

Equivalent Circuit Modelling using Electrochemical Impedance Spectroscopy for Different Materials of SOFC

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Abstract – Suitable models are required to interpret the data for the characterization of the systems using EIS. On the basis of their interpretations, the models are divided into two kinds: process models and equivalent circuit models. These models use the experimental data for the estimation of the parameters which describes this data adequately and are used for the analysis of the system's behavior in different conditions. In this paper, the equivalent circuits for EIS of different cathode materials are modeled, which are most commonly used for the interpretation of the electrochemical impedance data. In the modeling of the electrochemical performance, these models are built using the passive elements like- inductors, resistors, and capacitors and also the distributed elements like-Warburg diffusion impedance, Gerischer diffusion impedance, CPE (Constant Phase Element). The different combinations of these elements are used to build the equivalent circuits. Each element has some physical meaning in the equivalent circuits.

Key Words: Solid oxide Fuel Cell –SOFC, Electro impedance Spectroscopy – EIS, Impedance Modeling.

I. INTRODUCTION

As the strength value and phase of alternating current impedance depends on the frequency, so we use a sinusoidal voltage signal for measurements to excite an LTI system, and hence AC current is obtained, having the same frequency as voltage signal. These voltage and current expressions are then converted from a time to a frequency domain.

So in turn, the time and frequency domain expressions are related to each other. Most often the Nyquist's plot and Bode's plots are represented for giving a clearer picture of this alternating current impedance. The electrical and electrochemical characteristics of vague manganese oxide as well as MnO_2 /Carbon Vulcan nanocomposite is been investigated and compared in order to recognize the most auspicious material for energy conservation with the assistance of super-capacitors [14, 15]

A. Electrochemical Impedance Spectroscopy (EIS)

EIS is a powerful method and tool for the interpretation of performance of electrochemical systems and also in the

investigation of the polarization processes in an SOFC. As the polarization loss mechanisms have different responses of time constant and frequency, therefore this fact is used for explaining electrochemical mechanisms, characterizing the different electrode materials with their performances and also their ions transportation properties. The EIS is generated after a sinusoidal AC voltage or current is applied on the top of a DC bias for different ranges of frequencies. The sizes and shapes of the plots obtained reflects the useful information about the conditions of operation, microstructure and material as well as its composition. The appropriate models of the systems are built to understand these experimental impedance data obtained, and after impedance spectra is fitted with the data, we can get its parameters. These obtained models depict its parameters as a physical or chemical meaning and helps to give the description of the system. Ideally each process has its arc in the EIS. But their capacitive nature gives very less time to relax during the change in the boundary conditions and hence overlapped arcs are obtained in the EIS. Quite often, at high and low frequencies, inductive or capacitive impedance in the EIS can also be observed which are obtained because of the impedance of the measurement leads.

B. Electrochemical Impedance Modeling of SOFCs

As discussed above about the two modeling processes, in general, equivalent circuit modeling is widely used. This modeling type provides well enough overall performance comparisons, but usually because of the overlapping of the arcs obtained for various physiochemical processes, explanation of the physical source of the SOFC losses lacks accuracy. Hence, interpretations of the chemical as well as physical parameters may often be quite a challenge.

C. Elements Used for the Impedance Modeling:

- 1) **Resistance** It has only real part and is independent of the frequency. The current through it and voltage are both in phase to each other. Some uses of resistance in electrochemical phenomenon:
- a) **Ohmic resistance (R_o)** it is also called the uncompensated resistance. It is the potential difference between the

working and the reference electrode. The ohmic resistance depends on the conductivity of the electrolyte and the geometry of the electrode. In the Nyquist plot, at the high frequency end, the intersection of real axis and the impedance arc gives the R_o .

- b) **Polarization resistance (R_p)** The electrode gets polarized when the potential difference is higher than its open circuited. The polarized electrode results in a flow of current due to the reactions on its surface.
2. **Capacitance** Its impedance has imaginary part and is a function of the freq. Its impedance has the inverse proportional relation with the frequency. The current through it lags in phase by 90° with the voltage. Some uses of capacitance in electrochemical phenomenon:
 - a. **Double Layer-capacitance (C_{dl})** At the electrolyte/electrode interfaces exist an electrical double layer. The double layer thus formed when ions approach electrode surface from the solution. The charges of these ions and the charges in electrode are separated. The double layer-capacitance's value depends on number of variables like- impurity adsorption, temperature, ionic concentrations, electrode roughness, types of ions, electrode potential, oxide layers, etc.
 - b. **Coating-Capacitance (C_c)** Typically, coatings' dielectric constants are in ranges '3-4' & of water is around '80'. When coating gets penetrated by water, the dielectric constant is increased, and hence coating capacitance is also increased. Therefore, C_c is used for measuring the amount of water absorbed by coating.
3. **Constant-Phase Element (CPE)** Modeling with an ideal capacitor assumes that the surface investigated is homogeneous which is not the case normally. This lacked homogeneity is modeled as a Q element, used to represent the CPE: $Z_Q = 1 / [Y_o (j\omega)^n]$, where, $Y_o \rightarrow$ admittance of the ideal capacitance and $n \rightarrow$ empirical constant (range: 0 – 1). And when $n = 1$, CPE acts like a pure capacitor; when $n = 0$, CPE acts like a pure resistor. Further, if $n = 0.5$, CPE is the equivalent of the Warburg element, described in below. Double layer-capacitance and coating-capacitance, described above, are usually modeled by CPE.
4. **Inductance** An electrochemical cell's impedance can appear as to be inductive due to the surface's reactants adsorption & it can be modeled as an 'Inductance'. This behavior of inductance can also be formed from potentiostat non-idealities, inductance of cell cables, non-uniform current distribution and slow response of reference electrodes. In such cases, appearance of inductance shows the presence of error in the electrochemical impedance spectroscopy measurements.
5. **Warburg Impedance** Diffusion of ions at the interfaces of cell is common in electrochemical systems, which is modeled by using this impedance. For semi-infinite-

diffusion layer, impedance: $Z_W = 1 / [Y_o (j\omega)^{0.5}]$, where, Y_o is the diffusion admittance. Warburg impedance has been characterized which have identical imaginary and real contributions, which results in 45° phase angle.

6. **Gerischer Element (G)** Gerischer element in the circuit at the beginning was derived for the chemical reactions taking place in bulk sol. at first. On the Nyquist-plot, it looks like thin-layer diffusion element. It is given by the following equation:

$$Y(\omega) = Y_o \sqrt{k + j\omega}$$

Where, $Y_o \rightarrow$ admittance parameter, and $k \rightarrow$ rate constant parameter.

TABLE I. CIRCUIT ELEMENT USED IN MODELLING WITH THEIR IMPEDANCES AND ADMITTANCES

Elements	Admittance	Impedance
R	(1/R)	R
L	1/(j ω L)	(j ω L)
C	(j ω C)	1/(j ω C)
CPE	$[Y_o (j\omega)^n]$	$1/[Y_o (j\omega)^n]$
Warburg	$[Y_o j\omega]^{0.5}$	$1/[Y_o j\omega]^{0.5}$
Gerischer	$1/Y_o \sqrt{k + j\omega}$	$Y_o \sqrt{k + j\omega}$

In the complex impedance plane, such impedance yields a semicircle with diameter (Fig.1a). It is clear that in the limit $\omega \rightarrow 0$ the influence of the capacitance has to vanish, and the dc resistance R is obtained. At higher frequencies, the real part of the impedance Z_{real} decreases due to the dielectric "opening" of the capacitance (displacement current), whereas the imaginary part Z_{imag} (or the phase shift between the currents going through the resistor and the capacitor) increases. The frequency where these two currents are equal and the imaginary part of the impedance reaches its maximum is the relaxation frequency, ω_R , of the RC element. It is given by;

$$\omega_R = 1/RC$$

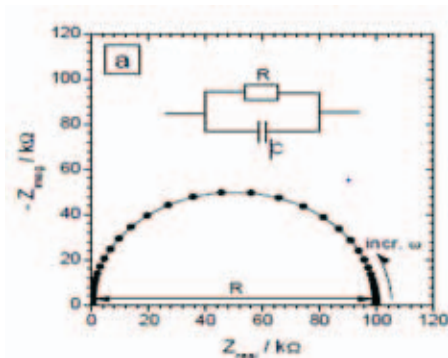


Fig1(a) Impedance spectra of one RC element

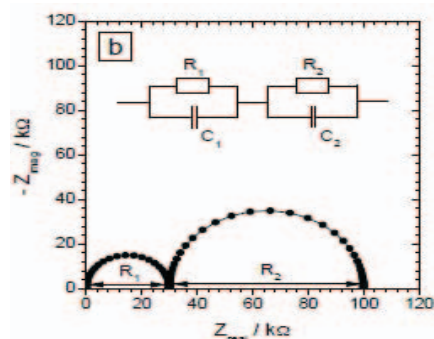


Fig.1b impedance spectra of two RC element

There are two circuits shown in figure.1a and figure.1b which shows two different impedance spectra with different time constants. Two serial RC elements lead to two well-separated semicircles in the complex impedance plane if their relaxation frequencies are sufficiently different (Fig.1b). In a real system, this may for example be realized by a large difference in the magnitude of the capacitances and similar values for the resistances. Hence, if a measurement yields one or several well separated semicircles, the resistances and relaxation frequencies of the underlying processes can immediately be read from the Cole-Cole plot, and thus a capacitance can be calculated for each process. The magnitude of a capacitance is often already a strong indication of its physical origin. Generally, Nyquist plot shows the real impedance v/s the imaginary impedance which shows the inductive and capacitive characteristics. Also, these plots have some advantages that controlled activation processes with different constants of time shows the impedance arcs and their shape gives an idea of its mechanisms or its governed phenomenon.

II. DISCUSSION

It is clearly seen from the table that some physics-based equivalent circuit models are proposed, and electrochemical impedances of corresponding SOFCs have been fitted well accordingly by using EIS [14]. Fitting of the curves give reaction rate constant, effective gas diffusions, absorption equilibrium constant, oxygen surface diffusions, etc. Electrochemical impedance plots often contain several semicircles which may be perfect or may be suppressed semicircles. Each suppressed semicircle usually shows to a specific reaction or process. However, such an approach is often not a correct approximation since processes can be coupled. Examples of coupled processes include the Finite-Length-Warburg (FLW) impedance element, gas diffusion coupled with gas conversion, the Gerischer impedance element describing a coupling between diffusion and reaction¹². While plotting each process' response (cathode Gerischer type surface adsorption/diffusion, inductance, anode Warburg gas diffusion, high frequency charge transfer reaction) individually, their separate peak frequency and contribution can be seen from their EIS curves as shown in table. A vertical line can be seen

at highest freq. region at the fourth quadrant due to the inductance or it may be in low frequency region which is due to lead inductance or due to some inductive properties of fuel cell; a small arc is formed due to the RC in parallel in high freq. region; A semicircle followed by a 45° line can be seen which are given by the Warburg and Gerischer type impedance, however their responses are greatly overlapped in the medium to low freq. region as we have discussed above. We also observe that with the increasing of the thickness, time constants of the dynamics increase so the resistance from diffusion also increases [13]. We have also observed one more shortcoming of the Nyquist Plots. While looking at the plot's data points, we can't tell what freq. was used to record that point. But we can find that frequency by using Bode plot in EIS. As we can see from the figure, we can use any of the above circuits for two time constants but generally we prefer Fig.2.C for modeling for ease of calculations. In two time constants circuit, one RC circuit is due to high frequency and another one is due to low frequency. [2] In many situations, however, the required equivalent circuit representation and thus the interpretation of impedance spectra are more complicated. Difficulties emerge if two serial processes having similar relaxation frequencies. In such a case the two semicircles overlap, and the resulting impedance behavior may appear as a single, distorted arc in the complex impedance plane.

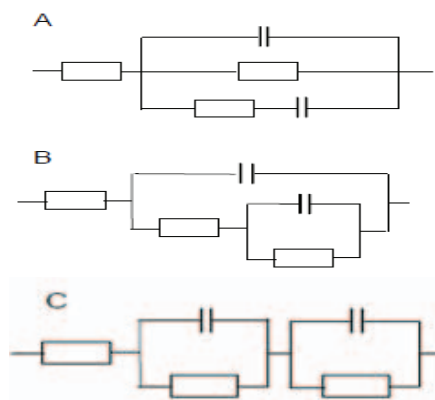
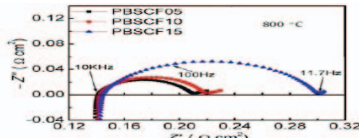
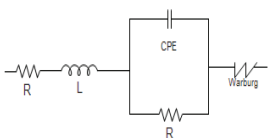


Fig. 2: Equivalent circuit models with two time constants.

The decision on whether or not such a distorted semicircle consists of two components is aggravated by the empirical fact that experimental semicircles are always "non-ideal" to some degree, i.e. more or less depressed, even if they are caused by a "single" electrochemical process. Apparently, an RC element generally oversimplifies the real situation. A path frequently followed in order to deal with depressed semicircles is to replace the capacitor of an RC element by a so-called constant phase element CPE. Resistance can be a charge transfer resistance, polarization resistance, ohmic resistance etc. and capacitance can be double layer capacitance, etc. as per characterization of fuel cell.

TABLE II. DIFFERENT SOFC CATHODE MATERIALS WITH THEIR EIS CURVES AND THEIR PROPOSED EQUIVALENT ELECTRICAL CIRCUITS.

Sr. No.	SOFC Cathode Materials	Electrochemical Impedance Spectroscopy (EIS)Data	Proposed Equivalent Electrical Circuits	Ref.
1.	La0.8Sr0.2MnO3- δ			[1]
2.	LSM-CGO (La0.6Sr1.4MnO4+ δ)			[2]
3.	SSC (Sm0.5Sr0.5CoO3- δ)			[3]
4.	LCF			[4]
5.	NSFCx NdxSr1-xFe0.8Cu0.2O3- δ (0.3 ≤ x ≤ 0.7)			[5]
6.	LSCF (La0.6Sr0.4Co0.8Fe0.2O3- δ)			[6]
7.	BSCF-GDC (Ba0.5Sr0.5Co0.8Fe0.2O3- δ) (Gd0.1Ce0.9O1.95)			[7]
8.	Nd2NiO4+ δ			[8]
9.	NBCO (NdBaCo2O5+ δ)			[9]
10.	PBCO(PrBaCo2O5+ δ - Ce0.8Sm0.2O1.9)			[10]

11.	PBSCF ($\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{2-\delta}\text{Fe}_{\delta}\text{O}_{5+\delta}$) ($x=0.5, 1.0, 1.5$)			[11]
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III. CONCLUSION

Modeling the equivalent circuit of EIS data for different kinds of cathode materials have been used to obtain physical properties of the system by the impedance data modeling in terms of an equivalent electrical circuit composed of resistance, capacitance, inductance etc. The values of these impedances can be easily calculated by using basic laws of KVL and KCL theoretically and also by using EIS fitting. We can also find the rate limiting step in SOFC performance with the help of EIS data and corresponding equivalent electrical circuits by finding the low frequency or high frequency region in EIS study. We have also concluded that the values of impedances depend upon the operating temperature of fuel cell, if we change the operating temperature then corresponding impedance values will change accordingly.

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