

Estimation and optimization of the quality of electrochemical impedance data in the silver electrodeposition system

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In view of a rigorous kinetic characterisation of the electrodeposition of silver from thiosulphate complexes ($1,2\text{-Ag}(\text{S}_2\text{O}_3)_2^{3-}$), Electrochemical Impedance Spectroscopy (EIS) is used to estimate all the relevant physical parameters together with their confidence intervals. Though, prior to any physical interpretation of the experimental impedance measurements, a thorough data analysis is essential. Firstly, this analysis consists in the identification of the stochastic error structure which indicates the weight that should be assigned to each data point while regressing an impedance model. Secondly, while regressing an electric impedance model that is intrinsically Kramers-Kronig consistent, biased data points are recognized and can be excluded from the data set for further physical interpretations (1-3).

Hence, knowing the stochastic error structure is the main key for a careful data analysis. Unfortunately, the time-varying character of electrodeposition systems has prevented direct experimental determination of the stochastic error structure. As a response for this common problem in electrochemistry, Agarwal *et al.* presented a method, by which the stochastic error structure can be determined, even for systems for which successive measurements are not replicate (2). The procedure is based on the use of a Voigt measurement model acting as a tool for detecting and filtering a lack of replicacy. An additional filtering step, eliminating the contributions due to a lack of fit of the model, enables the approximation of the stochastic error structure.

The application of Agarwal's strategy on the above mentioned Ag system starts with collecting a set of repeated spectra. Taking a Ag predeposition on the working electrode into account, two types of data collections can be constructed. The first one consists of a series of successive impedance spectra recorded subsequently to one preconditioning of the electrode. When overlaying the ten 'successive' spectra in a Nyquist plot (see Figure 1a), a nonstationary drift, preventing the direct estimation of the stochastic error structure, is clearly seen. The second type of data set is acquired by measuring several series of 'successive' spectra and collecting the spectra with the same serial number. Accordingly, each scan of this collection is preceded by a newly applied predeposition. However, assembling useful 'corresponding' spectra is often complicated by a lack of reproducibility of the electrode preconditioning step. As an example, Figure 1b represents two 'corresponding' spectra (the fifth ones) ensuing from two different series. Supported by complimentary chronoamperometric measurements (see (4)), the picture unfortunately denounces a strong lack of replicacy, with variations between 'corresponding' spectra being larger than those observed between 'successive' scans.

Therefore, an alternative electrode preconditioning method is proposed in this work. Its impact on subsequent impedance measurements is analysed following the strategy developed by Agarwal *et al.* The included

Kramers-Kronig tests will reveal if the newly proposed preconditioning has improved the quality of the impedance data. Furthermore, the assessment of the stochastic error structure will be employed for weighting the data points during physical modelling steps. Optionally, and apart from the attempts to improve the quality of the impedance data by adapting the experimental set-up, an alternative data analysis strategy, using a transfer function based measurement model (4,5), will be considered.

References

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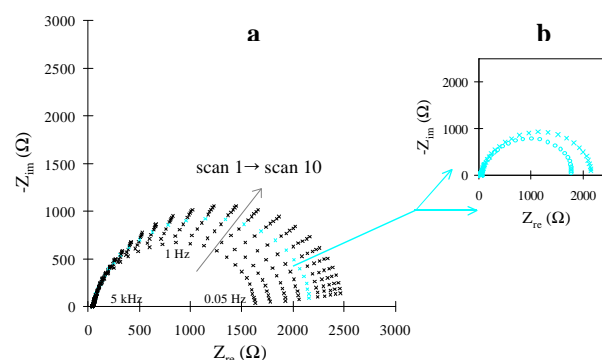


Fig. 1a: Consecutive impedance scans for the reduction of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ on a rotating Ag disk ($\varnothing = 5.96$ mm) subsequent to an electrode conditioning method.

Fig 1b: (x) fifth scan of the series presented in Fig. 1a, (O) fifth scan of a second series, for equal experimental conditions.