Chapter 2

Literature study

In this chapter the fundamentals of electrochemistry and the working principle of electrochemical cells like electrolysers and fuel cells are discussed. Various electrochemical characterisation methods along with an overview of equivalent electric circuits are also provided. Lastly, the applicability of system identification and the use of pseudo random binary sequence as perturbation signals are discussed.

2.1 Electrochemical cells

In chemistry the interrelationship between chemical and electrical effects are known as electrochemistry [2]. Electrochemical principles are used for various applications like electrophoresis, electrochromic displays and the electroplating of metals. In electrochemical systems, chemical processes are related to the flow of electric current and the production of electrical energy through chemical reactions.

An electrochemical cell consists of two electrodes and an electrolyte. The electrodes are used for electrical conduction and the electrolyte for ionic conduction. The electrode where oxidation occurs is referred to as the anode and the electrode where reduction takes place is called the cathode [2]. An electrochemical cell in which the chemical reactions occur spontaneously are referred to as a galvanic cell [2]. When the chemical reactions are non-spontaneous the electrochemical cell is called an electrolytic cell [2]. A depiction of a galvanic cell and an electrolytic cell is given in Figure 2.1. Galvanic cells are often utilised for generating electrical energy from chemical compounds that react spontaneously (e.g., fuel cells and batteries). Electrolytic cells are used for industrial purposes like the large scale production of aluminium and chlorine, and the production of hydrogen [2].

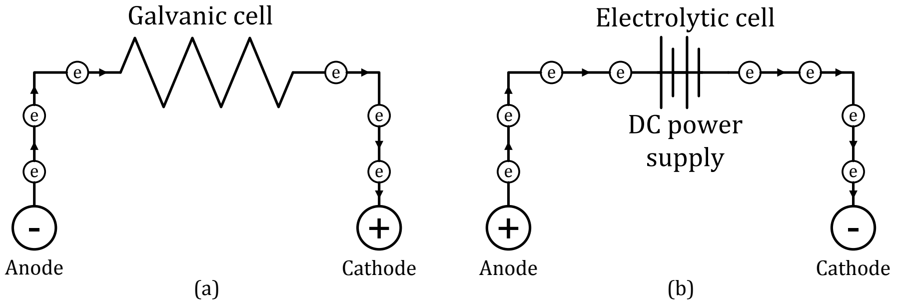


Figure 2.1: Electrochemical systems: a) Galvanic cell b) Electrolytic cell [2]

2.1.1 Fuel cells

A fuel cell is a galvanic type electrochemical cell, since the chemical reactions occur spontaneously. The chemical reactions that take place are:

Anode half reaction:

$$2H_2 \rightarrow 4H^+ + 4e^- \tag{2.1}$$

Cathode half reaction:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{2.2}$$

Overall reaction:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{2.3}$$

A depiction of a PEM fuel cell is provided in Figure 2.2. From Figure 2.2 it can be seen that hydrogen is supplied at the anode and is split into protons and electrons. The protons are transported through the electrolyte and the electrons move through an external load. At the cathode oxygen is supplied and combines with the protons and the electrons to form water. The moving electrons creates an electrical current

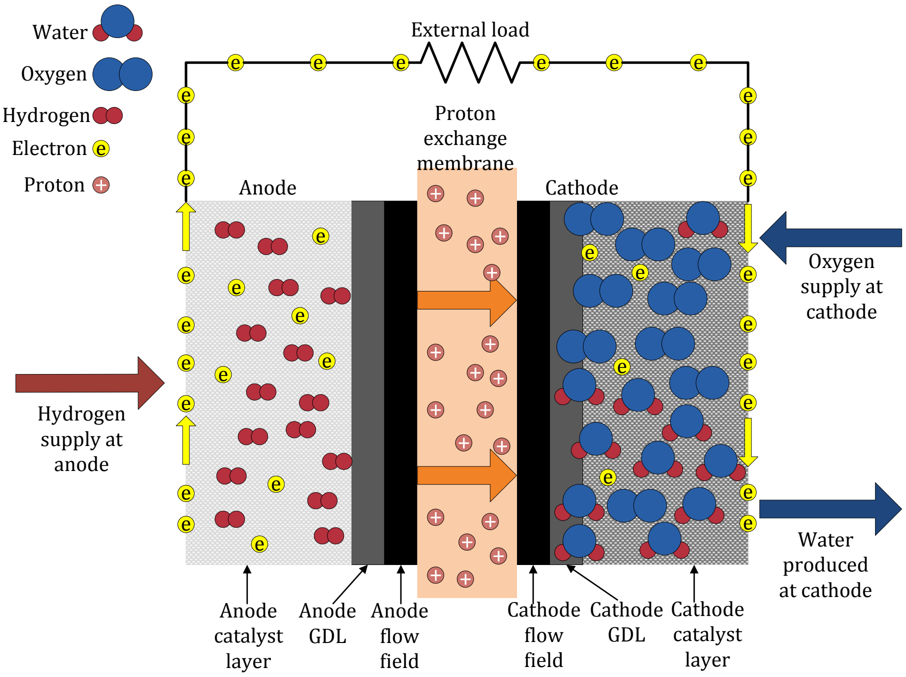


Figure 2.2: PEM fuel cell

2.1.2 Electrolysers

An electolyser is an electrolytic type electrochemical cell, since an external voltage higher than the open circuit voltage is required to drive the reactions. In Figure 2.3 is a depiction of a PEM electrolyser [2].

At the anode water is supplied and dissociated into protons, electrons and oxygen gas. The protons are transferred through the PEM and the electrons are transported from the anode to the cathode via the power source. At the cathode the protons combine with the electrons to form hydrogen. At times, small amounts of water are sometimes transported through the PEM during hydrogen production. The water is removed from the cathode and fed back to the anode.

Anode reaction :

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{2.4}$$

Cathode reaction:

$$4H^+ + 4e^- \rightarrow 2H_2 \tag{2.5}$$

Overall reaction:

$$2H_2O \rightarrow 2H_2 + O_2 \tag{2.6}$$

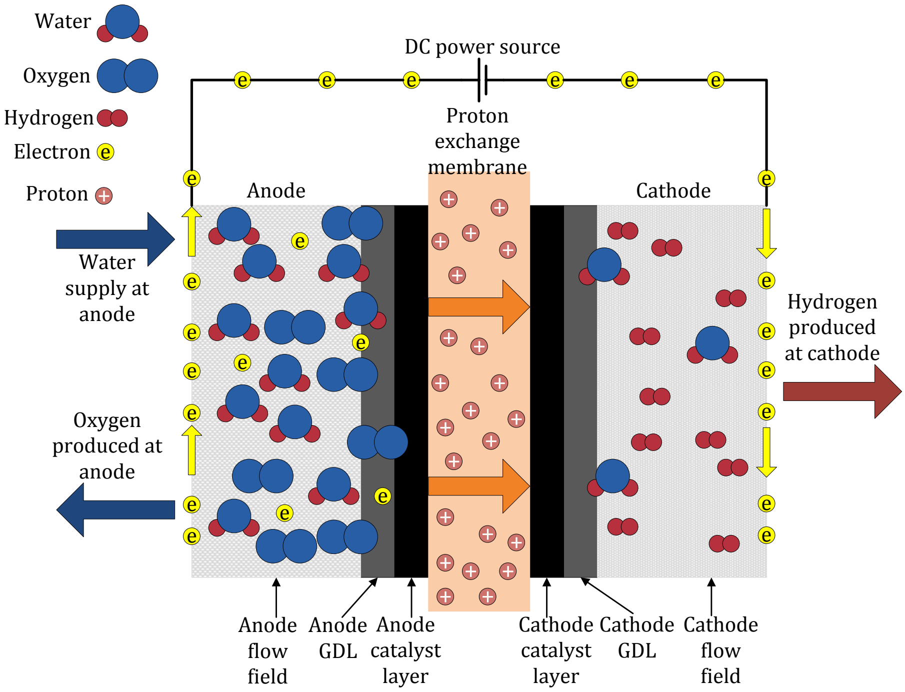


Figure 2.3: PEM electrolyser

2.2 Electrochemical fundamental principles

The basic electrochemical principles of electrochemical cells are discussed in this section. The Nernst equation is used to understand the thermodynamics and the Butler-Volmer equation is used to understand the reaction rates of electrochemical reactions.

The overpotential describes the thermodynamic potentials of electrochemical cells. The interrelationship between the overpotential and exchange current density is discussed. The theory provides an overview of the working principles of electrochemical cells.

2.2.1 Nernst equation

The Nernst equation can be used to specify the Oxidation Reduction Potential (ORP) at equilibrium. For an electrochemical cell where the following chemical reaction occurs,

$$O + ne^{-} \rightarrow R, \tag{2.7}$$

the equation for the Gibbs free energy is given in (2.8),

$$\Delta G_{fe1} = \Delta H - T\Delta S, \tag{2.8}$$

where ΔH is the change in enthalpy, ΔS is the change in entropy and T is the absolute temperature. The enthalpy (H) is the total energy of a thermodynamic system [3].

Enthalpy (H) is a thermodynamic potential, but can not be measured directly. The change in enthalpy (ΔH) is more useful as it shows how the energy of the system changes as the reaction takes place [9].

The entropy (S) of a thermodynamic system is a measure of how much energy is available for useful work in the thermodynamic process [9]. Entropy is governed by the second law of thermodynamics, the entropy of a segregate system always increases or remains constant [9].

Gibbs free energy can alternatively be expressed as:

$$\Delta G_{fe2} = \Delta G^{0} + RT \ln \frac{[R]}{[O]}, \tag{2.9}$$

where ΔG^0 is the standard free energy, R is the universal gas constant, T is the absolute temperature, [R] is the activity of the product (reduction, electron gain), and [O] is the activity of the reactant (oxidation, electron loss).

The electrical potential of an electrochemical reaction is dependant on the Gibbs free energy since it is a measure of the electrical work done by the electrochemical reaction. It can be explained by the following equation:

$$\Delta G = -nFE, \tag{2.10}$$

where $-nFE$ represents the electrochemical work done by the reaction, n is the number of electrons present in the reaction, F is the Faraday constant and E is the electrode potential.

From (2.10) and (2.9), the electrode potential can be expressed as:

$$E = E^0 - \frac{RT}{nF} \ln \frac{[R]}{[O]}, \tag{2.11}$$

where E^0 is the standard thermodynamic potential at 25 °C, R is the universal gas constant, T is the absolute temperature and F is the Faraday constant. The electrode potential in (2.11) is also known as the Nernst equation [3].

A PEM electrolyser dissociates water into hydrogen and oxygen gas and the chemical expression is given by:

$$H_2O(l) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g). \tag{2.12}$$

2.2.2 Butler-Volmer equation

The Nernst equation can be used to provide information on the reaction direction and the thermodynamic potentials at the electrodes [3]. A shortcoming of the Nernst eqaution is that it can't indicate the rate of the electrochemical reaction. Therefore, the Butler-Volmer equation is used to indicate the relationship between the reaction rate and the electrode potential.

For the following chemical reaction:

$$O + ne^- \rightleftharpoons R, \tag{2.13}$$

the expression for the forward reaction rate in terms of the current density is

$$i_{frr} = i_0 \exp\left(\frac{-\alpha F \eta}{RT}\right), \tag{2.14}$$

and the backward reaction rate in terms of the current density is

$$i_{brr} = i_0 \exp\left(\frac{(1-\alpha) F \eta}{RT}\right), \tag{2.15}$$

where i_{frr} is the forward reaction current density, i_{brr} is the backward reaction current density, η is the overpotential and α is the charge transfer coefficient. The values of the charge transfer coefficient is usually between 0.3 and 0.7 [3]. The Butler-Volmer equation is obtained by subtracting the backward reaction from the forward reaction rate and is given in (2.16).

$$i = i_{frr} - i_{brr} = i_0 \left(\exp\left(\frac{-\alpha F \eta}{RT}\right) - \exp\left(\frac{(1-\alpha) F \eta}{RT}\right)\right), \tag{2.16}$$

where i is the total current density and i_0 is the exchange current density. If the reaction is purely chemical the Butler-Volmer equation can't be used. The Butler-

Volmer equation is only valid when the electrode reaction is controlled by the electrical charge transfer at the electrode, since it is used to indicate the interrelationship between the current density and the overpotential [3]. If the multi-electron transfers occur within an electrochemical reaction the Butler-Volmer equation can also be expressed as follows:

$$i = i_0 \left(exp \left(-\frac{\alpha n_\alpha \eta}{RT} \right) - exp \left(\frac{(1-\alpha) n_\alpha F \eta}{RT} \right) \right), \tag{2.17}$$

An example of an electrochemical reaction where multi-electron transfers occur is the Hydrogen Oxidation Reaction (HOR) and Oxygen Reduction Reaction (ORR) reactions which involve two and four electrons, respectively [3]. (2.17) is only an approximation of the Butler-Volmer equation for reactions with multi-electron transfers. α is the charge transfer coefficient and n_α is the apparent electron number of the multi-electron equation [3].

2.2.3 Overpotential

In electrochemistry the extra potential, potential above the thermodynamic requisite, needed to drive an electrochemical reaction at a specific rate is referred to as the overpotential [2]. As shown in (2.13), if the net rate of the forward and backward reactions equals zero, equilibrium is reached. The potential at equilibrium conditions are referred to as the Nernst potential or the thermodynamic potential [3]. The difference between the enforced potential and the Nernst potential is given by:

$$\eta = E - E^0 \tag{2.18}$$

where η is the overpotential, E is the enforced potential and E^0 is the Nernst potential. From the Butler-Volmer equation it is seen that the current density is directly related to the overpotential. The higher the overpotential the higher the current density. To ensure efficiency during the operation of an electrochemical cell, the overpotential has to be kept as small as possible [3].

2.2.4 Exchange current density

For the chemical reaction given in (2.13), no net reaction takes place at equilibrium and the forward reaction rate is equal to the backward reaction rate [3]. During equilibrium no net concentration change of the reactants and products takes place in the forward and backward reactions [3]. This causes no net current to flow, since the forward and backward current densties are equal. The exchange current density is a measure of how effortlessly an electrochemical reaction takes place on the electrode surface. Therefore the exchange current density is dependent on the electrode surface used during an electrochemical experiment [3]. The exchange current density is directly proportional to the current density and indirectly proportional to the overpotential as shown in (2.17).

Just some of the basic electrochemistry principles are discussed in this section. For a more comprehensive description of electrochemical fundamentals the reader is referred to a book written by A.J. Bard and L.R. Faulkner [2].

2.3 Electrochemical characterisation methods

The analytical expressions that describe the various electrochemical aspects of electrochemical cells, depend on parameters that can't always be easily measured. Electrochemical characterisation methods are used to gather experimental data, in the form of voltage and current signals. The information is then related to the electrochemical aspects of the electrochemical cells.

The electrochemical characterisation methods which are mostly employed are the PC, the EIS and the CI method [8]. These methods are used to understand electrolyser dynamics, to indicate diagnostic failure modes and degradation, to alleviate performance losses and indicate other important characteristics [10]. When these issues are addressed the durability and cost of electrolyser can be improved.

2.3.1 Polarisation curve

The polarisation curve is a standard way of representing the cell voltage versus the cell current density [10]. Two variants of the PC exists, namely a steady state PC and a non-steady state PC. The steady state PC is generated by plotting the voltage as the current density changes within the electrochemical cell [8]. The PC method is widely utilised to benchmark the performance losses of electrolysers and fuel cells [10]. The PC provides a broad overview of the electrolyser performance losses, but it is not possible to extract information on individual components within the electrolyser [10].

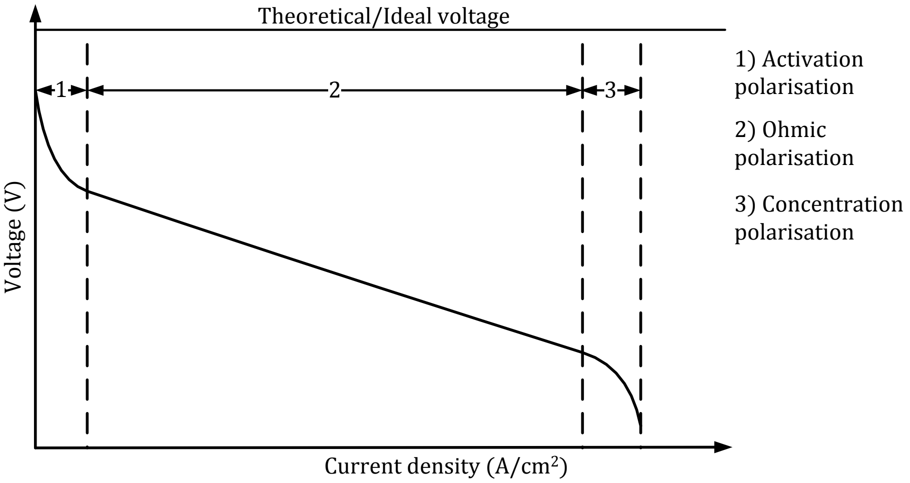


Figure 2.4: Generic polarisation curve of a fuel cell

In Figures 2.4 and 2.5 shows PCs for a fuel cell and electrolyser, respectively. There are three regions of interest within a PC, namely the activation polarisation, the ohmic polarisation and the concentration polarisation region. The activation losses occur at the low current densities and are caused by the slow kinetics of the ORR [8]. The effects of activation losses tends to be non-linear. The low current density is caused by the low charge transfer kinetics as indicated by the Butler-Volmer equation [10]. The ohmic polarisation is caused by resistive elements within the electrolyser or fuel cell. The resistive effects are caused by the transportation of ions through the electrolyte and the transportation of electrons through the electrode [10].

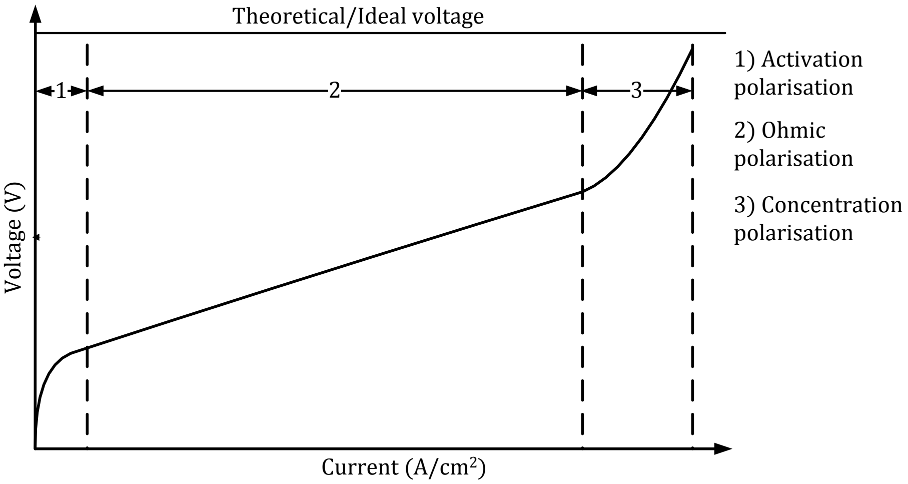


Figure 2.5: Generic polarisation curve of an electrolyser

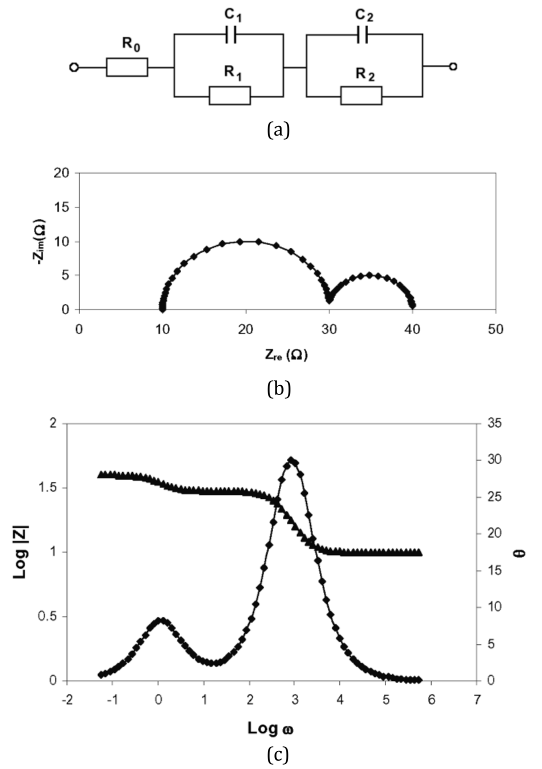
The concentration losses are caused by the mass transport effects that occur at high current densities [8]. This is due to reaction rate being higher than the transfer speed of reactants and products [10].

2.3.2 Electrochemical impedance spectroscopy

The EIS method is used to provide an equivalent electric circuit of an electrochemical cell. The EIS consists of applying a small AC voltage or current perturbation signal to the electrochemical cell and measuring the resulting response. If a small AC current is used as the perturbation the resulting voltage response is measured and vice versa. From the perturbation and response signals the impedance of the PEM electrolyser is calculated by dividing the voltage by the current [3]. Since AC signals are used, EIS can be applied over a wide frequency range.

The data from the EIS method is usually represented by an equivalent electrical circuit, a Nyquist plot and a Bode plot [8]. A Nyquist plot is used to depict the complex impedance of an equivalent electric circuit over a specific frequency range. In Figure

2.6 is an equivalent electric circuit, with its corresponding Nyquist plot and bode plot, for a fuel cell are shown.



(a)

(b)

(c)

Figure 2.6: General electric circuit and Nyquist plot of a fuel cell [3]

2.3.3 Current interrupt method

Another important characterisation tool is the CI method and is conventionally used for estimation of the ohmic losses within an electrochemical system. The CI method can be implemented on various electrochemical cells like batteries, fuel cells and electrolysers. In Figure 2.7 is a depiction of the CI waveform for an electrolyser and a fuel cell.

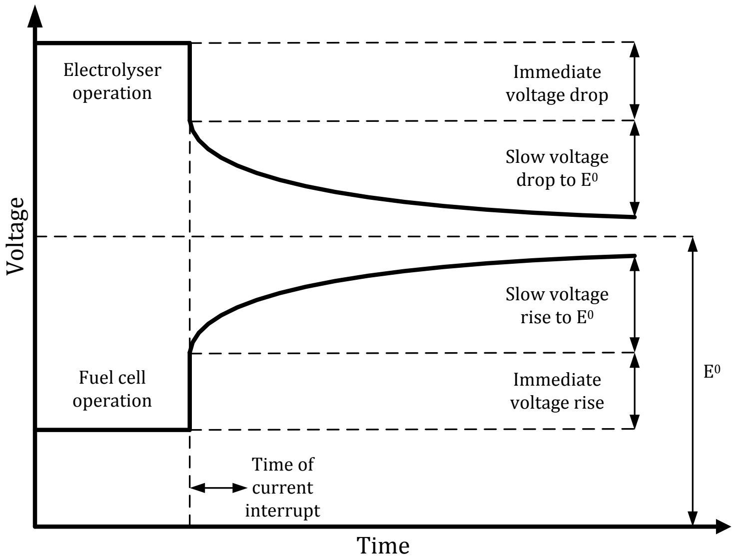


Figure 2.7: Current interrupt waveform for electrolyser and fuel cell

Consider the CI curve for electrolyser operation. From Figure 2.7 it can be seen that the electrolyser is operated at a steady state voltage. At a specific time the current is interrupted and a voltage transition is observed. The first voltage drop is caused by the membrane resistance and is observed immediately [3]. The second voltage transition is caused by slow disappearance of the electrochemical overvoltage towards the standard electrochemical voltage (E^0).

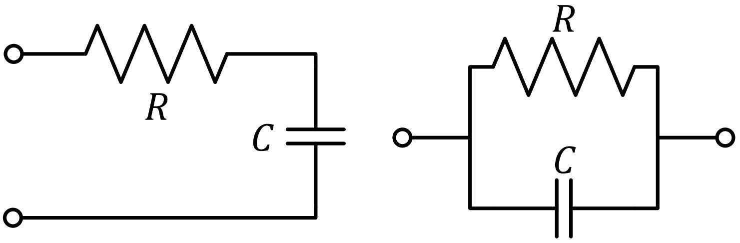
The membrane resistance is calculated by dividing the first voltage change by the current value before interruption. In order to observe the immediate voltage drop after current interruption, the voltage transition needs to be sampled at a high frequency. An estimation of the membrane resistance for a fuel cell was done by Abe [11]. It was reported that the voltage drop after the current is interrupted occurs within 5 μs [11].

2.4 Equivalent electric circuits

EECs are used to represent the impedance of an electrochemical system. The EEC contains electrical components like resistors, capacitors and/or inductors [3]. An EEC can be used to model specific electrochemical characteristics. Various EEC models have been developed for electrochemical systems and a few are discussed in this section.

RC equivalent electric circuit

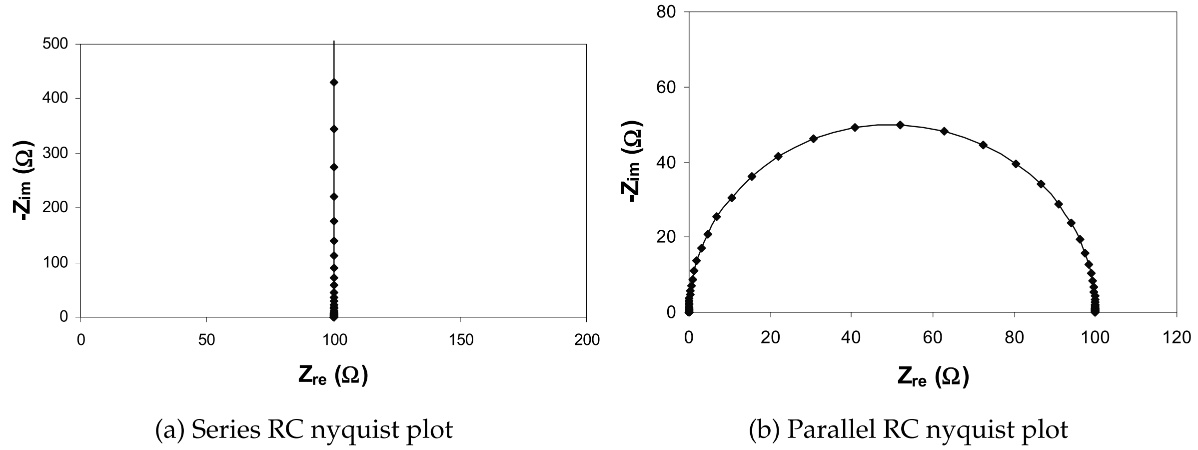
The simplest form of an EEC model is represented by RC electrical circuits. A representation of a RC EEC is presented in Figure 2.8. The connection between the resistor and capacitor can be either series or parallel. For a series connected EEC, the total impedance is the summation of every component's impedance. For a parallel connected EEC, the total admittance (inverse of impedance) is the summation of every components admittance. The impedance of a parallel connected RC circuit can be calculated by taking the inverse of the admittance.



(a) Series RC circuit (b) Parallel RC circuit

Figure 2.8: RC equivalent electric circuits [3]

The RC EEC can be used to model an ideal polarised electrode [3]. For such a model it is assumed that neither charge transfer nor the concentration losses are present within the system [3]. Typical Nyquist plots of the RC EECs are depicted in Figure 2.9.



(a) Series RC nyquist plot

(b) Parallel RC nyquist plot

Figure 2.9: Nyquist plots of RC electric circuits [3]

2.4.1 Randles cell

A depiction of the Randles cell is presented in Figure 2.10. It consists of a membrane resistance (R_m), the double layer capacitance (C_{dl}) and the charge transfer resistance (R_{ct}). The membrane resistance is associated with the ohmic losses, where charge transfer resistance is associated with the activation losses [3].

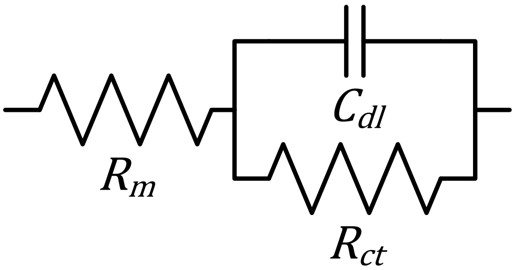


Figure 2.10: Randles cell equivalent electric circuit [3]

The double layer capacitance (C_{dl}) is associated with the electrochemical double layer [3]. The electrochemical double layer is the narrow region between the electrode and electrolyte interface within an electrochemical system [2]. A typical Nyquist plot of the Randles cell is depicted in Figure 2.11.

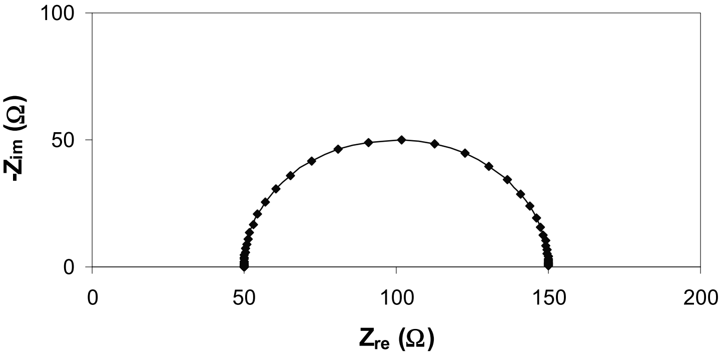


Figure 2.11: Nyquist plot of Randles cell [3]

2.4.2 Randles-Warburg cell

The Randles-Warburg cell consists of the Warburg impedance (Z_{wbg}) and the components of the Randles cell. The Randles-Warburg cell can be used to model the activation losses, the ohmic losses and the concentration losses of an electrochemical system. A depiction of the Randles-Warburg cell is presented in Figure 2.12. A typical Nyquist plot of the Randles-Warburg cell is depicted in Figure 2.13.

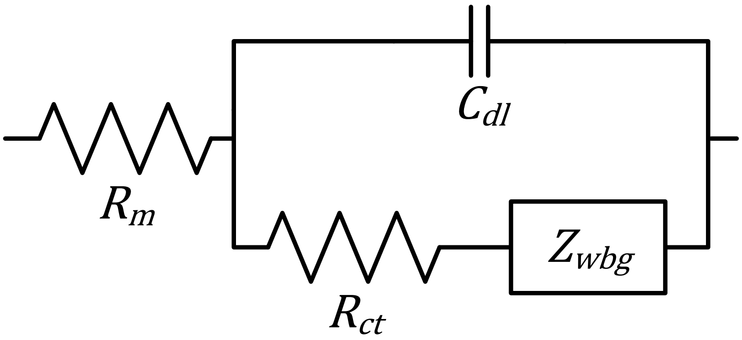


Figure 2.12: Randles-Warburg cell of electrochemical system [3]

The Warburg impedance (Z_{wbg}) is used to model the concentration losses. The Warburg impedance is most significant at low frequencies and high current densities [2]. In order to model the concentration losses, an appropriate characterisation method is needed to calculate Z_{wbg}. Since Z_{wbg} is frequency dependent, system identification techniques can be used to model it.

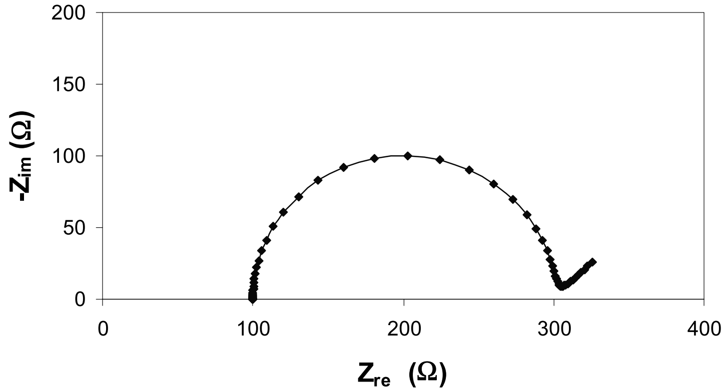


Figure 2.13: Nyquist plot of Randles-Warburg cell [3]

2.5 System identification

System identification can be used to model or estimate complex systems from noisy data [12]. The objective of System Identification (SI) is to derive a mathematical model of a dynamic or static system from experimental data [13]. Examples of system identification are the following: finding a mathematical model for controller design, understanding physical processes like machine learning or to estimate the model of a signal in filter design [4].

In Figure 2.14 is a basic depiction of a dynamic system, with $x(t)$ the input signal, $p(t)$ the perturbation (disturbance) signal and $y(t)$ the output signal. The output signal varies with the input and perturbation signal. The measured input and output signals are used to model the dynamic system.

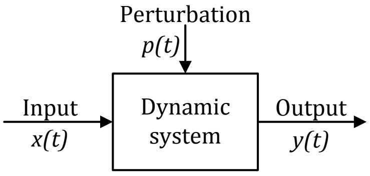


Figure 2.14: Dynamic system [4]

With system identification various types of models can be implemented to represent the dynamic system. These models include time domain or frequency domain, linear or non-linear, time invariant or time varying, continuous time or discrete time and parametric or non-parametric [4].

Time domain models are usually represented by differential equations or impulse responses. Frequency domain models may be represented by means of transfer functions in either the Fourier or Laplace domain. A linear model satisfies superposition and homogeneity whereas a non-linear model does not [4].

A continuous time model represents the system at any given instance of time. Discrete models are used to represent the system at distinct instances of time.

Non-parametric models implies that the system is not represented by parameters, but rather by curves or functions. This may be the time content of an impulse or step response in the time domain, the frequency content of a transfer function in the frequency domain. In theory, the system needs to be represented by an infinite number of measurements. In practice, the system is accurately modelled by a large number of measurements [13].

Parametric models are used to represent the system with a limited set of parameters and assumptions on the model structure is required. The parametric approach may be more complex than the non-parametric approach, since all the information in a model structure is used. However, this approach produces a more powerful model of the system.

2.5.1 Identification procedure

To model a dynamic system by means of system identification, four basic steps are required: First, information of the system are collected. Then an appropriate model structure is needed to represent the dynamic system. Model parameters are chosen to fit the model as accurately as possible to the measured data. Lastly, the model is validated [12].

A form of knowledge about the system is required for classification of the system identification problem. If the system is classified as a black box it means that nothing about the basic properties of the system is known and is exceptionally difficult to solve. In such an instance, assumptions about the system have to be made before the system can be solved. If the system is classified as a grey box, the elementary features of the system are known, but the dynamic equation or model coefficient value may be unknown [13]. A flow diagram of the system identification process is depicted in Figure 2.15.

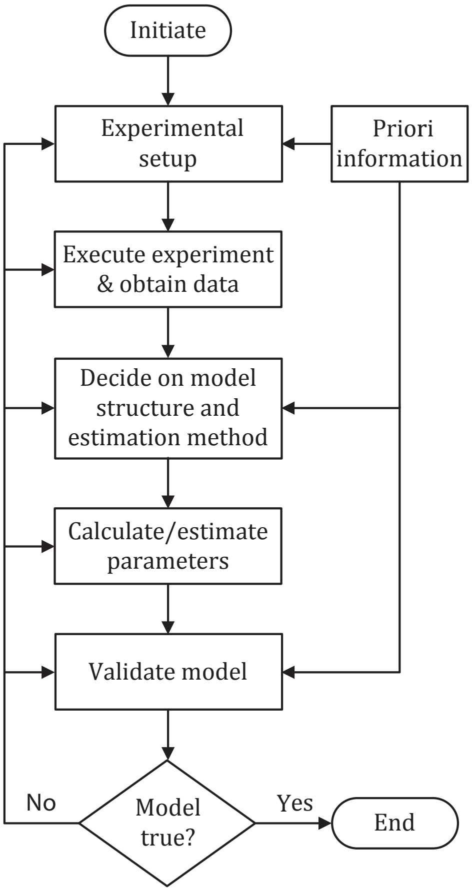


Figure 2.15: System identification process [4]

Firstly the process is initiated by developing the experimental setup. The objective of the experimental setup is to ensure that the collected data is maximally informative. The different types of perturbation signals and what the input/output signals should be, is of great importance [4].

The experiment is implemented and the necessary data is obtained. Next, a model structure is developed and an applicable estimation method is selected. The parameters are estimated and the results are validated. The model is validated by making sure the model output relates to the data observed [12]. If model validation is successful, the system identification process is completed. If the model fails, the previous steps are repeated until a true model is obtained.

2.5.2 Perturbation signals

Various perturbation signals can be used for the system identification process. Selecting the correct perturbation signal is crucial, since it has a significant effect on the parameter estimation process [4]. The various perturbation signal types include the following:

- Step function
- Sinusoidal signal
- Multi-sinusoidal signal
- Pseudo random binary sequence

A depiction of the step function is given in Figure 2.16 and is defined by:

$$x(t) = \begin{cases} 0 & \text{if } t < 0 \\ x_0 & \text{if } t \geq 0, \end{cases}$$

with, $x_0(t)$ the amplitude [14]. The step function can be used in systems with large signal-to-noise ratios and when a basic model is required. The step response can be associated with rise times, overshoots and static gain, etc.

The sinusoidal signal is depicted in Figure 2.17 and is expressed by the following equation:

$$x(t) = a(sin(2\pi f t + \phi)), \tag{2.19}$$

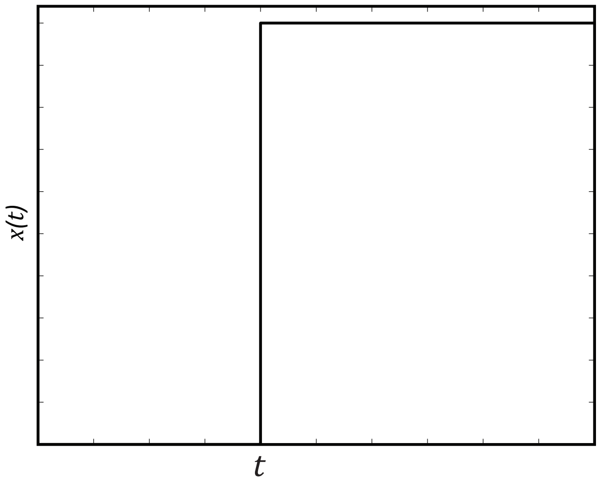


Figure 2.16: Step function

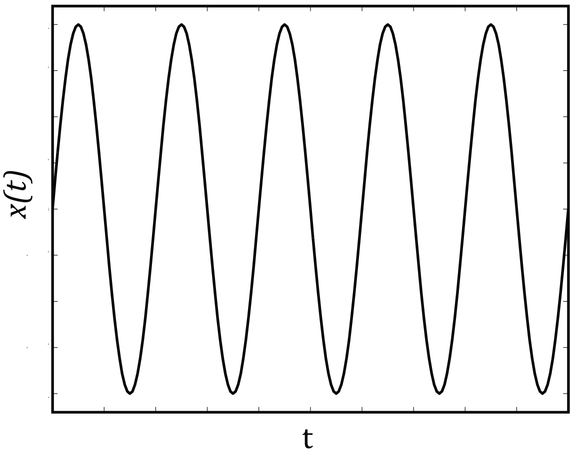


Figure 2.17: Sinusoidal function

with f the frequency and ϕ the phase shift. Sinusoidal signals can be employed to model continuous time systems. A sinusoidal signal can easily be generated for a frequency of interest. A disadvantage of the sinusoidal signal is that it is limited to one test frequency. A number of experiments with different excitation frequencies needs to be performed in order to obtain an adequate and accurate model of the system.

In order to model a system at various frequencies, a multi-sinusoidal signal can be used. A depiction of a multi-sinusoidal signal is presented in Figure 2.18 and the expression is given by:

$$x(t) = \sum_{k=1}^{n} a(sin(2\pi kft + \phi_k)) \tag{2.20}$$

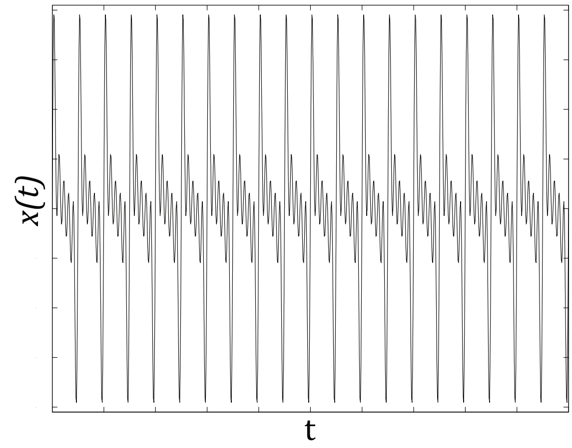


Figure 2.18: Multi-sinusoidal function

Another perturbation signal is the pseudo random binary sequence. It is a periodic and deterministic signal which can excite a frequency range of interest [12]. It is easy to implement and appropriate for the current switching method. The PRBS signal is discussed in more detail in the following section.

Since frequency dependent parameters, like C_{dl} and Z_{wbg}, exist within the EEC models it is required to characterise these components with an appropriate method. Therefore, system identification and the PRBS perturbation signal can be implemented to model these EEC components.

2.6 Pseudo random binary sequence

Pseudo random signal processing was initially developed for space and military applications in the early 1960's [15]. Other important applications of pseudo random signal processing includes spread spectrum communications, ranging and navigation systems, scrambling and cryptology [15]. A widely held choice is the use of random binary signals in system identification methods, since it can be easily generated and implemented [16]. The basic characteristics of a PRBS are the following [16]:

- The signal consists of two levels and is switched from one level to the other at a specific time t = 0, Δt, 2Δt, ...
- The level change within a PRBS signal is predetermined which causes the signal to be deterministic and repeatable.
- The PRBS signal has a specific period $T = N\Delta t$, with N an odd number.

2.6.1 Autocorrelation

Correlation functions can be used to indicate the level of similarity between different signals. Typically cross-correlation and auto-correlation are used to differentiate between the similarity of signals. Signal sets are typically used to describe physical, technical and biological systems [15]. Signal sets should exhibit at least one of the following characteristics [15]:

- Every signal contained in the signal set can easily be differentiated from a shifted version of itself.
- Every signal contained in the signal set can be easily differentiated from every other signal and a shifted version of these signals.

The auto-correlation function is the cross-correlation of the signal itself [17]. The auto-correlation function can be used for finding repeating patterns, such as finding a periodic signal contained in noisy data [17].

Figure 2.19 (a) shows a typical representation of a PRBS signal with its associated autocorrelation function in Figure 2.19 (b). The autocorrelation function of a PRBS signal is given by:

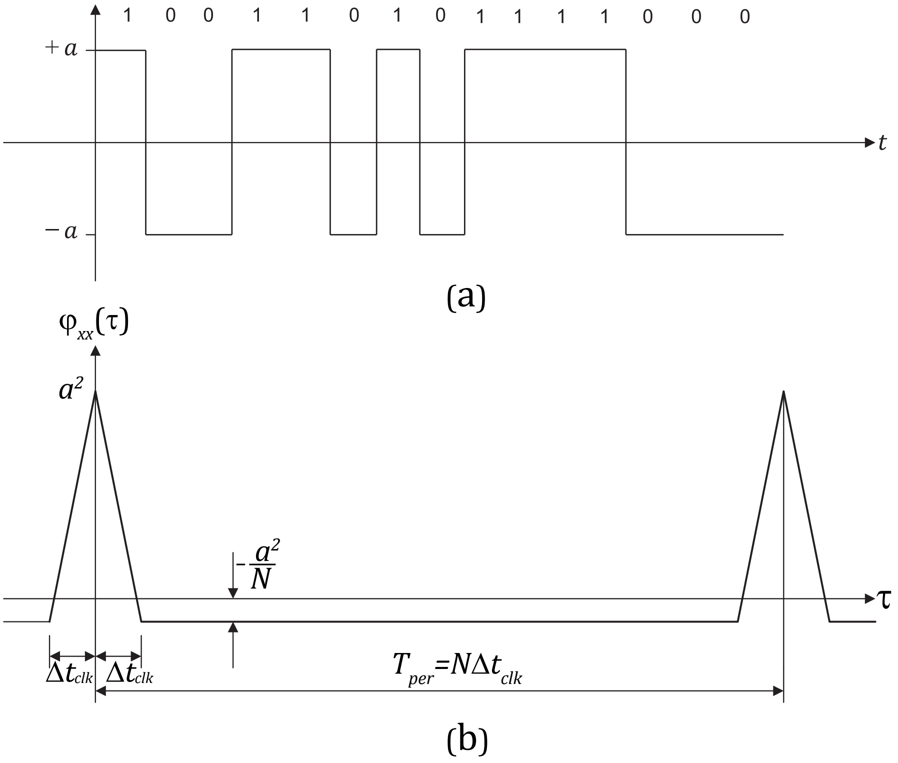


Figure 2.19: (a) Typical PRBS signal (b) Autocorrelation response of PRBS signal [5]

$$\begin{aligned}\varphi_{xx}(\tau) &= \frac{1}{N}\sum_{j=1}^{N} x(j)x(j+k)\\ &= \frac{N+1}{N}a^2\left(1-\frac{\tau}{\Delta t_{clk}}\right)-\frac{a^2}{N}\\ &= \frac{-a^2}{N}.\end{aligned} \tag{2.21}$$

2.6.2 Power spectral density

Various characteristics of signals can be obtained by examining the frequency content. The Power Spectral Density (PSD) specifies the frequency domain characteristics of different types of signals. The PSD of a signal is calculated by taking the Fourier transform of the Autocorrelation Function (ACF) [15]. The PSD can also be used to indicate the randomness characteristic of a PRBS signal. A signal is considered more random-like if the signal power is uniformly distributed with respect to frequency [15].

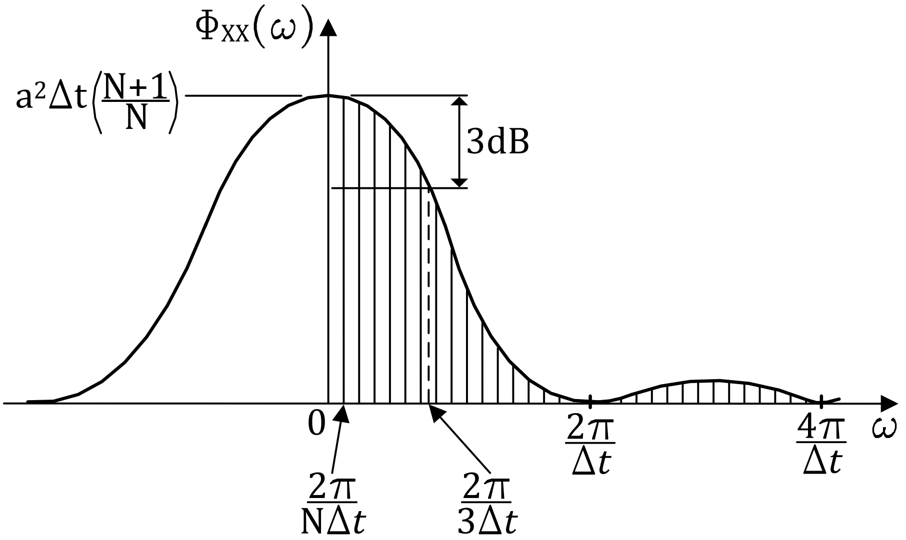


Figure 2.20: Power spectral density of a PRBS signal [5]

The PSD of a PRBS signal is shown in Figure 2.20. The PSD provides information on the available frequency band of the PRBS signal, and is given by:

$$\Phi_{xx}(\omega) = \frac{a^2(N+1)}{N}\left(\frac{sin(w\Delta t/2)}{w\Delta t/2}\right)^2. \tag{2.22}$$

A PRBS signal is band limited and is designed to excite a frequency range of interest. The lower (ω_{low}) and upper (ω_{up}) frequency bands of the PRBS are given by

$$\omega_{low} = \frac{2\pi}{N\Delta t}, \tag{2.23}$$

and

$$\omega_{up} = \frac{2\pi}{3\Delta t}. \tag{2.24}$$

2.6.3 Sequence properties

In order to ensure a valid and true PRBS signal, it has to comply with specific properties. These properties are [5]:

a) Balance property. In every period of the sequence the number of logic zeros and the number of logic ones, subtracted from one another, should not differ by more than one.

b) Run property. "Among the runs of one, two three, etc. in the period half should be of length 1, a quarter of length 2, an eighth of length 3 et. and there should be as many of each run of logic one as logic zero states." [5]

c) Correlation property. If a cyclic shift of the sequence, in any period of the sequence, is compared term by term, the number of differences should not be more than one.

2.6.4 Sequence generation

Various types of PRBS classes exist namely, Maximum Length Sequence (MLS)s, quadratic residue codes, twin prime sequences and Hall sequences. A common way of implementing a PRBS signal is by means of the MLS class. A MLS signal is generated by means of a Linear Feedback Shift Register (LFSR) as depicted in Figure 2.21. The shift register consists of n flip flop and modulo 2 addition at specific feedback points. The length of a MLS is given by:

$$N = 2^n - 1 \tag{2.25}$$

where, n is the number of flip flops within the LFSR and N is the number of binary levels within the PRBS. The first stage of the MLS is determined by the feedback of the modulo two sum, or by the binary 'exclusive or' function, of the last stage and earlier stages.

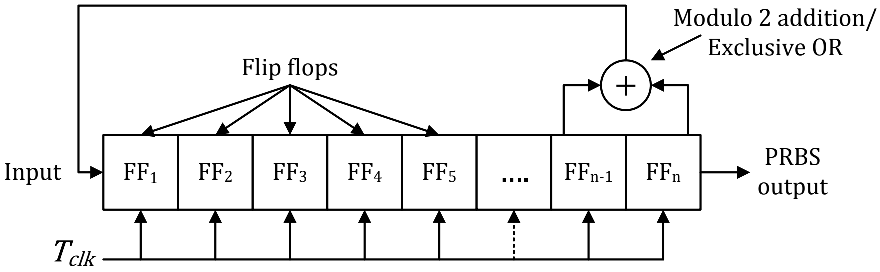


Figure 2.21: n-Stage LFSR PRBS generator [5]

The feedback should be taken from the correct registers, since an incorrect sequence with a length less than the maximum will be generated. The feedback configuration of a LFSR for generating a n stage MLS is given in Table 2.1.

Table 2.1: MLS feedback configuration for LFSR

n	Feedback from stages
2	1, 2
3	2, 3
4	3, 4
5	3, 5
6	5, 6
7	4, 7
8	2, 3, 4, 8 [5]
	4, 5, 6, 8 [16]
9	5, 9
10	7, 10

2.7 Critical overview

Various electrochemical characterisation methods have been utilised to characterise electrochemical systems [8]. One of these methods, namely the CI method, was used to obtain equivalent electrical circuits for other electrochemical cells like batteries [18], and fuel cells [19].

Current interrupt methods for electrical circuit modelling is presented in [20]. An EEC was developed to model the anode, the cathode and the membrane resistance. The EEC consisted of Faradaic resistances, capacitances and the electrolyte resistance.

The equipment needed to perform the CI method was presented in [21]. They developed electronic hardware to interrupt the current at a specific period. They considered the open and closed circuit electrode voltages. They found the current interrupt times to be in the range of 2 μs to 2 s.

Current switching was used to estimate the equivalent electric circuit parameters of a PEM fuel cell [22]. The Randles cell was used to model the fuel cell impedance. A current loading and current interrupt technique were used to estimate the parameters of the Randles cell.

The current interrupt method was implemented, by [23,24], to model the EEC of a fuel cell. The EEC consisted of the membrane resistance and a second order impedance transfer function. The impedance consisted of the membrane resistance, the double layer capacitance, the charge transfer resistance and the Warburg impedance. The experimental setup consisted of the fuel cell, a load resistance and a switch. The switch is controlled by a perturbation signal.

A 5 kHz pulse train was applied to the switch and the resulting current and voltage waveforms were recorded. The membrane resistance was estimated by dividing the change in voltage by the change in current. System identification was used to estimate the parameters of the impedance. A PRBS was used as the perturbation signal. The resulting current and voltage waveforms was used to obtain the parameters of the impedance.

Most of the research regarding electrochemical characterisation methods focused on modelling fuel cells [19, 22–24]. In this study, two variants of the CI method will be considered to model the impedance of a PEM electrolyser through an EEC. Two EECs will be used to model the impedance of the PEM electrolyser.

The first EEC, namely the Randles cell, will be estimated using the NVR method. The voltage response after current interruption, and the value of the current before interruption is analysed to obtain the parameters of the Randles cell. The Randles cell is a basic EEC model and provides information on the activation losses and the ohmic losses of the PEM electrolyser.

It is important to model the concentration losses of the PEM electrolyser, since the electrical losses turn out to be very high in this region. Therefore, the CS method is investigated to model the Randles-Warburg cell. A different approach is followed to model the Randles-Warburg cell. The Randles-Warburg cell will be modelled through a third order impedance transfer function, rather than to model it as the membrane resistance and a second order transfer function. The combination of the NVR and the CS method will be considered to obtain the parameters of the Randles-Warburg cell.