Electrodeposition Fueled by Newman and Tobias

by Elizabeth J. Podlaha, Hariklia Deligianni, and Gery Stafford

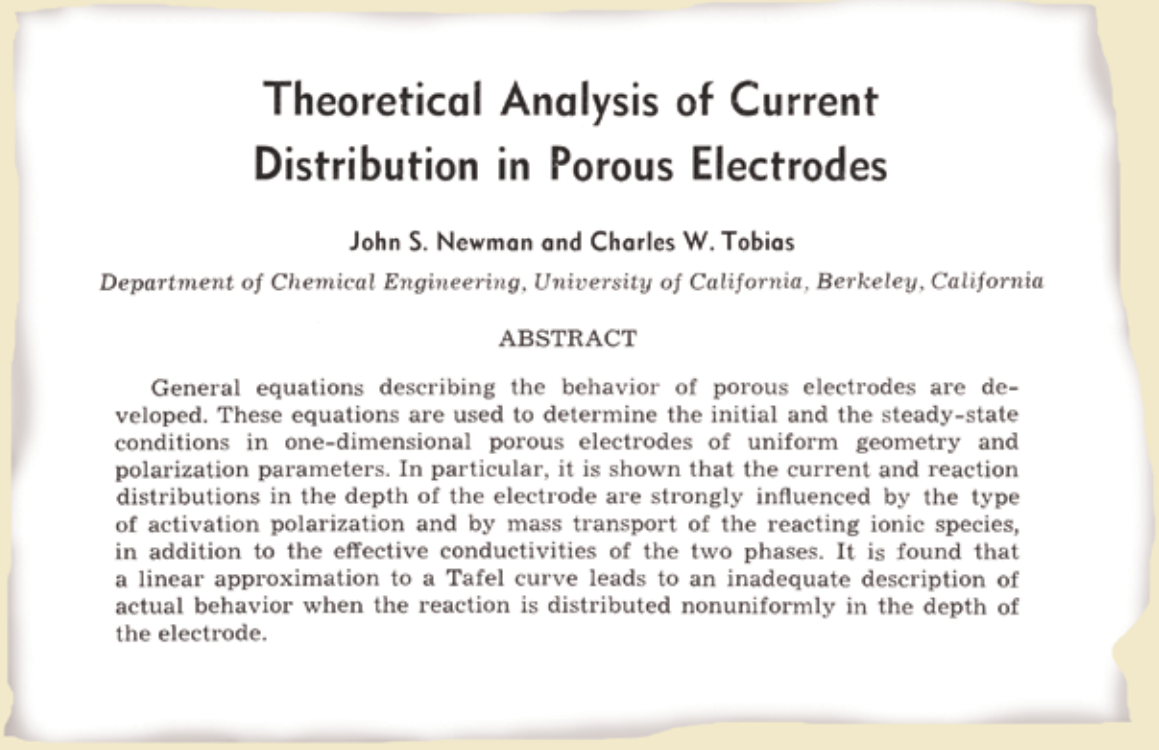
It would be remiss not to attribute progress in the understanding, design, and implementation of electrodeposition processes, and their associated assessment tools, on the wealth of mathematical modeling endeavors that adopt a continuum, microscopic level approach. Elements of the seminal publication of Newman and Tobias have breathed life into many theoretical descriptions of electrochemical phenomena, among them a variety of aspects important to the electrodeposition community (Fig. 1). Their paper establishes a straightforward treatment of porous electrode media, without the need for a detailed depiction of the exact geometry, which is most obviously adapted to battery systems. The current distribution concepts, trade-offs in kinetic, transport, and ohmic resistances, and the dimensionless representation of governing equations are key to electrodeposition modeling. Perhaps the most translational application is the analogous porous electrode-current distribution problem encountered in porous reactors with forced convection for the reduction of heavy metal ions from waste water.

The fundamentals of current distribution are however critically important to many electrodeposition processes such as: the electrodeposition of metals in micron and submicron-patterned substrates for the semiconductor industry; structural elements for micro-electro-mechanical systems (MEMS); in the analyses of electrodeposition tools, such as with the paddle, fountain, and Hull cell; and the now commonplace rotating disk electrode (RDE), and other similar rotating electrodes with controlled hydrodynamics and defined current distribution.

The Paper

In 1962, Newman and Tobias described the current distribution in a porous electrode, presenting equations in a general form with Butler-Volmer kinetics, the three modes of transport: diffusion, migration, and convection, and the equation of conservation of charge. To adapt a microscopic-scale model to a porous structure a continuum, macrohomogeneous approach was presented that provided a depiction of the current distribution as a function of average quantities, incorporating effective values such as the effective conductivity and diffusivity. The structure, partitioned into a matrix and solution phase, is considered to be so small that changes in current/potential and mass distribution can be treated as continuous over the overall dimension of the electrode, thus rendering a very complicated problem into a tractable

FROM:
J. Newman and C. W. Tobias, "Theoretical Analysis of Current Distribution in Porous Electrodes," *J. Electrochem. Soc.*, **109**, 1183 (1962).



Theoretical Analysis of Current Distribution in Porous Electrodes

John S. Newman and Charles W. Tobias

Department of Chemical Engineering, University of California, Berkeley, California

ABSTRACT

General equations describing the behavior of porous electrodes are developed. These equations are used to determine the initial and the steady-state conditions in one-dimensional porous electrodes of uniform geometry and polarization parameters. In particular, it is shown that the current and reaction distributions in the depth of the electrode are strongly influenced by the type of activation polarization and by mass transport of the reacting ionic species, in addition to the effective conductivities of the two phases. It is found that a linear approximation to a Tafel curve leads to an inadequate description of actual behavior when the reaction is distributed nonuniformly in the depth of the electrode.

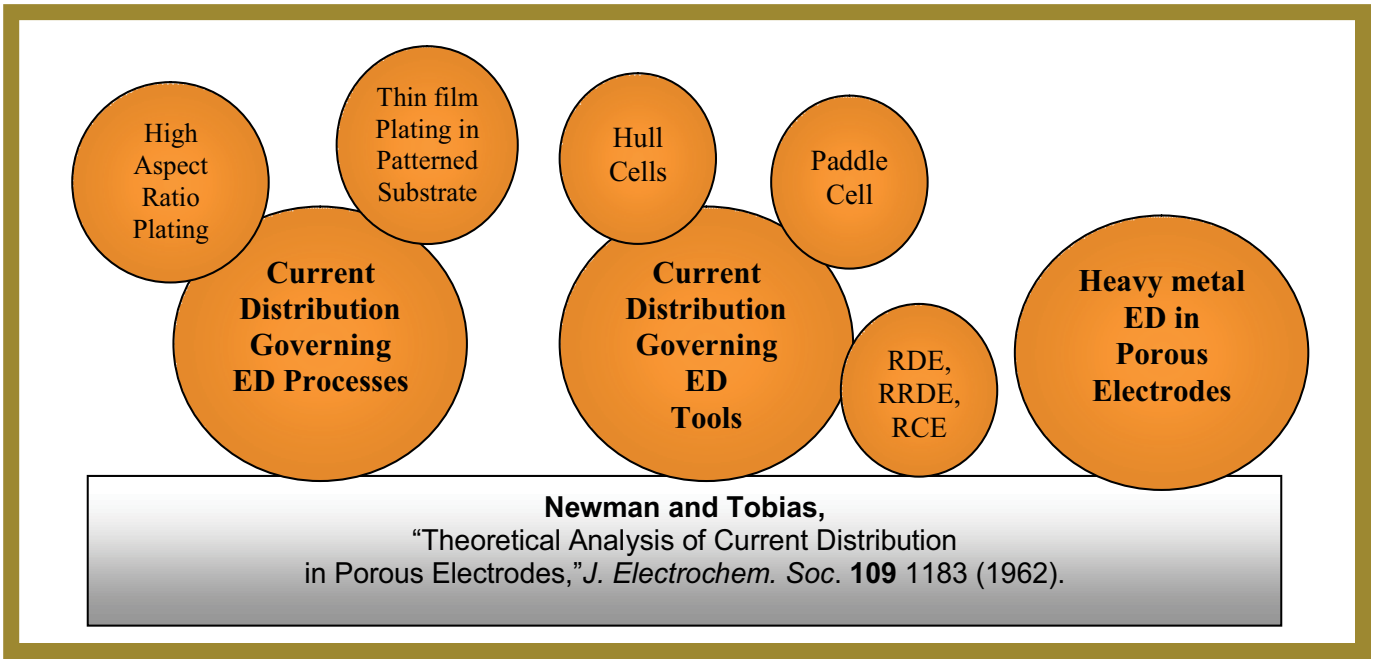


Fig. 1. *Electrodeposition examples marked by Newman and Tobias theory.*

one. The entire electrode volume is then considered to have a homogeneous distribution of pores that at a certain time occupy bulk porosity and have a uniform specific interfacial area.

The current distribution within the electrode can vary dramatically from each end, depending on the dominating resistances. For example, a large effective solution conductivity accompanied with rapid kinetics tends to create high current density changes near the current collector, farthest from the porous electrode/free solution boundary (Fig. 2a); and small values of the solution conductivity compared to the matrix conductivity, results in the opposite behavior with a high current density near the solution interface. A difference in the ratio of the solid to solution phase conductivity can shift the non-uniformity from one boundary to the other, and when they are comparable (Fig 2b), there is a high reaction rate near each end of the porous electrode. In either case, the current distribution can be made more uniform as the extent of the kinetic resistance increases, described by a smaller value of the δ term in Fig 2. Concentration distributions within the electrode tend to diminish the reaction rate near the back of the electrode as the reaction species' concentration decrease as it penetrates the porous electrode. The approach is particularly well suited for electrodeposition applications as it lays the foundation for current distribution problems and assumes dilute electrolytes, unlike the concentrated solution formulations necessary in most battery systems described by Newman and Tiedemann.[1]

Electrodeposition Applications

Electrodeposition into lithographically patterned substrates has had a great impact on our industrial sector in the magnetic recording, packaging, semiconductor, and microelectromechanical systems (MEMS) community. The first implementation of electroplating within a well-defined lithographic pattern on a semiconductor chip was the C4 solder interconnection.[2] The deposits today serve numerous functions from conductors in packaging modules, magnetic components in micro-devices, and as absorber elements in mask lithography. The principles established in the Newman and Tobias paper set forth the current distribution principles necessary to predict and control the elemental or alloy deposit thickness and composition, such as in the description of kinetic or transport controlled reaction distributed over a pattern with variable surface density regions[3-4] or into deep recesses,[5-6] of particular interest to X-ray lithography (*i.e.,* LIGA) fabrication and chip wiring technology.

The Newman and Tobias current distribution methodology has also been integrated with additive interaction models to help describe and control interconnect wiring deposition today.[7-8] The range of dimensions found in these problems offers the possibility of mixing micro- and macrostructures fabricated with extreme precision. Current distribution issues in electrodeposition over lithographically patterned substrates have challenges at multiple length scales, from the scale of the lithographic features within the pattern to that of the overall wafer. Multiscale problems have been recognized,[9] and present continued areas of interest to utilize and expand the principles put forth in the Newman and Tobias paper.

Electrodeposition tools are critical to the design of the industrial electrodeposition process and the control of current distribution. The one single tool that has perhaps had the most impact in the electrodeposition community is Romankiw's paddle cell,[10] where the unsteady mass transfer effects nicely demonstrate the increased modeling complexity.[11-12] The paddle cell agitates the electrolyte and controls the boundary layer near the electrode surface. The design attributed to Romankiw includes a pair of opposing rectangular prisms that moves back and forth over a horizontal working electrode wafer at a constant oscillating frequency, parallel to a counterelectrode; and was a significant innovation to achieve uniform current distribution along the wafer, providing a more meaningful alternative to the fountain cell. The modeling of the transport boundary layer thickness,[11] established by the periodic wake trailing the paddle as it passes over the cathode, helped to create a significant design tool in widespread use today.

In contrast, electroplating tools are also designed with an intentional current distribution, and a case in point is the Hull cell, introduced in 1939 by Hull.[13] The effect of current distribution on deposit morphology and alloy composition is readily assessed by a varying current density along the cathode length. The trapezoidal design

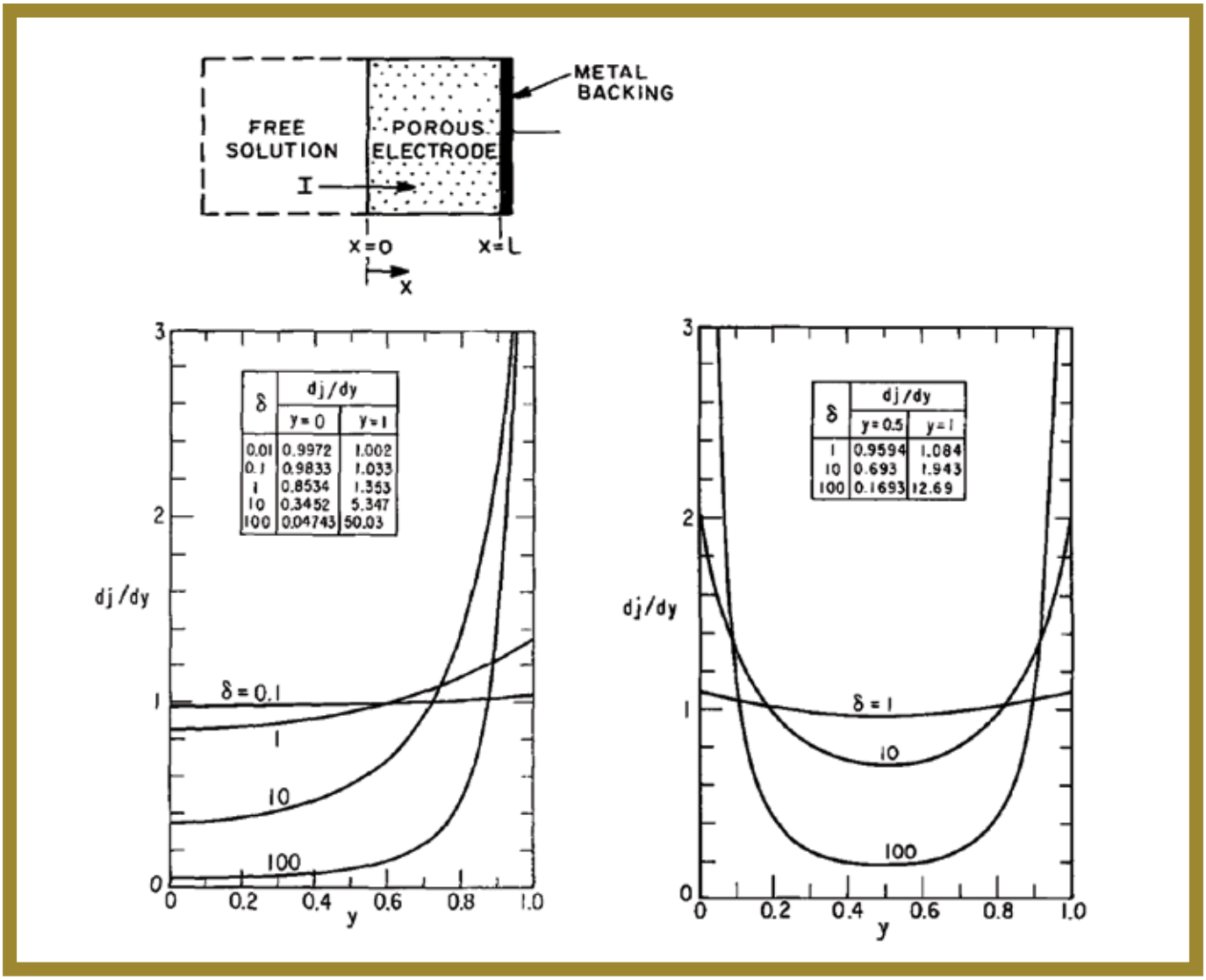


Fig. 2. *Normalized current distribution modeled within a three-dimension electrode from the solution interface at x = 0 (y = x/L) to the current collector backing at the opposite end of the electrode at y = 1, assuming no concentration gradients; (a.) high solution effective conductivity, κ, relative to a kinetic controlled reaction rate; and (b.) comparable quantities of solid, σ, and solution, κ, conductivity; δ is a dimensionless value comparing the reaction Tafel parameter,* $\beta = {}^{\alpha nF}/_{RT}$ *or* ${}^{(1-\alpha)nF}/_{RT}$, *with the effective conductivities,* $\delta = L|I|\beta\left(\frac{1}{\kappa}+\frac{1}{\sigma}\right)$.

of the cathode-anode juxtaposition induces a current distribution, at a maximum when ohmic control dominates the electrochemical reaction. Following the approach of the Newman and Tobias paper, the understanding and description of current distribution in a Hull cell was realized by Newman's former students[14-15] describing a secondary current distribution case. The methodology was subsequently applied to a rotating version of the Hull design. The rotating cylinder Hull cell (RCHC) introduces an additional functionality to electroplaters and researchers by controlling the electrolyte agitation, and hence transport boundary layers, while at the same time providing a readily assessable variation of the current density,[16-19] and can be described with a similar model.[20] By understanding the current distribution, it is then possible to deconvolute the partial current densities of individual, overall metal ion reduction reactions directly from an alloy's composition and thickness, providing a step forward in alloy electrodeposition analysis.

Many modeling approaches in electrodeposition are applied to non-porous electrodes where the reaction is restricted to the plane of the metal-solution interface. A key aspect of the Newman paper is that it provides a methodology to capture the essential features of a porous material, without the need for the exact description of a very complicated geometry. Nowhere is the application of the treatment of current distribution in porous systems more relevant in electrodeposition than in the recovery and reclamation of metal ions from waste solutions, particularly from dilute solutions, where the enhanced reaction area can help to counter the small current density that results from low limiting current densities as a consequence of the drop in bulk concentration. The Newman group[21-22] addressed this issue in the design of different electrode configurations with respect to the flow of solution and current. Based on the macroscopic viewpoint of the porous structure, the design of reactors for solution flow arrangements where the flow is either parallel to the current flow (flow-through) or perpendicular to it (flow-by) have been well described.

Some authors have shown that in some circumstances the flow-by arrangement can be superior to the flow-through orientation.[17,23] Porous electrodes in the flow-through arrangement have been investigated with various porous materials including granular graphite,[6,24] polyurethane foam,[25] and reticulated vitreous carbon (RVC).[26-28] Similar materials have also been characterized with the flow-by configuration as well.[5,29-30] Further development of modeling multiple metal deposition reactions in porous electrodes have been realized,[31] as a means of predicting deposition rate, its distribution, and effectiveness over a

wide range of operating conditions. As our need for a greener planet intensifies and electrolytes become more complex with multiple ions and with deposition reactions that have interacting, coupled characteristics, the methodologies presented in the Newman and Tobias paper will be a foundation to future porous electrode reactor models.

Conclusions

To capture the essence of electrodeposition, a mathematical description is key. To date, many of the electrodeposition current distribution models are based on the themes presented by Newman and Tobias and those fundamentals will help bridge the electrodeposition community in its future growth.

About the Authors

Elizabeth J. Podlaha is an associate professor in chemical engineering at Northeastern University, recipient of the ECS Student Research Award of the Battery Division (1991), and an NSF CAREER Award (2000). She may be reached at e.podlaha-murphy@neu.edu.

Hariklia (Lili) Deligianni is a research manager at IBM's T. J. Watson Research Center who has received two IBM Corporate Awards (2001, 2006), the National Medal of Technology for significant contributions to Semiconductor Technology (2006), and the Inventor of the Year Award, NY State (2006). She may be reached at lili@us.ibm.com.

Gery Stafford is a Research Chemist at NIST (Metallurgy Division), a Fellow of The Electrochemical Society, and a past Chair of the ECS Electrodeposition Division. He may be reached at gery.stafford@nist.gov.

References

1. J. Newman and W. Tiedemann, *AIChE J.*, **21**, 25 (1975).
2. M. Datta, R. V. Shenoy, C. Jahnes, P. C. Andricacos, J. W. Horkans, J. O. Dukovic, L. T. Romankiw, J. Roeder, H. Deligianni, H. Nye , B. Agarwala, H. M. Tong, and P. Totta, *J. Electrochem. Soc.*, **142**, 3779 (1995).
3. S. Mehdizadeh, J. O Dukovic, P.C. Andricacos, L. T. Romankiw and H. Y. Cheh, *J. Electrochem. Soc.*, **139**, 78 (1992).
4. S. Mehdizadeh, J. O. Dukovic, P..C. Andricacos, L. T. Romankiw, and H. Y. Cheh, *J. Electrochem. Soc.*, **140**, 3497 (1992).
5. J.-M. Lee, J. T. Hachman, J. J. Kelly, and A. C. West, *J. Microlith. Microfab. Microsys.*, **3**, 146 (2004).
6. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, and H. Deligianni, *IBM J. Res. Develop.*, **42**, 567 (1998).
7. Y. Qin, X. Li, F. Xue, P. M. Vereecken, P. Andricacos, H. Deligianni, R. D. Braatz, and R. C. Alkire, *J. Electrochem. Soc.*, **155**, D223 (2008).
8. T. P. Moffat, D. Wheeler, S.-K. Kim, and D. Josell, *J. Electrochem. Soc.*, **153**, C127 (2006).
9. J. O. Dukovic, *IBM J. Res. Develop.*, **34**, 693 (1990).
10. L. T. Romankiw, *U.S. Patent*, 3853715 (1974); E.E. Castellani, J. V. Powers, and L. T. Romankiw, *U.S. Patent*, 410275 (1978).
11. D. T. Schwartz, B. G. Higgins, P. Stroeve, and D. Borowski, *J. Electrochem. Soc.*, **134**, 1639 (1987).
12. G. J. Wilson and P. R. McHugh, *J. Electrochem. Soc.*, **152**, C356 (2005).
13. R. O. Hull, *J. Am. Electroplat. Soc.*, **27,** 52 (1939).
14. M. Matlosz, C. Creton, C. Clerc, and D. Landolt, *J. Electrochem. Soc.* **134**, 3015 (1987).
15. C. Madore, A. C. West, M. Matlosz, and D. Landolt, *Electrochim. Acta,* **37**, 69 (1992).
16. C. Madore and D. Landolt, *Plat. Surf. Finish.*, **80**, 73 (1993).
17. H. Tannenberger, *Galvanotechnik*, **93**, 938 (2002).
18. C. T. J. Low, C. Ponce de Leon, and F. C. Walsh, *Aust. J. Chem.,* **58**, 246 (2005).
19. C. T. J. Low, E. P. L. Roberts, and F. C. Walsh, *Electrochim. Acta,* **52**, 3831 (2007).
20. C. Madore, A. C. West, M. Matlosz, and D. Landolt, *Electrochim. Acta,* **37**, 69 (1992).
21. D. N. Bennion and J. Newman, *J. Appl. Electrochem.*, **2**, 113 (1972).
22. J. A. Trainham and J. Newman, *Electrochim. Acta*, **26**, 455 (1981).
23. P. S. Fedkiw, *J. Electrochem. Soc.*, **128**, 831 (1981).
24. R. S. Wenger and D. N. Bennion, *J. Appl. Electrochem.*, **6**, 385 (1976).
25. A. Tentorio and U. Casolo-Ginelli, *J. Appl. Electrochem.*, **8**, 195 (1978).
26. M. Fleischmann and A. Saraby-Reintjes, *Electrochim. Acta*, **29**, 69 (1984).
27. M. Matlosz and J. Newman, *J. Electrochem. Soc.*, **133**, 1850 (1986).
28. E. J. Podlaha and J. M. Fenton, *J. Appl. Electrochem.*, **25** 299 (1995).
29. D. Pletcher, I. White, F. C. Walsh, and J. P. Millington, *J. Appl. Electrochem.*, **23**, 82 (1993).
30 S. Langlois and F. Coeuret, *J. Appl. Electrochem.*, **19**, 51 (1989).
31. D. Pilone and G. H. Kelsall, *J. Electrochem. Soc.*, **153** D85 (2006).