

Investigating sputtered thin film Pt-containing electrocatalysts for SO₂(aq) electro-oxidation

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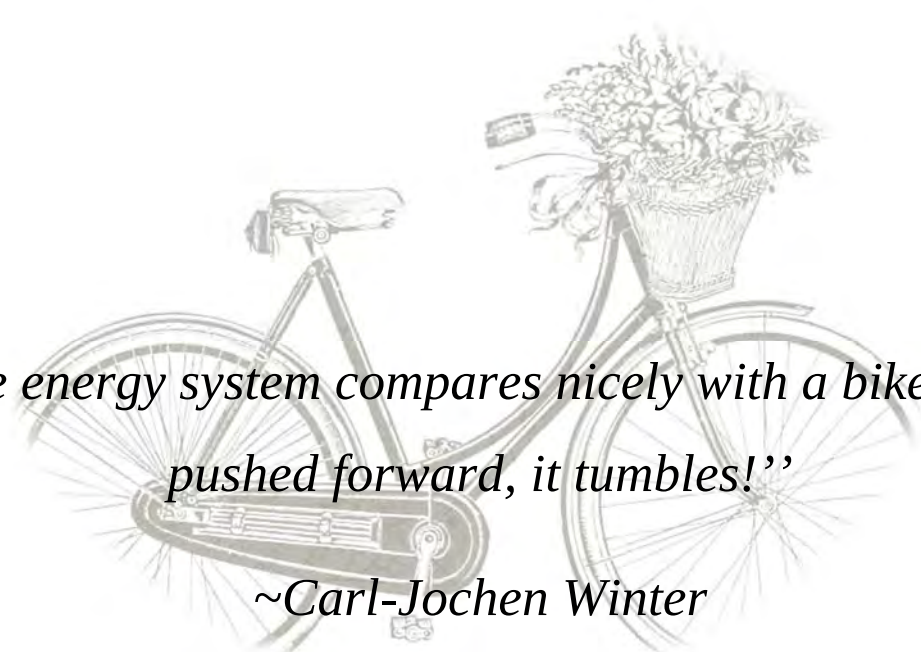
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Co-supervisor: Dr. V.A. Badets

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“The energy system compares nicely with a bike, if not pushed forward, it tumbles!”

~Carl-Jochen Winter

Declaration

I, Anzel Falch, declare that the thesis entitled: “*Investigating sputtered thin film Pt-containing electrocatalysts for SO₂(aq) electro-oxidation*”, submitted in fulfilment of the requirements for the degree *Philosophiae Doctor* in Chemistry, is my own work, except where acknowledged in the text, and has not been submitted in whole or in part to any other tertiary institution.

Signed at North-West University (Potchefstroom Campus)



Anzel Falch



Acknowledgements

First and most important, I want to thank my heavenly Father, for everything, for everything I am and have on earth is grace.

“Ek is tot alles in staat deur Hom wat my krag gee.”

Filippense 4:13

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LIST OF ABBREVIATIONS

AES	auger electron spectroscopy	PV	photovoltaics
AFM	atomic force microscopy	PVD	physical vapour deposition
Al	aluminium	PVDF	polyvinylidene fluoride
AMI	Advanced Metals Initiative	QCM	quartz crystal microbalance
aq	aqueous	RBT	rigid band theory
CATSA	Catalysis Society of South Africa	RDE	rotating disk electrode
CRB	Chemical Resource Beneficiation	RF	radio frequency
CSIR	Council for Scientific and Industrial Research	RMS	root mean square
CV	cyclic voltammetry	rpm	rotations per minute
DC	direct current	RTA	rapid thermal annealing
DMS	dimethyl sulphide		
EASA	electrochemical active surface area	SAIMM	The South African Institute of Mining and Metallurgy
EDGAR	Emission Database for Global Atmospheric Research	SCE	Saturated calomel electrode
EDX	energy dispersive X-ray spectroscopy	SDe	SO ₂ depolarised electrolysis
ESI	electronic supplementary information	SDE	SO ₂ depolarised electrolyser
f.c.c.	face centred cubic	SEM	scanning electron microscopy
FBR	fast breeder reactor	SHE	standard hydrogen electrode
FGD	flue gas desulphurisation	SNL	Sandia National Laboratories
GC	glassy carbon	SRNL	Savannah River National Laboratory
HTC	high-throughput and combinatorial	STDV	standard deviation
HyS	hybrid sulphur	UK	United Kingdom
IEA	International Energy Agency	USA	United States of America
IR	infrared	XPS	X-ray photoelectron spectroscopy
ISI	International Scientific Indexing	XRD	X-ray diffraction analysis
JNC	Japan Nuclear Cycle Development Institute		
LP	linear polarisation		
LSV	linear sweep voltammetry		
MEA	membrane electrode assembly		
MSE	mixed solvent electrolyte		
Mt	million tones		
NMP	n-methyl-2-pyrrolidone		
NRF	National Research Foundation		
NWU	North-West University		
OOC	Outotec Open Cycle		
PEM	proton exchange membrane		
PMDN	Precious Metals Development Network		
PolyPt	Polycrystalline Platinum		
ppm	parts per million		

LIST OF SYMBOLS

E°	standard reduction potential
$^\circ\text{C}$	degrees Celsius
V	Volt
μ	micro
K	Kelvin
R_s	surface roughness factor
s	second
M	molar
j	current density
E	potential
cm	centimetre
L	litre
A	Ampere
η	overpotential
j_0	exchange current density
k^0	heterogeneous rate constant
F	Faraday
A	active area
c_{SO_2}	SO ₂ concentration
E_a	activation energy
J	Joule
R	gas constant
W	Watt
E_{ocp}	open circuit potential
E_{low}	lower potential limit
%	percentage
θ	theta
C	Coulomb
h	hour
min	minute
eV	electron volt
R_a	average roughness
R_t	vertical distance between the highest and lowest points
§	paragraph

PREFACE

The research conducted and the results presented in this thesis are devoted to the field of energy, with the focus on aspects of electrocatalysis and materials science. Recent challenges and progress regarding the current and future state of the energy system are reviewed with particular emphasis on the development of electrocatalytic surfaces catalysing the oxidation of aqueous sulphur dioxide (SO₂), a key reaction in the hybrid sulphur (HyS) process as a means of producing hydrogen. The principle research techniques employed include a combination of modern high-throughput and combinatorial (HTC) methods in conjunction with the intermittent use of traditional apparatus and techniques to synthesise, characterise and evaluate the performance of various thin film electrocatalyst surfaces for electro-oxidising SO₂(aq). This thesis was submitted in article format, as is allowed by the North-West University (NWU) and stated in the General Academic Rules 2015 for doctoral studies ¹. This entails that the article(s) must be added to the thesis, with the requirement that at least one article has been accepted for publication ². The thesis must, however, be presented as a unit, as required by the General Academic Rules 2015 and therefore, should be supplemented with an inclusive problem statement, a focused literature study and a general conclusion. The article format thus results in the exclusion of the conventional ‘Experimental’, as well as the ‘Results and Discussion’ chapters, since the relevant information is contained in the respective articles. The chapters related to the different articles in this thesis are not necessarily a verbatim reproduction of the published articles as minor improvements and/or additions have been made to the text. For ease of access the published articles are included within Appendix A. In this regard some repetition of ideas/text/figures will occur in some of the chapters and in the included articles. The guidelines of the journal concerned is also required to be communicated. The framework, within which this doctoral degree may be compiled, is prescribed in the faculty rules and reads as follows:

N.9 Rules for the degree Philosophiae doctor

N.9.7 Exit level outcomes

“The student in this programme will attain the following specific outcomes:

- He/She will write a thesis of high technical quality (with reference to language usage, illustrations, tables, graphic representations, etc.) that will demonstrate: his/her command of an applied competency in an applicable quantitative and qualitative research methodology and in scientific penmanship; his/her ability to identify a relevant research problem in a natural science or health science discipline by integrating the above-mentioned skills and by thoroughly investigating existent knowledge as reflected in appropriate scientific literature;
- his/her ability to carry out the desired research in view of solving the problem;

- his/her ability to evaluate the results scientifically in the context of the problem statement;
- his/her ability to communicate the results scientifically.

The student will demonstrate by means of a literature investigation that he/she has a thorough and in-depth knowledge of related scientific literature; has the ability to interpret and debate different viewpoints and theories on a scientific basis; has looked up a large enough quantity of recent and appropriate historic primary and secondary sources in the speciality area.

The student will provide proof by means of problem identification that he/she has a sound insight into the nature and aim of the research; has the ability to circumscribe the research topic properly at the level of a doctorate.

Apart from the literature investigation the student will demonstrate that the research method is appropriate to the speciality area in view of handling the problem identified and that the research method has been selected in a reflexive and responsible manner.

By scientific evaluation and communication of the results the student will demonstrate the following:

- scientific processing of the thesis, with reference to the handling of appropriate quantitative or qualitative research methods and/or techniques, such as modelling, mathematical techniques of proof, experiments, observations, systematisation, founding of scientific statements, etc., as may be relevant to the problem investigated;
- the ability to formulate clearly; the ability to present a logical structure; a critical attitude and personal insight;
- the ability to formulate scientifically justified recommendations.

Summarised:

Students will have to demonstrate their ability to make a specific contribution to the development of new knowledge and skills in the field of specialisation by providing proof they have mastered knowledge of the theory and principles in the field; they are capable of integrating theory and practice in the field; of critical analysis of existing methodologies in the field; of analysis and interpretation of research data and results; of reporting research results in a scientifically acceptable format.”

*This section was reproduced from the Yearbook 2015 for the Faculty of Natural Sciences, Potchefstroom Campus*³.

Rationale in submitting the thesis in article format

The candidate's decision to submit in article format was based on the quality of the thesis. By submitting the article(s) to peer reviewed journals throughout the course of the degree, the candidate is exposed to constructive criticism by experts in the field, hence maintaining a high level of quality and relevance to the research. A prerequisite for handing in a PhD thesis in article format (stipulated in the Quality Manual) at the NWU is that at least one article must already have been approved for publication by an accredited journal². However, the candidate prepared four articles, of which one was published in a symposium series subjected to peer review and three were accepted for publication in an International Scientific Indexing (ISI) accredited journal. The prerequisite of the NWU has therefore been exceeded.

Contributions to articles

The origin of this work, substantiated by ideas and recommendations, was suggested by Dr. R.J. Kriek (supervisor). The conceptualisation, acquisition of data, decisions/interpretation and compilation of articles, were done by myself, A. Falch, with participation and assistance by Dr. R.J. Kriek and Dr. V.A. Badets (co-supervisor, maiden name Lates). H.S. Kotzé assisted in conducting some of the experimental work under my orders and supervision. Dr. C. Labrugère assisted in XPS analysis conducted at the University of Bordeaux.

Formatting and current status of articles

The thesis is written in British English. All articles were written in the English required by the journals. One article has been published in the The Precious Metals Development Network (PMDN) Symposium Series S77 of The Southern African Institute of Mining and Metallurgy. In addition, three articles were published in *Electrocatalysis*, a Springer journal. This specific journal was selected for communicating the research outcomes and results as the focus of this study is aligned with the scope of *Electrocatalysis*, which provides a unique international forum solely dedicated to the exchange of novel ideas in electrocatalysis for academic, government, and industrial researchers. The articles are inserted into the thesis in chapter format and in addition each publication is included in Appendix A in the published format. The author guidelines that were followed in preparation of the four articles are available at the following links: <http://www.saimm.co.za/guidelines-for-authors>, and <http://www.springer.com/chemistry/electrochemistry/journal/12678>, which are related to Chapter 2 and Chapters 3 to 5, respectively.

Consent by co-authors

All the co-authors, i.e. R.J. Kriek, V.A. Badets, H.S. Kotzé and C. Labrugère, as well as the Symposium Series and Electrocatalysis journal (see Appendix B for details) were informed that the Ph.D. thesis would be submitted in article format for examination and they gave their consent.



I, Dr. Roelof Jacobus Kriek, hereby give my permission that Anzel Falch may submit the article(s)/manuscript(s) for degree purposes.

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I, Dr. Christine Labrugère, hereby give my permission that Anzel Falch may submit the article(s)/manuscript(s) for degree purposes.

A handwritten signature in blue ink, reading "C. Labrugère".

Conference oral presentations

- o *Ternary sputtered electrocatalysts towards SO₂ electro-oxidation*, **A. Falch**, V.A. Badets, R.J. Kriek and C. Labrugère, Conference of the Catalysis Society of South Africa 2015, Arabella Hotel and Spa, Kleinmond, South Africa, November 2015.
- o *Sputtered Pt_xPd_y catalysts towards the electro-oxidation of aqueous sulphur dioxide*, H.S. Kotzé, **A. Falch** and R.J. Kriek, Conference of the Catalysis Society of South Africa 2015, Arabella Hotel and Spa, Kleinmond, South Africa, November 2015.
- o *A combinatorial sputtering system for the multiple syntheses and high-throughput testing of thin film catalysts for aqueous SO₂ electro-oxidation*, R.J. Kriek, **A Falch**, V.A. Lates, Conference of the Catalysis Society of South Africa 2014, Saint Georges Hotel and Conference Centre, Pretoria, South Africa, November 2014.
- o *The electrochemical oxidation of aqueous SO₂ on sputtered Pt/GC electrodes*, **A Falch**, V.A. Lates and R.J. Kriek, AMI in association with SAIMM, Precious Metals 2013, The Precious Metals Development Network Conference (PMDN), Protea Hotel President, Cape Town, South Africa, October 2013.
- o *The electro-oxidation of sulphur dioxide*, M. Bjorketun, A. Calitz, **A. Falch**, V.A. Lates, M. Potgieter, J. Rossmeisl, S. Siahrostami, M. Steyn, ISE-13th Topical Meeting of the International Society of Electrochemistry, 2013, Pretoria- CSIR International Convention Center, South Africa, April 2013.

Conference poster presentations

- o *The electrochemical oxidation of aqueous SO₂ on sputtered Pt/GC and Ru/GC*, **A. Falch**, V.A. Lates and R.J. Kriek, Conference of the Catalysis Society of South Africa 2013, Wild Coast, South Africa, November 2013.

Outline of thesis

The structure of this thesis as an article model will include the following as per the requirements for a thesis (from a description in the University's Quality Manual ²):

- ∞ Title page
- ∞ Declaration
- ∞ Acknowledgements
- ∞ Table of contents
- ∞ A preface comprising the following:

- A statement that the article format has been selected
 - The student's share in the research in the case of co-authors for the article(s)/manuscript(s)
 - Permission from co-authors that the article(s)/manuscript(s) can be submitted for degree purposes with a link to the guidelines for authors for the journal concerned
 - List of conference oral presentations
 - List of conference poster presentations
- ∞ An abstract
 - ∞ Literature review
 - ∞ Manuscripts
 - ∞ Bibliography for each chapter
 - ∞ Conclusion
 - ∞ Appendix A which includes the articles published from this study in published format
 - ∞ Appendix B which includes permission from the respective journals

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Abstract

Environmental concerns, social, economic and political pressure, and new technologies are the main factors driving change in energy systems around the globe. Human life and development are inevitably dependent on energy and the world is currently significantly reliant on mainly fossil fuels to meet its energy requirements. Fossil fuels together with nuclear energy both have negative implications for the health of humans and the quality of the environment. A worthy competitor that can serve as a solution to the depleting and destructive nature of fossil fuels and nuclear energy is renewable energy. Hydrogen, not only a non-carbon-containing energy carrier, but the most abundant atom on earth is considered the ultimate clean energy carrier to be generated from renewable resources. As hydrogen is only found as part of compounds on earth, it is fairly energy intensive to separate hydrogen into its molecular form, which goes hand in hand with huge amounts of environmental pollutants being emitted to the atmosphere. The hybrid sulphur (HyS) cycle, a thermo-electrochemical water splitting process, through the electrochemical oxidation of SO_2 , serves as a means of producing hydrogen in a usable form without emitting any harmful pollutants. Although there are various ways to produce hydrogen, interest in the non-carbon-based HyS cycle as a potential large scale hydrogen production process, results from the fact that, whereas the anodic reaction for regular water electrolysis, as another means of producing hydrogen, occurs at a standard potential of 1.23 V (SHE), the anodic reaction in the SO_2 depolarised electrolyser (SDE¹) occurs at a standard potential of 0.17 V (SHE), which translates into an energy gain of more than one volt that makes the HyS cycle more favourable. Insufficient electrocatalyst activity, stability and economic viability are among the most challenging issues related to technologies for electrochemical energy conversion. An aspect that can improve the SDE performance and economic viability is improving the anodic reaction of electrochemically oxidising aqueous SO_2 . This can be achieved by improving the electrocatalyst for the anodic reaction.

In an effort to address these barriers, combinatorial sputtering, high-throughput screening, and traditional methods were employed to investigate various thin film electrocatalyst combinations containing alternately varying content of platinum (Pt), palladium (Pd) and aluminium (Al), towards the electro-oxidation of aqueous SO_2 . Throughout the investigation the thin film electrocatalysts were exposed to different physical and electrochemical treatments and characterisation techniques, resulting in new insights gained. Included in the list of techniques and methods are combinatorial sputtering, photolithography, high-throughput screening, cyclic voltammetry, linear polarisation, rapid thermal annealing treatment (RTA), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and scanning electron microscopy (SEM).

¹ Note in the list of abbreviations the difference between the use of SDE and SDe

The combinatorial sputtering approach, based on magnetron enhanced plasma sputtering and photolithography, was developed and employed in the syntheses of the thin film electrocatalysts. A multi-channel potentiostat, connected to a custom manufactured multi-working electrode electrochemical cell, allowed for high-throughput parallel screening of the deposited electrocatalysts towards the electro-oxidation of aqueous SO₂. Employing onset potential and current output as the screening criteria together with stability tests and the results obtained from physical characterisation (by employment of the above mentioned techniques), thin films exhibiting satisfactory performance were identified. A Pt₃Pd₂ thin film, annealed at 800 °C, and a ternary combination of Pt₄₀Pd₅₇Al₃, annealed at 900 °C, were identified as potential contenders to compete with pure Pt that is currently being employed as the anode material for electrochemically catalysing the electro-oxidation of SO₂. Both Pt₃Pd₂ and Pt₄₀Pd₅₇Al₃ thin films contain less Pt than a pure Pt thin film, while exhibiting increased electrocatalytic activity, and can serve as a basis for future studies.

Keywords: *Combinatorial sputtering, sulphur dioxide, annealing, stability, HyS process, SO₂ electro-oxidation, hydrogen production, electrocatalyst, high-throughput screening*

Opsomming

Omgewingskwessies, sosiale, ekonomiese en politieke druk, en nuwe tegnologie is die belangrikste faktore wat verandering in energiestelsels regoor die wêreld dryf. Menselebens en ontwikkeling is onvermydelik afhanklik van energie en die wêreld is tans besonder afhanklik van hoofsaaklik fossielbrandstowwe om in sy energiebehoefte te voorsien. Fossielbrandstowwe en kernkrag het albei negatiewe gevolge vir die gehalte en gesondheid van die mens en die omgewing. 'n Waardige mededinger wat as 'n teenvoeter vir die afbrekende en vernietigende aard van fossielbrandstowwe en kernkrag kan dien, is hernubare energie. Waterstof is nie net 'n nie-koolstofbevattende energiedraer nie, maar dit is die volopste atoom op aarde en word beskou as die uitnemendste skoon energiedraer wat gegenereer word uit hernubare bronne. Aangesien waterstof slegs gevind word in verbindinge op die aarde, is dit redelik energie-intensief om waterstof in sy molekulêre vorm te verkry, wat gepaard gaan met die vrystelling van groot hoeveelhede omgewingbesoedelaars wat in die atmosfeer vrygestel word. Die hibriede swaelsiklus (HyS), 'n termo-elektrochemiese watersplytproses d.m.v. die elektrochemiese oksidasie van SO_2 , dien as 'n metode vir die vervaardiging van waterstof in 'n bruikbare vorm sonder die vrystelling van enige skadelike besoedelingstowwe. Alhoewel daar verskeie maniere is om waterstof te produseer, is belangstelling in die nie-koolstof-gebaseerde HyS-siklus as 'n potensiële grootskaalse waterstofproduksieproses te danke aan die feit dat, terwyl die anodereaksie vir gewone waterelektrolise, as 'n ander manier van waterstofvervaardiging, plaasvind by 'n standaardpotensiaal van 1.23 V (SHE), die anodereaksie in die SO_2 gedepolariseerde elektroliseerder (SDE²) plaasvind by 'n standaardpotensiaal van 0.17 V (SHE), wat 'n wins van meer as een volt beteken, en wat die HyS-siklus bevoordeel. Onvoldoende elektrokatalis-aktiwiteit, stabiliteit en ekonomiese lewensvatbaarheid is van die uitdagendste kwessies i.v.m. die tegnologie vir elektrochemiese energie-omskakeling. 'n Aspek wat die SDE-prestasie en ekonomiese lewensvatbaarheid kan verbeter, is die verbetering van die anodereaksie van elektrochemies-oksiderende waterige SO_2 . Dit kan bereik word deur die verbetering van die elektrokatalis vir die anodereaksie.

In 'n poging om hierdie hindernisse te oorkom, is kombinatoriese deponering, hoëdeurset-sifting, en tradisionele metodes gebruik om verskeie dunfilm elektrokatalis-kombinasies wat wisselende hoeveelhede platinum (Pt), palladium (Pd) en aluminium (Al) bevat, ondersoek gedurende die elektro-oksidasie van waterige SO_2 . Gedurende die ondersoek is die dunfilm-elektrokatalis blootgestel aan verskillende fisiese en elektrochemiese behandelings- en karakteriseringstegnieke, wat gelei het tot nuwe insigte. Die lys van tegnieke en metodes gebruik, sluit in kombinatoriese deponering, foto-litografie, hoëdeurset-sifting, sikliese voltammetrie, lineêre polarisasie, snel hitte-uitgloeïing (RTA), energie-dispersiewe X-straal-

² Let wel in die lys van afkortings dat daar 'n verskil in die gebruik van SDE en SDe is

spektroskopie (EDX), X-straaldiffraksie-analise (XRD), X-straal-foto-elektron spektroskopie (XPS), atoomkragnmikroskopie (AFM) en skandeer-elektronmikroskopie (SEM).

Die kombinatoriese deponering-benadering, gebaseer op magnetron-versterkte plasmadeponering en fotoligrafie, is ontwikkel en gebruik vir die sintese van die dunfilm elektrokataliste. 'n Multikanaal-potentiostaat, gekoppel aan 'n persoonlike vervaardigde multi-werkelektrode elektrochemiese sel, het hoë-deurset parallelle sifting van die gedeponeerde elektrokatalis teenoor die elektro-oksidase van waterige SO_2 moontlik gemaak. Deur gebruikmaking van die aanvang-potensiaal en stroom-uitset as die keuringskriteria, saam met stabiliteitstoetse en die resultate wat verkry is d.m.v. fisiese karakterisering (deur gebruik van die bogenoemde tegnieke), is dunfilms wat bevredigende prestasie vertoon het, geïdentifiseer. 'n Pt_3Pd_2 - dunfilm, uitgegloeï by $800\text{ }^\circ\text{C}$, en 'n ternêre kombinasie van $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$, uitgegloeï by $900\text{ }^\circ\text{C}$, is geïdentifiseer as potensiële kandidate om met suiwer Pt te kompeteer, wat huidig aangewend word as die anodemateriaal vir die elektrochemiese katalisering in die elektro-oksidase van SO_2 . Beide Pt_3Pd_2 - en $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ -dunfilms bevat minder Pt as suiwer Pt-dunfilms, met verhoogde elektrokatalitiese aktiwiteit, en kan dien as 'n basis vir toekomstige studies.

Slutelwoorde: *Kombinatoriese deponering, swaeldioksied, uitgloeïing, stabiliteit, HyS-proses, SO_2 -elektro-oksidase, waterstofproduksie, elektrokatalis, hoëdeurset-sifting*

Chapter 1

Introduction

This chapter is intended to serve as an introduction to the general theme of the thesis, which includes a motivation, background (substantiated by a concise literature overview), a problem statement, as well as the aim and objectives of the thesis.

Please note that as this thesis is in article format, the literature referred to in the following sections of Chapter 1 is in addition to the literature used in the introduction of the published articles listed in Chapters 2 to 5, and in that regard overlap may occur.

1.1 Motivation

Human life and development are inevitably dependent on energy and the world is currently almost exclusively reliant on mainly fossil fuels to meet its energy requirements, with fossil fuels being responsible for contributing ~80% of the world's energy demand. Renewable and nuclear energy are only contributing ~13.5% and ~6.5%, respectively, of the remaining 20% of the total global energy need ¹. The use of fossil fuels, to satisfy the supply and demand of world energy, will be under pressure in terms of long term sustainability in the near future due to the multiple challenges they face. These challenges include mainly depletion of the current state of fossil fuel reserves, the primary and secondary effects of global warming, and legislative, political and military conflicts. Fossil fuels and nuclear energy both have effects that diminish the quality and health of humans and the environment. This stems from fossil fuels that release pollutants, which, apart from various metals, result from (i) sulphur (S, 15-20%) that can produce SO₂ and in turn can react to produce acid rain, (ii) nitrogen (1-12%) which contributes to the formation of toxic nitrogen oxides (NO_x), and (iii) the direct release of carbon dioxide (CO₂) that is predominantly responsible for the greenhouse effect ². Renewable energy, on the other hand, is a worthy contender that can serve as a long-term solution to the depleting and destructive nature of fossil fuels and nuclear energy. Given adequate support, renewable energy has the potential to be inexhaustible, widely available and environmentally accommodating, while meeting the present and future world energy demand ¹.

1.2 Background & literature overview

1.2.1 Energy supply and demand

The global community is at present rapidly consuming available non-renewable (fossil fuel) sources of energy that have accumulated over many years, putting increasing strain on energy supply and demand over the coming years. This is, among other things, a direct result of the gradual increase in the world population, urbanisation, modernisation and economic growth. An estimation of the global population in 1800 was

approximately 1 billion, and over 200 years later the global population has increased to 6 billion people and thereby resulted in an estimated twenty fold increase in energy use levels ³. In 2050 the population is expected to stabilise at 11 billion resulting in a 16-fold increase in global energy utilisation ⁴. Although the International Energy Agency (IEA) projects a growth of 37% by 2040 in energy demand, it is expected that the growing population and economy will be less energy-intensive compared to the present situation ⁵. By 2040 it is also expected that the world's energy supply will depend on coal, oil, gas and low-carbon sources, which are all not depleted as yet, but they do all face distinct challenges ⁵. The future of oil is influenced in part by investments (requiring around \$900 billion per year to meet demand) and the political situation in participating oil countries/regions, which include among others the United States (USA), the Middle East, Asia, and Russia. Demand for natural gas will almost double and will account for almost 60 % of the global energy growth. One of the uncertainties facing natural gas is whether gas can be supplied at an attractive price to consumers while still maintaining large capital investments in gas supply. Global demand for coal is expected to increase by 15% by 2040 and the supply of coal is projected to be abundant and secure ⁵. However, implementation of coal as energy source will be hampered by strict measures to combat pollution and reduce CO₂ emissions (refer to Figure 1.1 for projected world CO₂ emissions in million tonnes (Mt) ¹), thus requiring optimised technologies (low carbon systems) in using coal as a source of energy ⁵.

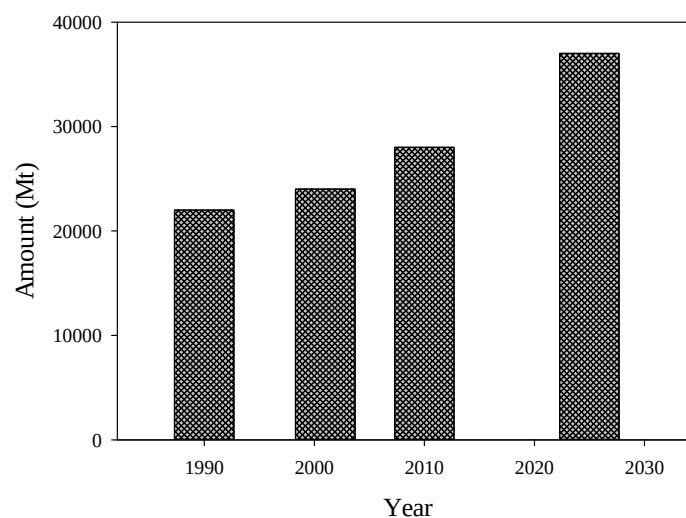


Figure 1.1: CO₂ global emissions.

Problems related to the existing energy systems, ranging from security of supply to environmental impact issues, are acknowledged and strategies to address these problems are evident in both political statements and model projects all over the world ⁶. This has contributed to the growing topic of renewable and sustainable energy over the last few decades, which can serve as an alternative to the growing challenges in the existing energy systems.

1.2.2 Production of hydrogen from renewable and sustainable sources

Renewable energy refers to abundant and widely available natural resources, which, if subjected to appropriate technologies, can be utilised for sustainable energy supply with basically zero harmful and destructive by-products that can negatively impact humans and the environment. Included in the list of renewable energies, but not limited to, are wind, solar, hydro, photovoltaic, biomass and geothermal power. The renewable sector is currently growing faster than the growth in the overall energy market and could increase from the current 13.5% contribution to the global energy demand to up to 50% in the 21st century with appropriate policies and advanced technology evolution ¹. A possible vision for an alternative renewable and sustainable energy system, which has been able to unite global economic growth and environmental concerns, is that of the hydrogen economy ⁷⁻⁹. Transitions from solid to liquid to gaseous energy sources, with hydrogen being forecasted as the source of energy for the future, are clearly depicted in Robert Hefner's illustration (Figure 1.2) of the historical and future projections of global energy systems

¹⁰.

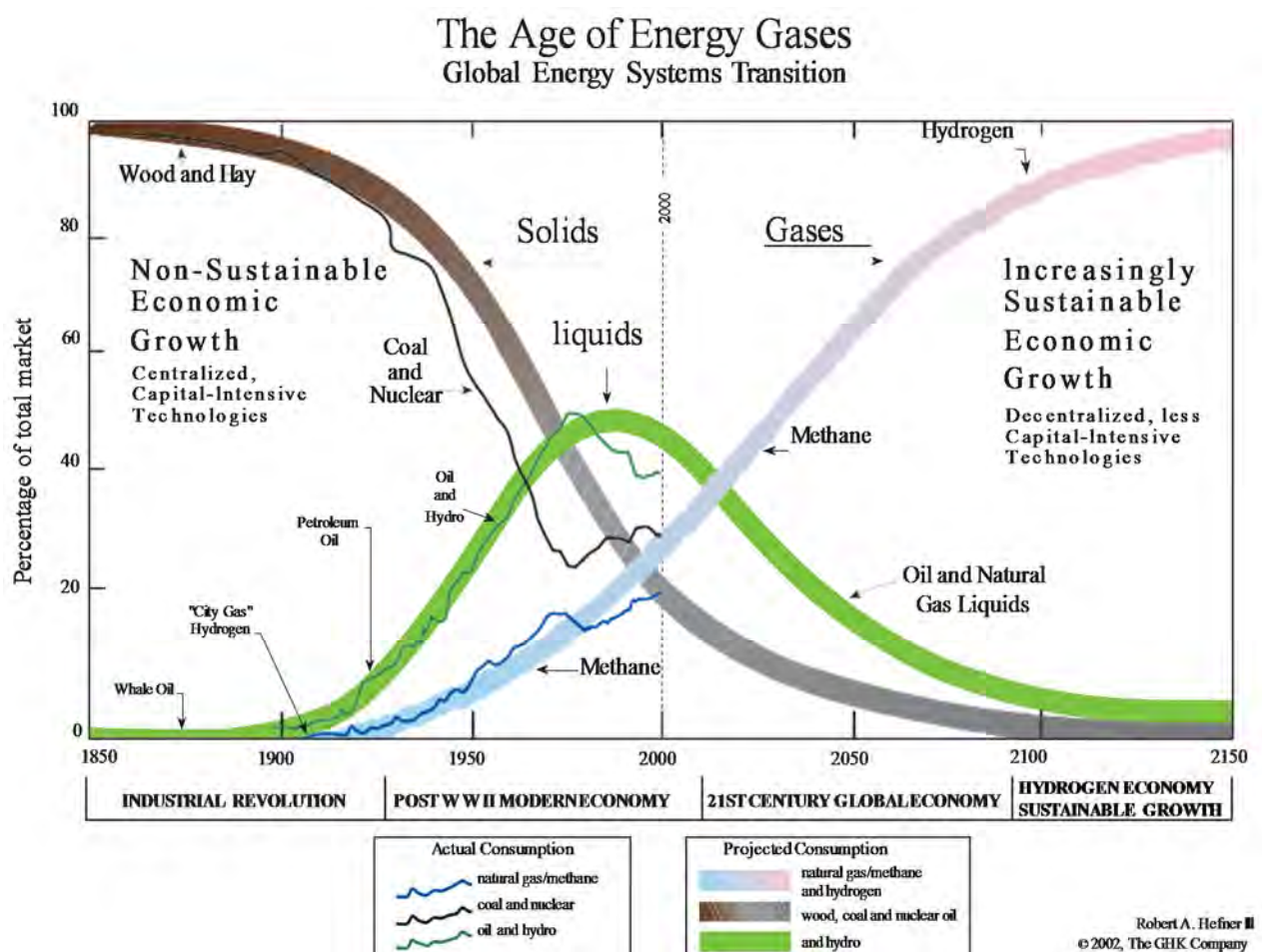


Figure 1.2: Global energy system transition, 1850-2150 (Permission granted by Elsevier, see Appendix B ¹⁰).

Hydrogen is the most abundant atom on earth ¹¹. In its molecular form it is considered as the ultimate clean energy carrier to be generated from renewable sources ^{2, 12, 13} as it can be transported to where it is needed and be delivered to consumers in an usable form ¹⁴. However, as hydrogen is present in compounds on earth, it is energy intensive to separate hydrogen in its molecular form ¹¹. Within the growing hydrogen economy ¹¹ numerous ways of producing hydrogen are being investigated, discussed, communicated and applied ^{6, 15-17}. At present the majority of hydrogen produced, is from fossil fuels conversion, such as natural gas reforming (Figure 1.3) ¹⁸.

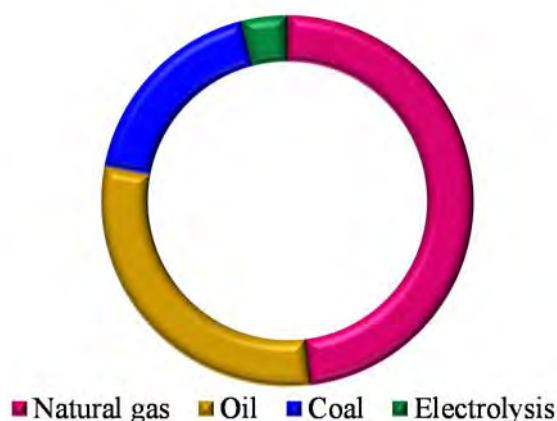


Figure 1.3: Annual global hydrogen production share (%) by source ¹⁸.

If hydrogen is to become a major energy (re)source, several obstacles have to be overcome. The energy/feedstock required to produce hydrogen has to be decreased in order to improve production efficiency so as to alleviate the current problem of hydrogen being a more expensive energy (re)source than traditional energy sources. In addition, infrastructure to transport and distribute hydrogen safely and efficiently should be improved ¹⁹. Realising the many advantages that the use of hydrogen offers, i.e. abundant availability, utilisation of a variety of feedstocks and a variety of production technologies, combined efforts of government and private entrepreneurs can expedite the progress in transitioning to efficient and economic viable hydrogen production ^{19, 20}. A number of alternative technologies (Figure 1.4) have the potential (with some already performing promising) for the production of hydrogen ^{6, 18}.

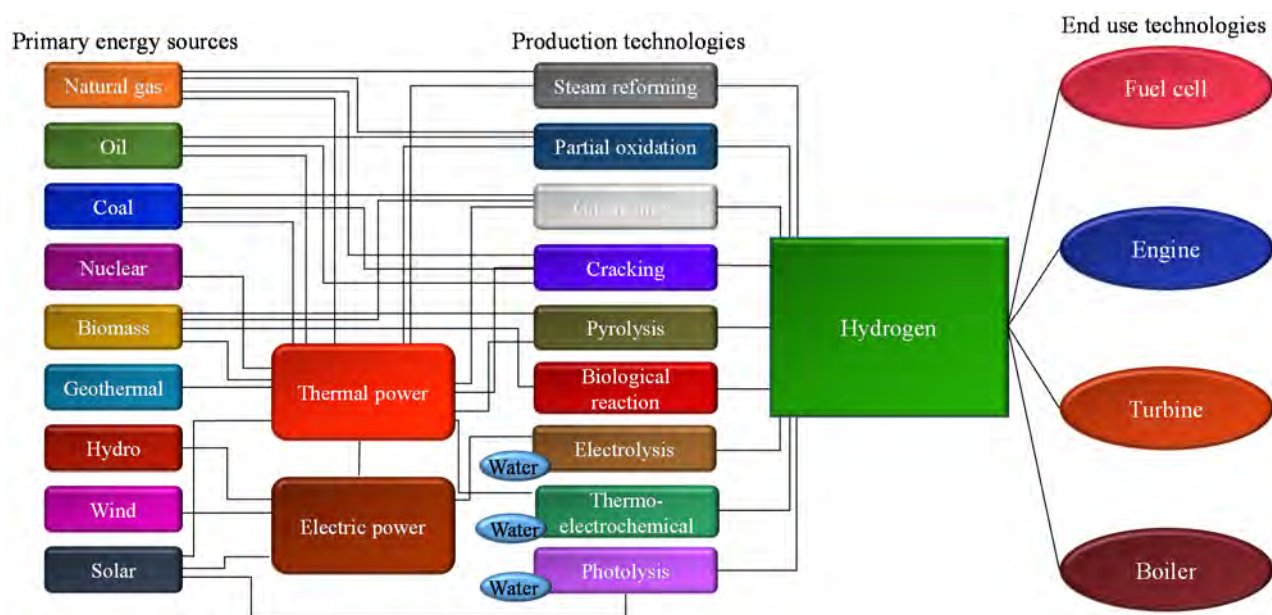


Figure 1.4: Main alternative methods of producing hydrogen from various energy sources (reproduced from Balat ⁶).

The range of hydrogen production processes can roughly be divided into hydrocarbon-based (steam-methane reforming and coal gasification), non-hydrocarbon-based (water electrolysis and thermochemical water decomposition) and integrated (steam-methane reforming linked to non-hydrocarbon-based) processes ²¹. Thermochemical processes produce hydrogen through a series of chemical reactions of which water splitting is one of the main reactions. All other chemical species included in the process are recycled back into the cycle at hand, resulting in the consumption of only heat and water to produce hydrogen and oxygen. Since hydrocarbons are not used in these thermochemical processes, no harmful emissions such as CO₂ are produced, and the hydrogen produced is extremely pure ²². Although there are various thermochemical cycles that can produce hydrogen from water, one of the leading candidates is the HyS cycle (a sulphur-based cycle), which is a promising thermo-electrochemical cycle for the future ²²⁻²⁷. The HyS cycle is being developed as a hydrogen generating technology driven by either nuclear or solar power ^{9, 28}, employing a combination of thermochemical and electrolytic reactions ¹⁹.

1.2.3 Sulphur dioxide and the HyS process

SO₂ is a colourless, non-flammable gas with a sharp and pungent odour ²⁹, which can be detected by taste and smell in the range of 0.001-0.003 ppm ^{30, 31}. Acute and chronic exposures to SO₂ have detrimental effects on the environment, as well as human and animal well-being. Included in these effects are, among others, bronchial constriction, increased pulmonary resistance, swelling of mucosal tissues and irritation of the respiratory tract, skin and eyes ³¹. Emission sources of SO₂ can roughly be divided into natural and anthropogenic sources. Volcanoes and volcanic vents as a sporadic source of SO₂, the decaying of organic matter, solar action on seawater and the oxidation of dimethyl sulphide (DMS) emitted from the ocean, can

all be categorised as natural sources of SO₂^{31, 32}, whereas the greatest anthropogenic sources include the combustion of fossil fuels and the smelting of sulphide ores³². Approximately 90% of global anthropogenic SO₂ emissions are emitted in the northern hemisphere, as can be depicted in Figure 1.5, with coal-fired power generation being the biggest attributer³⁰. Prominently illustrated by Figure 1.5, is that around the 1970s SO₂ emissions peaked (Figure 1.5a and Figure 1.6), subsequently declining (Figure 1.5b) as a direct result of the implementation of focused abatement technologies³⁰. Countries which attributed significantly to the diminishing of SO₂ emissions from 1970 to 2008 include North America, Europe, Japan, as well as Russia and the Ukraine. Countries that clearly disregard the focus on reducing SO₂ emissions include China, and to a lesser extent India (Figure 1.5b), releasing in the order of 33 Mt and 6 Mt of SO₂ per annum respectively (based on 2005 data)³³.

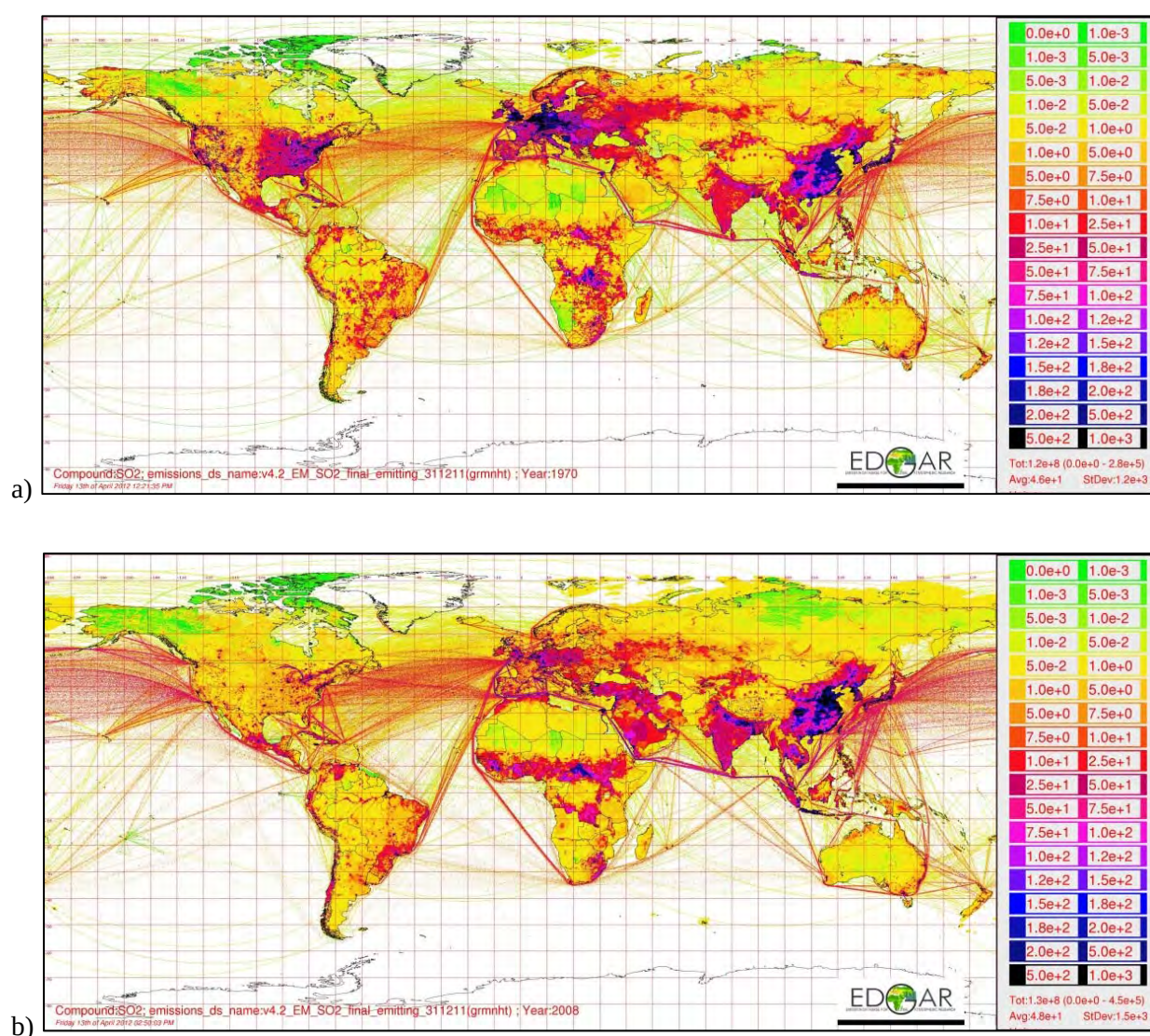


Figure 1.5: Spatial distribution maps for SO₂ drafted by the European Commission's Joint Research Centre using their Emission Database for Global Atmospheric Research (EDGAR) for (a) 1970, and (b) 2008 (EC-JRC/PBL, 2010)^{30, 34}.

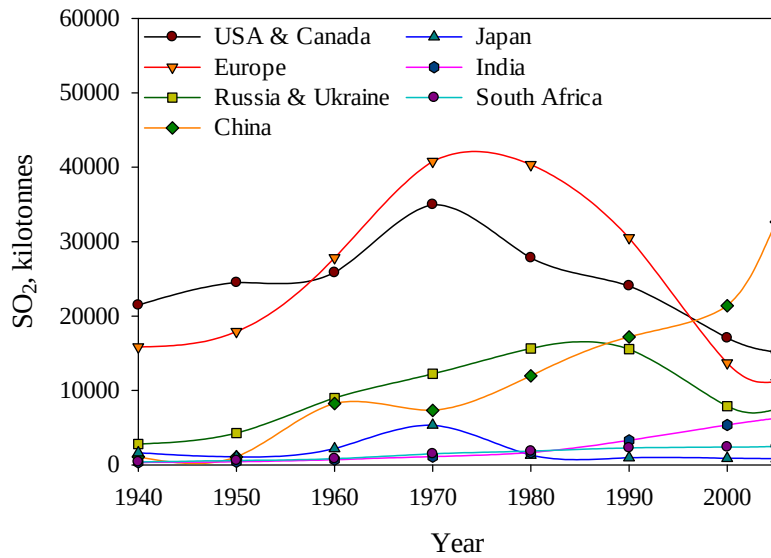


Figure 1.6: SO₂ emissions for specific countries and regions since 1940 ^{30, 33}.

The SO₂ accumulated in the atmosphere can be converted to sulphuric acid (H₂SO₄) according to the following reactions steps, through a number of pathways or any combination thereof. The possible pathways include a homogeneous gas-phase pathway, a homogeneous aqueous-phase pathway, or a heterogeneous pathway on the surface of particulate matter ^{30, 35, 36}.



In addition to the above-mentioned pathways, the following catalytic pathway contributes to the removal of SO₂ from the atmosphere ³⁷:



This sulphuric acid forming in the atmosphere, can then be deposited on the earth's surface, affecting vegetation, agricultural crops, natural waterways, and decay of buildings and monuments ³⁰.

A means of addressing the release of SO₂ into the atmosphere is by implementing abatement technologies for processes prone to support SO₂ pollution. Included among other applications, flue gas desulphurisation (FGD) ³⁸ is the current technology applied for the removal of SO₂ from exhaust flue gases of coal-fired power plants. In general, employed FGD technologies can be categorised as wet (SO₂ recovery efficiency of 93-98%), dry (SO₂ recovery efficiency of 50-60%) or “semi-dry” and based on the products formed, as

once-through (without recycle) or as re-generable (with recycle). According to a review done by Srivastava *et al.* ³⁹ on the SO₂ removal performance of scrubbers, it appears that 90% SO₂ removal can be achieved by wet limestone and lime spray drying installations and 95% SO₂ removal is achievable by state-of-the-art wet scrubber systems ³⁹. Dry methods are recommended for cases where SO₂ emissions are low with “semi-dry” methods applicable to small to medium sized industrial boilers ⁴⁰. Thus, depending on the process and the amount of emitted SO₂, an appropriate FGD can be applied, producing either saleable, recyclable or disposable waste products.

An aspect which has also gained a reasonable amount of interest over the years with regard to SO₂, is that of fundamental electrocatalysis ⁴¹⁻⁴⁶ (SO₂ oxidation). This reaction (SO₂ oxidation) in aqueous solution is of industrial relevance and the mechanism of this reaction has been investigated extensively for application in the HyS cycle ⁴⁷⁻⁵². The HyS cycle, as first proposed by the Westinghouse Corporation ⁵³⁻⁵⁵ and also known as the Ispra Mark 11 cycle ^{19, 56}, underwent extensive development in the 1970s ^{44, 56-58} and 1980s ^{56, 59, 60}. For the subsequent 20 years, further development nearly ceased ⁹ as advanced nuclear technologies gained increased interest ⁵⁶. After this period, interest in the HyS cycle revived with the HyS cycle having been rated among the top of 115 thermochemical cycles considered ^{27, 61}.

Table 1.1: General research into the HyS cycle over recent years.

Year	Short description	Ref
2005	Proof of concept for the production of hydrogen via SO ₂ -depolarised water electrolysis by employing a PEM electrochemical cell which can function at room temperature and pressure ranging up to 2 bar. SO ₂ dissolved in sulphuric acid was used for the first time to depolarise water electrolysis in the PEM cell.	⁶²
2006	Japan Nuclear Cycle Development Institute (JNC) proposed a lower temperature range thermochemical and electrolytic hybrid hydrogen production process (based on the Westinghouse process) for sodium cooled Fast Breeder Reactor (FBR).	⁶³
2007	A common step in the sulphur-iodine and HyS thermochemical cycles is the decomposition of sulphuric acid. A distinct description on the development of a dedicated solar receiver-reactor for the decomposition of sulphuric acid is discussed.	⁶⁴
2007	Improved electrochemical conversion in a PEM electrolyser was obtained when carrying out the anode reactions: (a) SO ₂ to H ₂ SO ₄ and H ₂ ; and (b) HBr to Br ₂ and H ₂ , in the gas phase.	²²
2008	Electrical/thermal coupling of an individual filter press electrolysis cell for the preliminary design of a future test pilot employing equations developed through Flux Expert [®] interface elements.	⁶⁵

Table 1.1: ... continued

2008	Analysis on energy losses occurring in a single cell SO ₂ depolarised electrolyser (SDE) from individual components. Identified losses are employed to optimise the membrane-electrode structure and materials. Improved performance as a result of binary and ternary catalysts containing Pt and other transition metals were also investigated.	66
2009	Design calculations of a composite reactor which serves to concentrate, preheat and decompose sulphuric acid for hydrogen production processes.	67
2009	The production of hydrogen by splitting water is investigated and discussed in terms of a conceptual design for the HyS process using PEM electrolysis and a bayonet decomposition reactor.	24
2009	An investigation of varying Pt loading amount and the resulting effect on the SO ₂ oxidation reaction in the HyS process.	68
2009	The application of Nafion® and sPEEK membranes in the electrochemical hybrid sulphur process is investigated by measuring their SO ₂ transport properties employing an electrochemical reaction cell.	69
2009	The employment of a high-temperature nuclear heat source for the splitting of water in the HyS process towards the production of hydrogen was investigated which combined proton exchange membrane (PEM) SDE technology, SRNL, with bayonet reactor sulphuric acid decomposition technology, Sandia National Laboratories (SNL).	24
2009	The thermodynamic properties of the aqueous SO ₂ /H ₂ SO ₄ system was investigated by using the OLI System Mixed Solvent Electrolyte (MSE) model in conjunction with Aspen Plus to elucidate the effect that sulphuric acid concentration, temperature and pressure have on SO ₂ solubility.	70
2010	Key properties of electrocatalysts, cation-ion exchange membranes and operating conditions that limit the formation of an undesired sulphur-rich layer between the cathode and membrane, for optimised SDE performance are discussed.	71
2011	Conceptual design and economic analysis for a large scale solar hydrogen production plant (100 TPD) based on the HyS process, matched to a particle receiver-based solar tower.	72
2011	The possible use of photovoltaics (PV) to supply the electrical demand of the electrolyser in the HyS cycle as a viable zero carbon production process was investigated.	73
2013	Elucidating the effect membrane electrode assembly (MEA) preparation and optimization have on the electrolysis performance of SO ₂ depolarised electrolysis (SDe).	74
2014	Evaluation of MEA properties including pressure and time during membrane manufacturing, as well as membrane thickness, catalyst loading and active area, for SO ₂ electrolysis.	75
2015	Insight into the effect H ₂ S has on the operating performance of a PEM SO ₂ electrolyser	76
2016	An investigation of the components that comprise the cell voltage of SO ₂ -depolarized electrolysis in hybrid sulphur process.	25

Table 1.1: ... continued

2016	This study explores the carry-over of SO ₂ and sulphur formation on the cathode in a real case operating SDE and the effect on the overall cell performance and H ₂ production.	77
2016	A range of operating conditions (current, temperature, etc.) and design variations (membrane type, thickness etc.) results are reported for a patented gas-fed SDE.	28

Within the HyS cycle (Figure 1.7) sulphuric acid is thermally decomposed to produce SO₂, water and oxygen (reaction 5)²⁴ by employing a high temperature heat source (>800 °C). The resulting SO₂ is fed to a SDE, which depending on design, can be a gas-fed system, liquid-fed system or a humidified SO₂ anode supply (only one published journal article on this method)⁷⁸. In the gas-fed system, gaseous SO₂ is fed to the anode⁷⁹ and in the liquid-fed system sulphuric acid saturated with SO₂ is employed as the anolyte²³. Nevertheless, not depending on which design is implemented for the SDE, the SO₂ is fed to the anode and electro-oxidised to produce sulphuric acid as well as hydrogen ions (reaction 6). The hydrogen ions migrate through the membrane of the electrolyser to the cathode where it is reduced to hydrogen gas (reaction 7), while the electrochemically produced sulphuric acid is recirculated back to the decomposition reactor. The net SDE reaction therefore involves the conversion of SO₂ into sulphuric acid and hydrogen gas (reaction 8), while the net HyS cycle reaction is that of water being split into hydrogen and oxygen (reaction 9).

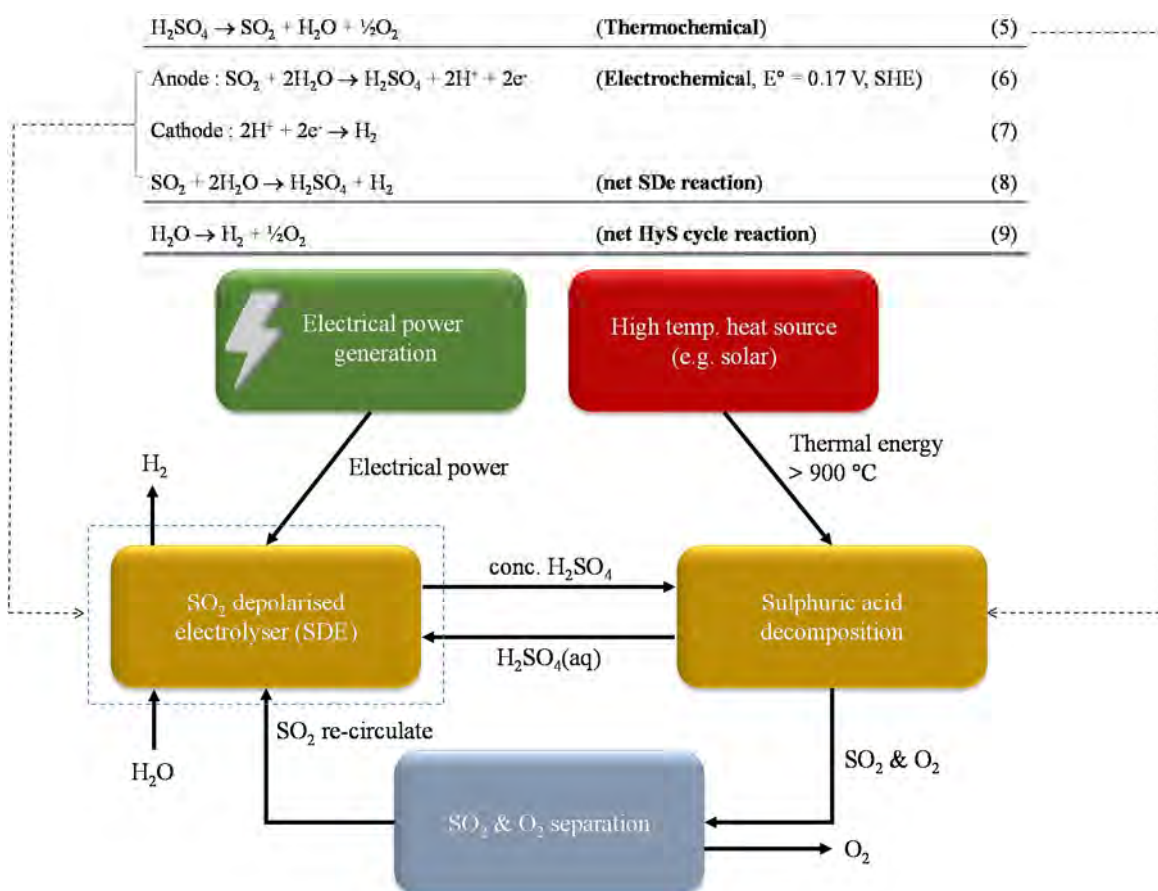


Figure 1.7: The Westinghouse HyS process⁸⁰.

Apart from the fact that the SDE process is part of the closed HyS cycle, which utilises SO_2 to produce hydrogen and oxygen as products while recycling the H_2SO_4 , it can also potentially be employed as a SO_2 sink together with, for example, a smelter or coal fired power plant (serving as the source of SO_2)⁹. This has also been proposed by Outotec and is termed the Outotec[®] Open Cycle (OOC, Figure 1.8), so as to produce hydrogen and sulphuric acid as products for sale^{81, 82}, while reducing the amount of vented SO_2 . In essence, hydrogen is produced as part of a remediation process of this detrimental environmental pollutant, and a portion of the energy input for the remediation process is returned in the form of hydrogen.

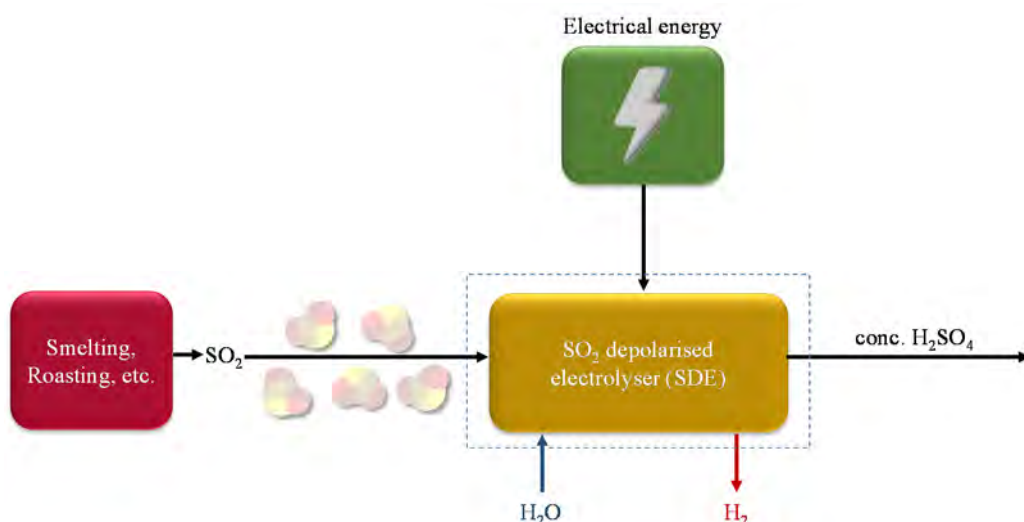


Figure 1.8: Simplified schematic of the Outotec[®] Open Cycle.

Although numerous studies have been conducted with the aim of elucidating the mechanism governing the oxidation of SO_2 , conflicting conclusions exist in literature, dating back to around 1965^{47, 83, 84}. This widespread disagreement can, in part, be attributed to a lack of adequate electrocatalyst surface control, as well as a lack of attention to a variety of sulphur species taking part in the overall mechanism³⁰. The complexity of the mechanism of SO_2 oxidation most probably varies depending on the electrode material and on the concentration/pH of the solution. This has recently (2010) been highlighted and confirmed by a review article published by O'Brien *et al.*⁸⁵. Portrayed in Table 1.2 is (i) a possible pathway, and (ii) the most widely accepted pathway according to which the oxidation of SO_2 proceeds. These mechanisms all oxidise SO_2 according to the same net chemical reaction. However, they all follow a slightly different reaction pathway, i.e. different intermediate compounds of which the lifetimes are unknown. The different intermediates in themselves lead to mechanistic uncertainty as it is not always known which reaction is the rate determining step, and which intermediate may complicate the expected mechanism by means of participating in possible side reactions³⁰.

Table 1.2: Possible pathways for the oxidation of SO₂.

Possible pathway with M representing an active site on the electrode surface	Widely accepted pathway with modifications	
	SO ₂ (aq) + 2H ₂ O(l) → H ₂ SO ₄ (aq) + 2H ⁺ (aq) + 2e ⁻ (13)	
M + H ₂ O → MOH + H ⁺ + e ⁻ (10)	A slight modification as suggested by Samec and Weber (1975) ⁴⁴ , is that HSO ₄ ⁻ forms after which combination with one proton occurs.	Another variation, as suggested by Seo and Sawyer (1965) ⁸³ , is that the probability of SO ₂ oxidising to SO ₄ ²⁻ exists, which then subsequently combines with two individual protons.
MOH → MO _{ads} + H ⁺ + e ⁻ (11)		
SO ₂ + H ₂ O + MO _{ads} → H ₂ SO ₄ + M (12)		

A thermodynamic study on a sulphur-water system conducted by Valensi *et al.*^{86, 87}, reports on the existence of stable and metastable sulphur species. Compounds classified as metastable can undergo further oxidation or reduction, depending on what is thermodynamically favourable. Sulphur, H₂SO₄ and hydrogen sulphide (H₂S) can therefore be categorised as stable compounds whereas S₂O₃²⁻, S₂O₄²⁻, dithionate ions (S₂O₆²⁻) and tetrathionate ion (S₄O₆²⁻), are all metastable compounds in acid solution. All of these compounds, except tetrathionate ions, can be produced electrochemically⁸⁸, and only the dithionate ion can be produced from the oxidation of SO₂⁸⁶. In turn, the dithionate ion can be reduced to form H₂SO₃ according to reactions 14 to 16.



As H₂SO₃ can presumably only be formed under cryogenic conditions and the fact that it is highly unstable at both room and elevated temperatures (resulting in it to have never been isolated), the pathway is highly unlikely⁸⁹. Within the SDE, both the anode electrocatalyst and the membrane electrode assembly (MEA) are susceptible to the interference of these unwanted compounds that can be produced in the mechanism(s) of oxidising SO₂, with sulphur and H₂S posing the greatest threat. Sulphur deposition can proceed electrochemically according to reactions 17 to 19^{30, 41}, or non-electrochemically according to a disproportionation reaction (reaction 20), as reported by Noyes and Steinour⁹⁰.



This reaction (reaction 20) does, however, proceed at a negligible rate, except at elevated temperatures, i.e. over 100 °C, which is within the operating temperature of the SDE. Indicated in the Pourbaix diagram for the sulphur-water system at 100 °C in Figure 1.9, it is clear that both sulphur and H₂S are stable within the pH and potential operating range of the SDE (section 1.2.4).

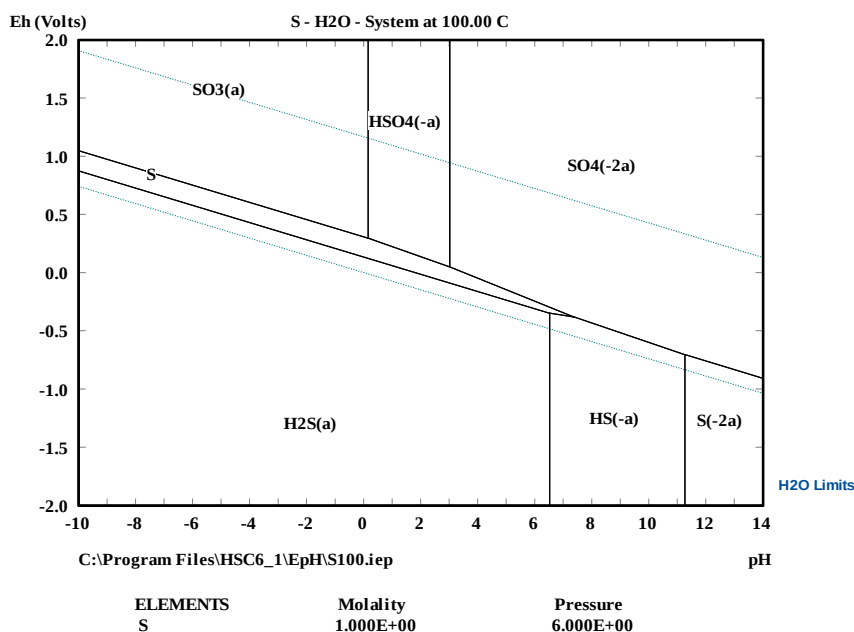
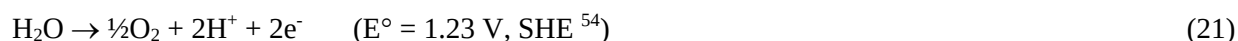


Figure 1.9: Pourbaix diagram of the sulphur water-system at 6 bar pressure (HSC 6 software) ³⁰.

Various studies have proved that the presence of adsorbed sulphur species on the surface of electrocatalyst materials changes the reactions considerably ^{41, 91, 92}. It is therefore evident that sulphur species play a key role in the efficient performance of the SDE, effecting both electrochemical oxidation and reduction at the anode and cathode, respectively ³⁰. Understanding these processes will benefit the efficient performance of the SDE, and with more research current disagreements, especially on the mechanism of SO₂ oxidation, may systematically be resolved.

1.2.4 Electrocatalyst research for the SDE

Interest in the HyS cycle (Figure 1.7) results from the fact that, whereas the anodic reaction for regular water electrolysis (reaction 21) occurs at a standard potential of 1.23 V (SHE)⁹³, the anodic reaction for the SDE (reaction 6) occurs at a standard potential of 0.17 V (SHE)⁹⁴ or 0.157 V (SHE)⁹⁵. This translates into an energy gain of more than one volt, which makes SO₂ depolarised electrolysis (as a means of producing hydrogen) more favourable^{24, 79}.



In the SDE two electrocatalysts are required on either side of the membrane, one for the anode and another for the cathode. In comparison, the rate of electrochemical reaction at the cathode is much higher than the rate of reaction occurring at the anode, resulting in the anode attributing to the inefficiencies in the effective operation of the SDE^{23, 41}. For the SDE an optimal operational target of 500 mA.cm⁻² at a cell potential of approximately 0.6 V has been proposed by Gorensek and Summers^{24, 96}. This target has reportedly been achieved by Staser *et al.*⁹⁷ employing a gaseous SO₂ feed design, although no additional reports supporting this finding could be obtained. This target can potentially be achieved through the development of an effective electrocatalyst for the anodic electro-oxidation of SO₂ and in that regard the properties of the anode are regarded as pivotal for improving the entire HyS process^{68, 98}.

With regard to electrocatalysts investigated for the electrochemical oxidation of SO₂, a limited number of studies were conducted on this topic over the years, especially for multicomponent electrocatalysts. Seo and Sawyer (1965) studied this reaction on platinum and gold electrodes and made comparisons with carbon paste and boron carbide. They employed voltammetric, chronopotentiometric and galvanostatic measurement and reported on the effects of pre-conditioning and electrolyte pH on the mechanism of SO₂ oxidation. Two mechanisms were suggested, the one a pure electron-transfer process and the other a chemical oxidation by means of a metal oxide forming electrolytically. The electron-transfer process is, however, predominating for active platinum and active gold⁸³. A study conducted by Comtat and Mahenc (1969)⁹⁹, on quantitative determinations of current/potential characteristics for various proposed SO₂ mechanisms, confirmed the findings of Seo and Sawyer (1965)⁸³. The findings of Seo and Sawyer and that of Comtat and Mahenc can be extended to the work done by Wiesner (1973) when employing catalyst-containing carbon electrodes (i.e. aluminium-vanadium mixed oxides with traces of platinum)¹⁰⁰.

Samec and Weber (1975) studied the oxidation of SO₂ on both a stationary⁴⁴ and rotating⁴⁵ gold electrode and emphasised the importance of pretreatment of the electrode. Pretreatment was observed to strongly effect the rate of SO₂ oxidation. This effect is connected to the formation of two different forms of adsorbed “reduced SO₂”, apparently adsorbed S and H₂S, reducing at potentials below +0.4 V (SHE).

Appleby and Pinchon (1979) conducted a systematic investigation of the mechanism of SO₂ oxidation on platinum (smooth and high surface area) in concentrated H₂SO₄, at different concentrations and temperatures, not exceeding a pressure of 1 atm. The oxidation of SO₂ was found to be extremely complex,

highly irreversible and is kinetically second order for both SO₂ and water ⁴⁷. Appleby and Pinchon (1980) investigated noble metals and found Pt to perform better than Pd ⁴⁸. They also found carbon materials (graphites and carbides) to be catalytically inactive, and activated carbon and carbon black as intermediately active, with regard to the oxidation of SO₂. Work done by Lu and Ammon (1980) ⁵⁰ supports the findings of Appleby and Pinchon (1980), with both studies suggesting the use of catalysed carbon as catalyst support for best results ^{41, 101}. Included in the work of Lu and Ammon (1980) ⁵⁰ was the investigation of the electrocatalytic activities of pre-anodised electrodes of Pt, Au, Ru, Pd, Ir, Re, and Rh for the oxidation of SO₂. Pd and PdO_x containing catalysts were identified as performing better than Pt.

Struck *et al.* (1980) studied the oxidation of SO₂ as a function of H₂SO₄ concentration, pressure and temperature and reported on the activity of various heterogeneous and homogeneous catalysts. About fifty non-noble heterogeneous catalysts (seen as cheap materials) were tested and did not show promising results for the oxidation of SO₂. Included in these heterogeneous catalysts are borides, nitrides, sulphides, carbides, bronzes, organic catalysts, tungsten (W) and cobalt (Co), in the form of powders adsorbed on graphite felt. In the form of solid materials, Ti, Nb, Zr, Ta, Pb, Mo and Duriron were investigated. Untreated graphite and vitreous carbon were also found to be inactive with only activated carbon showing response to oxidising SO₂. Noble metals were also listed as heterogeneous catalyst, and did show activity; however, noble metals do not qualify as cheap materials and hence focus was shifted to homogeneous materials. The most promising homogeneous catalyst exhibiting good performance for oxidising SO₂, was graphite plus very small amounts of hydrogen iodide (HI) in the electrolyte ⁹⁴.

A variety of Pt loadings supported on porous graphite sheet electrodes were investigated for the oxidation of SO₂ employing various SO₂ concentrations by Lyke and Langer (1991). Controlled reductive pre-treatment of the porous electrodes resulted in the formation of a sulphur-modified platinum surface, which resulted in enhanced steady-state oxidation ¹⁰². This effect is, however, not limited to platinum supported on graphite electrodes, but seems to be a general observation for platinum electrodes with high surface areas ¹⁰².

A study conducted by Lee and Langer (1995) found that adding a small amount of Al to Pt, supported on carbon black, resulted in an electrocatalytic activity increase for SO₂ oxidation. Quijada *et al.* (1995) reports on the electrochemical behaviour of aqueous SO₂ at Pt electrodes by employing cyclic voltammetry and in situ Fourier transform infra-red (FTIR). S(VI) was detected as being generated during both the forward and reverse sweeps with (bi)sulphate detected as the only SO₂ oxidation product ¹⁰³. Quijada *et al.* (2000) also reported on an interesting observation, that of polycrystalline gold performing better than generally accepted Pt. The best performance of gold was observed when the gold surface was covered with a 0.5 adlayer of S, thus suggesting that sulphur was in part responsible for the observed catalytic behaviour ¹⁰⁴.

A study conducted by Colon-Mercado and Hobbs (2007) found that Pt/C exhibited lower potentials with higher currents than Pd/C, which furthermore proved the enhanced catalytic activity of Pt above that of Pd, except for the conflicting observation made by Lu and Ammon ⁵⁰. The dissolution of Pd was also observed

by the authors, suggesting that Pd is less stable than Pt. A report compiled by Colon-Mercado *et al.* (2010) for SRNL examined the activity of Pt based electrocatalysts in 30 wt% H₂SO₄. Pt alloyed with non-noble transition metals such as Co, Cr and Fe exhibited increased activity while Pt alloyed with noble metals, such as Ir or Ru, exhibited a decrease in both kinetic activity and stability¹⁰⁵.

O'Brien *et al.* (2012) focussed on Pt and Au substrates, with Au being more active than Pt. The authors furthermore stated that Au electrocatalysts did not need to be modified with sulphur to exhibit high activity⁹⁵.

In addition to the study conducted by Lee and Langer (1995), one of the first studies conducted on a two-component catalyst, and the preliminary study conducted by SRNL¹⁰⁵, Xue *et al.* (2014) conducted a study on Pt-based bimetallic catalysts. Included in the investigation were Pt-Pd/C, Pt-Rh/C, Pt-Ru/C, Pt-Ir/C, and Pt-Cr/C. The catalyst exhibiting the highest electrocatalytic activity for SO₂ depolarised electrolysis was 60 wt% Pt-Cr/C⁹⁸.

Santasalo-Aarnio *et al.* (2016) proved that bipolar plates covered with a thin layer of Au could be utilised as an economic catalysts for SDe. The Au coated plate served a bifunctional role: providing an electrocatalytic active surface and prevents corrosion of the underlying stainless steel plate⁸¹.

The majority of studies on noble metals as catalysts, consistently found Pt to have high activity, although the results were somewhat mixed for the other noble metals⁴¹. Despite all these observations, carbon supported platinum electrodes are commonly used in the MEA assemblies of the SDE^{41, 98}. Operating at high temperatures and high sulphuric acid concentration, the anode electrocatalyst has to be not only active, but must also be able to withstand this harsh operating environment. While platinum is generally considered the standard anode electrocatalyst for the SDE^{28, 41}, efforts are underway to find an electrocatalyst other than platinum. In an effort to reduce platinum content it could be alloyed/combined with either a more cost effective noble metal(s) or base metal(s). Although results obtained for platinum alloyed with non-noble metals show good activity¹⁰⁵, platinum alloyed with noble metals show similar to or even higher activity than that of pure platinum. As studies on this subject are limited⁹⁸ the need exists to research and develop new as well as improved electrocatalysts for the electro-oxidation of SO₂^{22, 106, 107}. The development and optimisation of new and/or improved materials in general recently gained a fair amount of interest and are driven by the challenges renewable energy poses in the near future¹⁰⁸.

1.2.5 Combinatorial and high-throughput methods

A prominent observation of the 21st century is that many technological solutions depend on the development and/or optimisation of materials with new and/or improved properties¹⁰⁹, which ideally can be economically attractive, exhibit enhanced performance and that are environmentally friendly. A very powerful means of parallel synthesis, property characterisation and identification of novel functional materials is by employing a combination of high-throughput and combinatorial methodologies. The recognition of combinatorial and high-throughput experimentation, especially in the field of materials discovery and optimisation, results from avoiding time-consuming synthesis and testing of numerous

material candidates accompanied by the increase in complexity exhibited by the structural and functional properties of materials ¹¹⁰. In material science, composition, morphology, microstructure and preparation to name a few, all contribute to the properties exhibited by a material. HTC enables the fabrication of a great number of materials and offers extremely powerful abilities of characterising a vast amount of properties, resulting overall in accelerated material development ¹⁰⁹. The terms “combinatorial” and “high-throughput” can interchangeably be used for describing all types of automated parallel and/or rapid sequential synthesis and evaluation process permutations ¹¹⁰. One of the very first remarks, with regard to multiple-sample syntheses and testing, was made by Hanak in 1970 who emphasise the fact that the search for new materials suffers due to the fact that handling one sample at a time, in the process of synthesis and chemical testing, is an expensive and time-consuming approach, which prevents the researcher to take full advantage of his/her talents and keeps the level of progress low ¹¹¹. He suggested the abandonment of the tedious efforts of single sample synthesis and testing, and the adoption of methods to process multiple materials simultaneously. As the need to explore efficient and systematic means of searching for alternative binary, ternary and higher materials grew, the field of combinatorial science gained growing interest ^{107, 112-116} and really took off around 1995 ^{110, 117} with the majority of HTC developments happening within the pharmaceutical and medical fields ¹⁰⁹ (Table 1.3).

Table 1.3: A short list of some review publications on the topic of HTC.

Title	Year	Ref
“Generation and utilization of synthetic combinatorial libraries”	1995	118
“Combinatorial libraries of transition-metal complexes, catalysts and materials”	1998	119
“Combinatorial libraries: studies in molecular recognition”	1998	120
“Transition-metal-mediated reactions in combinatorial synthesis”	1998	121
“Catalyst discovery through combinatorial chemistry”	1998	122
“Combinatorial catalyst discovery”	1999	123
“Combinatorial materials science and catalysis”	1999	124
“Combinatorial chemistry: a tool for the discovery of new catalysts”	2001	125
“High-throughput approaches to catalyst discovery”	2003	126
“Combinatorial and high-throughput materials science”	2007	127
“A review of high throughput and combinatorial electrochemistry”	2011	109
“High speed screening technologies in heterogeneous catalysis”	2011	128

Table 1.3: ... continued

“Combinatorial and High-Throughput Screening of Biomaterials”	2011	129
“Combinatorial and High-Throughput Screening of Materials Libraries: Review of State of the Art”	2011	110
“Application of parallel synthesis and high-throughput characterisation in photocatalyst discovery”	2011	130
“Liquid-phase combinatorial library synthesis: recent advances and future perspectives”	2014	131
“Combinatorial electrochemistry–Processing and characterization for materials discovery”	2015	132

Taking into account the vast number of starting materials, measurement parameters and testing conditions, several millions of catalysts could be investigated. However, even with the availability of existing tools aimed at achieving exactly this, it has to be realised that the testing of every possible candidate will still be too costly, result in massive amounts of instant data and is time prohibitive. This process should therefore be governed by scientific intuition, applicability and a little serendipity. Thus, planning the HTC approach is essential and four general classes of HTC planning can be summarised ¹¹⁰: (i) a traditional statistical design approach with the aim of generating reliable conclusions from a limited number of experiments, (ii) characterisation of a group of samples by employing a “diversity” of methods to a specific area of interest, (iii) using “search” methods by employing a sequence of experiments to intelligently work through the experiment space, and (iv) combining different (hybrid) methods to develop a series of experiments with an increased focus on the expected outcome ¹³³⁻¹³⁷.

HTC affords the ability to discover and optimise new materials that have broad applicability, with the areas of biomaterials, polymer-based industrial coatings, electronic and functional materials, sensing materials and catalysis being mostly impacted ¹¹⁰. As approximately 90% of all chemical processes are catalysed ¹³⁸ a lot of effort is poured into the design and optimisation of new and improved catalysts (heterogeneous, homogeneous or biocatalysts) for specific applications. To this regard HTC has been identified as indispensable ¹¹⁰. For heterogeneous catalysts in particular, the number of possible catalyst variations is staggering due to the great number of elements on the periodic table. If the heterogeneous catalysts are solids it will be even more complex to specify them completely, as solid state materials are characterised not only by composition, but also by crystallinity, interphase properties, bulk and surface property differences, polymorphic form and much more, which increases the diversity of possibilities on a systematic basis. Although various strategies have evolved over time to assist with heterogeneous catalyst design ^{110, 139-141}, one means of reducing the number of possible catalysts to be tested is by employing computational

chemistry¹⁴², and another by applying known knowledge about the system to be catalysed and required performance outcomes when planning/designing catalysts. It has to be stressed, however, that a HTC approach (with significant planning and aiming at parallelisation) does not always allow for highly accurate and precise experimentation compared to conventional experimentation (mainly linear and sequential)¹⁰⁶.¹²⁷ It is aimed rather at investigating observable trends in the material of interest, such as catalytic activity for example, subsequent to which the initial observation is confirmed and optimised with more precise kinetic data^{107, 108} that have been obtained by means of more traditional methods.

HTC is a rather new paradigm for many electrochemical researchers^{109, 117, 132} and the supremacy of HTC approaches makes it very attractive in pursuing high-throughput combinatorial electrochemistry¹⁰⁹ as electrochemical methods allow precise control of voltage and current whether manual or by automated programming. One of the first examples of employing combinatorial electrochemistry involved generating a 645-member electrode array of Pt, Ru, Os, Ir and Rh, employing a modified inkjet printer with metal salt 'inks' and subsequently screening the catalysts for methanol oxidation¹⁴³. Numerous studies have followed in which electrocatalysts were investigated for a number of chemical reactions¹⁴⁴⁻¹⁴⁶. However, no research has been conducted on high-throughput combinatorial electrocatalyst development for SO₂ electro-oxidation as part of the HyS cycle.

1.3 Problem statement

The current state of energy supply, demand, sustainability and legislation is a global matter of urgency/concern. In an attempt to avoid future detrimental issues in the area of energy and environmental security, it is necessary to evaluate alternative technologies. With the aim of producing clean and sustainable energy from renewable resources, hydrogen as an energy carrier, among various possible energy systems, is considered a possible and viable solution. The future economic supply of environmentally clean energy is, however, not a certainty¹¹ and requires immediate commitment and evolution in research, development and application. One possible alternative method, which has already been proposed in the 1970s by the Westinghouse Corporation, is the three step closed HyS cycle as a means to produce clean hydrogen from water and SO₂ gas. The HyS cycle process releases no harmful pollutants that could impact negatively on humans and the environment as it converts a harmful pollutant SO₂(g) to H₂SO₄ and H₂. Basic parameters which influence the successful operation of the HyS cycle can be categorised as follows: (a) *parameters to be increased*: (i) kinetics of SO₂ oxidation, (ii) catalytic activity and stability of the catalysts, and (iii) membrane ion conductivity; (b) *parameters to be decreased, reduced or eliminated*: (i) overpotential, (ii) cell resistance (membrane and electrolyte), and (iii) side reactions. Of these parameters, the electrochemical oxidation of SO₂ at the anode of a SDE (within the HyS cycle), is the current area of interest as it is the critical step in the overall process. The anode kinetics in comparison to the cathode kinetics, are much slower which contributes to the overall 'inefficient' operation of the HyS cycle. Improving the performance of the SDE will therefore result from the identification of a suitable anodic

electrocatalyst material that can compete or replace the currently employed pure Pt for the electro-oxidation of SO_2 . This will serve to improve electrode kinetics, i.e. lowering the overpotential, increasing current outputs, as well as increasing the operational lifetime of the electrocatalyst. As discussed in section 1.2.4 only a limited number of papers have been published over the last 50 years related to electrocatalyst development with Pt still being regarded as the catalyst of choice. From the published literature it has been ascertained that Pd competes to some extent with Pt in the electro-oxidation of aqueous SO_2 , while the addition of small amounts of Al would seem to alter electrocatalytic activity for the better for this reaction. This research project therefore aims to investigate (i) pure Pt, (ii) Pt combined with another noble metal, with specific reference to Pd, and (iii) Pt combined with Pd as well as a third base metal, with specific reference to Al, for the electro-oxidation of SO_2 by employing a combination of HTC and traditional methods. The electrocatalysts will be ranked based on onset potential, current output and stability with the results being elucidated by characterisation methods such as SEM, EDX, XRD, AFM and XPS.

1.4 Aim and objectives

In view of the above-mentioned, the following comprehensive aim has been compiled:

Fundamentally investigating and developing potential electrocatalysts, for the electro-oxidation of $\text{SO}_2(\text{aq})$, with the focus on reducing the amount of Pt by means of combining Pt with either a less expensive noble metal and by employing a less expensive non-noble metal, while still maintaining (or increasing) (i) catalytic activity, and (ii) sufficient stability.

To achieve the above-mentioned aim, the following objectives are set:

- i. Investigation of the available literature that will serve as a guideline for electrocatalyst development, characterisation and evaluation with regard to the electrochemically catalysed oxidation of aqueous SO_2 .
- ii. Preliminary investigation of a sputtered Pt electrocatalyst compared to an industrially manufactured Pt electrocatalyst together with the associated literature.
- iii. Designing and establishing a feasible HTC methodology by employing a physical vapour deposition (PVD) combinatorial sputtering system for electrocatalyst development in conjunction with a multiple channel potentiostat for high-throughput characterisation.
- iv. Commissioning of a specialised electrochemical cell for testing multiple working electrodes simultaneously (up to 64 working electrodes).
- v. Defining specific parameters for effective identification and evaluation of electrocatalysts for further traditional investigation.
- vi. Electrochemically investigating the onset potential, current output and stability of the selected electrocatalysts on standard electrochemical equipment.
- vii. Characterising physical properties of the electrocatalyst materials employing conventional methods (SEM, EDX, XRD, AFM and XPS) in an attempt to elucidate on possible structure-activity relations.

- viii. Comparing and validating (where possible) the results obtained in this study with available results found in literature.

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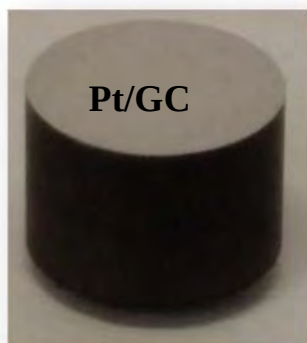
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Chapter 2

The electrochemical oxidation of aqueous SO₂ on sputtered Pt/glassy carbon electrodes*

Chapter overview

A comparative investigation with regard to the activity of an industrial manufactured polycrystalline platinum (PolyPt) electrode and platinum deposited on glassy carbon (GC) electrodes, prepared by sputtering with a physical vapour deposition system (PVD), towards the oxidation of aqueous sulphur dioxide (SO₂), was conducted using a combination of stationary and rotating electrode voltammetric methods. It was found that the thin film Pt/GC catalysed the oxidation of aqueous SO₂ at a lower onset potential, with higher current density and smaller electrochemical active surface area (EASA) compared to PolyPt, indicating better Pt utilisation. The thin film Pt/GC furthermore required a lower activation energy of $E_A = 52.4 \text{ kJ.mol}^{-1}$, compared to $E_A = 56.8 \text{ kJ.mol}^{-1}$ for PolyPt, confirming the sputtered thin film Pt/GC electrode as being a slightly better electrocatalyst for the oxidation of aqueous SO₂.



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2.1 Introduction

Sulphur dioxide electrochemistry has attracted a wide and varied research interest over the last few decades, due to the relevance of this reaction to the HyS cycle. The electrochemical oxidation of sulphur dioxide has been studied extensively on platinum electrodes ¹⁻⁵, which serve to increase the efficiency of the SDE employed in the HyS cycle. Hydrogen is the product evolved on the cathode (reaction 1) of the SDE while sulphur dioxide is oxidised to sulphuric acid and hydrogen ions (reaction 2) on the anode:



O'Brien *et al.* ¹ investigated the influence of various parameters on the electrode behaviour of polycrystalline platinum, which include acid concentration, lower potential limit (E_{low}) and temperature. Activity was divided into three scenarios, which varied between limited, catalytic and inhibited oxidation depending on sulphur coverage and acid concentration. Recently, work done by Steimke and Steeper ^{6, 7} and Sivasubramanian *et al.* ⁸ focused on utilising Pt/C as catalyst on the anode of the SDE as a means to improve the performance of SO_2 oxidation. They found that Pt/C catalysts exhibited improved performance, both from a catalytic and economical point of view, as improved Pt utilisation resulted in a reduction of the amount of Pt used. These Pt catalysts were prepared by mixing 20 wt% Pt/C catalysts powder with NMP (n-methyl-2-pyrrolidone) solution, containing polymeric binder polyvinylidene fluoride (PVDF). In this paper the oxidation of aqueous SO_2 is investigated on platinum deposited on glassy carbon prepared by sputtering in a PVD system and compared to industrially manufactured polycrystalline Pt (Pine Instruments). Sputtering affords one with short preparation times of sputtered electrocatalysts, achieving metal loading in the microgram range, as will be discussed in the experimental section. Sputtering furthermore ensures obtaining pure catalysts in that other synthesis factors that would influence results are circumvented.

2.2 Experimental

2.2.1 Equipment

Potentiostatic and potentiodynamic techniques were carried out using a BioLogic potentiostat (VSP) and processing of data with EC-lab 10.21 software. A three electrode setup was employed that consisted of a saturated calomel electrode (SCE, Radiometer Analytical REF 421) as reference electrode (all potentials reported vs SHE were converted employing the standard SCE literature value of 0.244 V at 25 °C), a spiral Pt wire as the counter electrode and either a platinum (PolyPt) disk insert electrode (Pine Instruments) or sputtered Pt/GC (platinum covered glassy carbon) insert as the working electrode. Both types of working electrodes had a geometrical surface area of 0.196 cm².

2.2.2 Electrode cleaning and preparation

2.2.2.1 Polycrystalline Pt (PolyPt)

The electrode cleaning procedure involved soft polishing on polishing cloths (Pine Instruments) using 5 μm and 0.05 μm alumina particle suspensions, respectively. The electrode was then sonicated in Milli-Q water for 5 min before final electrochemical cleaning in 1 mol.L^{-1} H_2SO_4 that involved repeated cyclic voltammetry (CV) scans between the hydrogen and oxygen evolution regions (see 2.2.4).

2.2.2.2 Pt/GC

The Pt/GC inserts were prepared by polishing the glassy carbon inserts in 4 steps. Firstly coarse paper was used followed by a coarse cloth with final polishing on soft polishing cloths (all Pine Instruments products) using 5 μm and 0.05 μm alumina particle solutions respectively. The inserts were then sonicated in Milli-Q water (10 min), acetone (10 min) and propanol (10 min). Sputtering of the Pt (42 $\mu\text{g.cm}^{-2}$, 19.2 nm) was done by a physical vapour deposition system (PVD Products) with the settings listed in Table 2.1.

Table 2.1: Settings used for sputtering Pt onto glassy carbon inserts.

Parameter	Value
Base pressure	1×10^{-6} Torr
Chamber Pressure	8 mTorr
Argon flow rate	0.015 L.min^{-1}
Power	90 Watt
Time of deposition	1 min

2.2.3 Solutions

A 1 mol.L^{-1} acid solution was prepared by dilution of 95.1 wt% H_2SO_4 (SAAR5885124LP), purchased from MERCK, with Milli-Q water. This solution was degassed with N_2 for 10 min before preconditioning started. A stock solution of 1 mol.L^{-1} Na_2SO_3 (Sigma Aldrich) was used as the SO_2 source (see reaction 3 for in situ production of SO_2). This solution was not degassed prior to addition to the H_2SO_4 and some dissolved oxygen might be present as a result. All experiments were conducted in a water-jacketed electrochemical cell (100 ml) with the temperature controlled through an external circulation water bath (Julabo F12 ED).



2.2.4 Procedures

Electrode preconditioning procedures involved scanning the electrode between 0.041 V vs SHE and 1.441 V vs SHE, starting at E_{OCP} (open circuit potential) with a scan rate of 50 mV.s^{-1} for 25 cycles. Secondly, three cycles were scanned, changing only the anodic potential to 1.741 V vs SHE and lastly the first step was repeated but only for three cycles, hence the 28 cycles reported in Figure 2.1. Linear sweep voltammetry (LSV) $E_{\text{low}} = 0.2 \text{ V vs SHE}$ to 1.441 V vs SHE (based on the results O'Brien *et al.* obtained¹) runs were conducted at different rotation rates (0 rpm, 200 rpm, 600 rpm, 1500 rpm and 2500 rpm) and different temperatures (298.15 K, 308.15 K, 318.15 K and 328.15 K) for investigating the oxidation of SO_2 . The PolyPt insert was polished between runs as described in the electrode cleaning section. With regard to the Pt/GC inserts, a new Pt/GC insert was used for each run.

2.3 Results and discussion

2.3.1 Cyclic voltammetry

Figure 2.1a and Figure 2.1b show the typical consecutive CVs for PolyPt and Pt/GC, respectively. The CVs were performed as a means to assess the stability (short term, long term stability is addressed in Chapter 4 and Chapter 5) and activity (active area) of the surfaces in H_2SO_4 as electrolyte. The CVs reveal that the hydrogen desorption region increased and the strong and weak hydrogen desorption peaks became more distinct with cycling for both electrocatalysts. A clear difference between the Pt/GC and PolyPt electrodes were the smaller, almost non-existing strong and weak hydrogen adsorption/desorption peaks noticed for Pt/GC, which gradually formed as the cycling proceeded, which implies that the sputtered Pt/GC electrode had not been crystalline at the outset, but that a degree of crystallinity was induced through preconditioning.

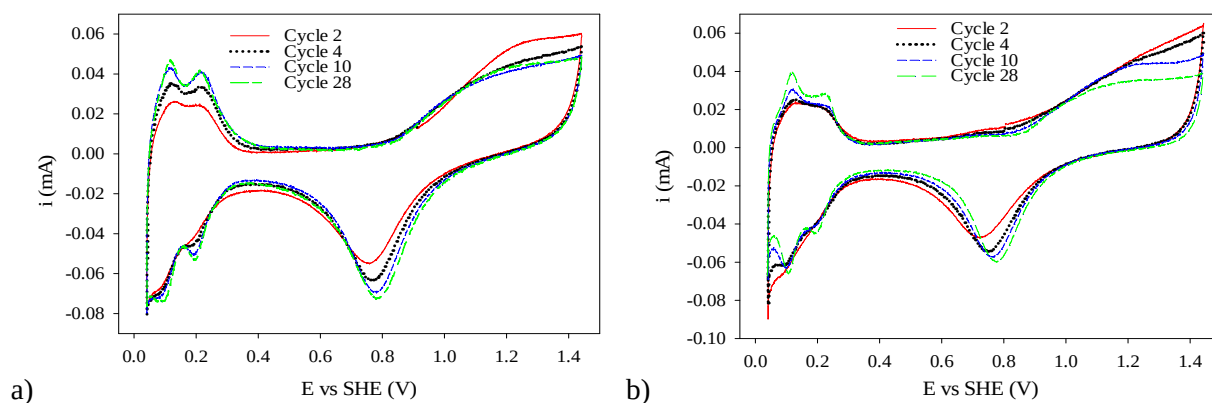


Figure 2.1: Cyclic voltammograms after consecutive cycling for a) PolyPt and b) Pt/GC in $1 \text{ mol.L}^{-1} \text{H}_2\text{SO}_4$ purged with N_2 at room temperature at a sweep rate of 50 mV.s^{-1} . The Pt catalyst layer on the GC consists of a total metal loading of $42 \text{ }\mu\text{g.cm}^{-2}$.

The electrochemical active surface area (EASA) value for both Pt/GC and PolyPt was determined for the hydrogen desorption region by integration of the current over time in the potential region of 0.04 – 0.45 V vs SHE and also subtracting the double-layer charging current from the total hydrogen desorption current. The values obtained were then divided by the adsorption charge corresponding to formation of a hydrogen monolayer, 210 $\mu\text{C}.\text{cm}^{-2}$ for Pt ⁹. The resulting EASA values obtained for Pt/GC and PolyPt were 0.5 cm^2 and 0.781 cm^2 , respectively, resulting in surface roughness values ($R_s = A_{\text{real}} / A_{\text{geo}}$) of 2.55 and 3.98, respectively. These EASA values were employed to convert the current values (mA) to current density values ($\text{mA}.\text{cm}^{-2}$) for the results given in Figure 2.2.

2.3.2 Linear sweep voltammetry

Work conducted by O'Brien *et al.* ¹ include an in-depth study of the influence different experimental parameters have on the behaviour of the electrode towards the reaction of interest. In their study the effect of E_{low} and acid concentration were studied extensively. For our study, based on their results, we chose 0.2 V vs SHE as our E_{low} in 1 $\text{mol}.\text{L}^{-1}$ H_2SO_4 electrolyte solution for all our experiments due to the substantial increase in catalytic activity compared to the other E_{low} values and acid concentrations. In order to compare the electrodes relative to one another and to literature, in terms of onset potential, the two most employed methods for deriving onset potential were employed. The first method involves determining the onset potential from the anodic sweep and transforming the LSV graph (Figure 2.2) into an inverse Tafel plot (overpotential (η) vs $\log |i|$) and taking the y-axis intercept as described by O'Brien *et al.* ¹. The second method involves calculating the onset potential using the intercept of two straight lines tangent to the LSV curve as described by Cooper & McGinn ¹⁰. The onset potentials are listed in Table 2.2 and it is evident that the sputtered Pt/GC shows competitive behaviour in comparison with PolyPt.

Table 2.2: Comparison of onset potentials for different electrodes.

Electrode	Supplier	Onset potential (V vs SHE)		Conditions
		O'Brien <i>et al.</i> ²	Cooper & McGinn ¹⁰	
Pt/GC	Custom made	0.436 ± 0.012	0.575 ± 0.002	$E_{\text{low}} = 0.2 \text{ V vs SHE}$, 1 $\text{mol}.\text{L}^{-1}$ H_2SO_4 , 298.15 K, 0 rpm, 100 mM SO_2 , 5 $\text{mV}.\text{s}^{-1}$
PolyPt	Pine instruments	0.471 ± 0.004	0.585 ± 0.003	$E_{\text{low}} = 0.2 \text{ V vs SHE}$, 1 $\text{mol}.\text{L}^{-1}$ H_2SO_4 , 298.15 K, 0 rpm, 100 mM SO_2 , 5 $\text{mV}.\text{s}^{-1}$
PolyPt	Pine Instrument-E4 series	0.464 ²	N.A.	$E_{\text{low}} = 0.2 \text{ V vs SHE}$, 1 $\text{mol}.\text{L}^{-1}$ H_2SO_4 , $295.15 \pm 1 \text{ K}$, 0 rpm, 100 mM SO_2 , 1 $\text{V}.\text{s}^{-1}$ ²

Comparing the RDE data for both the PolyPt and Pt/GC (Figure 2.2) it is clear that they do not reach diffusion limited conditions and become inhibited at $E > 0.9 \text{ V}$. From the current density values (Figure 2.2) it is clear that Pt/GC produces higher current densities with a smaller EASA compared to PolyPt, which

means that Pt utilisation on the Pt/GC is better than on the PolyPt. One can therefore conclude that Pt/GC is performing better than the PolyPt electrocatalyst.

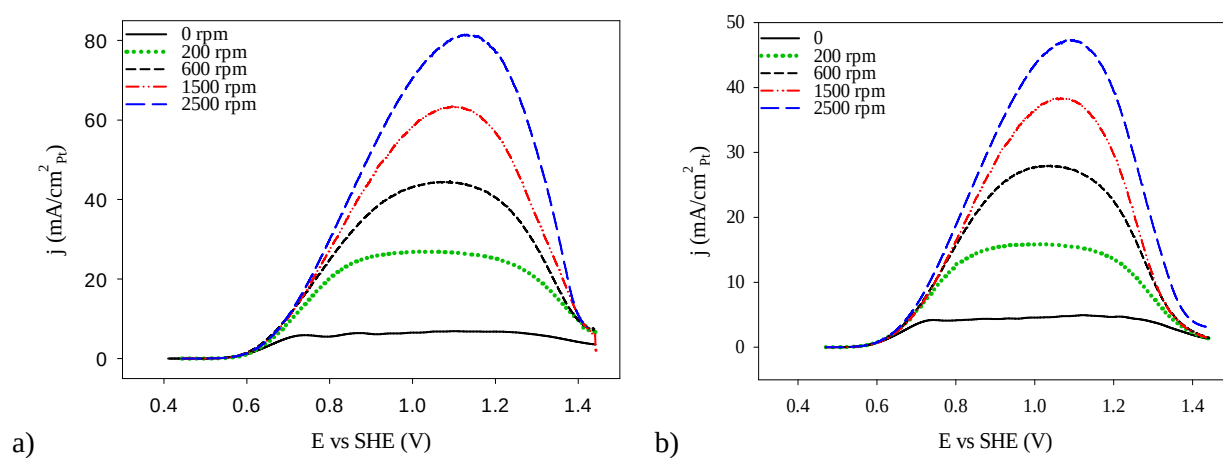


Figure 2.2: RDE behaviour of a) Pt/GC and b) PolyPt electrodes. Conditions: 1 mol.L⁻¹ H₂SO₄, 100 mM SO₂, 5 mV.s⁻¹, E_{low} = 0.2 V vs SHE, 298.15 ± 1 K.

2.3.3 Exchange current density and activation energy

The effect of temperature on the reaction was quantitatively analysed by deducing the activation energy from the results obtained from Tafel plots. Tafel plots (not shown) have been constructed from the LSV runs at 0 rpm at different temperatures. From these Tafel plots the exchange current density, j_0 (mA.cm⁻²), was obtained as described by Bard and Faulkner ¹¹ (See Table 2.3), and used to calculate the standard heterogeneous rate constant, k^0 (cm⁻¹.s⁻¹), by employing the following equation ¹.

$$j_0 = F A k^0 c_{\text{SO}_2}$$

where F is the Faraday constant, A is the active area and c_{SO_2} the SO₂ concentration.

Table 2.3: Exchange current densities (mA.cm⁻²) for the Pt/GC and PolyPt electrodes at different temperatures.

Temperature (K)	Exchange current density (mA.cm ⁻²)	
	Pt/GC	PolyPt
298.15	3.4×10^{-12}	6.4×10^{-11}
308.15	7.9×10^{-12}	1.0×10^{-10}
318.15	1.1×10^{-11}	1.6×10^{-10}
328.15	2.5×10^{-11}	5.8×10^{-10}

The Arrhenius plot (Figure 2.3) was subsequently constructed from the natural log of the calculated k^0 value and the inverse of the temperatures according to the following equation:

$$\ln k^0 = \ln(M) - \frac{E_a}{RT}$$

where E_a is the activation energy of the reaction (J.mol^{-1}) and M a constant.¹¹ From this analysis it was found that the Pt/GC (52.4 kJ.mol^{-1}) has a lower activation energy compared to PolyPt (56.8 kJ.mol^{-1}), which in turn correlates very well with the literature value of 51 kJ.mol^{-1} . This is not a significant difference between the two electrocatalysts, but still proves the potential that sputtered Pt/GC electrocatalysts exhibit toward catalyzing the electro-oxidation of SO_2 .

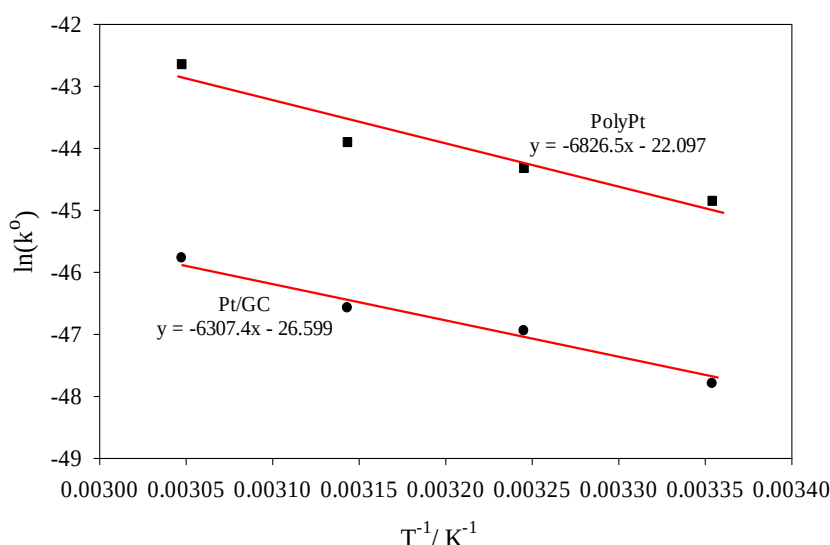


Figure 2.3: Arrhenius plots for Pt/GC and PolyPt. Conditions: 100 mM SO_2 in 1 mol.L⁻¹ H_2SO_4 with $E_{\text{low}} = 0.2 \text{ V}$ vs SHE.

2.4 Conclusion

The catalytic activity and stability of Pt/GC and PolyPt were studied in a 1 mol.L⁻¹ sulphuric acid solution at different rotation rates and at temperatures ranging from 298.15 K to 328.15 K. The results showed that both Pt/GC and PolyPt exhibited good stability (short term) and activity, but that PolyPt was slightly less active for the oxidation of SO_2 . Lower onset potentials and higher current densities for the electro-oxidation of SO_2 on Pt/GC compared to PolyPt were obtained. Furthermore, the activation energy for the oxidation of SO_2 on Pt/GC was a little less than that of PolyPt, which supports the potential sputtered electrocatalysts exhibit for electrocatalysis. Future work will include annealing of the glassy carbon electrocatalysts to investigate potential increase in stability, as well as activity of the Pt/GC electrodes. The main focus of

future work also includes investigating combinations of metals (Pt:X, X being another metal), being either binary, ternary, or quaternary metallic/alloys of the combinations.

References

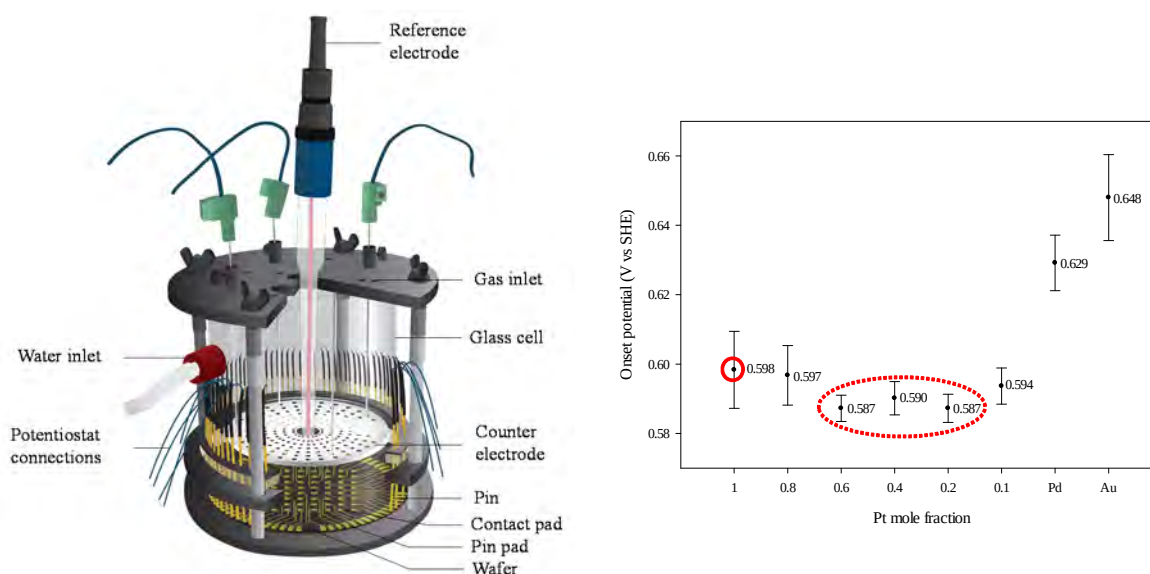
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Chapter 3

Combinatorial plasma sputtering of Pt_xPd_y thin film electrocatalysts for aqueous SO_2 electro-oxidation*

Chapter overview

A combinatorial sputtering system, based on magnetron enhanced plasma sputtering, was employed in the syntheses of Pt_xPd_y thin film catalysts and a multi-channel potentiostat allowed for high-throughput parallel screening of the deposited electrocatalysts for the electro-oxidation of aqueous sulphur dioxide (SO_2). Employing onset potential as the screening criterion it was found that three Pt_xPd_y bimetallic combinations exhibited satisfactory performance with the best compositions being that of Pt_3Pd_2 and PtPd_4 . Both these combinations exhibited the same lower onset potential of 0.587 ± 0.004 V, SHE compared to that of pure Pt (0.598 ± 0.011 V, SHE) and in addition contain less Pt.



*A. Falch, V. Lates and R.J. Kriek, Combinatorial Plasma Sputtering of Pt_xPd_y Thin Film electrocatalysts for Aqueous SO_2 Electro-oxidation, *Electrocatalysis*, 2015, **6**, 322-330.

3.1 Introduction

The HyS cycle, proposed by the Westinghouse Corporation ¹, has received a fair amount of attention as a thermochemical water splitting cycle ²⁻⁴. Sulphuric acid is thermally decomposed to produce aqueous sulphur dioxide (reaction 1), which is fed to a SDE and electro-oxidised at the anode to again produce sulphuric acid, as well as hydrogen ions (reaction 2). The hydrogen ions migrate through the membrane of the electrolyser to the cathode where they are reduced to hydrogen gas (reaction 3) while the electrochemically produced sulphuric acid is recirculated back to the decomposition reactor. The net SDE reaction therefore involves the conversion of aqueous sulphur dioxide into sulphuric acid and hydrogen gas (reaction 4), while the net HyS cycle reaction is that of water being split into hydrogen and oxygen (reaction 5):



Interest in the HyS cycle results from the fact that, whereas the anodic reaction for regular water electrolysis (reaction 6) occurs at a standard potential of 1.23 V, SHE ⁶, the anodic reaction for the SDE (reaction 2) occurs at a standard potential of 0.17 V, SHE ⁵, which translates into an energy gain of more than 1 V.



The possibility, however, exists for the SDE to be employed as a SO₂ sink, whereby SO₂ together with water is used as feedstock to convert an environmental pollutant into useable commodities, i.e. sulphuric acid and hydrogen gas. In contrast to regular water electrolysis systems the SDE runs at a lower cell voltage and some of the electrical energy input is ‘returned’ in the form of an energy carrier, i.e. hydrogen gas, which translates into a substantial economic benefit ⁷.

For the SDE an operational target of 500 mA.cm⁻² was set at a cell potential of approximately 0.6 V ⁸. This target can only be achieved through the development of an effective electrocatalyst for the anodic electro-oxidation of SO₂ and in that regard the properties of the anode is regarded as pivotal for improving the entire HyS process ⁴. While platinum is still considered the standard anode catalyst for the SDE, several studies have been conducted on the subject, which amongst others include those listed in Table 3.1. As is the case with the oxygen reduction reaction in a fuel cell, efforts are underway to find an electrocatalyst other than platinum. Operating at about 100 °C and high sulphuric acid concentration, the

anode electrocatalyst has to be, not only active, but must also be able to withstand this harsh environment. In an effort to reduce platinum content it could be alloyed with either a more cost effective noble metal or base metals. Although results obtained for platinum alloyed with non-noble metals show good activity ³, platinum alloyed with noble metals show similar to or even higher activity than that of pure platinum. However, studies on this subject are limited ⁴.

Table 3.1: Studies on the catalyst of the anode as a means of improving the electrolysis performance of the HyS process.

Year	Catalyst	Ref
1973	Al-V mixed oxides with traces of Pt	9
1980	Pt, Pd, Au, Ru, Re, Ir and Rh	10
2007	Pt/C and Pd/C	11
2010	Pt-M/C (M = Co, Cr, Fe, Ru, Ir)	3
2012	Pt and Au	2
2014	Pt-M/XC72R (M = Pd, Rh, Ru, Ir and Cr)	4

The need therefore exists to research and develop new, as well as improved catalysts for the electro-oxidation of SO₂ ^{12, 13}. A fast and effective means of achieving this is by employing high-throughput combinatorial screening ¹³⁻¹⁶, which is a technique that has gained a lot of interest over recent years. One of the very first remarks, with regard to multiple-sample syntheses and testing, was made by Hanak in 1970 who emphasised the fact that the search for new materials suffered due to the fact that handling one sample at a time, in the process of synthesis and chemical testing, was an expensive and time-consuming approach, which prevented the researcher to take full advantage of his/her talents and kept the level of progress low ¹⁷. He suggested the abandonment of the tedious efforts of single sample synthesis and testing, and the adoption of methods to process multiple materials simultaneously. As the need to explore efficient and systematic means of searching for alternative binary, ternary and higher materials grew, the field of combinatorial science gained interest ^{13, 18-22}. Some of the techniques that have been applied to a combinatorial approach include (i) sputtering ²³, (ii) evaporation and molecular beam epitaxy ²⁴, and (iii) pulsed laser deposition ²⁵, employing either a form of the composition spread technique ^{17, 23} or using a discrete composition approach ^{18, 20}. It has to be stressed, however, that a high-throughput approach does not always allow for highly accurate and precise experimentation compared to conventional experimentation ^{12, 26}. It is aimed rather at investigating observable trends in the material of interest, such as catalytic activity for example, subsequent to which the initial observation is confirmed and optimised with more precise kinetic data ¹³. One of the first examples of combinatorial electrochemistry involved

generating a 645-member electrode array of Pt, Ru, Os, Ir and Rh, employing a modified inkjet printer with metal salt ‘inks’ and subsequently screening the catalysts for methanol oxidation ²⁷. Numerous studies have followed in which electrocatalysts have been investigated for a number of chemical reactions ²⁸⁻³⁰. However, little research has been conducted on high-throughput combinatorial electrocatalyst development for SO₂ electro-oxidation as part of the HyS cycle.

In this study we describe the high-throughput syntheses and screening of Pt_xPd_y thin films for the electro-oxidation of SO₂. Palladium was chosen to ‘alloy’ with platinum as some experimental studies ^{10, 31}, as well as a theoretical molecular modelling study ³² pointed towards palladium as being potentially more active than platinum for the electro-oxidation of aqueous SO₂. The thin films were obtained by employing a vacuum sputtering system for the physical deposition of a library, with the dimensions of each pad being 3 mm x 3 mm. This was followed by simultaneous electrochemical screening of the thin films by employing a specially designed electrochemical cell connected to a multi-channel potentiostat. The thin films (Pt_xPd_y combinations) were furthermore characterised by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Their activities were compared to the activity of pure sputtered Pt in the oxidation of aqueous SO₂ using onset potential as the evaluative criterion.

3.2 Experimental approach

3.2.1 Photolithography

Photolithography is employed to microfabricate a Ti-Au electrical circuit onto a SiO₂ wafer (Microchemicals, Germany), adapted from Strasser *et al.* ¹³ and Warren *et al.* ³³. The wafer has a diameter of 100 mm, with a thickness of 500-550 µm and consists of two semi standard flats with an orientation of (100). A thin, uniform, 10 µm thick layer of positive photoresist (PL177, Microchemicals) is put down onto the wafer by controlled addition of the photoresist (Performus dispensing system, EFD Nordson) and spin coating (Spin 150, SPS Ltd.) subsequent to which the wafer is dried at 80 °C for 15 minutes. The image mask of the circuit pattern is accurately fitted onto the wafer and the exposed ink is developed by exposure to 5 mW/cm² UV light for 1 minute in a UV box (Pluvex 1410, Mega Electronics, UK). The wafer is then placed in a developer solution (RS Universal developer) for 20 seconds and subsequently rinsed with water and dried with N₂. The size of the contact pad, onto which the thin film will be deposited, is 0.09 cm² with 2.5 mm spacing and the size of the pin pad, which connects the individual contact pad to the potentiostat, is 2.5 × 6 mm with 1-1.5 mm spacing. Subsequent to development the wafer is ready for deposition of the circuit by DC-magnetron vacuum sputtering. A 106.8 nm thick Ti-Au layer (calibration of Ti and Au is done as described in section 3.3.1) is deposited onto the patterned wafer, employing the aperture as depicted in Figure 3.2a, which allows the Ti and Au plasma to deposit on the entire wafer.

The conditions for sputtering the circuit are as follows: vacuum base pressure of 5 x 10⁻⁷ Torr, chamber pressure of 8 mTorr, argon gas flow rate of 0.015 L.min⁻¹, Ti DC power of 50 W for 235 seconds and on

top of the Ti layer a Au layer, DC power of 50 W for 280 seconds. The negative part of the circuit pattern is then stripped off so as to remove the sputtered metal not forming part of the circuit. This is done by placing the wafer in acetone and bubbling N₂ to impose agitation so as to speed up the process of stripping. The wafer is again covered with a layer of photoresist, after which only the contact pads and pin pads are developed by exposure to UV light for 1 minute followed by 20 seconds in the developer. In order to confirm that the lines are insulated, each contact pad, line and pin pad combination of the circuit is scrutinized and tested employing a digital multimeter. This insulation step ensures that each contact pad, line and pin pad combination is insulated from all other combinations and to ensure that only the pads are exposed for electrochemical testing.

3.2.2 Combinatorial deposition system

The combinatorial deposition system (Figure 3.1) used for vacuum sputtering was custom designed and supplied by PVD Products, USA.

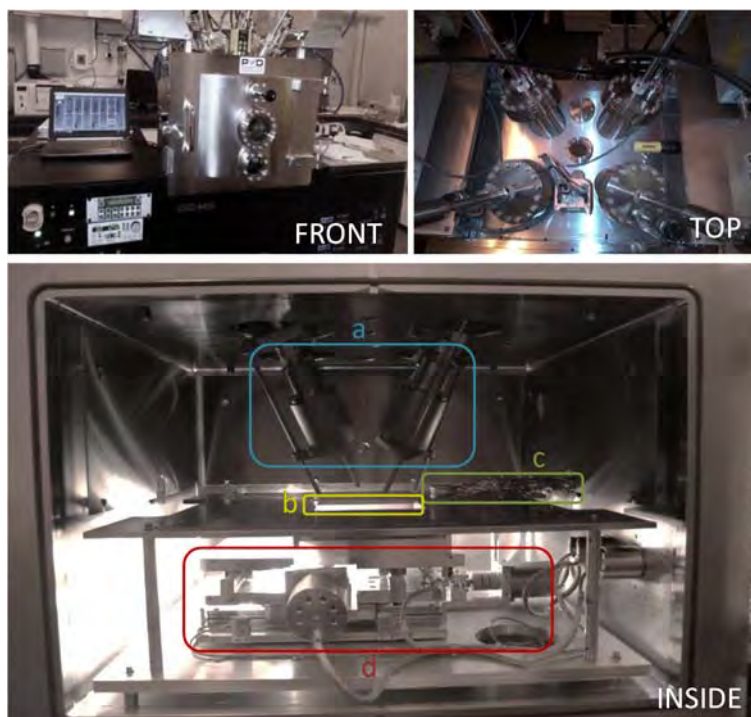


Figure 3.1: Different views of the combinatorial deposition system. (a) Four downward facing magnetron guns, (b) variable aperture, (c) quartz crystal microbalance (QCM), and (d) programmable x-y stage.

The system is a sputter down setup with four water-cooled magnetron guns (Figure 3.1a) hosting one target/metal disk each. The target diameter and thickness are fixed to 38.1 mm and 3.2 mm, respectively and were obtained from ACI Alloys (Inc), California. The magnetron guns hosting the targets are focused onto the aperture (Figure 3.1b and Figure 3.2a-d) of choice and the target to substrate distance is constant

at 90 mm. A computer-controlled shutter allows for the opening and closing of the target. Various holders and apertures (Figure 3.2) were customised to allow for the following alternatives of sputtering: (a) on a 100 mm diameter SiO₂ wafer (see holder in Figure 3.2f) and on 16 glassy carbon (GC) electrodes (see holder in Figure 3.2e), (b) on 4 GC electrodes at a time, (c) on only one square contact pad among a maximum of 64 electrode pads on the SiO₂ wafer, and (d) on only one circular GC electrode.

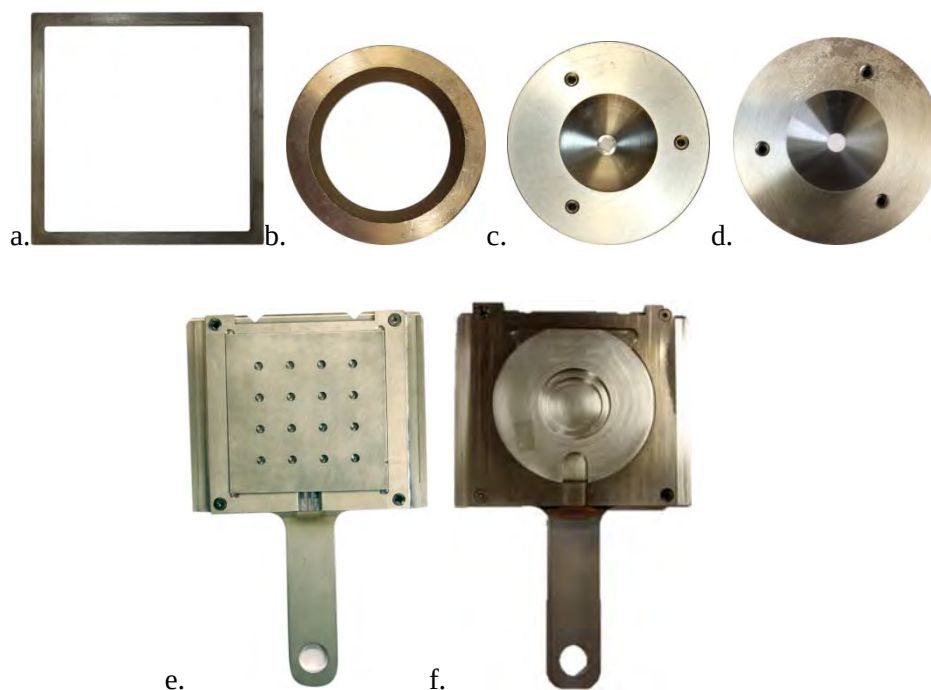


Figure 3.2: Various apertures for sputtering on a) a 100 mm diameter SiO₂ wafer and 16 GC electrodes; b) on 4 of 16 GC electrodes at a time; c) only on one electrode among the 64 electrodes of the SiO₂ wafer and d) only on one GC electrode. Images e and f are holders for 16 GC electrodes and a SiO₂ wafer, respectively, which is placed on the programmable x-y stage.

Prior to sputtering, the sputtering chamber is ‘pumped down’ to a base pressure of $\sim 5 \times 10^{-7}$ Torr using a rough pump (≥ 250 mTorr) and turbo pump (< 250 mTorr) combination. The maximum power of the four direct current (DC) magnetron guns is 100 W and two of these can switch to radio frequency (RF) mode when required (for example sputtering insulating targets, i.e. oxides) with a maximum power of 100 W. The programmable parameters that determine the composition and thickness of the sputtered films include the deposition time, regulated by the position of the shutter (open or closed) or by the on-off state of the magnetron, the power of the magnetron, as well as the argon pressure and flow rate. Calibration (refer to section 3.3.1 for details) of each target, taking these parameters into consideration, was conducted by employing the built-in quartz crystal microbalance (QCM, Figure 3.1c), which measured the change in the mass deposited per unit area as a change in frequency of a quartz crystal resonator.

3.2.3 Deposition of thin film catalysts

The library of thin films is deposited one-by-one in a pre-defined sequence during which the sputtering parameters, derived from the calibration data, are specified in such a way so as to obtain a gradient of discrete compositions across the library. In this work, different molar ratio combinations of Pt and Pd were produced by simultaneously sputtering (co-depositing) the individual metals to obtain bimetallic materials. The different combinations were compared to pure Pt and Pd towards the oxidation of aqueous SO₂. Random positions were chosen for each Pt_xPd_y ratio (in triplicate) so as to validate whether the position of a specific electrocatalyst did not influence the electrical signal (performance) of the catalyst as the length of the contact lines did vary. In that regard, the contact pads that were not sputtered with Pt and Pd, consisted of Au (the sputtered circuit). The programmable parameters that determine the composition and thickness of the sputtered films are listed in Table 3.2.

Table 3.2: Power and time of deposition used for the syntheses of sputtered films with variable molar composition (Pt_xPd_y) and fixed thickness (40 nm). Base pressure - 5×10^{-7} Torr, chamber pressure - 8 mTorr, argon flow rate - 0.015 L.min⁻¹.

Composition		DC power (Watt)		Time (s)
Pt	Pd	Pt	Pd	
0	1.0	0	50	150
0.1	0.9	17	90	74
0.2	0.8	24	60	99
0.4	0.6	62	60	74
0.6	0.4	50	22	138
0.8	0.2	85	15	106
1.0	0	50	0	226

3.2.4 Physical characterisation

Catalyst ratios were investigated non-destructively with reduced area analysis by employing SEM with an integrated XMax 20 EDX system (Oxford Instruments). Prior to determining catalyst ratios, mapping was performed (SEM with an integrated XMax 20 EDX system) to validate homogeneous sputtering. The whole wafer was fitted into the microscope chamber and the catalyst compositions were measured sequentially. Subsequent to electrochemical investigation, the wafer containing the circuit and thin film

catalysts, was cut to obtain a cross section view using scanning electron microscopy (FEI Quanta FEG 250), which allowed the measurement and validation of the film thickness.

3.2.5 Electrochemical characterisation

3.2.5.1 Solutions for electrochemical measurements

In order to ensure that the electrocatalysts were all in the same electrochemical condition, preconditioning (section 3.2.5.3) was conducted in degassed (N₂ bubbled for 20 min) 0.1 mol.L⁻¹ HClO₄ (Merck). A 1 mol.L⁻¹ H₂SO₄ acid solution (pH = 0.55) was made up by dilution of 95 wt% H₂SO₄ (Merck). This solution was degassed with N₂ for 15 min prior to linear polarisation. A stock solution of 1 mol.L⁻¹ Na₂SO₃ (Sigma Aldrich) was used as an in-situ SO₂ source (reaction 7).



All experiments were conducted in a water-jacketed electrochemical cell (300 mL) with the temperature (25 °C) controlled through an external circulation water bath (Julabo F12 ED). In all instances Milli-Q water (Millipore Milli-Q ultrapure water system; 18.2 MΩ.cm) was used.

3.2.5.2 Combinatorial electrochemical cell

Electrochemical testing was conducted by employing a specially designed electrochemical cell (Figure 3.3), which had been adapted from the cell reported by Cooper *et al.*³⁴. The wafer containing the sputtered electrocatalysts was placed at the bottom of the cylindrical double-wall glass cell body such that the catalysts were facing upward so as to be exposed to the electrolyte solution. The electrocatalysts and electrolyte were sealed off from the pin pads by an O-ring seal incorporated into the bottom wall of the bottomless cylindrical double-wall glass cell body. A Pt plated Ti mesh electrode with a 7 cm diameter was placed parallel to the wafer at a distance of about 2.5 cm and served as a common counter electrode. A saturated calomel electrode (SCE, Radiometer Analytical REF 421) was used as the reference electrode and was placed above the working electrode array, protruding through an opening in the middle of the counter electrode. The distance between the capillary tip of the reference electrode and the working electrode pads at the centre and at the edge of the array ranged from about 1.5 to 2 cm. This distance was chosen so as to minimise the differences in the uncompensated ohmic resistance between the electrocatalysts. Voltage drops across the electrolyte between the reference electrode tip and individual working electrode pads were considered negligible¹³, given the conductivity of the electrolyte and the magnitude of the measured currents.

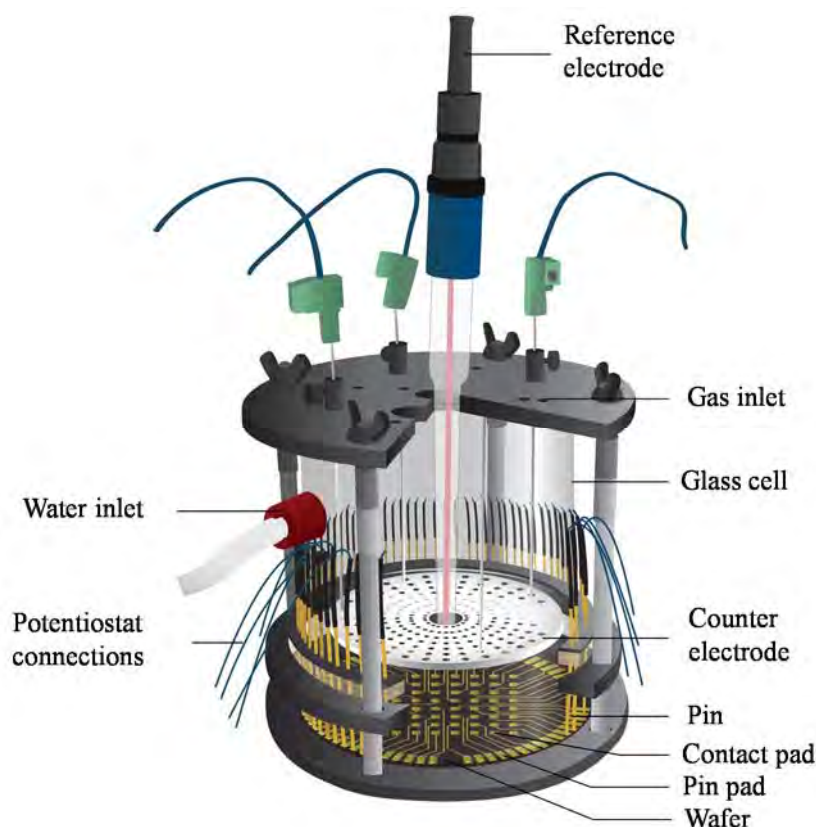


Figure 3.3: A cutaway schematic drawing of the designed electrochemical cell (adapted from ³⁴).

3.2.5.3 Electrochemical measurements on the wafer

All electrochemical measurements were performed simultaneously with a 64-channel potentiostat (Arbin Instruments). The electrode preconditioning procedure involved, as a first step, conducting cyclic voltammetry (CV) scans between 1.441 V vs SHE to 0.041 V vs SHE starting at E_{ocp} (open circuit potential) for 25 cycles employing a scan rate of 50 mV.s^{-1} . This was followed with three CV scan cycles changing the anodic potential to 1.741 V vs SHE and finally the first step was repeated but only for three cycles. This preconditioning procedure was necessary to ensure obtaining repeatable results for subsequent linear polarisation scans (for SO_2 electro-oxidation). Linear polarisation runs ($E_{low} = 0.2 \text{ V vs SHE}$ to 1.441 V vs SHE, based on the results of O'Brien *et al.* ³⁵) in the SO_2 containing solution were conducted at a scan rate of 10 mV.s^{-1} . Electrodes were, however, not held at the E_{low} potential for 2 min to deposit sulphur on the surface, as was done by O'Brien *et al.* ³⁵, since depositing sulphur would alter the surface composition. The activity of each composition was evaluated, based on the potential defined by the onset of the SO_2 oxidation reaction. This potential was calculated using the intercept of two straight lines that bound the curve as described by Cooper & McGinn ²⁹. A catalyst composition that has a low onset potential in the short term may excel in application conditions and this screening test was only designed to identify promising compositions. The catalyst ratio(s) that exhibit(s) promising activity will

undergo future analysis on glassy carbon disk inserts employing a conventional three electrode setup, which does not form part of the scope of this study.

3.3 Results and discussion

3.3.1 Calibration of sputtering rate

To ensure control over catalyst thickness and composition, critical attention was paid to the calibration of the sputtering or deposition rate. Calibration is enabled by employing a built-in retractable and computer controlled quartz crystal microbalance (QCM). The QCM is positioned in the centre of the four magnetron guns (Figure 3.1c) and allows for the in-situ measurement of the sputtering rate expressed as nm/min based on the frequency change of the oscillator and well-known relationships. The sputtering rate is influenced by the DC power of the sputtering gun, as well as the chamber pressure (Figure 3.4). The direct relationship between the DC power of each gun and the corresponding sputtering rate was evaluated for each metal (Ti, Au, Pd, Pt) and a representative graph (Figure 3.5) was constructed. The calibration lines (equations in Figure 3.5) were then used to calculate the time of deposition for the various electrocatalysts at a specific power setting.

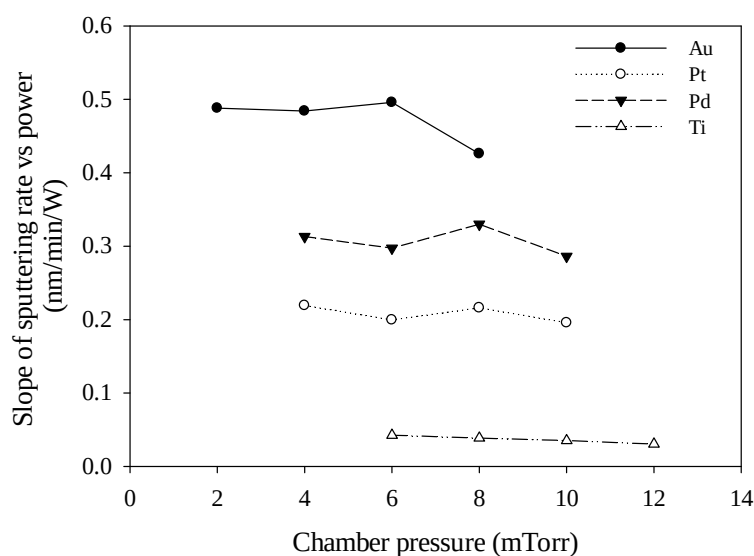


Figure 3.4: The influence of the chamber pressure on the slope of the deposition rate versus DC power. The slope is obtained from calibration graphs similar to those in Figure 3.5. Experimental conditions: vacuum base pressure, 5×10^{-7} Torr; argon gas flow rate, 0.015 L.min^{-1} ; deposition time, 1 min.

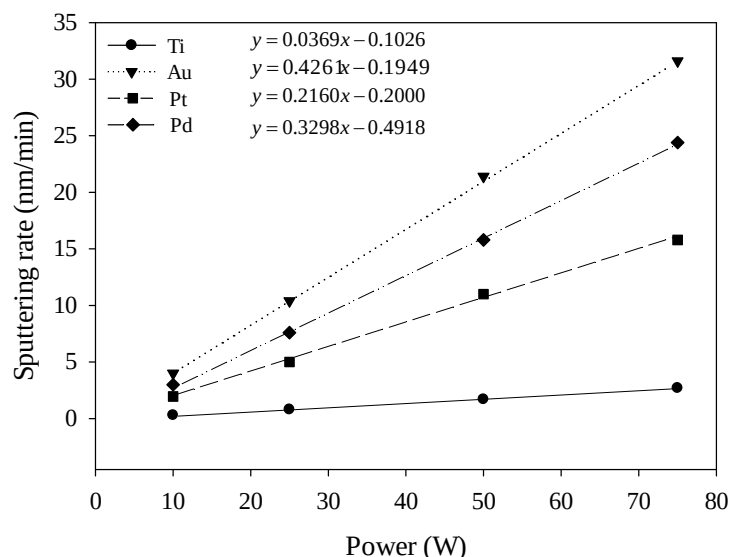


Figure 3.5: A calibration curve for deposition rate versus power. Conditions: vacuum base pressure, 5×10^{-7} Torr; argon gas flow rate 0.015 L.min^{-1} , chamber pressure 8 mTorr.

In addition, calibration curves were obtained for each metal at chamber pressures between 2 and 30 mTorr. A very good correlation (R^2 higher than 0.99) was found as long as the chamber pressure was kept between 2 and 12 mTorr. For higher chamber pressures, the sputtering rate was quite low and hence the errors due to reading of the QCM values were higher. Figure 3.4 shows the slope of the calibration graph obtained for different chamber pressures. As a global trend it can be observed that the higher the chamber pressure the lower the sputtering rate becomes. It was also observed that low chamber pressures, e.g. 2 and 4 mTorr, were not achievable for the deposition of Pt and Ti as the plasma could not be ignited. On the other hand, a chamber pressure higher than 10 mTorr was only achievable for the Ti target. As the chamber pressure is a crucial parameter for co-sputtering of two or more metals it has to be convenient for all metals being sputtered. A pressure of 8 mTorr was subsequently chosen as a general pressure at which the deposition of any metal is possible. This combinatorial sputtering system is furthermore equipped with inlets for argon and oxygen, which can be used for reactive sputtering, with the flow rate of each sputtering gas that can be independently varied. In the case when only argon is used, as is the case for this study, the flow rate should not influence the sputtering rate. This was confirmed for the sputtering of Ti at a fixed chamber pressure and different DC powers of the magnetron gun (Figure 3.6). As expected no variation of the sputtering rate was observed with a change in the flow of argon, which confirmed the proper functioning of the combinatorial sputtering setup.

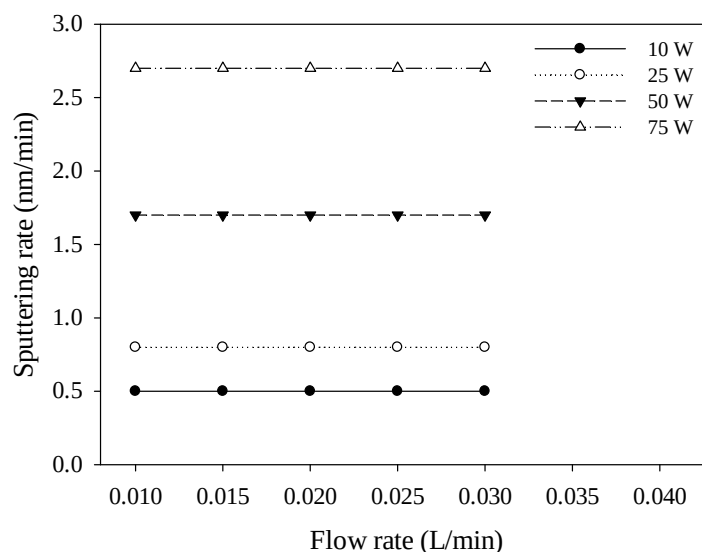


Figure 3.6: The influence of the Ar flow rate on the final thickness of a Ti film for different values of the magnetron power. Experimental conditions: vacuum base pressure, 5×10^{-7} Torr; chamber pressure, 8 mTorr; deposition time, 1 min.

3.3.2 Characterisation of sputtered films by scanning electron microscopy

In order to investigate the morphology and stoichiometry of the sputtered thin films, SEM and EDX were conducted employing representative mapping of the co-deposited thin film electrocatalysts as a means of revealing the distribution of the Pt and Pd metals. As an example, Pt_3Pd_2 is shown in Figure 3.7.

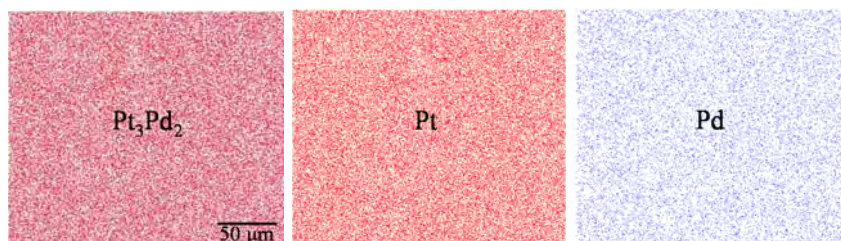


Figure 3.7: Elemental mapping of as-deposited Pt_3Pd_2 electrocatalyst.

In general, the metals are seen to be homogeneously distributed as is expected from co-deposition, and as a result the bulk composition is representative of the surface composition. To investigate the calibration (see section 3.3.1) of the PVD, the sputtered ratios were investigated by EDX analysis (Table 3.3). The results obtained from EDX deviated from the expected calibrated values in that the thin films were Pd deficient, with the PtPd_9 exhibiting a large standard deviation (STDV, obtained from 3 different positions on the wafer). A similar observation was made by Cooper *et al.* who sputtered PtRu combinations for methanol oxidation and found their thin films to be Ru deficient³⁶. A similar trend was observed in that both Pd and Ru have a lower density than Pt, and in each case it was the metal with the lower density that

was deficient in the sputtered thin film. This clearly illustrates that for sputtered thin films, each composition has to be measured independently by a secondary method to obtain true compositional values.

Table 3.3: Atomic ratio (%) of sputtered Pt_xPd_y thin film electrocatalysts.

Catalyst (%)		Measured atomic %		
Pt	Pd	Pt	Pd	STDV
80	20	83.14	16.86	1.49
60	40	67.92	32.08	0.63
40	60	49.08	50.92	0.100
20	80	31.93	68.14	1.89
10	90	25.64	74.37	5.90

SEM analysis was also conducted on a cross section of the pin pad to measure the thickness of the sputtered circuit layer (Figure 3.8). This was done subsequent to electrochemical testing as SEM analysis requires cutting of the wafer. The thickness of the layer as measured by SEM analysis was 105.374 nm and is in accordance with our calibrated values.

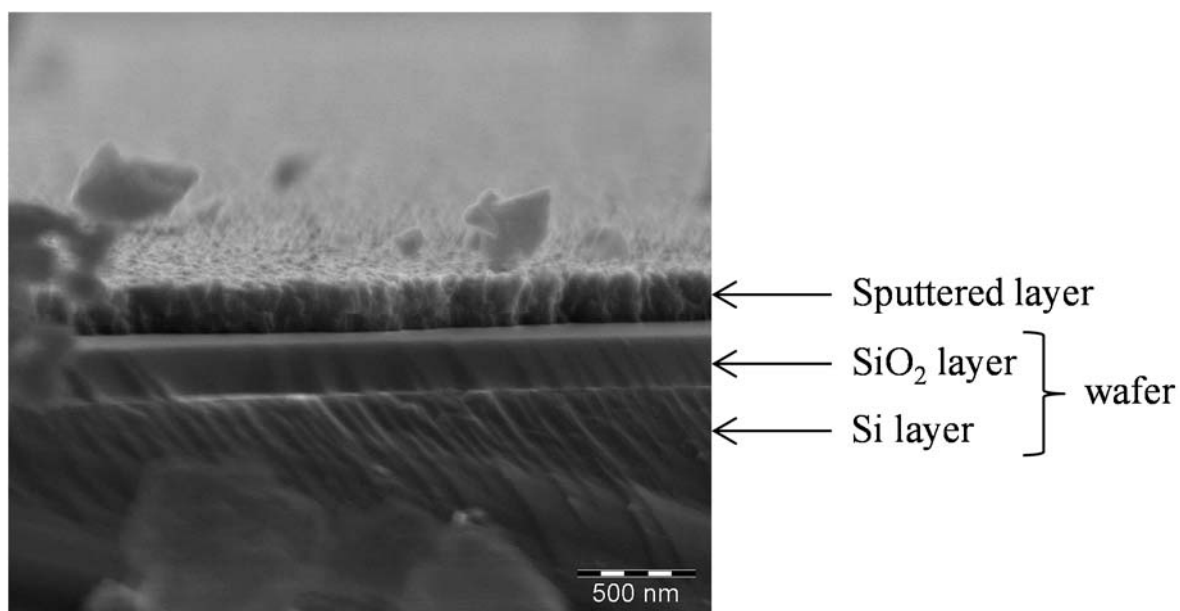


Figure 3.8: Cross view of the Si-SiO₂-TiAu layers of a wafer.

3.3.3 Electrochemical activity for SO₂ oxidation

To validate the repeatability of the fabrication process of a sputtered electronic circuit two wafers were fabricated employing the exact same steps and parameters. These two wafers, containing the exact same set of electrocatalysts, were independently electrochemically tested and compared for the electro-oxidation of aqueous SO₂. Each wafer contained three of each electrocatalyst sputtered on different positions in order to investigate the potential influence that different positions might have on the electric signal. The fabrication of two wafers furthermore served to investigate repeatability between wafers.

Onset potential is considered by many authors^{29, 37-39} to be one of the indicators for catalytic activity of a catalyst and whether a catalyst is effective for the reaction of interest. With the onset potential of Pt being the target potential for the electro-oxidation of aqueous SO₂, every library contained several Pt sputtered catalysts as reference points. From a plot of the average onset potentials for Au, Pt, Pd and Pt_xPd_y electrocatalysts (Figure 3.9) it is clear that Au exhibited the worst performance, followed by Pd, Pt, and the Pt_xPd_y combinations all being in close proximity of Pt. The average onset potential of 0.598 ± 0.011 V (SHE) for Pt, for the electro-oxidation of SO₂, agrees well with literature^{2, 35}, which serves as the first confirmation that the data generated by the experimental system is acceptable. This average value is calculated from the average of the two wafers for a set of three electrocatalysts on each wafer. An example of composing this average onset potential value and standard deviation (STDV) is given in Table 3.4. The overall average difference between the two wafers for all the electrocatalysts was calculated as 0.728%, which is very good taking into account all the steps required in fabricating a wafer, sputtering the thin film catalysts onto the wafer and conducting electrochemical screening.

Table 3.4: Example of composing the average onset potential value and standard deviation for Pt.

Pt	Wafer 1	Wafer 2
Onset potential (V, SHE)	0.609 0.603 0.581	0.606 0.600 0.591
Pad-to-pad reproducibility	0.598 ± 0.015	0.599 ± 0.008
Wafer-to-wafer reproducibility	0.598 ± 0.011	

The electrocatalysts that exhibited promising activity are Pt₃Pd₂, Pt₂Pd₃, and PtPd₄, indicating that the addition of Pd results in a slight improvement, as their onset potentials are slightly lower than that of pure Pt (Figure 3.9). With a decrease in Pt content it is clear that no trend is observed with regard to the change in onset potential. Pt₂Pd₃ exhibited the highest onset potential of the three promising electrocatalysts (see rectangular box in Figure 3.9), while Pt₃Pd₂ and PtPd₄ resulted in the same lowest average onset potential,

making them potentially alternative catalysts compared to Pt. The Pt₃Pd₂ catalyst contained ~32% less Pt, while the PtPd₄ catalyst contained ~68% less Pt than the pure Pt catalyst (based on EDX analysis). Possible reasons for deviation in the onset potential values may be that Pt is sensitive to minute amounts of inorganic and organic contaminants that may remain on the surface due to the photolithographic processing that the electrocatalysts are exposed to^{29, 40} and also the deviation in composition measured by EDX. The combinations tested have two commonalities, i.e. the fact that they catalyse the oxidation of SO₂ having a lower onset potential, as well as the undeniable fact that they all use less Pt to achieve this.

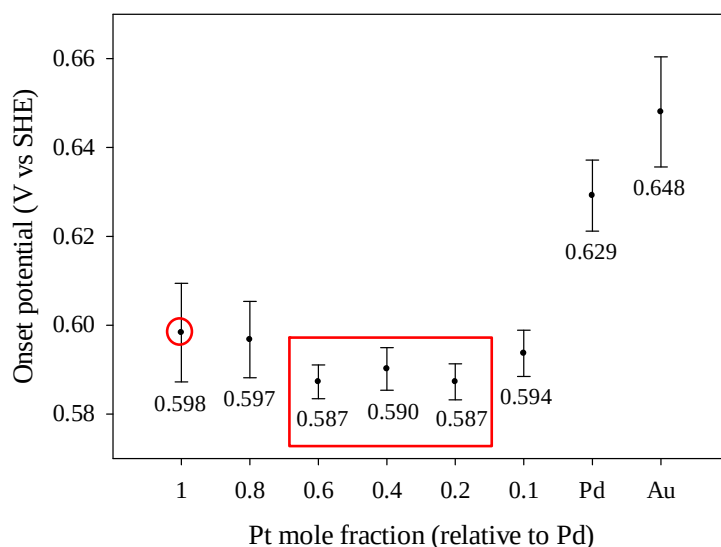


Figure 3.9: Average onset potentials for Au, Pd, Pt and Pt_xPd_y electrocatalysts on a SiO₂ wafer. Conditions: 1 mol.L⁻¹ H₂SO₄, 100 mmol.L⁻¹ SO₂, 25 °C, 10 mV.s⁻¹.

Current density, as another characteristic indicator of catalyst activity, was not employed during this investigation, because to make a worthy comparison using current density the real active surface area is required. The real active surface area of a pure Pt surface is mostly determined by examining and integrating the monolayer hydrogen adsorption area after consecutive potential sweeps⁴¹⁻⁴³. The combinatorial approach investigated here includes varying catalysts like Au and Pd, which do not contain any Pt at all. Hence, the method of oxygen adsorption from solution should be used for the estimation of real surface area as this method is common to all the metals under investigation⁴³. Multiple runs to a set of upper potential limits, at which oxygen is chemisorbed in a monoatomic layer with a one-to-one correspondence with the surface metal atoms, have to be conducted⁴⁴. This requires the catalyst surface to be identical at the commencement of each run, and since our various catalysts are positioned on a wafer which cannot undergo physical polishing/cleaning, they will have to undergo some form of electrochemical cleaning and/or other means of obtaining a repeatable surface. Furthermore, for the

electro-oxidation of aqueous SO₂ sulphur, as well as other intermediate oxidation products, has variable adsorption/binding strengths on the different metals and metal combinations, which will affect the specific technique that is employed to determine the real active surface area³². Whichever method is employed to determine the real active surface area, all have their advantages and limitations⁴¹. In this instance, after weighing the advantages and limitations of using oxygen adsorption from solution as a means to determine the real active surface area of the variety of catalysts prepared, employing our combinatorial setup, it was decided not to disregard the method, but that it deserves a dedicated investigation²⁹. One could use geometric area, as stated by Cooper & McGinn³⁴, but employing the real active surface area is preferred as it is sure to differ from the geometric area for different catalyst compositions. Hence, for this investigation only onset potential was employed as a means to quickly identify promising compositions from a catalyst library for the electro-oxidation of aqueous SO₂³⁴.

In order to clearly identify a possible alternative catalyst compared to pure Pt, further in-depth investigations have to be conducted on the Pt₃Pd₂ and PtPd₄ catalysts. This will entail sputtering these combinations onto GCs to (i) investigate and improve catalyst stability, (ii) conduct real active surface area measurements so as to calculate and compare current densities, and (iii) conduct linear polarisation scans at different temperatures in order to calculate activation energy.

3.4 Conclusions

A combinatorial method for the synthesis and electrochemical screening of novel functional materials has been described. Pure Au, Pt, Pd and bimetallic Pt_xPd_y electrocatalysts were sputtered onto a silica wafer and screened for activity towards the electro-oxidation of aqueous SO₂, employing onset potential as the screening criterion. On the wafer three Pt_xPd_y bimetallic combinations exhibited satisfactory performance (compared to pure Pt) with the best compositions being Pt₃Pd₂ and PtPd₄. Both these combinations exhibited the same lower onset potential of 0.587 ± 0.004 V, SHE compared to that of pure Pt (0.598 ± 0.011 V, SHE). It has been shown that Pt content can be significantly reduced through the development of a bimetallic electrocatalyst for the electro-oxidation of aqueous SO₂, whilst not sacrificing catalytic activity (based on onset potential).

3.5 Acknowledgements

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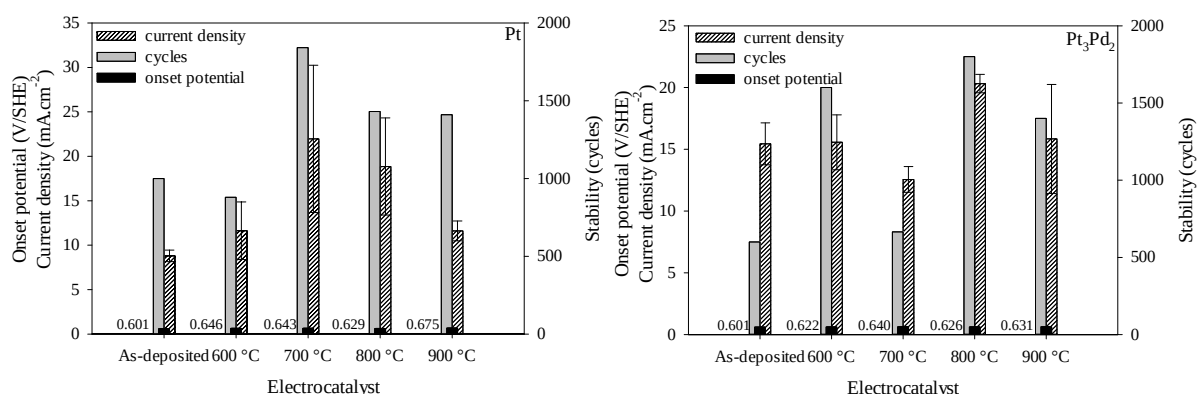
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Chapter 4

The effect of rapid thermal annealing on sputtered Pt and Pt₃Pd₂ thin film electrocatalysts for aqueous SO₂ electro-oxidation*

Chapter overview

Insight into the effect that rapid thermal annealing (RTA) has on the structural and electrochemical characteristics of sputtered Pt and Pt₃Pd₂ thin film electrocatalysts is communicated. The DC magnetron sputtered thin films were rapidly annealed at temperatures ranging from 600 °C to 900 °C under an Ar atmosphere. The microstructural changes and electrochemical properties (onset potential, current density and stability) induced by rapid thermal annealing were investigated towards the electro-oxidation of aqueous SO₂. An increase in annealing temperature induced different degrees of crystallinity and the surfaces changed from being smooth and granular to surfaces exhibiting defined grain boundaries. Electrochemical characterisation, employing linear polarisation (LP) and cyclic voltammetry (CV), revealed improved catalytic activity for the Pt₃Pd₂ thin film catalysts (compared to Pt) exhibiting lower onset potentials, competitive currents and acceptable stability. The Pt₃Pd₂ thin film, annealed at 800 °C, proved to be a promising contender, by competing with pure Pt for the electro-oxidation of aqueous SO₂.



*A. Falch, V.A. Lates, H.S. Kotzé, R.J. Kriek, The effect of rapid thermal annealing on sputtered Pt and Pt₃Pd₂ thin film electrocatalysts for aqueous SO₂ electro-oxidation, in *Electrocatalysis*, Springer, 2016, 33-41.

4.1 Introduction

Of concern in this paper is the oxidation of aqueous SO₂ at the anode of a SDE in the HyS process, which was proposed by Westinghouse Corp. as a means of producing hydrogen ¹, a clean alternative fuel, and subsequently mitigating environmental pollution. Sulphuric acid is thermally decomposed to produce SO₂, water and oxygen (reaction 1) ² by employing a high temperature heat source (>800 °C). The resulting SO₂ is fed to a SDE, which can be a gas-fed system or liquid-fed system depending on the design. In the gas-fed system, gaseous SO₂ is fed to the anode ³ and in the liquid-fed system, sulphuric acid saturated with SO₂ is employed as the anolyte ⁴. The gas-fed system is, however, more complex as the gaseous SO₂ that is required, is obtained from the thermochemical step (reaction 1), but the oxygen that is also present should first be separated from the mix to obtain pure SO₂, which is not the case with the liquid-fed system. Nevertheless, irrespective of which design is implemented for the SDE, the SO₂ is fed to the anode and electro-oxidised to produce sulphuric acid as well as hydrogen ions (reaction 2). The hydrogen ions migrate through the membrane of the electrolyser to the cathode where they are reduced to hydrogen gas (reaction 3) while the electrochemically produced sulphuric acid is recirculated back to the decomposition reactor. The net SDe reaction therefore involves the conversion of SO₂ into sulphuric acid and hydrogen gas (reaction 4), while the net HyS cycle reaction is that of water being split into hydrogen and oxygen (reaction 5).

Table 4.1: Steps in the HyS cycle.

$\text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$	(Thermochemical)	(1)
Anode : $\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^-$	(Electrochemical, $E^\circ = 0.17 \text{ V}$, SHE ⁵)	(2)
Cathode : $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$		(3)
$\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2$	(net SDe reaction)	(4)
$\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$	(net HyS cycle reaction)	(5)

For the electro-oxidation of SO₂ to be effective, electrocatalysts need to be employed that can perform under optimal working conditions (increase the reaction rate with low electrode overpotentials and show satisfactory lifetime), both from an economical and environmental point of view. While platinum has been the electrocatalyst of choice due to its high electrocatalytic activity and inert character ^{6, 7}, a number of studies (Table 4.2), in addition to those already communicated ⁸, have been conducted in an effort to reduce/replace the platinum as it is an expensive metal. Recent research has revealed that multimetallic electrocatalyst compositions provide enhanced performance in terms of activity, stability and/or selectivity compared to their corresponding monometallic components and as a consequence research into multimetallic compositions is increasing ^{6, 9-12}. It has also been revealed that annealing of metallic compositions serve to increase their activity and stability ¹³⁻¹⁵.

Table 4.2: Some studies conducted on the anode catalyst of the SDE.

Year	Catalyst	Ref.
1965	Pt and Au	16
1975	Au	17
1980	Graphite (carbon) with small amounts of HI, borides, carbides, nitrides, sulfides, organic catalysts, bronzes, W, Co, Ti, Nb, Zr, Ta, Pb, Mo, Au, Pd and Duriron	18
1983	Activated carbon	19
1991	Pt supported in a porous graphite sheet	20
1995	Pt-Al	6
2000	Polycrystalline Au	21
2012	Pt and Au	22
2015	Pt _x Pd _y combinations	8

In previous work ⁸ we identified Pt₃Pd₂ as a potential candidate for the electro-oxidation of aqueous SO₂. Palladium was chosen to ‘alloy’ with platinum as some experimental studies ^{23, 24}, as well as a theoretical molecular modelling study ²⁵ pointed towards palladium being potentially more active than platinum for the electro-oxidation of aqueous SO₂ ⁸. For pure Pd and Pt_xPd_y combinations it was observed that, with increasing Pd content (Pt₂Pd₃, PtPd₄ and PtPd₉), the stability in acidic solution decreased as signs of delamination occurred. Of the combinations investigated, the PtPd₄ thin film combination exhibited the same low onset potential as the Pt₃Pd₂ thin film combination, but did not withstand the harsh acidic environment sufficiently and was prone to almost immediate delamination. Hence, we decided to focus our attention on investigating the effect that rapid thermal annealing has on the properties of Pt and Pt₃Pd₂ sputtered thin films, specifically focusing on the activity and stability of the electrocatalysts towards electro-oxidising aqueous SO₂. The thin films were furthermore characterised by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) with integrated energy dispersive X-ray spectroscopy (EDX). The electrochemical SO₂ oxidation trends (activity and stability) were determined by linear polarisation and cyclic voltammetry.

4.2 Experimental

4.2.1 Preparation of glassy carbon electrode inserts and deposition of thin films

Glassy carbon electrodes (GCs, Sigradur G, HTW Germany) were polished to promote reproducible electrochemical surfaces (geometric area of 0.196 cm²) ²⁶. Firstly, microcloth (Buehler polishing kit) with

1 μm diamond paste (DP-Paste M, Struers) was used for 50 cycles. The GCs were subsequently rinsed with water (Milli-Q Plus ultra-pure water (specific resistance = $18.2\text{ M}\Omega\cdot\text{cm}$) was used in all instances, before transferring to the second microcloth so as to ensure that the second microcloth stayed free of diamond particles). On the second microcloth the GC was subjected to 25 cycles employing $0.05\text{ }\mu\text{m}$ deagglomerated alumina suspension (Gamma Micropolish II, Buehler) as polishing medium. The inserts were then sonicated in toluene (HiPerSolv for HPLC, BDH Laboratory Supplies) for 15 min, ethanol (Merck) for 15 min, Milli-Q water for 15 min and iso-propanol (Merck) for 15 min, after which the GCs were dried with N_2 . The thin films (60 nm) were prepared by means of physical vapour deposition and four identical thin films were deposited simultaneously onto four polished glassy carbon surfaces by employing the method and conditions as communicated earlier⁸.

4.2.2 Annealing procedure

The as-deposited samples were annealed ex-situ employing a rapid thermal annealing oven (Accuthermo AW610) and the temperature regimes employed (temperature time periods and temperature ramps) are illustrated in Figure 4.1. Maximum temperatures ranged from $600\text{ }^\circ\text{C}$ to $900\text{ }^\circ\text{C}$ in steps of $100\text{ }^\circ\text{C}$.

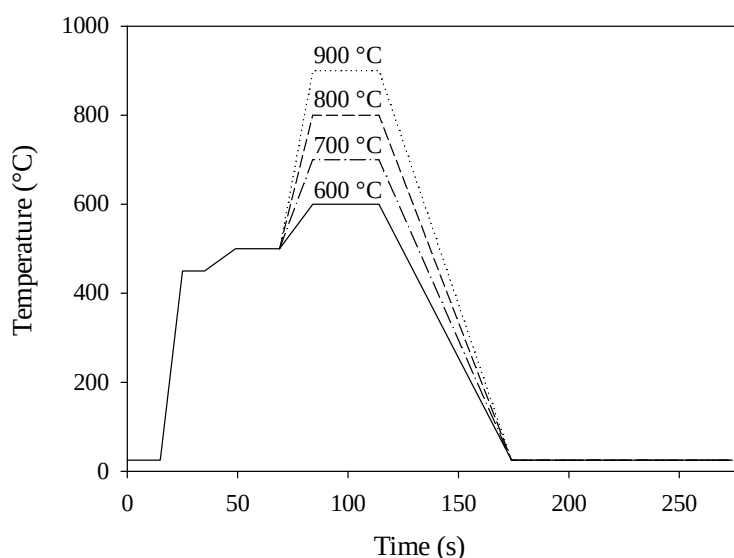


Figure 4.1: The temperature regime employed for annealing Pt and Pt_3Pd_2 thin films.

4.2.3 Characterisation of thin films

In order to investigate the stoichiometry and morphology of the electrocatalysts, SEM (FEI Quanta FEG 250) with an integrated XMax 20 EDX system (Oxford Instruments) was performed before and after annealing. EDX was performed in moving average mode employing a collection time of 100 s. XRD patterns were collected to investigate any change in crystallinity of the thin films employing a XPERT-PRO diffractometer with a $\text{Cu K}\alpha$ radiation source. The Bragg angles were scanned from 5° to 110° at $0.1^\circ/\text{min}$. Electrochemical measurements were performed in a standard three electrode setup, employing a

Pt spiral wire as the counter electrode and a saturated calomel electrode (SCE, Radiometer Analytical REF 421) as the reference electrode. Preconditioning was conducted in degassed (N_2 was bubbled for 20 min) $0.1 \text{ mol.L}^{-1} \text{ HClO}_4$ (Merck). A $1 \text{ mol.L}^{-1} \text{ H}_2\text{SO}_4$ acid solution was made up by dilution of 95 wt% H_2SO_4 (SAAR5885124LP, Merck). This solution was degassed with N_2 for 15 min prior to linear polarisation. A stock solution of $1 \text{ mol.L}^{-1} \text{ Na}_2\text{SO}_3$ (Sigma Aldrich) was used as an in-situ SO_2 source (reaction 6).



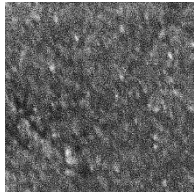
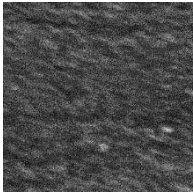
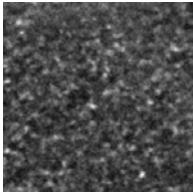
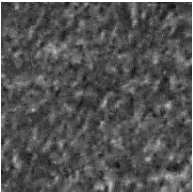
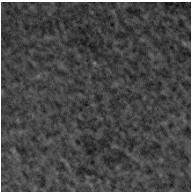
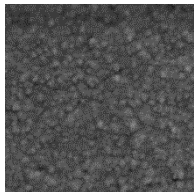
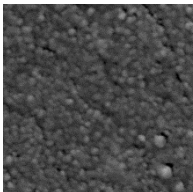
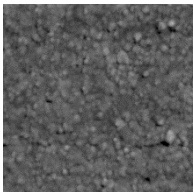
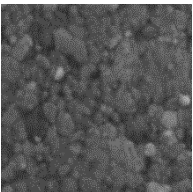
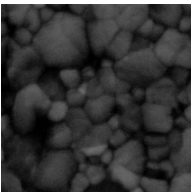
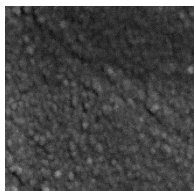
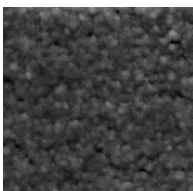
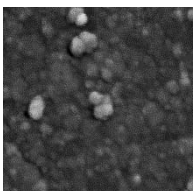
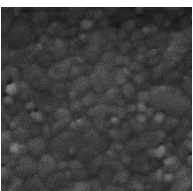
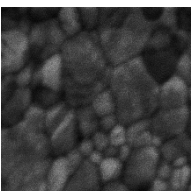
Linear polarisation was conducted ($E_{\text{low}} = 0.2 \text{ V vs SHE}$ to 1.441 V vs SHE at a scan rate of 10 mV.s^{-1}) to determine the onset potentials and current density (criterion for activity²⁷) for the thin films exposed to the different annealing regimes. Current densities were calculated by employing the electrochemical active surface area (EASA) determined by evaluating the reduction charge of O atoms adsorbed from solution²⁸. Cyclic voltammetry (CV) was employed as a relatively simple means of obtaining information with regard to stability²⁹⁻³¹ of the as-deposited and annealed samples in a $1 \text{ mol.L}^{-1} \text{ H}_2\text{SO}_4$ ($\text{pH} = 0.55$) electrolyte environment. CVs were recorded at a scan rate of 100 mV.s^{-1} and within a potential window of 0.041 V vs SHE and 1.441 V vs SHE at 25°C .

4.3 Results and discussion

4.3.1 SEM and EDX characterisation

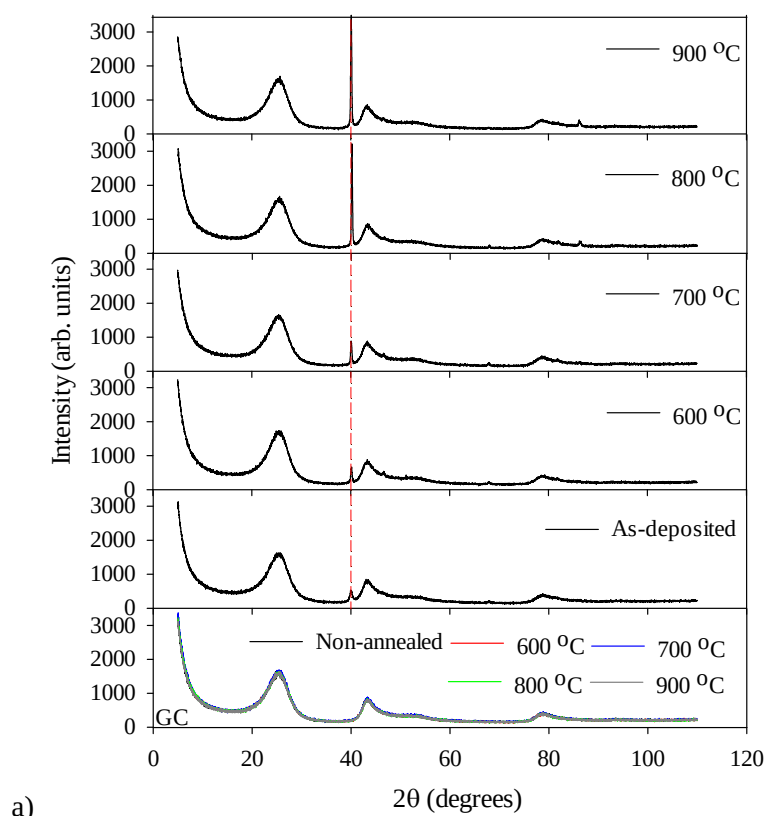
The stoichiometry of the electrocatalysts were investigated by EDX (Table 4.3) and the evolution of the surface morphologies of the electrocatalysts were investigated by SEM, both before and after annealing. SEM micrographs of the as-deposited and annealed GC, Pt and Pt_3Pd_2 sputtered thin films annealed at 600°C , 700°C , 800°C and 900°C are presented in Table 4.3. GCs annealed in this temperature range are unaffected as these GCs are high temperature resistant. The as-deposited samples of Pt and Pt_3Pd_2 show smooth, crack-free surfaces and adapt to the GC surface. Annealing up to 900°C resulted in discontinuous grain growth surfaces³² with islands of grains surrounded by well-defined grain boundaries³³. A question that now arises is whether the Pt_3Pd_2 electrocatalyst can be referred to as a bimetallic or alloy catalyst, as these are interpreted and defined in different ways³⁴? According to literature of the early 1900s^{35, 36}, the rigid band theory (RBT) was used to define an alloy as being another/new metal in which the individual components are no longer distinguishable; thus any change in catalytic activity is explained as being due to electronic change in the alloy as a whole, with the surface composition being regarded as not important³⁴. Not everyone accepted this theory and regarded the individual properties of the contributing metals to still be preserved in the alloy³⁷. This debate is, however, still continuing³⁴ and we are adopting the more recent definition of an alloy that is defined as a metal consisting of two or more components irrespective of how the components are mixed³⁸. Thus, the as-deposited and annealed samples of Pt_3Pd_2 are seen as alloys, but with changing properties as annealing temperature increases.

Table 4.3: Visual surface analysis of glassy carbon and as-deposited and annealed thin films at different annealing temperatures.

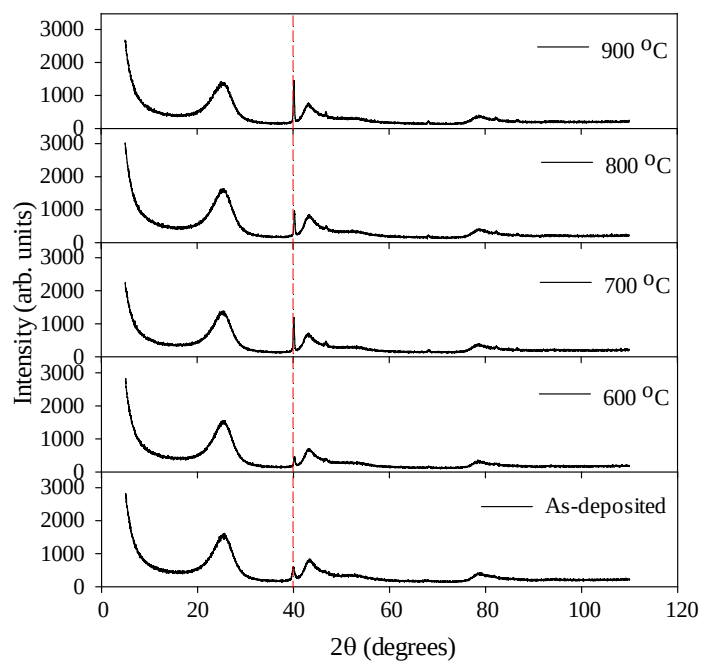
	200 nm	As-deposited	600 °C	700 °C	800 °C	900 °C
GC						
Pt (100%)						
Pt₃Pd₂ (60.43:39.57 ± 3.60%)						

4.3.2 XRD characterisation

As a means to evaluate annealing-induced changes in the crystal structure, XRD was obtained for the different thin film electrocatalysts at the different annealing temperatures (Figure 4.2). As a reference, XRD spectra were also obtained for blank GCs at the different temperatures. The GCs were not affected by annealing temperatures up to 900 °C, supporting the results obtained from SEM analysis. Overall the XRD patterns of the Pt and Pt₃Pd₂ thin films exhibited an increase in the degree of polycrystallinity for the different temperatures. This is clear from the peak observed at 40°(2θ) (as a means to evaluate the degree of crystallinity) for both the as-deposited Pt and Pt₃Pd₂ sputtered thin films, that grow into sharper peaks ((111) plane) as the temperature increases. In addition to the peak at 40°(2θ) for both thin films (Pt and Pt₃Pd₂), the (200), (220), (311) and (222) planes ³⁹, characteristic of face centred cubic (f.c.c.) crystal structure ⁴⁰ emerges as the temperature increases. No peaks characteristic of Pt oxide and Pd oxide were present. Both Pt and Pd exist in f.c.c. lattices and the unit cell dimensions are 3.92 Å and 3.89 Å for Pt and Pd, respectively ⁴¹, which makes it difficult to distinguish between the two metals ⁴² in the Pt₃Pd₂ thin film alloy. The (111) reflection peak at the Bragg angle of 40°(2θ) was used to calculate the crystallite size of the different thin films incorporating the Debye-Scherrer equation. In general, both the Pt and Pt₃Pd₂ thin films annealed at different temperatures exhibited larger crystallite size in comparison to the as-deposited thin films ranging from ~18 nm (as-deposited films) to ~60 nm (annealed thin films).



a)



b)

Figure 4.2: XRD spectra of a) blank GC, Pt and b) Pt₃Pd₂, at the different annealing temperatures. (Red dashed line indicates the (111) reflection).

4.3.3 Electrochemical characterisation

4.3.3.1 Electrochemical active surface area determination

As it is a known fact that the activity of electrocatalysts is proportional to their real EASA (as geometrical area can be misleading), it is inevitable that the real EASA of the thin films of interest should be determined, as was stated by Bard *et al.* ⁴³. In this study Pt and Pd are employed as the main components in the electrocatalysts as they show potential for the oxidation of aqueous SO₂. The EASA of Pt has been studied extensively in various catalyst forms (foils, thin layers, nano-particles ⁴⁴) employing different methods (underpotential deposition of metals ^{44, 45}, CO stripping ⁴⁶ and double layer capacitance ⁴⁴), with hydrogen adsorption/desorption ⁴⁷ having been employed the most frequently for determining the EASA. However, as Pd is one of the metals being investigated, employing the hydrogen adsorption method is not feasible, as hydrogen is not adsorbed onto Pd but is rather absorbed into the Pd ⁴⁸. A method that has shown reliable results for surfaces containing Pd involves the integration of the charge of a full monolayer of PdO ^{28, 48-51}, which is also applicable for Pt, making normalised comparison between the different thin film electrocatalysts possible. Cyclic voltammetry was employed by scanning the electrode from 0.3 V to 1.2-1.7 V, respectively (Figure 4.3a), with a scan rate of 0.05 V.s⁻¹. The reduction charge of the surface oxide was evaluated by integrating the area of the oxide peak, not including the double layer charge (Figure 4.3b). For this method it is essential to know the upper potential limit where O atoms are chemisorbed in a monolayer with a one-to-one correspondence to the available Pt- and Pd-surface sites. This is indicated by a change in slope of a straight line plot between charge (μC) and upper potential limit (V) ^{45, 48, 51}, as can be seen in Figure 4.3c.

The charge corresponding to the monolayer coverage was converted to an area value (cm²) by employing the well-known values of 208 μC.cm⁻² for Pt and 212 μC.cm⁻² for Pd for a one electron transfer per site ⁵². For the Pt₃Pd₂ electrocatalyst 60% of the surface will correspond to the value of Pt and 40% to the value of Pd, and since the charge evaluated is due to oxide reduction, a two electron transfer per site value was calculated as being 419.2 μC.cm⁻². The values for real EASA obtained by the method of oxide reduction for the Pt and Pt₃Pd₂ thin film electrocatalysts are shown in Figure 4.4.

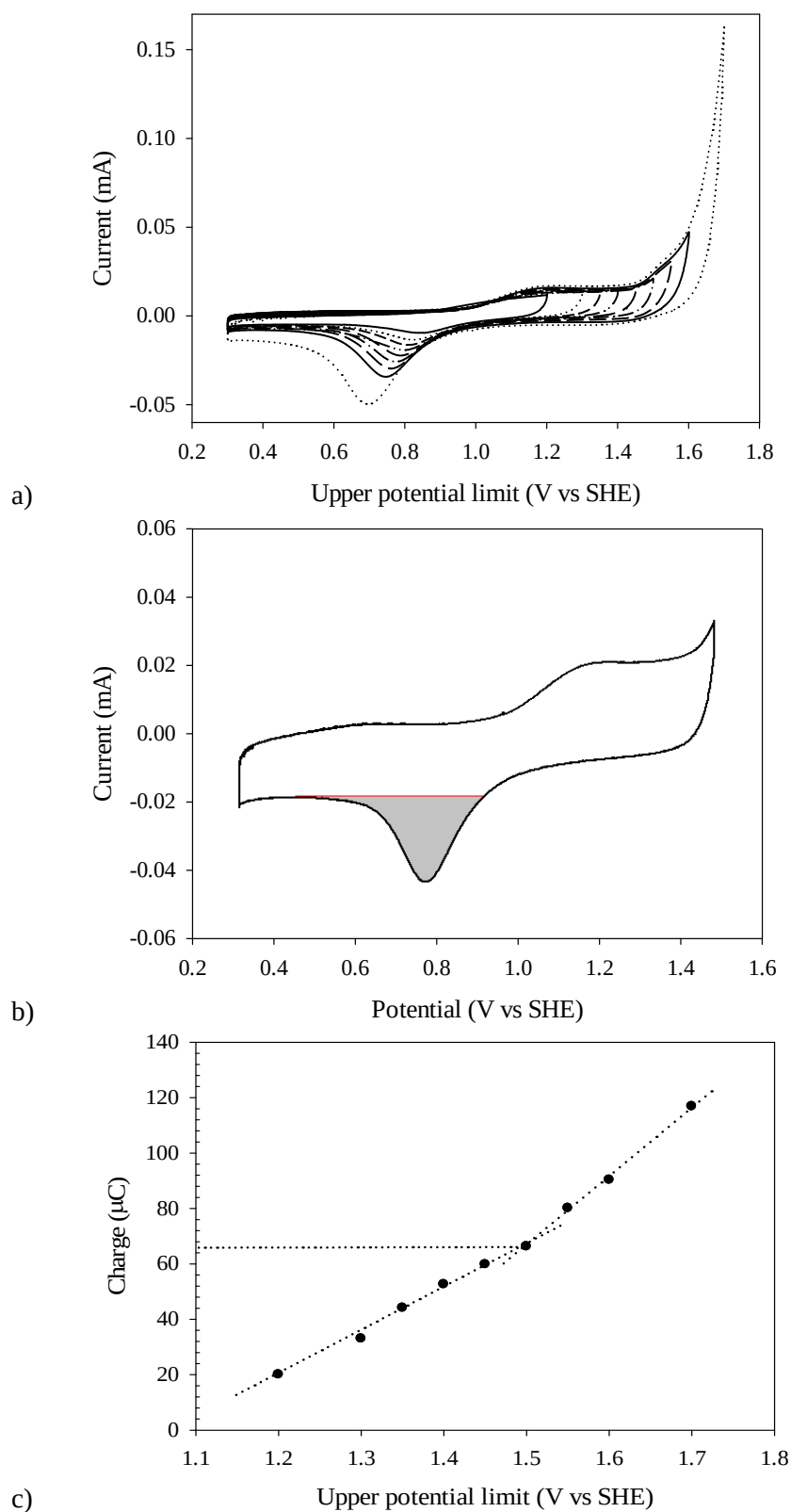


Figure 4.3: a) Typical cyclic voltammograms of Pt_3Pd_2 annealed at 800°C showing the growth of surface oxide, b) the red line indicating the base line for the integrated grey region used for EASA calculations, and c) charge vs. upper potential limit indicating where O atoms are chemisorbed in a monolayer with a one-to-one correspondence with the available surface atoms.

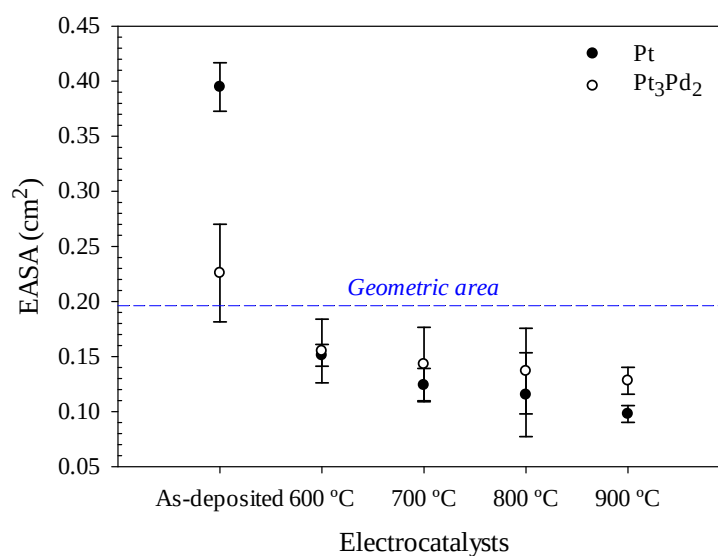


Figure 4.4: EASA values determined for Pt and Pt₃Pd₂ electrocatalysts.

It is clear that an increase in annealing temperature correlates with a general decrease in the EASA for both Pt and Pt₃Pd₂, with the values for Pt being smaller than that of Pt₃Pd₂ and with the difference between the individual Pt and Pt₃Pd₂ electrocatalysts increasing with increasing annealing temperature. A similar observation was made for Pt_xCu_y catalysts by Mani *et al.* who observed that the measured (by means of evaluating the charge for monolayer hydrogen adsorption/desorption) electrochemical surface area decreased significantly with increasing annealing temperatures (600 °C to 950 °C), ascribing it to particle growth¹⁵. For the as-deposited non-annealed samples the EASA for Pt is almost double that of Pt₃Pd₂. Another intriguing observation is the fact that the EASA values for the as-deposited thin films are larger than the geometrical area while the EASA values for the annealed thin films are smaller than the geometrical area. It is therefore unlikely that surface roughening occurred¹⁵ and it is likely that the activity of the catalysts is a result of geometric (topology of surface sites) and/or electronic effects (interaction between the molecular orbitals of reactants and the d-orbitals of available surface sites)^{15, 53-55}. One of the first researchers who recognised a relationship between the surface and activity of a catalyst was Taylor in 1925⁵⁶, who stated that the reaction being catalysed determines the amount of surface being catalytically active and that all extremes exist, ranging from all the surface atoms being active to that in which only a few atoms are active. It can therefore be assumed that determining the active surface area electrochemically as a means to obtain current density (mA.cm⁻²) is a way of normalising current, as the action of adsorbing O atoms on the surface will differ from the reactants participating in SO₂ electro-oxidation²⁵. Understanding the properties of surfaces and establishing which properties are responsible for chemical activity is, however, a long term goal of surface science^{53, 55}.

4.3.3.2 Linear sweep voltammetry, stability and current density

The performance of the as-deposited and annealed Pt and Pt₃Pd₂ thin films for the electro-oxidation of aqueous SO₂ was investigated and ranked, based on their variation in onset potential, stability and current density (Figure 4.7a & b). The onset potential was calculated using the intercept of two straight lines tangent to the LP curve (Figure 4.5 point **B**) as described by Cooper & McGinn⁵⁷, while stability was determined by the number of cycles until signs of delamination occurred on the electrocatalyst surface. Current was taken at the highest point on the SO₂ oxidation peak (Figure 4.5 point **A**) and converted to current density by employing the determined EASA values (section 4.3.3.1).

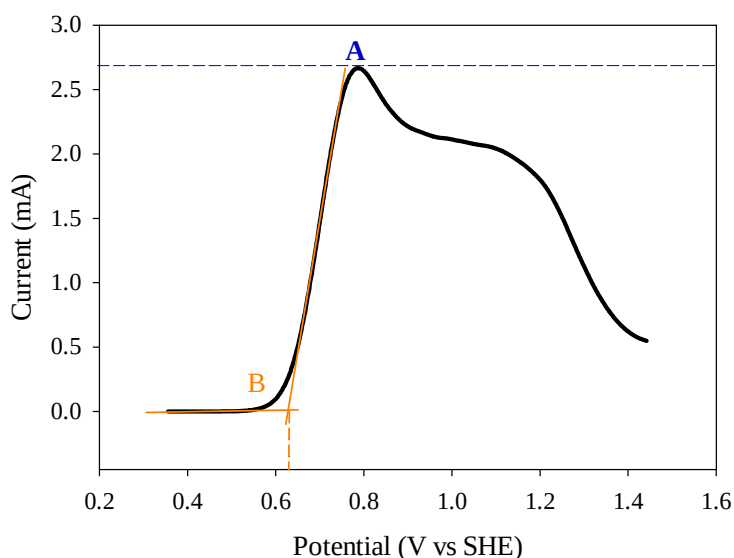
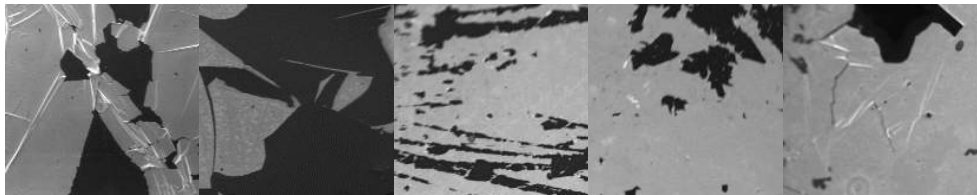


Figure 4.5: Linear polarisation curve for Pt₃Pd₂ annealed at 800 °C with (A) indicating the highest point on the SO₂ oxidation peak and (B) the onset potential defined by the intercept of two tangent lines⁵⁷.

In general, the onset potentials of the individual annealed Pt₃Pd₂ electrocatalysts were lower than that of the annealed Pt electrocatalysts at the respective temperatures. For both Pt and Pt₃Pd₂ the annealed thin films exhibited higher onset potentials than the as-deposited thin films. Annealing therefore had no positive influence on the onset potential as no improvement (lowering of the onset potential) was observed.

As it is important to realise a long operational lifetime for the electrocatalyst in the electrolyser, consecutive CVs were conducted to investigate the stability of the thin film electrocatalysts in a sulphuric acid environment (in the absence of SO₂). This technique of consecutive cycling has previously been employed to evaluate the durability of electrocatalysts in a short period of time⁵⁸. During the recording of the CVs, the electrocatalyst surface was visually monitored for signs of delamination as an indication of the level of resistance of the thin films to a sulphuric acid environment (Table 4.4).

Table 4.4: Different degrees of delamination observed for Pt and Pt₃Pd₂ thin films.

	1 mm	As-deposited	600 °C	700 °C	800 °C	900 °C
Pt (100%)						
Pt₃Pd₂ (60.43:39.57 ± 3.60%)						

As a result of prolonged consecutive cycling an interesting observation was made for the different electrocatalysts. As a result of consecutive cycling, all the electrocatalysts exhibited various degrees of distinct growth in the hydrogen absorption/desorption regions, with no specific trend (Figure 4.6). Clarification of these changes requires in-depth characterisation, but was not the focus of this study as the thin films still delaminated from the glassy carbon surface. Attention must therefore first be given to improving the adhesion of the thin film to the support of interest, followed by in-depth characterisation of the effect of prolonged consecutive cycling, for example the possible formation of a Pt skin on the surface of the Pt₃Pd₂ catalyst ⁵⁹.

As can be observed in Figure 4.7 RTA clearly increased the lifetime of the electrocatalysts (in an acidic environment) for both the Pt and Pt₃Pd₂ thin film electrocatalysts. The Pt annealed at 700 °C and the Pt₃Pd₂ annealed at 800 °C were the most stable in a sulphuric acid environment. In terms of hours, the lifetime of as-deposited Pt₃Pd₂, for example, increased from ~ 4 h 40 min to ~ 14 h 20 min by annealing at 800 °C. If the onset potentials and stability are considered together, it is evident that the Pt₃Pd₂ annealed at 800 °C is the superior electrocatalyst as it exhibits both good stability and comparable onset potential compared to all the annealed Pt samples. Another indicator of activity that was evaluated, in the search of finding a possible alternative electrocatalyst, is current density. RTA resulted in the annealed thin films all exhibiting almost equal to or higher current densities than the corresponding as-deposited thin films. However, the advantage obtained of increased stability and improved current density by annealing at 800 °C for the Pt₃Pd₂ specifically, overrides the fact that the as-deposited Pt₃Pd₂ and Pt thin films exhibit the lowest onset potentials overall. Taking into account all three parameters, the Pt₃Pd₂ thin film electrocatalyst annealed at 800 °C would seem to be the superior electrocatalyst for the oxidation of aqueous SO₂, exhibiting (i) lower onset potential compared to pure Pt, (ii) improved normalised current density, and (iii) increased stable lifetime in a sulphuric acid environment.

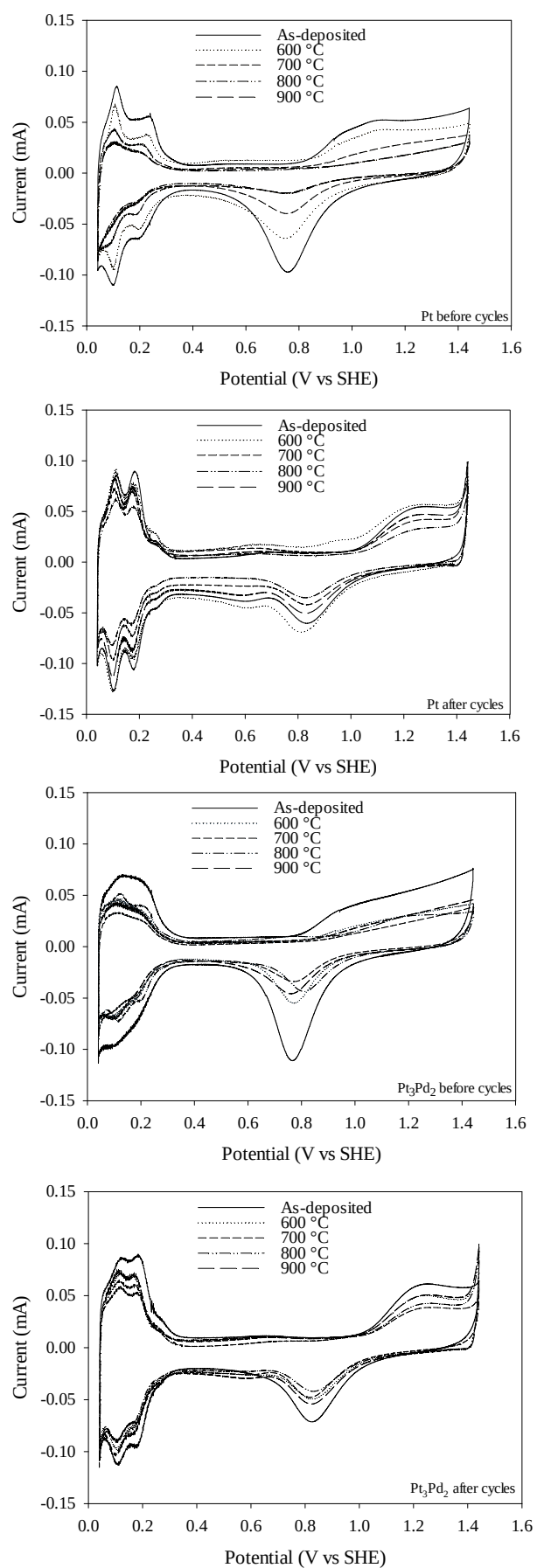


Figure 4.6: Consecutive cycling of Pt and Pt₃Pd₂ thin film electrocatalysts.

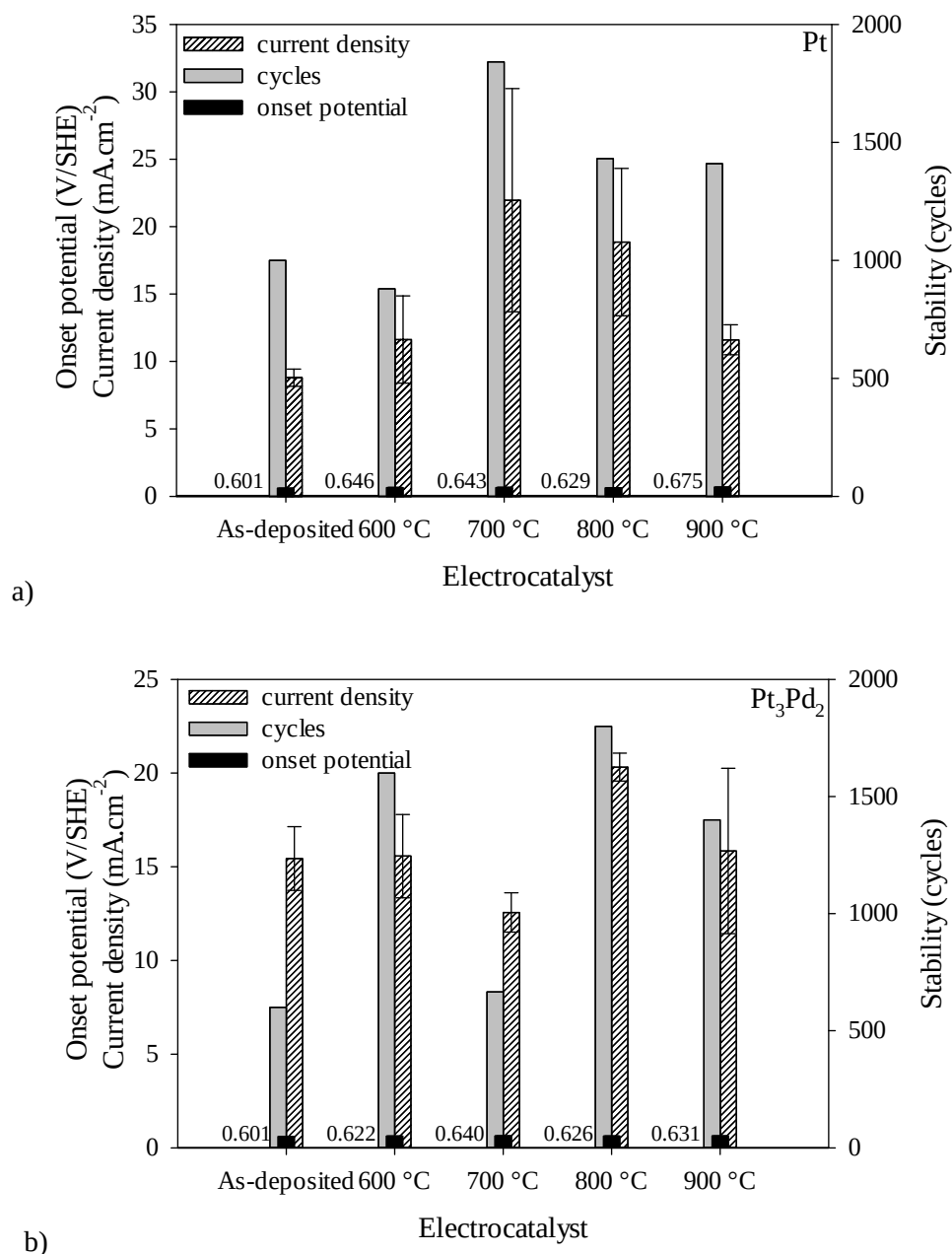


Figure 4.7: Comparison of the onset potential, current density and number of cycles for as-deposited and annealed a) Pt and b) Pt₃Pd₂ at different temperatures. Standard deviations for onset potentials are included in the graph, but are negligibly small.

4.4 Conclusion

Thin film electrocatalysts were subjected to rapid thermal annealing at different temperatures and the changes induced by annealing were investigated by physical and electrochemical characterisation. From the physical characterisation analysis, which included SEM and XRD, it was found that: (a) the thin films visually showed to form well-defined grains with grain boundaries as the annealing temperature increased, (b) the thin films transformed into more crystalline thin films as the temperature increased, and (c) the crystallite size for the annealed thin films was larger compared to that of the as-deposited thin films. The

effect of these observed physical changes (induced by rapid thermal annealing) on the electrochemical properties of Pt and Pt₃Pd₂ thin films towards the oxidation of SO₂ in an acidic environment was investigated. From electrochemical characterisation it was found that RTA did not improve the onset potential of the annealed thin films, but did however, improve current density and substantially improved the lifetime of the thin films in an acidic environment. The Pt₃Pd₂ thin film electrocatalyst annealed at 800 °C seems to be the superior electrocatalyst for the oxidation of aqueous SO₂, exhibiting lower onset potential than all pure annealed Pt, as well as improved normalised current density and increased stable lifetime within a sulphuric acid environment.

In summary, the highlights that have been achieved thus far in searching for a potential alternative electrocatalyst, that is competitive compared to Pt, can be listed as follows:

- i) a thin film electrocatalyst (Pt₃Pd₂) with ~ 40% less Pt than pure Pt has been identified to exhibit a similar onset potential compared to 100% Pt; and
- ii) exposing the thin film electrocatalysts to RTA, as a means to improve the properties of the thin film electrocatalysts, resulted in the majority of annealing temperatures improving the electrochemical properties of the thin films, with the Pt₃Pd₂ thin film electrocatalyst annealed at 800 °C being a promising contender in competing with pure Pt towards the electro-oxidation of aqueous SO₂.

4.5 Acknowledgements

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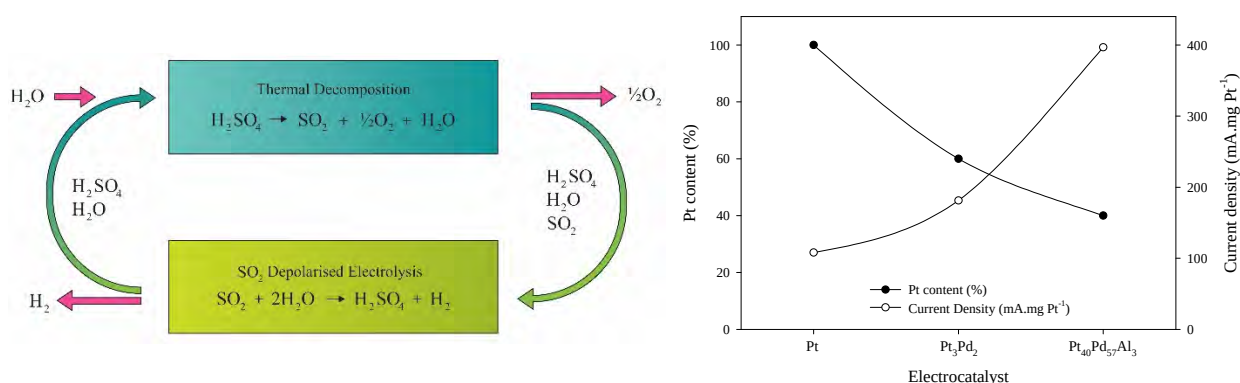
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Chapter 5

Co-sputtered $\text{Pt}_x\text{Pd}_y\text{Al}_z$ thin film electrocatalysts for the production of hydrogen via $\text{SO}_2(\text{aq})$ electro-oxidation*

Chapter overview

A co-sputtered $\text{Pt}_x\text{Pd}_y\text{Al}_z$ ternary system was investigated for potential use as anode catalyst for the electro-oxidation of aqueous sulphur dioxide (SO_2), a key reaction in the hybrid sulphur (HyS) process for splitting water into hydrogen and oxygen. Combining the noble metals Pt and Pd with Al resulted in no significant improvement in onset potential, however, current output was improved for the majority of the electrocatalysts evaluated. Of these electrocatalysts only a single ternary composition exhibited improved stability when compared to pure Pt. It was found that a combination of $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ (annealed at 900°C) exhibited superior performance when compared to pure Pt and the previously determined best binary electrocatalyst, i.e. Pt_3Pd_2 . Current density (mA.mg Pt^{-1}) increased from 108.11 to 181.21 and finally to 396.73 for Pt, Pt_3Pd_2 and $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$, respectively, indicating an increase in activity that correlates with a decrease in Pt content. Atomic force microscopy (AFM) revealed an increase in surface roughness for Pt, Pt_3Pd_2 and $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$, while the occurrence of metal interaction and certain degrees of Al migration (a result of annealing) was confirmed for $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction analysis (XRD).



*A. Falch, V.A. Badets, C. Labrugère, R.J. Kriek, Co-sputtered $\text{Pt}_x\text{Pd}_y\text{Al}_z$ thin film electrocatalysts for the production of hydrogen via $\text{SO}_2(\text{aq})$ electro-oxidation, in *Electrocatalysis*, Springer, 2016, 7, 376-390.

5.1 Introduction

Hydrogen, the only non-carbon containing energy carrier, is the most abundant atom on earth ¹ and is considered as the ultimate clean energy carrier (in molecular form) to be generated from renewable resources ². The range of hydrogen production processes can roughly be divided into hydrocarbon-based (steam-methane reforming and coal gasification), non-hydrocarbon based (water electrolysis and thermochemical water decomposition) and integrated (steam-methane reforming linked to non-hydrocarbon based) ³. As hydrogen is only found as part of compounds on earth, it is fairly energy intensive to separate hydrogen into its molecular form ¹, and goes hand in hand with huge amounts of environmental pollutants being emitted to the atmosphere. If, however, hydrogen can be returned/produced as part of a remediation process of these detrimental environmental pollutants, a portion of the energy input for the remediation process can be returned in the form hydrogen. This is exactly what the HyS cycle, a thermo-electrochemical water splitting process, accomplishes through the electrochemical oxidation of aqueous sulphur dioxide (Figure 5.1). Thermochemical processes produce hydrogen through a series of chemical reactions with water-splitting being the net reaction. Since hydrocarbons are not used in these thermochemical processes no harmful emissions such as carbon dioxide (CO₂) are produced, with the hydrogen produced being extremely pure ⁴. There are various thermochemical cycles (a combination of thermochemical and electrochemical reactions ⁵) that can produce hydrogen from water with the HyS cycle (reactions 1 – 4) being the most promising ^{4, 6-8}.

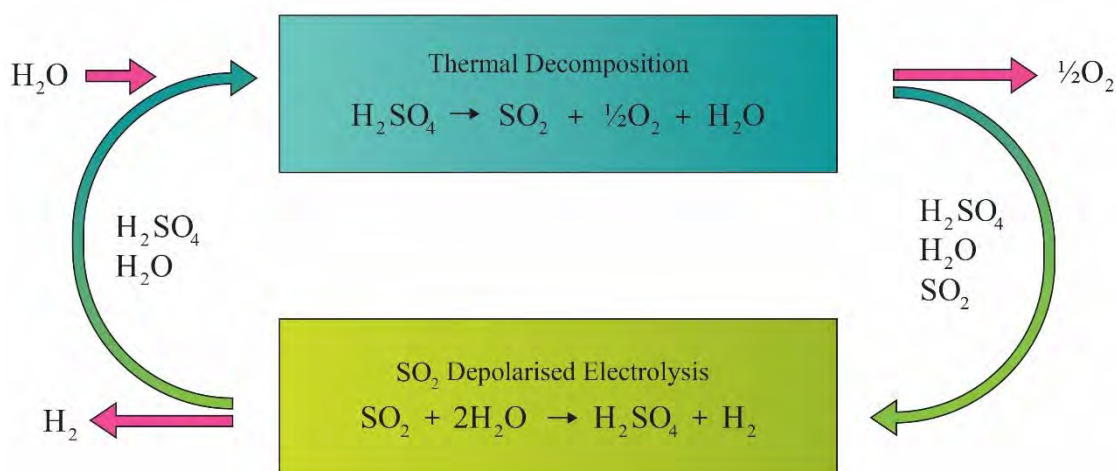
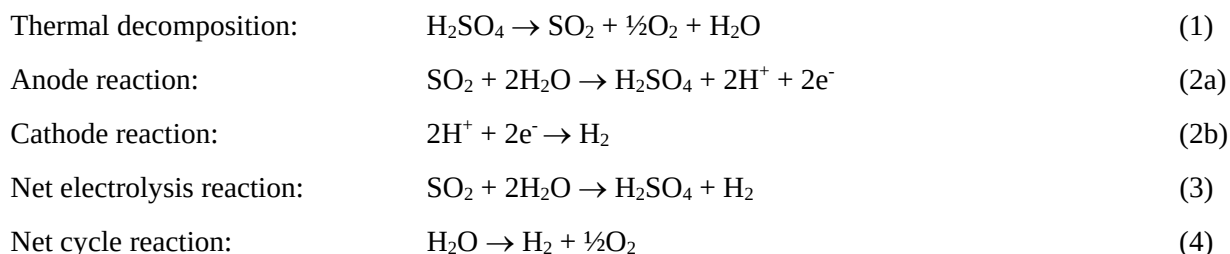


Figure 5.1: The thermo-electrochemical HyS cycle for the splitting of water.

The HyS cycle undergone extensive development in the 1970s^{9, 10} and 1980s^{10, 11}. For the subsequent 20 years, further development nearly ceased as advanced nuclear technologies gained increased interest¹⁰. After this period, interest in the HyS cycle revived and the HyS cycle was subsequently rated among the top of 115 thermochemical cycles considered¹². Interest in the HyS cycle results from the fact that, whereas the anodic reaction for regular water electrolysis occurs at a standard potential of 1.23 V (SHE)¹³, the anodic reaction for SDe occurs at a standard potential of 0.17 V (SHE)¹⁴, which translates into an energy gain of more than one volt^{7, 15}. In SDe the rate determining step occurs at the anode, which results in the anode attributing to the inefficiencies of the SDE¹⁶. In this regard, an optimal operational target of 500 mA.cm⁻², at a cell potential of approximately 0.6 V, has been proposed for SDe by Gorenssek and Summers^{7, 17}. This target can potentially be achieved through the development of an effective electrocatalyst for the anodic electro-oxidation of SO₂ and in that regard the properties of the anode are regarded as pivotal for improving the entire HyS process^{18, 19}.

While platinum is generally considered the standard anode catalyst for the SDE^{8, 16}, efforts are underway to identify an electrocatalyst other than platinum (see^{20, 21} for a detailed list of investigated catalysts). As Pt is costly the development and implementation of a catalyst with increased or equal catalytic activity and reduced cost (less Pt) will be advantageous. Platinum content could be reduced by alloying/combining it with either a more cost effective noble metal or base metals in an effort to still maintain acceptable catalytic activity^{20, 21}. An earlier investigation by us (employing sputtered thin films) has shown that Pt content can indeed be reduced by combination with Pd, i.e. Pt_xPd_y, without sacrificing electrocatalytic activity²¹. A thin film combination of Pt₃Pd₂ has specifically been found to exhibit competitive performance compared to pure Pt for the electro-oxidation of aqueous SO₂, with annealing further improving performance²¹. For this study aluminium (Al) was introduced as a third component in an attempt to lower the content of both Pt and Pd (both noble metals). Al is considered a metal of great electrochemical potential²² and a study by Lee²³ on Pt and Al combinations proved that only small amounts of Al is effective in improving catalytic performance in aqueous SO₂ electro-oxidation. This study by Lee was brief and no subsequent investigations were pursued²⁴. For this investigation we employed combinatorial evaporative sputtering and high-throughput parallel screening in search of Pt_xPd_yAl_z electrocatalysts for the electro-oxidation of SO₂. Identified compositions that merit more thorough investigation were evaluated by employing conventional methods.

5.2 Experimental

5.2.1 Preparation, deposition, screening and annealing of thin films

The wafer and glassy carbon preparation, thin film deposition and electrochemical testing have previously been described in-depth^{20, 21}. Employing a built-in quartz crystal microbalance (QCM)²⁰ and Pt, Pd and Al targets, all with a purity of 99.99% (ACI alloys), the conditions for physical vapour deposition (PVD) were

derived for the chosen compositions. The thin films (~60 nm) were subsequently deposited in triplicate by PVD, onto an annular arrangement (Roelof Jacobus Kriek, Combinatorial Screening Array, PCT/IB2016/056830 (PCT Application)) of 64 square working electrode pads (0.09 cm² each), developed through photolithography ²⁰ (Figure 5.2). The electrode pads were connected by a network of traces to individual rectangular pin pads on the outer perimeter of the wafer. The network of traces were provided with reinforced bending points to prevent braking of the lines/traces. For the conventional electrochemical testing glassy carbon inserts (0.196 cm² each) were employed as substrate onto which the thin metal films were deposited. Electrochemical testing was performed on the wafer containing the various thin film compositions, in a dedicated electrochemical cell ²⁰, with each working electrode connected individually to a multichannel potentiostat (Arbin MSTAT) for high-throughput screening while conventional testing commenced in a standard three electrode setup ²¹. Preconditioning was conducted in degassed 0.1 mol.L⁻¹ HClO₄ (Merck), scanning from 0.041 V vs SHE to 1.441 V vs SHE starting at E_{ocp} (open circuit potential) for 25 cycles, followed by 3 cycles up to 1.741 V vs SHE and finally the first step was repeated but only for three cycles, employing a scan rate of 50 mV.s⁻¹ respectively. Linear polarisation (LP) was conducted in 1 mol.L⁻¹ H₂SO₄ (Merck, pH = 0.55) in the potential window 0.2 V vs SHE to 1.441 V vs SHE at a scan rate of 10 mV.s⁻¹. This solution was degassed with N₂ for 15 min prior to linear polarisation. A stock solution of 1 mol.L⁻¹ Na₂SO₃ (Sigma Aldrich) was used as an in-situ SO₂ source ²⁰. These electrochemistry testing parameters were identical for the thin films deposited onto the wafer and the glassy carbon inserts. Subsequent to the deposition of the selected thin film combinations onto the glassy carbon substrates (designated with letters of the alphabet as a means to ease comprehension throughout the article), some were kept as fresh (as-deposited) thin films while the rest of the thin films were annealed ex-situ under an Ar atmosphere, employing a rapid thermal annealing oven (Accuthermo AW610), with the maximum temperatures ranging from 600 °C to 900 °C with intervals of 100 °C ²¹.

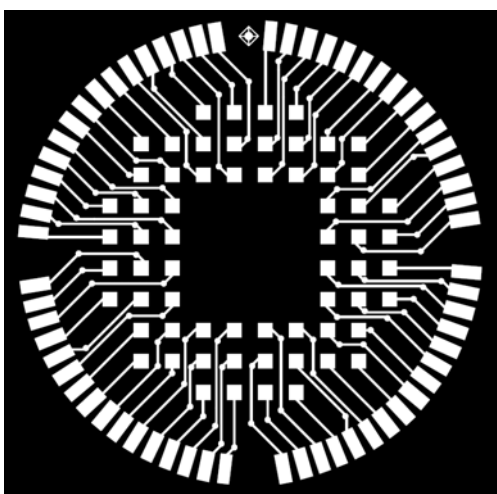


Figure 5.2: Annular arrangement of 64 square working electrode pads (Roelof Jacobus Kriek, Combinatorial Screening Array, PCT/IB2016/056830 (PCT Application)).

5.2.2 Physical characterisation of thin films

Energy-dispersive X-ray spectroscopy (EDX, employing INCA software) analysis, in moving average mode employing a collection time of 100 s and a 15 keV electron source, was conducted in triplicate before and after electrochemical testing, so as to evaluate thin film composition. Atomic force microscopy (AFM, Nanoscope V Multimode from Veeco) was used to investigate surface roughness, deriving various surface roughness parameters by employing Nanoscope Analysis (Veeco) software. In addition, surface properties of the thin films were characterised employing X-ray photoelectron spectroscopy (XPS). A Thermo Fisher Scientific K-ALPHA spectrometer was used for surface analysis with a monochromatised Al K α source ($h\nu = 1486.6$ eV) and a 200 micrometer spot size. A pressure of 10^{-7} Pa was reached in the chamber when transferring the samples. The full spectra (0-1100 eV) were obtained with a constant pass energy of 200 eV and high resolution spectra (C1s, Pd3p-O1s, Al2p-Pt4f, Pd3d, Al2s) at a constant pass energy of 40 eV. Charge neutralisation was applied during analysis. Sputtering was performed with Ar⁺ ions at 500 eV. High resolution spectra were fitted and quantified (Scofield sensitivity factors used for quantification) using the AVANTAGE software provided by Thermo Fisher Scientific.

5.3 Results and discussion

5.3.1 Combinatorial sputtering and high-throughput screening of the Pt_xPd_yAl_z system

With the focus on identifying a possible ternary anode composition for application in the electro-oxidation of SO₂, Pt_xPd_y compositions were evaluated previously^{20, 21} and characterised so as to establish a standard for comparison with ternary Pt_xPd_yAl_z anode compositions²⁵. The initial binary combinations investigated, included a wide compositional range (Pt_xPd_y) that spanned from pure Pt to pure Pd using mainly 10% content increments (refer to reference²⁰ for in-depth details). Pt₃Pd₂ was identified to be the optimum binary composition and extensive characterisation was conducted on it²¹, with annealed Pt₃Pd₂ (at 800 °C) proving to be a worthy contender to compete with pure Pt for the electro-oxidation of SO₂. In producing a ternary electrocatalyst the combination of Pt and Pd with a base metal will result in an electrocatalyst containing less noble metal with Al making up the balance. Due to the vast number of electrocatalyst combinations that can statistically be formulated using the three components, Pt, Pd, and Al, our selection of electrocatalysts to be subjected to high-throughput screening was aligned in accordance to the high-throughput experimental planning strategies as categorised by R. Potyrailo, which includes a hierarchical development of the experiment starting out from a broad base with an increased and more detailed focus as the area of interest narrows²⁶. The finding of our previous work, i.e. that a Pt₃Pd₂ combination annealed at 800 °C exhibited competing performance, was employed as a guideline for the development of a possible ternary anode composition that includes a base metal. To this regard ternary compositions were mainly focused, but not limited to, that area where Pt is less than 60%, Pd less than 40% (i.e. Pt₃Pd₂) and random Al content. Al, however, could not be increased above 60% as (i) Al deposits at a much lower rate in contrast to Pt and Pd resulting in very long deposition times, while operating the PVD apparatus at its limit,

(ii) Al is not very resistant in strong acidic environments with degradation being almost immediate in sulphuric acid, and (iii) a report found in literature, on Pt and Al combinations, proved that only small amounts of Al is effective in improving catalytic performance²³. Linear polarisation response of the various compositions were obtained through high-throughput parallel screening, which is a simple means of quickly identifying an active composition that may work well in the SDE environment. The average of the polarisation graphs (conducted in triplicate) were used to determine the onset potential for each ratio employing the method reported by Cooper & McGinn with the current density based on (a) geometric area^{20, 25, 27}, and (b) mass Pt present in the thin film.

Before and immediately subsequent to electrochemical testing each of the catalyst pads were visually evaluated for signs of corrosion. Some of the compositions did corrode during electrochemical testing (Figure 5.3), which was also observed by Cooper & McGinn for their Pt-Ru-W thin film anode catalysts for direct methanol fuel cells²⁵.

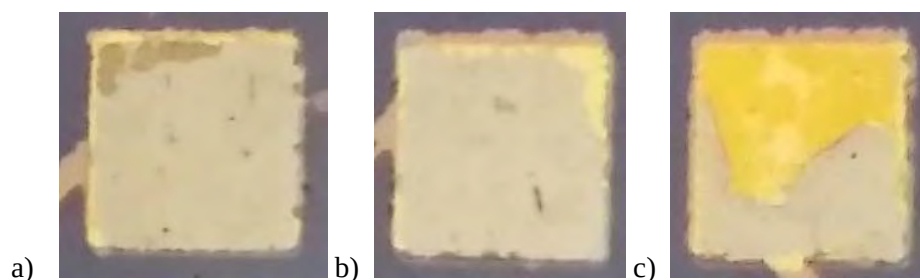


Figure 5.3: Examples of varying degrees of corrosion occurring after linear polarisation for (a) $\text{Pt}_{34}\text{Pd}_{22}\text{Al}_{44}$, (b) $\text{Pt}_{43}\text{Pd}_{46}\text{Al}_{11}$, and (c) Al.

In the event that the greatest portion of the pad revealed corrosion, it was not included in the results, as it would in essence be the gold circuit that participated in the electro-oxidative reaction. Gold shows a high onset potential for SO_2 electro-oxidation, hence obtaining low onset potentials eliminated the possible interference of gold. Onset potential, as a means of evaluating catalyst activity, is a suitable measure in the event of possible corrosion as it is not influenced by any change in surface roughness²⁵. As only some catalyst pads revealed signs of severe corrosion, which were subsequently eliminated, current density based on geometric area and mass of Pt present in the thin film were also employed to evaluate thin film combinations. Current density, in contrast to onset potential, is influenced by both surface roughness and composition and by applying both these parameters to identify thin film candidates during the screening phase limits the occurrence of systematic errors. Screening of the various thin film combinations, for the electro-oxidation of SO_2 , are summarised in Figure 5.4 as ternary plots in terms of (a) onset potential (V), (b) current density ($\text{mA}\cdot\text{cm}^{-2}$), and (c) mass-specific current density ($\text{mA}\cdot\mu\text{g Pt}^{-1}$). Employing these criteria eight thin film composition, three based on lowest onset potential value, three based on highest geometric current density (normalised by geometric area), and two based on highest mass-specific current density (normalised by Pt mass), were selected for additional testing employing conventional testing techniques with glassy carbon inserts as substrate.

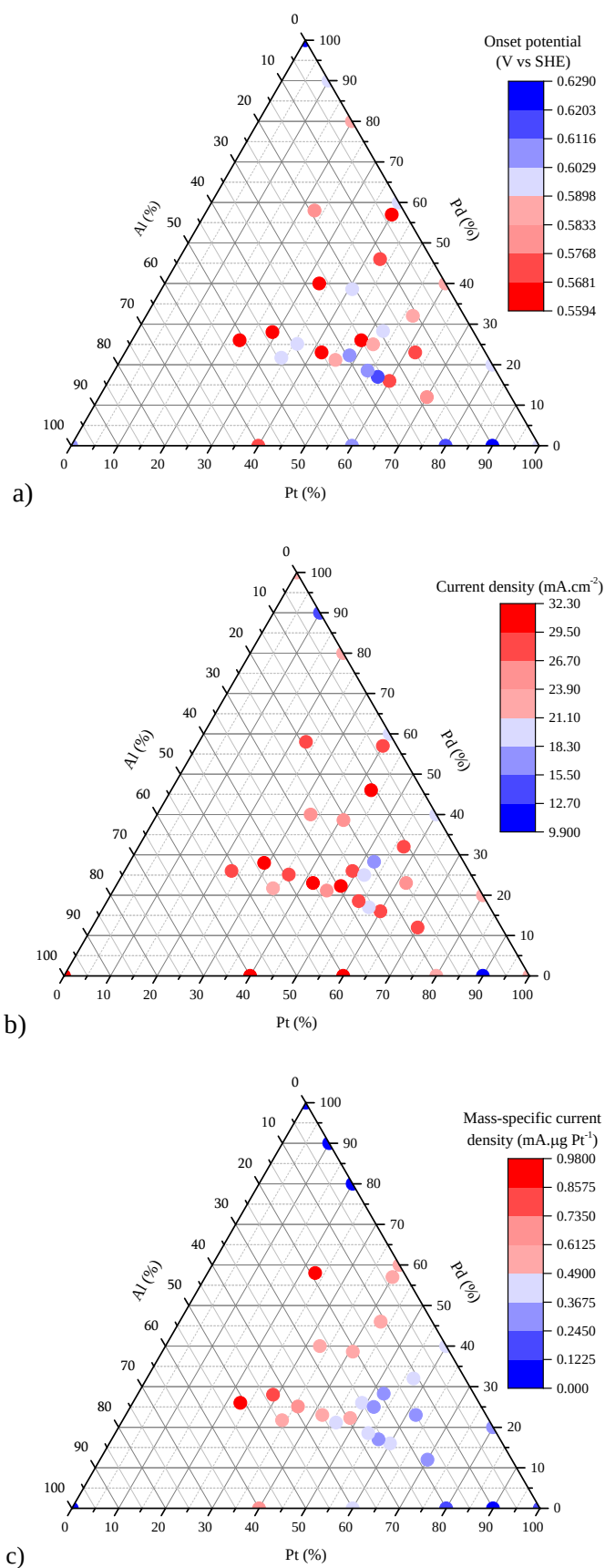


Figure 5.4: Ternary plots for (a) onset potential, (b) current density normalised by geometric area, and (c) mass-specific normalised current density, towards SO_2 electro-oxidation for the $\text{Pt}_x\text{Pd}_y\text{Al}_z$ system.

5.3.2 Composition of the thin films prior to conventional electrochemical testing

The bulk stoichiometry of the eight best electrocatalysts was investigated in triplicate by EDX, both before and after annealing. EDX analysis revealed that the expected theoretical compositions, predicted by employing the built-in QCM, correlate well with the actual sputtered bulk stoichiometry (Figure 5.5). No difference between as-deposited thin films and their corresponding annealed states were observed.

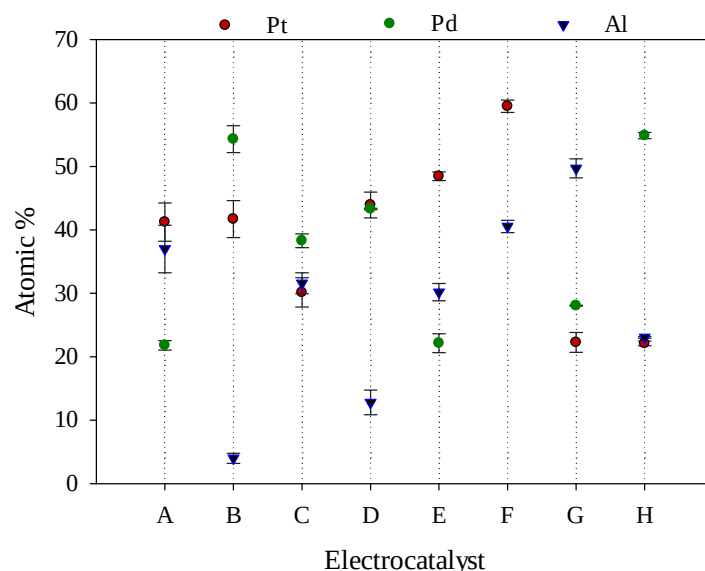


Figure 5.5: EDX after sputtering verifying that the actual sputtered ratios correlate with the expected sputtered ratios of (A)-Pt₄₂Pd₂₃Al₃₅, (B)-Pt₄₀Pd₅₇Al₃, (C)-Pt₃₃Pd₄₀Al₂₇, (D)-Pt₄₃Pd₄₆Al₁₁, (E)-Pt₄₈Pd₂₃Al₂₉, (F)-Pt₆₀Al₄₀, (G)-Pt₂₃Pd₂₆Al₅₁, and (H)-Pt₂₃Pd₅₈Al₁₉.

5.3.3 Conventional electrochemical evaluation

5.3.3.1 Linear polarisation and subsequent EDX characterisation

Employing physical vapour deposition and high-throughput screening accelerates the complex process of new catalyst design and improves performance identification. However, it is not sufficiently suited for in-depth investigation and characterisation, and conventional methods, such as rotating disk electrode (RDE) linear polarisation, are more suitable. Hence, Figure 5.6 exhibits the electrocatalytic performance of the eight selected thin films (in the as-deposited (AD) and annealed state (on glassy carbon as substrate)) that did not show signs of corrosion (mainly in the form of delamination) during/after electrochemical testing. (I)-700 °C, referring to Pt, and previously identified (J)-800 °C, referring to Pt₃Pd₂, are taken as the baseline against which all ternary combinations are compared. In general, it is evident that no significant improvement in onset potential was achieved, with the majority of electrocatalysts exhibiting similar onset potentials (within error), when compared to (I)-700 °C and (J)-800 °C. However, (E)-AD, 700 °C, 800 °C and (D)-AD performed well. As the results obtained from onset potential are not sufficient for identifying

an alternative electrocatalyst, mass-specific current density was also investigated. From Figure 5.6b it is evident that the majority of the ternary electrocatalysts exhibited an increase in current density.

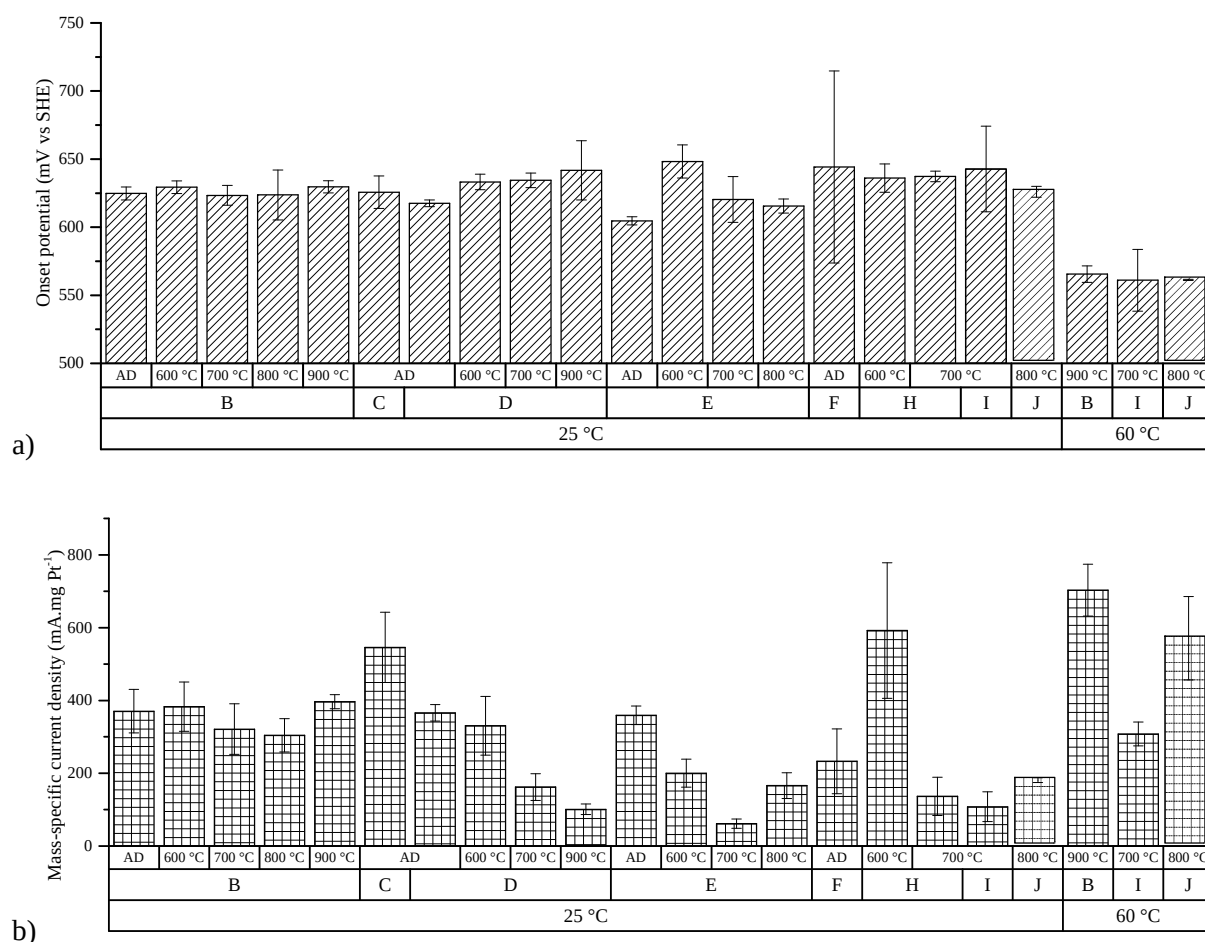


Figure 5.6: Onset potential values (a) and mass-specific current density values (b) for (B)-Pt₄₀Pd₅₇Al₃, (C)-Pt₃₃Pd₄₀Al₂₇, (D)-Pt₄₃Pd₄₆Al₁₁, (E)-Pt₄₈Pd₂₃Al₂₉, (F)-Pt₆₀Al₄₀, (H)-Pt₂₃Pd₅₈Al₁₉, (I)-Pt, and (J)-Pt₃Pd₂.

Subsequent to electrochemical testing (Figure 5.6) the thin film electrocatalysts were analysed by EDX so as to evaluate any change in composition that could not be visually detected (an indication of short term stability). Overall, all the catalysts exhibit a slight change in compositional ratio with no specific trend (Figure 5.8), when compared to the compositional ratios directly after sputtering (Figure 5.5), with (B)-AD, (F)-AD, (H)-600 °C and (H)-700 °C showing the largest deviation in compositional ratio. This is however not sufficient in identifying a stable electrocatalyst, and additional evaluation on the stability is required. In an attempt to identify a stable electrocatalyst, in conjunction with having a low onset potential and acceptable current output, consecutive cycling in a sulphuric acid environment was conducted (Figure 5.9). For all the electrocatalysts under investigation, the only electrocatalyst that exhibited improved stability, compared to (I)-700 °C and (J)-800 °C, was (B)-900 °C, lasting about 1.4 times longer. Taking all three parameters (onset potential, mass-specific activity, and stability) into consideration that are indicative of an

improved electrocatalyst, (B)-900 °C can therefore be considered the ternary candidate exhibiting the most potential in competing with (I)-700 °C and (J)-800 °C. Compared to the baseline, i.e. Pt and Pt_3Pd_2 , $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ (annealed at 900 °C) performed the best in that current density (mA.mg Pt^{-1}) increased from 108.11, to 181.21 and finally to 396.73 for Pt, Pt_3Pd_2 and $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ respectively, indicating an increase in activity that correlates with a decrease in Pt content (Figure 5.7).

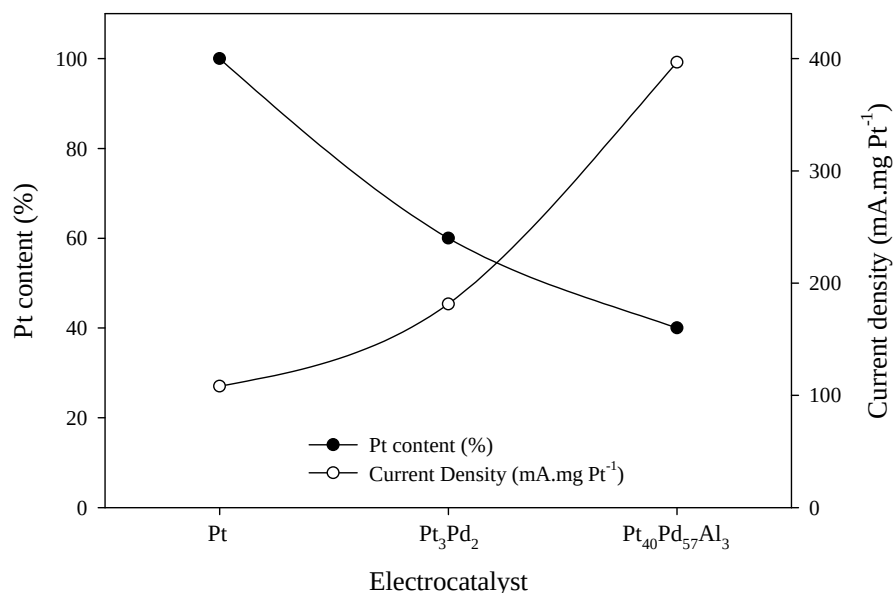


Figure 5.7: Correlation of current density (mA.mg Pt^{-1}) with Pt content (%).

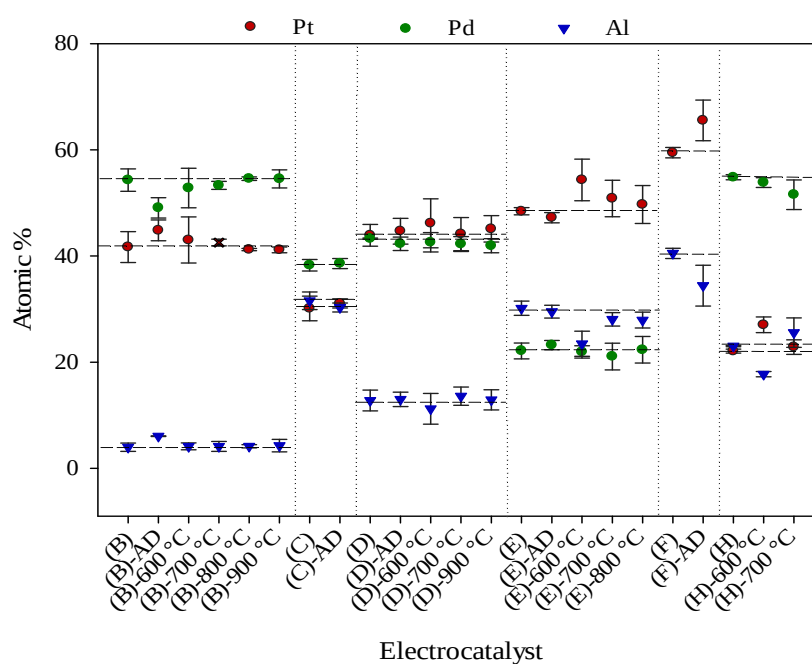


Figure 5.8: EDX analysis subsequent to LP runs for (B)- $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$, (C)- $\text{Pt}_{33}\text{Pd}_{40}\text{Al}_{27}$, (D)- $\text{Pt}_{43}\text{Pd}_{46}\text{Al}_{11}$, (E)- $\text{Pt}_{48}\text{Pd}_{23}\text{Al}_{29}$, (F)- $\text{Pt}_{60}\text{Al}_{40}$, and (H)- $\text{Pt}_{23}\text{Pd}_{58}\text{Al}_{19}$.

To put (B)-900 °C further to the test, it was subsequently evaluated under an increased electrolyte temperature of 60 °C (using a SCE reference electrode above this temperature is not advised, due to the instability of Hg_2Cl_2) with the results also being depicted in Figure 5.6 and Figure 5.9. At this elevated temperature the same phenomena were observed for (B)-900 °C, (I)-700 °C and (J)-800 °C as in the case of 25 °C, with no significant difference in onset potential having been observed. However, an improved performance was evident in terms of current output and durability. The (B)-900 °C thin film (at 25 °C) furthermore exhibited totally different behaviour in terms of visible signs of corrosion when compared to all the other tested electrocatalysts. This was evident in that the (B)-900 °C thin film (at 25 °C) dissolved gradually into solution (visually monitored until the film was so thin, that glassy carbon started to appear), keeping its active surface (Figure 5.10a) as only the thin film thickness decreased, while all the other electrocatalysts, including the target electrocatalysts ²¹, clearly delaminated. (B)-900 °C (at 60 °C), in contrast, only started to exhibit the normal signs of delamination nearer to the end of its stability lifetime, with the last cycle subsequently being lower in the hydrogen adsorption/desorption region than the first cycle (Figure 5.10b), as a part of the thin film delaminated from the surface.

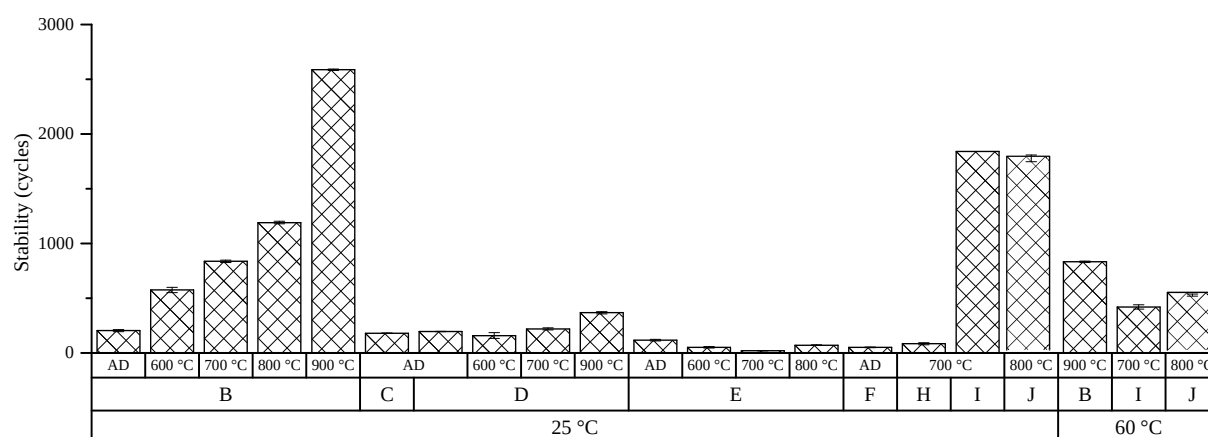


Figure 5.9: Consecutive cycling of thin film electrocatalyst for stability evaluation with (B)- $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$, (C)- $\text{Pt}_{33}\text{Pd}_{40}\text{Al}_{27}$, (D)- $\text{Pt}_{43}\text{Pd}_{46}\text{Al}_{11}$, (E)- $\text{Pt}_{48}\text{Pd}_{23}\text{Al}_{29}$, (F)- $\text{Pt}_{60}\text{Al}_{40}$, (H)- $\text{Pt}_{23}\text{Pd}_{58}\text{Al}_{19}$, (I)-Pt, and (J)- Pt_3Pd_2 . Conditions: scan rate of 100 mV.s^{-1} and potential window of 0.041 V vs SHE to 1.441 V vs SHE at 25 °C and 60 °C.

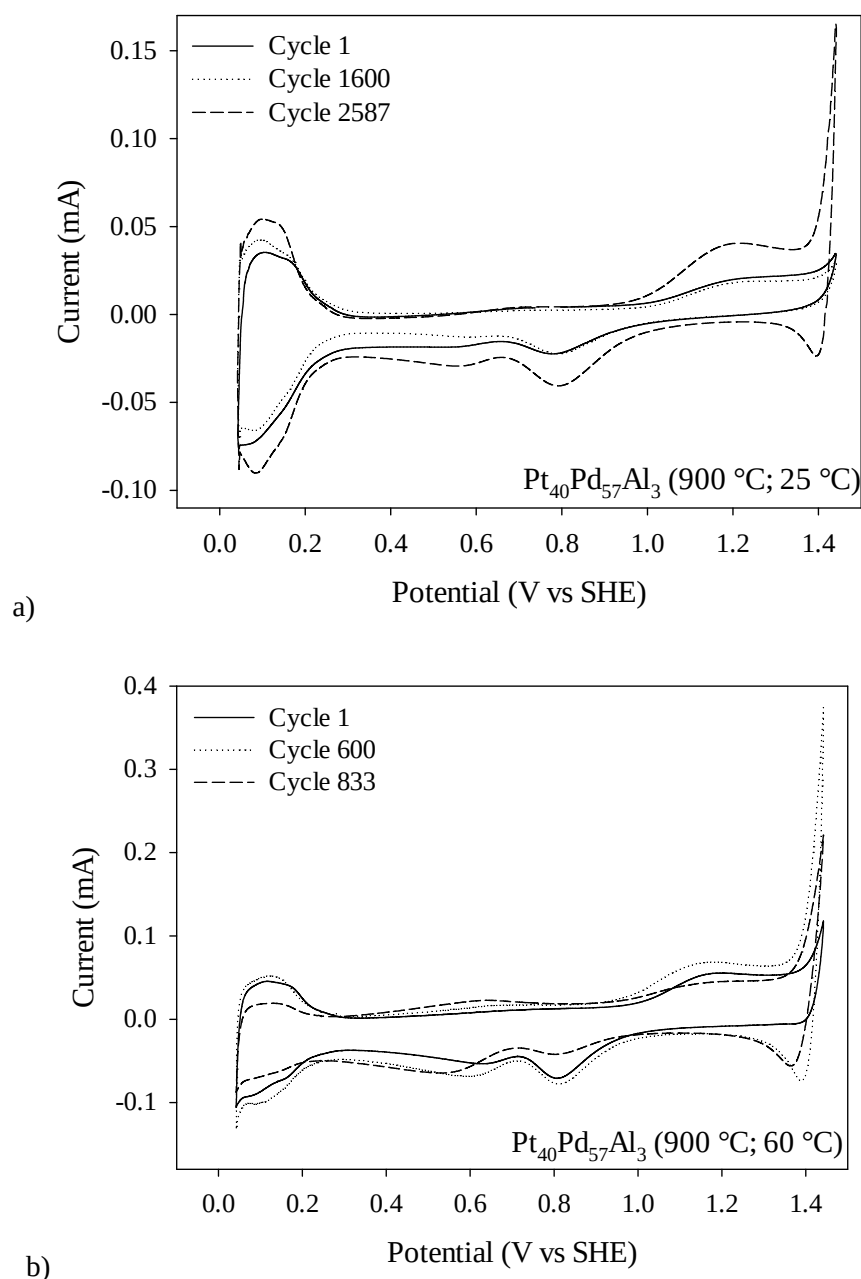


Figure 5.10: Consecutive cycling of (B)-Pt₄₀Pd₅₇Al₃ annealed at 900 °C in H₂SO₄ at (a) 25 °C, and (b) 60 °C.

5.3.4 Further characterisation and discussion

AFM and XPS analyses were conducted on the most promising binary ²¹ and ternary thin film electrocatalysts in competition with pure Pt for SO₂ electro-oxidation, with the aim being to gain more insight into the physical and electronic properties of these thin films. Pt thin films (as-deposited and the best performing annealed form) were also included in these analyses, serving as the primary reference/target electrocatalyst.

5.3.4.1 AFM analysis

AFM allows, among other things, meticulous observation and evaluation of the morphological and topographical characteristics of thin film surfaces. Three-dimensional (3D) AFM scans were recorded over a substrate area of $2\ \mu\text{m} \times 2\ \mu\text{m}$, for each sample, at three different locations on the thin film. Roughness parameters were calculated from 2 different positions within each of the three individual locations so as to provide reliable average roughness values representative of the whole thin film surface.

Table 5.1: 2D and 3D AFM images for electrocatalysts (I)-Pt (700 °C), (J)-Pt₃Pd₂ (800 °C), and (B)-Pt₄₀Pd₅₇Al₃ (900 °C).

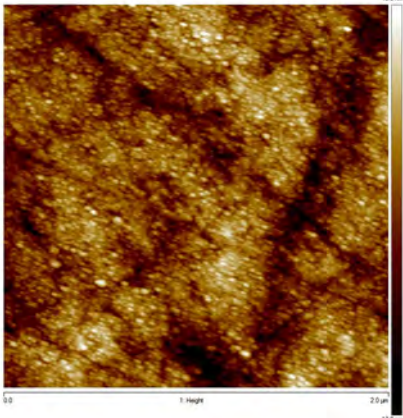
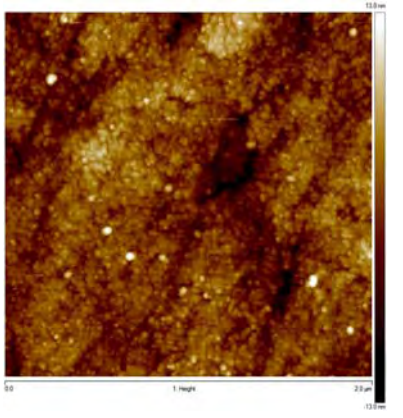
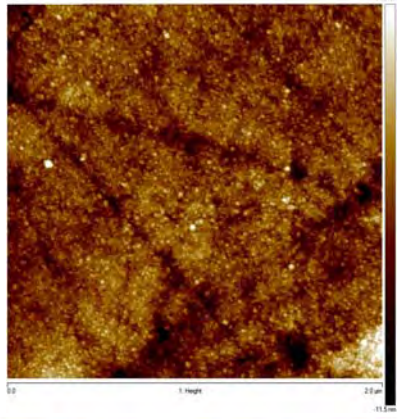
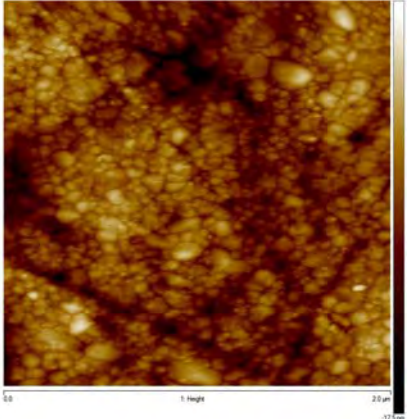
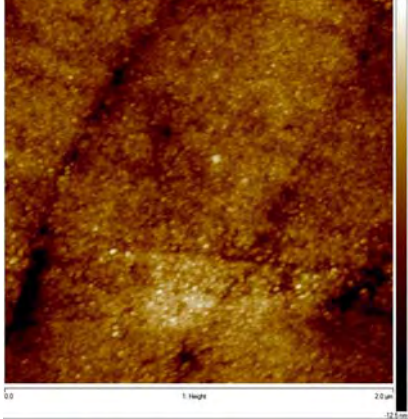
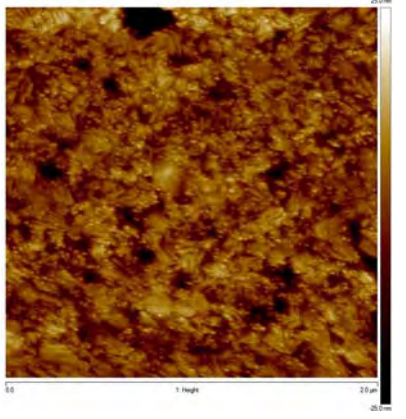
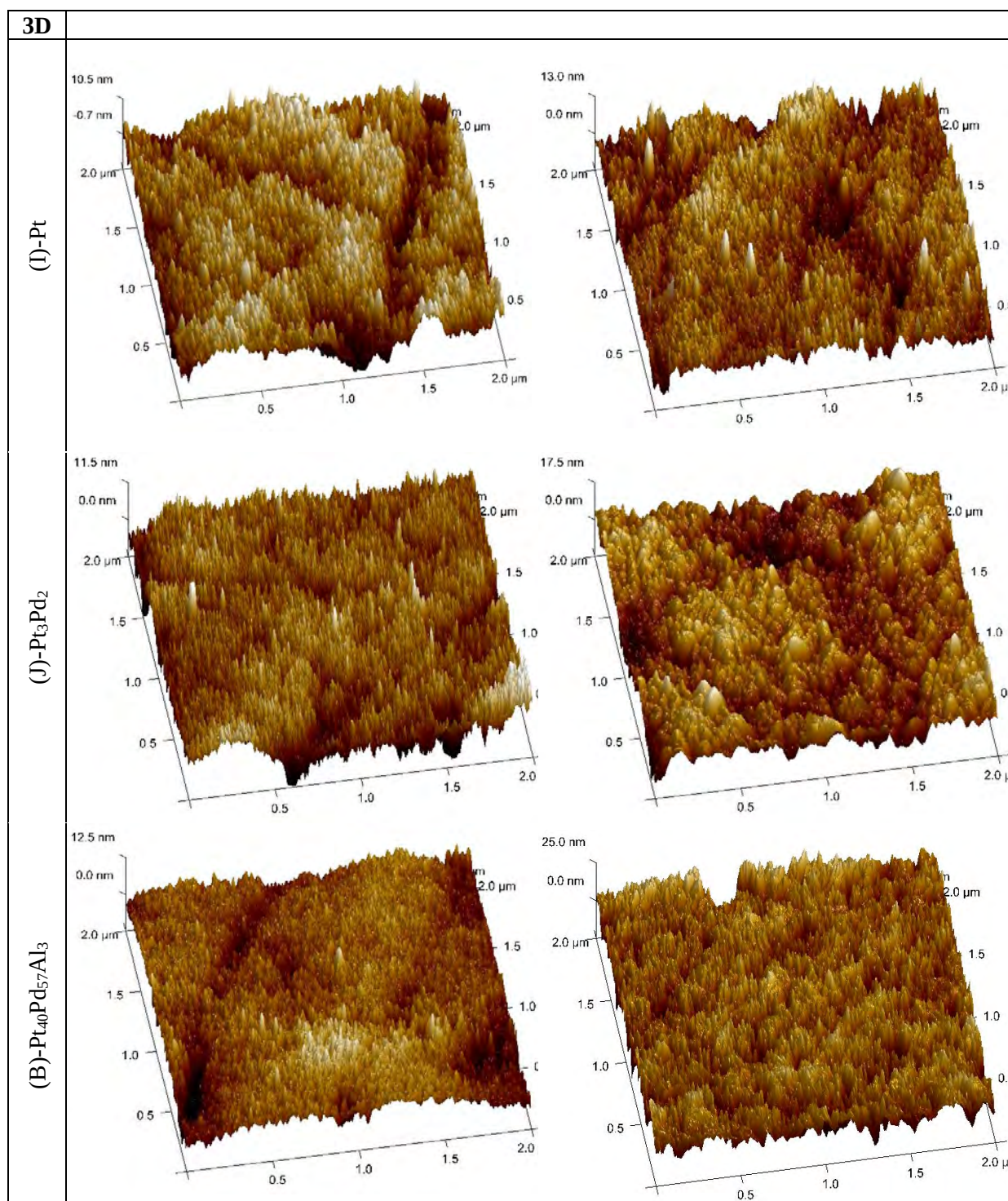
2D	As-deposited	Annealed
(I)-Pt		
(J)-Pt ₃ Pd ₂		
(B)-Pt ₄₀ Pd ₅₇ Al ₃		

Table 5.1: ... continued



From the 2D and 3D AFM images shown in Table 5.1, it is clear that the thin films in the as-deposited form all exhibit a fine distribution of metal particles, adapting the profile of the underlying glassy carbon surface, with unavoidable grooves clearly visible resulting from polishing. Upon annealing the as-deposited thin films evolved from exhibiting a finely distributed appearance to clearly exhibiting different degrees of

crystal formation with the least amount of change being visible for (I)-700 °C. (J)-800 °C transformed into a surface with clearly defined grain boundaries, evidence of a polycrystalline nature²¹. (B)-900 °C exhibited crystal growth of a totally different nature when compared to (J)-800 °C, with a type of random agglomerated distribution of small ‘sheets’ of crystals varying in orientation with sharp corners emerging from the surface. It is remarkable how only ~3% Al metal content can induce such an extreme difference in surface/bulk structure upon annealing. This type of crystal growth might be one of the reasons for observing a prominent improvement in catalyst performance for (B)-900 °C, especially the stability performance observed for this electrocatalyst in a sulphuric acid environment for both 25 °C and 60 °C (Figure 5.9), when compared to (I)-700 °C and (J)-800 °C.

In addition to 2D and 3D imaging, the following surface roughness profile parameters (Figure 5.11) were acquired: (i) average roughness (R_a), which is based on mean height roughness, (ii) vertical distance between the highest and lowest points (R_t), and (iii) root mean square (RMS) of the distribution of surface height making it a bit more sensitive than R_a ²⁸.

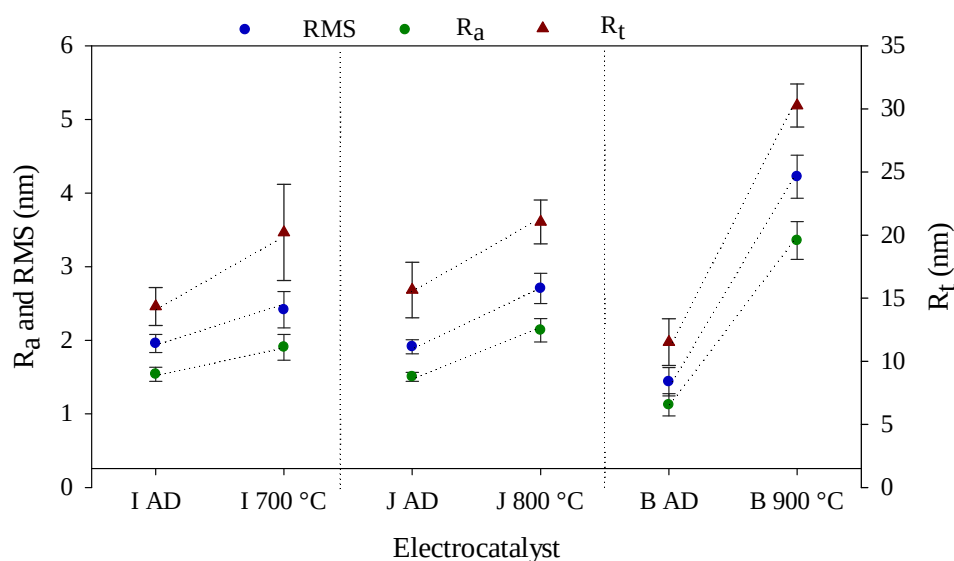


Figure 5.11: Surface roughness profile parameters of (I)- Pt as-deposited (I AD) and annealed at 700 °C, (J)- Pt₃Pd₂ as-deposited (J AD) and annealed at 800 °C, and (B)- Pt₄₀Pd₅₇Al₃ as-deposited (B AD) and annealed at 900 °C.

In general, as is evident from Figure 5.11, (I)-700 °C and (J)-800 °C exhibited similar values for all the roughness parameters with (B)-AD showing a smoother surface (lower values) overall. As for the different annealed forms of the individual thin films, the roughness parameters all increased from the as-deposited state to the specific annealed form, with (B)-900 °C being the most influenced by annealing treatment and also exhibiting totally different crystal growth compared to (I)-700 °C and (J)-800 °C (Table 5.1 2D). Overall, (B)-900 °C exhibited the highest roughness values for all three roughness parameters acquired,

which has a direct and positive effect on the higher current output observed when compared to (I)-700 °C and (J)-800 °C. The rapid thermal annealing of catalyst (B)-900 °C has a positive influence on the performance and stability of this catalyst towards SO₂ electro-oxidation in a sulphuric acid environment.

5.3.4.2 XPS

In an attempt to further elucidate the observed electrocatalytic performance of the most promising binary²¹ and ternary thin film electrocatalysts, in competition with pure Pt for SO₂ electro-oxidation, XPS surface analysis and depth profiling on the thin film samples were conducted so as to gain information regarding their composition and chemical environment. Knowing the overlapping that occurs between Pd3p3-O1s and Al2p-Pt4f peaks, high resolution spectra were collected to ensure that the best fitted quantified results are obtained, especially for materials J and B (cf. Electronic Supplementary Information (ESI) Figure S1 and S2 for fitted XPS spectra after 10s Ar⁺ etching for (B)-AD and (B)-900 °C). The fits were conducted subsequent to linear background subtraction using a product of Gaussian and Lorentzian functions, as defined in the AVANTAGE software. Figure 5.12 reveals comparative information for the AD and annealed states with regard to the extreme surface (top outer layer) of the thin films for Pt4f, Pd3d and Al2s. Figure 5.13 exhibits compositional information (derived from the C1s, O1s, Pt4f_{7/2}, Pd3d_{3/2} and Al2s peak areas), related to the depth of the metallic Pt and Pt-based thin films deposited on glassy carbon as substrate. It must be kept in mind that (i) XPS remains a semi-quantitative analysis to follow atomic compositional change with depth (not to be directly correlated with previous EDX results), and (ii) XPS has an accuracy within 5 to 10% of absolute atomic % compositional information²⁹.

In the as-deposited state, no shift in the Pt4f_{7/2} peak at ~71.15 eV was observed for (I), (J) and (B), which is a direct indication that no significant change in the chemical environment occurred during/as a result of physical vapour deposition. Upon annealing, again no shift in the Pt4f_{7/2} binding energy was observed for (I)-700 °C and (J)-800 °C; however, a clear change was observed for (B)-900 °C, exhibiting a slight negative shift in the Pt4f_{7/2} (Figure 5.12d) and Pd3d_{5/2} peaks (Figure 5.12e), which could possibly be ascribed to the occurrence of metal-metal interactions as a result of annealing temperature³⁰. In addition, (B)-900 °C (Figure 5.12f) exhibited an increase in Al content at the surface (15 at.%) when compared to (B)-AD (only 2 at.%), which is expected if explained in terms of fundamental properties of monometallic metals (atomic radius)³¹. For the metals present in (B)-900 °C, the order of decreasing size with regard to atomic radii is Al (143 pm) > Pt (139 pm) > Pd (137 pm)³². In general, lattice strain is expected to contribute to the segregation/migration of the atom with the largest atomic radius to the surface, which in the case of (B)-900 °C is Al. This supports the observation obtained from XPS data that Al2s mainly appears on the extreme surface subsequent to annealing (Figure 5.12f), which clearly points towards the migration of Al to the surface upon annealing.

While the previous XPS measurements (Figure 5.12) focused on the surface, depth profiles of the Pt and Pt-based samples (Figure 5.13) were obtained by combining a sequence of Ar⁺ ion gun etch cycles with XPS measurements from the current exposed surface. The objective of obtaining depth profiles was to validate that the observed electrocatalytic performance was not as a result of a ‘skin’ formed, as a result of severe segregation/migration to the surface, but rather being the result of a homogeneous composition throughout the depth of the thin film. The first observation for all the electrocatalysts, in both the as-deposited and annealed states, is (i) the presence of inescapable C, N, Si and Cl impurities, due to ambient pollution on the metal surface layer, disappearing after only 10 s of Ar⁺ etching, and (ii) a constant ~55 nm thin metallic layer (validating the calibrated sputtered layer of ~60 nm) recorded by XPS etching for all the analysed thin films. Subsequent to Ar⁺ etching through the thin metallic film, it is clear that at a depth of ~40 nm carbon from the substrate appears. Carbon, however, is present almost throughout the depth of the annealed surfaces (especially sample (B)-900 °C), which can be explained either by possible diffusion of the substrate through the Pt/Pd/Al thin film at high temperature (which is unlikely as these specific glassy carbon inserts are stable under high temperatures) or as a result of XPS detecting possible ‘exposed’ substrate carbon as a result of the roughness of the (B)-900 °C thin film (R_t around 30 nm, Figure 5.11). It is furthermore evident that contraction of the different sputtered layers occurs upon annealing with increased contraction as the temperature increases.

For (B), Al seems to be in the oxidised state throughout the entire thickness of the layer (118.5 eV binding energy Figure 5.12f, only data for the top layer is shown). As Al gets oxidised easily in air, it is very probable that the samples were oxidised from the moment when the thin films were exposed to air. In addition, XPS depth profiling for (B)-900 °C supports the previous observation (Figure 5.12f) of a degree of migration of Al towards the surface after annealing and that all three metals are present throughout the depth of the thin film. Concerning Pd3d_{5/2} peak fitting (cf. ESI Figure S1 and S2), the absence of PdO bonding usually located at 337 eV is confirmed³³ as the maximum component is Pd metal at around 335 eV, while another 1 eV higher (~336 eV) could be attributed to Pd-O-X bonding namely Pd-O-Al.

As thin film (B), i.e. Pt₄₀Pd₅₇Al₃, presented itself as being a competitive electrocatalyst for SO₂ electro-oxidation, measured against Pt and the previously identified Pt₃Pd₂ composition, XRD spectra were furthermore recorded for (B)-AD and (B)-900 °C (cf. ESI Figure S3). (B)-AD is concluded to consist of a PtPd cubic phase, whereas (B)-900 °C consists of a possible Pt_{2.84}Al_{1.16} cubic phase that may support the slight negative shift observed for the Pt4f_{7/2} (Figure 5.12d) and Pd3d_{5/2} peaks (Figure 5.12e), which are indicative of alloy formation.

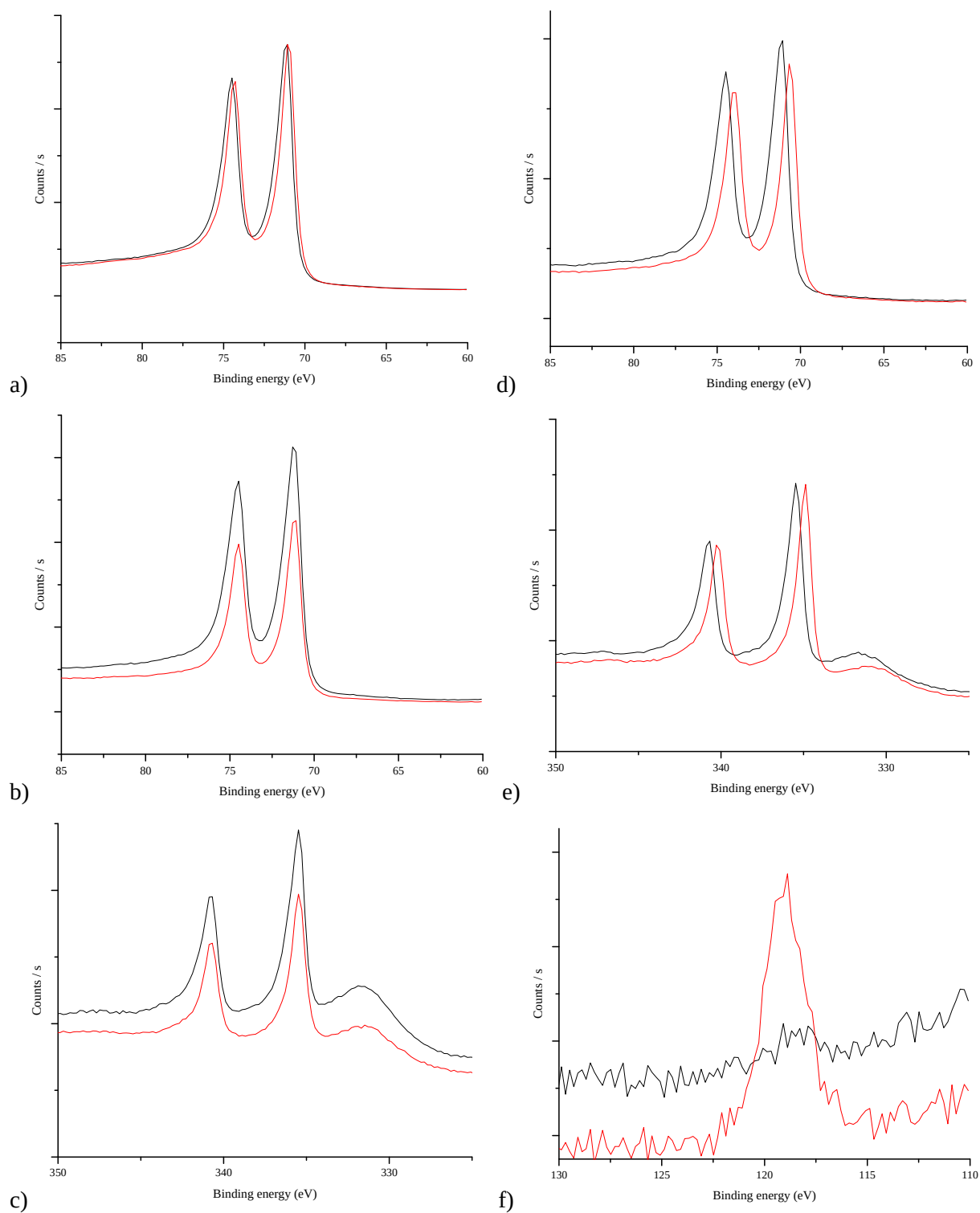


Figure 5.12: Pt4f, Pd3d and Al2s XPS spectra on the extreme surface, i.e. the top outer layer, of both the as-deposited (AD) (black curve) and annealed states (red curve) of (I)-Pt (a), (J)-Pt₃Pd₂, (b, c) and (B)-Pt₄₀Pd₅₇Al₃ (d, e, f).

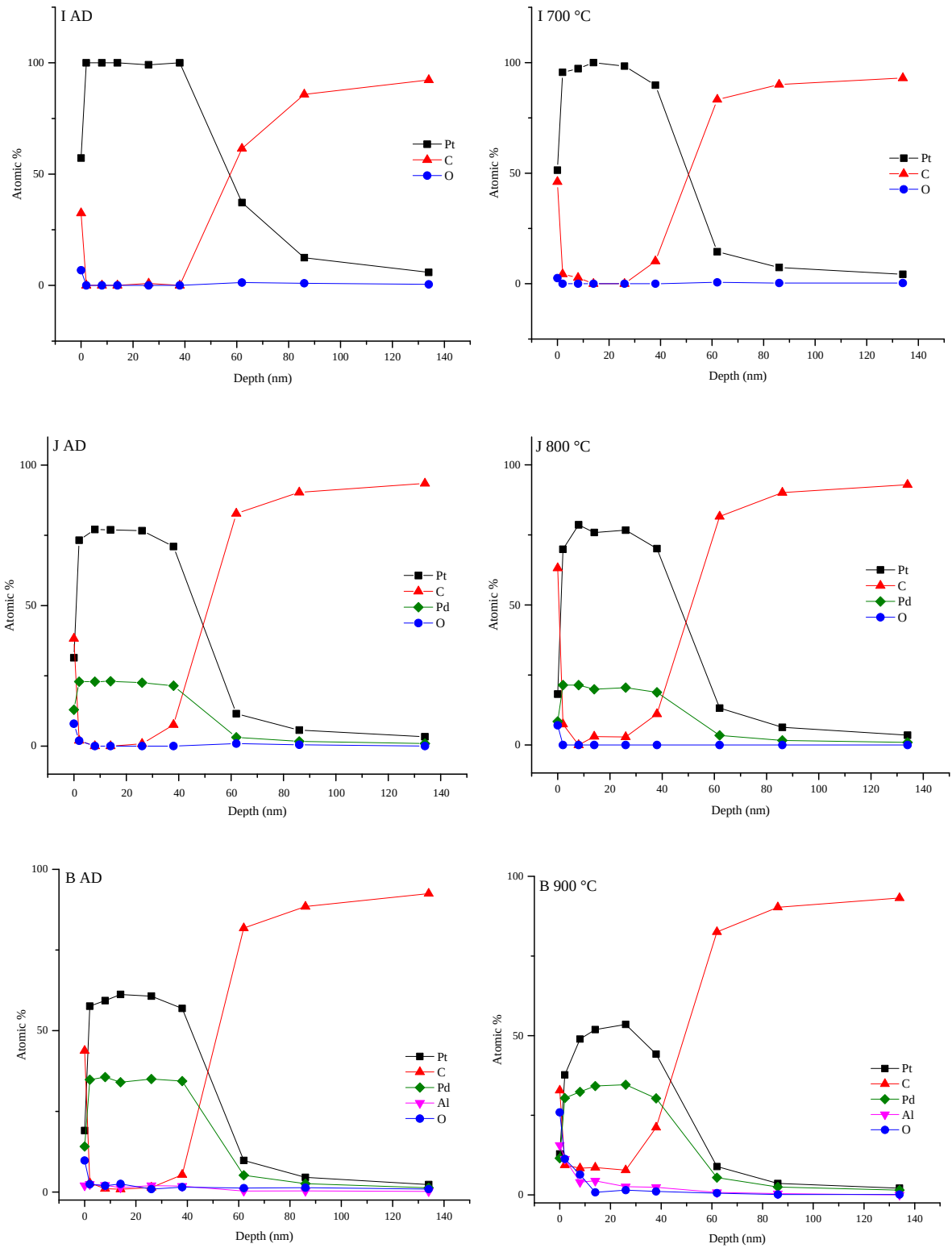


Figure 5.13: Depth profiles of (I)-Pt, (J)-Pt₃Pd₂ and (B)-Pt₄₀Pd₅₇Al₃, for both the as-deposited (AD) and annealed states. The etch-rate was estimated 0.2 nm/s on each material.

5.4 Conclusion

As is evident from literature, only a limited number of surfaces have been investigated thus far for catalysing the electro-oxidation of aqueous SO_2 . It is furthermore clear that widespread disagreement and non-reproducible behaviour exist²⁴, as this reaction is very sensitive and highly influenced by the prevailing conditions (electrode material, pH, temperature, preconditioning, pressure, applied anodic potential, etc.). The mechanism of SO_2 electro-oxidation is highly contested and proposed mechanisms mainly include (a) indirect oxidation via a dithionate intermediate³⁴⁻³⁶ or involving bulk SO_2 together with an unspecified S(VI) intermediate³⁷, and (b) direct oxidation via an adsorbed reactant³⁵. The sensitivity of this reaction to the electrocatalytic surface, combined with the mechanistic complexity of this reaction³⁸, requires that the performance of a specific active electrocatalyst of interest will be better understood through an in-depth and detailed mechanistic investigation, that takes into account various factors such as temperature, acid concentration, sulphur coverage, etc. The majority of mechanistic studies on SO_2 oxidation, however, were mainly conducted on platinum and single component electrode materials. The extensive effort devoted to understanding the mechanism by which SO_2 is electro-oxidised by Pt substantiates the fact that the necessary mechanistic characterisation of any identified multi-component electrocatalyst, e.g. $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$, is bound to be challenging and will require meticulous and repeatable evidence so as to be fundamentally sound.

From our investigation, identifying a possible alternative anode catalyst that can compete with pure Pt, it is clear that a lot of scope and room for improvement still exist for improving the catalytic activity and stability of the electrocatalyst. In general, it is primarily the surface properties of a catalyst in conjunction with the secondary bulk effects, which are credited for any observed catalytic improvements/weakening. We have highlighted the influence that a secondary/tertiary metal, in conjunction with annealing, can have on the catalytic performance of the thin film by effecting only slight changes in composition and temperature treatment.

The addition of a third component to the noble metals Pt and Pd, in the form of Al, i.e. $\text{Pt}_x\text{Pd}_y\text{Al}_z$, enhanced the electrocatalytic performance towards the electro-oxidation of aqueous SO_2 with the Al content kept below ~3%. In excess of ~3% Al the electrocatalytic performance was severely hampered. Overall onset potential, however, did not improve significantly for any of the evaluated electrocatalysts, while improvements in current output and stability (lasting ~1.4 times longer than both pure Pt (the (I)-700 °C sample) and Pt_3Pd_2 (the (J)-800 °C sample)) was achieved specifically for $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ (the (B)-900 °C sample), both in 25 °C and 60 °C testing environments. We have shown that electrocatalytic activity for the electro-oxidation of aqueous SO_2 can be achieved by substantially lowering the Pt content in that current density (mA.mg Pt^{-1}) increased from 108.11 to 181.21 and finally to 396.73 for Pt, Pt_3Pd_2 and $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ respectively, indicating an increase in activity that correlates with a decrease in Pt content.

Furthermore, additional information obtained from XPS analysis has shown that Pt₄₀Pd₅₇Al₃ ((B)-900 °C) exhibited an increase in Al content at the surface (~15 at.%) when compared to (B)-AD (only ~2 at.%) although no sign of a distinctive skin of one metal (or more in the case of Pt₄₀Pd₅₇Al₃) was present near the surface for the Pt₃Pd₂ and Pt₄₀Pd₅₇Al₃ thin films (as-deposited and annealed). This confirmed that the observed activity of the thin films was a result of all the metals being present in the thin film surface to a certain degree, however XPS analysis after cycling is recommended to validate that a possible induced skin does not form ³⁹. XRD analysis of the annealed Pt₄₀Pd₅₇Al₃ thin film ((B)-900 °C) has highlighted the presence of some degree of alloy formation.

The power of alternately employing combinatorial and high-throughput methods with conventional electrochemical and characterisation methods, for electrocatalysts development, has clearly been shown, and resulted in the identification of a catalyst that contains a lot less platinum while exhibiting increased catalytic activity and stability.

5.5 Acknowledgements

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5.6 Electronic Supplementary Information (ESI)

5.6.1 X-ray photoelectron spectroscopy (XPS)

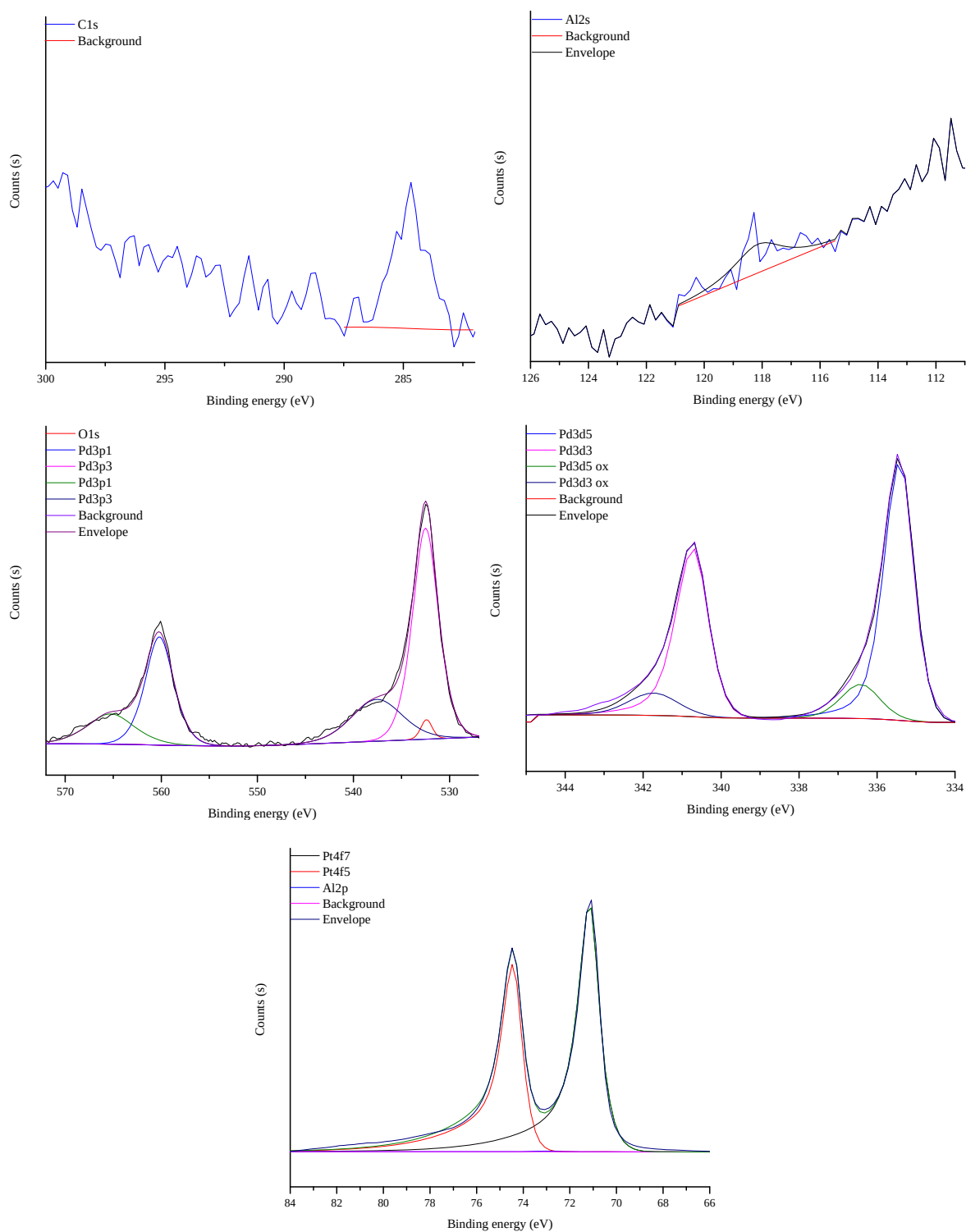


Figure S1: Fitted XPS spectra after 10s Ar⁺ etching for (B)-AD.

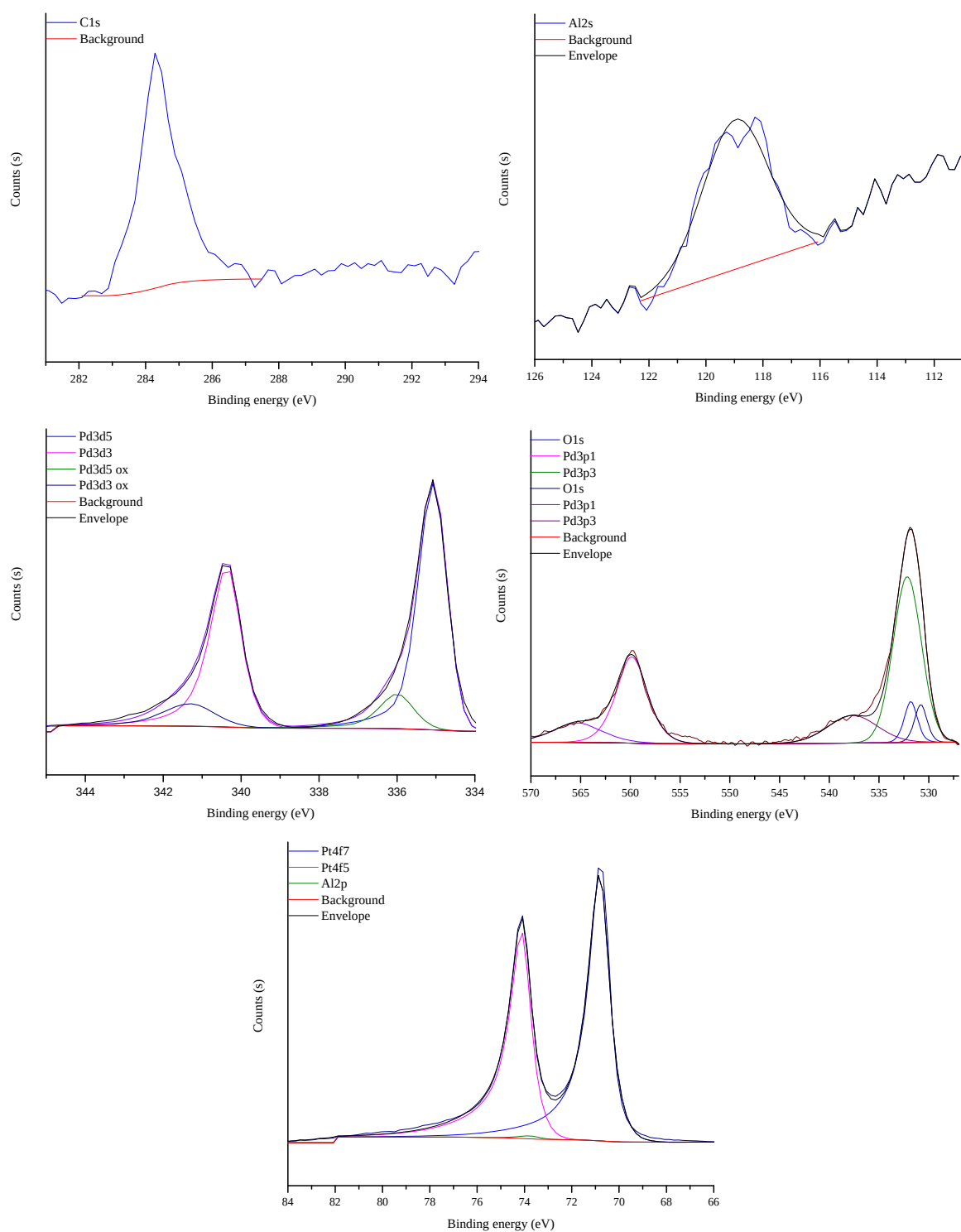


Figure S2: Fitted XPS spectra after 10s Ar⁺ etching for (B)-900 °C.

5.6.2 X-ray diffraction analysis (XRD)

X-ray diffraction (XRD) patterns were collected on a PANalytical X'pert MPD-PRO Bragg-Brentano θ - θ geometry diffractometer equipped with a secondary monochromator, a 3X15 positions sample changer and an X'celerator detector over an angular range of $2\theta = 8$ - 80° . Each acquisition lasted for 3 hours. The Cu- $K\alpha$ radiation was generated at 45 KV and 40 mA ($\lambda = 0.15418$ nm).

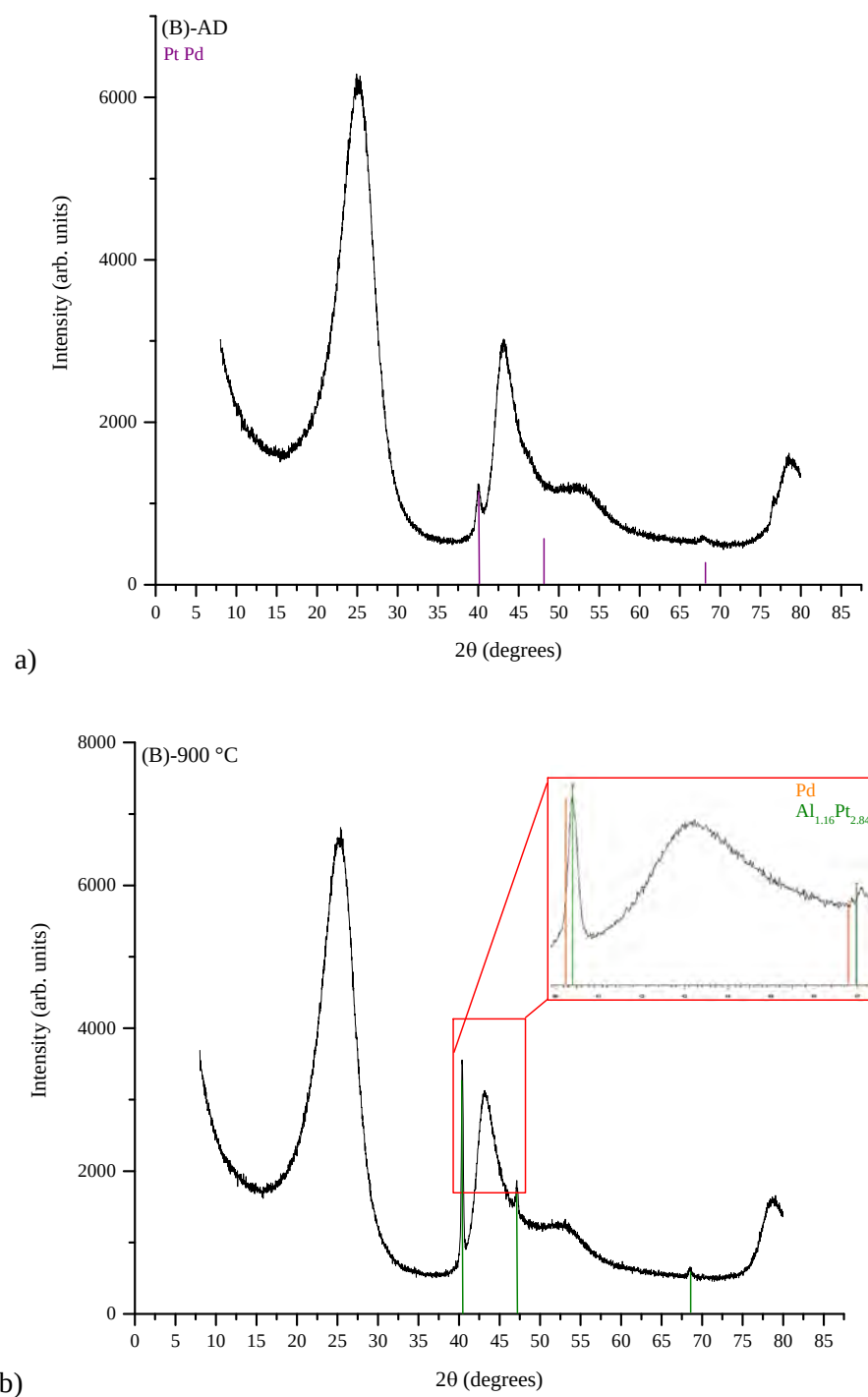


Figure S3: XRD spectra for a) (B)-AD, b) (B)-900 °C.

Chapter 6

Summative evaluation and recommendations

The purpose of this chapter is to reiterate, assess and encapsulate the key findings presented in Chapters 2-5. Subsequently, areas of possible improvements are identified and recommendations for possible future work are specified.

6.1 Reiteration of the problem statement, aim and objectives

The HyS cycle, as first proposed by the Westinghouse Corporation ¹, has of late gained renewed interest as an energy production cycle that is clean if linked to renewable energy. The rate determining step for this process is the electro-oxidation of SO₂ on the anode of the SDE. At present Pt is the electrocatalyst of choice and from literature it is clear that very little work has been conducted on identifying new and improved electrocatalysts for this reaction. With this said, the area of interest was formulated (§1.3) and the aim and objectives (§1.4) were set.

As stated in Chapter 1, the aim of this study was to fundamentally develop and investigate possible alternative electrocatalysts for the electro-oxidation of SO₂(aq), with the main focus being on reducing the amount of Pt by combining Pt (435.98 ZAR/g ²) with either a less expensive noble metal (Pd, (337.36 ZAR/g ²) and by employing a less expensive non-noble metal (Al, 0.03 ZAR/g ²), while maintaining or increasing catalytic activity and sufficient stability. As a means to achieve this multifaceted aim, the main objectives were:

- i. Preliminary investigation of the potential of a sputtered Pt electrocatalyst, through physical vapour deposition (PVD), in comparison with an industrially manufactured Pt polycrystalline electrocatalyst,
- ii. Designing and establishing a feasible HTC methodology by employing a PVD combinatorial sputtering system for electrocatalyst development in conjunction with a multi-channel potentiostat for high-throughput characterisation,
- iii. Commissioning of a specialised electrochemical cell for testing multiple working electrodes simultaneously (up to 64 working electrodes),
- iv. Defining specific parameters for effective identification and evaluation of electrocatalysts for further traditional investigation,
- v. Electrochemically investigating the onset potential, current output and stability of the selected electrocatalysts on standard electrochemical equipment, and

- vi. Characterising the physical properties of the electrocatalyst materials employing conventional methods (SEM, EDX, XRD, AFM and XPS) in an attempt to elucidate possible structure-activity relations.

In the following sections it will be illustrated that the above-mentioned objectives were successfully achieved (§6.2) and areas for improvement (§6.3) will be discussed.

6.2 Thesis overview

The development of any catalyst (material design) is extremely demanding ³. It is essential to formulate relative simple rules and theories which minimise the experimental efforts in the attempt to identify at least suitable candidates for further optimisation ³. In addition it requires acute detail and understanding of methods and techniques (depending on the demands required from the catalysts at hand) employed during material design. Ideally it will be advantageous to be able to explain certain observed phenomena of surface-structure-composition-activity relations. In the case of successful material design and acceptable performance outcomes for a given process/situation, is the next step to then implement the materials into a testing system to evaluate activity and stability accurately for possible large scale application. If all these steps can eventually be successfully achieved for a certain material of interest, the process of material design can be considered essentially complete and successful, keeping in mind that refinement and improvement will always be inevitable.

After reviewing and considering the available literature on the current and future situation of global energy challenges, and possibilities of addressing these challenges, it was decided to divide the main body of this thesis into four separate, but succeeding articles to clearly illustrate the approaches of addressing the problem statement (§1.3) and set objectives (§1.4).

Knowing the goal at hand, the first step was to decide which methods, materials and parameters will be employed of the available methods and techniques for material design, to assist in the process of identifying and investigating a possible alternative electrocatalyst(s) for the electro-oxidation of SO₂. Consequently, it was decided to employ a combinatorial sputtering system to synthesise electrocatalysts in the form of sputtered thin films. Subsequent to achieving full and successful operation of the custom built vapour deposition system the sputtering rate of the relevant metals was calibrated (only reported in Chapter 3). As a preliminary investigation (Chapter 2), Pt (as the catalyst of choice) was sputtered onto GC electrode inserts and directly compared to an available pure polycrystalline Pt electrode insert as a means to evaluate if an electrocatalyst in the sputtered form/state exhibits any potential for the electro-oxidation of SO₂. It was found that Pt in the sputtered state exhibited comparable activity in terms of onset potential, current output (in terms of current density and exchange current density), Pt utilisation, and activation energy, and therefore merited further investigation. Sputtering furthermore ensures the obtaining of pure catalysts in a

fast and controllable manner, and other synthesis factors that may influence results (as in the case of multistep synthesis) are circumvented.

Based on the promise exhibited by the preliminary investigation of sputtered Pt on GC, the PVD combinatorial sputtering technique was scrutinized and reported (Chapter 3). The investigation focused on sputtered thin films consisting of Pt, Pd and Pt_xPd_y combinations employing a SiO_2 wafer as substrate, followed with high-throughput screening by employing a multi-channel potentiostat. This investigation entailed (i) mastering the art of photolithography (using a SiO_2 wafer as substrate), as a first step in the multistep process of circuit development, (ii) calibration of both the sputtering system (for multiple metals) and the multi-channel potentiostat, (iii) commissioning of a combinatorial electrochemical cell, and (iv) intermittent validation of the individual steps. Electrochemical and physical information were successfully obtained for the Pt, Pd and Pt_xPd_y system, which proved the reliability and applicability of the chosen approach for electrocatalyst design and synthesis. Employing onset potential as the initial screening criterion, it was found that three Pt_xPd_y bimetallic combinations exhibited satisfactory performance with the best compositions being that of Pt_3Pd_2 and $PtPd_4$, with both containing substantially less Pt. The potential of (a) combining Pt and Pd as binary electrocatalysts, and (b) employing HTC methods in conjunction with traditional methods, were realised and the published paper served as the basis for the subsequent papers that form the core of this thesis.

In Chapter 4 it was attempted to optimise the structure of the best performing electrocatalyst (identified in Chapter 3), which will have a direct influence on the electrochemical performance of the electrocatalyst catalysing the electro-oxidation of SO_2 . The effect of RTA was investigated using high temperature resistant GCs as substrate with the main reasons being the following:

- Performing RTA on the thin film electrocatalysts, using the Ti-Au circuit on a SiO_2 wafer as substrate, will result in the circuit material inevitably interfering with the electrocatalyst composition and structure, as the high temperature treatment result in different degrees of migration and interactions of the metals present. This possibility of circuit material being present in the electrocatalyst composition responsible for electrocatalytic performance is obviously unwanted and detrimental.
- In practice the substrate of use in the SDE is mainly carbon (e.g. carbon ink ⁴, carbon black ((XC-72CB) ^{5,6}, Vulcan XC-72R ⁷, and carbon cloth ⁸) and in that regard employing GCs as substrate serves better for comparative purposes as it eliminates the interference of underlying circuit material that can influence results.

In general it was found that exposing the thin film electrocatalysts to RTA, as a means to improve the properties of the thin film electrocatalysts, was advantageous. It resulted in the majority of the annealing temperatures improving the electrochemical properties of the thin films, with the Pt_3Pd_2 thin film

electrocatalyst annealed at 800 °C being a promising contender in competing with pure Pt for the electro-oxidation of aqueous SO₂.

The key aspects/findings of Chapters 3 and 4 were taken into Chapter 5 with the aim of decreasing the Pt and total noble metal content (Pt and Pd) by the incorporation of a base metal, specifically Al, while still maintaining, or preferably, improving electrode performance. Multiple initial combinations were evaluated by means of HTC employing a SiO₂ wafer as substrate with the eight best performing electrocatalysts having been identified in terms of onset potential, mass-specific current density and geometric current density. These 8 electrocatalysts were reproduced employing GCs as substrate and exposed to RTA subsequent to which they were evaluated by means of conventional electrochemistry in terms of onset potential, current density and stability. The electrocatalysts not showing any deterioration during the short term characterisation (linear polarisation) were evaluated for long term stability. Based on these results the best electrocatalysts were selected and exposed to further in-depth characterisation (electrochemical and physical) as a means to gain possible insight into structure-activity relations. It was found that a combination of Pt₄₀Pd₅₇Al₃ annealed at 900 °C exhibited noteworthy performance when compared to pure Pt and to the best binary Pt₃Pd₂ electrocatalyst. Atomic force microscopy (AFM) exhibited an increase in surface roughness for Pt, Pt₃Pd₂ and Pt₄₀Pd₅₇Al₃, as a result of annealing treatment, with the occurrence of metal interaction and certain degrees of migration for Pt₄₀Pd₅₇Al₃ confirmed by X-ray photoelectron spectroscopy (XPS). From Figure 5.7 is clear that an increase in mass specific current density was achieved with a decrease in Pt content with the highest current density resulting from Pt₄₀Pd₅₇Al₃, the catalyst with the lowest Pt content.

The power of employing combinatorial and high-throughput methods, together with conventional electrochemical and characterisation methods, for electrocatalysts development, has clearly been shown. This has resulted in a methodology for the identification of possible candidate electrocatalysts that contain reduced amounts of Pt, while still exhibiting acceptable catalytic activity and stability. The identified ternary electrocatalyst, Pt₄₀Pd₅₇Al₃, is by no means considered as being the ultimate electrocatalyst for SO₂ electro-oxidation, but this study merely highlights the process of employing HTC and traditional methods for electrocatalyst design with the electro-oxidation of SO₂ in mind, and room for improvement does exist. With this said, the following section includes relevant recommendations to be considered for improving future work.

6.3 Recommendations

6.3.1 Thermal treatment

Different types of circuit materials and manufacturing processes exist, depending on, among other things, the expectations of the application. If the need exists to anneal electrocatalyst combinations on a wafer containing an underlying circuit, it is a requirement that the circuit material does not migrate or interfere

with the catalyst layer under investigation when exposed to thermal treatment. The investigation of other circuit materials, that are chemically non-reactive, conductive and stable to thermal treatment, and the process of constructing this circuit, for example through reactive sputtering (e.g. TiN) or physical assembly, is required to eliminate any possible interference of the circuit during measurements. In this study there was not an immediate need to anneal compositions present on a wafer and for this reason the circuit material employed throughout the course of this study was Ti-Au. This ensured that comparisons between the results of the consecutive papers forming the core of this thesis were not compromised. However, it is recommended that the design of the circuit be altered according to the type of information that is sought.

6.3.2 Substrate material

Apart from identifying and characterising an improved catalyst material the identification of a suitable substrate material is key, as this directly affects the quality and performance of the catalyst material it supports. As a possible electrocatalyst composition was identified in this study, a recommendation is to investigate alternative substrate materials. The investigation of alternative substrate materials may improve, among other things, the stability of the catalyst layer so as to possibly prevent delamination. The delamination observed through-out this study can be speculated to have been a result of either the intrinsic properties of the thin layer itself or due to a lack of coherence between the properties of the thin film layer and the substrate, which results in the substrate being responsible (in part) for poor stability. By changing the underlying substrate, it is furthermore expected that it may influence the type of crystal growth, subsequent to sputtering and/or thermal treatment, and as a result change the catalyst surface area. However, this is merely speculation and needs to be investigated.

6.3.3 Additional areas of improvement

In addition to the above mentioned recommendations, other areas of improvement in general related to this type of study include:

- (i) different temperature regimes (as only one profile was used throughout this study and XPS revealed the great influence thermal treatment has on the structure of the electrocatalyst),
- (ii) different film thicknesses (affecting both the amount of material included in the catalyst layer and the growth of the crystal structure when exposed to thermal treatment ⁹),
- (iii) in the case of optimum conditions (i.e. substrate material, film composition and thermal treatment regime) in-depth mechanistic studies related to the reaction under investigation may contribute to the effective characterisation of the electrocatalyst. This can potentially clarify how the structure and composition affects the catalytic mechanism (e.g. is it limited to an active site morphology role or is there an electronic effect?),
- (iv) relative currents were employed through-out the course of this study, however as current is a measure of reaction rate, it can be convoluted by ohmic and mass transport phenomena which

in essence form part of mechanistic studies. It would be good to ensure that the currents obtained and reported are truly in an activation controlled regime, and if not, to correct for ohmic and transport components, and

- (v) implement the identified material into a SDE system to evaluate activity and stability accurately for possible large scale application.

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THE ELECTROCHEMICAL OXIDATION OF AQUEOUS SO₂ ON SPUTTERED Pt/GC ELECTRODES

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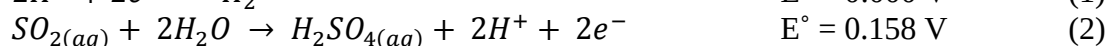
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Abstract

A comparative investigation with regards to the activity of an industrial manufactured polycrystalline platinum (PolyPt) electrode and platinum deposited on glassy carbon (GC) electrodes, prepared by sputtering with a physical vapor deposition system (PVD), towards the oxidation of aqueous sulfur dioxide (SO₂), has been conducted using a combination of stationary and rotating electrode voltammetric methods. It was found that Pt/GC catalysed the oxidation of aqueous SO₂ at a lower onset potential, with higher current density and smaller electrochemical active surface area (ECSA) compared to PolyPt, indicating better Pt utilization. Pt/GC also required an activation energy of $E_A = 52.4 \text{ kJ.mol}^{-1}$ compared to PolyPt with an activation energy of $E_A = 56.8 \text{ kJ.mol}^{-1}$, confirming the unique sputtered Pt/GC electrode as being a slightly better electrocatalyst for the oxidation of SO₂.

1. Introduction

Sulfur dioxide electrochemistry presents a wide and varied research interest over the last few decades, due to the relevance this reaction has in relation to the hybrid sulfur cycle (HyS). The electrochemical oxidation of sulfur dioxide has been studied extensively on platinum electrodes¹⁻⁵, which plays an important part in the efficiency of the sulfur dioxide depolarised electrolyser (SDE) used in the HyS cycle. Fundamentally, hydrogen is the product evolved on the cathode of the SDE and sulfur dioxide is oxidised to sulfuric acid on the anode:



O'Brien *et al.*¹ investigated the influence of various parameters on the electrode behavior of polycrystalline platinum. Parameters varied include acid concentration, lower potential limit (E_{low}) and temperature. Activity was divided into three scenarios which varied between limited, catalytic and inhibited oxidation depending on sulfur coverage and acid concentration. Recently, work done by Steimke and Steeper^{6,7} and Sivasubramanian *et al.*⁸ focused on utilizing Pt/C catalyst on the anode of the SDE as a means to improve the performance of SO₂ oxidation. They found that Pt/C catalysts exhibited an improved performance, both from a catalytic and economical point of view, as improved Pt utilization resulted in a reduction of the amount of Pt used. These Pt catalysts were

prepared by mixing 20 wt % Pt/C catalysts powder with NMP (n-methyl pyrrolidone) solution containing polymeric binder poly-vinylidene fluoride (PVDF). In this paper the oxidation of aqueous SO₂ has been investigated on platinum deposited glassy carbon prepared by sputtering with a PVD system and compared to industrially manufactured polycrystalline Pt (Pine Instruments). Sputtering affords one with short preparation times of sputtered electrocatalysts, achieving metal loading in the microgram range, as will be discussed in the experimental section. Sputtering furthermore ensures obtaining pure catalysts in that other synthesis factors that would influence results are circumvented.

2. Experimental

2.1. Equipment

Potentiostatic and potentiodynamic techniques were carried out using a BioLogic potentiostat (VSP) and processing of data with EC-lab 10.21 software. A three electrode setup was employed that consisted of a saturated calomel electrode (Radiometer Analytical REF 421) as a reference electrode, a spiral Pt wire as the counter electrode and a Pine Instruments platinum disk (PolyPt) insert electrode and sputtered Pt/GC (platinum covered glassy carbon) inserts as the working electrodes, respectively. Both types of working electrodes have a geometrical surface area of 0.196 cm².

2.2. Electrode cleaning and preparation

2.2.1. Polycrystalline Pt (PolyPt)

The electrode cleaning procedure involved soft polishing on polishing cloths (Pine Instruments) using 5 µm and 0.05 µm alumina particle solutions respectively. The electrode was then sonicated in Milli-Q water for 5 min before final electrochemical cleaning in 1 M H₂SO₄ that involved repeated CV scans between hydrogen and oxygen evolution regions, see 2.2.4.

2.2.2. Pt/GC

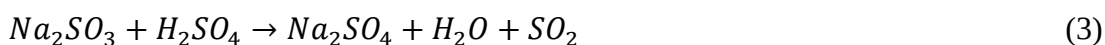
The Pt/GC inserts were prepared by polishing the glassy carbon inserts in 4 steps. First coarse paper was used followed by a coarse cloth with final polishing on soft polishing cloths (All Pine Instruments products) using 5 µm and 0.05 µm alumina particle solutions respectively. The inserts were then sonicated in Milli-Q water (10 min), acetone (10 min) and propanol (10 min). Sputtering of the Pt (42 µg.cm⁻²) was done by a physical vapour deposition system (PVD Products) with the settings listed in Table 1.

Table 1: Settings used for sputtering Pt onto glassy carbon inserts.

Parameter	Value
Base pressure	1x10 ⁻⁶ Torr
Chamber Pressure	8 mTorr
Argon flow rate	15 sccm
Power	90 Watt
Time of deposition	1 min

2.2.3. Solutions

A 1 M acid solution was made by dilution of 95.1 wt % H₂SO₄ (SAAR5885124LP), purchased from MERCK, with Milli-Q water. This solution was degassed with N₂ for 10 min before preconditioning started. A stock solution of 1 M Na₂SO₃ (Sigma Aldrich), was used as the SO₂ source (see reaction 3 for in situ production of SO₂). This solution was not degassed before addition to the H₂SO₄ and some dissolved oxygen may be present as a result. All experiments were conducted in a water-jacketed electrochemical cell (100 ml) with the temperature controlled through an external circulation water bath (Julabo F12 ED).



2.2.4. Procedures

Electrode preconditioning procedures involved scanning the electrode between 1.2 V vs SCE to -0.2 V vs SCE starting at E_{OCP} (open circuit potential) with a scan rate of 50 mV.s⁻¹ for 25 cycles. Secondly, three cycles were scanned changing only the anodic potential to 1.5 V vs SCE and lastly the first step was repeated but only for three cycles, hence the 28 cycles reported in Figure 1. Linear polarisation (E_{low}=0.2 V vs SHE to 1.43 V vs SHE, based on the results O'Brien *et al.* obtained¹) runs were conducted at different rotation rates (0 rpm, 200 rpm, 600 rpm, 1500 rpm and 2500 rpm) and different temperatures (298.15 K, 308.15 K, 318.15 K and 328.15 K) respectively for investigating the oxidation of SO₂. The PolyPt insert was polished between runs as described in the electrode cleaning section. With regards to the Pt/GC inserts, a new Pt/GC insert was used for each run.

3. Results and discussion

3.1. Cyclic voltammetry

Figure 1a and Figure 1b show the typical consecutive CVs for PolyPt and Pt/GC respectively. The CVs were performed as a means to assess the stability and activity (active area) of the surface in H₂SO₄ as electrolyte. The CVs reveal that the hydrogen desorption region increased and the strong and weak hydrogen desorption peaks became more distinct with cycling for both electrocatalyst. A clear difference between the Pt/GC and PolyPt electrodes were the smaller, almost non-existing strong and weak hydrogen adsorption/desorption peaks noticed for Pt/GC, which gradually formed as the cycling proceeded, which implies the sputtered Pt/GC electrode are not crystalline to start with, but that a degree of crystallinity is induced through preconditioning. The electrochemical active surface area (ECSA) value for both Pt/GC and PolyPt were determined for the hydrogen desorption region by integration of the current over time in the potential region of 0.04 – 0.45 V vs SHE and also subtracting the double-layer charging current from the total hydrogen desorption current. The values obtained were then divided by the adsorption charge corresponding to formation of a hydrogen monolayer, 210 µC.cm⁻² for

Pt⁹. The resulting ECSA values obtained for Pt/GC and PolyPt are 0.5 cm² and 0.781 cm² respectively, resulting in surface roughness values ($R_s = A_{\text{real}} / A_{\text{geo}}$) of 2.55 and 3.98 respectively. These ECSA values are also used to convert current values (mA) to current density values (mA.cm⁻²) for the results given in Figure 2.

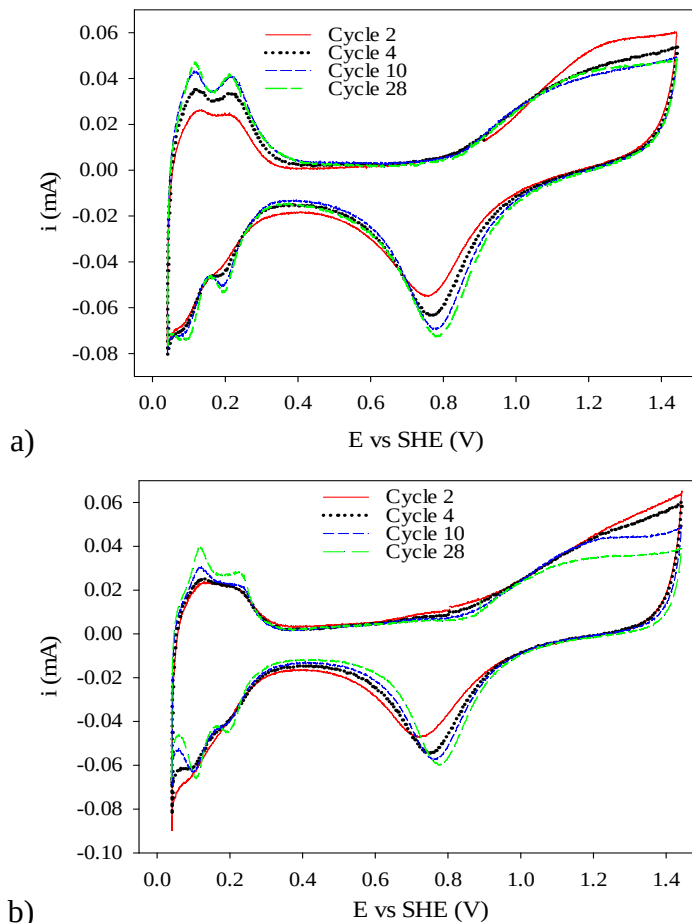


Figure 1: Cyclic voltammograms after consecutive cycling for a) PolyPt and b) Pt/GC in 1 M H₂SO₄ purged with N₂ at room temperature at a sweep rate of 50 mV.s⁻¹. The Pt catalysts layer on the GC consists of a total metal loading of 42 µg.cm⁻².

3.2. Linear sweep voltammetry

Work done by O'Brien *et al.*¹ include an in-depth study of the influence different experimental parameters have on the behaviour of the electrode towards the reaction of interest. In their study the effect of E_{low} and acid concentration were studied extensively. For our study, based on their results, we chose 0.2 V vs SHE as our E_{low} in 1 M H₂SO₄ electrolyte solution for all our experiments due to the substantial increase in catalytic activity compared to the other E_{low} values and acid concentrations. In order to compare electrodes, the onset potential was determined from the anodic sweep and transforming the LSV graph (Figure 2) into an inverse Tafel plot (over potential (η) vs log|i|) taking

the y-axis intercept as describe by O'Brien *et al.* ¹. The second method involves calculating the onset potential using the intercept of two straight lines tangent to the LSV curve as described by Cooper & McGinn ¹⁰. The overpotential and the onset potentials are listed in Table 2 and is it evident that the sputtered Pt/GC shows competitive behaviour in comparison with PolyPt.

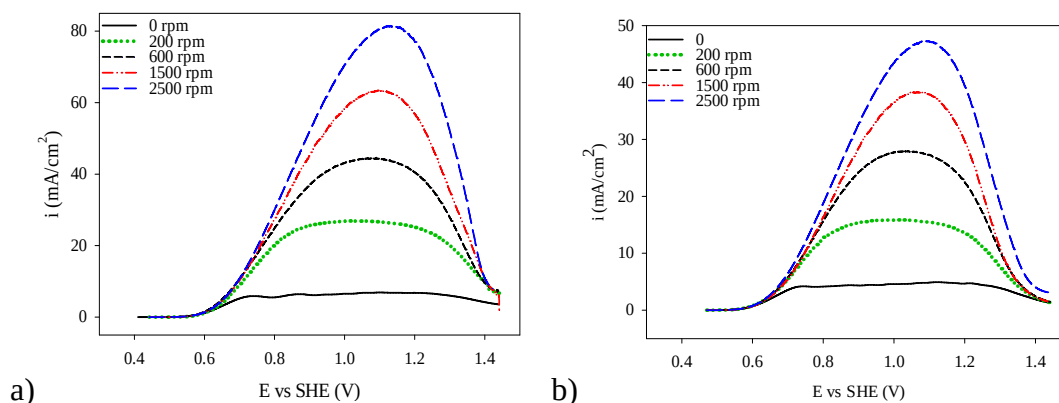


Figure 2: RDE behaviour of a) Pt/GC and b) PolyPt electrodes. Conditions: 1 M H₂SO₄, 100 mM SO₂, 5 mV.s⁻¹, E_{low} = 0.2 V vs SHE, 298.15 ± 1 K.

Table 2: Comparison of onset potentials (in terms of over potential) for different electrodes

Electrode	Supplier	Onset potential (V vs SHE)		Conditions
		O'Brien <i>et al.</i> ²	Cooper & McGinn ¹⁰	
Pt/GC	Custom made	0.436 ± 0.012	0.575 ± 0.002	E _{low} = 0.2 V vs SHE, 1 M H ₂ SO ₄ , 298.15 K, 0 rpm, 100 mM SO ₂ , 5 mV.s ⁻¹
PolyPt	Pine instruments	0.471 ± 0.004	0.585 ± 0.003	E _{low} = 0.2 V vs SHE, 1 M H ₂ SO ₄ , 298.15 K, 0 rpm, 100 mM SO ₂ , 5 mV.s ⁻¹
PolyPt	Pine Instrument-E4 series	0.464 ²	N.A.	E _{low} = 0.2V vs SHE, 1 M H ₂ SO ₄ , 295.15 ± 1 K, 0 rpm, 100 mM SO ₂ , 1 V.s ⁻¹

Comparing the RDE data for both the PolyPt and Pt/GC, it is clear that they do not reach diffusion limited conditions and becomes inhibited at E > 0.9 V. Correlating the ECSA values with the current density values (Figure 2) it seem that Pt/GC gives higher current density with a lower ECSA compared to polycrystalline Pt which means that Pt utilization

on the Pt/GC is higher than on the PolyPt. It is therefore evident to conclude that Pt/GC is performing better than the PolyPt electrocatalyst.

3.3. Exchange current density and activation energy

The effect of temperature on the reaction was quantitatively analysed by deducting the activation energy from the results obtained from Tafel plots. Tafel plots (not shown) have been constructed from the LSV runs at 0 rpm at different temperatures. From these Tafel plots the exchange current density, i_0 (mA.cm⁻²) was obtained (Table 3), as described by Bard and Faulkner¹¹, and used to calculate the standard heterogeneous rate constant, k^0 (cm⁻¹.s⁻¹) by employing the following equation¹

$$i_0 = F A k^0 c_{SO_2}$$

where F is the Faraday constant, A is the active area and c_{SO_2} the SO₂ concentration. The Arrhenius plot (Figure 3) was then constructed from the natural log of the calculated k^0 value and the inverse of the temperatures according to the following equation

$$\ln k^0 = \ln(M) - \frac{E_a}{RT}$$

where E_a is the activation energy of the reaction (J.mol⁻¹) and M a constant.¹¹ From this analysis it was found that the Pt/GC (52.4 kJ.mol⁻¹) has a lower activation energy compared to PolyPt (56.8 kJ.mol⁻¹), which in turn correlates very well with the literature value of 51 kJ.mol⁻¹. This is not a significant difference between the two

electrocatalysts, but still makes Pt/GC the better electrocatalyst of the two to catalyse the reaction.

Table 3: Exchange current densities (mA.cm⁻²) for the Pt/GC and PolyPt electrodes at different temperatures

Temperature (K)	Exchange current density (mA.cm ⁻²)	
	Pt/GC	PolyPt
298.15	3.4 x 10 ⁻¹²	6.4 x 10 ⁻¹¹
308.15	7.9x 10 ⁻¹²	1.0 x 10 ⁻¹⁰
318.15	1.1 x 10 ⁻¹¹	1.6 x 10 ⁻¹⁰
328.15	2.5x 10 ⁻¹¹	5.8 x 10 ⁻¹⁰

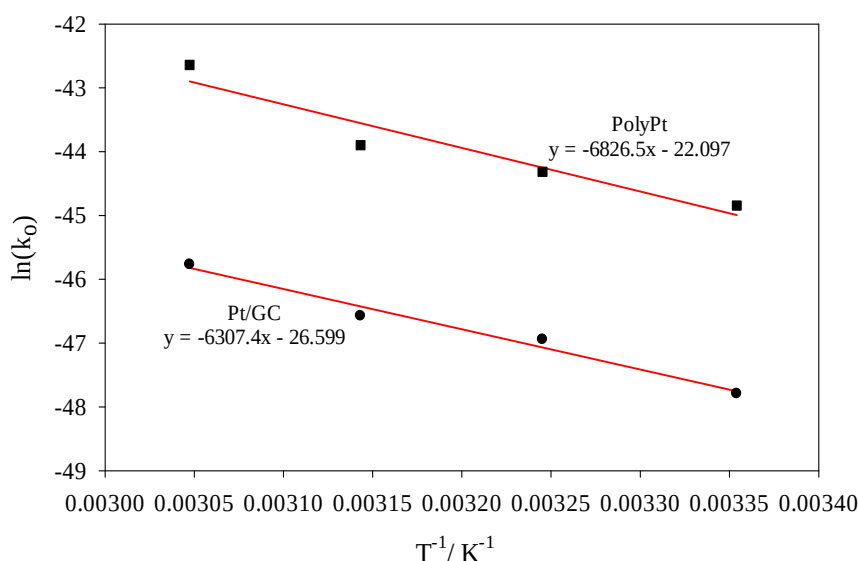


Figure 3: Arrhenius plots for Pt/GC and PolyPt. Conditions: 100 mM SO₂ in 1 M H₂SO₄ with $E_{low} = 0.2$ V vs SHE.

4. Conclusion

The catalytic activity and stability of Pt/GC and PolyPt were studied in a 1 M sulfuric acid solution at different rotation rates and at temperatures ranging from 298.15 K to 328.15 K. The results showed that both Pt/GC and PolyPt exhibited good stability and activity, but that PolyPt was a bit less active for the oxidation of SO₂. Lower onset potentials and higher current densities for the oxidation of SO₂ on Pt/GC compared to PolyPt was obtained. Furthermore, the activation energy for the oxidation of SO₂ on Pt/GC is a little less than that of PolyPt. Future work will include annealing of the glassy carbon electrocatalysts to increase stability and hopefully also the activity of the Pt/GC electrodes. The main focus of future work also includes investigating combinations of metals (Pt:X, X being another metal), being either binary, ternary, or quaternary metallic/alloys of the combinations.

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Combinatorial Plasma Sputtering of Pt_xPd_y Thin Film Electrocatalysts for Aqueous SO_2 Electro-oxidation

A. Falch, V. Lates & R. J. Kriek

Electrocatalysis

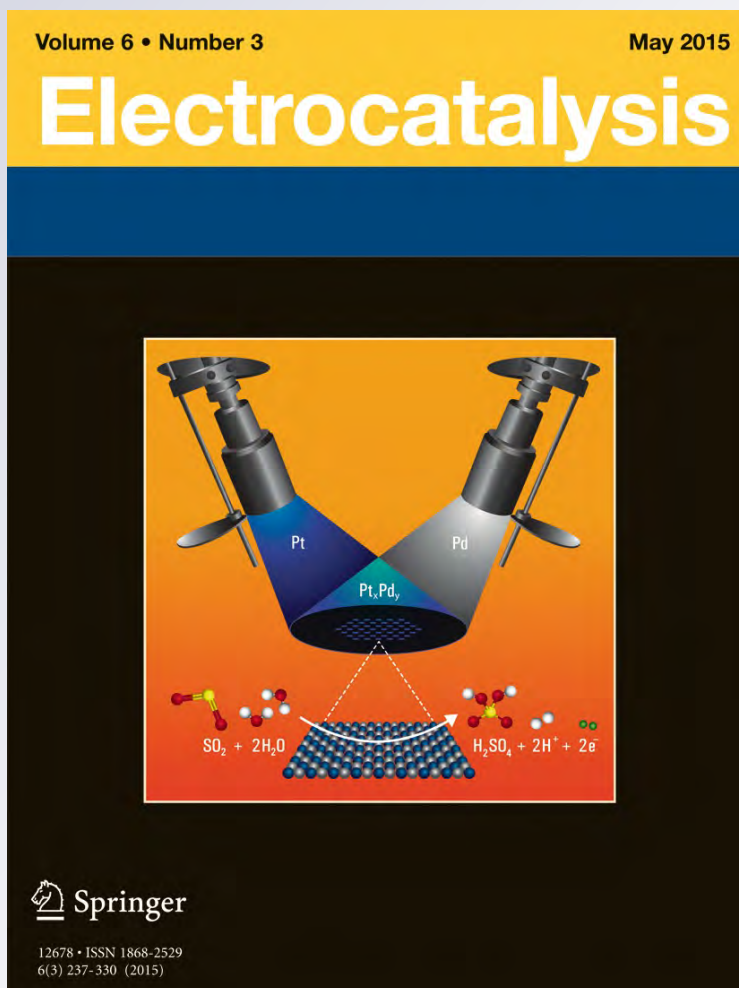
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Combinatorial Plasma Sputtering of Pt_xPd_y Thin Film Electrocatalysts for Aqueous SO₂ Electro-oxidation

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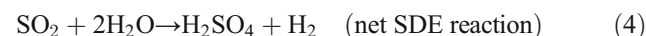
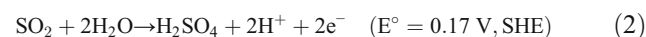
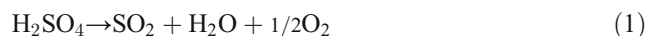
Abstract A combinatorial sputtering system, based on magnetron enhanced plasma sputtering, was employed in the syntheses of Pt_xPd_y thin film catalysts, and a multi-channel potentiostat allowed for high-throughput parallel screening of the deposited electrocatalysts towards the electro-oxidation of aqueous sulphur dioxide (SO₂). Employing onset potential as the screening criterion, it was found that three Pt_xPd_y bimetallic combinations exhibited satisfactory performance with the best compositions being that of Pt₃Pd₂ and PtPd₄. Both these combinations exhibited the same lower onset potential of 0.587±0.004 V, SHE compared to that of pure Pt (0.598±0.011 V, SHE), and in addition contain less Pt in achieving these onset potentials.

Keywords Combinatorial sputtering · Sulphur dioxide · Electro-oxidation

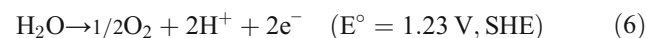
Introduction

The hybrid sulphur cycle (HyS cycle), proposed by the Westinghouse Corporation [1], has received a fair amount of attention as a thermo-chemical water splitting cycle [2–4]. Sulphuric acid is thermally decomposed to produce aqueous sulphur dioxide (reaction 1), which is fed to a sulphur depolarised electrolyser (SDE) and electro-oxidised at the anode to again produce sulphuric acid as well as hydrogen ions (reaction 2). The hydrogen ions migrate through the membrane of the electrolyser to the cathode where it is reduced to hydrogen

gas (reaction 3), while the electrochemically produced sulphuric acid is recirculated back to the decomposition reactor. The net SDE reaction therefore involves the conversion of aqueous sulphur dioxide into sulphuric acid and hydrogen gas (reaction 4), while the net HyS cycle reaction is that of water being split into hydrogen and oxygen (reaction 5):



Interest in the HyS cycle results from the fact that, whereas the anodic reaction for regular water electrolysis (reaction 6) occurs at a standard potential of 1.23 V, SHE [5], the anodic reaction for the SDE (reaction 2) occurs at a standard potential of 0.17 V, SHE [6], which translates into an energy gain of more than 1 V.



The possibility, however, exists for the SDE to be employed as a SO₂ sink, whereby SO₂ together with water is used as feedstock to convert an environmental pollutant into useable commodities, i.e. sulphuric acid and hydrogen gas. In contrast to regular water electrolysis systems, the SDE runs at a lower cell voltage and some of the electrical energy input is ‘returned’ in the form of an energy carrier, i.e. hydrogen gas, which translates into a substantial economic benefit [7].

For the SDE, an operational target has been set of 500 mA cm⁻² at a cell potential of approximately 0.6 V [8]. This target can only be achieved through the development of an effective electrocatalyst for the anodic electro-oxidation of SO₂, and to that regard, the properties of the anode is regarded as pivotal for improving the entire HyS process [4]. While

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platinum is still considered the standard anode catalyst for the SDE, several studies have been conducted on the subject, which amongst others include those listed in Table 1. As is the case with the oxygen reduction reaction in a fuel cell, efforts are underway to find an electrocatalyst other than platinum. Operating at about 100 °C and high sulphuric acid concentration, the anode electrocatalyst has to be not only active but must also be able to withstand this harsh environment. In an effort to reduce platinum content, it could be alloyed with either a more cost-effective noble metal or base metals. Although results obtained for platinum alloyed with non-noble metals show good activity [3], platinum alloyed with noble metals shows similar to or even higher activity than that of pure platinum. However, studies on this subject are limited [4].

The need therefore exists to research and develop new as well as improved catalysts for the electro-oxidation of SO₂ [12, 13]. A fast and effective means of achieving this is by employing high-throughput combinatorial screening [13–16], which is a technique that has gained a lot of interest over recent years. One of the very first remarks, with regards to multiple-sample syntheses and testing, was made by Hanak in 1970 who emphasised the fact that the search for new materials suffers due to the fact that handling one sample at a time, in the process of synthesis and chemical testing, is an expensive and time-consuming approach, which prevents the researcher to take full advantage of his/her talents and keeps the level of progress low [17]. He suggested the abandonment of the tedious efforts of single sample synthesis and testing, and the adoption of methods to process multiple materials simultaneously. As the need to explore efficient and systematic means of searching for alternative binary, ternary and higher materials grew, the field of combinatorial science gained interest [13, 18–22]. Some of the techniques that have been applied to a combinatorial approach include (i) sputtering [23], (ii) evaporation and molecular beam epitaxy [24], and (iii) pulsed laser deposition [25], either employing a form of the composition spread technique [17, 23] or using a discrete composition approach [18, 20]. It has to be stressed, however, that a high-throughput approach does not always allow for highly accurate and precise experimentation compared to conventional experimentation [12, 26]. It is aimed

rather at investigating observable trends in the material of interest, such as catalytic activity for example, subsequent to which the initial observation is confirmed and optimised with more precise kinetic data [13]. One of the first examples of combinatorial electrochemistry involved generating a 645-member electrode array of Pt, Ru, Os, Ir and Rh employing a modified inkjet printer with metal salt ‘inks’ and subsequently screening the catalysts for methanol oxidation [27]. Numerous studies have followed where electrocatalysts have been investigated for a number of chemical reactions [28–30]; however, little research has been conducted on high-throughput combinatorial electrocatalyst development for SO₂ electro-oxidation as part of the HyS cycle.

In this study, we describe the high-throughput syntheses and screening of Pt_xPd_y thin films for the electro-oxidation of SO₂. Palladium was chosen to ‘alloy’ with platinum as some experimental studies [10, 31] as well as a theoretical molecular modelling study [32] pointed towards palladium being potentially more active than platinum for the electro-oxidation of aqueous SO₂. The thin films are obtained employing a vacuum sputtering system for the physical deposition of a discrete composition library with the dimensions of each pad being 3 mm×3 mm. This is followed by simultaneous electrochemical screening of the thin films by employing a specially designed electrochemical cell connected to a multi-channel potentiostat. With this multi-channel potentiostat, a rapid electro-analytical technique is applied to all synthesised materials as it does not require calibration and it is independent of the composition of the tested materials. The thin films (Pt_xPd_y combinations) were furthermore characterised by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Their activities are compared to the activity of pure sputtered Pt towards the oxidation of aqueous SO₂ using onset potential as the evaluative criterion.

Experimental Approach

Photolithography

Photolithography is employed to microfabricate a Ti-Au electrical circuit onto a SiO₂ wafer (Microchemicals, Germany), adapted from Strasser et al. [13] and Warren et al. [33]. The wafer has a diameter of 100 mm, with a thickness of 500–550 µm and consists of two semi-standard flats with an orientation of (100). A thin, uniform, 10-µm-thick layer of positive photoresist (PL177, Microchemicals) is put down onto the wafer by controlled addition of the photoresist (Performus dispensing system, EFD Nordson) and spin coating (Spin 150, SPS Ltd.) subsequent to which the wafer is dried at 80 °C for 15 min. The image mask of the circuit pattern is accurately fitted onto the wafer and the exposed ink is

Table 1 Studies on the catalyst of the anode as a means of improving the electrolysis performance of the HyS process

Year	Catalyst	Ref.
1973	Al-V mixed oxides with traces of Pt	[9]
1980	Pt, Pd, Au, Ru, Re, Ir and Rh	[10]
2007	Pt/C and Pd/C	[11]
2010	Pt-M/C (M=Co, Cr, Fe, Ru, Ir)	[3]
2012	Pt and Au	[2]
2014	Pt-M/XC72R (M=Pd, Rh, Ru, Ir and Cr)	[4]

developed by exposure to 5 mW/cm^2 UV light for 1 min in a UV box (Pluvex 1410, Mega Electronics, UK). The wafer is then placed in a developer solution (RS Universal developer) for 20 s and subsequently rinsed with water and dried with N_2 . The size of the contact pad, onto which the thin film will be deposited, is 0.09 cm^2 with 2.5-mm spacing, and the size of the pin pad, which connects the individual contact pad to the potentiostat, is $2.5 \times 6 \text{ mm}$ with 1–1.5-mm spacing. Subsequent to development, the wafer is ready for deposition of the circuit by DC-magnetron vacuum sputtering. A 106.8-nm-thick Ti-Au layer (calibration of Ti and Au is done as described in the “Calibration of Sputtering Rate” section) is deposited onto the patterned wafer, employing the aperture as depicted in Fig. 2a, which allows the Ti and Au to deposit on the entire wafer.

The conditions for sputtering the circuit are as follows: vacuum base pressure of 5×10^{-7} Torr, chamber pressure of 8 mTorr, argon gas flow rate of 0.015 L min^{-1} , Ti DC power of 50 W for 235 s, and on top of the Ti layer a Au layer, DC power of 50 W for 280 s. The negative part of the circuit pattern is then stripped off so as to remove the sputtered metal from the black sections. This is done by placing the wafer in acetone and bubbling N_2 to impose agitation so as to speed up the process of stripping. The wafer is again covered with a layer of photoresist, where after only the contact pads and pin pads are developed by exposure to UV light for 1 min followed by 20 s in the developer. In order to confirm that the lines are insulated, each contact pad, line and pin pad combination of the circuit is scrutinised and tested employing a digital multimeter. This insulation step ensures that each contact pad, line and pin pad combination is insulated from all other combinations and to ensure that only the pads are exposed for electrochemical testing.

Combinatorial Deposition System

The combinatorial deposition system (Fig. 1) used for vacuum sputtering was custom-designed and supplied by PVD Products, USA.

The system is a sputter down setup with four water-cooled magnetron guns (Fig. 1a) hosting one target/metal disk each. The target diameter and thickness are fixed to 38.1 and 3.2 mm respectively and were obtained from ACI Alloys (Inc), California. The magnetron guns hosting the targets are focussed onto the aperture (Figs. 1b and 2a–d) of choice, and the target to substrate distance is constant at 90 mm. A computer-controlled shutter allows for the opening and closing of the target. Various holders and apertures (Fig. 2) were customised to allow for the following alternatives of sputtering: (a) on a 100-mm-diameter SiO_2 wafer (see holder in Fig. 2f) and on 16 glassy carbon (GC) electrodes (see holder in Fig. 2e), (b) on 4 GC electrodes at a time, (c) on only one

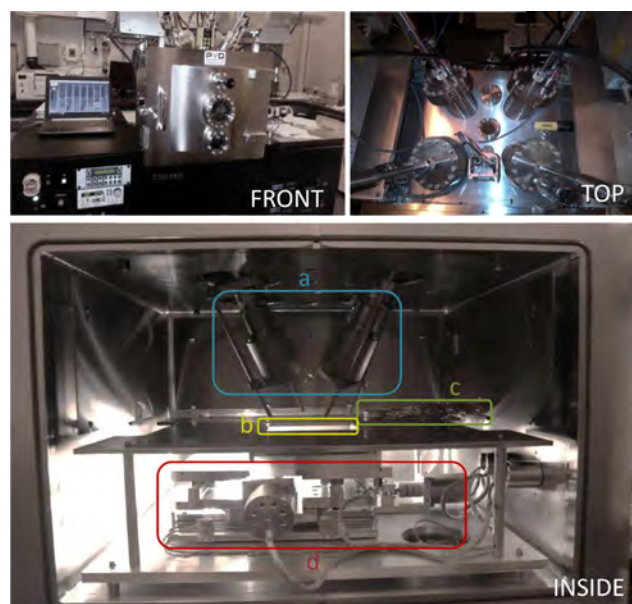


Fig. 1 Different views of the combinatorial deposition system. **a** Four downward facing magnetron guns, **b** variable aperture, **c** quartz crystal microbalance (QCM), and **d** programmable x-y stage

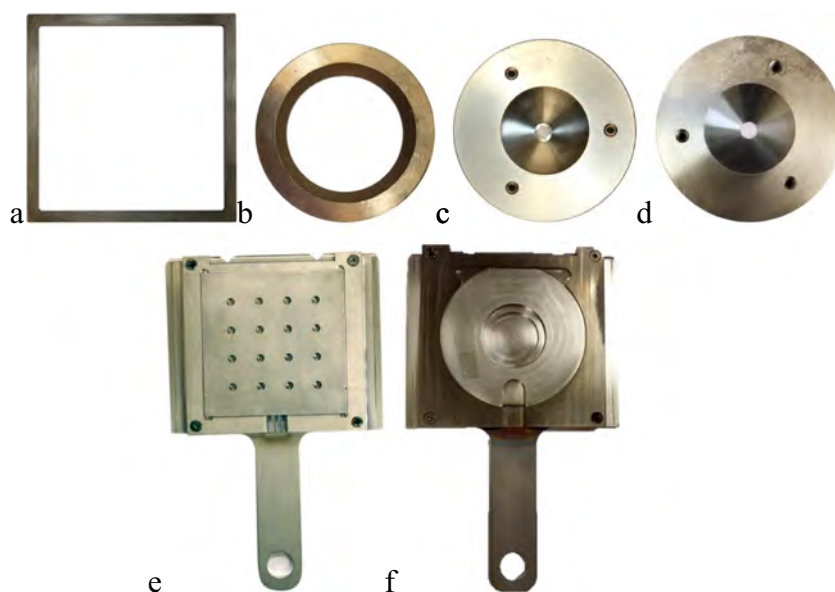
square contact pad among a maximum of 64 electrode pads on the SiO_2 wafer, and (d) on only one circular GC electrode.

Prior to sputtering, the sputtering chamber is ‘pumped down’ to a base pressure of $\sim 5 \times 10^{-7}$ Torr using a rough pump (≥ 250 mTorr) and turbo pump (< 250 mTorr) combination. The maximum power of the four direct current (DC) magnetron guns is 100 W, and two of these can switch to radio frequency (RF) mode when required (for example sputtering non-conductive targets, i.e. oxides) with a maximum power of 100 W. The programmable parameters that determine the composition and thickness of the sputtered films include the deposition time, regulated by the position of the shutter (open or closed) or by the on-off state of the magnetron, the power of the magnetron, and the argon pressure and flow rate. Calibration (refer to the “Calibration of Sputtering Rate” section for details) of each target, taking these parameters into consideration, was conducted by employing the built-in quartz crystal microbalance (QCM, Fig. 1c), which measures the change in the mass deposited per unit area as a change in frequency of a quartz crystal resonator.

Deposition of Thin Film Catalysts

The library of thin films is deposited one-by-one in a pre-defined sequence during which the sputtering parameters, derived from the calibration data, are specified in such a way so as to obtain a gradient of discrete compositions across the library. In this work, different molar ratio combinations of Pt and Pd were produced by simultaneously sputtering (co-depositing) the individual metals to obtain bimetallic materials. The different combinations were compared to pure Pt

Fig. 2 Various apertures for sputtering on **a** a 100-mm-diameter SiO₂ wafer and 16 glassy carbon (GC) electrodes, **b** on 4 of 16 glassy carbon (GC) electrodes at a time, **c** only on one electrode among the 64 electrodes of the SiO₂ wafer, and **d** only on one GC electrode. Images **e** and **f** are holders for 16 GC electrodes and a SiO₂ wafer respectively which is placed on the programmable x-y stage



and Pd towards the oxidation of aqueous SO₂. Random positions were chosen for each Pt_xPd_y ratio (in triplicate) so as to validate whether the position of a specific electrocatalyst does not influence the electrical signal (performance) of the catalyst as the length of the contact lines do vary. To that regard, the contact pads that were not sputtered with Pt and Pd consisted of Au (the sputtered circuit). The programmable parameters that determine the composition and thickness of the sputtered films are listed in Table 2.

Physical Characterisation

Catalyst ratios were investigated non-destructively with reduced area analysis by employing SEM with an integrated XMax 20 EDX system (Oxford Instruments). Prior to determining catalyst ratios, mapping was performed (SEM with an integrated XMax 20 EDX system) to validate homogeneous

Table 2 Power and time of deposition used for the syntheses of sputtered films with variable molar composition (Pt_xPd_y) and fixed thickness (40 nm)

Composition		DC power (Watt)		Time (s)
Pt	Pd	Pt	Pd	
0	1.0	0	50	150
0.1	0.9	17	90	74
0.2	0.8	24	60	99
0.4	0.6	62	60	74
0.6	0.4	50	22	138
0.8	0.2	85	15	106
1.0	0	50	0	226

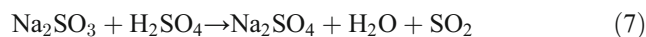
Base pressure, 5×10^{-7} Torr; chamber pressure, 8 mTorr, argon flow rate, 0.015 L min⁻¹

sputtering. The whole wafer was fitted into the microscope chamber and the catalyst compositions were measured sequentially. Subsequent to the electrochemical investigation, the wafer, containing the circuit and thin film catalysts, was cut to obtain a cross section view using scanning electron microscopy (FEI Quanta FEG 250), which allowed the measurement and validation of film thickness.

Electrochemical Characterisation

Solutions for Electrochemical Measurements

In order to ensure that the electrocatalysts are all in the same electrochemical condition, preconditioning (see the “[Electrochemical Measurements on the Wafer](#)” section) was conducted in degassed (N₂ bubbled for 20 min) 0.1 mol L⁻¹ HClO₄ (Merck). A 1 mol L⁻¹ H₂SO₄ acid solution (pH=0.55) was made up by dilution of 95 wt% H₂SO₄ (Merck). This solution was degassed with N₂ for 15 min prior to linear polarisation. A stock solution of 1 mol L⁻¹ Na₂SO₃ (Sigma Aldrich) was used as an in situ SO₂ source (reaction 7).



All experiments were conducted in a water-jacketed electrochemical cell (300 mL) with the temperature (25 °C) controlled through an external circulation water bath (Julabo F12 ED). In all instances, Milli-Q water (Millipore Milli-Q ultra-pure water system; 18.2 MΩ cm) was used.

Combinatorial Electrochemical Cell

Electrochemical testing was conducted employing a specially designed electrochemical cell (Fig. 3), which has been adapted

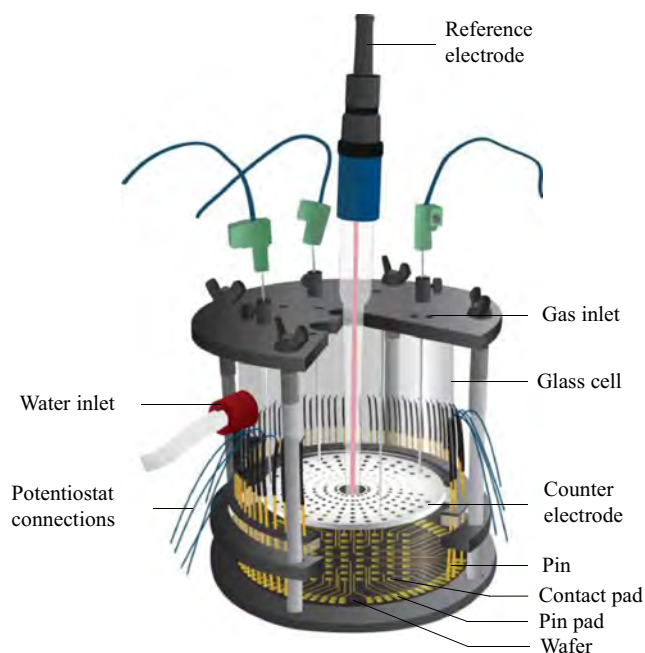


Fig. 3 A cutaway schematic drawing of the designed electrochemical cell (adapted from [34])

from the cell reported by Cooper et al. [34]. The wafer containing the sputtered electrocatalysts was placed at the bottom of the cylindrical double-wall glass cell body such that they were facing upward so as to be exposed to the electrolyte solution. The electrocatalysts and electrolyte were sealed off from the pin pads by an O-ring seal incorporated into the bottom wall of the bottomless cylindrical double-wall glass cell body. A Pt-plated Ti mesh electrode with a 7-cm diameter was placed parallel to the wafer at a distance of about 2.5 cm and served as a common counter electrode. A saturated calomel electrode (SCE, Radiometer Analytical REF 421) was used as the reference electrode and was placed above the working electrode array, protruding through an opening in the middle of the counter electrode. The distance between the capillary tip of the reference electrode and the working electrode pads at the centre and at the edge of the array ranged from about 1.5 to 2 cm. This distance was chosen so as to minimise the differences in the uncompensated ohmic resistance between the electrocatalysts. Voltage drops across the electrolyte between the reference electrode tip and individual working electrode pads were considered negligible [13] given the conductivity of the electrolyte and the magnitude of the measured currents.

Electrochemical Measurements on the Wafer

All electrochemical measurements were performed simultaneously with a 64-channel potentiostat (Arbin Instruments). The electrode preconditioning procedure involved, as a first step, conducting cyclic voltammetry (CV) scans between

1.441 V versus SHE to 0.041 V versus SHE starting at E_{ocp} (open circuit potential) for 25 cycles employing a scan rate of 50 mV s^{-1} . This was followed up with three CV scan cycles changing the anodic potential to 1.741 V versus SHE and finally the first step was repeated but only for three cycles. This preconditioning procedure is necessary to ensure obtaining repeatable results for subsequent linear polarisation scans (for SO_2 electro-oxidation). Linear polarisation runs ($E_{\text{low}} = 0.2 \text{ V vs SHE}$ to 1.441 V vs SHE , based on the results of O'Brien et al. [35]) in the SO_2 -containing solution were conducted at a scan rate of 10 mV s^{-1} . Electrodes were, however, not held at the E_{low} potential for 2 min to deposit sulphur on the surface, as was done by O'Brien et al. [35], since depositing sulphur will alter the surface. The activity of each composition was evaluated based on the potential defined by the onset of the SO_2 oxidation reaction. This potential was calculated using the intercept of two straight lines that bound the curve as described by Cooper & McGinn [29]. A catalyst composition that has a low onset potential in the short term may excel in application conditions, and this screening test was only designed to identify promising compositions. The catalyst ratio(s) that exhibit(s) promising activity will undergo future analysis on glassy carbon disk inserts employing a conventional three-electrode setup, which does not form part of the scope of this study.

Results and Discussion

Calibration of Sputtering Rate

To ensure control over catalyst thickness and composition, critical attention was paid to the calibration of the sputtering or deposition rate. Calibration is enabled by employing a built-in retractable and computer-controlled quartz crystal microbalance (QCM). The QCM is positioned in the centre of the four magnetron guns (Fig. 1c) and allows for the in situ measurement of the sputtering rate expressed as nm/min based on the frequency change of the oscillator and well-known relationships. The sputtering rate is influenced by the DC power of the sputtering gun as well as the chamber pressure (Fig. 4). The direct relationship between the DC power of each gun and the corresponding sputtering rate was evaluated for each metal (Ti, Au, Pd, Pt), and a representative graph (Fig. 5) was constructed. The calibration lines (equations in Fig. 5) are then used to calculate the time of deposition for the various electrocatalysts at a specific power setting.

In addition, calibration curves were obtained for each metal at chamber pressures between 2 and 30 mTorr. A very good correlation (R^2 higher than 0.99) was found as long as the chamber pressure was kept between 2 and 12 mTorr. For higher chamber pressures, the sputtering rate was quite low and hence the errors due to reading of QCM values were

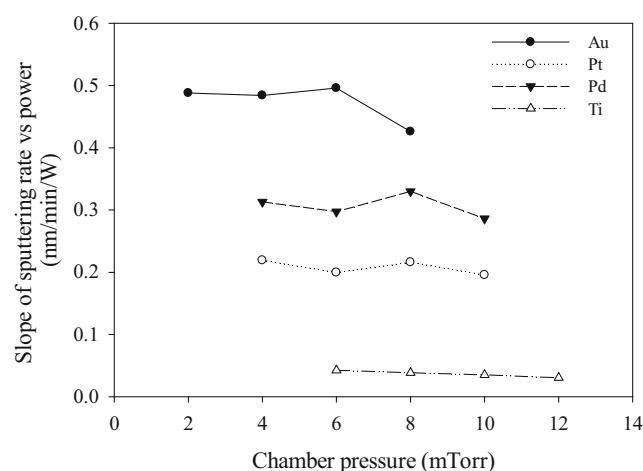


Fig. 4 The influence of the chamber pressure on the slope of the deposition rate versus DC power. The slope is obtained from calibration graphs similar to those in Fig. 5. Experimental conditions: vacuum base pressure, 5×10^{-7} Torr; argon gas flow rate, 0.015 L min^{-1} ; and deposition time, 1 min

higher. Figure 4 shows the slope of the calibration graph obtained for different chamber pressures. As a global trend, it can be observed that the higher the chamber pressure, the lower the sputtering rate becomes. It was also observed that low chamber pressures, e.g. 2 and 4 mTorr, were not achievable for the deposition of Pt and Ti as the plasma could not be ignited. On the other hand, a chamber pressure higher than 10 mTorr was only achievable for the Ti target. As the chamber pressure is a crucial parameter for co-sputtering of two or more metals, it has to be convenient for all metals being sputtered. A pressure of 8 mTorr was subsequently chosen as a general pressure at which the deposition of any metal is possible. This combinatorial sputtering system is furthermore

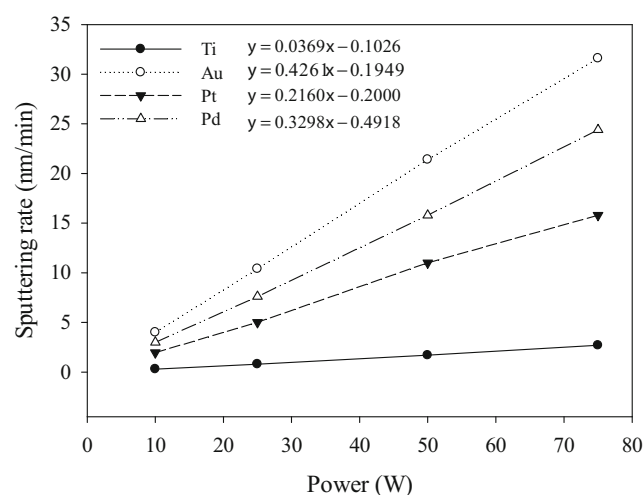


Fig. 5 A calibration curve for deposition rate versus power. Conditions: vacuum base pressure, 5×10^{-7} Torr; argon gas flow rate, 0.015 L min^{-1} ; chamber pressure, 8 mTorr

equipped with inlets for argon and oxygen, which could be used for reactive sputtering, with the flow rate of each sputtering gas that can be independently varied. In the case when only argon is used, as is the case for this study, the flow rate should not influence the sputtering rate. This was confirmed for the sputtering of Ti at a fixed chamber pressure and different DC powers of the magnetron gun (Fig. 6). As expected, no variation of the sputtering rate was observed with a change in the flow of argon, which confirms the proper functioning of the combinatorial sputtering setup.

Characterisation of Sputtered Films by Scanning Electron Microscopy

In order to investigate the morphology and stoichiometry of the sputtered thin films, SEM and EDX were conducted employing representative mapping of the co-deposited thin film electrocatalysts as a means of revealing the distribution of the Pt and Pd metals. As an example, Pt_3Pd_2 is shown in Fig. 7.

In general, the metals are seen to be homogeneously distributed as is expected from co-deposition, and as a result, the bulk composition is representative of the surface composition. To investigate the calibration (see the “Calibration of Sputtering Rate” section) of the PVD, the sputtered ratios were investigated by EDX analysis (Table 3). The results obtained from EDX deviated from the expected calibrated values in that the thin films were Pd deficient, with the PtPd_9 exhibiting a large standard deviation (STDV, obtained from three different positions on the wafer). A similar observation was made by Cooper et al. who sputtered PtRu combinations for methanol oxidation and found their thin films to be Ru

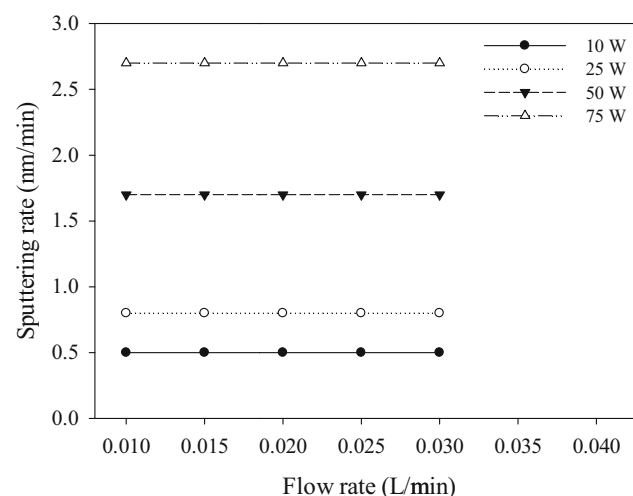
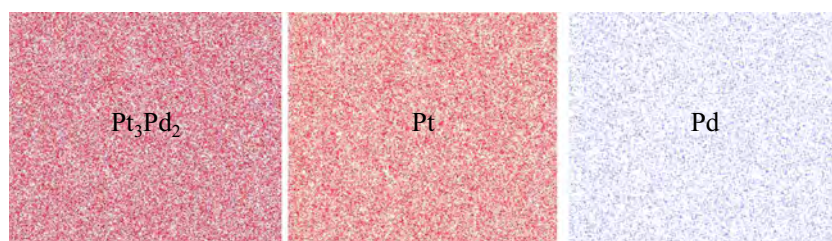


Fig. 6 The influence of the Ar flow rate on the final thickness of a Ti film for different values of the magnetron power. Experimental conditions: vacuum base pressure, 5×10^{-7} Torr; chamber pressure, 8 mTorr; deposition time, 1 min

Fig. 7 Elemental mapping of as-deposited Pt₃Pd₂ electrocatalyst

deficient [36]. A similar trend is observed in that both Pd and Ru have a lower density than Pt, and in each case, it is the metal with the lower density that is deficient in the sputtered thin film. This clearly illustrates that for sputtered thin films, each composition has to be measured independently by a secondary method to obtain true compositional values.

SEM analysis was also conducted on a cross section of the pin pad to measure the thickness of the sputtered circuit layer (Fig. 8). This was done subsequent to electrochemical testing as SEM analysis requires cutting of the wafer. The thickness of the layer as measured by SEM analysis was 105.375 nm and is in accordance with our calibrated values.

Electrochemical Activity for SO₂ Oxidation

To validate the repeatability of the fabrication process of a sputtered electronic circuit, two wafers were fabricated employing the exact same steps and parameters. These two wafers, containing the exact same set of electrocatalysts, were independently electrochemically tested and compared for the electro-oxidation of aqueous SO₂. Each wafer contained three of each electrocatalyst sputtered on different positions in order to investigate the potential influence that different positions might have on the electric signal. The fabrication of two wafers furthermore served to investigate repeatability between wafers.

Onset potential is considered by many authors [29, 37–39] to be one of the indicators for catalytic activity of a catalyst and whether a catalyst is effective for the reaction of interest. With the onset potential of Pt being the target potential for the electro-oxidation of aqueous SO₂, every library contained

several Pt sputtered catalysts as reference points. From a plot of the average onset potentials for Au, Pt, Pd and Pt_xPd_y electrocatalysts (Fig. 9), it is clear that Au exhibited the worst performance, followed by Pd, Pt, and the Pt_xPd_y combinations all being in close proximity of Pt. The average onset potential of 0.598±0.011 V (SHE) for Pt, for the electro-oxidation of SO₂, agrees well with literature [2, 35], which serves as the first confirmation that the data generated by the experimental system is acceptable. This average value is calculated from the average of the two wafers for a set of three electrocatalysts on each wafer. An example of composing this average onset potential value and standard deviation (STDV) is given in Table 4. The overall average difference between the two wafers for all the electrocatalysts was calculated as 0.728 %, which is very good taking into account all the steps required for fabricating a wafer, sputtering the thin film catalysts onto the wafer and conducting electrochemical screening.

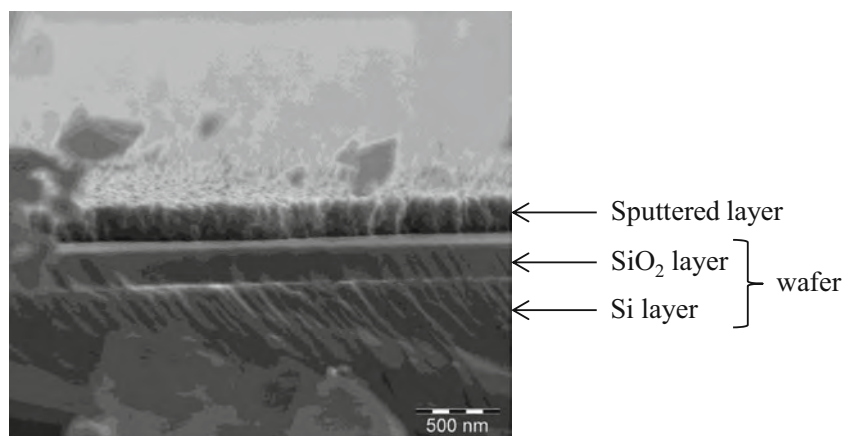
The electrocatalysts that exhibited promising activity are Pt₃Pd₂, Pt₂Pd₃ and PtPd₄, indicating that the addition of Pd results in a slight improvement as their onset potentials are slightly lower than that of pure Pt (Fig. 9). With a decrease in Pt content, it is clear that no trend is observed with regard to the change in onset potential. Pt₂Pd₃ exhibits the highest onset potential of the three promising electrocatalysts (see rectangular box in Fig. 9), while Pt₃Pd₂ and PtPd₄ resulted in the same lowest average onset potential, making them potential alternative catalysts compared to Pt. The Pt₃Pd₂ catalyst contains ~32 % less Pt, while the PtPd₄ catalyst contains ~68 % less Pt than the pure Pt catalyst (based on EDX analysis). Possible reasons for deviation in the onset potential values may be that Pt is sensitive to minute amounts of inorganic and organic contaminants that may remain on the surface due to the photolithographic processing that the electrocatalysts are exposed to [29, 40] and also the deviation in composition measured by EDX. The combinations tested have two commonalities, i.e. the fact that they catalyse the oxidation of SO₂ having a lower onset potential as well as the undeniable fact that they all use less Pt to achieve this.

Current density, as another characteristic indicator of catalyst activity, was not employed during this investigation for, to make a worthy comparison using current density, the real active surface area is required. The real active surface area of a pure Pt surface is mostly determined by examining and integrating the monolayer hydrogen adsorption area after

Table 3 Atomic ratio (%) of sputtered Pt_xPd_y thin film electrocatalysts

Catalyst (%)		Measured atomic %		
Pt	Pd	Pt	Pd	STDV
80	20	83.137	16.863	1.487
60	40	67.920	32.080	0.626
40	60	49.083	50.917	0.100
20	80	31.928	68.137	1.888
10	90	25.635	74.365	5.904

STDV standard deviation

Fig. 8 Cross view of the Si-SiO₂-TiAu layers of a wafer

consecutive potential sweeps [41–43]. The combinatorial approach investigated here includes varying catalysts like Au and Pd, which do not contain any Pt at all. Hence, the method of oxygen adsorption from solution should be used for the estimation of real surface area as this method is common to all the metals under investigation [43]. Multiple runs to a set of upper potential limits, at which oxygen is chemisorbed in a monoatomic layer with a one-to-one correspondence with the surface metal atoms, have to be conducted [44]. This requires the catalyst surface to be identical at the commencement of each run, and since our various catalysts are positioned on a wafer which cannot undergo physical polishing/cleaning, they will have to undergo some sort of electrochemical cleaning and/or other means of obtaining a repeatable surface. Furthermore, for the electro-oxidation of aqueous SO₂, sulphur as well as other intermediate oxidation products has variable adsorption/binding strengths on the different metals and metal combinations, which will affect the specific technique that is employed to determine the real active surface area [32]. Whichever method is employed to determine the real active surface area, all have their advantages and limitations [41]. In this instance, after weighing the advantages and limitations of using oxygen adsorption from solution as a means to determine the real active surface area of the variety of catalysts prepared employing our combinatorial setup, it was decided not to disregard the method, but that it deserves a dedicated investigation [29]. One could use geometric area, as stated by Cooper & McGinn [34], but employing the real active surface

area is preferred as it is sure to differ from the geometric area for different catalyst compositions. Hence, for this investigation, only onset potential was employed as a means to quickly identify promising compositions from a catalyst library for the electro-oxidation of aqueous SO₂ [34].

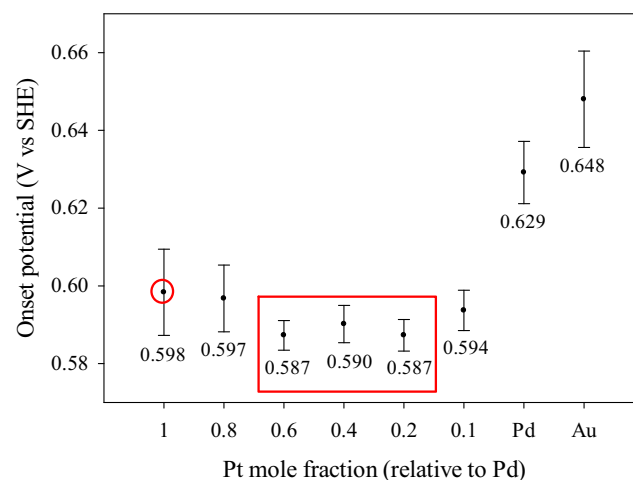
In order to clearly identify a possible alternative catalyst compared to pure Pt, further in-depth investigations have to be conducted on the Pt₃Pd₂ and PtPd₄ catalysts. This will entail sputtering these combinations onto GCs to (i) investigate and improve catalyst stability, (ii) conduct real active surface area measurements so as to calculate and compare current densities, and (iii) conduct linear polarisation scans at different temperatures in order to calculate activation energy.

Conclusions

A combinatorial method for the synthesis and electrochemical screening of novel functional materials has been described. Pure Au, Pt, Pd and bimetallic Pt_xPd_y electrocatalysts were

Table 4 Example of composing the average onset potential value and standard deviation for Pt

Pt	Wafer 1	Wafer 2
Onset potential (V, SHE)	0.609	0.606
	0.603	0.600
	0.581	0.591
Pad-to-pad reproducibility	0.598±0.015	0.599±0.008
Wafer-to-wafer reproducibility	0.598±0.011	

**Fig. 9** Average onset potentials for Au, Pd, Pt and Pt_xPd_y electrocatalysts on a SiO₂ wafer. Conditions: 1 mol L⁻¹ H₂SO₄, 100 mmol L⁻¹ SO₂, 25 °C, 10 mV s⁻¹

sputtered onto a silica wafer and screened for activity towards the electro-oxidation of aqueous SO_2 , employing onset potential as the screening criterion. On the wafer, three Pt_xPd_y bimetallic combinations exhibited satisfactory performance (compared to pure Pt) with the best compositions being Pt_3Pd_2 and PtPd_4 . Both these combinations exhibited the same lower onset potential of 0.587 ± 0.004 V, SHE compared to that of pure Pt (0.598 ± 0.011 V, SHE). It has been shown that Pt content can be significantly reduced, through the development of a bimetallic electrocatalyst for the electro-oxidation of aqueous SO_2 , whilst not sacrificing catalytic activity (based on onset potential).

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The Effect of Rapid Thermal Annealing on Sputtered Pt and Pt₃Pd₂ Thin Film Electrocatalysts for Aqueous SO₂ Electro-Oxidation

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Abstract Insight into the effect that rapid thermal annealing (RTA) has on the structural and electrochemical characteristics of sputtered Pt and Pt₃Pd₂ thin film electrocatalysts is communicated. The DC magnetron sputtered thin films were rapidly annealed at temperatures ranging from 600 to 900 °C under an Ar atmosphere. The microstructural changes and electrochemical properties (onset potential, current density and stability) induced by rapid thermal annealing were investigated towards the electro-oxidation of aqueous SO₂. An increase in annealing temperature induced different degrees of crystallinity, and the surfaces changed from being smooth and granular to surfaces exhibiting defined grain boundaries. Electrochemical characterisation, employing linear polarisation (LP) and cyclic voltammetry (CV), revealed improved catalytic activity for the Pt₃Pd₂ thin film catalysts (compared to Pt) exhibiting lower onset potentials, competitive currents and acceptable stability. The Pt₃Pd₂ thin film, annealed at 800 °C, proved to be a promising contender in competing with pure Pt towards the electro-oxidation of aqueous SO₂.

Keywords Sulphur dioxide · Electro-oxidation · Annealing · Stability

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Introduction

Of concern in this paper is the oxidation of aqueous SO₂ at the anode of a SO₂-deloxygenated electrolyser (SDE) in the hybrid sulphur (HyS) process (Table 1), which was proposed by Westinghouse Corp. as a means of producing hydrogen [1], a clean alternative fuel, and subsequently mitigating an environmental pollutant. Within a decomposition, sulphuric acid is thermally decomposed to produce SO₂, water and oxygen (reaction 1) [2] by employing a high-temperature heat source (>800 °C). The resulting SO₂ is fed to a SDE, which can be a gas-fed system or liquid-fed system depending on the design. In the gas-fed system, gaseous SO₂ is fed to the anode [3], and in the liquid-fed system, sulphuric acid saturated with SO₂ is employed as the anolyte [4]. The gas-fed system is however a more complex system, as the gaseous SO₂ that is required is obtained from the thermochemical step (reaction 1), but the oxygen that is also present should first be separated from the mix to obtain pure SO₂, which is not the case with the liquid-fed system. Nevertheless, irrespective of which design is implemented for the SDE, the SO₂ is fed to the anode and electro-oxidised to produce sulphuric acid as well as hydrogen ions (reaction 2). The hydrogen ions migrate through the membrane of the electrolyser to the cathode where it is reduced to hydrogen gas (reaction 3) while the electrochemically produced sulphuric acid is recirculated back to the decomposition reactor. The net SDE reaction therefore involves the conversion of SO₂ into sulphuric acid and hydrogen gas (reaction 4), while the net HyS cycle reaction is that of water being split into hydrogen and oxygen (reaction 5).

For the electro-oxidation of SO₂ to be effective, electrocatalysts need to be employed that can perform under optimal working conditions (increase the reaction rate with low electrode overpotentials and show satisfactory lifetime), both from an economical and environmental point of view.

Table 1 Steps in the HyS cycle

$\text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$	(Thermochemical)	(1)
Anode: $\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^-$	(Electrochemical, $E^\circ = 0.17$ V, SHE [5])	(2)
Cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$		(3)
$\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2$	(net SDE reaction)	(4)
$\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$	(net HyS cycle reaction)	(5)

While platinum has been the electrocatalyst of choice, due to its high electrocatalytic activity and inert character [6, 7], a number of studies (Table 2), in addition to those already communicated [8], have been conducted in an effort to reduce/replace the platinum as it is an expensive metal. Recent research reveals that multimetallic electrocatalyst compositions provide enhanced performance in terms of activity, stability and/or selectivity compared to their corresponding monometallic components, and as a consequence, research into multimetallic compositions is increasing [6, 9–12]. It has also been revealed that annealing of metallic compositions serves to increase their activity and stability [13–15].

In previous work [8], we identified Pt_3Pd_2 to be a potential candidate for the electro-oxidation of aqueous SO_2 . Palladium was chosen to ‘alloy’ with platinum as some experimental studies [23, 24] as well as a theoretical molecular modelling study [25] pointed towards palladium being potentially more active than platinum for the electro-oxidation of aqueous SO_2 [8]. For pure Pd and Pt_xPd_y combinations, it was observed that, with increasing Pd content (Pt_2Pd_3 , PtPd_4 and PtPd_9), the stability in acidic solution decreased as signs of delamination occurred. Of the combinations investigated, the PtPd_4 thin film combination exhibited the same low onset potential as the Pt_3Pd_2 thin film combination, but does not withstand the harsh acidic environment sufficiently and is prone to almost immediate delamination. Hence, we decided to focus our attention on investigating the effect that rapid thermal annealing has on the properties of Pt and Pt_3Pd_2 sputtered thin films, specifically focusing on the activity and stability of the electrocatalysts towards electro-oxidising aqueous SO_2 . The thin films were

furthermore characterised by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) with integrated energy dispersive X-ray spectroscopy (EDX). The electrochemical SO_2 oxidation trends (activity and stability) were determined by linear polarisation and cyclic voltammetry.

Experimental

Preparation of Glassy Carbon Electrode Inserts and Deposition of Thin Films

Glassy carbon electrodes (GCs, Sigradur G, HTW Germany) were polished to promote reproducible electrochemical surfaces (geometric area of 0.196 cm^2) [26]. Firstly, microcloth (Buehler polishing kit) with $1\text{-}\mu\text{m}$ diamond paste (DP-Paste M, Struers) was used for 50 cycles. The GCs were subsequently rinsed with water (Milli-Q Plus ultra-pure water was used in all instances, $18.2 \text{ M}\Omega \text{ cm}$) before transferred to the second microcloth so as to ensure that the second microcloth stays free of diamond paste particles. On the second microcloth, the GC was subjected to 25 cycles employing $0.05 \text{ }\mu\text{m}$ deagglomerated alumina suspension (Gamma Micropolish II, Buehler) as a polishing medium. The inserts were then sonicated in toluene (HiPerSolv for HPLC, BDH Laboratory Supplies) for 15 min, ethanol (Merck) for 15 min, Milli-Q water for 15 min and iso-propanol (Merck) for 15 min, after which the GCs were dried with N_2 . The thin films (60 nm) were prepared by means of physical vapour deposition, and four identical thin films were deposited simultaneously onto

Table 2 Some studies conducted on the anode catalyst of the SDE

Year	Catalyst	Reference
1965	Pt and Au	[16]
1975	Au	[17]
1980	Graphite (carbon) with small amounts of HI, borides, carbides, nitrides, sulphides, organic catalysts, bronzes, W, Co, Ti, Nb, Zr, Ta, Pb, Mo, Au, Pd and Duriron	[18]
1983	Activated carbon	[19]
1991	Pt supported in a porous graphite sheet	[20]
1995	Pt-Al	[6]
2000	Polycrystalline Au	[21]
2012	Pt and Au	[22]
2015	Pt_xPd_y combinations	[8]

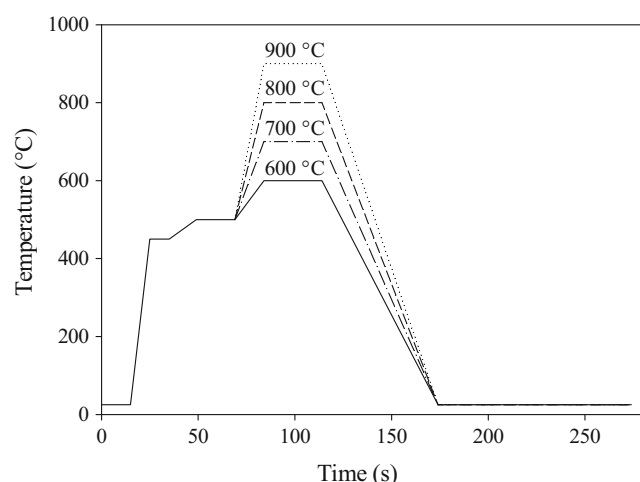


Fig. 1 The temperature regime employed for annealing Pt and Pt₃Pd₂ thin films

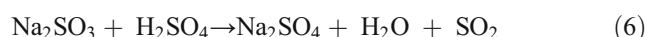
four polished glassy carbon surfaces by employing the method and conditions as communicated earlier [8].

Annealing Procedure

The as-deposited samples were annealed ex situ employing a rapid thermal annealing oven (AccuThermo AW610), and the temperature regime employed (temperature time periods and temperature ramps) is illustrated in Fig. 1. Maximum temperatures ranged from 600 to 900 °C with intervals of 100 °C.

Characterisation of Thin Films

In order to investigate the stoichiometry and morphology of the electrocatalysts, SEM (FEI Quanta FEG 250) with an integrated XMax 20 EDX system (Oxford Instruments) was performed before and after annealing. EDX was performed in moving average mode employing a collection time of 100 s. XRD patterns were collected to investigate any change in crystallinity of the thin films employing a XPERT-PRO diffractometer with a Cu K α radiation source. The Bragg angles were scanned from 5° to 110° at 0.1° min⁻¹. Electrochemical measurements were performed in a standard three-electrode set-up, employing a Pt spiral wire as the counter electrode and a saturated calomel electrode (SCE, Radiometer Analytical REF 421) as the reference electrode. Preconditioning was conducted in degassed (N₂ was bubbled for 20 min) 0.1 mol L⁻¹ HClO₄ (Merck). A 1 mol L⁻¹ H₂SO₄ acid solution was made up by dilution of 95 wt% H₂SO₄ (SAAR5885124LP, Merck). This solution was degassed with N₂ for 15 min prior to linear polarisation. A stock solution of 1 mol L⁻¹ Na₂SO₃ (Sigma Aldrich) was used as an in situ SO₂ source (reaction 6).



Linear polarisation was conducted ($E_{\text{low}} = 0.2$ V vs SHE to 1.441 V vs SHE at a scan rate of 10 mV s⁻¹) to determine the onset potentials and current density (criterion for activity [27]) for the thin films exposed to the different annealing regimes.

Table 3 Visual surface analysis of glassy carbon and as-deposited and annealed thin films at different annealing temperatures

200 nm		As-deposited	600 °C	700 °C	800 °C	900 °C
GC						
	Pt					
	(100 %)					
Pt ₃ Pd ₂						
	Pt ₃ Pd ₂					
	(60.43:39.57 ± 3.60 %)					

Current densities were calculated by employing the electrochemical active surface area (EASA) determined by evaluating the reduction charge of O atoms adsorbed from solution [28]. Cyclic voltammetry (CV) was employed as a relatively simple means of obtaining information with regard to stability [29–31] of the as-deposited and annealed samples in a 1 mol L⁻¹ H₂SO₄ (pH=0.55) electrolyte environment. CVs were conducted at a scan rate of 100 mV s⁻¹ and within a potential window of 0.041 V vs SHE and 1.441 V vs SHE at 25 °C.

Results and Discussion

SEM and EDX Characterisation

The stoichiometry of the electrocatalysts was investigated by EDX (Table 3), and the evolution of the surface morphology of the electrocatalysts was investigated by SEM, both before and after annealing. SEM micrographs of the as-deposited and annealed GC, Pt and Pt₃Pd₂ sputtered thin films annealed at 600, 700, 800 and 900 °C are presented in Table 3. GCs annealed over this temperature range are unaffected as these are high temperature-resistant GCs. The as-deposited samples of Pt and Pt₃Pd₂ show smooth, crack-free surfaces and adopt the GC surface. Annealing up to 900 °C resulted in discontinuous grain growth surfaces [32] with islands of grains surrounded by well-defined grain boundaries [33]. A question that now arises is whether the Pt₃Pd₂ electrocatalyst can be referred to as a bimetallic or alloy catalyst, as this is being interpreted and defined in different ways [34]? According to

literature of the early 1900s [35, 36], the rigid band theory (RBT) was used to define an alloy as being another/new metal in which the individual components are no longer distinguishable; thus, any change in catalytic activity is explained as being due to electronic change in the alloy as a whole, with the surface composition being regarded as not important [34]. Not everyone was accepting this theory and regarded the individual properties of the contributing metals to still be preserved in the alloy [37]. This debate is however still continuing [34], and we are adopting the more recent definition of an alloy that is defined as a metal consisting of two or more components irrespective of how the components are mixed [38]. Thus, the as-deposited and annealed samples of Pt₃Pd₂ are seen as alloys, but with changing properties as annealing temperature increases.

XRD Characterisation

As a means to evaluate anneal-induced changes in the crystal structure, XRD was obtained for the different thin film electrocatalysts at the different annealing temperatures (Fig. 2). As a reference, XRD spectra were also obtained for blank GCs at the different temperatures. The GCs were not affected by annealing temperatures up to 900 °C, supporting the results obtained from SEM analysis. Overall, the XRD patterns of the Pt and Pt₃Pd₂ thin films exhibited an increase in the degree of polycrystallinity for the different temperatures. This is clear from the peak observed at 40°(2θ) (as a means to evaluate the degree of crystallinity) for both the as-deposited Pt and Pt₃Pd₂ sputtered thin films that grows into sharper peaks ((111) phase) as the temperature increases. In addition to the peak at 40°(2θ) for both

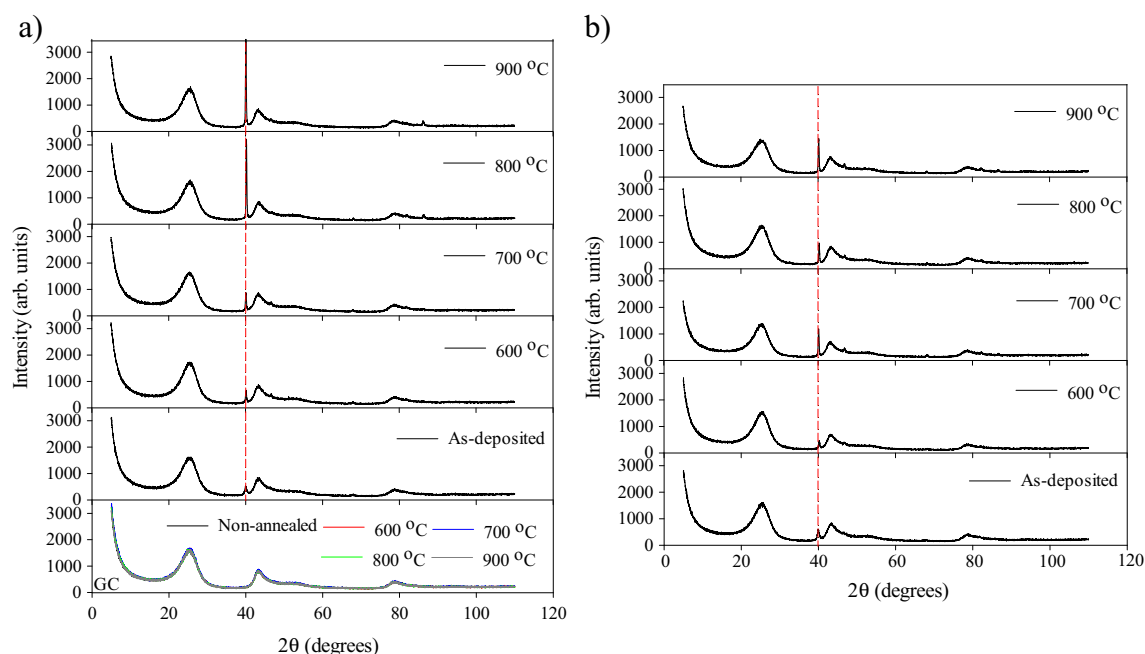


Fig. 2 XRD spectra of **a** blank GC, Pt and **b** Pt₃Pd₂, at the different annealing temperatures. (Red dashed line indicates the (111) phase)

thin films (Pt and Pt₃Pd₂), the (200), (220), (311) and (222) planes [39] characteristic of face-centred cubic (f.c.c.) crystal structure [40] emerge as the temperature increases. No peak characteristics of Pt- and Pd-oxide were present. Both Pt and Pd exist in f.c.c. lattices, and the unit cell dimensions are 3.92 and 3.89 Å for Pt and Pd, respectively [41], which makes it difficult to distinguish between the two metals [42] in the Pt₃Pd₂ thin film alloy. The (111) reflection peak at the Bragg angle of 40°(2 θ) was used to calculate the crystallite size of the different thin films incorporating the Debye-Scherrer equation. In general, both the Pt and Pt₃Pd₂ thin films annealed at different temperatures exhibited larger crystallite size in comparison to the as-deposited thin films ranging from ~18 nm (as-deposited films) to ~60 nm (annealed thin films).

Electrochemical Characterisation

Electrochemical Active Surface Area Determination

As it is a known fact that the activity of electrocatalysts is proportional to their real EASA (as geometrical area can be misleading), it is inevitable that the real EASA of the thin films of interest should be determined, as was stated by Bard et al. [43]. In this study, Pt and Pd are employed as the main

components in the electrocatalysts as they show potential for the oxidation of aqueous SO₂. The EASA of Pt has been studied extensively in various catalyst forms (foils, thin layers, nano-particles [44]) employing different methods (underpotential deposition of metals [44, 45], CO stripping [46] and double layer capacitance [44]), with hydrogen adsorption/desorption [47] having been employed the most frequently for determining the EASA. However, as Pd is one of the metals being investigated, employing the hydrogen adsorption method is not feasible, as hydrogen is not adsorbed onto Pd but is rather absorbed into the Pd [48]. A method that has shown reliable results for surfaces containing Pd involves the integration of the charge of a full monolayer of PdO [28, 48–51], which is also applicable for Pt, making normalised comparison between the different thin film electrocatalysts possible. Cyclic voltammetry was employed by scanning the electrode from 0.3 to 1.2–1.7 V, respectively (Fig. 3a), with a scan rate of 0.05 V s⁻¹. The reduction charge of the surface oxide was evaluated by integrating the area of the oxide peak, not including the double layer charge (Fig. 3b). For this method, it is essential to know the upper potential limit where O atoms are chemisorbed in a monolayer with a one-to-one correspondence to the available Pt and Pd surface sites. This is indicated by a change in slope of a straight line plot between

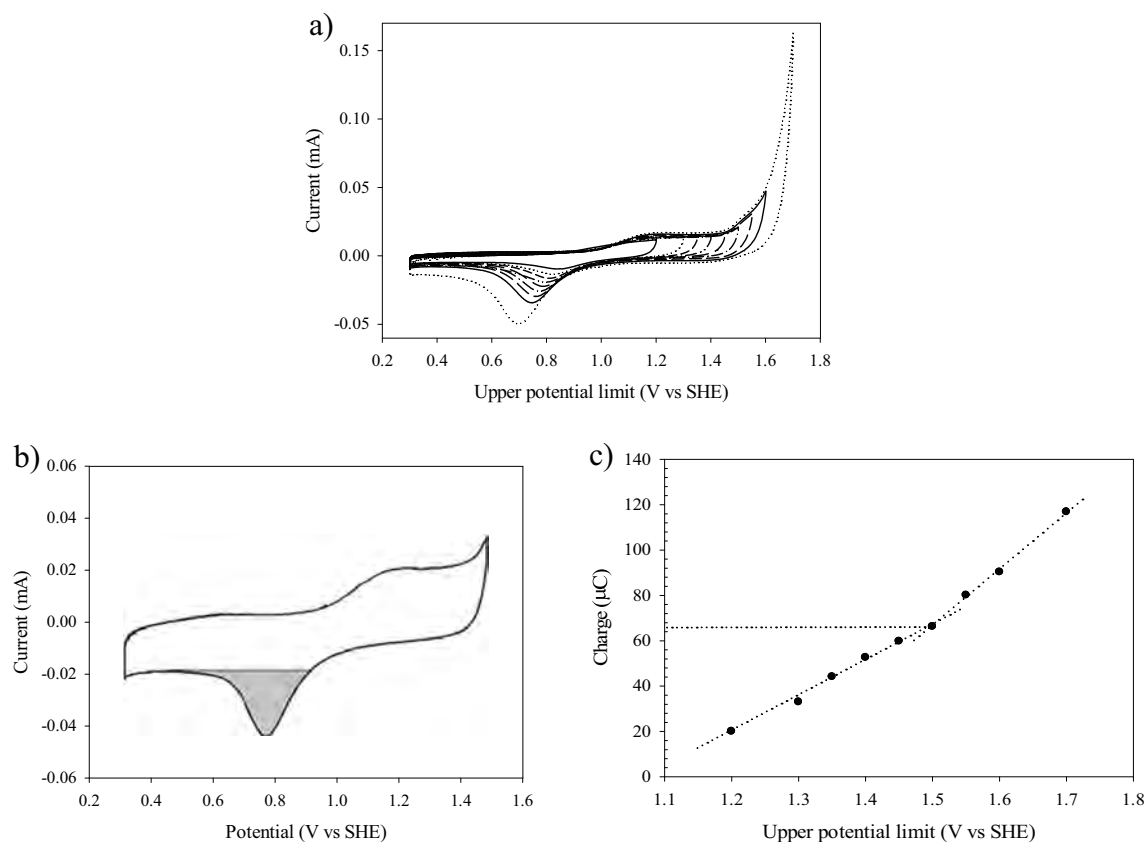


Fig. 3 **a** Typical cyclic voltammograms of Pt₃Pd₂ annealed at 800 °C showing the growth of surface oxide. **b** The red line indicates the base line for the integrated grey region used for EASA calculations. **c** Charge vs

upper potential limit indicating where O atoms are chemisorbed in a monolayer with a one-to-one correspondence with the available surface atoms

charge (μC) and upper potential limit (V) [45, 48, 51], as can be seen in Fig. 3c.

The charge corresponding to the monolayer coverage was converted to an area value (cm^2) by employing the well-known values of $208 \mu\text{C cm}^{-2}$ for Pt and $212 \mu\text{C cm}^{-2}$ for Pd for a one-electron transfer per site [52]. For the Pt_3Pd_2 electrocatalyst, 60 % of the surface will correspond to the value of Pt and 40 % to the value of Pd, and since the charge evaluated is due to oxide reduction, a two-electron transfer per site value was calculated as being $419.2 \mu\text{C cm}^{-2}$. The values for real EASA obtained by the method of oxide reduction for the Pt and Pt_3Pd_2 thin film electrocatalysts are shown in Fig. 4.

It is clear that an increase in annealing temperature correlates with a general decrease in the EASA for both Pt and Pt_3Pd_2 with the values for Pt being smaller than that of Pt_3Pd_2 and with the difference between the individual Pt and Pt_3Pd_2 electrocatalysts increasing with increasing annealing temperature. A similar observation was made for Pt_xCu_y catalysts by Mani et al. who observed that the measured (by means of evaluating the charge for monolayer hydrogen adsorption/desorption) electrochemical surface area decreased significantly with increasing annealing temperatures (600 to 950°C), owing it to particle growth [15]. In contrast, for the as-deposited non-annealed samples, the EASA for Pt is almost double that of Pt_3Pd_2 . Another intriguing observation is the fact that the EASA values for the as-deposited thin films are larger than the geometrical area while the EASA values for the annealed thin films are smaller than the geometrical area. It is therefore unlikely that surface roughening occurred [15], and it is likely that the activity of the catalysts is a result of geometric (topology of surface sites) and/or electronic effects (interaction between the molecular orbitals of reactants and the d-orbitals of available surface sites) [15, 53–55]. One of the first researchers who recognised a relationship between the surface and activity of a catalyst was Taylor in 1925 [56], who stated that the reaction being catalysed determines the amount of

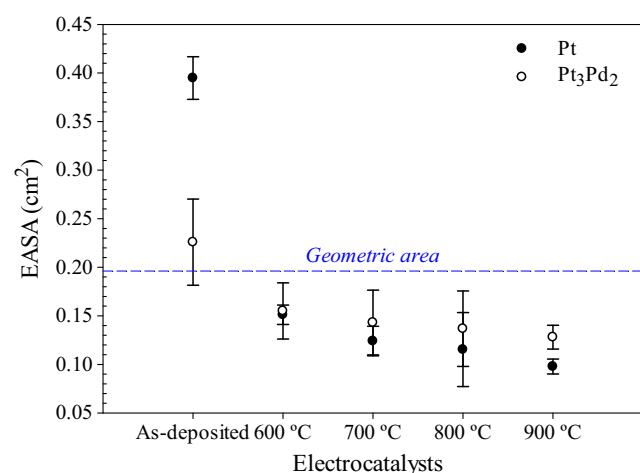


Fig. 4 EASA values determined for Pt and Pt_3Pd_2 electrocatalysts

surface being catalytically active and that all extremes exist, ranging from all the surface atoms being active to that in which only a few atoms are active. It can therefore be assumed that determining the active surface area electrochemically as a means to obtain current density (mA cm^{-2}) is a way of normalising current, as the action of adsorbing O atoms on the surface will differ from the reactants participating in SO_2 electro-oxidation [25]. Understanding the properties of surfaces and establishing which properties are responsible for chemical activity are however a long-term goal of surface sciences [53, 55].

Linear Sweep Voltammetry, Stability and Current Density

The performance of the as-deposited and annealed Pt and Pt_3Pd_2 thin films for the electro-oxidation of aqueous SO_2 was investigated and ranked based on their variation in onset potential, stability and current density (Fig. 7a, b). The onset potential was calculated using the intercept of two straight lines tangent to the linear polarisation (LP) curve (Fig. 5 point B) as described by Cooper and McGinn [57], while stability was determined by the number of cycles until signs of delamination occurred on the electrocatalyst surface. Current was taken at the highest point on the SO_2 oxidation peak (Fig. 5 point A) and converted to current density by employing the determined EASA values (section “[Electrochemical active surface area determination](#)”).

In general, the onset potentials of the individual annealed Pt_3Pd_2 electrocatalysts were lower than that of the annealed Pt electrocatalysts at the respective temperatures. For both Pt and Pt_3Pd_2 , the annealed thin films exhibited higher onset potentials than the as-deposited thin films. Annealing therefore has no positive influence on the onset potential as no improvement (lowering of the onset potential) was observed.

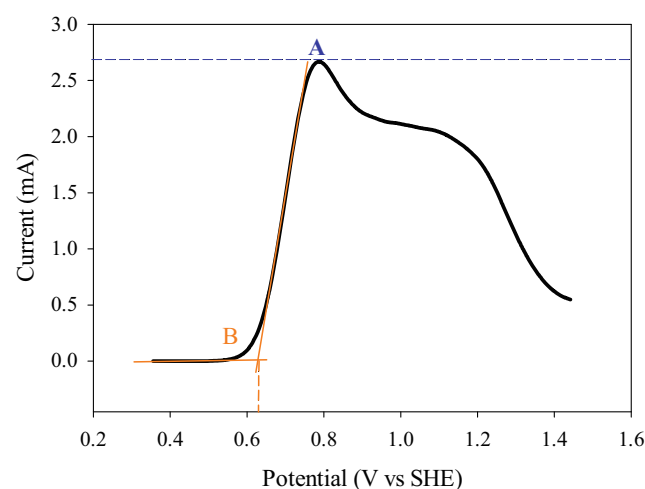
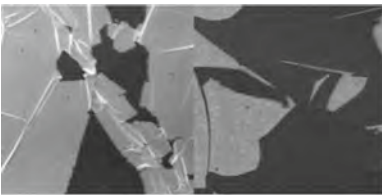
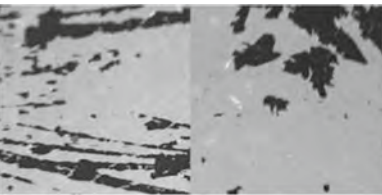
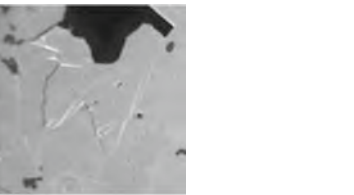
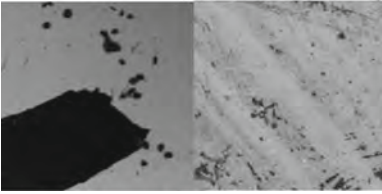
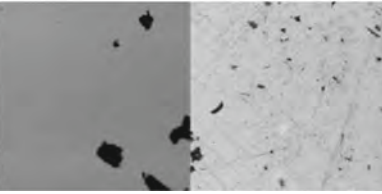
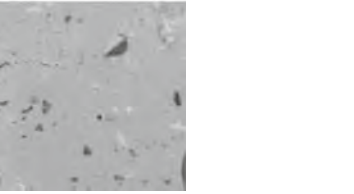


Fig. 5 Linear polarisation curve for Pt_3Pd_2 annealed at 800°C with A indicating the highest point on the SO_2 oxidation peak and B the onset potential defined by the intercept of two tangent lines [57]

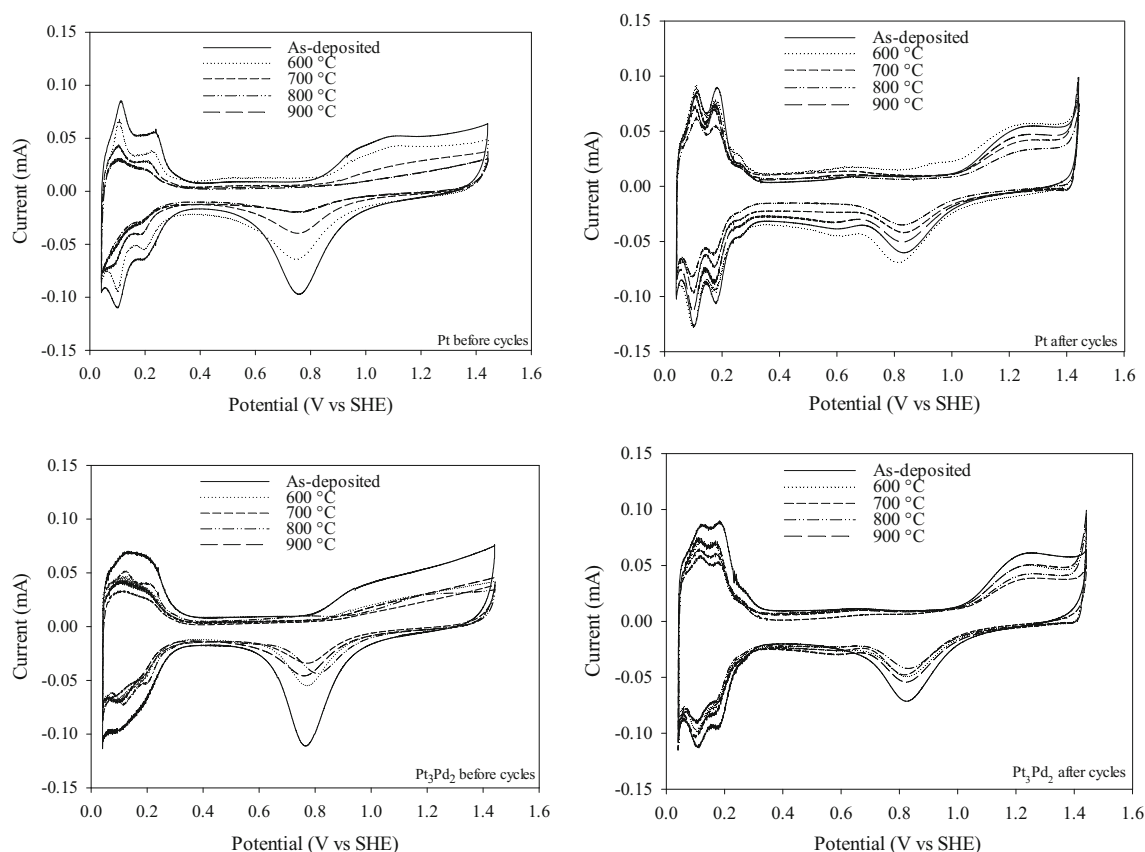
Table 4 Different degrees of delamination observed for Pt and Pt₃Pd₂ thin films

	1 mm	As-deposited	600 °C	700 °C	800 °C	900 °C
Pt (100 %)						
Pt ₃ Pd ₂ (60.43:39.57 ± 3.60 %)						

As it is important to realise a long operational lifetime for the electrocatalyst in the electrolyser, consecutive CVs were conducted to investigate the stability of the thin film electrocatalysts in a sulphuric acid environment (in the absence of SO₂). This technique of consecutive cycling has previously been employed to evaluate the durability of

electrocatalysts in a short period of time [58]. During the CVs, the electrocatalyst surface was visually monitored for signs of delamination as an indication of the level of resistance of the thin films to a sulphuric acid environment (Table 4).

As a result of prolonged consecutive cycling, an interesting observation was made for the different electrocatalysts. As a

**Fig. 6** Consecutive cycling of Pt and Pt₃Pd₂ thin film electrocatalysts

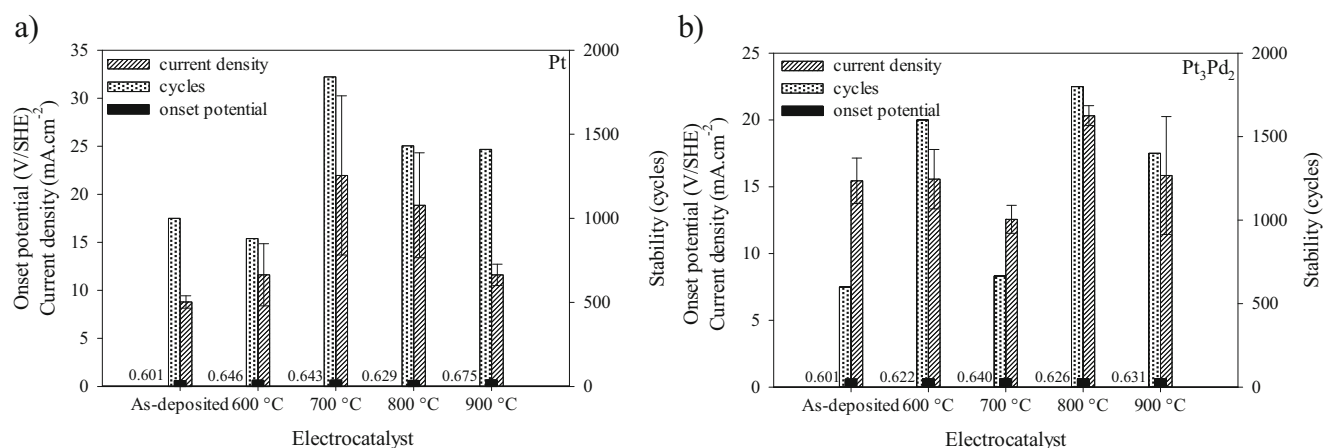


Fig. 7 Comparison of the onset potential, current density and number of cycles for as-deposited and annealed **a** Pt and **b** Pt₃Pd₂, at different temperatures. Standard deviations for onset potentials are included in the graph but are negligibly small

result of consecutive cycling, all the electrocatalysts exhibited various degrees of distinct growth in the hydrogen absorption/desorption regions, with no specific trend (Fig. 6). Clarification of these changes requires in-depth characterisation, but was not the focus of this study as the thin films still delaminated from the glassy carbon surface. Attention must therefore first be given to improve the adhesion of the thin film to the support of interest, followed by in-depth characterisation of the effect of prolonged consecutive cycling.

As can be observed from Fig. 7, rapid thermal annealing (RTA) clearly increased the lifetime of the electrocatalysts (in an acidic environment) for both the Pt and Pt₃Pd₂ thin film electrocatalysts. The Pt annealed at 700 °C and the Pt₃Pd₂ annealed at 800 °C are the most stable within a sulphuric acid environment. In terms of hours, the lifetime of as-deposited Pt₃Pd₂ as an example, increased from ~3 h and 8 min to ~9 h and 24 min by annealing at 800 °C. If the onset potentials and stability are considered together, it is evident that the Pt₃Pd₂ annealed at 800 °C is the superior electrocatalyst as it exhibits both good stability and comparable onset potential compared to all the annealed Pt samples. Another indicator of activity that was evaluated, in the search of finding a possible alternative electrocatalyst, is current density. RTA resulted in the annealed thin films all exhibiting almost equal to or higher current densities than the corresponding as-deposited thin films. However, the advantage of the obtained increased stability and improved current density by annealing at 800 °C for the Pt₃Pd₂ specifically overrides the fact that the as-deposited Pt₃Pd₂ and Pt thin films exhibit the lowest onset potentials overall.

Taking into account all three parameters, the Pt₃Pd₂ thin film electrocatalyst annealed at 800 °C would seem to be the superior electrocatalyst for the oxidation of aqueous SO₂, exhibiting (i) lower onset potential compared to pure Pt, (ii) improved normalised current density and (iii) increased stable lifetime within a sulphuric acid environment.

Conclusion

Thin film electrocatalysts were subjected to rapid thermal annealing at different temperatures, and the changes induced by annealing were investigated by physical and electrochemical characterisation. From the physical characterisation analysis, which included SEM and XRD, it was found that (a) the thin films visually showed to form well-defined grains with grain boundaries as the annealing temperature increased, (b) the thin films transformed into more crystalline thin films as the temperature increased and (c) the crystallite size for the annealed thin films was larger compared to that of the as-deposited thin films. The effect of these observed physical changes (induced by rapid thermal annealing) on the electrochemical properties of Pt and Pt₃Pd₂ thin films towards the oxidation of SO₂ in an acidic environment was investigated. From electrochemical characterisation, it was found that RTA did not improve the onset potential of the annealed thin films, but did however improve current density and substantially improved the lifetime of the thin films in an acidic environment. The Pt₃Pd₂ thin film electrocatalyst annealed at 800 °C seems to be the superior electrocatalyst for the oxidation of aqueous SO₂, exhibiting lower onset potential than all pure annealed Pt, as well as improved normalised current density and increased stable lifetime within a sulphuric acid environment.

In summary, the highlights that have been achieved thus far in searching for a potential alternative electrocatalyst that is competitive compared to Pt can be listed as follows:

- A thin film electrocatalyst (Pt₃Pd₂) with ~40 % less Pt than pure Pt has been identified to exhibit a similar onset potential compared to 100 % Pt, and
- Exposing the thin film electrocatalysts to RTA, as a means to improve the properties of the thin film electrocatalysts, resulted in the majority of annealing temperatures improving the electrochemical properties of the thin films, with the Pt₃Pd₂ thin film

electrocatalyst annealed at 800 °C being a promising contender in competing with pure Pt towards the electro-oxidation of aqueous SO₂.

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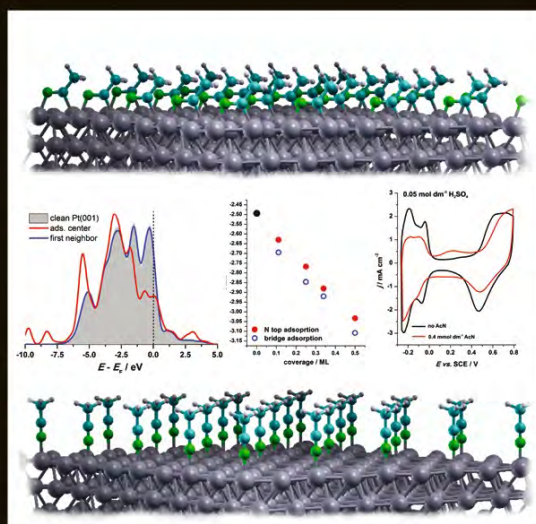
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Co-sputtered $\text{Pt}_x\text{Pd}_y\text{Al}_z$ thin film electrocatalysts for the production of hydrogen via $\text{SO}_2(\text{aq})$ electro-oxidation

A. Falch¹ · V. A. Badets² · C. Labrugère³ · R. J. Kriek¹

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Abstract A co-sputtered $\text{Pt}_x\text{Pd}_y\text{Al}_z$ ternary system was investigated for potential use as anode catalyst for the electro-oxidation of aqueous sulphur dioxide (SO_2), a key reaction in the hybrid sulphur (HyS) process for splitting water into hydrogen and oxygen. Combining the noble metals Pt and Pd with Al resulted in no significant improvement in onset potential; however, current output was improved for the majority of the electrocatalysts evaluated. Of these electrocatalysts, only a single ternary composition exhibited improved stability when compared to pure Pt. It was found that a combination of $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ (annealed at 900 °C) exhibited superior performance when compared to pure Pt and the previously determined best binary electrocatalyst, i.e. Pt_3Pd_2 . Current density (mA.mg Pt^{-1}) increased from 108.11 to 181.21 and finally to 396.73 for Pt, Pt_3Pd_2 and $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$, respectively, indicating an increase in activity that correlates with a decrease in Pt content. Atomic force microscopy (AFM) revealed an increase in surface roughness for Pt, Pt_3Pd_2 and $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$, while the occurrence of metal interaction and certain degrees of Al migration (a result of annealing) was confirmed for

$\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction analysis (XRD).

Keywords SO_2 electro-oxidation · Hydrogen production · Electrocatalyst · High-throughput screening

Introduction

Hydrogen, the only non-carbon containing energy carrier, is the most abundant atom on earth [1] and is considered as the ultimate clean energy carrier to be generated from renewable resources [2]. The range of hydrogen production processes can roughly be divided into hydrocarbon-based (steam-methane reforming and coal gasification), non-hydrocarbon based (water electrolysis and thermochemical water decomposition) and integrated (steam-methane reforming linked to non-hydrocarbon based) [3]. As hydrogen is only found as part of compounds on earth, it is fairly energy-intensive to separate hydrogen into its molecular form [1], and goes hand in hand with huge amounts of environmental pollutants being emitted to the atmosphere. If, however, hydrogen can be returned/produced as part of a remediation process of these detrimental environmental pollutants, a portion of the energy input for the remediation process can be returned in the form hydrogen. This is exactly what the hybrid sulphur (HyS) cycle, a thermo-electrochemical water splitting process, accomplishes, through the electrochemical oxidation of aqueous sulphur dioxide (Fig. 1). Thermochemical processes produce hydrogen through a series of chemical reactions with water-splitting being the net reaction. Since hydrocarbons are not used in these thermochemical processes, no harmful emissions such as carbon dioxide (CO_2) are produced, with the hydrogen produced being extremely pure [4]. There are various thermochemical cycles (a combination of thermochemical and

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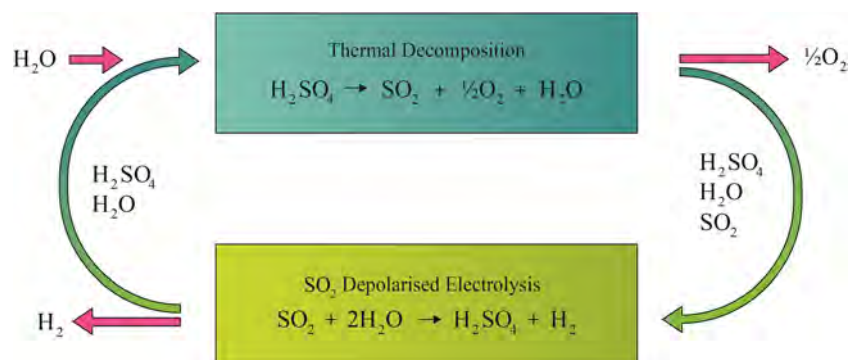
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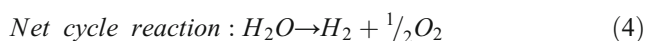
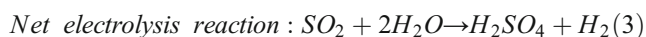
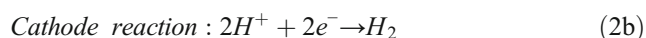
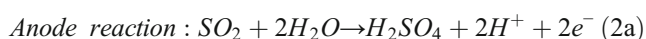
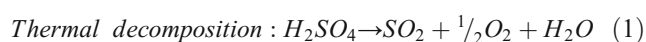
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Fig. 1 The thermo-electrochemical HyS cycle for the splitting of water



electrochemical reactions [5]) that can produce hydrogen from water with the HyS cycle (reactions 1–4) being the most promising [4, 6–8].



The HyS cycle undergone extensive development in the 1970s [9, 10] and 1980s [10, 11]. For the subsequent 20 years, further development nearly ceased as advanced nuclear technologies gained increased interest [10]. After this period, interest in the HyS cycle revived, and the HyS cycle was subsequently rated first among 115 thermochemical cycles considered [12]. Interest in the HyS cycle results from the fact that, whereas the anodic reaction for regular water electrolysis occurs at a standard potential of 1.23 V (SHE) [13], the anodic reaction for SO_2 depolarised electrolysis (SDE) occurs at a standard potential of 0.17 V (SHE) [14], which translates into an energy gain of more than one volt [7, 15]. In SDE the rate determining step occurs at the anode, which results in the anode contributing to the inefficiencies of the SDE [16]. To this regard, an optimal operational target of $500 \text{ mA}\cdot\text{cm}^{-2}$, at a cell potential of approximately 0.6 V, has been proposed for SDE by Gorenssek and Summers [7, 17]. This target can potentially be achieved through the development of an effective electrocatalyst for the anodic electro-oxidation of SO_2 and to that regard the properties of the anode is regarded as pivotal for improving the entire HyS process [18, 19].

While platinum is generally considered the standard anode catalyst for the SDE [8, 16], efforts are underway to identify an electrocatalyst other than platinum (see [20, 21] for a detailed list of investigated catalysts). As Pt is costly the development and implementation of a catalyst with increased or equal catalytic activity and reduced cost (less Pt) will be advantageous. Platinum content could be reduced by alloying/combining it with either a more cost effective noble metal or base metals in an effort to still maintain acceptable catalytic activity [20, 21]. An earlier

investigation by us (employing sputtered thin films) has shown that Pt content can indeed be reduced by combination with Pd, i.e. Pt_xPd_y , without sacrificing electrocatalytic activity [21]. A thin film combination of Pt_3Pd_2 has specifically been found to exhibit competitive performance compared to pure Pt for the electro-oxidation of aqueous SO_2 with annealing further improving performance [21]. For this study aluminium (Al) was introduced as a third component in an attempt to lower the content of both Pt and Pd (both noble metals). Al is considered a metal of great electrochemical potential [22] and a study by Lee [23] on Pt and Al combinations proved that only small amounts of Al is effective in improving catalytic performance towards aqueous SO_2 electro-oxidation. This study by Lee was brief and no subsequent investigations were pursued [24]. For this investigation we employed combinatorial evaporative sputtering and high-throughput parallel screening in search of $\text{Pt}_x\text{Pd}_y\text{Al}_z$ electrocatalysts for the electro-oxidation of SO_2 . Identified compositions that merit more thorough investigation were evaluated employing conventional methods.

Experimental

Preparation, deposition, screening and annealing of thin films

The wafer and glassy carbon preparation, thin film deposition and electrochemical testing have previously been described in-depth [20, 21]. Employing a built-in quartz crystal microbalance (QCM) [20] and Pt, Pd and Al targets, all with a purity of 99.99 % (ACI alloys), the conditions for physical vapour deposition (PVD) were derived for the chosen compositions. The thin films (~60 nm) were subsequently deposited in triplicate by PVD, onto an annular arrangement (Patent Application No. 2015/08424) of 64 square working electrode pads (0.09 cm^2 each), developed through photolithography [20] (Fig. 2). The electrode pads were connected by a network of traces to individual rectangular pin pads on the outer perimeter of the wafer. The network of traces were provided with

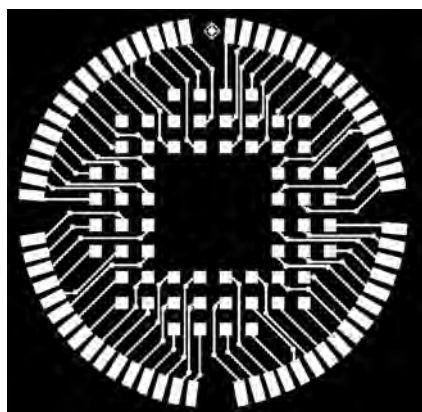


Fig. 2 Annular arrangement of 64 square working electrode pads (Patent Application No. 2015/08424)

reinforced bending points to prevent breaking of the lines/traces. For the conventional electrochemical testing, glassy carbon inserts (0.196 cm^2 each) were employed as substrate onto which the thin metal films were deposited. Electrochemical testing was performed on the wafer containing the various thin film compositions, in a dedicated electrochemical cell [20], with each working electrode connected individually to a multichannel potentiostat (Arbin MSTAT) for high-throughput screening while conventional testing commenced in a standard three electrode setup [21]. Preconditioning was conducted in degassed $0.1 \text{ mol.L}^{-1} \text{ HClO}_4$ (Merck), scanning from 0.041 V vs SHE to 1.441 V vs SHE starting at E_{ocp} (open circuit potential) for 25 cycles, followed by 3 cycles up to 1.741 V vs SHE and finally the first step was repeated but only for three cycles, employing a scan rate of 50 mV.s^{-1} , respectively. Linear polarisation (LP) was conducted in $1 \text{ mol.L}^{-1} \text{ H}_2\text{SO}_4$ (Merck, $\text{pH}=0.55$) in the potential window 0.2 V vs SHE to 1.441 V vs SHE at a scan rate of 10 mV.s^{-1} . This solution was degassed with N_2 for 15 min prior to linear polarisation. A stock solution of $1 \text{ mol.L}^{-1} \text{ Na}_2\text{SO}_3$ (Sigma Aldrich) was used as an in situ SO_2 source [20]. These electrochemistry testing parameters were identical for the thin films deposited onto the wafer and the glassy carbon inserts. Subsequent to the deposition of the selected thin film combinations onto the glassy carbon substrates (designated with letters of the alphabet as a means to ease comprehension throughout the article), some were kept as fresh (as-deposited) thin films while the rest of the thin films were annealed ex situ under an Ar atmosphere, employing a rapid thermal annealing oven (Accuthermo AW610), with the maximum temperatures ranging from 600 to 900°C with intervals of 100°C [21].

Physical characterisation of thin films

Energy-dispersive X-ray spectroscopy (EDX, employing INCA software) analysis, in moving average mode employing a collection time of 100 s and a 15 keV electron source, was

conducted in triplicate before and after electrochemical testing, so as to evaluate thin film composition. Atomic force microscopy (AFM, Nanoscope V Multimode from Veeco) was used to investigate surface roughness, deriving various surface roughness parameters by employing Nanoscope Analysis (Veeco) software. In addition, surface properties of the thin films were characterised employing X-ray photoelectron spectroscopy (XPS). A Thermo Fisher Scientific K-ALPHA spectrometer was used for surface analysis with a monochromatised Al $K\alpha$ source ($h\nu=1486.6 \text{ eV}$) and a $200 \mu\text{m}$ spot size. A pressure of 10^{-7} Pa was reached in the chamber when transferring the samples. The full spectra ($0\text{--}1100 \text{ eV}$) were obtained with a constant pass energy of 200 eV and high resolution spectra (C1s , Pd3p-O1s , Al2p-Pt4f , Pd3d , Al2s) at a constant pass energy of 40 eV . Charge neutralisation was applied during analysis. Sputtering was performed with Ar^+ ions at 500 eV . High-resolution spectra were fitted and quantified (Scofield sensitivity factors used for quantification) using the Advantage software provided by Thermo Fisher Scientific.

Results and discussion

Combinatorial sputtering and high-throughput screening of the $\text{Pt}_x\text{Pd}_y\text{Al}_z$ system

With the focus on identifying a possible ternary anode composition for application in the electro-oxidation of SO_2 , Pt_xPd_y compositions were evaluated previously [20, 21] and characterised so as to establish a standard for comparison with ternary $\text{Pt}_x\text{Pd}_y\text{Al}_z$ anode compositions [25]. The initial binary combinations investigated include a wide compositional range (Pt_xPd_y) that spanned from pure Pt to pure Pd using mainly 10 % content increments (refer to an earlier paper [20] for additional detail). Pt_3Pd_2 was identified to be the optimum binary composition and extensive characterisation was conducted on it [21], with annealed Pt_3Pd_2 (at 800°C) proving to be a worthy contender to compete with pure Pt for the electro-oxidation of SO_2 . In producing a ternary electrocatalyst, the combination of Pt and Pd with a base metal will result in an electrocatalyst containing less noble metal with Al making up the balance. Due to the vast number of electrocatalyst combinations that can statistically be formulated using the three components, Pt, Pd and Al, our selection of electrocatalysts to be subjected to high-throughput screening was aligned in accordance to the high-throughput experimental planning strategies as categorised by R. Potyrailo, which includes a hierarchical development of the experiment starting out from a broad base with an increased and more detailed focus as the area of interest narrows [26]. The finding of our previous work, i.e. that a Pt_3Pd_2 combination annealed at 800°C exhibited competing performance, was employed as a guideline

for the development of a possible ternary anode composition that includes a base metal. To this regard, ternary compositions were mainly focused, but not limited to, that area where Pt is less than 60 %, Pd less than 40 % (i.e. Pt_3Pd_2) and random Al content. Al, however, could not be increased above 60 % as (1) Al deposits at a much lower rate in contrast to Pt and Pd resulting in very long deposition times, while operating the PVD apparatus at its limit, (2) Al is not very resistant in strong acidic environments with degradation being almost immediate in sulphuric acid and (3) a report found in literature, on Pt and Al combinations, proved that only small amounts of Al is effective in improving catalytic performance [23]. Linear polarisation response of the various compositions were obtained through high-throughput parallel screening, which is a simple means of quickly identifying an active composition that may work well in the SDE environment. The average of the polarisation graphs (conducted in triplicate) were used to determine the onset potential for each ratio employing the method reported by Cooper and McGinn with the current density based on (a) geometric area [20, 25, 27] and (b) mass Pt present in the thin film.

Before and immediately, subsequent to electrochemical testing each of the catalyst pads were visually evaluated for signs of corrosion. Some of the compositions did corrode during electrochemical testing (Fig. 3), which was also observed by Cooper and McGinn for their Pt-Ru-W thin film anode catalysts for direct methanol fuel cells [25].

In the event that the greatest portion of the pad revealed corrosion, it was not included in the results, as it would in essence be the gold circuit that participated in the electro-oxidative reaction. Gold shows a high onset potential for SO_2 electro-oxidation, hence obtaining low onset potentials eliminated the possible interference of gold. Onset potential, as a means of evaluating catalyst activity, is a suitable measure in the event of possible corrosion as it is not influenced by any change in surface roughness [25]. As only some catalyst pads revealed severe signs of corrosion, which were subsequently eliminated, current density based on geometric area and mass of Pt present in the thin film were also employed to evaluate thin film combinations. Current density, in contrast to onset potential, is influenced by both surface roughness and composition and by applying both these parameters to identify thin

film candidates during the screening phase, limited any systematic errors made. Screening of the various thin film combinations, for the electro-oxidation of SO_2 , are summarised in Fig. 4 as ternary contour plots in terms of (a) onset potential (V), (b) current density ($\text{mA}\cdot\text{cm}^{-2}$) and (c) mass-specific current density ($\text{mA}\cdot\mu\text{g Pt}^{-1}$). Employing these criteria, eight thin film compositions, three based on lowest onset potential value, three based on highest geometric current density (normalised by geometric area) and two based on highest mass-specific current density (normalised by Pt mass), were selected for additional testing employing conventional testing techniques with glassy carbon inserts as substrate.

Composition of the thin films prior to conventional electrochemical testing

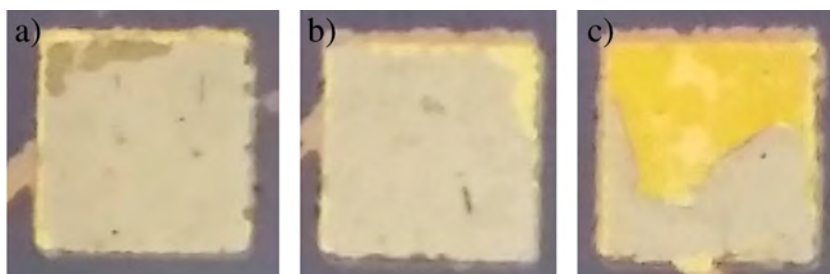
The bulk stoichiometry of the eight best electrocatalysts was investigated in triplicate by EDX, both before and after annealing. EDX analysis revealed that the expected theoretical compositions, predicted by employing the built-in QCM, correlate well with the actual sputtered bulk stoichiometry (Fig. 5). No difference between as-deposited thin films and their corresponding annealed states were observed.

Conventional electrochemical evaluation

Linear polarisation and subsequent EDX characterisation

Employing physical vapour deposition and high-throughput screening accelerates the complex process of new catalyst design and improves performance identification. However, it is not sufficiently suited for in-depth investigation and characterisation, and conventional methods, such as rotating disk electrode (RDE) linear polarisation, are more suitable. Hence, Fig. 6 exhibits the electrocatalytic performance of the eight selected thin films (in the as-deposited (AD) and annealed state (on glassy carbon as substrate)) that did not show signs of corrosion (mainly in the form of delamination) during/after electrochemical testing. (I)-700 °C, referring to Pt, and previously identified (J)-800 °C, referring to Pt_3Pd_2 , are taken as the baseline to which all ternary combinations are compared against. In general, it is evident that no significant

Fig. 3 Examples of varying degrees of corrosion occurring after linear polarisation for (a) $\text{Pt}_{34}\text{Pd}_{22}\text{Al}_{44}$, (b) $\text{Pt}_{43}\text{Pd}_{46}\text{Al}_{11}$, and (c) Al



improvement in onset potential was achieved, with the majority of electrocatalysts exhibiting similar onset potentials (within error), when compared to (I)-700 °C and (J)-800 °C. However, (E)-AD, 700 °C, 800 °C and (D)-AD performed well. As the results obtained from onset potential are not sufficient for identifying an alternative electrocatalyst, mass-specific current density was also investigated. From Fig. 6, it is evident that the majority of the ternary electrocatalysts exhibits an increase in current density. Compared to the baseline, i.e. Pt and Pt₃Pd₂, Pt₄₀Pd₅₇Al₃ (annealed at 900 °C) performed the best in that current density (mA.mg Pt⁻¹) increased from 108.11 to 181.21 and finally to 396.73 for Pt, Pt₃Pd₂ and Pt₄₀Pd₅₇Al₃, respectively, indicating an increase in activity that correlates with a decrease in Pt content (Fig. 7).

Subsequent to electrochemical testing (Fig. 6) the thin film electrocatalysts were analysed by EDX so as to evaluate any change in composition that could not be visually detected (an indication of short term stability). Overall, all the catalysts exhibit a slight change in compositional ratio with no specific trend (Fig. 8), when compared to the compositional ratios directly after sputtering (Fig. 5), with (B)-AD, (F)-AD, (H)-600 °C and (H)-700 °C showing the largest deviation in compositional ratio. This is however not sufficient in identifying a stable electrocatalyst, and additional evaluation on the stability is required. In an attempt to identify a stable electrocatalyst, in conjunction with having a low onset potential and acceptable current output, consecutive cycling in a sulphuric acid environment was conducted (Fig. 9). For all the

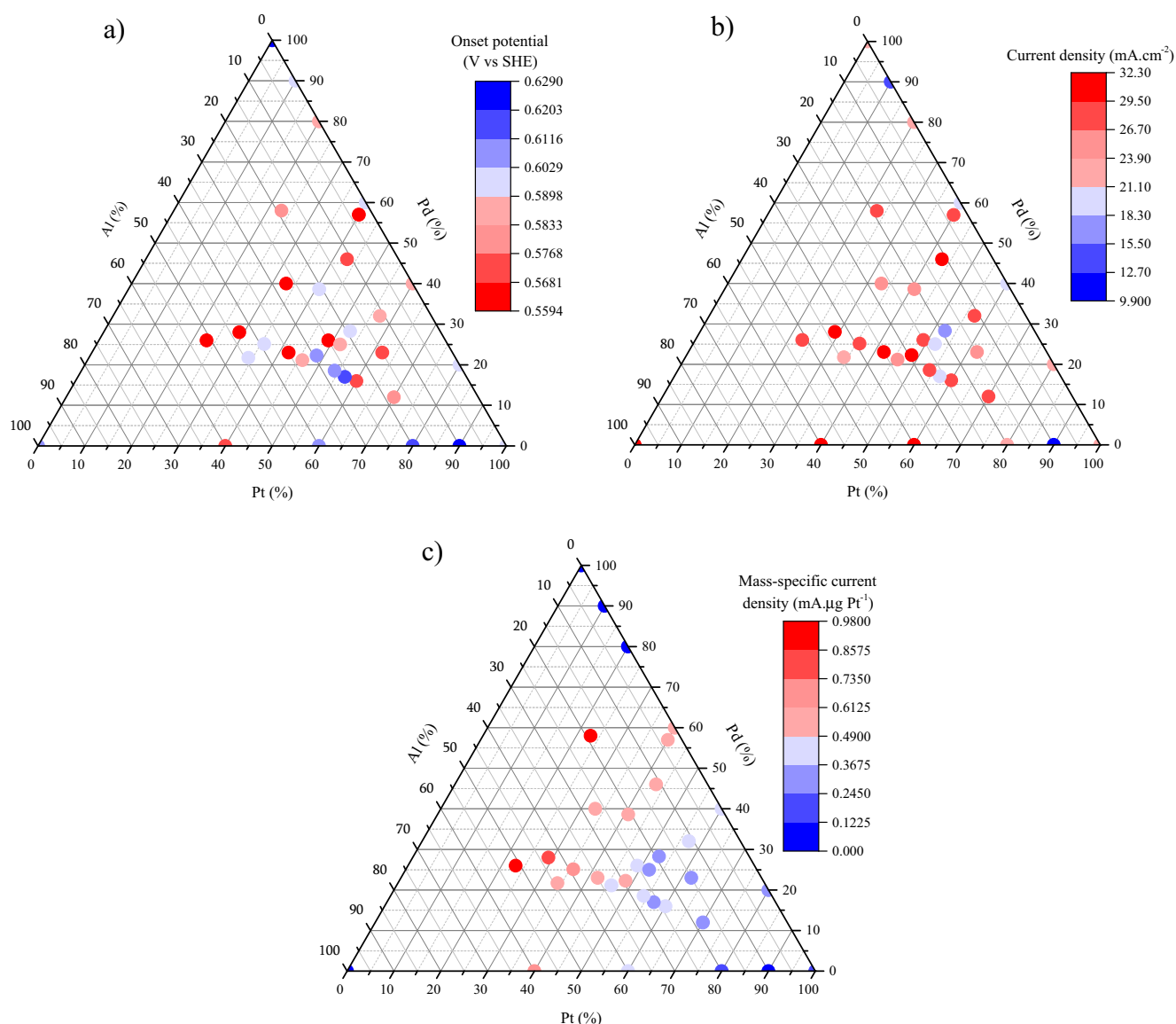


Fig. 4 Ternary contour plots for (a) onset potential, (b) current density normalised by geometric area and (c) mass-specific normalised current density, towards SO₂ electro-oxidation for the Pt_xPd_yAl_z system

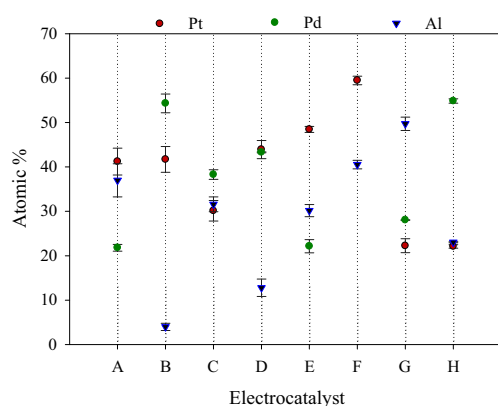


Fig. 5 EDX after sputtering verifying that the actual sputtered ratios correlate with the expected sputtered ratios of (A)-Pt₄₂Pd₂₃Al₃₅, (B)-Pt₄₀Pd₅₇Al₃, (C)-Pt₃₃Pd₄₀Al₂₇, (D)-Pt₄₃Pd₄₆Al₁₁, (E)-Pt₄₈Pd₂₃Al₂₉, (F)-Pt₆₀Al₄₀, (G)-Pt₂₃Pd₂₆Al₅₁, and (H)-Pt₂₃Pd₅₈Al₁₉

electrocatalysts under investigation, the only electrocatalyst that exhibited improved stability, compared to (I)-700 °C

and (J)-800 °C, was (B)-900 °C, lasting about 1.4 times longer. Taking all three parameters (onset potential, mass-specific activity, and stability) into consideration that are indicative of an improved electrocatalyst, (B)-900 °C can therefore be considered the ternary candidate exhibiting the most potential in competing with (I)-700 °C and (J)-800 °C.

To put (B)-900 °C further to the test, it was subsequently evaluated under an increased electrolyte temperature of 60 °C (using a SCE reference electrode above this temperature is not advised, due to the instability of Hg₂Cl₂) with the results also being depicted in Figs. 6 and 9. At this elevated temperature the same phenomena was observed for (B)-900 °C, (I)-700 °C and (J)-800 °C as in the case of 25 °C, with no significant difference in onset potential having been observed. However, an improved performance was evident in terms of current output and durability. The (B)-900 °C thin film (at 25 °C) furthermore exhibited totally different behaviour in terms of visible signs of corrosion when compared to all the other tested electrocatalysts. This was evident in that the (B)-900 °C

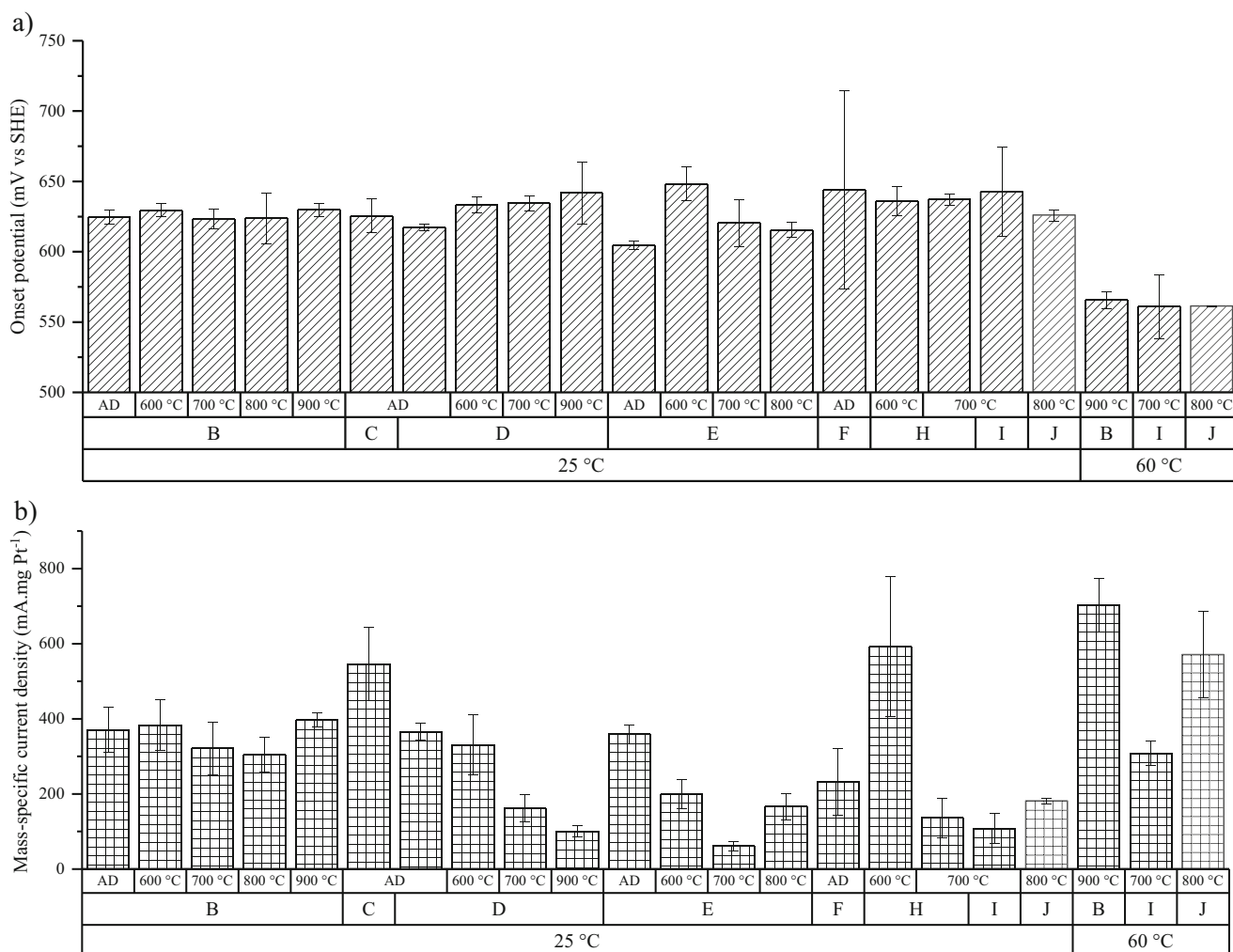
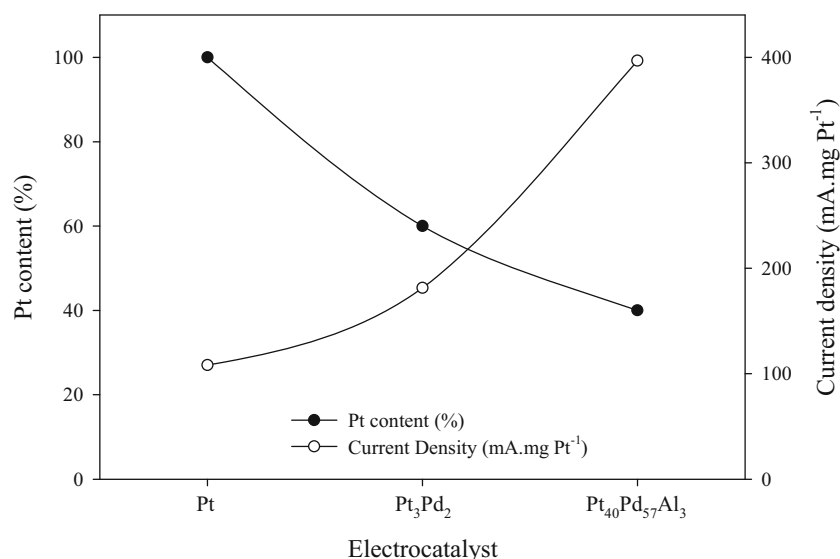


Fig. 6 Onset potential values (a) and mass-specific current density values (b) for (B)-Pt₄₀Pd₅₇Al₃, (C)-Pt₃₃Pd₄₀Al₂₇, (D)-Pt₄₃Pd₄₆Al₁₁, (E)-Pt₄₈Pd₂₃Al₂₉, (F)-Pt₆₀Al₄₀, (H)-Pt₂₃Pd₅₈Al₁₉, (I)-Pt, and (J)-Pt₃Pd₂

Fig. 7 Correlation of current density (mA.mg Pt^{-1}) with Pt content (%)



thin film (at 25 °C) dissolved gradually into solution (visually monitored until the film was so thin, that glassy carbon started to appear), keeping its active surface (Fig. 10a) as only the thin film thickness decreased, while all the other electrocatalysts, including the target electrocatalysts [21], clearly delaminated. (B)-900 °C (at 60 °C), in contrast, only started to exhibit the normal signs of delamination nearer to the end of its stability lifetime, with the last cycle subsequently being lower in the hydrogen adsorption/desorption region than the first cycle (Fig. 10b), as a part of the thin film delaminated from the surface.

Further characterisation and discussion

AFM and XPS analysis were conducted on the most promising binary [21] and ternary thin film electrocatalysts in competing with pure Pt for SO_2 electro-oxidation, with the aim being to gain more insight into the physical and electronic properties of these thin films. Pt thin films (as-deposited and the best performing annealed form) were also included in these analyses, serving as the primary reference/target electrocatalyst.

AFM analysis

AFM allows, among other things, meticulous observation and evaluation of the morphological and topographical characteristics of thin film surfaces. Three-dimensional (3D) AFM scans were recorded over a substrate area of $2 \times 2 \mu\text{m}$, for each sample, at three different locations on the thin film. Roughness parameters were calculated from two different positions within each of the three individual locations so as to provide reliable average roughness values representative of the whole thin film surface. From the 2D and 3D AFM images shown in Table 1, it is clear that the thin films in the as-

deposited form all exhibit a fine distribution of metal particles, adapting the profile of the underlying glassy carbon surface, with unavoidable grooves clearly visible resulting from polishing. Upon annealing, the as-deposited thin films evolved from exhibiting a finely distributed appearance to clearly exhibiting different degrees of crystal formation with the least amount of change being visible for (I)-700 °C. (J)-800 °C transformed into a surface with clearly defined grain boundaries, evident of a polycrystalline nature [21]. (B)-900 °C exhibited crystal growth of a totally different nature when compared to (J)-800 °C, with a type of random agglomerated distribution of small ‘sheets’ of crystals varying in orientation with sharp corners emerging from the surface. It is remarkable how only ~3 % Al metal content can induce such

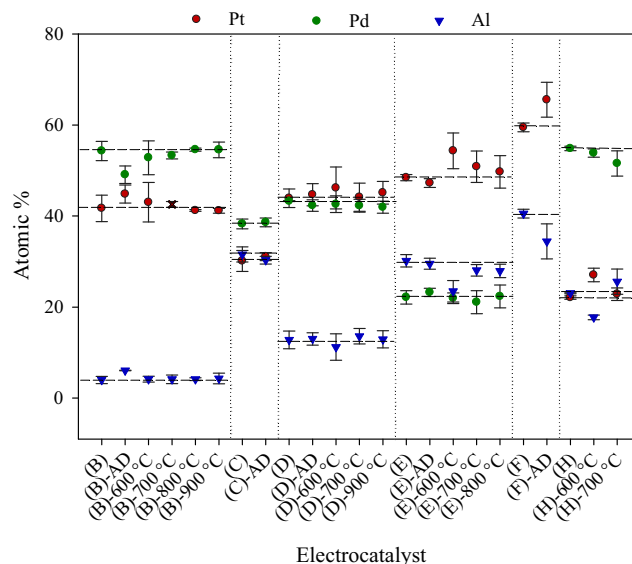


Fig. 8 EDX analysis subsequent to LP runs for (B)-Pt₄₀Pd₅₇Al₃, (C)-Pt₃₃Pd₄₀Al₂₇, (D)-Pt₄₃Pd₄₆Al₁₁, (E)-Pt₄₈Pd₂₃Al₂₉, (F)-Pt₆₀Al₄₀, and (H)-Pt₂₃Pd₅₈Al₁₉

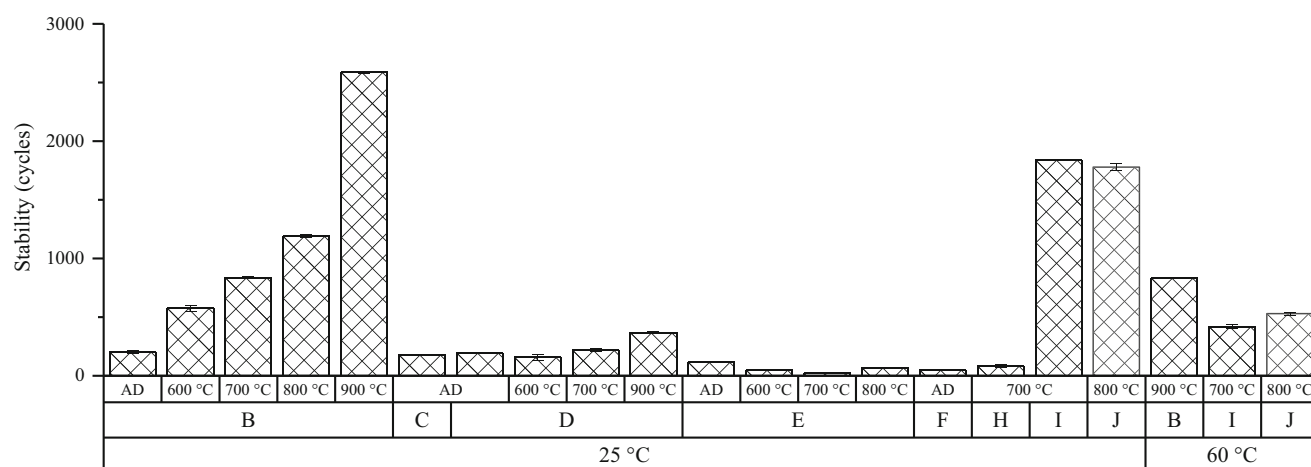


Fig. 9 Consecutive cycling of thin film electrocatalyst for stability evaluation with (B)-Pt₄₀Pd₅₇Al₃, (C)-Pt₃₃Pd₄₀Al₂₇, (D)-Pt₄₃Pd₄₆Al₁₁, (E)-Pt₄₈Pd₂₃Al₂₉, (F)-Pt₆₀Al₄₀, (H)-Pt₂₃Pd₅₈Al₁₉, (I)-Pt, and (J)-Pt₃Pd₂.

Conditions: scan rate of 100 mV.s⁻¹ and potential window of 0.041 V vs SHE to 1.441 V vs SHE at 25 °C and 60 °C

an extreme difference in surface/bulk structure upon annealing. This type of crystal growth might be one of the reasons for observing a prominent improvement in catalyst performance for (B)-900 °C, especially the stability performance observed for this electrocatalyst in a sulphuric acid environment for both 25 °C and 60 °C (Fig. 9), when compared to (I)-700 °C and (J)-800 °C.

In addition to 2D and 3D imaging, the following surface roughness profile parameters (Fig. 11) were acquired: (1) average roughness (R_a), which is based on mean height roughness, (2) vertical distance between the highest and lowest points (R_t), and (3) root mean square (RMS) of the distribution of surface height making it a bit more sensitive than R_a [28].

In general, as is evident from Fig. 11, (I)-700 °C and (J)-800 °C exhibited similar values for all the roughness parameters with (B)-AD showing a smoother surface (lower values) overall. As for the different annealed forms of the individual thin films, the roughness parameters all increased from the as-deposited state to the specific annealed form, with (B)-900 °C

being the most influenced by annealing treatment and also exhibiting totally different crystal growth compared to (I)-700 °C and (J)-800 °C (Table 1 2D). Overall, (B)-900 °C exhibited the highest roughness values for all three roughness parameters acquired, which has a direct and positive effect on the higher current output observed when compared to (I)-700 °C and (J)-800 °C. The rapid thermal annealing of catalyst (B)-900 °C has a positive influence on the performance and stability of this catalyst towards SO₂ electro-oxidation in a sulphuric acid environment.

XPS

In an attempt to further elucidate the observed electrocatalytic performance of the most promising binary [21] and ternary thin film electrocatalysts, in competing with pure Pt for SO₂ electro-oxidation, XPS surface analysis and depth profiling on the thin film samples were conducted so as to gain information

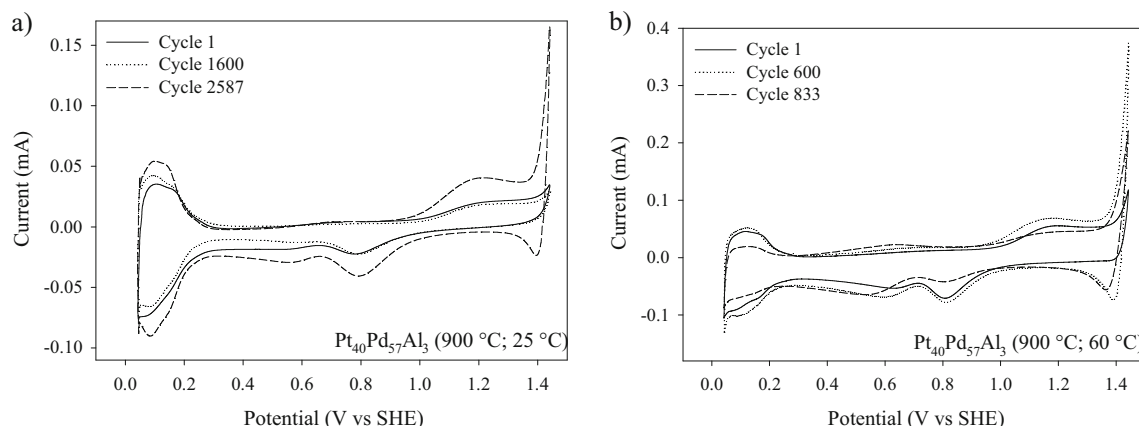
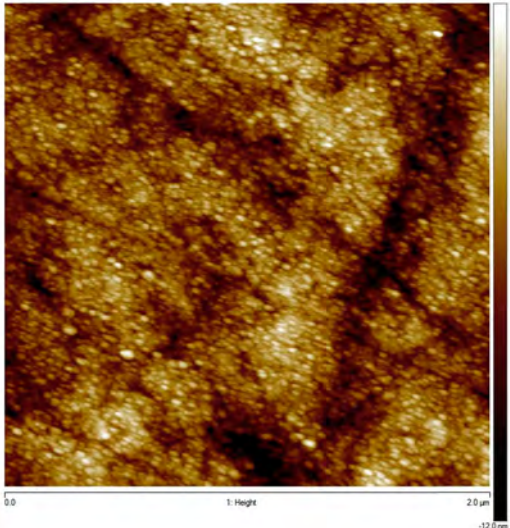
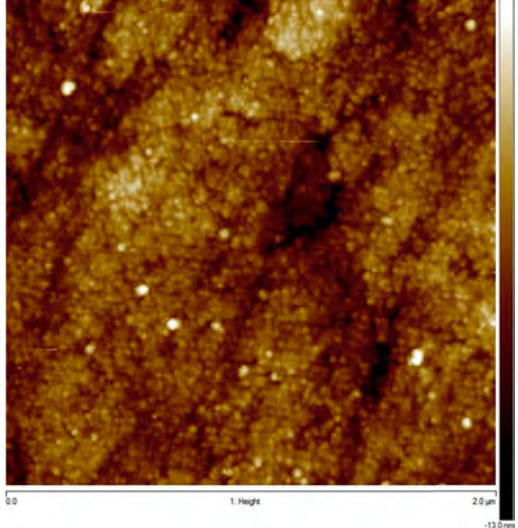
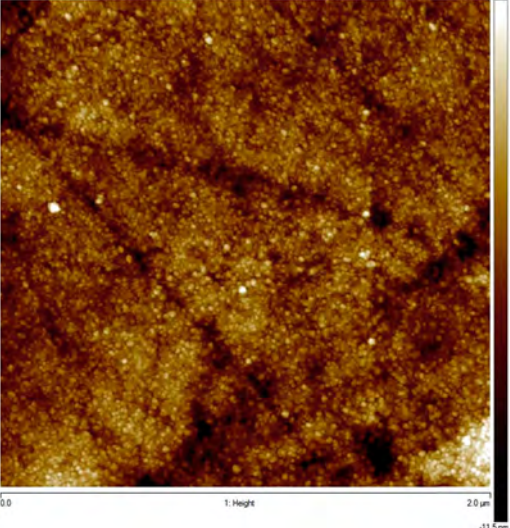
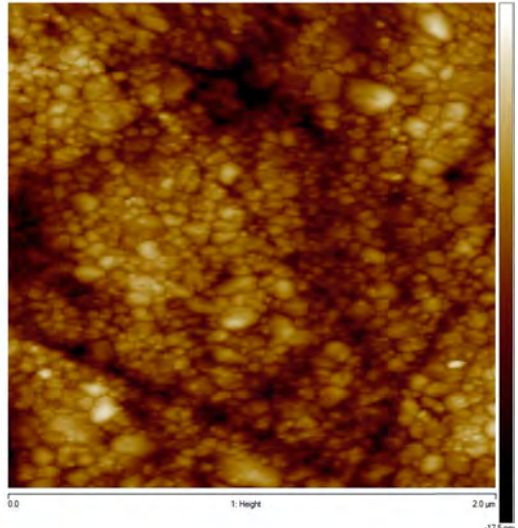
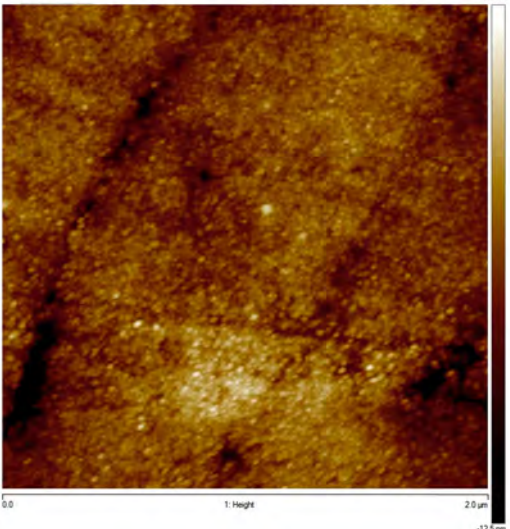
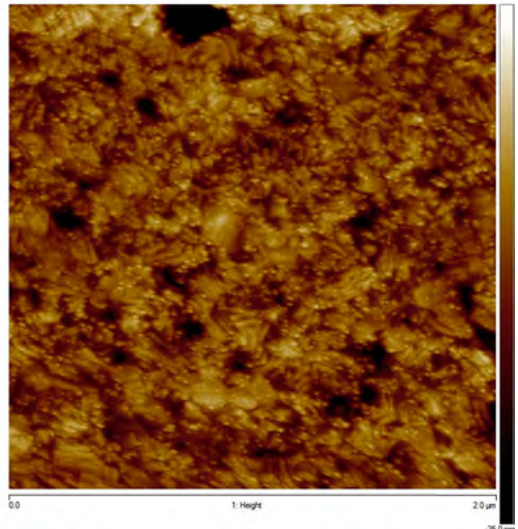
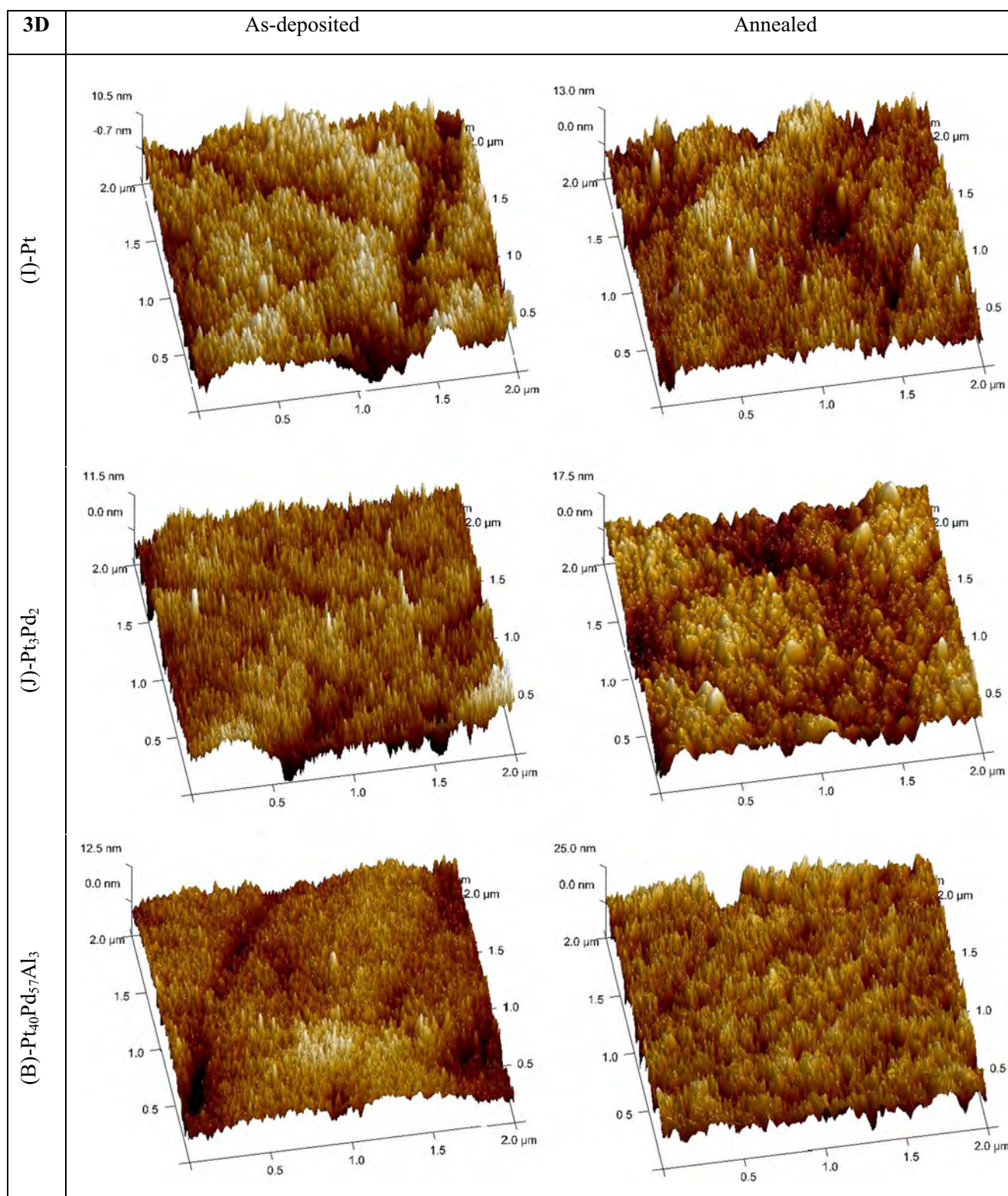


Fig. 10 Consecutive cycling of (B)-Pt₄₀Pd₅₇Al₃ annealed at 900 °C in H₂SO₄ at (a) 25 °C, and (b) 60 °C

Table 1 2D and 3D AFM images for electrocatalysts (I)-Pt (700 °C), (J)-Pt₃Pd₂ (800 °C), and (B)-Pt₄₀Pd₅₇Al₃ (900 °C)

2D	As-deposited	Annealed
(I)-Pt		
(J)-Pt ₃ Pd ₂		
(B)-Pt ₄₀ Pd ₅₇ Al ₃		



regarding their composition and chemical environment. Knowing the overlapping that occurs between Pd3p3-O1s and Al2p-Pt4f peaks, high-resolution spectra were collected to ensure that the best fitted quantified results are obtained,

especially for materials J and B (cf. Electronic Supplementary Information (ESI) Figs. S1 and S2 for fitted XPS spectra after 10s Ar⁺ etching for (B)-AD and (B)-900 °C). The fits were conducted subsequent to linear background subtraction using

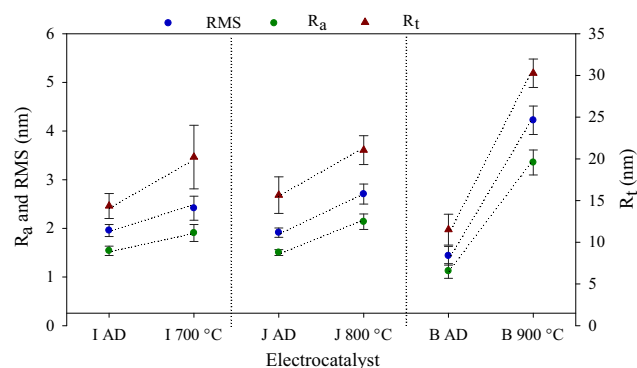


Fig. 11 Surface roughness profile parameters of (I)- Pt as-deposited (I AD) and annealed at 700 °C, (J)- Pt₃Pd₂ as-deposited (J AD) and annealed at 800 °C, and (B)- Pt₄₀Pd₅₇Al₃ as-deposited (B AD) and annealed at 900 °C

a product of Gaussian and Lorentzian functions, as defined in the Advantage software. Figure 12 reveals comparative information for the AD and annealed states with regard to the extreme surface (top outer layer) of the thin films for Pt_{4f}, Pd_{3d} and Al_{2s}. Figure 13 exhibits compositional information (derived from the C1s, O1s, Pt_{4f}_{7/2}, Pd_{3d}_{3/2} and Al_{2s} peak areas), related to the depth of the metallic Pt and Pt-based thin films deposited on glassy carbon as substrate. It must be kept in mind that (1) XPS remains a semi-quantitative analysis to follow atomic compositional change with depth (not to be directly correlated with previous EDX results), and (2) XPS has an accuracy within 5 to 10 % of absolute atomic % compositional information [29].

In the as-deposited state, no shift in the Pt_{4f}_{7/2} peak at ~71.15 eV was observed for (I), (J) and (B), which is a direct indication that no significant change in the chemical environment occurred during/as a result of physical vapour deposition. Upon annealing, again no shift in the Pt_{4f}_{7/2} binding energy was observed for (I)-700 °C and (J)-800 °C, however a clear change was observed for (B)-900 °C, exhibiting a slight negative shift in the Pt_{4f}_{7/2} (Fig. 12d) and Pd_{3d}_{5/2} peaks (Fig. 12e), which could possibly be ascribed to the occurrence of metal-metal interactions as a result of annealing temperature [30]. In addition, (B)-900 °C (Fig. 12f) exhibited an increase in Al content at the surface (15 at. %) when compared to (B)-AD (only 2 at. %), which is expected if explained in terms of fundamental properties of monometallic metals (atomic radius) [31]. For the metals present in (B)-900 °C, the order of decreasing size with regard to atomic radii is Al (143 pm) > Pt (139 pm) > Pd (137 pm) [32]. In general, lattice strain is expected to contribute to the segregation/migration of the atom with the largest atomic radius to the surface, which in the case of (B)-900 °C is Al. This supports the observation obtained from XPS data that Al_{2s} mainly appears on the extreme surface subsequent to annealing (Fig. 12f), which clearly points towards the migration of Al to the surface upon annealing.

While the previous XPS measurements (Fig. 12) focused on the surface, depth profiles of the Pt and Pt-based samples (Fig. 13) were obtained by combining a sequence of Ar⁺ ion gun etch cycles with XPS measurements from the current exposed surface. The objective of obtaining depth profiles was to validate that the observed electrocatalytic performance was not as a result of a ‘skin’ formed, as a result of severe segregation/migration to the surface, but rather being the result of a homogeneous composition throughout the depth of the thin film. The first observation for all the electrocatalysts, in both the as-deposited and annealed states, is (1) the presence of unescapable C, N, Si and Cl impurities, due to ambient pollution on the metal surface layer, disappearing after only 10 s of Ar⁺ etching and (2) a constant ~55 nm thin metallic layer (validating the calibrated sputtered layer of ~60 nm) recorded by XPS etching for all the analysed thin films. Subsequent to Ar⁺ etching through the thin metallic film, it is clear that at a depth of ~40 nm carbon from the substrate appears. Carbon, however, is present almost throughout the depth of the annealed surfaces (especially sample (B)-900 °C), which can be explained either by possible diffusion of the substrate through the Pt/Pd/Al thin film at high temperature (which is unlikely as these specific glassy carbon inserts are stable under high temperatures) or as a result of XPS detecting possible ‘exposed’ substrate carbon as a result of the roughness of the (B)-900 °C thin film (*R_t* around 30 nm, Fig. 11). It is furthermore evident that contractions of the different sputtered layers occur upon annealing with increased contraction as the temperature increases.

For (B), Al seems to be in the oxidised state throughout the entire thickness of the layer (118.5 eV binding energy Fig. 12f, only data for the top layer is shown). As Al gets oxidised easily in air, it is very probable that the samples were oxidised from the moment when the thin films were exposed to air. In addition, XPS depth profiling for (B)-900 °C supports the previous observation (Fig. 12f) of a degree of migration of Al towards the surface after annealing and that all three metals are present throughout the depth of the thin film. Concerning Pd_{3d}_{5/2} peak fitting (cf. EIS Figure S1 and S2), the absence of PdO bonding usually located at 337 eV is confirmed [33] as the maximum component is Pd metal at around 335 eV, while another 1 eV higher (~336 eV) could be attributed to Pd-O-X bonding namely Pd-O-Al.

As thin film (B), i.e. Pt₄₀Pd₅₇Al₃, presented itself as being a competitive electrocatalyst for SO₂ electro-oxidation, measured against Pt and the previously identified Pt₃Pd₂ composition, XRD spectra were furthermore recorded for (B)-AD and (B)-900 °C (cf. ESI Fig. S3). (B)-AD is concluded to consist of a PtPd cubic phase, whereas (B)-900 °C consist of a possible Pt_{2.84}Al_{1.16} cubic phase that may support the slight negative shift observed for the Pt_{4f}_{7/2} (Fig. 12d) and Pd_{3d}_{5/2} peaks (Fig. 12e), which are indicative of alloy formation.

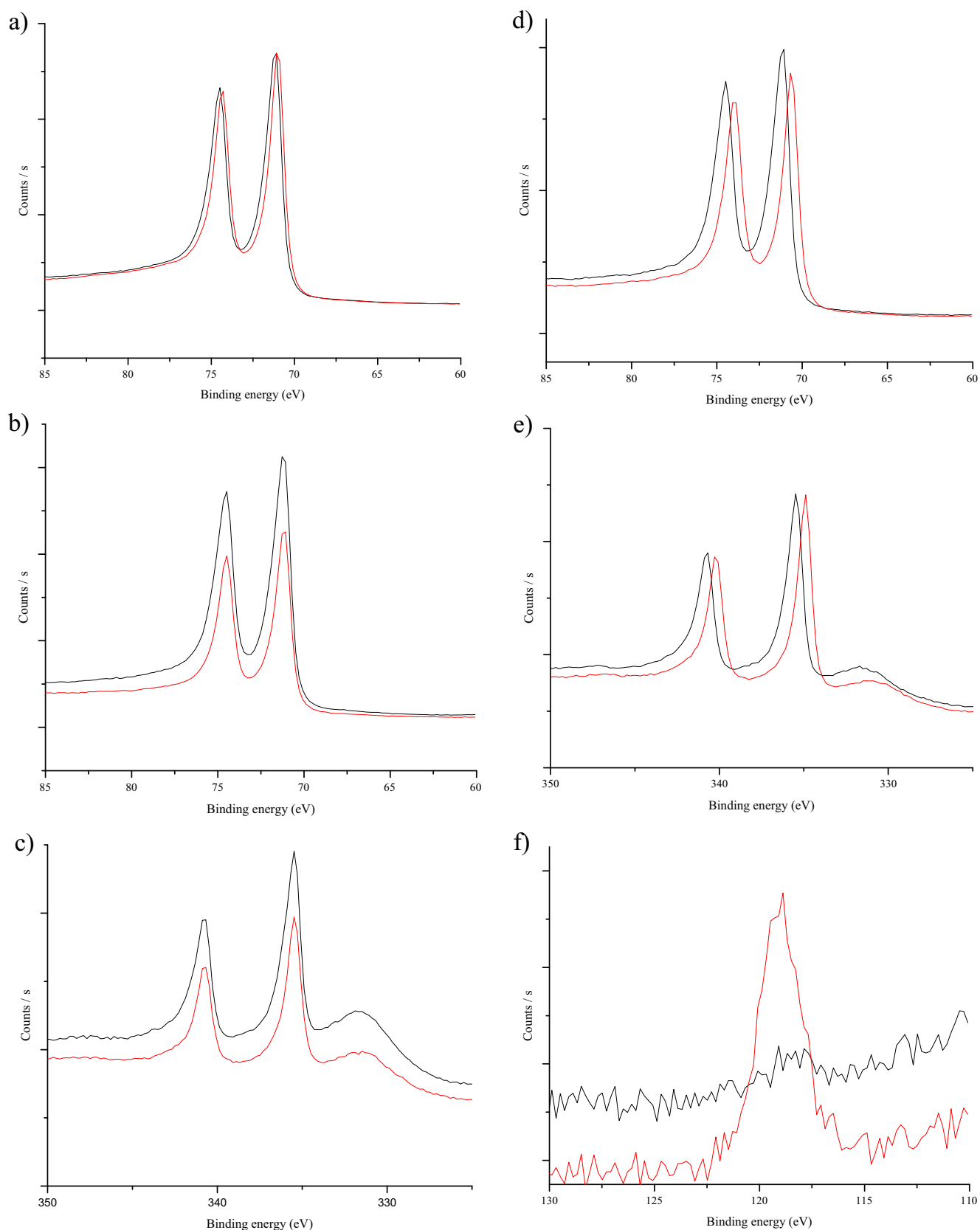


Fig. 12 Pt4f, Pd3d and Al2s XPS spectra on the extreme surface, i.e. the top outer layer, of both the as-deposited (AD) (black curve) and annealed states (red curve) of (I)-Pt (a), (J)-Pt₃Pd₂, (b, c) and (B)-Pt₄₀Pd₅₇Al₃ (d, e, f)

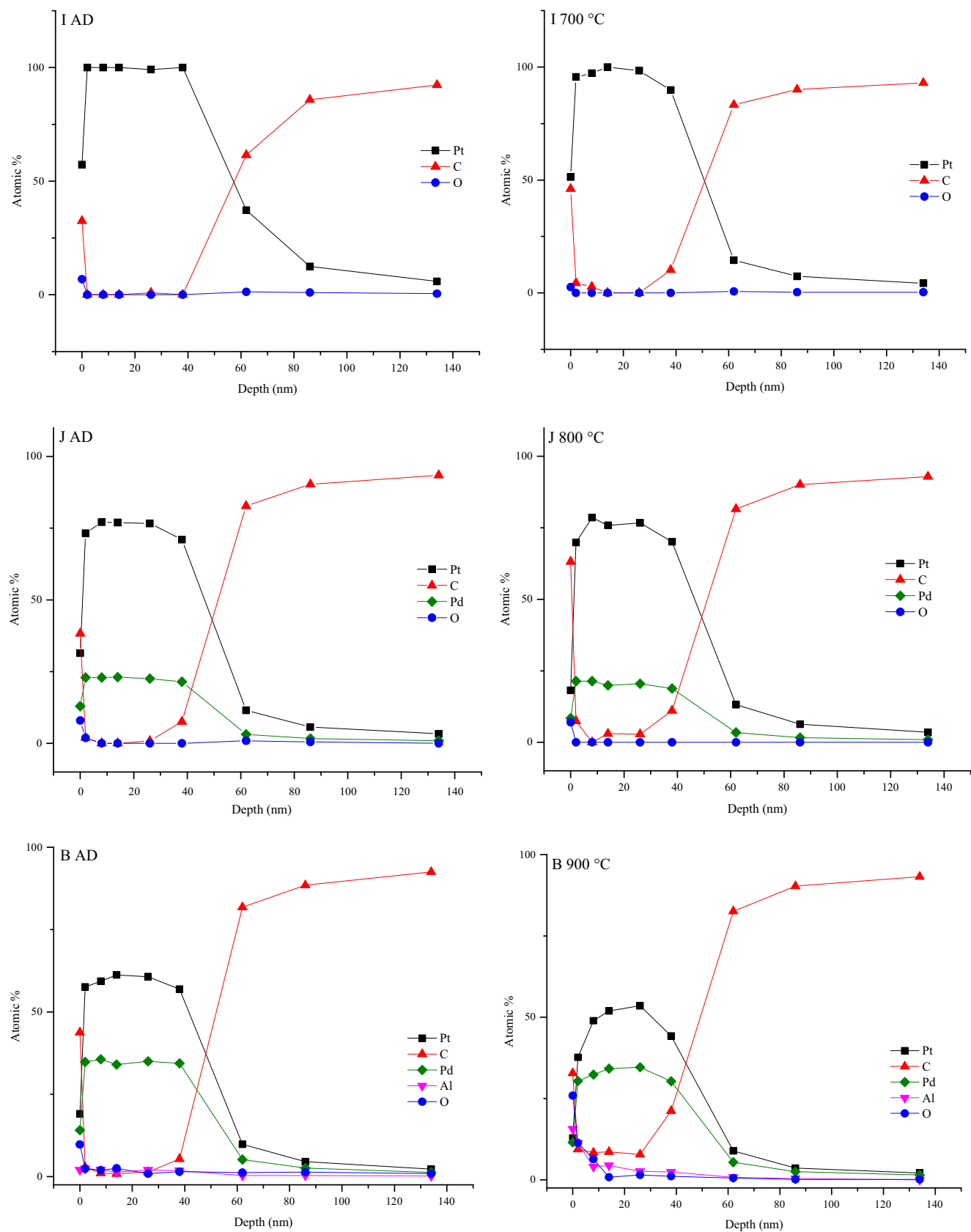


Fig. 13 Depth profiles of (I)-Pt, (J)-Pt₃Pd₂ and (B)-Pt₄₀Pd₅₇Al₃, for both the as-deposited (AD) and annealed states. The etch-rate was 0.2 nm/s on each material

Conclusion

As is evident from literature, only a limited number of surfaces have been investigated thus far for catalysing the electro-oxidation of aqueous SO_2 . It is furthermore clear that widespread disagreement and non-reproducible behaviour exist [24], as this reaction is very sensitive and highly influenced by the prevailing conditions (electrode material, pH, temperature, preconditioning, pressure, applied anodic potential, etc.). The mechanism of SO_2 electro-oxidation is highly contested and proposed mechanisms mainly include (a) indirect oxidation via a dithionate intermediate [34–36] or involving bulk SO_2 together with an unspecified S(VI) intermediate [37], and (b) direct oxidation via an adsorbed reactant [35]. The sensitivity of this reaction to the electrocatalytic surface, combined with the mechanistic complexity of this reaction [38], requires that the performance of a specific active electrocatalyst of interest will be better understood through an in-depth and detailed mechanistic investigation, that takes into account various factors such as temperature, acid concentration, sulphur coverage, etc. The majority of mechanistic studies on SO_2 oxidation, however, were mainly conducted on platinum and single component electrode materials. The extensive effort devoted to understanding the mechanism by which SO_2 is electro-oxidised by Pt substantiates the fact that the necessary mechanistic characterisation of any identified multi-component electrocatalyst, e.g., $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$, is bound to be challenging and will require meticulous and repeatable evidence so as to be fundamentally sound.

From our investigation, identifying a possible alternative anode catalyst that can compete with pure Pt, it is clear that a lot of scope and room for improvement still exist for improving the catalytic activity and stability of the electrocatalyst. In general, it is primarily the surface properties of a catalyst in conjunction with the secondary bulk effects, which are credited for any observed catalytic improvements/weakening. We have highlighted the influence that a secondary/tertiary metal, in conjunction with annealing, can have on the catalytic performance of the thin film by effecting only slight changes in composition and temperature treatment.

The addition of a third component to the noble metals Pt and Pd, in the form of Al, i.e. $\text{Pt}_x\text{Pd}_y\text{Al}_z$, enhanced the electrocatalytic performance towards the electro-oxidation of aqueous SO_2 with the Al content kept below ~3 %. In excess of ~3 % Al the electrocatalytic performance was severely hampered. Overall onset potential, however, did not improve significantly for any of the evaluated electrocatalysts, while improvements in current output and stability (lasting ~1.4 times longer than both pure Pt (the (I)-700 °C sample) and Pt_3Pd_2 (the (J)-800 °C sample)) was achieved specifically for $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ (the (B)-900 °C sample), both in 25 °C and 60 °C testing environments. We have shown that electrocatalytic activity for the electro-oxidation of aqueous SO_2 can be

achieved by substantially lowering the Pt content in that current density (mA.mg Pt^{-1}) increased from 108.11 to 181.21 and finally to 396.73 for Pt, Pt_3Pd_2 and $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$, respectively, indicating an increase in activity that correlates with a decrease in Pt content.

Furthermore, additional information obtained from XPS analysis has shown that $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ ((B)-900 °C) exhibited an increase in Al content at the surface (~15 at. %) when compared to (B)-AD (only ~2 at. %) although no sign of a distinctive skin of one metal (or more in the case of $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$) was present near the surface for the Pt_3Pd_2 and $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ thin films (as-deposited and annealed). This confirmed that the observed activity of the thin films was a result of all the metals being present in the thin film surface. XRD analysis of the annealed $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ thin film ((B)-900 °C) has highlighted the presence of some degree of alloy formation.

The power of alternately employing combinatorial and high-throughput methods with conventional electrochemical and characterisation methods, for electrocatalysts development, has clearly been shown, and resulted in the identification of a catalyst that contains a lot less platinum while exhibiting increased catalytic activity and stability.

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