

APPENDIX A: The Equivalent Circuit Model (ECM) Approach

For Nyquist plot with depressed semicircle, the equivalent circuit can be represented as shown in Fig. A.1 and Fig. A.2.

Equivalent circuit are

The impedance is given by

$$\frac{1}{Z} = \frac{1}{R} + \frac{1}{Z_{CPE}}$$

$$= \frac{1}{R} + \frac{1}{k\omega^{-p} \left[\cos\left(\frac{\pi p}{2}\right) - j \sin\left(\frac{\pi p}{2}\right) \right]}$$

Hence,

$$\frac{1}{Z} = \frac{k\omega^{-p} \left[\cos\left(\frac{\pi p}{2}\right) - j \sin\left(\frac{\pi p}{2}\right) \right] + R}{Rk\omega^{-p} \left[\cos\left(\frac{\pi p}{2}\right) - j \sin\left(\frac{\pi p}{2}\right) \right]}$$

$$= \frac{k\omega^{-p} \left[\cos\left(\frac{\pi p}{2}\right) - j \sin\left(\frac{\pi p}{2}\right) \right] + R}{Rk\omega^{-p} \left[\cos\left(\frac{\pi p}{2}\right) - j \sin\left(\frac{\pi p}{2}\right) \right]} \times \frac{\left[\cos\left(\frac{\pi p}{2}\right) + j \sin\left(\frac{\pi p}{2}\right) \right]}{\left[\cos\left(\frac{\pi p}{2}\right) + j \sin\left(\frac{\pi p}{2}\right) \right]}$$

$$\begin{aligned}
&= \frac{k\omega^{-p} \left[\cos^2\left(\frac{\pi p}{2}\right) - j^2 \sin^2\left(\frac{\pi p}{2}\right) \right] + R \left[\cos\left(\frac{\pi p}{2}\right) + j \sin\left(\frac{\pi p}{2}\right) \right]}{Rk\omega^{-p} \left[\cos^2\left(\frac{\pi p}{2}\right) - j^2 \sin^2\left(\frac{\pi p}{2}\right) \right]} \\
&= \frac{k\omega^{-p} + R \left[\cos\left(\frac{\pi p}{2}\right) + j \sin\left(\frac{\pi p}{2}\right) \right]}{Rk\omega^{-p}}
\end{aligned}$$

Inverting the equation gives

$$\begin{aligned}
Z &= \frac{Rk\omega^{-p}}{k\omega^{-p} + R \cos\left(\frac{\pi p}{2}\right) + jR \sin\left(\frac{\pi p}{2}\right)} \\
&= \frac{R + R^2 k^{-1} \omega^p \cos\left(\frac{\pi p}{2}\right)}{1 + 2Rk^{-1} \omega^p \cos\left(\frac{\pi p}{2}\right) + R^2 k^{-2} \omega^{2p}} - j \frac{R^2 k^{-1} \omega^p \sin\left(\frac{\pi p}{2}\right)}{1 + 2Rk^{-1} \omega^p \cos\left(\frac{\pi p}{2}\right) + R^2 k^{-2} \omega^{2p}}
\end{aligned}$$

Hence,

$$\begin{aligned}
Z' &= \frac{R + R^2 k^{-1} \omega^p \cos\left(\frac{\pi p}{2}\right)}{1 + 2Rk^{-1} \omega^p \cos\left(\frac{\pi p}{2}\right) + R^2 k^{-2} \omega^{2p}} \\
Z'' &= \frac{R^2 k^{-1} \omega^p \sin\left(\frac{\pi p}{2}\right)}{1 + 2Rk^{-1} \omega^p \cos\left(\frac{\pi p}{2}\right) + R^2 k^{-2} \omega^{2p}}
\end{aligned}$$

of the Nyquist plot takes the form of A as in Fig. A.3, the equivalent circuit is as shown in Fig. A.4

Equivalent circuit are

Fig. A.4

Fig. A.3

The impedance is given by

$$Z = R + k \frac{\left[\cos\left(\frac{\pi p}{2}\right) - j \sin\left(\frac{\pi p}{2}\right) \right]}{\omega^p}$$

Hence,

$$Z' = R + \frac{k \cos\left(\frac{\pi p}{2}\right)}{\omega^p}$$

$$Z'' = \frac{k \sin\left(\frac{\pi p}{2}\right)}{\omega^p}$$

For Nyquist plot with depressed semicircle and spike in Fig. A.5., the equivalent circuit is as shown in Fig. A.6.

Equivalent circuit are

The derivation of equation is given by:

$$Z = Z_1 + Z_2$$

Where,

$$Z_1 = \frac{R + R^2 k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right)}{1 + 2Rk_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-2} \omega^{2p_1}} - j \frac{R^2 k_1^{-1} \omega^{p_1} \sin\left(\frac{\pi p_1}{2}\right)}{1 + 2Rk_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-2} \omega^{2p_1}}$$

$$Z_2 = k_2 \frac{\left[\cos\left(\frac{\pi p_2}{2}\right) - j \sin\left(\frac{\pi p_2}{2}\right) \right]}{\omega^{p_2}}$$

Thus,

$$Z = \left[\frac{R + R^2 k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right)}{1 + 2Rk_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-2} \omega^{2p_1}} + k_2 \frac{\cos\left(\frac{\pi p_2}{2}\right)}{\omega^{p_2}} \right] - j \left[\frac{R^2 k_1^{-1} \omega^{p_1} \sin\left(\frac{\pi p_1}{2}\right)}{1 + 2Rk_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-2} \omega^{2p_1}} + k_2 \frac{\sin\left(\frac{\pi p_2}{2}\right)}{\omega^{p_2}} \right]$$

Hence,

$$Z_r = \frac{R + R^2 k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right)}{1 + 2Rk_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-2} \omega^{2p_1}} + \frac{k_2 \cos\left(\frac{\pi p_2}{2}\right)}{\omega^{p_2}}$$

$$Z_i = \frac{R^2 k_1^{-1} \omega^{p_1} \sin\left(\frac{\pi p_1}{2}\right)}{1 + 2Rk_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-2} \omega^{2p_1}} + \frac{k_2 \sin\left(\frac{\pi p_2}{2}\right)}{\omega^{p_2}}$$

Theoretical Background

The fundamental property of a polymer electrolyte is conductivity. Conductivity in principle is the product of charge carrier number density (n), charge carrier mobility (μ) and their diffusivity which can be represented by the diffusion coefficient (D). the diffusion coefficient can be calculated using the Nernst-Einstein equation. This equation can be related to the conductivity and hence to the mobility since $\sigma = n\mu e$ where e is elementary charge. The conductivity can be calculated if thickness, area and bulk resistance of the polymer electrolyte are known. The bulk resistance can be determined

from Nyquist plot which can be established through impedance spectroscopy. Knowing the bulk resistance, conductivity can be calculated from the equation

$$\sigma = \frac{2d}{R_b A} \quad (1)$$

where σ is conductivity, d is sample thickness, R is bulk resistance and A is electrode/electrolyte contact area. An example of a Nyquist plot is as shown in Fig. 1.

The Nyquist plot shown in Fig. 1 can be considered to be made up of a depressed semicircle and a tilted spike. The depressed semicircle can be represented by an equivalent circuit comprising a “leaky capacitor” and a resistor connected in parallel and the spike can be represented by a constant phase element (CPE). The equivalent circuit can be illustrated as shown in Fig. 2 [10].

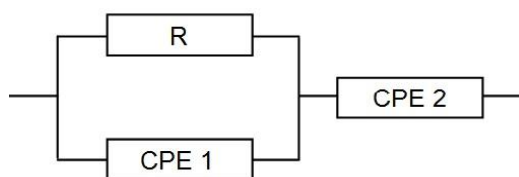


Fig. A.7. Equivalent circuit represent Nyquist plot.

The impedance of the equivalent circuit, Z_{eq} can be obtained as follows:

$$Z_{eq} = Z_r + jZ_i \quad (2)$$

where

$$Z_r = \frac{R + R^2 k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right)}{1 + 2Rk_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-2} \omega^{2p_1}} + \frac{k_2 \cos\left(\frac{\pi p_2}{2}\right)}{\omega^{p_2}} \quad (3)$$

$$Z_i = \frac{R^2 k_1^{-1} \omega^{p_1} \sin\left(\frac{\pi p_1}{2}\right)}{1 + 2Rk_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-2} \omega^{2p_1}} + \frac{k_2 \sin\left(\frac{\pi p_2}{2}\right)}{\omega^{p_2}} \quad (4)$$

The values of ω , p_1 , p_2 and R can be obtained by from Nyquist plot but the values of k_1 and k_2 can be obtained by trial and error. The impedance of the equivalent circuit when given the appropriate values will fit the Nyquist plot satisfactorily. A “leaky capacitor” is usually represented by a CPE. The resistor and CPE can be arranged in series, parallel and series-parallel combination. For the Nyquist plot shown in Fig. 1, the equivalent circuit consists of a resistor in parallel with a CPE and the combination is in series with a second CPE as shown in Fig. 2.

The inverse of k_1 i.e. k_1^{-1} is the capacitance of the bulk sample, since the bulk sample is represented by the depressed semicircle. At the peak of the depressed semicircle, the relaxation time can be estimated from the ideal Debye relation:-

$$\omega_m \tau_1 = 1 \quad (5)$$

Hence,

$$\tau_1 = \frac{1}{\omega_m} = \frac{1}{2\pi f_m} \quad (6)$$

Where f_m is frequency at the peak of depressed semicircle.

At the same time,

$$\tau_1 = Rk_1^{-1} \quad (7)$$

Here, R is the bulk resistance. τ_1 is the characteristics time constant. This implies that

$$k_1^{-1} = \frac{1}{2\pi f_m R} \quad (8)$$

Likewise, k_2^{-1} is the capacitance of the “leaky capacitor”.

$$k_2^{-1} = \frac{\epsilon_r \epsilon_o A}{\lambda} \quad (9)$$

Where λ is the thickness of the electrical double layer (EDL) that is formed when the ions accumulate at the electrodes during impedance measurement. ϵ_r is the dielectric constant of the material. ϵ_0 is vacuum permittivity (8.85×10^{-14} F cm⁻¹) and A is cross section area. According to Bandara and Mellander [9],

$$\lambda = (D\tau_2)^{1/2} \quad (10)$$

Here, D is the diffusion coefficient and τ_2 is $\frac{1}{\omega_2}$ with ω_2 being angular frequency corresponding to minimum in imaginary parts of the impedance, Z_i . From equation (9) and (10), we can write

$$(D\tau_2)^{1/2} = k_2 \epsilon_r \epsilon_0 A \quad (11)$$

and

$$D = \frac{(k_2 \epsilon_r \epsilon_0 A)^2}{\tau_2} \quad (12)$$

since $\mu = \frac{eD}{kT}$, where k is Boltzmann constant (1.38×10^{-23} J K⁻¹), T is absolute temperature in Kelvin and e is the electron charge (1.602×10^{-19} C), we can have

$$\mu = \frac{e(k_2 \epsilon_r \epsilon_0 A)^2}{kT\tau_2} \quad (13)$$

and from $\sigma = n\mu e$, we can write

$$n = \frac{\sigma k T \tau_2}{(e k_2 \epsilon_r \epsilon_0 A)^2} \quad (14)$$

Reference,

1. Linford, R. G. *Solid State Ionics Devices* 551-571 (World Scientific, Singapore, 1988).