

From Mathematical Models to New Experimental Methods and From Experimental Methods to New Mathematical Models: An Integrated Approach.

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The goal of the electrochemist is either to analyze an interfacial mechanism by kinetic characterization and chemical identification of the reaction intermediates or to estimate a parameter characteristic of some process (i.e., corrosion rate, deposition rate, and state of charge of a battery) from the measurement of a well-defined quantity. Verification of a new model for an electrochemical system may require development of a new specific experiment as the usual experimental methods are not always appropriate. On the other hand, a new experimental technique devoted to a specific phenomenon must be analyzed with a new mathematical model.

The kinetic description of electrochemical impedance involving the surface coverage of intermediates was especially promoted by Epelboin et al.¹ They considered that, for a reaction mechanism involving few reactions, some reaction intermediates adsorb following a Langmuir isotherm and are characterized by a surface coverage θ_i . In this framework, all the loops except the diffusion ones are semicircles centered on the real axis. These semicircles could be capacitive or inductive loops. Recently,² it was assumed that the double layer capacitance C_d is linked to the surface coverage θ_i , where C_d is a function of frequency due to the frequency dependence of θ_i . To explore the role of surface coverage on the modulation of double layer capacitance, a new technique was invented to measure this frequency dependence, and, in this way, to verify directly the theory developed thirty years ago.³

In the beginning of the seventies Bruckenstein et al.⁴ introduced a new technique to study mass transport in electrochemical systems in which the current response to a speed modulation of a rotating disk electrode was analyzed. A few years later, in 1977, Deslouis et al.⁵ used the usual device for impedance measurement to obtain the first diagrams in the whole frequency range. The corresponding model for a uniform accessible electrode was proposed by Tribollet and Newman in 1983.⁶ This technique, called EHD impedance, was used for different systems. When applied to electrodissoolution at high rates, the EHD results indicated that the viscosity gradient near the electrode played a significant role. The experimental work motivated a substantial refinement to existing models for the impedance of electrodissoolution systems.^{7,8}

Scale deposit from natural water provokes drastic problems in industry as well as in domestic installations. Numerous investigations were performed in order to understand the mechanism of scale deposition.^{9,10} In particular, an electrochemical method consisted of accelerating the CaCO_3 crystallisation by means of an electrode polarized at the oxygen reduction potential. This well known technique led to information about the scaling power of different waters. A new experimental device measuring, *in situ*, three experimental parameters, current of oxygen reduction, mass of CaCO_3 deposit and images of CaCO_3 crystals growing on the electrode surface was recently developed.^{11,12} The optical observation was performed through the electrode itself, the electrode being a SnO_2 electrode coated by a very thin layer of the metal under investigation. It provides new information about the nucleation process and the growth rate of the different crystals: aragonite and calcite. A corresponding model is in development.

The examples presented here demonstrate an intimate coupling between deterministic models and experimental techniques. In some cases, development of new mathematical models leads to invention of new

experimental methods. In other cases, results from experimental methods motivate development of refined mathematical models.

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