PEM Fuel Cell Diagnostic Tools
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Electrochemical Impedance Spectroscopy

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3.1 Introduction

The need for an efficient, nonpolluting power source for vehicles in urban environments, emphasized by legislative initiatives, has resulted in increased attention to the option of fuel-cell-powered vehicles of high efficiency and low emissions. Recently, fuel cells are also used in a variety of new applications like portable devices (e.g., radio communications, mobiles, laptop, etc.), residential applications (combined heat and power generation), and other transport applications (e.g., submarines, ships, rail-guided vehicles, etc.).

Fuel cells can continuously convert the chemical energy of a fuel (hydrogen, methanol, methane, etc.) and an oxidant into electrical energy at up to 83% efficiency with very low pollutant emissions. Depending on the type of electrolyte used in a fuel cell, one can distinguish the following six main types:

1. Alkaline fuel cell (AFC)
2. Proton exchange membrane fuel cell (PEMFC)—also called polymer electrolyte fuel cell (PEFC) or solid polymer fuel cell (SPFC)
3. Direct methanol fuel cell (DMFC)
4. Phosphoric acid fuel cell (PAFC)
5. Molten carbonate fuel cell (MCFC)
6. Solid oxide fuel cell (SOFC)

The first four types of fuel cells operate at temperatures below 200°C, MCFC and SOFC operate at temperatures higher than 650°C.

In order to increase the reaction area (triple phase boundary) electrodes used in fuel cells are porous electrodes with highly dispersed catalysts grains (agglomerates) linked to an ionic conductor.
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The key technical problems common to all types of fuel cell are the optimal design, stability, and durability of such porous electrodes. Other R&D challenges are the investigation of the reaction mechanism and kinetic at each electrode/electrolyte interface, determination of degradation (poisoning) mechanism, production of cheap and efficient electrodes with low catalyst loading, development of suitable catalysts, long-term stability, and so on. In order to solve these problems, a better understanding of the electrochemical reactions and mass transport in the fuel cell is essential. Moreover, quality control and understanding of degradation require new nondestructive methods and a better understanding of experimental results based on modeling and simulation. However, EIS is such an in situ investigation method that is increasingly applied in fuel cell research and development.

### 3.2 Principle of EIS

Impedance analysis is a very popular, nondestructive measurement technique that provides detailed diagnostic information about a wide range of electrochemical phenomena including charge transfer reaction at the interface electrode/electrolyte, reaction mechanisms, state of charge of batteries, electrode material properties, and state of health of fuel cells, and so on. The technique involves applying a low-level alternative current (AC) waveform to the electrochemical system (half cell, single cell, stack, etc.) under investigation and measuring the response of the cell to this stimulus (the AC voltage across the cell and the AC current through the cell). The impedance of the cell is obtained by taking the ratio of AC voltage/AC current (Figure 3.1). Since a low-level AC voltage or AC current excitation signal (stimulus) is used, no damage or change is suffered by the cell. Typically, a swept frequency sinewave is used as the stimulus so that the impedance can be evaluated across the frequency range of interest, in most cases from 1 mHz to 100 kHz. The AC waveform is usually applied to the cell via a potentiostat that provides signal conditioning, amplification and DC/AC level control so that the programmed voltage or current is correctly applied. Connections are made from the cell to the potentiostat so that the potential across the cell and the current through the cell may be monitored. The potentiostat provides buffering of the voltage input signals (reference inputs) so that voltage measurements may be performed with minimal disturbance to the cell. In addition, the potentiostat provides current to voltage conversion circuitry to convert the AC current passing through the cell into an AC voltage waveform that can be measured by a frequency response analyzer (FRA) to

FIGURE 3.1 Schematic representation of EIS applied to fuel cell characterization.
provide impedance analysis. EIS, initially applied by Graham (1947) and later by Delahay (1965) to study the double layer capacitance and also applied in AC polarography (Schmidt and Stackelberg, 1963) to separate the double-layer charging current and Faradaic current from the total current, is now applied to characterize electrode processes and complex interfaces. The analysis of the system response yields information about the reactivity and structure of the interface, also about the electrochemical reactions and mass transport limitations taking place there. Its importance recently increased due to the modern computer-controlled devices and the corresponding analytical software. Accordingly, the fields of application and therefore the number of publications and recommendable textbooks (Lasia, 1999; Bard and Faulkner, 2001; Wagner, 2005, 2009; Orazem and Tribollet, 2008; Yuan et al., 2010) increased in the last 10 years.

First impedance measurements and interpretation of EIS performed to characterize PEMFC were reported in Srinivasan et al. (1988), Fletcher (1992), Wilson et al. (1993), and Poltarzewski et al. (1992).

3.2.1 Impedance Elements and Equivalent Circuits Used for PEMFC Characterization

During oxidation of the fuel at the anode and reduction of the oxygen at the cathode different chemical and electrochemical reactions can take place in front or on the electrode surface. In addition, concentration gradient or mass transport hindrance has an impact on the fuel cell performance. A schematic representation of the different steps and their location during the electrochemical reactions as a function of distance from the electrode surface is given in Figure 3.2.

Fortunately, these different reaction steps proceed with different time constants ranging from microsecond to month, as schematically shown in Figure 3.3 and described by Wagner and Friedrich (2009).

After transformation of the time constants into the frequency domain the different electrochemical processes can be distinguished from each other. In the high-frequency range of measured EIS at the PEMFC electrolyte ($R_\Omega$) and contact resistances can be determined. At lower frequencies mainly the double-layer charging and charge transfer reactions can be determined and in the lowest frequency range slow processes such as diffusion processes are observed. Given by the different reaction rates of the involved charge transfer reactions hydrogen oxidation and oxygen reduction, as well as the time

![FIGURE 3.2 Schematic representation of the different steps and their location during the electrochemical reactions as a function of distance from the electrode surface.](image-url)
The constant of these reactions, will be different and in most cases are distinguishable from each other as schematically shown in Figure 3.4.

The most common representations of electrochemical impedance spectra are the Bode plots, where the logarithm of impedance magnitude $|Z|$ and the phase-shift ($\alpha$) are plotted versus the logarithm of the frequency ($f$) and Nyquist plots, where the imaginary part of the impedance is plotted versus the real part of the impedance. Both plots are useful. The Bode plot is used when the impedance magnitude covers a large range of sizes. From the shape of the Nyquist plot one can

**FIGURE 3.3** Overview of the wide range of dynamic processes in fuel cells.

**FIGURE 3.4** Bode plot of EIS measured at different current densities, PEMFC operated at 80°C with H$_2$ and O$_2$ at 2 bar.
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distinguish between different diffusion processes and evaluate the deviation of the double-layer capacity from ideal behavior, that is, constant phase element behavior. The electrode/electrolyte interface can be represented by an equivalent circuit which contains various impedance elements representing the involved reaction steps. These elements are generally represented as ohmic, capacitive or inductive components with particular dependencies of their complex impedance upon the frequency of the AC signal. The particular linking of these impedance elements is based on the relationship between the processes represented by these elements. Subsequently occurring steps are represented by a series connection of the elements while steps occurring simultaneously are represented by a connection in parallel. In the case of fuel cells with conversion of chemical energy into electrical energy generally an equivalent consists of the so-called Faradaic impedance $Z_F$ in parallel to a capacitive element $C$ (Figure 3.5).

The simplest electrode/electrolyte interface is the case when the Faradaic impedance can be described by only a charge transfer resistance $R_{ct}$ and the capacitive element is the double-layer capacity $C_{dl}$. The impedance spectrum of such an equivalent circuit is represented in Figure 3.6 as Bode plot and Figure 3.7 as Nyquist plot.

![Figure 3.5](image_url)

**Figure 3.5** Common equivalent circuit describing the frequency response of a fuel cell (left) and simplest case of an equivalent circuit with charge transfer resistance parallel to the double-layer capacity.

![Figure 3.6](image_url)

**Figure 3.6** Bode plot of the impedance spectra simulated in the frequency range from 10 mHz to 10 kHz with the equivalent circuit from Figure 3.5.
From Figure 36 one can estimate the electrolyte resistance and charge transfer resistance. The value of the double-layer capacity can be calculated with the simple equation given below:

\[
2\pi f_{\text{max}} = \left( \frac{1}{R_{\text{el}}C_{\text{dl}}} \right) \left( 1 + \frac{R_{\text{ct}}}{R_{\text{el}}} \right)^{1/2}
\]  

(3.1)

In a similar way one can estimate from the Nyquist plot the electrolyte resistance, the charge transfer resistance is given by the diameter of the semicircle and from \( f_{\text{max}} \) the double-layer capacity \( C_{\text{dl}} \) can be calculated with another simple equation:

\[
2\pi f_{\text{max}}\omega_{\text{max}} = \frac{1}{C_{\text{dl}}R_{\text{ct}}}
\]  

(3.2)

For more complicated processes when the Faradaic impedance consisting of more than only the charge transfer resistance the evaluation of measured EIS is more complicated and is performed via a fit procedure that is usually implemented in the software of commercial available electrochemical workstations. Other processes during fuel cell reactions can be diffusion and adsorption processes. These particular diffusion processes can be described by different impedance elements like Warburg impedance, Nernst impedance, spherical diffusion impedance, and so on. For details see one of the textbooks.

The Faradaic impedance can be described as connections of different impedance elements (Göhr and Schiller, 1986), each of which is associated with a single process. Such an impedance element is the relaxation impedance, describing the surface relaxation of the interface and explains the development of the pseudo-inductive behavior in the low-frequency range (frequency <3 Hz) in the impedance spectra of the fuel cell. This behavior was first found by Müller et al. (1999) during poisoning the anode of a PEMFC.
with a mixture of H₂/CO and will be discussed in detail in Section 3.3.2. The surface relaxation impedance represents a Faradaic impedance ($Z_F$) at nonequilibrium potential with a potential-dependent transfer reaction rate: $k = k(\varepsilon)$ and its time-dependent relaxation according to Equations 3.3 and 3.4:

\[
Z_F = \frac{R_{ct}}{1 + R_{ct}/Z_K} \quad (3.3)
\]

\[
Z_K = \frac{1 + j\omega \tau_K}{I_F \cdot d\ln k/d\varepsilon} \quad (3.4)
\]

In Equation 3.3 $R_{ct}$ denotes the charge transfer resistance, $Z_K$ is defined as the relaxation impedance and is schematically shown as series combination of $R_K$ and $L_K$ as well as the box surrounding $R_{ct}$ in Figure 3.8. According to Equation 3.4, where $I_F$ denotes the Faraday current, $\tau_K$ the time constant of relaxation and the expression of $d\ln k/d\varepsilon$ is the first derivative of the logarithm of the reciprocal relaxation time constant ($k = 1/\tau_K$) against the potential $\varepsilon$. According to its frequency dependence, $Z_K$ can be split up into the relaxation resistance $R_K$ and the relaxation inductivity $X_K$, with the pseudo-inductance $L_K = \tau_K \cdot R_K$, which is proportional to the relaxation time constant $\tau_K$.

\[
R_K = \frac{1}{I_F \cdot d\ln k/d\varepsilon} \quad (3.5)
\]

\[
X_K = j\omega \tau_K \cdot R_K = j\omega \cdot L_K \quad (3.6)
\]

### 3.2.2 Modeling and Theory of Porous Electrodes

Porous electrodes are used in electrocatalysis. In catalysis, generally, there is a great advantage in increasing the real surface area, especially the electrochemical active area of electrodes. First, investigations of porous electrodes with EIS were applied by De Levie (1963, 1964, and 1967), presenting the transmission line model, a model describing the pores of a porous electrode as essentially circular cylindrical channels of uniform diameter of semi-infinite length (Figure 3.9). On the basis of AC impedance measurements, Göhr et al. (1983) and Göhr (1997) investigated porous lead electrodes in sulfuric acid, and proposed another model of the porous electrode represented...
schematically in Figure 3.10. In this model the cylindrical pore was considered as a transmission line made of a large number of infinitesimally thin sections, with impedance elements of pore’s ground surface \( Z_n \), pores electrolyte \( Z_p \), pore’s wall surface \( Z_q \), porous layer \( Z_s \), and surface layer \( Z_o \).

\[
R_{\text{electrode}} = \frac{(R_{\text{por}} \cdot R_{\text{ct}})^{1/2}}{\tanh\left(\frac{R_{\text{por}}}{R_{\text{ct}}} \right)^{1/2}}
\]  

(3.7)

In the case of Göhrs’s model (Figure 3.10) a simple equation (Equation 3.7) for the resistance \( R_{\text{electrode}} \) of the porous electrode can be derived if only the pores electrolyte resistance \( Z_p = R_{\text{por}} \) and from the pore’s wall surface \( Z_q \) the charge transfer resistance \( R_{\text{ct}} \) are considered.

A review, describing gas diffusion electrodes and flooded electrodes is given in Szpak (1991). The great number of very interesting publications, regarding AC impedance measurements on porous electrodes and model electrodes known in the literature, shows the importance and wide applications of the method, from porous layers to fuel cell electrodes. The existing models can be classified into different groups:

- Thin-film model (Will, 1963)
- Surface migration model (Winsel, 1962; Mund, 1975)
- Biporosity model (Grens, 1970; Giordano et al., 1991)
- Flooded agglomerates (Giner and Hunter, 1969; Jaouen et al., 2002)
- Thin film agglomerate model (Raistrick, 1990)
- Cantor block model (Sarangapani et al., 1996; Kötz and Carlen, 2000; Eikerling et al., 2005)
- Triple pore structure (Itagaki et al., 2010)

3.3 Applications of EIS

3.3.1 Steady-State Applications

The most used method to characterize the performance of a fuel cell consists of measuring a steady-state current/potential curve. From such a graph, one obtains information about the entire fuel cell comprising the sum of the electrochemical behavior of the electrode/electrolyte interfaces, conductivity of the electrolyte, the influences of the gas supply and the electrical contacts between the individual components.

In order to determine current/potential curves, one either scans the whole potential range continuously, beginning from the open-circuit potential (OCP) to full load, with a constant voltage scan rate.
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lying between 0.1 and 10 mV s$^{-1}$ and records the resulting current, or one gradually alters the potential and the steady-state current is recorded after reaching a steady state or waiting for a definite time period. Another method to characterize the performance of fuel cells is EIS. In this chapter different applications of the EIS for the characterization of fuel cells will be given.

**Conversion of Resistance to Performance Losses of the Fuel Cell during Operation**

With measurements over the entire performance range of operation one tries to separate the single contributions to the performance loss of a fuel cell during load or even at OCP.

The correlation between impedance measurements and current/potential curve was first described by Wagner (2002) and is given schematically in Figure 3.11.

The DC resistance of the cell measured at $U_n$ corresponds to the tangent to the current/potential curve at that potential. The DC resistance of the cell ($R_{\text{cell}}$) is the impedance at frequencies near 0 Hz where only ohmic parts attract attention. To obtain the DC resistance of the cell, one have to extrapolate the measured data or the simulated impedance (model) at very low frequency (e.g., 1 nHz) or summing up the individual resistances, obtained after fitting the measured spectra with an equivalent circuit.

Assuming that the current/potential curve can be expressed by an Equation 3.8 of second order and the resistance is defined by Equation 3.9, then, the parameters $a_n$, $b_n$, and $c_n$ from Equation 3.4 are given by Equations 3.10 through 3.12.

\[ U_n = a_n I_n^2 + b_n I_n + c_n \]  
\[ R_n = \frac{\partial U}{\partial I} \bigg|_{n} \]  

with

\[ a_n = \frac{R_{n+1} - R_n}{2(I_{n+1} - I_n)} \]  
\[ b_n = R_{n+1} - 2a_n I_{n+1} \]  
\[ c_n = U_{n-1} - a_n I_{n-1}^2 - b_n I_{n-1} \]  

**FIGURE 3.11** Schematic representation of the correlation between DC resistances (anode, cathode, and cell) of fuel cell and measured current/voltage curve.
Over the last 10–15 years a lot of key barriers for the development of PEMFC for terrestrial applications have been successfully overcome. However, there is still need for further research and development effort, an important goal is to increase the efficiency and to produce efficient and cheap electrodes, and membrane-electrode assemblies (MEA) with low noble metal catalyst loading, high CO tolerance, and long lifetime. Actually, the R&D efforts are focused on the development of nanodispersed catalysts, nonnoble metal catalyst, and production techniques, which allow production of MEAs with low noble metal catalyst loading and are suitable for mass production, development of high-temperature membranes to enhance the electrode kinetics and to lower the CO influence (up to 160°C), and integration of the MEA into a fuel cell system with simplified water management, gas conditioner, bipolar plate, fuel storage systems, and so on.

To investigate the physical and electrochemical origins of the performance loss in PEMFCs, operated at different conditions like high-current densities, fuel composition (neat H₂, H₂ + 100 ppm CO, H₂O), flow rates, temperatures, air or pure oxygen, and so on, electrochemical impedance studies on different PEMFC systems with different electrodes and membranes were performed (Wagner, 2005).

Applying a classical three electrode cell with one reference electrode is extremely difficult for the investigation of electrochemical systems with solid electrolytes. However, since the anode and cathode transfer functions at OCP can be determined independently without a reference electrode using a symmetrical gas supply of hydrogen or oxygen at the two electrodes of the cell, cathode impedance at OCP can be determined directly with two independent experiments (Wagner, 2002).

By varying some experimental conditions such as current load (Figures 3.12 and 3.13), temperature, gas composition, hydrogen humidification, and membrane thickness (Andreaus et al., 2002), electrode composition (Wagner et al., 2008) measured cell impedance can be split up into anode impedance, cathode impedance, and electrolyte resistance without using reference electrodes. These results were used to derive appropriate equivalent circuits for the analysis of impedance spectra measured on fuel cells operated with H₂/O₂, H₂/air, and H₂ + 100 ppm CO/O₂. The variation of the experimental conditions is also a useful method to confirm the accuracy of the equivalent circuit.

To identify and separate the different diffusion processes, it is useful to represent the measured impedance spectra in both the Bode and Nyquist diagrams (Figure 3.13). In the Nyquist diagram one...
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... can observe the finite diffusion as an additional loop at the lowest part of the frequency range and the infinite diffusion as a straight line with a slope of 1 (real part = imaginary part). In the Bode diagram (Figure 3.12) the difference between the two kinds of diffusion cannot be seen so clearly due to the logarithmic scale. In general, the Bode plot provides a clearer description of the electrochemical system's frequency-dependent behavior than the Nyquist plot, in which frequency values are implicit.

Starting with EIS measured with symmetrical gas supply, an equivalent circuit for the complete PEMFC can be applied for the simulation of the measured impedance spectra of the PEMFC. Each electrode/electrolyte interface can be represented by an equivalent circuit presented in Figure 3.5. In addition to the charge transfer reaction at higher current densities a diffusion process can be seen.

![Figure 3.13](image-url)  
**FIGURE 3.13** Bode diagram of the measured impedance spectra, PEMFC at 80°C, at different cell voltages: (○) 600 mV and (□) 320 mV.

![Figure 3.14](image-url)  
**FIGURE 3.14** Equivalent circuit (EC) used for the simulation of PEMFC inserted into SEM picture of a PEMFC cross section.
the single fuel cell an equivalent circuit shown in Figure 3.14 was used. Besides a series of resistance (electrolyte or membrane resistance $R_e$), the equivalent circuit contains three time constants of parallel R/C. In the simulation the capacitance (C) was replaced by constant phase element (CPE) due to the porous structure of the electrodes. The cathode can be described using a time constant for the charge transfer through the double layer ($R_{ctC}/CPE_{dlC}$, the exponent of the CPE is around 0.85, for an exponent of 1 the CPE is equal with the capacitance), a time constant for the finite diffusion of water with a Nernst-impedance-like behavior ($R_{NN}/CPE_{NN}$, the exponent of the CPE is around 0.95), and finally the time constant of the anode ($R_{ctA}/CPE_{dlA}$, the exponent of the CPE is around 0.80).

Applying Equations 3.8 through 3.12 and using the current density dependency of the resistances ($R_N, R_{ctA}, R_{dl}$, and $R_{ctC}$) represented in Figure 3.15, gained from the simulation with the equivalent circuit from Figure 3.14 the individual performance losses (overpotentials) can be determined (Figure 3.16).

At low-current densities the cell overpotential is given mainly by the cathodic overpotential. At higher current densities ($i > 400$ mA cm$^{-2}$) an additional diffusion overpotential becomes noticeable. The increase in the anodic overpotential with increasing current density can be explained by assuming a partially dry out of the interface membrane/anode with simultaneous increasing of the water content.

**FIGURE 3.15** Current density dependency of the resistances after evaluation of the impedance spectra evaluated with EC from Figure 3.14.

**FIGURE 3.16** Individual performance losses of the PEMFC at 80°C in function of current density, calculated by integration of the individual resistances at different current densities.
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depending electrolyte resistance inside the pore \( Z_p = R_{pore} \) — applicable only in the case of impregnated electrodes or electrodes with electrolyte powder inside (see Section 3.3.1.1) the electrode and can be minimized by appropriate water management. Therefore, a further refinement of the equivalent circuit is useful and can be made if one uses the porous electrode model.

### 3.3.1.1 Influence of MEA Composition

In order to optimize the electrode composition and performance of PEMFC and to reduce the production cost of MEAs, different MEAs using different catalyst powders, carbon-supported and unsupported catalysts with different proton conducting solid electrolyte powder (Nafion) contents were produced by using a dry powder spraying technique (Gülzow et al., 1999, 2000). The electrochemical characterization was performed by recording current–voltage curves and electrochemical impedance spectra in a galvanostatic mode of operation at 500 mA cm\(^{-2}\). The evaluation of the measured impedance spectra (Figure 3.17) using the porous electrode model (Figure 3.10) for each electrode shows that the cathode of the fuel cell is very sensitive to the electrode composition whereas the contribution of the anode is very small and invariant to the electrode composition. Furthermore, it could be shown that using electrolyte powder in the electrodes the charge transfer of the cathode decreasing monotonically with increasing electrolyte content in the cathode. These findings suggest that with increasing electrolyte content in the electrodes, in particular in the cathode, the utilization degree of the catalyst increases linearly with increasing electrolyte content in the electrode (Wagner et al., 2008). Taking into account the change of the catalyst loading with electrode composition and normalizing the charge transfer resistance per unit weight catalyst content \( R_{\text{cath, norm}} \), one can find a very distinct correlation between cell performance and electrode composition. This correlation is shown in Figure 3.18. If one takes into account only the results from MEAs with Nafion one can find even a linear correlation of the cathode

![Figure 3.17](image-url)  
**FIGURE 3.17**  Impedance spectra (Bode plot) of a MEA produced with different carbon-supported Pt catalyst (20% Pt/C, 60% Pt/C, and Pt black 100%), without electrolyte in the electrode, operated with H\(_2\)/air at 500 mA cm\(^{-2}\).
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charge transfer resistance with Nafion content in the electrode (Figure 3.19). These results show for the first time such an explicit behavior and correlation of cell performance and electrode composition.

### 3.3.1.2 Influence of Cathodic Gas Composition

One of the major sources of performance loss during operation of fuel cells is the slow kinetics of the oxygen reduction reaction (ORR). Therefore, many investigations were performed to understand the

---

**FIGURE 3.18** Dependency of the cathodic charge transfer resistance $R_{\text{cath}}$ and normalized cathodic charge transfer resistance $R_{\text{cath,norm}}$ from the catalyst layer composition after evaluation of the EIS measured at different MEAs, operated with H$_2$/air at 500 mA cm$^{-2}$.

---

**FIGURE 3.19** Cathodic charge transfer resistance $R_{\text{cath}}$ and normalized cathodic charge transfer resistance $R_{\text{cath,norm}}$ in function of the catalyst layer composition after evaluation of the EIS measured at different MEAs with Nafion, operated with H$_2$/air at 500 mA cm$^{-2}$.
 reaction mechanism of the ORR. During operation of the cell with air instead of pure oxygen one can find two sources of performance loss at the cathode:

- Decreasing of charge transfer reaction rate with decreasing partial pressure of oxygen corresponding to an increase in the charge transfer resistance ($R_{ct,C}$)
- Appearance of an additional diffusion impedance term in the low-frequency range of the impedance spectra, for example, at 3 Hz in Figure 3.20

For different fuel cell applications like mobile applications the use of air instead of pure oxygen should be reasonable. For space applications or high-power density applications pure oxygen should be used.

In addition, by changing the cathodic gas composition during galvanostatic mode of fuel cell operation one can distinguish and validate the different contributions to the overall cell impedance.

In Figures 3.21 and 3.22, two EIS spectra measured at the same current are shown. The used MEA was N111 IP from Ion Power Inc., operated with 2.7-fold ($\lambda$) oxygen and air, respectively. Given by the high gas flow rate in the case of operation with air, one can recognize in the high-frequency range of the EIS an increase of the membrane resistance determined by an improper humidification of the cathode. Under such operation conditions the cell performance decreases and one would expect a limited durability of the cell.

### 3.3.2 Time-Resolved Electrochemical Impedance Spectroscopy

A prerequisite for the development and the improvement of fuel cells is the knowledge of the mechanistic processes that take place during operation. The understanding of the kinetic behavior of the fuel cells requires the variation of different experimental parameters. Often, the variation of distinct parameters causes situations where steady-state conditions are no longer fulfilled. In practice, EIS analysis often suffers from the fact that the steady-state condition is violated due to time instability of the examined...
systems. While an EIS measurement is running, the examined system should not change its dynamic behavior. Unfortunately, the violation of steady-state conditions complicates the evaluation of experimentally obtained impedance spectra because all relevant physical models for the interpretation of the data are based on steady-state conditions. The time- and frequency-dependent relationship between current and voltage of an electrochemical system is often called “two-pole impedance transfer function” (TTF). All properties, which are influencing the current–voltage dependence, must be stable in this time interval. Otherwise, the TTF will be falsified in a way that is equivalent to a violation of causality.
Nevertheless, it is possible to investigate such “drifting” systems and to obtain relevant data for the development of fuel cells using EIS. Enhanced numerical procedures like real-time-drift compensation, time-course interpolation and causal transfer functions are required to compensate or to eliminate the drift effects of systems with states that change with time.

**Real-time-drift compensation:** During recording an impedance spectrum a potential drift due to change of the state of the system can occur. The magnitude of drift is frequency dependent and should be compensated by the software during the measurement.

**Time-course interpolation:** Recording an impedance spectrum one frequency after another requires a finite time, while the measurement at high frequencies requires less time than the measurement at low frequencies. As a consequence, the system at the start is in a different state from at the end if the system changes the state during the impedance measurement.

It is impossible to eliminate the drift that is caused by the finite measuring time, performing only a single spectrum. Especially the data recorded at low frequencies are affected and a mathematical procedure has to be applied to check the data with respect to causality and linearity (Z-HIT) to avoid erroneous interpretations resulting from a fit of the drift-affected data.

According to the idea of Savova-Stoynov (Savova-Stoynov and Stoynov, 1985, 1992; Stoynov, 1990), recording a series of impedance measurements at distinct time intervals offers the possibility to eliminate the drift and therefore to reconstruct an impedance spectrum which is acquired in an “infinite” short time. Additionally, the elapsed time of the experiment is involved as a third parameter. As mentioned above, the measurement at lower frequencies requires a longer time for the registration and therefore, the measured curve is shifted to the back along the time axes. It should be noted, that the absolute value of the shift is frequency dependent because the acquisition time for each measured frequency is different. For the lowest frequency, a single impedance spectrum can be reconstructed by interpolating the impedance value from the time course of the series using an appropriate smoothing function at the time of the start of this distinct measurement. The interpolation procedure is repeated for each measured frequency resulting in a data set where the effect of finite measurement time is significantly reduced or even eliminated for each recorded spectrum of the series.

**Causal transfer functions:** Causality in the meaning of system theory forces couplings between the real and imaginary part, which are known as Kramers–Kronig relations (KKT) or Hilbert relations (HT).

These relations offer the possibility to examine measured transfer functions (impedance spectra) on errors caused by time instability or time drift. KK-checking techniques have fundamental problems in the application in practical measurements. Therefore, many attempts have been made to overcome these limitations by means of different interpolation procedures. An attempt is the Z-HIT (Agarwal et al., 1995; Ehm et al., 2000; Schiller et al., 2001) approximation, an approximation formula for the calculation of the impedance modulus course from the phase angle by integration.

During operation of fuel cells different time-dependent effects can occur, depending on the type of fuel cell and experimental conditions such as gas flow rates (flooding of the electrode, changing of the gas composition), temperature (corrosion or sintering), impurities in the hydrogen (CO) leading to poisoning of the anode in the case of PEMFCs, and degradation of the electrodes during long time of operation, and so on.

One has to assume that the system changes its state not only between two measurements but also during the recording of a single spectrum. The latter fact causes problems for the evaluation of the spectrum, because the recording of an impedance spectrum one frequency after another requires a finite time, while the measurement at high frequencies requires less time than the measurement at low frequencies. Due to the fact that the recording of a single spectrum in the frequency range, for example, from 10 kHz to 50 mHz requires about 20 min, the influence of the changed state on the measured spectrum is not negligible. For this reason, one of the fundamental prerequisites for the evaluation of impedance measurements is violated. Nevertheless, it is possible, to reconstruct “quasi steady state” (and therefore “quasi causal”) spectra from drift affected impedance data using improved evaluation techniques which are denoted as the real-time-drift compensation, the time-course interpolation, and the
Z-HIT refinement. These techniques were applied successfully to the interpretation of time-dependent impedance spectra of a fuel cell which exhibits nonsteady-state behavior.

Applying all three techniques to time-drifting systems, quasi steady-state impedance spectra, TREIS, at defined times can be obtained.

### 3.3.2.1 EIS during CO Poisoning of PEMFC Pt and Pt/Ru Anodes

Owing to the high-energy conversion rate and the harmless emission products, PEMFCs receive more and more attention especially in the case for powering electric vehicles. The highest performance is achieved with hydrogen (H₂) which is the preferred fuel for low-temperature fuel cells and pure oxygen. However, H₂ has several limitations. The storage systems for liquid or compressed H₂ are heavy and bulky. Furthermore, H₂ refuelling is costly and takes time. An additional obstacle is actually the lack of an infrastructure to distribute H₂ to the consumer (Cleghorn et al., 1997).

An alternative to the use of H₂ as fuel are methanol or hydrocarbons (e.g., natural gas, biogas) that can be transformed to hydrogen on board of the electric vehicle by a reformation reaction (Figure 3.23). This allows using the H₂-PEMFC cell which has a higher level of development. The reformate feed gas may contain up to 2.5% carbon monoxide (CO) by volume, which can be reduced to about 50 ppm CO using a selective oxidizer (Wilkinson and Thompsett, 1997).

The performance of platinum which is known as one of the most effective catalysts for the hydrogen oxidation in PEMFCs is influenced even by traces of CO. Compared with the use of pure hydrogen, the maximum power density is more than halved in the presence of only 5 ppm CO. One possible explanation for the decrease of the fuel cell performance is that the CO blocks or limits the active sites of the platinum catalyst due to adsorption which leads to an inhibition of the hydrogen oxidation reaction. In the last two decades, intensive work has been devoted to find electrocatalysts that are tolerant to CO in

![Fuel processing schematic](image_url)
hydrogen at operating temperatures below 100°C. This system has been the object to numerous studies using electrochemical methods like potentiostatic measurement, potentiodynamic measurement, and stripping voltammetry. Detailed kinetic studies were given in Vogel et al. (1975), Schmidt et al. (1998), and Koper et al. (2001).

First in situ impedance measurements were reported by Müller et al. (1999), who demonstrated the time dependence of impedance spectra in galvanostatic conditions for CO poisoning Pt anodes. Other publications, with detailed kinetic data were published later (Ciureanu and Wang, 1999, 2000; Kim et al., 2001; Wang et al., 2001; Leng et al., 2002; Wagner and Gülzow, 2004).

For the development of improved electrocatalysts that are less sensitive with respect to the presence of CO, a mechanistically understanding of the poisoning process of the anode is desirable. The progressive poisoning with CO of a fuel cell can be monitored using TREIS.

As shown in detail (Wagner and Schulze, 2003), the CO poisoning of the Pt- and PtRu-anode during galvanostatic mode of operation with H₂ + 100 ppm CO causes a change in the state of the fuel cell that is reflected by the decrease in the cell voltage during operation (Figure 3.24) and by time dependency on the recorded impedance spectra. Besides, an increase of the total impedance of the fuel cell, in the case of galvanostatic mode of operation, the occurrence and the increase of a pseudo-inductive behavior at frequencies lower than 3 Hz is observed. It is useful to operate the fuel cell in the galvanostatic mode of operation because at a constant current density, the impedance of the cathode and the membrane resistance can be assumed to be constant during the course of impedance measurements and the changes in the impedance spectra during poisoning the anode with CO can be attributed exclusively to the impedance of the anode.

Representative time-dependent impedance spectra of the series, that is, time-resolved impedance spectra are depicted in Figure 3.25 for the fuel cell with Pt anode as Nyquist plots whereby the experimental data are represented by dots and the solid lines in the Figure represents the modeled curves after fitting the experimental data with the equivalent circuit from Figure 3.26. For the PtRu, similar time-dependent impedance spectra were measured.

In series to both half cells, the resistance of the membrane itself—denoted as the electrolyte resistance (Rₑ)—as well as a parasitic wiring inductance (Lₑ) due to the mutual induction effect has to be taken into account. The impedance of the cathodic half cell (oxygen reduction) is approximated using a charge transfer resistance (Rₑ,c) in parallel to a constant phase element (CPE c). This simple equivalent circuit describes the partial impedance of the cathodic half-cell with sufficient accuracy. In contrast, the impedance of the anode (hydrogen oxidation) is more complicated due to the CO poisoning and appearance

![Figure 3.24](https://example.com/figure324.png)

**FIGURE 3.24** Evolution of cell voltage during CO poisoning of Pt/C (●) and PtRu/C (□) anodes in galvanostatic mode of fuel cell operation at 217 mA cm⁻² (5 A), 80°C.
of an inductive loop in the low-frequency range of the impedance spectra. The impedance of the anode is modeled using a porous electrode (PE) in series to a double-layer capacity ($C_{dl,A}$) which is in parallel to the Faradaic impedance ($Z_F$) that contains a surface relaxation impedance ($Z_K$) parallel to the charge transfer resistance ($R_{ct,A}$) in series with a finite diffusion impedance element (Nernst-impedance, $Z_N$) so that the expression for the Faradaic impedance from Equation 3.3 was extended and is given by

$$Z_F = \frac{R_{ct} + Z_N}{1 + R_{ct}/Z_K}$$  \hspace{1cm} (3.13)

On the basis of this model and equivalent circuit shown in Figure 3.26, the changes and differences, depending on the anode used in the fuel cell (Pt/C or PtRu/C) in the impedance spectra during the

**FIGURE 3.25** Nyquist plot of EIS measured at: (1) 0 s, (2) 3601 s, (3) 5402 s, (4) 7204 s, (5) 9605 s, and (6) 11,404 s during CO poisoning of Pt/C anode during galvanostatic mode of operation with $H_2 + 100$ ppm CO (anode), at 5 A (cell surface = 23 cm$^2$), 80°C, and oxygen (cathode).

**FIGURE 3.26** Equivalent circuit used for evaluation of interpolated (time-dependent) EIS measured during hydrogen oxidation and CO poisoning of the anode and oxygen reduction at the fuel cell cathode in galvanostatic mode of cell operation.
experiment are dominated by the changes of the charge transfer resistance of the anode \( R_{\text{ct,A}} \), the surface relaxation impedance \( R_K, \tau_K \) and the finite diffusion impedance \( Z_N \).

The time evolution of the charge transfer resistance of the anodes is shown in Figure 3.27 (Pt/C anode (●) and PtRu/C anode (□) as a function of the elapsed time). The Warburg parameter from the Nernst impedance \( Z_N \) represented in Figure 3.28 shows the greatest difference between the two anodes. The Nernst impedance \( Z_N \) contains two parameters: the Warburg parameter \( W \) and a diffusion time constant \( k_N \), determined by the constant of diffusion \( D_k \) and diffusion layer thickness \( d_N \). The Nernst impedance is calculated by Equations 3.14 and 3.15 and with Equation 3.16, one can calculate the Nernst resistance \( R_N \):

\[
Z_N = \frac{W}{\sqrt{j\omega}} \tanh \left( \frac{j\omega}{k_N} \right)
\]  

with

\[
R_N = \frac{w}{\sqrt{K_N}}
\]

\[
k_N = D_k / d_N^2
\]  

FIGURE 3.27 Time elapsed of the charge transfer resistance of the (●) Pt/C and (□) PtRu/C anodes after evaluation of the time-dependent impedance spectra with the equivalent from Figure 3.26.

FIGURE 3.28 Time elapsed of the Warburg parameter \( W \) from the Nernst impedance for the (●) Pt/C and (□) PtRu/C anodes after evaluation of the time-dependent impedance spectra with the equivalent from Figure 3.26.
3.3.2.2 EIS during the PEMFC Pt-Cathode Flooding

One of the major issues during PEMFC operation is the water management. Despite a proper humidification of the cell, often a drying out or flooding of the cell can occur. A drying out of the cell induces not only an increase in the membrane resistance because the proton conductivity strongly depends on the water content in the membrane but also has a major impact on the degree of reaction zone (triple phase boundary) especially in the case of electrodes impregnated with electrolyte suspension or electrolyte in form of electrolyte powder to increase the triple phase boundary. The other extreme condition during fuel cell operation is the case of flooding of the pores of the electrode with water. This water can result from improper humidification of the electrodes if the relative humidification is more than 100% or if the electrode surface is too hydrophilic and water is accumulated in the pores flooding the electrode. To examine the flooding of the cathode, a PEMFC was operated for 8 h with the cathode in the “dead end” mode of operation at 2 A, 80°C, oxygen and hydrogen at 2 bar. In the “dead end” mode of operation the outlet valve of the cathode was closed so that the formed water could not flow out of the cell. During the time-dependent flooding of the electrode also time-dependent impedance spectra were recorded (Figures 3.29 and 3.30). After time interpolation of the measured impedance spectra they were evaluated with the equivalent circuit described previously. In Figure 3.31, one can observe an increase in the charge transfer resistance of the cathode caused by the flooding of the electrode and a decrease of the active electrode surface. Also from Figure 3.32 an increase of the diffusion hindrance with operational time during the cathode flooding is observed.

During flooding of the cathode, a part of the catalyst can be dissolved and under certain conditions the catalyst can be deposited at other parts of the electrode, for example, in the gas diffusion layer. This loss of catalyst has an important impact on the cell durability and should be avoided during fuel cell operation.

3.3.2.3 EIS during Long-Term Operation (Degradation) of PEMFCs

One of the major key problems to be solved for the application of fuel cells is the long-term behavior and durability. To improve the durability one has to know and understand first the degradation mechanism.

![FIGURE 3.29 Bode representation of EIS (impedance vs. frequency) during flooding the cathode 400 min with water at 2 A, dead end.](image-url)
To investigate in detail the degradation mechanism of the electrodes in a PEM single cell, a MEA was operated over 1000 h galvanostatically at a current density of 500 mA cm$^{-2}$. At different times during operation several EIS measurements were performed without interrupting the fuel cell operation. The corresponding measurement time is indicated by arrows in Figure 3.33. As shown in Figure 3.33, after an operation time of 1000 h an additional nearly linear time-dependent voltage loss of about 140 mV

**FIGURE 3.30** Bode representation of EIS (phase shift vs. frequency) during flooding the cathode 400 min with water at 2 A, dead end.

**FIGURE 3.31** Time dependency of the charge transfer resistance of the cathode during flooding with water at 2 A, dead end.
could be observed, corresponding to a voltage loss (degradation) rate of 140 \( \mu \text{V h}^{-1} \) equivalent to a power density loss rate of 70 \( \mu \text{W h}^{-1} \text{ cm}^{-2} \). The measured data represented in the Bode diagram (Figure 3.34) as symbols and the modeled curves as lines also show a strong time dependency. A linear increase in the impedance with operating time, especially in the higher frequency range (1–20 kHz) of the impedance spectra could be observed.

After a complete shut down of the cell after an operating time of 1000 h and restarting the cell after 24 h at OCV, the cell showed nearly the same performance as at the beginning of the longtime test and the impedance spectra recorded directly after the restart shows similar values to the impedance spectra recorded at the beginning of the lifetime test.

For the evaluation of the measured spectra the same equivalent circuit as shown in Figure 3.14 was used. Besides a series resistance (membrane resistance \( R_M \)), the equivalent circuit contains three time
constants of parallel R/C. In the equivalent circuit $R_{ct(A)}$ and $R_{ct(C)}$ are related to charge transfer resistance on the anode and on the cathode, the capacitances $C_{dl(A)}$ and $C_{dl(C)}$ are related to the double-layer capacity of both electrodes. The diffusion processes will be simulated also by an RC-element ($R_N$ and $C_N$) and the membrane resistance by $R_M$. In the simulation, the capacitance ($C$) was replaced by CPE due to the porous structure of the electrodes. The cathode can be described using two time constants, one for the charge transfer through the double layer ($R_{ct(C)}/CPE_{dl(C)}$, the exponent of the CPE is around 0.85, for an exponent of 1 the CPE is equal with the capacitance) and one for the finite diffusion of water with a Nernst-impedance-like behavior ($R_{N}/CPE_{N}$, the exponent of the CPE is around 0.95). The time constant of the anode ($R_{ct(A)}/CPE_{dl(A)}$, the exponent of the CPE is around 0.80) is given by the charge transfer through the anode double layer.

The resistance of the membrane $R_M = 5.65 \pm 0.10$ mΩ and the resistance related to the diffusion $R_N = 2.50 \pm 0.5$ mΩ were both nearly constant during the whole experiment.

The most time-sensitive impedance elements are the charge transfer resistance of the anode $R_{ct(A)}$ and the charge transfer resistance of the cathode $R_{ct(C)}$. The time dependence of $R_{ct(A)}$ is shown in Figure 3.35. The contribution of $R_{ct(A)}$ to the overall cell impedance increased at the beginning of the experiment from 2.5 to nearly 9 mΩ after 1000 h of operation. After a new start-up of the cell, the resistance reached nearly at the same value (3.0 mΩ) as at the beginning of the experiment.

The time dependence of $R_{ct(C)}$ is shown in Figure 3.36. The contribution of $R_{ct(C)}$ to the overall cell impedance increased at the beginning of the experiment from 10.5 to nearly 16 mΩ after 1000 h of operation. After the new start-up of the cell, the charge transfer resistance of the cathode decreased at a value of 14 mΩ, thus the reversible part, defined as the difference between the value after 1000 h of operation (16 mΩ) and the value after start-up (14 mΩ) is 2 mΩ. The irreversible part is defined as the difference between the value after start-up and the value at the beginning of the long-term operation (10.5 mΩ).

Taking into account that the surface area of the cell is 23 cm² and the current density is 0.5 A cm⁻², we obtain the total current of 11.5 A. Using Ohm's law and the exact resistance values from Figures 3.35 and 3.36, we are able to calculate and to separate the voltage losses of the cell during long-term operation.
into reversible and irreversible voltage losses and furthermore into contributions of the anode and cathode. The result of the separation into different voltage losses is shown in Figure 3.37.

From this we can calculate that total voltage loss of the cell during 1000 h of operation is 137.4 mV. The greatest part of the voltage loss is a reversible loss (88.8 mV) and 48.6 mV is an irreversible voltage loss. The voltage loss related to the anode can be revoked and the irreversible part of voltage loss is small at the anode (5.4 mV) compared to the irreversible voltage loss at the cathode (43.2 mV).

In addition to EIS surface science investigations were performed that allow one to identify the degradation processes. Two different degradation processes were identified: the agglomeration of the platinum catalyst mainly in the cathode and the disintegration of the PTFE and the correlated decrease of the hydrophobic degree. The loss of the hydrophobicity is more significant on the anode than on the cathode (Schulze et al., 2007).

The irreversible degradation is probably attributable to a catalyst structure change that is detected by surface analytical methods. The platinum catalyst agglomerates during fuel cell operation. As a consequence the active surface of the catalyst in the cathode decreases and the electrochemical performance decreases concurrently. In contrast to the decrease of the hydrophobicity the loss of active surface area cannot be compensated by modification of the operation conditions. This degradation is therefore an irreversible process. Under extreme operation conditions when the electrodes are flooded with water the platinum can move across the gas diffusion layer. This indicates that the mobility of the platinum is related to a liquid water phase.

**FIGURE 3.35** Time dependence of charge transfer resistance of the anode $R_{ct,A}\text{.}$

**FIGURE 3.36** Time dependence of charge transfer resistance of the cathode $R_{ct,C}\text{.}$
The reversible degradation is related to the decomposition of the PTFE and, respectively, the decrease in the hydrophobicity and the correlated alteration of the water balance. This degradation process will mainly affect the performance of the anodes. So the electrochemical performance increases after an interruption of operation and drying of the fuel cell. The changed hydrophobicity or the related alteration of the PTFE yields a decrease of the electrochemical performance that can be compensated by modification of the water balance; for example, the water balance can be modified by adding purging intervals and adapting the periods between purging and the length of the purging intervals.

The quantification of the effects of both degradation processes has shown that the reversible degradation processes are more significant than the irreversible processes. Therefore, it is very important for long-term experiments and for the long-term stability to take the experimental conditions into account that are used to determine degradation values, especially if the experimental setup eliminates the effect of the reversible degradation process.

3.3.3 Locally Resolved Applications: EIS Using Segmented Cells

To achieve optimum performance and long lifetime of fuel cells for commercial use, a homogeneous electrochemical activity over the electrode area is obligatory. Inhomogeneous current distribution causes low reactant and catalyst utilization as well as reduced efficiency, fast degradation, and low durability. Therefore, the knowledge of the current density distribution is essential for the development of MEAs and stack design as well as for the adaptation of the operation conditions in fuel cells.

In the following, two tools for locally resolved electrochemical measurements is described. The first technique is based on individual segments that are externally connected with resistances for the current measurements in each segment. A photograph and a schematic diagram of this approach are shown in Figure 3.38, respectively. The cell shown in Figure 3.38 has an active are of $5 \times 5$ cm$^2$ and 16 segments. All segments are isolated with PTFE among each other and the frame. Each segment is connected by a resistance to the current collector.
All segments must be positioned individually. In order to fit the surface of all segments in the same plane on the backside of the segments an elastic plate is used. If the elastic plate is too soft it is not possible to apply a high contact pressure from the flow field onto the GDL, which can result in high electrical contact resistance. As a result, the variation of the contact resistances for the individual segments with the GDL can be high. If the elastic plate is too hard, the segments will not be assembled in the same plane, and consequently the contact pressures and contact resistances for the individual segments with the GDL can vary as well. Therefore, it is necessary to choose the elastic material according to the specific MEA and GDL. In addition, the segments have to be manufactured very precisely in order to minimize the in plane positioning problem. Therefore, this approach to locally resolved measurements is time intensive and cost intensive.

An additional problem of the individual positioning of the segments is that a complex flow field increases the experimental problems. Therefore, a chocolate wafer structure with perpendicular channels of 1 mm depth and 1 mm width is used. Typically, the segmented side is used as anode because in a hydrogen-supplied fuel cell the effect of the transport processes on the anode side has a lower influence on the cell performance compared to the cathode. Alternately, a segmented cathode side is used with pure oxygen in order to investigate the anode flow fields. Caused by the external connection of the segments and the thickness of this measurement device, the technique is only suitable for single cells or at outer cells in short stacks.

An advantage of this approach is that each segment can be operated as an individual cell, whereas all cells are parallely connected by the in-plane conductivity of the GDL. This tool can not only be used to measure current density distribution but also to impress a current density onto the cell by using individual loads. The current generated in a certain region of the MEA flows through the corresponding segment and a small series resistance. Its voltage drop along the 16 resistances is scanned and the resulting current distribution density is registered. Exemplary, the change in current distribution as a result of cathode flooding in a PEMFC is shown in Figure 3.39. This routinely used tool helps to detect unfavorable operating conditions, to avoid damage of the PEMFC due to hot spots in the MEA and finally to improve gas distributor structures.

Using the segmented cell from Figure 3.38 locally resolved impedance measurements were performed. Depending on the problem to be solved different cells should be operated under the relevant conditions. In Figures 3.40 and 3.41, the locally resolved impedance spectra measured at open cell voltage are shown. Similar measurements with segmented cells are reported by Schneider et al. (2009).
**FIGURE 3.39** Change in distribution of current density while flooding the cathode of a PEMFC operating in dead-end mode.

**FIGURE 3.40** Bode plot (impedance vs. frequency) of EIS measured with the segmented cell.
3.4 Recent Advances of EIS Technique: Applications of EIS for PEMFC Stack Characterization

There is a great interest in characterizing and monitoring fuel cell stacks during operation. Fuel cell stacks have a higher power output than single cells and therefore the hardware used for electrochemical characterization should be able to handle high currents and high voltages. At the moment only a few labs worldwide are able to measure impedance spectra at a stack level.

Given by the serial connection of single cells in the case of fuel cell stack it is very important to monitor the individual cell voltage. The failure of one cell can damage the complete stack. Therefore, we build a test rig (Figure 3.42) with four electronic loads: three work as slaw consuming only power and the fourth as the measuring unit.

To reduce the measuring time of the stack a new electrochemical workstation is used with 16 parallel impedance channels so that 16 cells of the stack can be measured simultaneously. These measurements are performed in a galvanostatic operation mode of the stack. The AC current excitation signal is applied over the whole fuel cell stack and the AC response voltage is collected at the corresponding single cell of the stack. This technique is a great improvement compared to the sequential multiplexer technique.

3.5 Concluding Remarks

EIS is a very powerful method for the characterization of fuel cells and stacks. It is the most used, in situ nondestructive steady-state measurement technique that provides detailed diagnostic information over a wide range of electrochemical phenomena occurring during PEMFC operation. EIS can be applied for in situ failure analysis using a more or less complex equivalent circuit, as shown in detail in this chapter. There are a great number of advantages using EIS but also some limitations of the method. Given by the high currents flowing through a large cell and low impedance in the high-frequency range of the spectra some artifacts restrict the application to fuel cells with large surface. This restriction can be overcome.
Electrochemical Impedance Spectroscopy

by twisting the cell connectors or by using in addition the current interrupt method to extend the high-frequency range of EIS. EIS is well established for single fuel cell and cell components characterization. In the near future, EIS is expected to be used for monitoring PEMFC stacks and individual cells of the stack during operation.

References


