



Diffusion within a Layered, Graphite-Like, Spherical Electrode Theoretical Aspects

Paul B. Antohi,^a Philip L. Taylor,^a and Daniel A. Scherson^{b,*}

^aDepartment of Chemistry, and ^bDepartment of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7078, USA

A method of analysis is presented whereby one may determine from chronocoulometric measurements whether a spherical electrode is isotropic or anisotropic. To be examined theoretically is diffusion of a species within a collection of flat impermeable disks stacked parallel to and at equal distance from each other, forming an enveloping spherical surface. Within this model, which mimics a layered, graphite-like spherical electrode, species can enter (or leave) each of the disks only through the edge, *i.e.*, transport across the faces of the disks is not allowed. The functional form of the transient dimensionless flux for this stratified structure, following a concentration step at the surface, was found to be very similar to that of an isotropic sphere of the same radius subject to otherwise identical conditions. However, the times required for the two types of spheres to achieve a prescribed fraction of their maximum capacity were found to differ, particularly for short times. Provided the number of disks is known, a parameter that can be easily obtained from the size of the particle and the interplanar distance of the layered material, the analysis presented in this work affords means of extracting from the experimental data the correct diffusion coefficient of the species within the stratified lattice, and thus assessing the error involved by assuming the sphere to be isotropic.

© 2005 The Electrochemical Society. [DOI: 10.1149/1.1939107] All rights reserved.

Manuscript submitted December 8, 2004; revised manuscript received February 9, 2005. Available electronically June 27, 2005.

Efforts toward further performance optimization of Li⁺ batteries have generated renewed interest into experimental and theoretical aspects of mass transport within solid media.^{1,2} Of particular interest is to develop and implement methods for a reliable determination of diffusion coefficients. Much progress in this area has been made via an analysis of potential-step,^{3,6} galvanostatic discharge,⁷ and impedance spectroscopy^{3-5,8,9} measurements, in which the lattice is assumed to be isotropic. Although justified for most cathode materials in view of their structure, such an assumption is not valid for layered materials such as graphite, for which Li⁺ transport occurs along, but not across, the graphene sheets.

This contribution examines from a theoretical viewpoint mass transport within a structure composed of disks stacked at equal distance from each other and forming an enveloping spherical surface of radius r_0 subject to a concentration step at the surface, which renders insertion into (or release from) each disk under strict diffusion control. Such conditions are realized in practice in potential-step (or chronocoulometric) experiments involving materials of relevance to Li⁺ battery electrodes, for which the diffusion coefficients of Li⁺ are orders of magnitude smaller than those in electrolyte solutions. Although the Li⁺ insertion materials in technical electrodes are present as a collection of irregularly shaped particles on the order of micrometers in characteristic dimension, the choice of a spherical particle simplifies considerably the mathematical analysis, allowing essential aspects of the phenomenon to be illustrated. One of the primary objectives of this work is to compare the transient current response of an anisotropic layered spherical particle of the type described above following a potential (concentration) step with that of an isotropic sphere of the same radius subject to identical conditions.

Theoretical Formalism

Diffusion within a disk and within an isotropic sphere has been extensively studied and is only briefly reviewed here.¹ As is well known, the governing differential equations for both of these two geometries differ only in the magnitude of the factor that multiplies the term inversely proportional to the radial distance, r , *i.e.*, 1 for the disk and 2 for the sphere (see Eq. I.1 in Table I). The boundary conditions (see Eq. I.2) selected in this work represent a concentration step at the edge of the disk or the surface of the sphere, $r = r_0$, which simulate a potential-step (or chronopotentiometry) ex-

periment that induces incorporation (or release) of species into (from) the structure under strict diffusion control. By defining a common set of dimensionless variables (see Eq. I.3), one may reduce Eq. I.1 and I.2 to Eqs. I.3 and I.4. The solutions for the disk and for the (isotropic) sphere can be expressed in terms of Bessel functions, J , of order 0 and 1, and of spherical Bessel functions, j , also of order 0 and 1, respectively (see Eq. I.5). Also shown in Table I are surface flux and its time integral, which are proportional to the current and the accumulated charge, respectively. The surface flux is proportional to the spatial derivative of the dimensionless concentration, $C = (c/c_0) - 1$, with respect to the dimensionless radial distance $\rho = r/r_0$, evaluated at $\rho = 1$, the surface of the sphere or the edge of the disk. This is denoted as $I(\theta)$ (Eq. I.6), where $\theta = Dt/r_0^2$ is the dimensionless time, while the integral of $I(\theta)$ with respect to θ is written as $Q(\theta)$ (Eq. I.7).

Diffusion within an anisotropic layered sphere.—It is assumed in what follows that the anisotropic sphere consists of a finite collection of disks stacked on top of each other, forming a stratified quasi-spherical structure of radius r_0 , as shown schematically in Fig. 1. It is important to stress that the faces of the disks form an impenetrable barrier, so that transport of species occurs within but not across the disks. Because the concentration of the species at the edge of each of the disks is assumed to be constant at all times following application of the step, the response of the stratified sphere can be obtained by simply adding the contributions due to all of the disks. In this model, the total flux, $I_{\text{sph}}^{\text{ani}}(t)$, and the total integral of the flux, $Q_{\text{sph}}^{\text{ani}}(t)$, for this anisotropic sphere are given in terms of dimensionless variables by the following expressions

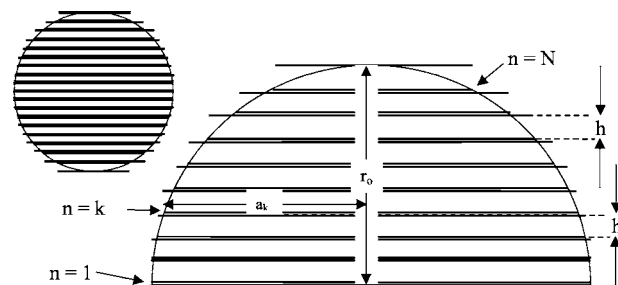


Figure 1. Schematic diagram of the model employed to represent a layered spherical particle composed of a collection of stacked disks of varying diameters, a_k , and thickness $h = r_0/N$.

* Electrochemical Society Active Member.

^z E-mail: dxs16@po.cwru.edu

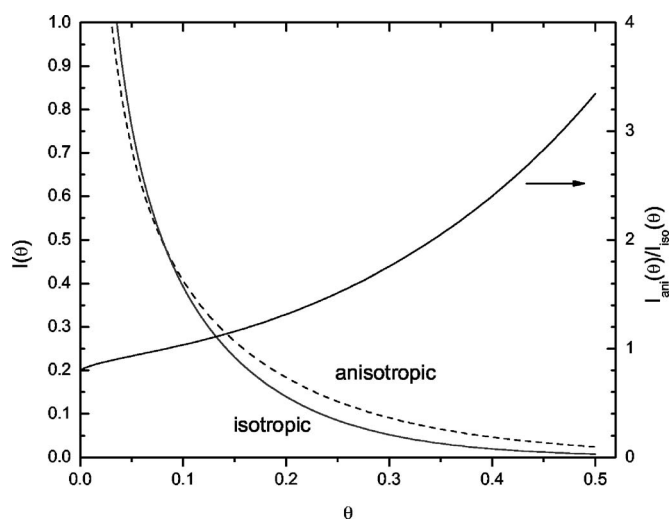


Figure 2. Plots of $I(\theta)$ vs θ for an anisotropic sphere consisting of 3000 disks (see dashed line and text for details) and an isotropic sphere of the same radius (see solid curve, left ordinate) following application of a concentration step at the surface at $\theta = 0$. $I(\theta)$ is proportional to the current measured in a chronocoulometric experiment. Also shown in this figure (see right ordinate) is a plot of the ratio $I_{\text{ani}}(\theta)/I_{\text{iso}}(\theta)$ to highlight the quantitative differences between the results obtained for the anisotropic and isotropic spheres.

$$I_{\text{sph}}^{\text{ani}}(t) = -8\pi D_{\text{ani}} c_0 r_0 \sum_{n=1}^N \sum_{l=1}^{\infty} \frac{1}{N} \times \exp\left[-(\alpha_l^{(0)})^2 \frac{D_{\text{ani}} t}{r_0^2} \left(\frac{1}{1 - [(n-1)/N]^2}\right)\right] \quad [1]$$

$$Q_{\text{sph}}^{\text{ani}}(t) = 8\pi c_0 r_0^3 \sum_{n=1}^N \sum_{l=1}^{\infty} \frac{1 - (n-1)^2/N^2}{N(\alpha_l^{(0)})^2} \times \left\{ 1 - \exp\left[-(\alpha_l^{(0)})^2 \frac{D_{\text{ani}} t}{r_0^2} \left(\frac{1}{1 - [(n-1)/N]^2}\right)\right] \right\} \quad [2]$$

where $\alpha_l^{(0)}$ are the zeroes of the Bessel function of order 0, and $2N$ is the number of disks.

The form of $Q_{\text{sph}}^{\text{ani}}(t)$ obtained in this way is superficially similar to the result for an isotropic sphere (Eq. I.8). At small times the rate

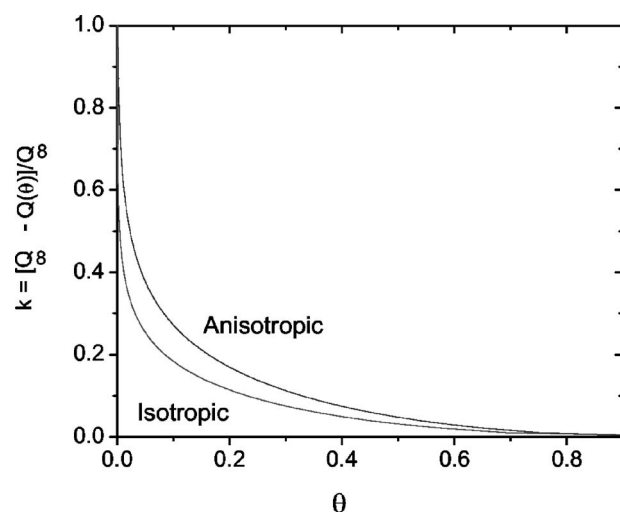


Figure 3. Plots of the accumulated charge ratio $[Q_{\infty} - Q(\theta)]/Q_{\infty}$ vs θ for an anisotropic sphere consisting of 3000 disks (see upper curve and text for details) and an isotropic sphere of the same radius (lower curve) following application of a concentration step at the surface at $\theta = 0$, where Q_{∞} is proportional to the charge injected in the limit as $\theta \rightarrow \infty$.

at which charge enters is almost independent of the presence of impermeable layers, as the flow is essentially one-dimensional. At large times the functional forms are also identical, as the long-time behavior is dominated by the smallest value of $\alpha_1^{(0)}$ (or $\beta_1^{(0)}$), making the decay essentially exponential. The important distinction, however, lies in the fact that this rate of exponential decay differs by a factor close to 60%, *i.e.*, the ratio of $\alpha_1^{(0)}/\beta_1^{(0)}$ between the two configurations. This similarity of form over a wide range of times can be seen in Fig. 2, which shows a plot of $I(\theta)$ vs θ for an anisotropic sphere consisting of 3000 disks ($N = 1500$) and for an isotropic sphere of the same radius. In the case of graphite, for which the interlayer distance is 0.311 nm, the number of disks selected would correspond to a particle of *ca.* 10 μm in radius. As can be seen from this figure, it would be difficult in practice to determine whether the particle is isotropic or anisotropic from a simple fitting of theoretical and experimental curves.

Because the long-time behavior dominates the form of the response, a numerical fit to the equation that describes diffusion within an anisotropic sphere, *i.e.*

Table I. Differential equations and boundary conditions, and their corresponding expressions in dimensionless variables, solutions, and reduced currents and charges for diffusion into a sphere and a disk following application of a concentration step at the boundary.

System	Disk	Sphere	
Differential equations	$\partial c / \partial t = D[\partial^2 c / \partial r^2 + (1/r)\partial c / \partial r]$	$\partial c / \partial t = D[\partial^2 c / \partial r^2 + (2/r)\partial c / \partial r]$	I.1
Boundary conditions	$c(r = r_0, t) = c_0; c(r < r_0, t = 0) = 0$	$c(r = r_0, t) = c_0; c(r < r_0, t = 0) = 0$	I.2
Dimensionless variables	$\theta = Dt/r_0^2, \rho = r/r_0, C = (c/c_0) - 1$	$\theta = Dt/r_0^2, \rho = r/r_0, C = (c/c_0) - 1$	I.3
Differential equations	$\partial C / \partial \theta = \partial^2 C / \partial \rho^2 + (1/\rho)\partial C / \partial \rho$	$\partial C / \partial \theta = \partial^2 C / \partial \rho^2 + (2/\rho)\partial C / \partial \rho$	I.4
Boundary conditions	$C(\rho = 1, \theta) = 0; C(\rho < 1, \theta = 0) = -1$	$C(\rho = 1, \theta) = 0; C(\rho < 1, \theta = 0) = -1$	I.5
Solutions	$C(\rho, \theta) = -2\sum_{n=1}^{\infty} [J_0(\alpha_n^{(0)}\rho) / \alpha_n^{(0)} J_1(\alpha_n^{(0)})] e^{-(\alpha_n^{(0)})^2 \theta}$	$C(\rho, \theta) = -2\sum_{n=1}^{\infty} [j_0(\beta_n^{(0)}\rho) / \beta_n^{(0)} j_1(\beta_n^{(0)})] e^{-(\beta_n^{(0)})^2 \theta}$	I.6 ^a
Flux at the surface	$I(\theta) = -2\sum_{n=1}^{\infty} e^{-(\alpha_n^{(0)})^2 \theta}$	$I(\theta) = -2\sum_{n=1}^{\infty} e^{-(\beta_n^{(0)})^2 \theta}$	I.7 ^a
Integral of $I(\theta)$	$Q(\theta) = 2\sum_{n=1}^{\infty} (1 - e^{-(\alpha_n^{(0)})^2 \theta}) / (\alpha_n^{(0)})^2$	$Q(\theta) = 2\sum_{n=1}^{\infty} (1 - e^{-(\beta_n^{(0)})^2 \theta}) / (\beta_n^{(0)})^2$	I.8 ^a

^a $\alpha_n^{(0)}$ and $\beta_n^{(0)}$ in Eq. I.6-I.8 represent the zeroes of the corresponding Bessel functions.

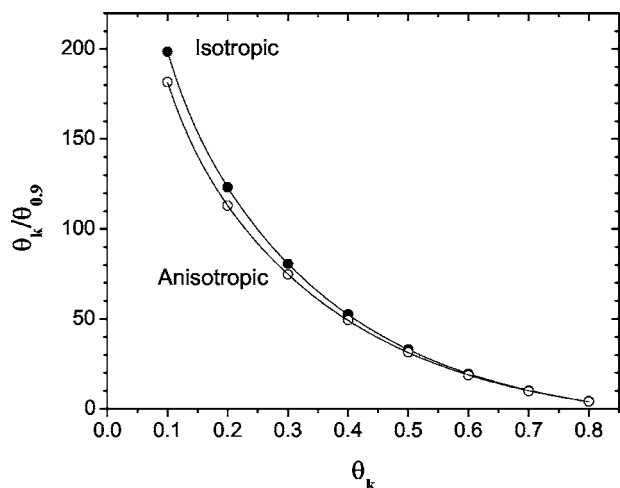


Figure 4. Plots of $\theta_k/\theta_{0.9}$ vs θ_k , where $k = [Q_\infty - Q(\theta_k)]/Q_\infty$, for the response of (●) isotropic and (○) anisotropic spheres of the same radius following application of a concentration step at the surface at $\theta = 0$. The curves represent best fits to the calculated points; hence, interpolated values should not be used for quantitative calculations.

2. In contrast, the ratio of times required to achieve two prescribed fractions of the saturation value do provide a means of assessing whether or not the particle is isotropic.

3. Provided the number of layers in the anisotropic sphere is known, it becomes possible to extract from the chronocoulometric response the intrinsic value of the diffusion coefficient.

Implicit in the treatment herein presented is the absence of staging effects of the type found in graphite; the results obtained are only valid for a single stage.

Acknowledgments

This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Science, and by NASA Glenn Research Center.

Case Western Reserve University assisted in meeting the publication costs of this article.

References

1. For general aspects of diffusion within solids, see W. Jost, *Diffusion in Solids, Liquids, Gases*, Academic, New York (1960).
2. For diffusion problems of relevance to electrochemical measurements, see A. J. Bard and L. R. Faulker, *Electrochemical Methods*, Wiley, New York (1986).
3. K. Dokko, M. Mohamedi, Y. Fujita, T. Itoh, M. Nishizawa, M. Umeda, and I. Uchida, *J. Electrochem. Soc.*, **148**, A422 (2001).
4. K. Dokko, M. Mohamedi, M. Umeda, and I. Uchida, *J. Electrochem. Soc.*, **150**, A425 (2003).
5. Y. Luo, W.-B. Cai, and D. A. Scherson, *J. Electrochem. Soc.*, **149**, A1100 (2002).
6. For applications of electrochemical techniques to the study of transport within particles other than Li^+ intercalation electrodes, see, for example, H.-S. Kim, M. Nishizawa, and I. Uchida, *Electrochim. Acta*, **45**, 483 (1999).
7. V. R. Subramanian, J. A. Ritter, and R. E. White, *J. Electrochem. Soc.*, **148**, E444 (2001).
8. J. P. Meyers, M. Doyle, R. M. Darling, and J. Newman, *J. Electrochem. Soc.*, **147**, 2930 (2000).
9. M. D. Levi and D. Aurbach, *J. Phys. Chem. B*, **108**, 11693 (2004).