Chapter 17
Conclusions

Electrochemical impedance spectroscopy is a mature technique, and its fundamental mathematical problems are well understood. Impedances can be written for any electrochemical mechanism using standard procedures. Modern electrochemical equipment makes it possible to acquire data in a wide range of frequencies and with various impedance values. The validity of experimental data can be verified by standard procedures involving Kramers-Kronig transforms. Several programs either allow for the use of predefined simple and distributed elements in the construction of electrical equivalent circuits or directly fit data to equations (which should be defined by the user).

The biggest challenge is correctly interpreting the experimental data and assigning correct circuits/equations to the models. Formal fitting of the experimental impedances to electrical equivalent circuits is simple and represents the most widely used procedure; however, this procedure generally conveys little information about the electrochemical mechanism. The biggest problem in the analysis of impedances is correctly assigning a physical meaning to the observed features (physicochemical modeling). A casual perusal of the literature reveals that experimental data are often misinterpreted. It must be stressed that correct modeling is the most difficult part of analyzing impedance data. First, the steady-state current-potential characteristics must be well understood. Next, additional experiments with modifications to the concentration/partial pressure, temperature, hydrodynamic conditions, electrode surface, and morphology might be necessary.

Finally, once a correct physicochemical model is found and its parameters determined, then one may set about determining the kinetic parameters of the system. It should be emphasized that impedance parameters (e.g., resistances, capacitances, or other mechanism-related parameters) are derivatives of rates of electrochemical and chemical reactions and are complex functions of the rate constants and other parameters, for example, adsorption and concentration. Such analyses are carried out using nonlinear approximations of the impedance parameters as functions of the electrode potential and other experimental parameters, and these analyses are being performed on an increasingly frequent basis. Of course, one cannot neglect error analysis to check the reliability of the procedure.

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Although most impedance spectra are relatively simple, in some cases – most often in corrosion – they are very complex. Macdonald [1] suggested doing analysis by pattern recognition using artificial neural networks coupled with extensive libraries of reaction mechanisms. However, although such tools are very promising they are still rarely used [620] and not yet commercially available.