Circuit Elements Used in Electrochemistry

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Abstract: Equivalent circuit fitting is an important task when dealing with electrochemical devices. The purpose is to find a circuit that best models the behavior of the electrochemical device so that it can be used in future simulation softwares to describe the behavior of the device. Because the regular resistor, capacitor and inductor only cannot accurately model the behavior of electrochemical devices, some conceptual circuit elements have been developed for the purpose. The paper gives an account of some of the elements.

Keywords: Equivalent Circuit, Warburg, Tanhyperbole, Cothyperbole, Gerischer

I. INTRODUCTION

Electrochemical Impedance Spectroscopy is an experimental method used in determining the complex impedance of a material over a certain range of frequency, from which analysis is performed on the results obtained. One of such analysis is to obtain an equivalent circuit of the device.

The most familiar circuit elements used in modeling the behavior of devices are resistors, capacitors and inductors. Apart from these elements, there are some conceptual elements used in electrochemistry to model the behavior of a device. Some of these devices are the Constant Phase Element, Warburg Impedance, Tanhyperbole, O circuit element and Gerisher, most of which are available in commercial equivalent circuit fitting softwares [1].

Using these circuit elements makes us sometimes arrive at an equivalent circuit model that best fits the behavior of the device. For example, the earlier Randle’s circuit that describes the behavior of a super capacitor has a Warburg impedance element in it [2]. Though, there are now other models developed by scholars that model the behavior of a super capacitor better than it. This paper gives a brief description of some of the elements.

II. CONSTANT PHASE ELEMENT (CPE).

Constant phase element is a circuit element having impedance expressed by:

\[ Z = \frac{1}{Q_0(j\omega)\alpha} \]

Where:
- \( \omega \) - Radial frequency.

Where \( Q_0 \) takes the value of the admittance at \( \omega = 1 \text{rad/s} \) with a unit of S.s. The phase angle of the impedance does not depend on frequency and has an angle of \((-90^\circ \alpha)\). When \( \alpha = 1 \), the impedance has no difference with that of a capacitor. In an instance where \( \alpha \) approaches 1, its response resembles that of a capacitor with a constant phase angle less than 90°.

The CPE behavior is usually caused by electrode roughness, surface disorder, slow adsorption or diffusion reactions, non-uniformity of current and voltage, electrode geometry and porosity. Fractal electrodes normally exhibit this behavior [2 -5].

III. WARBURG IMPEDANCE.

Warburg impedance is as a result of diffusion transport to electrodes. It is dependent on the frequency of the alternating signal. Whenever the frequency is high its value is small because the distance moved by diffusing reactants is small. At lower frequencies the reactants have to move a greater distance there by increasing the Warburg impedance. It is mathematically represented by the equation

\[ Z_w = \sigma(\omega)^{-0.5}(1 - j) \]

This forms a line with an angle of 45° to the real axis on the Nyquist plot.

The variable \( \sigma \), in equation (2) is the Warburg coefficient expressed as:
\[ \sigma = \frac{RT}{n^2F^2A^2} \left(\frac{1}{C_{o}^{2}/D_{o}} + \frac{1}{C_{R}^{2}/D_{R}}\right) \]  

Where: \( R \) - Ideal gas constant \((8.314472 \text{ J K}^{-1} \text{ mol}^{-1})\).
\( T \) - Thermodynamic temperature.
\( n \) - Number of electrons involved.
\( F \) - Faraday constant.
\( A \) - Surface area of the electrode.
\( C_{o}^{*} \) - Bulk concentration of the oxidant.
\( D_{o} \) - Diffusion coefficient of the oxidant.
\( C_{R}^{*} \) - Bulk concentration of the reactant.
\( D_{R} \) - Diffusion coefficient of the reactant.

The unit of \( \sigma \) is \( \Omega \text{s}^{0.5} \). It could either be determined using equivalent circuit fitting using a circuit that has a Warburg element in it or by finding the slope under its plot. Equivalent circuit fitting softwares mostly return an admittance value for the Warburg element from which the Warburg coefficient can be computed using the relationship [6]:

\[ \sigma = \frac{1}{\sqrt{2Y_{o}}} \]  

When \( \sigma \) is known, the magnitude of the Warburg impedance could be determined using:

\[ |Z_{w}| = \frac{\sqrt{2\sigma}}{\omega^{0.5}} \]  

Equation (2) only applies when the diffusion layer has an infinite thickness. In some cases the diffusion layer has a finite thickness. The following equation then applies:

\[ Z = \sigma \omega^{-\frac{1}{2}}(1 - j)\tanh\left(\delta \left(\frac{\omega}{B}\right)^{0.5}\right) \]  

Where \( \delta \) is the Nernst diffusion layer thickness and \( D \) is the diffusion coefficient of the electro active species [7].

More over in the case in which the diffusion layer is finite, the Tangent (T) circuit element and Open Finite-Length Diffusion (OFLD, sometimes shortened ‘O’) circuit element can be used to model the behavior of the super capacitor or any electrochemical device [8].

IV. T CIRCUIT ELEMENT (TANHYPERBOL)

The impedance behavior of the T circuit element is similar to that of the Warburg impedance at high frequencies. However, at lower frequencies, its behavior resembles that of a series combination of a resistor and a capacitor with:

\[ R = \frac{(B/Y_{o})}{3} \]  

\[ B = \frac{\delta}{\sqrt{D}} \]

Where: \( R \) is resistance.
\( B \) is time constant which has a unit of \( \sec^{0.5} \).
\( Y_{o} \) is an admittance parameter.
\( \delta \) is the thickness of the thin layer.
\( D \) is the diffusion coefficient.

\[ Z'' = \frac{B}{Y_{o}} \]

Equation (8) is the admittance parameter expressed as:

\[ Y_{o} = \frac{n^2F^2A}{RT \left(\frac{1}{c_{o}D_{o}^{2/3}} + \frac{1}{c_{R}D_{R}^{2/3}}\right)} \]  

Figure 1. Impedance behavior of a T circuit element [8].

Its impedance is given by:

\[ \tilde{Z}(\omega) = \left(\frac{1}{Y_{o}\sqrt{\omega}}\right) \coth\left[B\sqrt{\omega}\right] \]  

\[ Y_{o} \] is an admittance parameter expressed as:

\[ Y_{o} = \frac{n^2F^2A}{RT \left(\frac{1}{c_{o}D_{o}^{2/3}} + \frac{1}{c_{R}D_{R}^{2/3}}\right)} \]
The T element derives its name from the tan hyperbolic function in its admittance when equation (7) is inverted. This is the reason why sometimes it is described as a “Tanhyperbole” circuit element.

V. O CIRCUIT ELEMENT (COTHYPERTHOL)

The behavior of the O circuit element shown in figure 2 is as a result of the use of a rotating electrode (RDE) in impedance studies. In this type of system, there exists a region near the electrode in which mass transport happens by diffusion alone because a thin layer of unstirred solution (Nernst diffuse layer (NDL)) exists which has a large source of material outside it.

Sandwiched in between these regions is a porous membrane in which molecules can diffuse. At high frequencies its behavior is similar to the Warburg impedance while at low frequencies it shows the behavior of a Randles cell [9], [10].

Figure 2. Impedance behavior of an O circuit element [9].

Its impedance is given by:

$$ Z(\omega) = \left( \frac{1}{\sqrt{j\omega}} \right) \tanh \left[ B \sqrt{j\omega} \right] $$ (11)

B depends on the NDL which also depends on the speed of rotation of the electrodes [10]. It is called a “Cothyperbole” because its admittance has a Cothyperbole when equation (9) is inverted.

VI. GERISCHER (G)

Another circuit element used in impedance spectroscopy is the Gerischer (G) which also has the behavior of Warburg impedance at high frequencies sharing some resemblance with the O circuit element at low frequencies as shown in figure 3.

Figure 3. Impedance Behavior of a G circuit Element [11].

It results from a chemical reaction happening in the bulk solution called the common electrode (CE) mechanism. Its impedance is given by:

$$ Z(\omega) = \frac{1}{\sqrt{j\omega}} \left( 1 + \frac{k}{\sqrt{j\omega}} \right) $$ (12)

Where: k is a rate constant parameter having a unit per second (s\(^{-1}\)) [4].

VII. CONCLUSION

The paper has presented some conceptual circuit elements used in electrochemistry, specifically in equivalent circuit fitting. These elements are readily available in some equivalent circuit fitting softwares and have been used by several researchers and scholars in modeling impedance spectroscopy data.
VIII. REFERENCES


Usman Sammani Sani graduated from Bayero University, Kano in 2008, where he obtained a bachelor degree of electrical engineering. He then furthered his studies, in which he obtained M.Sc. in Electronic Communications and Computer Engineering from The University of Nottingham Malaysia Campus in 2011.

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