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COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in the **Physical Review.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on ''Modeling of metal electrodeposits: Analytical solutions''

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When the equations of ionic motion for electrodeposition in a one-dimensional cell filled with a dilute binary electrolyte are solved under fixed-boundary conditions, a diffusion-limited current, independent of applied potential, is obtained. This result is well expected in the framework of the quasineutrality approximation. In this framework, the assumption by Huang and Hibbert [Phys. Rev. E. **52**, 5065 (1995)] of an electrical-migration term in the evolution equation for the concentration is incorrect. However, a term of the same form, though smaller, may appear either from the concentration dependence of the mobilities or from an electro-osmotic effect if the electrolyte is embedded in a gel or a porous medium. [S1063-651X(96)06010-2]

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In a recent paper [1], Huang and Hibbert rediscuss the modeling of ionic motion in electrodeposition from binary electrolytes. Specifically, they reconsider the model originally proposed by Chazalviel [2] and later extended to the convective case by Fleury, Kaufman, and Hibbert [3]. According to Huang and Hibbert, earlier models did not include electrical migration properly, hence leading to the unphysical prediction that current should not depend upon potential, and they propose an alternate model which allegedly includes migration terms in a simpler and more effective manner. We think that their criticism of Refs. [2,3] is not founded and the proposed model is incorrect. Models [2,3] did include migration terms, as can be seen from their initial equations

$$\frac{\partial C_c}{\partial t}=D_c\Delta C_c-\mu_c\mathbf{E}\cdot\boldsymbol{\nabla}C_c-\mu_cC_c\boldsymbol{\nabla}\cdot\mathbf{E}-\mathbf{v}\cdot\boldsymbol{\nabla}C_c, \tag{1}$$

$$\frac{\partial C_a}{\partial t}=D_a\Delta C_a+\mu_a\mathbf{E}\cdot\boldsymbol{\nabla}C_a+\mu_aC_a\boldsymbol{\nabla}\cdot\mathbf{E}-\mathbf{v}\cdot\boldsymbol{\nabla}C_a. \tag{2}$$

The second and third terms in the second members of these equations do arise from electrical migration. The fourth terms describe advective motion and were only considered in [3]. However, these equations are coupled through a Poisson equation

$$\boldsymbol{\nabla}\cdot\mathbf{E}=(z_cC_c-z_aC_a)/\varepsilon\varepsilon_0. \tag{3}$$

The quasineutrality approximation, invoked by [1], amounts to letting ε_0 formally tend to zero in the above three equations. Equation (3) then reduces to $z_cC_c=z_aC_a$, which can be renamed C, and Eqs. (1) and (2) can be linearly combined into the equivalent system of charge conservation ($\boldsymbol{\nabla}\cdot\mathbf{J}=0$), plus the equation

$$\frac{\partial C}{\partial t}=D\Delta C-\mathbf{v}\cdot\boldsymbol{\nabla}C, \tag{4}$$

where $D=(D_c\mu_a+D_a\mu_c)/(\mu_\alpha+\mu_c)$ is the ambipolar diffusion constant. This is the well-known advection-diffusion equation for the concentration [4]. Here the terms involving the electric field have completely disappeared. The physical origin of this disappearance is that migration pushes cations and anions in opposite directions, but Poisson's equation forces neutrality very efficiently, hence leading to a cancellation of the electric-field terms. At the level of the calculation, this disappearance occurs because the $\mu C\boldsymbol{\nabla}\cdot\mathbf{E}$ terms in Eqs. (1) and (2) *are not negligible*, in contrast to the assumption of Ref. [1], and they essentially cancel the $\mu\mathbf{E}\cdot\boldsymbol{\nabla}C$ terms. The residual effect of the electric field is shrouded in the ambipolar diffusion coefficient. This is a classical effect in electrochemistry as well as in semiconductor physics, and motion of the electroactive species in the vicinity of an electrode is indeed well known to be limited by diffusion [5].

In this respect, the result of [2,3] that the steady-state current is independent of the imposed potential is not surprising. In the steady state, most of the applied potential drop will occur very close to the cathode across a narrow space-charge layer and the current will be limited by diffusion in the quasineutral region across the cell. In practical ramified electrodeposition experiments, such a steady state will of course never be attained, just because of the occurrence of other phenomena (ramified growth, electroconvection, hydrogen-gas evolution, ...) and the current will depend upon the applied potential as explained in [2,3].

The presence of an electrical-migration term $-\mu E\partial C/\partial x$ in Eq. (1) of Ref. [1] then appears basically incorrect to us. One might argue that the above Eqs. (1)–(3)

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are written in the approximate framework of very dilute electrolytes. In practice, the mobilities and diffusion coefficients depend upon concentration in a complex way [6], hence terms involving $\nabla\mu_c$, $\nabla\mu_a$, ∇D_c, and ∇D_a must appear in Eqs. (1) and (2), and the exact cancellation of the electric-field terms in Eq. (4) may then break down. This will be the case if μ_a and μ_c vary with concentration in a different way. These effects will lead to a term of the same form as the electrical-migration term in Eq. (1) of Ref. [1]. However, this is a rather subtle higher-order effect, and the corresponding coefficient is not just a mobility μ, but rather $C(\mu_a d\mu_c/dC-\mu_c d\mu_a/dC)/(\mu_a+\mu_c)$. Alternately, a term of the migration form might arise if cation and anion concentrations were not equal, due to the presence of fixed ions, for example, in a supporting medium (porous medium or gel). A global motion of the electrolyte (electroendosmosis) would then result [7]. The μ coefficient in Eq. (1) of Ref. [1] could then be regarded as an electro-osmotic mobility. Such an effect might play a rôle in growth experiments performed on filter paper [8], but can hardly be present in usual thin-cell experiments performed with simple liquid electrolytes.

In conclusion, the treatment of Ref. [1] as such is incorrect. However, it can be relevent to special cases where terms involving the electric field survive in the quasineutrality approximation, provided μ in their Eq. (1) is given the appropriate meaning. The same criticism may be applied to Eq. (1) of a more recent paper by the same authors [9].

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