Process simulations as an integrated step in the global identification of electrochemical processes on a rotating disc electrode

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At our department, the investigation of the silver electrodeposition started some years ago as an answer for the need to understand more thoroughly the physical background behind the development of a silver image for photographic purposes. Meanwhile, a lot of insight has been achieved in the thermodynamics as well as in the kinetics of the electrocrystallisation and the subsequent quasi-stationary growth stage. To model the quasi-stationary electroreduction of silver on a preplated rotating disc electrode starting from thiosulphate complexes, a chemical-electrochemical reaction scheme has been adopted (1). Most of the kinetic parameters were evaluated through regression of the appropriate impedance model to electrochemical impedance spectra. However, one was still concerned with the fact that the diffusion coefficient of the oxidans had to be determined independently from steady state observations to avoid convergence problems. This was even more odd to establish observing that diffusion processes are governing the kinetics. Summarizing, while a lot of knowledge was acquired, a lot of questions remained unresolved.

At this point, where one could have doubts about both the appropriateness of the proposed reaction model and the quality of the data, it was decided to choose for a more integrated approach where the error analysis of impedance data would be an initial step in the global identification problem. Accordingly, repeated impedance measurements were performed resulting in the identification of the error structure (2). This was realized using the measurement model toolbox developed by the group of Orazem (3-5). Having more insight in the quality of the data, one can focus now on the refinement of the physical model.

In this second step, results from the initial error analysis still provide some useful indications. As an example for the silver system, the error analysis showed that thanks to an improved electrode pretreatment reliable information could be obtained up to lower frequencies. Moreover, at those lower frequencies, at least one physical process with an inductive behavior was established (6). According to the literature, this low frequent inductive behavior can be caused by adsorption phenomena. This assumption may find its confirmation in an investigation carried out by Gonnissen *et al.*, since the author suggested the existence of a chemisorbed $1,1-Ag(S_2O_3)^-$ surface complex by means of Surface Enhanced Raman Spectroscopy (7). In view of modeling the experimentally observed frequency behavior in the silver system, one could then adopt an equivalent circuit, which has been invoked in literature to describe adsorption phenomena. However then, there is this risk that one will end up with elements (e.g. Constant Phase Elements) which fit the data but don't help to understand thoroughly the physical processes taking place. Moreover, in the same way as there exists no unique relation between an equivalent circuit and a given impedance spectrum, no one could affirm that there is a one-one relation between an equivalent circuit and a given reaction mechanism. Therefore, in an effort to model the experimental results without ever losing the physical link, it was decided to simulate the response of a proposed reaction mechanism starting from the set of physicochemical laws dictating the electrochemical system. Those calculations are performed with the PIRoDE software, which is a powerful tool to simulate electrode processes on a uniformly accessible rotating disc electrode following the dilute solution model (8). It is based on an accurate application of the physicochemical laws on one hand, and the opportunity to specify the thermodynamics and kinetics of the probable physical processes on the other hand. As a result, PIRoDE is able to visualize the concentration and potential profiles, as well as the current responses for each specified electrode reaction. The feature which will be explored here is the possibility to propose a reaction mechanism involving homogeneous chemical reactions, electron transfer reactions, adsorption or electrosorption reactions. Based on the comparison between the simulated and the experimental signal response, a proposed reaction mechanism will be rejected or retained.

As a result, those process simulations will be conceived as a fully integrated step in the global system identification procedure, which can be split up in three moves. Firstly, a rigorous error analysis is performed to meet the quality of the data set. Secondly, the simulation tool is applied to understand the physics of the system under study. This will lead to the identification of the parameters of which the values will be fitted. Finally, having a fairly good idea of the most appropriate physical model, efforts can be concentrated on estimating the parameter values with a known reliability while taking into account the error content of the data set.

References

1. S. Vandeputte, E. Verboom, A. Hubin, and J. Vereecken, J. Electroanal. Chem., **397**, 249 (1995)
2. L. Pauwels, W. Simons, A. Hubin, J. Schoukens, and R. Pintelon, Electrochim. Acta, **47**, 2138 (2002)
3. P. Agarwal, M.E. Orazem, and L.H. Garcia-Rubio, J. Electrochem. Soc., **139**, 1917 (1992)
4. P. Agarwal, O.D. Crisalle, M.E. Orazem, and L.H. Garcia-Rubio, J. Electrochem. Soc., **142**, 4149 (1995)
5. P. Agarwal, M.E. Orazem, and L.H. Garcia-Rubio, J. Electrochem. Soc., **142**, 4159 (1995)
6. L Pauwels, W. Simons, and A. Hubin, in Design and Mathematical Modeling of Electrochemical Systems, J.W. Van Zee, M.E. Orazem, C.M Doyle, Editors, Proceedings Volume at the occasion of the 201st ECS meeting, Philadelphia (PA), May 12-17, 2002, submitted for publication.
7. D. Gonnissen, W. Langenaeker, A. Hubin, and P. Geerlings, J. Raman Spectrosc., **29**, 1031 (1998)
8. PIRoDE software manual, www.elsyca.com