Summary

Electrochemistry is at the heart of a multitude of industrial activities like electrowinning and electrorefining of metals, plating, electrochemical forming and machining, *etc*. Therefore, a thorough understanding of electrochemical reactions is indispensable. Electrochemical impedance spectroscopy (EIS) is a powerful tool to elucidate the reaction mechanism of an electrochemical process. However, the interpretation of electrochemical impedance spectra is not straightforward and, therefore, modelling techniques (curve-fitting techniques) are required to obtain insight in the observed phenomena. With respect to this modelling, it was found that fundamental questions are often left unresolved. For example, how to decide whether a fit is satisfactory? If it is not, is this due to the poor quality of the experimental data or due to the inadequacy of the postulated model? Therefore, the object in this work is to set up a methodology for a sound statistical and accurate data modelling of electrochemical impedance spectra. The strategy consists in addressing issues specific to the two key elements in data modelling, namely the experimental data and the theoretical data.

With respect to the experimental data it is found that the intrinsic time dependency of electrochemical processes (the electroreduction of silver thiosulphate complexes is taken as a case study) has adverse influences on the acquisition of impedance measurements as well as on the proper error analysis of the experimental data. By combining a new electrode pretreatment procedure and a dedicated approach to error analysis (the measurement model approach) it is found that unbiased impedance data can be collected for an extended frequency region, and with a proper assessment of the level of stochastic measurement noise. As a result, the procedure yields experimental impedance spectra containing a higher amount of information with known reliability. It is stressed that the knowledge of the reliability of the experimental data enables to evaluate the statistical relevance of any subsequent regression.

In order to calculate theoretical data, it is proposed to build impedance models starting from the basic physical-electrochemical laws. In view of treating these types of models, a state-of-the-art numerical solver, Pirode, is evaluated by comparison with an analytical approach. Focus is on electrode kinetics influenced by adsorption and/or mass transfer since those phenomena are frequently encountered in industrial, complex processes. The interest in the study of adsorption phenomena is furthermore underlined due to the fact that the simulation of adsorption is new in Pirode. With the current state of developments, it is found that analytical models (despite their general lack of accuracy) are still needed to proceed to automate parameter estimation (*i.e.* curve fitting). On the other hand it is demonstrated that the numerical model of Pirode enables the simulation of theoretical data that describe more accurately the electrochemical processes under investigation. Then again, fitting possibilities are

missing so far in Pirode. Further developments are therefore expected in the integration of a statistically well-founded curve-fitting tool in powerful numerical solvers like Pirode. This would enable both accurate and precise parameter estimation without the need to elaborate analytical models.