An integrated approach to electrochemical impedance spectroscopy

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Abstract

A philosophy for electrochemical impedance spectroscopy is presented which integrates experimental observation, model development, and error analysis. This approach is differentiated from the usual sequential model development for given impedance spectra by its emphasis on obtaining supporting observations to guide model selection, use of error analysis to guide regression strategies and experimental design, and use of models to guide selection of new experiments. These concepts are illustrated with two examples taken from the literature. This work illustrates that selection of models, even those based on physical principles, requires both error analysis and additional experimental verification.
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1. Introduction

While impedance spectroscopy can be a sensitive tool for analysis of electrochemical and electronic systems, an unambiguous interpretation of spectra cannot be obtained by examination of raw data. Instead, interpretation of spectra requires development of a model which accounts for the impedance response in terms of the desired physical properties. Model development should take into account both the impedance measurement and the physical and chemical characteristics of the system under study.

It is useful to envision a flow diagram for the measurement and interpretation of experimental measurements such as impedance spectroscopy. Barsoukov and Macdonald proposed such a flow diagram for a general characterization procedure (Figure 1.2.1 in both references [1] and [2]) consisting of two blocks comprising the impedance measurement, three blocks comprising a physical (or process) model, one block for an equivalent electrical circuit, and blocks labeled curve fitting and system characterization. They suggested that impedance data may be analyzed for a given system by using either an exact mathematical model based on a plausible physical theory or a comparatively empirical equivalent circuit. The parameters for either model can be estimated by complex nonlinear least squares regression. The authors observed that ideal electrical circuit elements represent ideal lumped constant properties; whereas, the physical properties of electrolytic cells are often distributed. The distribution of cell properties motivates use of distributed impedance elements such as constant-phase elements (CPE). An additional problem with equivalent circuit analysis, which the authors suggest is not shared by the direct comparison to the theoretical model, is that circuit models are ambiguous and different models may provide equivalent fits to a given spectrum. The authors suggest that identification of the appropriate equivalent circuit can be achieved only by employing physical intuition and by carrying out several sets of measurements with different conditions.

A similar flow diagram was presented by Huang et al. [3] for solid-oxide fuel cells (SOFCs). The diagram accounts for the actions of measuring impedance data, modeling, fitting the model, interpreting the results, and optimizing the fuel cell for power generation. The authors emphasize that the interpreting action depends more on the electrochemical expertise of the researchers than on a direct mapping from model parameters to SOFC properties.

While helpful, the flow diagrams proposed by Barsoukov and Macdonald [2] and Huang et al. [3] are incomplete because they do not account for the role of independent assessment of exper-
2. Integration of measurements, error analysis, and model

A refined philosophical approach toward the use of impedance spectroscopy is outlined in Fig. 1 where the triangle evokes the concept of an operational amplifier for which the potential of input channels must be equal. Sequential steps are taken until the model provides a statistically adequate representation of the data to within the independently obtained stochastic error structure. The different aspects which comprise the philosophy are presented in this section.

2.1. Impedance measurement are integrated with experimental error analysis

All impedance measurements should begin with measurement of a steady-state polarization curve. The steady-state polarization curve is used to guide selection of an appropriate perturbation amplitude and can provide initial hypotheses for model development. The impedance measurements can then be performed at selected points on the polarization curve to explore the potential dependence of reaction rate constants. Impedance measurements can be performed as well as a function of other state variables such as temperature, rotation speed, reactant concentration. Impedance scans made at different points of time can be used to explore temporal changes in system parameters. Some examples include growth of oxide or corrosion-product.

The impedance measurements should also be conducted in concert with error analysis with emphasis on both stochastic and systematic bias errors. The bias errors can be defined to be those that result in data that are inconsistent with the Kramers–Kronig relations. An empirical error analysis can be undertaken using the measurement model approach suggested by Agarwal et al. [5–7] and Orazem [8]. It should be noted, however, that this approach is not definitive because Kramers–Kronig-consistent artifacts can be caused by electrical leads and the electronics. Use of dummy cells can help identify artifacts that are consistent with the Kramers–Kronig relations. As an alternative approach for identification of stochastic part of the error structure, Dygas and Breiter have shown that impedance instrumentation could, in principle, provide standard deviations for the impedance measurements at each frequency [9].

The feedback loop shown in Fig. 1 between EIS Experiment and Error Analysis indicates that the error structure is obtained from the measured data and that knowledge of the error structure can guide improvements to the experimental design. The magnitude of perturbation, for example, should be selected to minimize stochastic errors while avoiding inducing a nonlinear response. The frequency range should be selected to sample the system time constants, while avoiding bias errors associated with non-stationary phenomena. In short, the experimental parameters should be selected so as to minimize the stochastic error structure while, at the same time, allowing for the maximum frequency range that is free of bias errors.

2.2. Process model is developed in concert with other observations

The model identified in Fig. 1 represents a process model intended to account for the hypothesized physical and chemical character of the system under study. From the perspective embodied in Fig. 1, the objective of the model is not to provide a good fit with the smallest number of parameters. The objective is rather to use the model to gain physical understanding of the system. The model should be able to account for, or at least be consistent with, all experimental observations. The supporting measurements therefore provide a means for model identification. The feedback loop shown in Fig. 1 between Model and Other Observations is intended to illustrate that the supporting measurements guide model development and the proposed model can suggest experiments needed to validate model hypotheses. The supporting experiments can include both electrochemical and non-electrochemical measurements.

Numerous scanning electrochemical methods such as scanning reference electrodes, scanning tunneling microscopy, and scanning electrochemical microscopy can be used to explore surface heterogeneity. Scanning vibrating electrodes and probes can be used to measure local current distributions. Local electrochemical impedance spectroscopy provides a means of exploring the distribution of surface reactivity. Measurements can be performed across the electrode at a single frequency to
create an image of the electrode or, alternatively, performed at a given location to create a complete spectrum. Other experiments may include in situ and ex situ surface analysis, chemical analysis of electrolytes, and both in situ and ex situ visualization and/or microscopy. Transfer-function methods such as electrohydrodynamic (EHD) impedance spectroscopy allow isolation of the phenomena that influence the electrochemical impedance response [10].

2.3. Regression analysis accounts for error structure

The goal of the operation represented by the triangle in Fig. 1 is to develop a model that provides a good representation of the impedance measurements to within the noise level of the measurement. The error structure for the measurement clearly plays a critical role in the regression analysis. The weighting strategy for the complex nonlinear least squares regression should be based on the variance of the stochastic errors in the data, and the frequency range used for the regression should be that which has been determined to be free of bias errors. In addition, knowledge of the variance of the stochastic measurement errors is essential to quantify the quality of the regression.

Sequential steps are taken until the model provides a statistically adequate representation of the data to within the independently obtained stochastic error structure. The comparison between model and experiment can motivate modifications to the model or to the experimental parameters.

3. Examples

The systems described below illustrate the approach outlined in Fig. 1.

3.1. Deep-level states in GaAs diodes

Orazem et al. [11] and Jansen et al. [12] described the impedance response for an n-type GaAs Schottky diode with temperature as a parameter. The system consisted of an n-GaAs single crystal with a Ti Schottky contact at one end and a Au, Ge, Ni Schottky contact at the eutectic composition at the other end. This material has been well characterized in the literature and, in particular, has a well known EL2 deep-level state that lies 0.83–0.85 eV below the conduction band edge [13]. Experimental details are provided elsewhere [11,12].

The experimental data are presented in Fig. 2 (a) and (b) for the real and imaginary parts of the impedance, respectively, for temperatures ranging from 320 to 400 K. The logarithmic scale used in Fig. 2 emphasizes the scatter seen in the imaginary impedance at low frequencies. The impedance response is seen to be a strong function of temperature. The impedance-plane plots shown in Fig. 3 for data collected at 320 and 340 K approach the classic semicircle associated with a single relaxation process.

Jansen and Orazem showed that the impedance data could be superposed as given in Fig. 4 [12]. The impedance data collected at different temperatures were normalized by the maximum mean value of the real part of the impedance and plotted against a normalized frequency defined by

$$f^* = \frac{f}{f^\circ} \exp \left( \frac{E}{kT} \right)$$  \hspace{1cm} (1)

where $E = 0.827$ eV, and the characteristic frequency $f^\circ$ was assigned a value of $2.964 \times 10^{14}$ Hz such that the imaginary part of the normalized impedance values reached a peak value near $f^* = 1$. The data collected at different temperatures are reduced...
Fig. 4. Impedance data from Fig. 2 collected for an n-GaAs/Ti Schottky diode as a function of frequency $f^* = (f/f°) \exp(E/kT)$: (a) the real part of the impedance; and (b) the imaginary part of the impedance. Data taken from Jansen et al. [12]

to a single line. The extent to which the data are superposed is seen more clearly on the logarithmic scale shown in Fig. 5. The superposition shown in Figs. 4 and 5 suggest that the system is controlled by a single-activation-energy-controlled process.

A closer examination of Fig. 4(b) reveals that the maximum magnitude of the scaled imaginary impedance is slightly less than 0.5; whereas the corresponding value for a single-activation-energy-controlled process should be identically 0.5. Regression analysis using the traditional weighting strategies under which the standard deviation of the experimental values was assumed to be proportional to the magnitude of the impedance,

$$\sigma_r = \sigma_j = \alpha |Z|,$$

led to a single time constant with only a hint that other parameters could be extracted. Orazem et al. [11] and Jansen et al. [12] used the measurement model approach described by Agarwal et al. [5–7] and Orazem [8] to identify the stochastic error structure for the impedance data. When the data were regressed using this error structure for a weighting strategy, additional parameters could be resolved revealing additional activation energies. Thus, while the data do superpose nicely in Figs. 4 and 5, the impedance data do in fact contain information on minor activation-energy-controlled electronic transitions [11,12]. The information concerning these transitions could be extracted by regression of an appropriate process model using a weighting strategy based on the error structure of the measurement.

Two models have been proposed for the data presented above. Macdonald proposed a distributed-time-constant model which accounts for distributed relaxation processes [14]. This model fits the data very well and has the advantage that it requires a minimal number of parameters. A second model, presented in Fig. 6, accounts for discrete energy levels and provides a fit of equivalent regression quality at each temperature [11,12]. In Fig. 6, $C_n$ is the space-charge capacitance, $R_n$ is a resistance that accounts for a small but finite leakage current, and the parameters $R_1 \ldots R_k$ and $C_1 \ldots C_k$ are attributed to the response of discrete deep-level energy states. Parameters corresponding to deep-level states were added sequentially to the model, subject to the constraint that the $2\sigma$ (95.4%) confidence interval for each of the regressed parameters may not include zero. Including the space charge capacitance and leakage resistance, four resistor–capacitor pairs could be obtained from the impedance data collected at 300, 320, and 340 K; three resistor–$1/2$ capacitor pairs could be obtained from the data collected at 360, 380, and 400 K; and two resistor-capacitor pairs could be obtained from the data collected at 420 K [12].
This model has the disadvantage that up to eight parameters are required, depending on the temperature, as compared to the three parameters required for the distributed-time-constant model. The question to be posed then, “which is the better model for the measurements?”

If the goal of the regression is to provide the most parsimonious model for the data, the model with the smallest number of parameters and a continuous distribution of activation energies is the best model. If the goal of the regression is to provide a quantitative physical description of the system for which the data were obtained, additional measurements are needed to determine whether the activation energies are discrete or continuously distributed. In this case, deep-level transient spectroscopy (DLTS) measurements indicated that the n-GaAs diode contained discrete deep-level states. In addition, the energy levels and state concentrations obtained by regression of the second model were consistent with the results obtained by DLTS[12]. Thus, the second model with a larger number of parameters provides the more useful description of the GaAs diode. The choice between the two models could not be made without the added experimental evidence.

3.2. Side reactions in PEM fuel cells

Low-frequency inductive features [15–17] are commonly seen in impedance spectra for PEM fuel cells. Makharia et al. [15] suggested that side reactions and intermediates involved in the fuel cell operation can be possible causes of the inductive loop seen at low frequency. However, such low-frequency inductive loops could also be attributed to non-stationary behavior, or, due to the time required to make measurements at low frequencies, non-stationary behavior could influence the shapes of the low-frequency features.

A typical result is presented in Fig. 7 for the impedance response of a single 5 cm$^2$ PEMFC with hydrogen and air as reactants [18]. The measurements were conducted in galvanostatic mode for a frequency range of 1 kHz to 1 mHz with a 10 mA peak-to-peak sinusoidal perturbation. Roy and Orazem [19] used the measurement model approach developed by Orazem and coworkers [5–8] to demonstrate that, for the fuel cell under steady-state operation, the low-frequency inductive loops seen in Fig. 7 were consistent with the Kramers–Kronig relations. Therefore, the low-frequency inductive loops could be attributed to process characteristics and not to non-stationary artifacts.

Roy et al. [18] proposed that that the low-frequency inductive loops observed in PEM fuel cells could be caused by parasitic reactions in which the Pt catalyst reacts to form PtO and subsequently forms Pt$^+$ ions. They also showed that a reaction involving formation of hydrogen peroxide could yield the same inductive features. A comparison between the two models and the experimental results is shown in Fig. 8, and the corresponding values for the real and imaginary parts of the impedance are presented as a function of frequency in Fig. 9(a) and (b), respectively. The model calculations were not obtained by regression but rather by simulation using approximate parameter values. Regression was not used because the model was based on the assumption of a uniform membrane-electrode assembly (MEA); whereas, the use of a serpentine flow channel caused the reactivity of the MEA to be very nonuniform. The parameters were first selected to reproduce the current–potential curve and then the same parameters were used to calculate the impedance response.
for each value of current density. The potential (or current) dependence of model parameters was that associated with the Tafel behavior assumed for the electrochemical reactions.

While reaction parameters were not identified by regression to impedance data, the simulation presented by Roy et al. [18] demonstrates that side reactions proposed in the literature can account for low-frequency inductive loops. Other models can also account for low-frequency inductive loops so long as they involve potential-dependent adsorbed intermediates [20]. It is generally understood that equivalent circuit models are not unique and have therefore an ambiguous relationship to physical properties of the electrochemical cell. As shown by Roy et al. [18], even models based on physical and chemical processes are ambiguous. In the present case, the ambiguity arises from uncertainty as to which reactions are responsible for the low-frequency inductive features.

Resolution of this ambiguity requires additional experiments. The processes and reactions hypothesized for a given model can suggest experiments to support or reject the underlying hypothesis. For example, the proposed formation of PtO is consistent with a decrease in the active catalytic surface area and a loss of Pt ions in the effluent. Cyclic voltammetry after different periods of fuel cell operation could be used to explore reduction in electrochemically active area. Inductively coupled plasma mass spectroscopy (ICPMS) could be used to detect residual Pt ions in the fuel cell effluent, and ex situ techniques could detect formation of PtO in the catalyst layer. A different set of experiments could be performed to explore the hypothesis that peroxide formation is responsible for the inductive loops. Platinum dissolution has been observed in PEM fuel cells, [21] and peroxide formation has been implicated in the degradation of PEM membranes [22–24]. Thus, it is likely that both reactions are taking place and contributing to the observed low-frequency inductive loops.

4. Discussion

The example presented in Section 3.1 demonstrates the importance of coupling experimental observation, model development, and error analysis. The measurements conducted at different temperatures allowed identification of discrete activation energies for electronic transitions. Use of a weighting strategy based on the observed stochastic error structure increased the number of parameters that could be obtained from the regression analysis. Thus, four discrete activation-energy-controlled processes could be identified, but at the expense of a corresponding model that required eight parameters. A regression of almost the same quality could be obtained under the assumption of a continuous distribution of activation energies, and this model required only three parameters. Discrimination between the two models requires additional experimental observations, such as the DLTS identification of electronic transitions involving discrete deep-level states.

The example presented in Section 3.2 demonstrates the utility of the error analysis for determining consistency with the Kramers–Kronig relations. In this case, the low-frequency inductive loops were found to be consistent with the Kramers–Kronig relations at frequencies as low as 0.001 Hz so long as the system had reached a steady-state operation. The error analysis employed regression of a measurement model. The mathematical process models that were proposed to account for the low-frequency features were based on plausible physical and chemical hypotheses. Nevertheless, the models are ambiguous and require additional measurements and observations to identify the most appropriate for the system under study.

The philosophy described here cannot always be followed to convergence. Often the hypothesized model is inadequate and cannot reproduce the experimental results. Even if the proposed reaction sequence is correct, surface heterogeneities may introduce complications that are difficult to model. The accessible frequency range may be limited at high frequency for systems with a very small impedance. The accessible frequency range may be limited at low frequency for systems subject to significant non-stationary behavior. The experimentalist may need to accept a large level of stochastic noise for a system with a large impedance. In cases where the models are unable to explain all features of the experiment, the graphical

Fig. 9. Comparison of the impedance response for a PEM fuel cell operated at 0.2 A/cm² to model predictions generated using a reaction sequence involving formation of hydrogen peroxide and a reaction sequence involving formation of PtO: (a) real part of the impedance; and (b) imaginary part of the impedance. Results taken from Roy et al. [18].
methods presented by Orazem et al. [25] can nevertheless yield quantitative information.

5. Conclusions

The philosophy embodied in Fig. 1 integrates experimental observation, model development, and error analysis. It takes into account the observations that impedance spectroscopy is not a stand-alone technique and that other observations are required to validate a given interpretation of the impedance spectra. Within the context of the work presented here, the objective of modeling is not to provide a good fit with the smallest number of parameters, but, rather, to use the model to learn about the physics and chemistry of the system under study.

References