Chapter 2

Instruments and Experimental procedures
2.1 Scanning electron microscopy (SEM)

The scanning electron microscopy was used to determine the average crystallite size and the surface morphology of the solar cells. It gives information about the grain evolution and grain size in the solar cells. It also gives information about intergranular pores and their distribution of grains in the bulk samples. Figure 2.1 shows the schematic ray diagram of Scanning electron microscope. In this instrument, electrons emitted due to thermionic emission from a filament are accelerated using high accelerating potential typically between 0-50 kV and focused using magnetic field and electric field as fine beam. This focused beam is used to irradiate the sample. The secondary electrons emitted from the sample, are detected using a detector placed at a certain angle with respect to the sample.

Figure 2.1 The schematic ray diagram of Scanning electron microscope

The secondary electrons, backscattered electrons, auger electrons, characteristic X-rays and several other radiations are released from the specimen. Generally, the secondary electrons are collected by detector, originating from the subsurface depth having range of several angstroms. To avoid the charging effect due to the insulating behaviour of the samples, they were coated
with a conducting layer of gold, thickness of about 100 Å by using the DC magnetron sputtering.

2.2 Impedance Spectroscopy

In impedance spectroscopy measurements, the cell is perturbed with an alternating signal of small magnitude and the way in which the system follows the perturbation at steady state is observed.\(^{105-117}\) There are many advantages associated with this technique, among which the most important are (a) an experimental ability to make high-precision measurements because the response may be indefinitely steady and can therefore be averaged over a long term, (b) an ability to treat the response theoretically by linearized (or otherwise simplified) current-potential characteristics, and (c) measurement over a wide time (or frequency) range (\(10^4\) to \(10^6\) s or \(10^4\) to \(10^6\) Hz). Since one usually works close to equilibrium, one often does not require detailed knowledge about the behavior of the \(i-E\) response curve over great ranges of overpotential.

![Figure 2.2 Schematic representation of electrochemical workstation used for EIS of supercapacitors](image)

EIS normally involve excitation signals, \(E_{ac}\), of very low amplitude, and they depend essentially on the fact that current-overpotential relations are virtually linear at low overpotentials.\(^{118-122}\) In a linear system, excitation at frequency \(\omega\) provides a current also of frequency \(\omega\) (and only of frequency \(\omega\)). On the other hand, a nonlinear \(i-E\) relation gives a distorted response that is not purely sinusoidal; but it is still periodic and can be represented as a superposition of signals at frequencies \(\omega, 2\omega, 3\omega, \) etc. The current overpotential function for an electrode reaction is nonlinear over moderate ranges of overpotential, and the effects of this nonlinearity can be observed and put to use.\(^{123-126}\)
2.2.1 Response of electrical circuits

The application of an electrical perturbation i.e. current or potential to an electrical circuit causes the appearance of a response. Let us begin with the notion of an ideal resistor having resistance $R$. According to Ohm’s law, current ($I$) flowing through the resistor and voltage ($V$) across the two terminals of the resistor is expressed by the following relation:

$$V = IR$$

(2.1)

However, impedance is a more general concept than resistance because it involves phase difference.\(^{124}\) The ratio of the Laplace transforms of potential and current is expressed in the units of resistance and is called impedance. During impedance measurement, a small-amplitude modulated voltage $V(\omega, t)$ is applied over a wide range of frequency ($f = \omega/2\pi$) and the corresponding currents $I(\omega, t)$ are recorded, or vice versa. The resultant impedance $Z(\omega)$ of the system is calculated as\(^{127, 128}\)

$$Z(\omega) = \frac{V(\omega, t)}{I(\omega, t)}$$

(2.2)

provided that $I(\omega, t)$ is small enough to be linear with respect to $V(\omega, t)$, or vice versa. At a certain frequency $\omega$, $V(\omega, t)$ may have different amplitude and phase than that of $I(\omega, t)$ depending on the nature of the charge transfer and storage processes in the system. When the frequency of the applied perturbation is very low, the system is said to be driven with DC current and the impedance of the system coincides with its DC resistance ($R_{dc}$), that is, impedance with zero phase difference:\(^{128}\)

$$Z(0) = \frac{V(0)}{I(0)} = R_{dc}$$

(2.3)

It is to be noted here that there are other response quantities related to impedance such as admittance ($Y$), modulus function ($M$), and complex dielectric constant or dielectric permittivity ($\varepsilon$).\(^{128, 129}\) Switching the data between different representations is a very useful tool of analysis in EIS and the most frequently used functions are described in Table 2.1.

30
Table 2.1 Impedance representations

<table>
<thead>
<tr>
<th>Denomination</th>
<th>Definition</th>
<th>Real and imaginary parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impedance</td>
<td>$Z(\omega)$</td>
<td>$Z = Z' + iZ''$</td>
</tr>
<tr>
<td>Admittance</td>
<td>$Y(\omega) = 1/Z(\omega)$</td>
<td>$Y = Y' + iY''$</td>
</tr>
<tr>
<td>Phase angle</td>
<td>$\tan \delta = Z'' / Z'$</td>
<td></td>
</tr>
<tr>
<td>Complex capacitance</td>
<td>$C^*(\omega) = 1/i\omega Z(\omega)$</td>
<td>$C^* = C' + iC''$</td>
</tr>
<tr>
<td>Conductivity</td>
<td>$\sigma^*(\omega)$</td>
<td>$\sigma^* = \sigma' + i\sigma''$</td>
</tr>
<tr>
<td>Complex dielectric constant</td>
<td>$\varepsilon^*(\omega)$</td>
<td>$\sigma^* = i\omega \varepsilon^*$</td>
</tr>
<tr>
<td>Complex electric modulus</td>
<td>$M^*(\omega)$</td>
<td>$M^* = M' + iM''$</td>
</tr>
</tbody>
</table>

In complex number, a small-amplitude AC voltage can be described as $V(\omega, t) = V_0 \exp (j\omega t)$ and response to this potential is the AC current $I(\omega, t) = I_0 \exp \{j(\omega t - \theta)\}$, where $\theta$ is the phase difference between $V(\omega, t)$ and $I(\omega, t)$ and $j = \sqrt{-1}$. Therefore, Eq. (2.2) can be written as\(^{127}\)

$$Z(j\omega) = \frac{V_0}{I_0} \exp(j\theta) \quad (2.4)$$

Again, Eq. (2.4) can be rewritten in terms of magnitude ($Z_0$) as\(^{127}\)

$$Z(j\omega) = Z_0 \exp(j\theta) \quad (2.5)$$

Applying Euler’s relationship and replacing $Z_0$ with $|Z|$, Eq. (2.5) can be expressed as\(^{127}\)

$$Z(j\omega) = |Z| (\cos \theta + j\sin \theta) \quad (2.6)$$

In general, impedance is expressed as\(^{127}\)

$$Z = Z' + jZ'' \quad (2.7)$$
Where, $Z' = |Z| \cos \theta$ and $Z'' = |Z| \sin \theta$ are the real and the imaginary parts of the impedance, respectively. The real and imaginary parts of the impedance are related to the phase angle $\theta$ as

$$Z(\theta) = \tan^{-1}\left( \frac{Z''}{Z'} \right)$$

and the magnitude $|Z|$ as

$$|Z| = \sqrt{Z'^2 + Z''^2}$$

EIS data can be displayed in different ways. In the complex plane, $Z''$ is plotted against $Z'$. The complex plane plots are often termed as Nyquist plots. In Bode plot, both log $|Z|$ and $\theta$ are plotted against log $f$. Sometimes, it is helpful to plot log $Z''$ against log $f$.

In the frequency domain, current-voltage relations can be rearranged as Eq. (2.2). If a purely sinusoidal voltage $V(\omega, t) = V_0 \exp(j\omega t)$ is applied across a resistor with resistance $R$ then the current that flows through the resistor will be $I(\omega, t) = V(\omega, t)/R = V_0 \sin(\omega t)/R$, which can be written as $I(\omega, t) = I_0 \sin(\omega t)$. So, the impedance of the resistor, $Z_R(\omega)$, is

$$Z_R(\omega) = \frac{V(\omega, t)}{I(\omega, t)} = R$$

In this case, the applied voltage and the resultant current are in phase. If the voltage is applied to a capacitor having capacitance $C$ then the resultant current is $I(\omega, t) = C dV(\omega, t)/dt = \omega CV_0 \cos(\omega t)$, where $I = dq/dt$ and $q = CV$. The above expression for the current passing through the capacitor can be written as $I(\omega, t) = \omega CV_0 \cos(\omega t - \pi/2)$ or $I(\omega, t) = I_0 \sin(\omega t)$, where $I_0 = \omega CV_0$. The impedance of the capacitor, $Z_C(\omega)$, is thus,

$$Z_C(\omega) = \frac{V(\omega, t)}{I(\omega, t)} = \frac{1}{\omega C}$$

where $1/\omega C$ or in complex notation $1/j\omega C$ is the reactance of a capacitor and $-\pi/2$ is the phase difference. According to the above description, reactance for any electrical element can be deduced using fundamental relation between current and voltage for that element as summarized in Table 2.2.

<p>| Basic electrical elements and their current-voltage relation |</p>
<table>
<thead>
<tr>
<th>Component</th>
<th>Symbol</th>
<th>Fundamental relation</th>
<th>Impedance, $Z(\omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inductor</td>
<td>$L$</td>
<td>$V = L \frac{dI}{dt}$</td>
<td>$j\omega L$</td>
</tr>
<tr>
<td>Resistor</td>
<td>$R$</td>
<td>$V = I \times R$</td>
<td>$R$</td>
</tr>
<tr>
<td>Capacitor</td>
<td>$C$</td>
<td>$V = \frac{1}{C} \int I , dt$</td>
<td>$\frac{1}{j\omega C}$</td>
</tr>
<tr>
<td>Constant phase element</td>
<td>$Q_n$</td>
<td>$V = \frac{1}{Q_n} \int I , dt$</td>
<td>$\frac{1}{(j\omega)^n Q_n}$</td>
</tr>
</tbody>
</table>

An overview of the system facilitates the translation of the charge transfer, transport, and accumulation processes in the system to an electrical circuit composed of a lump of series and parallel combination of resistors, capacitors, inductors, and so forth. The equivalent circuit model constructed using Kirchoff’s rules is used to deduce the physically meaningful properties of the system.\textsuperscript{119,125} For example, if two elements are in series then the current passing through them is the same and if two elements are in parallel then the voltages across them are the same.

### 2.2.1.1 Series R-C circuit

The impedance of the series connection of resistance and capacitance is given by,

$$Z(\omega) = Z_R(\omega) + Z_C(\omega)$$ \hspace{1cm} (2.12)

where $Z_R(\omega)$ and $Z_C(\omega)$ are the impedance for $R$ and $C$, respectively. Eq. (2.12) can be written in terms of reactance as\textsuperscript{119}

$$Z(\omega) = R + \frac{1}{j\omega C}$$ \hspace{1cm} (2.13)

Rearranging Eq. (2.13), one gets

$$Z(\omega) = R - \frac{j}{\omega C}$$ \hspace{1cm} (2.14)
At the low frequency limit ($\omega \to 0$) the capacitive impedance is so large that the total impedance is infinity. Therefore, the DC resistance, $Z(0)$, of the system is infinity and there is no DC current to flow through the system. As the frequency increases the capacitive impedance decreases. At the limit of very high frequency ($\omega \to \infty$), the capacitor becomes short-circuited and there remains the resistance $R$ only. Impedance of such system can be modeled as a series combination of a resistor and a capacitor as shown in the inset of Figure 2.3 where $R_S$ is the series resistance and $C$ is the capacitance. However, complex plane plot does not tell us about the corresponding frequency of the impedance explicitly.

### 2.2.1.2 Parallel R-C circuit

For the parallel R-C connection, the impedance of the system is given by,

$$Z(\omega) = \frac{1}{\frac{1}{R} + j\omega C} = \frac{R}{1 + j\omega RC} = \frac{R}{1 + \omega^2 R^2 C^2} - \frac{j\omega R^2 C}{1 + \omega^2 R^2 C^2}$$  \hspace{1cm} (2.15)
Figure 2.4 Complex plane plot for the impedance corresponding to the equivalent circuit shown in the inset

There are two limits of the impedance: \( \omega = 0, \ Z' = R \) and \( \omega \to \infty, \ Z' = 0 \). The complex plane plot shows a semicircle of radius \( R/2 \) and the centre on the real axis while the frequency at the semicircle maximum is equal to \( \omega = 1/RC \).

2.2.1.3 Series R with parallel R-C circuit

The impedance of the series R with parallel RC circuit can be written as

\[
Z(\omega) = Z_S(\omega) + Z_{pl}(\omega)
\]  

(2.16)

where \( Z_S(\omega) = R_S \) and \( Z_{pl}(\omega) \) is the impedance of the parallel combination of the \( R \) and the \( C \). Thus, Eq. (2.16) can be written in terms of reactance as\(^{125}\)

\[
Z(\omega) = R_S + \frac{R}{1+\omega^2 R^2 C^2} - j \frac{\omega R^2 C}{1+\omega^2 R^2 C^2} = \left( R_S + R \right) \frac{1+j \omega \frac{R S C}{R^2 + R C}}{1+j \omega R C} \]  

(2.17)
Figure 2.5 Complex plane plot for the impedance corresponding to the simplified Randle’s circuit shown in the inset

Here, \( R_S + R/(1 + \omega^2 R^2 C^2) \) and \( -\omega R^2 C/(1 + \omega^2 R^2 C^2) \) are the real and imaginary parts of the impedance, respectively. Figure 2.5 shows the impedance of the system in complex plane plot. The plot has a semicircle, which is typical for a single RC circuit. When \( \omega \to \infty \), the capacitive impedance is short-circuited, and this eventually shunts the \( R \). Therefore, only the \( R_S \) remains at the high frequency intercept. As the frequency decreases the capacitive impedance increases. At the low frequency intercept the capacitive impedance is infinitely large but still there is the \( R \). So, the DC resistance \( Z(0) \) of this system is \( Z(0) = R_S + R \). It can be noticed from Eq. (2.17) that the maximum of the \( Z'' \) occurs at \( Z' = R_S + R/2 \), which corresponds to the characteristic frequency of the charge relaxation process (\( \omega_{\text{max}} \)).

### 2.2.1.4 Inductance

So far we have seen that the imaginary part of the impedances for different combination of resistances and capacitors showed negative values and the spectra appeared in the first quadrant of the complex plane. However, the imaginary parts sometimes take positive values and thus the spectra appear in both first and fourth quadrants due to the inductance of the contact wire, which often produces a tail at high frequencies (Figure 2.6). On the other hand, impedances of several types of solar cells show similar phenomenon, however at low frequency region, as a loop that forms an arc in the fourth quadrant (Figure 2.7).
Figure 2.6 Complex plane plot for the impedance showing inductive effects at the high frequency with the corresponding equivalent circuit shown in the inset

Figure 2.7 Complex plane plot for the impedance showing inductive effects at the low frequency with the corresponding equivalent circuit shown in the inset
2.2.2 Equivalent Circuit of Some Electrochemical Systems and Their Impedance

2.2.2.1 Semi-Infinite Diffusion

The current through resistance which is carried by electroactive species can create an impedance which is frequently known as the Warburg element. If the diffusion layer is assumed to have an unlimited thickness within the experimental AC frequency range, than a semi-infinite diffusion may become the rate determining step in the Faradaic kinetic process. The semi-infinite diffusion is modeled by a Warburg infinite diffusion component $Z_W$ that can be expressed as,$^{130}$

$$Z_W(\omega) = \sqrt{\frac{2}{j\omega}} \sigma$$  \hspace{1cm} (2.18)

Since $1/\sqrt{j} = (1 - j)/\sqrt{2}$, Eq. (2.18) can be written as

$$Z_W(\omega) = \frac{\sigma}{\sqrt{\omega}} (1 - j)$$  \hspace{1cm} (2.19)

The coefficient $\sigma$ is defined as$^{131}$

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}} \left( \frac{1}{c^*_O D_O} + \frac{1}{c^*_R D_R} \right)$$  \hspace{1cm} (2.20)

Where $c^*_O$ and $c^*_R$ are the bulk concentration of oxidant and reductant, respectively; $D_O$ and $D_R$ are the diffusion coefficients of the oxidant and reductant, respectively; $A$ is the surface area of the electrode; and $n$ is the number of electrons involved. The semi-infinite diffusion impedance cannot be modeled by simply connecting resistor and capacitor because of square root dependency on frequency ($\sqrt{\omega}$).$^{131}$

2.2.2.2 Randle’s Circuit

A typical electrochemical cell where polarization due to the combination of kinetic and diffusion phenomena modeled by a full Randle’s equivalent circuit is composed of a parallel addition of double layer capacitance and Faradaic impedance. This circuit also includes solution resistance (Figure 2.8). The impedance of the Randle’s circuit is expressed by,
\[ Z(\omega) = R_s + \frac{R_{ct} + Z_W}{1 + j\omega C_{dl}(R_{ct} + Z_W)} \]  

(2.21)

Figure 2.8 Complex plane plot for the impedance corresponding to Randle’s circuit shown in the inset

The complex plane plot (Figure 2.8) shows that the impedance of Faradaic process appears as a semicircle at high frequency edge and the diffusion process appears as a diagonal line with a slope of 45\(^\circ\) at the low frequency edge. In general, three characteristic frequency regions can be identified when an electrochemical system represented by a Randle’s circuit is characterized by EIS. The low-frequency region is identified for characterization of diffusion-limited mass transport through its characteristic frequency:

\[ \omega_D = \frac{D}{L_D^2} \]  

(2.22)

The second (typically higher) frequency is determined by the ratio of the Faradaic (mainly charge transfer) and capacitive double layer charging currents:

\[ \omega_{RC} = \frac{1}{R_{ct}C_{dl}} \]  

(2.23)

Above this critical frequency a high-frequency impedance region exists (\(\omega > \omega_{RC}\)) where the impedance is determined by the double-layer capacitance as well as the bulk-solution impedance, resistance of the wires, film thickness of bulk polymer, etc. In the second, medium-frequency (\(\omega_{RC} > \omega > \omega_D\)) region, the impedance characteristic depends on Faradaic charge
transfer and infinite diffusion impedances. The non-stationary diffusion layers are generated near the interface, while the concentration perturbations are zero outside these layers ($\omega > \omega_D$). For $\omega > \omega_D$ the species will not sense the boundary at $x = L_D$, and the system will be characterized by semi-infinite diffusion, with Warburg $-45^\circ$ response. At the low frequencies ($\omega_D > \omega$) the concentration distributions are quasi-stationary, and the diffusion impedance may become finite. $Z''$ decreases to the real axis at the onset of finite diffusion for transmitting or absorbing boundaries or rises at $-90^\circ$ as a purely capacitive response for blocking or reflecting boundaries.\textsuperscript{131, 132}

If the time constant ($\tau_F = 1/\omega_{\text{max}} = R_{ct} C_{dl}$) of the Faradaic or charge transfer kinetics is too fast compared to the time constant ($\tau_d = R_{ct}^2 / 2 \sigma^2$) of diffusion process then the system is said to be under diffusion control. On the other hand, the system will be under kinetic controls lower than that of diffusion.

### 2.2.2.3 Constant Phase Element

In an electrochemical system, a straight line with angle lower than $\frac{\pi}{2}$ is often observed in a complex plane plot. Such behavior may arise from (i) a microscopic roughness caused by scratches, pits, etc. always present on solid surfaces, which causes coupling of the solution resistance with the surface capacitance and (ii) a capacitance dispersion of interfacial origin connected with slow adsorption of ions and chemical in-homogeneities of the surface. In equivalent circuit model of an electrochemical system, the capacitance $C_{dl}$ is often replaced by a constant phase element (CPE) to account for the deviation of the $C_{dl}$ from an ideal capacitor. The impedance of the CPE is expressed as\textsuperscript{128, 133}

$$Z_{Q_n}(\omega) = \frac{1}{(j\omega)^n Q_n}$$  \hspace{1cm} (2.24)

Where, $Q_n$ and $n$ are the CPE pre-factor and index, respectively. If the index $n$ is equal to 1.0 the CPE coincides with a pure capacitor. Generally, $n$ varies from 1.0 to 0.5 to fit an experimental data. The impedance corresponding to the simplified Randle’s circuit with CPE can be expressed as

$$Z(\omega) = R_S + \frac{R_{ct}}{1 + (j\omega)^n R_{ct} Q_n}$$  \hspace{1cm} (2.25)
When the value of $n$ decreases from 1.0 to 0.5 the semicircle deviates to a depressed semicircle. In this case, the characteristic frequency $\omega_{\text{max}}$ is expressed as:

$$\omega_{\text{max}} = \frac{1}{(R_{ct}Q_n)^{1/n}}$$

(2.26)

From Eq. (2.32), we can see that the CPE response decelerates with the decrease of $n$. The equivalent capacitance ($C_{dl}$) of the electrochemical interface corresponding to the parallel combination of $R_{ct}$ and $Q_n$ can be calculated by,

$$C_{dl} = Q_n^{1/n} R_{ct}^{1/n-1}$$

(2.27)

### 2.2.2.4 Diffusion in a Thin Film

Diffusion occurs in thin film also, for example, diffusion of tri-iodide in the electrolyte solution of DSSCs. Moreover, diffusion can be coupled with reaction such as the electron diffusion-recombination at the positive electrode of DSSCs. Impedance of such diffusion is known as finite-length diffusion impedance. The impedance of the diffusion and recombination or diffusion and coupled reaction can be modeled as a finite-length transmission line (FTL) composed of distributed elements $r_m$, $r_k$, and $c_m$ as shown in Figures 2.9 and 2.10, where $r_k$ is given by:

$$r_k = R_k L = \frac{1}{\omega_{k} c_m}$$

(2.28)
In a thin film diffusion, the diffusion layer is bounded and the impedance at lower frequencies no longer obeys the equation for semi-infinite Warburg diffusion. Bisquert et al.\textsuperscript{134} has modeled various aspects of diffusion of particles with diffusion coefficient \( D \) in a thin film of thickness \( L \), where the characteristic frequency \( \omega_d \) is,

\[
\omega_d = \frac{D}{L^2} \tag{2.29}
\]

In a reflecting boundary condition, electrons, being injected at the interface between a conducting substrate and a porous semiconductor film, diffuse through the film to the outer edge of the film where electron transport is blocked. This diffusion phenomenon can be modeled as a FTL with short-circuit at the terminal similar to that in Figure 2.9, however, without \( r_k \) as the diffusion is not coupled with reaction. The diffusion impedance \( Z_{d,o} \) for a reflecting boundary condition is expressed as\textsuperscript{134}

\[
Z_{d,o}(\omega) = R_d \sqrt{\frac{\omega_d}{j\omega}} \coth \sqrt{\frac{j\omega}{\omega_d}} \tag{2.30}
\]

where \( R_d = r_m L \) and \( \omega_d = 1/r_m c_m \) are the diffusion resistance and characteristic frequency of diffusion, respectively. Complex plane plot of this impedance shows a straight line with 45° at high frequency and then vertically goes up at the low frequency (Figure 2.9). The high and the low frequency regions clearly show two distinct features separated by the characteristic frequency \( \omega_d \). When \( \omega \gg \omega_d \), the system behaves as a semi-infinite and Eq. (2.30) coincides with Eq. (2.18) as\textsuperscript{134}

\[
Z_{d,o}(\omega) = R_d \sqrt{\frac{\omega_d}{j\omega}} \tag{2.31}
\]
Figure 2.10 Complex plane plot of the impedance model for diffusion with the absorbing boundary condition and the corresponding Finite-length transmission line model of diffusion-reaction impedance is shown in the inset.

At the low frequency region, the impedance becomes\(^ {134}\)

\[
Z_{d,o}(\omega) = \frac{R_d}{3} + \frac{R_d \omega_d}{j \omega}
\]  

(2.32)

On the other hand, in an absorbing boundary condition, electrons are injected at \(p-n\) junction and are collected at the outer edge of the neutral \(p\) region of a semiconductor. The diffusion process can be modeled as a FTL with open-circuit at the terminus similar to that in Figure 2.10, of course, without \(r_k\). For absorbing boundary condition, the diffusion impedance \((Z_{d,c})\) can be expressed as\(^ {134}\)

\[
Z_{d,c}(\omega) = R_d \sqrt{\frac{\omega_d}{j \omega}} \tanh \sqrt{\frac{j \omega}{\omega_d}}
\]  

(2.33)

The impedance in complex plane plot appears as an arc at the low frequency region and a straight line with 45° showing semi-infinite behaviour at high frequency region that follows Eq. (2.31) as shown in Figure 2.10. The impedance of the diffusion and recombination for the reflective boundary condition \((Z_{dr,o})\) is expressed as\(^ {134}\)

\[
Z_{dr,o}(\omega) = \frac{(R_d R_k)}{(1+j \omega / \omega_k)} \cosh \left( \frac{\omega_k}{\omega_d} \right) \left( 1 + \frac{j \omega}{\omega_k} \right)
\]  

(2.34)
and the impedance for the absorbing boundary condition \(Z_{dr,c}\) is expressed as\(^\text{134}\)

\[
Z_{dr,c}(\omega) = \sqrt{\frac{(R_d R_k)}{(1+j\omega/\omega_k)}} \tanh \sqrt{\frac{\omega_k}{\omega_d}} \left(1 + \frac{j\omega}{\omega_k}\right)
\]

where \(R_d\) and \(\omega_d\) are the diffusion resistance and characteristic frequency for diffusion, respectively, as in Eq. (2.30) and Eq. (2.33). The additional terms \(R_k\) and \(\omega_k\) are the resistance corresponding to homogeneous reactions and the characteristic frequency of the reaction, respectively. Eq. (2.34) and Eq. (2.35) have three independent parameters, for example, \(R_d\), \(\omega_d\), and \(\omega_k\). The relation among the physicochemical parameters is expressed as\(^\text{134}\)

\[
\frac{R_k}{R_d} = \frac{\omega_d}{\omega_k} = \left(\frac{L_n}{L}\right)^2
\]

where \(L\) and \(L_n\) are the film thickness and the diffusion length, respectively. Comparing Eq. (2.29) and Eq. (2.36), one can write

\[
L_n = \frac{D}{\omega_k}
\]

When \(R_k\) is very large, Eq. (2.34) reduces to Eq. (2.31) of simple diffusion. In this case, the reaction resistor \(r_k\) in the transmission line model is open circuit. For a finite \(R_k\), the impedance takes two different shapes depending on the quotient of Eq. (2.36). If \(R_k > R_d\) the impedance at high frequency region \((\omega \gg \omega_d)\) follows Eq. (2.31) and at the low frequency region \((\omega \ll \omega_d)\) the expression is

\[
Z_{dr,o}(\omega) = \sqrt{\frac{(R_d R_k)}{(1+j\omega/\omega_k)}}
\]

Thus, the complex plane plot of the impedance has a small Warburg part at high frequency and a large arc at low frequency. In this case, the DC resistance is expressed as

\[
R_{dc} = Z(0) = \frac{1}{3} R_d + R_k
\]

When \(R_k < R_d\), Eq. (2.34) gives the expression

\[
Z_{dr,o}(\omega) = \sqrt{\frac{(R_d R_k)}{(1+j\omega/\omega_k)}}
\]

where the reaction time is shorter than the time for diffusion across the layer \((\omega_k \gg \omega_d)\). This is the case when diffusing species are lost before they reach the outer edge of the film. The
model corresponding to Eq. (2.40) is called Gerischer’s impedance and the DC resistance has the form \(135, 136\)

\[
R_{dc} = Z(0) = \sqrt{(R_dR_k)}
\]  

(2.41)

For a very large value of \(R_k\), Eq. (2.35) turns into Eq. (2.33) of simple diffusion as in Figure 2.10. The DC resistance of the impedance equals \(R_d\). If \(R_k > R_d\) Eq. (2.35) approximates to Eq. (2.33); however, the DC resistance is slightly less than that of the case for very large value of \(R_k\) due to additional contribution of \(r_k\). When \(R_k < R_d\), Eq. (2.35) reduces to Gerischer’s impedance of Eq. (2.40) and the DC resistance of the impedance is given by Eq. (2.41).

2.3 Electrochemical Systems

The measurement techniques and modeling approaches will be explained with the help of practical systems, which are extensively studied for supercapacitors and solid oxide fuel cells (SOFCs). These techniques are also applicable to other kinds of electrochemical energy converters; however, a complete introduction for all relevant electrochemical systems seems rather difficult. In this section, supercapacitors and SOFCs as representatives for electrochemical energy conversion systems are briefly categorized and explained.

2.3.1 General Electrochemical Systems

All devices which convert chemical energy into electrical energy and vice versa are part of the scientific discipline of electrochemistry. The term ‘system’ indicates that the most fundamental practical realization of such an energy converter, often also called a ‘cell’, can be viewed as a system that shows a systematic and often quite complex relation between its inputs and its outputs.

The most general definition of an electrochemical system, is that it consists of two electrodes separated by at least one electrolyte phase.\(^{121}\) The primary difference between an electrochemical reaction occurring in a cell and its complementary redox reaction is that oxidation and reduction do not occur at the same site but separated by the electrolyte as two half-reactions in the so-called ‘half-cells’.\(^ {137}\) During a chemical redox reaction one reactant accepts one or more electrons and the other donates one or more electrons. In order to maintain electroneutrality, ions are exchanged. For an electrochemical cell, these ions are exchanged via the ionic conducting electrolyte that blocks the direct exchange of electrons. These flows
through an external conductor\textsuperscript{121} where they can do work. The primary application of an electrochemical cell is thus to convert chemical energy into electrical energy.

In many cases these electrochemical reactions are reversible and electric energy can be used to convert a chemical substance with low internal chemical energy into a substance with higher internal chemical energy, like it is done in electrolysis. A comprehensive and practical introduction into electrochemical systems is given in Ref. [\textsuperscript{137}]. The fundamental works \textsuperscript{138}, \textsuperscript{139}, and \textsuperscript{140} also provide good introductions that reach from the fundamentals of electrochemistry to the components of an electrochemical cell. If an electrochemical system is able to provide an electrical current, it is called a galvanic cell.\textsuperscript{140} There are three types of galvanic cells:

\textit{Primary galvanic cells}. These are cells that contain the fuel to be converted into electrical energy during operation. This reaction is not reversible. After the fuel is depleted, the cell must be mechanically refilled to provide the possibility of further production of electrical energy. The first galvanic cell invented by Volta in 1800 was of this category.\textsuperscript{137}

\textit{Secondary galvanic cells}. The electrochemical reaction associated with this type of cells is reversible. That is why they have two operation modes – discharge, producing electrical energy out of chemical energy, and charge, converting electrical energy to chemical energy. All reactants and products are also contained in the cell. The supercapacitors discussed in this thesis and, more generally, secondary batteries belong to this category.\textsuperscript{141}

\textit{Tertiary galvanic cells}. The fuel for these cells is not contained in the device itself but is supplied externally. Hence, this type of galvanic element is normally referred to as fuel cell. Generally, all types of fuel cells belong to this category and the SOFC, which will be discussed in detail in this thesis, is one of the most prominent one. If the operation of a tertiary galvanic cell is reversed, it is operated in the so-called electrolysis mode, converting electrical energy into chemical energy and thereby producing fuel. This fuel may be externally stored and utilized later in the same cell operated in fuel cell mode to produce electrical energy, but is not restricted to this.

\textbf{2.3.2 Setup of Electrochemical Systems}

An electrochemical system consists of three basic components: the electrolyte, anode and cathode. In section 2.3.1 the major tasks for the three components are explained for all electrochemical cells that can be categorized as supercapacitors or fuel cells. Also other
important components are required for a practical realization of an electrochemical system is described there. The electrochemical reaction in an electrochemical system follows a fundamental law, the conservation of species that is introduced in section 2.3.4.

![Diagram of Electrochemical System](image)

**Figure 2.11 Setup of Electrochemical system**

### 2.3.3 Components of Electrochemical Systems

The necessary components of an electrochemical system are electrolyte, anode, and cathode. Their description is kept general in sections 2.3.3.1 to 2.3.3.3. As additional components for the practical realization of an electrochemical system, current collectors and the housing are briefly addressed in section 2.3.3.4.

#### 2.3.3.1 Electrolyte

The electrolyte is the defining part in an electrochemical system. Its primary purpose is to separate the anode and cathode volume spatially to prevent a spontaneous reaction of the reactants. The electrolyte must be an electronic insulator to prevent an internal short circuit. Even small electronic conductivities are unfavorable, because the energy of the current through the electrolyte cannot be used in the external circuit and is lost as heat to the surrounding environment.

The term ‘volume’ is used here with intent because the reactants and products in the electrodes can be gaseous (e.g. in a SOFC), solid (e.g. in a supercapacitor) or even liquid (e.g. in a Direct
Methanol Fuel Cell (DMFC)). The electrolyte itself can either take the form of a solid (e. g. in a SOFC) or liquid (e. g. in a supercapacitor). The second purpose of the electrolyte is to enable the direct transport of ions or charged molecules, while the residual electrons and holes provide electrical energy for the external electric circuit.

Materials, charge, and charged species that meet these requirements vary and this explains the many types of galvanic cells. A comprehensive list of different types of cells and the corresponding electrolyte materials, charge, and charged species can be found in Ref. [142] for batteries and in Ref. [143] for fuel cells.

### 2.3.3.2 Anode

The anodic reaction is an oxidation providing free electrons on the anode side. During operation the anode has a negative charge and acts as the negative pole in the electrochemical system. The anode must be electronically conductive to provide the electrical connection to the external electrical circuit. The second requirement is that the anode is responsible for the charge transfer from ions to electrons (for electrolytes conductive for negatively charged ions or molecules) or vice versa (for electrolytes conductive for positively charged ions, molecules or protons). For some configurations the charge carriers are incorporated in the anode material (as ions are in supercapacitor anodes), for others the anode has to be catalytically active to facilitate the reaction and to lower the polarization losses (as the Ni in SOFC anodes).

### 2.3.3.3 Cathode

In principle the cathode has the same function and requirements as the anode, only that the chemical reaction is a reduction and electrons are bound by the cathodic half reaction, so that holes and therefore a positive charge and positive pole emerges during the electrochemical reaction. It has to be electronically conductive and conduct the charge transfer from electrons to ions (for electrolytes conductive for negatively charged ions or molecules) or vice versa (for electrolytes conductive for positively charged ions, molecules or protons). A further benefit of a good cathode is to facilitate the cathodic reaction by catalytic activity. The requirements being the same as for the anode, the materials and microstructural properties that meet these requirements best will differ.
2.3.3.4 Additional Components

In order to make an electrochemical system applicable, two other important components have to be added:

Current Collectors. The role of a current collector is to provide the electronic connection of the electrodes to the outer circuit. The requirements for a current collector are high electronic conductivity as well as chemical compatibility with the materials and the ambient conditions of the cell components they are connected with. Due to the oxidizing environment on the cathode side and the reducing environment on the anode side, it is common to use different materials as current collector, respectively. For example, Cu is used to contact the anode of supercapacitor and Al for contacting the cathode. For SOFCs the term current collector is commonly also used for an additional highly porous electrode layer, that shows a good electronic conductivity. Such a layer is used for nano-sized cathodes with a thickness of only a few hundred nanometers, for example. These usually show lower porosities than standard electrodes and a direct metallic contacting is not easily achieved. That is why an additional current collector layer is applied between electrode and metallic current collector.

Housing. As described in section 2.3.1, in every electrochemical system an electrochemical reaction is split into two half cell reactions by the electrolyte. In order to avoid direct contact between the two reactants, the electrolyte has to be both impermeable and inert for these substances, but also a housing has to be provided, that prevents direct reactions among the reactants and with the surrounding environment. As the operating parameters for supercapacitor and SOFC are very different, also the requirements for the housings differ.

2.3.4 Electrical Properties of Electrochemical Systems

Like other sources of electrical energy, electrochemical systems are characterized by the terminal voltage $U_{\text{op}}$.

2.3.4.1 Open Circuit Voltage (OCV)

In this section the thermodynamic derivation of the OCV will be given in brief based on Ref. [138]. Other comprehensive derivations can be found in Ref. [137]. A deeper insight into the chemical context can be found in Ref. [145]. In this thesis, no distinction is drawn between the theoretical cell voltage and the terminal voltage under open circuit conditions $U_{OCV}$. 
In a galvanic cell, chemical energy is converted into electrical energy. This means there is a general chemical reaction of the type,

\[ A + B \rightarrow C + D \]

(\( I \))  (\( II \))

involved, associated with a change in free molar reaction enthalpy. \( \Delta G \) is the corresponding difference in molar free energy or Gibbs free energy. It is thus the maximum electrical energy that can be obtained from the transformation of one mole of reactants during a chemical reaction. At least the same amount of energy has to be introduced into the system for the reverse reaction, if applicable. \( \Delta G^0 \) is the standard value for \( \Delta G \). A list of values for \( \Delta G^0 \) relevant for different fuel cell reactions can be found in Ref. [146]. For LIBs the standard potentials of the applied materials are listed in Ref. [142, 147]. From these values, the standard cell voltage \( U^0_{OCV} \) can be calculated, as will be shown in equations (2.46) to (2.48). For a deeper insight into the energies associated with the electrochemical reaction [137, 138].

In order to understand the correlation of the electrical cell voltage \( U_{OCV} \) or OCV not assuming standard conditions and the chemical potential, the electrochemical potential \( \mu' \) has to be introduced,

\[
\mu'_n = \mu_n + z_n F \varphi
\]

(2.42)

where \( \mu_n \) is the chemical potential of the component \( n \),\(^{139}\)

\[
\mu_n = \mu_n^0 + RT \ln a_n
\]

(2.43)

The chemical potential consists of the standard value \( \mu_n^0 \) at standard conditions and a term that depends on the concentration of component \( n \). The latter part is determined by the chemical activity \( a \), which is a measure of the effective concentration.\(^{139}\) While electrochemical equilibrium is assumed,

\[
\mu'_n (I) = \mu'_n (II)
\]

(2.44)

the electrical potential difference \( \Delta \varphi \) or cell voltage \( U_{OCV} \) can be calculated by the so-called Nernst equation

\[
U_{OCV} = \Delta \varphi = \frac{\mu_n^0 (I) - \mu_n^0 (II)}{zF} + \frac{RT}{zF} \ln \frac{n_n a_n I}{n_n a_n I}
\]

(2.45)
The first part of the equation is material specific while the second part is concentration specific.

The material specific part of equation (2.45) equals

$$\frac{\mu_{n, I}^0 - \mu_{n, II}^0}{zF} = \frac{\Delta G^0}{zF},$$

because the sum of changed chemical potentials through the chemical reaction weighted by the stoichiometric factor $\nu$ equals the change in Gibbs free energy:

$$\Delta G = \sum_n \nu_n \mu_n.$$  \hspace{1cm} (2.47)

Therefore the cell voltage can be linked directly to the change in reaction enthalpy:

$$U_{OCV} = -\frac{\Delta G}{zF}, \text{ or for standard conditions } U_{OCV}^0 = -\frac{\Delta G^0}{zF}.$$ \hspace{1cm} (2.48)

### 2.3.4.2 Cell Voltage under Load

In a first approximation, the cell voltage of an electrochemical system behaves like a real voltage source – an ideal voltage source in series with a resistor, the so-called inner resistance of the voltage source. If a current is drawn from the real voltage source, the terminal voltage decreases. The reason for this behavior is the voltage drop at the inner resistance. In electrochemical systems a similar voltage drop is observable, which is due to ohmic and polarization losses. The voltage drop at the electrodes is called overpotential $\eta$ in electrochemistry,\textsuperscript{138} and $\eta_{tot} = U_{OCV} - U_{op}$ is defined as the total overpotential in this thesis. It is caused by the electrochemical reaction itself, which can be described by Butler-Vollmer kinetics or by the Tafel equation,\textsuperscript{121} or by transport mechanism such as solid state or gas diffusion. A comprehensive overview of the polarization processes relevant for SOFCs is provided in Ref. \textsuperscript{148}. For supercapacitor this is more difficult due to the different material systems and configurations. For small currents the voltage decrease is approximately linear and the Current/Voltage (C/V) characteristics are given as a decreasing line intersecting the ordinate at $U_{OCV}$.

Even though the equations describing the OCV and the voltage under load are valid for both SOFCs and supercapacitor, the static behavior under load is different for both systems. It is not possible to adjust a stable operating point with a current density $|J| > 0$ for a battery because of the associated change in SOC. Therefore the static C/V diagram is not a well-established display for the performance analysis for supercapacitors. The same relations account for
batteries, but are more difficult to determine and to handle. Charge/discharge characteristics are often addressed as substitute for the C/V characteristics of batteries.

2.3.4.3 Charge/Discharge Characteristics of Supercapacitors

The charge/discharge characteristics of a supercapacitor simply consist of the charge curve and the discharge curve. The performance of a supercapacitor can be rated by those curves. They exhibit the course of the cell voltage $U_{op}$ during a charge or discharge procedure maintaining a constant current density or $C$ rate. While the OCV is determined by the material properties of the supercapacitor, performance can be determined by the deviation of the operating voltage $U_{op}$ from the OCV at a constant $C$ rate. For every $C$ rate, a different charge/discharge curve is obtained. In principle, important cell parameters like the DC impedance $Z_{DC}$ can be deduced from these curves. In practice, this is rarely done.

Another common technique that should be mentioned in this context is known as Constant Current Constant Voltage (CCCV). For charging the supercapacitor, a constant current is applied, until the end-of-charge voltage is reached. After that, this voltage is kept constant, until the current has dropped below a certain value. The corresponding discharge is conducted with a constant current until the end-of-discharge voltage is reached. However, this technique is normally not used for the characterization of the supercapacitor but only to perform defined charge/discharge cycles.

2.3.4.4 Impedance of Electrochemical Systems

As mentioned above, the cell voltage $U_{op}$ decreases due to ohmic and polarization losses, if a positive current density are adjusted. More generally, in every electrochemical system, electrochemical processes occur, that are responsible for a voltage drop during operation and constitute a loss process. In the static characteristics introduced these processes are only represented as a sum and cannot be separated. Each of these losses is characterized by their relaxation time, or characteristic frequency. In other words, there are fast and slow processes; they have different rates. The impedance response can be reproduced by basic electrical components that constitute a so-called Equivalent Circuit Model (ECM). The literature on this topic is extremely extensive and versatile. The most cited, and probably most fundamental, work is Ref. [118]. A more recent and more practical textbook is Ref. [124]. In Ref. [149], a rather
brief but still comprehensive introduction into the topic is given. Apart from the information given in these publications, a large number of review and overview articles will be recommended in the corresponding subsections, as they become relevant to the discussion. Although the literature is extensive concerning the mathematical description and the underlying differential equations, practical explanations for the different time constants that arise in an electrochemical system, remain scarce.

2.3.5 Performance and Efficiency

An important goal of current research activities is to get impartial numbers for the performance and efficiency of an electrochemical system. Possible criteria to rate performance and efficiency are controversially applied throughout the literature with little consistency. Basically, the performance of an electrochemical system is determined by the physical quantities energy density and power (loss) density. Efficiency is the ratio between energy delivered by the system and energy supplied to the system. Supercapacitors are rated according to capacity and recommended C rate. These characteristics can be broken down to energy density and performance plus efficiency, respectively.

2.3.5.1 Energy Density

A high energy density is the most important performance related specification for a favourable electrode material for supercapacitors. The energy density can be expressed per unit volume or weight, depending on what is more relevant for a given application. Performance itself can be controlled to a certain extent by the micro- and macrostructure of the cell.

2.3.5.2 High Energy and High Power Cells

A supercapacitor cell is composed of the cell components introduced in section 2.3.3. In this paragraph it is briefly demonstrated, how the composition of a cell can be trimmed for high energy density and high power density. The measures that can be taken are explained for the three relevant cell components:

Separator with electrolyte. The thickness of the electrolyte does not contribute to storage and is reciprocal to the ohmic resistance of the cell. Therefore the electrolyte is as thin as possible to achieve both higher power and energy densities.
Current collectors. The thicker the current collectors, the lower the resistance caused by them. In high power cells, thick current collectors are used in order to increase the maximum current and decrease heat dissipation. However, as the thickness of the current collector increases, the thickness of the electrodes must decrease for equally sized cells. As a consequence of having thick current collectors, high power cells have less system energy density than other cells.

Electrodes. The thicker the electrodes the fewer number of layers is needed to achieve a given capacity. For this reason, high energy cells commonly have thicker electrodes than other cell types and the volume ratio between electrodes and current collectors in the overall volume is therefore higher. Due to few and thin current collectors, the maximum current is limited for this type of cells.

2.3.5.3 Efficiency

For supercapacitors the efficiency is given by the ratio of energy that is needed to charge the battery and the energy that can be used in the outer electrical circuit during discharge:

\[ \eta_C = \frac{E_{\text{discharge}}}{E_{\text{charge}}} \]  \hspace{1cm} (2.49)

The efficiency typically depends on the C rate at which the charge and discharge cycle is performed, but even at very low C rates, the voltage is higher during charging than during discharging at the same state of charge. This is mainly due to overpotentials and the hysteresis in supercapacitor. At high C rates the efficiency drops, because at higher currents, overpotentials rise and are thereby lowering the efficiency.