

On the contamination of membrane-electrode assemblies of water electrolyzers based on proton exchange membrane in the course of operation

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The issues of contamination of membrane-electrode assemblies (MEAs) of water electrolyzers based on proton exchange membrane (PEM) currently pose a subject for investigation. The analysis of structure and chemical composition of the MEA after its long-term testing shows, that the ions and/or the clusters of several contaminating elements (Ti, Pt, Ir, Fe, Ni, Cr, Si), originated from the constructional materials of MEA, electrolysis stack and external piping, are accumulated in the membrane and electrocatalytic layers. Quantitatively, the most predominant contaminating element is Ti (up to 12 wt. %). The cathode area (cathode active layer and membrane band adjacent to them) is extremely exposed to the contaminant's deposit.

Keywords: water electrolysis, proton exchange membrane, membrane-electrode assembly, electrocatalytic layer, contamination, impurity

INTRODUCTION

Pure aluminum and its low doped The aspects of stability of performances of PEM water electrolyzers have been actively studied [1-8] over the last years. In particular, investigations have been performed to study the dissolution, migration and aggregation of the catalytic nanoparticles inside the active layer [4-6], the thermo-oxidative degradation of PEM [7-8] and other factors which negatively affected on the performances and operating life of the electrolyser.

This study covers issues of MEA contamination by various impurities (Ti, Pt, Ir, Fe, Ni, Cr, Si) originated from the constructional materials of MEA, electrolysis stack and external piping. The control MEA was exposed to stability tests, and after that, its structure and chemical composition was studied using an energy-dispersive X-ray spectroscopy (EDX), transmission and scanning electron microscopy (TEM and SEM) in order to define contaminating impurities.

EXPERIMENTAL

The MEA fabrication and testing

The MEA with 25 cm² active surface area was assembled using Nafion® 117 membrane (EI. DuPont de Nemours Co., USA) and current collectors/gas diffusion electrodes fabricated from porous sheets based on titanium alloy (TPP-7 grade, 0.95 mm thickness and 37% porosity).

Prior to the MEA assembling, the electrocatalytic layers were fabricated by spraying of the catalytic ink onto the current collectors. The Ir black (1.5 mg/cm²) was synthesized as described in [9] and applied on the anode; 40 wt. % of Pt on Vulcan XC-72 (1.0 mg/cm² of total loading) was synthesized according to [10] and used on the cathode. 5 and 15 wt. % of D521 Nafion® polymer dispersion (EI. DuPont de Nemours Co., USA) were added to the anodic and cathodic electrocatalytic ink, respectively.

After preparation, the MEA was clamped in a lab-made thermally controlled electrolysis cell (figure 1). Both the cell holder and the flow-field plates were manufactured from titanium alloy (VT1-0 grade). External separators of hydrogen and oxygen were made of chemical glass; silicone tubes were used as a connecting piping. The anode was supplied with the bidistilled water additionally treated by the ion-exchange filter.

The control MEA underwent the stability test at 60°C and atmospheric pressure of gases. The electrolysis system operated in average for 6 hours every day. Then, prior to switching off for the night or weekend, the control measurement of current-voltage performances was implemented. The calculation of the operational time of MEA considered only its alive time (the idle time was not taken into account). Water changes were performed

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several times during the stability tests in the cases when water resistance exceeded the value of 18 MOhm*cm.

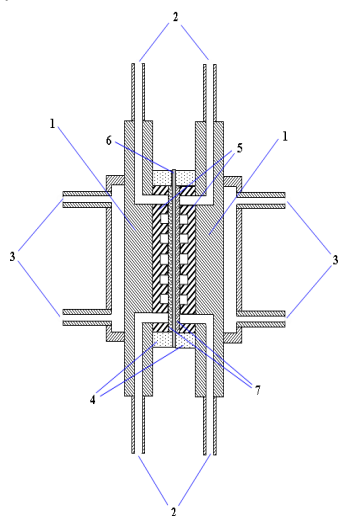


Fig. 1. Schematic diagram of the electrolysis cell. 1 – cell holder; 2 – fittings for reactant/products supply/removal; 3 – fittings for heating/cooling; 4 – sealants; 5 – flow-field plates; 6 – membrane; 7 – current collectors/gas diffusion electrodes with electrocatalytic layers

The electrolysis system operated under the above conditions within 4000 hours with daily measurements of current-voltage performances. Then, the system was shut down, the cell was disassembled, and the MEA structure and the chemical composition were examined.

Analysis of the MEA structure and chemical composition

The structure and chemical composition of the MEA after its long-term testing were investigated using the TEM, SEM and EDX. The MEA was locked using epoxy resin and cross-sliced using an ultramicrotome knife to produce thin (ca. 100-nm) strips.

The TEM and SEM micrographs of MEA cross-slices were obtained using the JEM 1200 EX TEMSCAN (JEOL) and Tescan Vega II LSU microscope (Oxford Instruments), respectively. The elemental analysis was performed using the Inca EDS micro-analysis system (Oxford Instruments).

RESULTS AND DISCUSSIONS

In the course of the stability test, the electrolysis cell voltage monotonously increased with an average rate ca. 35 μ V/hour. After 4000 of running hours of electrolysis system, the experiment was stopped, and the control MEA underwent the above structural and chemical analysis.

The typical TEM micrographs of various areas of MEA cross-slices are shown in figure 2. Numeric symbols in micrographs correspond to positions of performing the EDX resulted in figure 3. The SEM micrographs of MEA cathodic area with the marked positions of execution of the element analysis is shown in figure 4 (lower part). The linear scanning EDX-spectrum of Ti concentration distribution across the MEA thickness in cathodic area is shown in figure 4 (upper part). The chemical composition of the near-cathode membrane area marked by circle in figure 4 is shown in Table 1.

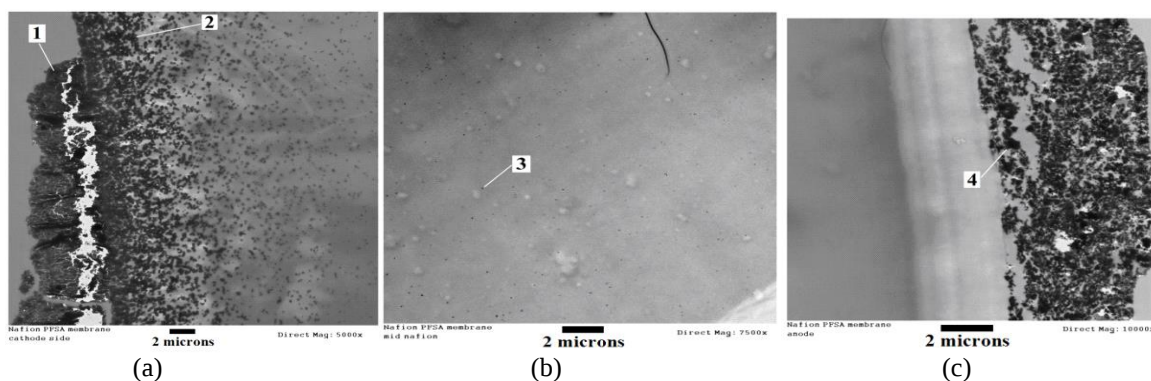


Fig. 2. TEM micrographs of MEA cross-section: (a) cathodic region of MEA, (b) membrane region equidistant from anode and cathode, (c) anodic region of MEA. Numbers in the micrographs correspond to positions of EDX measurements resulted in figure 3.

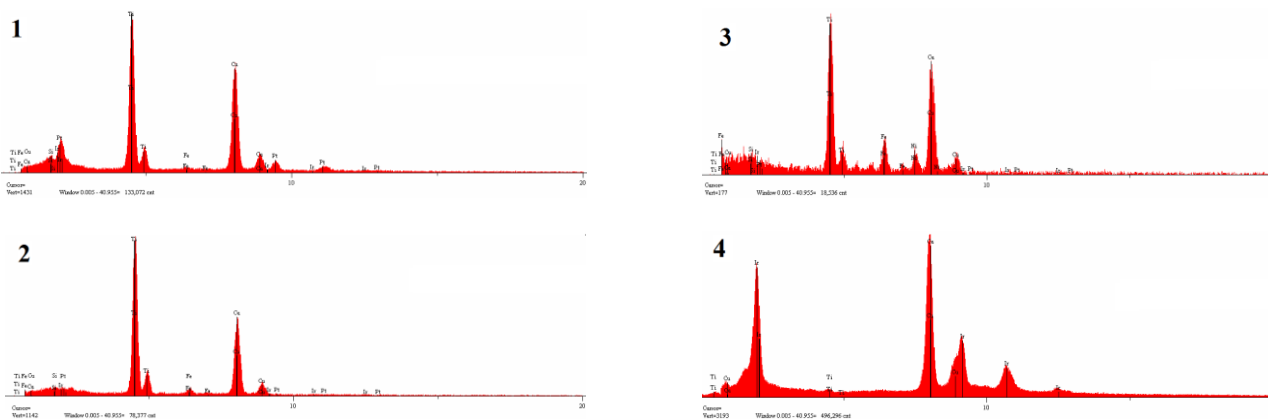


Fig. 3. Results of EDX analyses of electrocatalytic layers and membrane cross-sections. Numbers in spectra correspond to positions of EDX measurements specified in the micrographs provided on figure 2.

Figure 2 shows, that numerous agglomerates of contaminating particles are clearly seen in the near-cathode membrane area (figure 2(a)), whereas the individual impurity particles could only be seen in the membrane area located at the equal distance from the anode and the cathode (figure 2(b)), and no significant impurity inclusions are observed in the near-anode membrane zone (figure 2(c)). The size of the clusters formed by impurities and the density of their distribution decreases with increase of the distance from the cathode. Thus, the analysis of the

micrographs concludes that the cathode is the nucleation zone for impurity clusters in a membrane.

The assumption is that, mainly, the impurity ions transfer in a membrane (and active layers) in the course of water electrolysis is caused by the water flow initiated by the flow of protons and directed from the anode to the cathode. At the same time, as the impurity ions approach to the cathode, their reduction expedites the deposition of particles. The reduction process is most likely caused by interaction of ions with hydrogen and with already partially reduced impurity ions.

Table 1. Results of the element analysis of near-cathode membrane region marked by circle in figure 4

Element	Content, wt. %	Source(s)
C	36.32	Membrane material
O	7.85	
F	22.34	
S	0.79	
Ti	11.96	Current collectors, flow-field plates, cell holder
Cr	3.42	
Fe	5.15	
Ni	3.02	
Si	0.96	Current collectors, flow-field plates, cell holder, glass tank-separator and silicon tubes
Pt	7.34	
Ir	0.85	Cathodic active layer
Totals	100.00	Anodic active layer

The analysis of EDX spectra (figure 3) allowed to determine the main elements of the membrane and catalytic layers contamination: Ti, Fe, Pt, Ni, Si, Cr, Ir. The Cu peak on figure 3 is explained by the fact that the copper grid has been used as a specimen support for the studied MEA samples. Apparently, the sources of Pt and Ir are cathodic and anodic

electrocatalytic layers, respectively. Ti, Fe, Si, Cr and Ni are the components of titanium alloys (material of current collectors, flow-field plate and cell holder). In particular, according to the technical specifications, titanium alloy of TPP-7 grade (material of porous current collectors) contains up to 1.1 wt. % of Fe (Table 2).

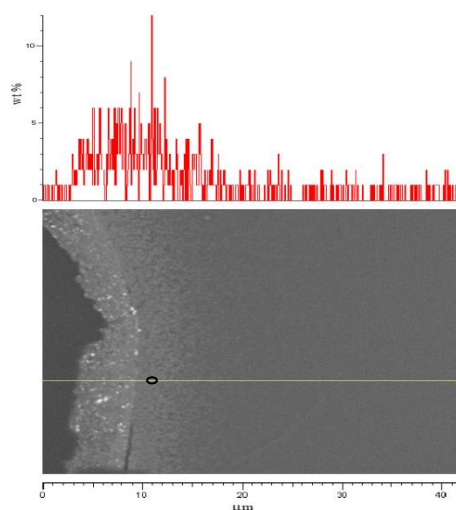
Table 2. Chemical composition of titanium alloys used as construction elements of MEA and electrolysis cell according to GOST 19807-91, TS 14-1-1895-76 and TS 1715-449-05785388-99. Contents of elements are given in wt. %.

Element		Ti	Fe	Si	H	O	N	Cl	C	Others (Ni, Cr, etc)
Grade of titanium alloy	VT1-0	97.00	0.25	0.10	0.01	0.20	0.04	-	0.07	0.30
	TPP-7	97.95	1.10	-	-	-	0.50	0.45	-	-

Technical titanium alloy of VT1-0 grade (material of flow-field plates and cell holder) according to the technical requirements contains Fe (0.25 wt. %), Si (0.10 wt. %) and others (Table 2). The EDX spectra show no traces of Ca, Mg, Na, K etc, which confirms that the purity of the water-reagent is high. The presence of Si can be explained by its outwashing with water from the glass tank-separator and the silicon tubes of the other piping elements (made of VT1-0 titanium alloy) of the electrolysis cell.

The results of the element analysis of a typical area of the near-cathode membrane region are shown in table 1. The first 4 elements (C, O, F and S) compose the membrane material and are not contaminants. However, the next elements are contaminating impurities. In particular, according to table 1, one of the main contaminants of the membrane and the cathode active layer is Ti and the other components of titanium alloys (Fe, Ni, Cr, Si). For instance, figure 4 shows, that the maximum Ti content in near-cathode contaminating band of membrane (2-3 μm from the boundary between the membrane and the cathodic active layer) is *ca.* 12 wt. %. Definitely, Ti, Fe, Ni, Cr and Si originate from the current collectors, flow-field plates and the cell holder. According to the diagram of potential – pH equilibrium (Pourbaix diagram) for titanium–water system [11], for the anode current collector and flow-field plate (working in 1.5-2.0 V potential range), the electrochemical corrosion of titanium with formation of hydroxides and TiO_2 oxide, and repassivation of titanium as a result of anode polarization, is thermo-dynamically possible. Therefore, the anode current collector and the flow-field plate may corrode during the electrolysis cell operation, and Ti^{2+} ions are passed into water and then oxidized to Ti^{3+} . Subsequently, the electroosmotic water flow with the dissolved titanium ions moves through a membrane from the anode to the cathode, and ions of titanium are reduced in a membrane with formation of clusters. A

similar mechanism could be considered for explanation of contamination by other components of titanium alloys. It is necessary to mention that the contaminating elements can form not only nanoparticles and clusters of metals (Ti, Fe, etc) in a membrane, but also their chemical compounds. In particular, it must not be excluded, that rather than the metallic iron, its oxides of the lowest valence and/or the mixed oxides are formed in the membrane matrix (being the acidic media).

**Fig. 4.** Spectrum of Ti concentration profile across the MEA thickness in cathodic region, and the SEM

Contamination by Pt and Ir is associated with degradation processes in electrocatalytic layers [4, 5]. Metallic particles are exposed to oxidation in the course of electrolysis, are dissolved in water as cationic species, which then are transferred with circulating water flow. At some distance from the cathode, they start to react with dissolved hydrogen that cross-permeates from the cathode (or with already reduced species) and are chemically reduced into metallic particles.

Rearrangement of chemical elements, entering into the construction materials of components of MEA, electrolysis cell and auxiliary systems, results

in at least several negative effects. In particular, the loss of Pt and Ir in electrocatalytic layers leads to a decrease in their activity as well as to a decrease in their internal electronic and proton conductivity (due to the loss in coherence of particles). On the other hand, incorporation of nanoparticles of inorganic substances into the ion-exchange membrane leads to essential modifications of the system of pores and channels, as well as to deterioration of transport properties of membrane [4]. In particular, with increase in concentration of impurity metallic particles in a membrane its proton conductivity falls [11] and the probability of local overheating and a membrane burn-through (due to ohmic heating of percolating metal clusters) increases [2, 5]. According to [1], the cations can occupy the ion-exchange sites of the Nafion® polymer electrolyte in the catalyst layers and membrane, which results in the increase of the anode and cathode overpotentials. The assumption is that in the course of stability test the increase of electrolysis cell voltage was related to the combination of the abovementioned factors. The use of the ion-exchange filters and/or regular change of water in electrolysis system can be recommended in order to decrease the MEA contamination.

CONCLUSIONS

The results of microstructural and chemical analyses indicated that in the course of operation of PEM water electrolyser, the membrane and electrocatalytic layers are contaminated by the impurity elements originated from the MEA and cell components (electrocatalytic layers, current collectors, flow-field plates, cell holder) and external cell piping. As a result of corrosion of these components, the ions of titanium, iron, silicon, nickel, chrome, platinum and iridium are dissolved in water-reagent circulating through them and are reduced in membrane and active layers. These phenomena lead to a number of adverse effects

(decrease of electrocatalytic layer activity and conductivity, deterioration of transport properties of membrane, etc), increasing the voltage of electrolysis cell. A use of ion-exchange filters and/or regular change of water in electrolysis system is recommended in order to reduce contamination of the membrane and electrocatalytic layers.

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REFERENCES

1. M. Lamberti, F. Escher, Food Rev. 1. S. Sun, Z. Shao, H. Yu, G. Li, B. Yi, *J. Power Sources*, **267**, 515 (2014).
2. P. Millet, A. Ranjbari, F. de Guglielmo, S.A. Grigoriev, F. Aupretre, *Int J Hydrogen Energy*, **37**, 17478 (2012).
3. M. Langemann, D.L. Fritz, M. Müller, D. Stolten, *Int J Hydrogen Energy*, **40**, 11385 (2015).
4. S.A. Grigoriev, D.G. Bessarabov, V.N. Fateev, *Russian Journal of Electrochemistry*, **53**, 318 (2017).
5. S.A. Grigoriev, K.A. Dzhus, D.G. Bessarabov, P. Millet, *Int J Hydrogen Energy*, **39**, 20440 (2014).
6. C. Rakousky, U. Reimer, K. Wippermann, S. Kuhri, M. Carmo, W. Lueke, D. Stolten, *J Power Sources*, **342**, 38 (2017).
7. F. Fouda-Onana, M. Chandesris, V. Medeau, S. Chelghoum, D. Thoby, N. Guillet, *Int J Hydrogen Energy*, **41**, 16627 (2016).
8. C. Rakousky, U. Reimer, K. Wippermann, M. Carmo, W. Lueke, D. Stolten, *J Power Sources*, **326**, 120 (2016).
9. S.A. Grigoriev, A.A. Kalinnikov, *Int J Hydrogen Energy*, **42**, 1590 (2017).
10. A.A. Fedotov, S.A. Grigoriev, P. Millet, V.N. Fateev, *Int J Hydrogen Energy*, **38**, 8568 (2013).
11. Mousavi Ehteshami S. Mohsen, Amirhooshang Taheri, S.H. Chan, *J. Industrial and Engineering Chemistry*, **34**, 1 (2016).

ЗАМЪРСЯВАНЕ В ПРОЦЕСА НА РАБОТА НА МЕМБРАННО-ЕЛЕКТРОДНИТЕ ПАКЕТИ ВЪВ ВОДНИ ЕЛЕКТРОЛИЗЬОРИ, БАЗИРАНИ НА ПРОТОННО-ОБМЕННА МЕМБРАНА

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(Резюме)

Проблемите на замърсяването на мембранно-електродните пакети (МЕАs) на водни електролизьори, базирани на протонно-обменна мембрана (РЕМ), понастоящем представляват обект на изследване. Анализът на структурата и химичния състав на МЕА след дългото му тестване показва, че йоните и / или клъстерите на няколко замърсяващи елементи (Ti, Pt, Ir, Fe, Ni, Cr, Si) произхождат от конструктивните материали на МЕА, електролитния стек и външните тръби и се натрупват в мембраната и електрокаталитичните слоеве. Количествено, най-преобладаващият замърсител е Ti (до 12 тегл.%). Катодната зона (катодният активен слой и мембранната лента в непосредствена близост до тях) е изключително изложена на отлагане на замърсителя.

Ключови думи: водна електролиза, протонно-обменна мембрана, мембранно-електроден пакет, електрокаталитичен слой, замърсяване, примеси