ARTICLES

Mesopores inside electrode particles can change the Li-ion transport mechanism and diffusion-induced stress

Stephen J. Harris
General Motors R&D Center—Electrochemistry and Battery Systems, Warren, Michigan 48090

Rutooj D. Deshpande
University of Kentucky, Department of Chemical and Materials Engineering, Lexington, Kentucky 40506-0046

Yue Qi
General Motors R&D Center—Chemical Sciences and Materials Systems Laboratory, Warren, Michigan 48090

Indrajit Dutta
Trison Business Solutions, Inc., Warren, Michigan 48098

Yang-Tse Cheng
University of Kentucky, Department of Chemical and Materials Engineering, Lexington, Kentucky 40506-0046

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Following earlier work of Huggins and Nix \cite{Huggins2000}, several recent theoretical studies have used the shrinking core model to predict intraparticle Li concentration profiles and associated stress fields. A goal of such efforts is to understand and predict particle fracture, which is sometimes observed in degraded electrodes. In this paper we present experimental data on LiCoO$_2$ and graphite active particles, consistent with previously published data, showing the presence of numerous internal pores or cracks in both positive and negative active electrode particles. New calculations presented here show that the presence of free surfaces, from even small internal cracks or pores, both quantitatively and qualitatively alters the internal stress distributions such that particles are prone to internal cracking rather than to the surface cracking that had been predicted previously. Thus, the fracture strength of particles depends largely on the internal microstructure of particles, about which little is known, rather than on the intrinsic mechanical properties of the particle materials. The validity of the shrinking core model for explaining either stress maps or transport is questioned for particles with internal structure, which includes most, if not all, secondary electrode particles.

I. INTRODUCTION

Following early work of Huggins and Nix,\cite{Huggins1992} several recent theoretical studies have modeled internal stresses generated during insertion and deinsertion of Li into electrode particles.\cite{Deshpande2008, Chen2005, Chen2006, Chen2007} A goal of such efforts is to explain and predict particle fracture, which is sometimes observed in degraded electrodes.\cite{Qi2008, Qi2009, Qi2010} These calculations have generally used a macrohomogeneous model\cite{Bolsterli1994, Bolsterli1995} to predict intraparticle Li concentration profiles and the associated stress fields. Macrohomogeneous models typically implicitly assume that active particles are internally solid, homogeneous, isotropic, and flawless and are in an isotropic environment, which naturally leads to the shrinking core model for lithium transport between the outside and the center of the particles. Under this model, as Li diffuses radially into or out of the particle, local variations in Li concentration cause local phase transitions, with phase boundaries separating the inner core from outer shells.\cite{Bolsterli1994, Bolsterli1995} However, there is little direct experimental evidence supporting the shrinking core model for Li-ion battery electrode particles. In fact, its appropriateness has been questioned for certain highly anisotropic materials, such as single-crystal LiFePO$_4$ particles,\cite{Bolsterli1994, Bolsterli1995, Bolsterli1996, Bolsterli1997} and experiment shows that for this material the shrinking core model is not valid.\cite{Bolsterli2000, Bolsterli2001} On the other hand, the shrinking core has been implicitly accepted as applying to secondary particles made from randomly oriented primary particles.\cite{Deshpande2008, Chen2005, Chen2006, Chen2007}

The validity of the shrinking core model must depend on the internal micro/nano structure of the active
electrode particles, but little such information is available. Joho et al.,\textsuperscript{18} however, have measured the specific Brunauer–Emmett–Teller (BET) area of graphite particles, and they suggested that the existence of mesopores (2–50 nm) inside graphite particles and the surface area of these mesopores contribute significantly to the electroactive surface area and the irreversible capacity loss during the first cycle due to SEI formation. In this paper we present experimental images (see also http://www.LithiumBatteryResearch.com) showing the presence of a complex internal structure for electrode particles, including what appear to be cracks, pores, and grain boundaries. These results are consistent with a previous study using a focused ion beam on graphite particles that also observed internal cracks.\textsuperscript{19} We then present new calculations showing that the free surfaces from even small internal mesopores substantially alter, both quantitatively and qualitatively, the Li diffusion transport and the internal stress distributions. The goal of this model is to illustrate the importance of including real microstructure of electrode particles in future battery performance and failure modeling.

II. EXPERIMENTAL PROCEDURE

Positive (LiCoO\textsubscript{2}) and negative (graphite) electrodes were removed from two newly purchased LR1865AH Lishen (Tianjin, China) 3.7 V 18650 laptop batteries. The electrodes were cut into small strips and vacuum embedded in epoxy (EpoFix, Struers, Inc., Cleveland, OH). The embedded samples were microtomed to a mirror finish using a Reichert-Jung Ultracut E. The surface of the sample was coated with a thin layer of Au–Pd to make it conductive for scanning electron microscopic (SEM) and energy-dispersive spectroscopic (EDS) analyses. High-resolution SEM images of the deposited surface layers and particle size measurements were obtained using a Carl Zeiss NVision 40 Crossbeam workstation with a LEO Gemini field emission column. A beam energy of 3 kV and WD of \(3.5 \text{ mm}\) was used for SEM images. EDS analysis was done using Apollo 40 SDD (EDAX Corp., Mahwah, NJ) detector and a beam energy of 15 kV.

III. RESULTS

Figure 1(a) shows an SEM image of the graphite electrode. The copper current collector is visible running through the center of the double-sided electrode. Vertical striations in the potting material from the microtome are observed on either side of the electrode. The EDS carbon map in Fig. 1(b) helps identify individual graphite particles, but conductive carbon, binder, and the epoxy (in pores) also contribute to the carbon signal. Figure 1(c), an EDS phosphorus map, indicates the presence of electrolyte salt, LiPF\textsubscript{6} and essentially outlines the pores and shows that the graphite particles have diameters in the range of 10 to 20 \(\text{\mu m}\). Figure 2(a) shows the analogous SEM image of the positive electrode, while Fig. 2(b) shows an EDS cobalt map at higher resolution, with LiCoO\textsubscript{2} particles in the range 10 to 30 \(\text{\mu m}\).

A high-resolution SEM image of the interior of an individual graphite particle, exposed by microtome cutting, is shown in Fig. 3(a). The full field of view, \(\sim 4 \text{ \mu m}\), is considerably smaller than the size of a single particle. Note particularly the highly anisotropic nature of the grains, from which we conclude that Li insertion is anisotropic, since it takes place only from the prismatic edges and not through basal planes. Particle size measurements of such grains have been carried out from several SEM images from two batteries and taking into account more than 35 grains. The numerical average particle diameter was found to be \(\sim 8.4 \text{ \mu m}\) with a standard deviation of 1.6 \(\text{\mu m}\). This value is smaller than the whole particle and indicates that the larger particles comprise smaller grains resulting in grain boundaries and internal pores. Figure 3(b) shows an analogous high-resolution SEM of the interior of a partial particle of LiCoO\textsubscript{2}, which is also a layered material that would be lithiated anisotropically. Considering that the microtome induces unidirectional striation marks [Fig. 1(a)], we
expect that the microtome might tend to align microstructural components within the particles. The fact that the grains show no apparent preferred orientation suggests that the orientational effects of the microtome are modest.

Analogous data have been published previously by Zhang et al.,19 who used a focused ion beam to expose the particle interiors. Because a focused ion beam20–22 is expected to cause much less surface damage on a scale of microns than a microtome, their observations of internal cracks/pores are particularly relevant here. Similar types of cracks were also observed in our investigation. Figure 3(c) shows a typical propagation of a hairline crack within a graphite particle. Note the bifurcation of the crack within the particle indicating the crack path is anisotropic in nature. Figure 3(d) shows a transgranular pore within a graphite particle. Pores of different sizes were observed in the graphite particles varying from surface defects to transgranular cracks as shown in Fig. 3(d). The presence of grain boundaries, cracks, and pores inside electrode particles suggests that if the electrolyte has access to the interior of such particles, then Li\(^+\) ion transport could take place by grain-boundary/pore diffusion as well as by bulk diffusion. Zhang et al.19 observed that internal crack/pore surfaces were coated with SEI, showing that electrolyte, and, therefore, lithium ions did in fact infiltrate into the particles. According to Joho’s measurement, it is the surface area including the mesopores inside graphite particles that correlates with Li loss resulting from SEI formation, not the external surface area of the particle. Clearly, the mesopore surfaces inside these particles contribute a large portion to the total electroactive surface.

With these images in mind, we next use analytical modeling to show that the presence of complex internal structure can impact the amplitude and structure of the internal stresses caused by lithium insertion and removal. Our model will consider a particle with a single pore. For real particles, such as those shown in Fig. 3, we expect that the presence of several free surfaces at different orientations will have an even more profound effect, both quantitative and qualitative, on the internal stress and strain fields as well as on internal Li transport mechanisms.

### IV. ANALYSIS FOR DIFFUSION-INDUCED STRESS

To calculate how the stress field evolves during lithium insertion into a spherical particle, recent papers have used the analogy between thermal stresses and diffusion-induced stresses (DIS).3,5 In this paper we use a slightly different approach to model stresses, where we take the electrode particle to be cylindrical with a coaxial pore to find the impact of a small internal mesopore on the stress distributions. The use of cylindrical symmetry is more appropriate for mimicking layered materials such as graphite and LiCoO\(_2\), which permit lithium insertion only from the edges. The mesopore diameter we consider is 1% of the (cylindrical) particle diameter, corresponding to \(1 \times 10^{-4}\) volume fraction. For an electrode particle of 10 \(\mu\)m diameter, the mesopore size would be 100 nm.

The concentration of Li\(^+\) ions at a particular radius can be defined with a diffusion equation in a cylindrical coordinate system

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right)
\]

where \(C\) is the molar concentration and \(D\) is diffusion coefficient of Li inside the electrode particle. Let us assume that the electrode is surrounded by a constant lithium ion concentration \(C_R\). For a cylindrical electrode
particle, we assume a finite concentration at the center where the initial lithium ion concentration inside the electrode is $C_0$. Now assume that there is a single small mesopore, coaxial with the cylinder, with radius $a$. This mesopore may or may not be accessible to electrolyte. We consider the following boundary conditions for concentration conditions of diffusion Eq. (1)

(i) Solid electrode, no mesopore:

$$
C(r, 0) = C_0, \quad \text{for } 0 \leq r \leq R; \\
C(R, t) = C_R, \quad \text{for } t \geq 0; \\
C(0, t) = \text{finite}, \quad \text{for } t \geq 0 .
$$

(ii) Pre-existing coaxial mesopore of radius $a$, filled with electrolyte

$$
C(r, 0) = C_0, \quad \text{for } 0 \leq r \leq R; \\
C(R, t) = C_R, \quad \text{for } t \geq 0; \\
C(a, t) = C_R, \quad \text{for } t \geq 0 .
$$

Solving Eq. (1) with the aforementioned boundary conditions yields the concentration profiles, from which we can model the stress evolution inside each particle. We assume the electrodes are made from an isotropic, linearly elastic solid. Although we find that this assumption cannot be used to give accurate predictions for stresses inside a real particle (Fig. 3), we believe that it is sufficient to give an estimate of the impact that the presence of a free surface would have on the local stress field. Using the analogy between thermal stresses and DISs we can write the radial strain as

$$
\varepsilon_{rr} - \frac{\Omega}{3} C = \frac{1}{E} [\sigma_r - v(\sigma_0 + \sigma_z)] .
$$

Similarly, the tangential strain and axial strain are defined as

$$
\varepsilon_{00} - \frac{\Omega}{3} C = \frac{1}{E} [\sigma_0 - v(\sigma_r + \sigma_z)] ,
$$

and

$$
\varepsilon_{zz} - \frac{\Omega}{3} C = \frac{1}{E} [\sigma_z - v(\sigma_r + \sigma_0)] .
$$

Here, $E$ is the Young’s modulus of the electrode and $\Omega$ is the partial molar volume of the solute. Because atomic diffusion in solids is a much slower process than elastic deformation, mechanical equilibrium is established on a time scale that is short compared with that for diffusive processes, and we treat this as a static equilibrium problem. In the absence of any body force, the equation for static mechanical equilibrium in the bulk of a cylinder is given by

$$
\frac{d\sigma_r}{dr} + \frac{(\sigma_r - \sigma_0)}{r} = 0 .
$$

FIG. 3. Scanning electron microscopic for the interior of (a) a graphite particle and (b) a LiCoO$_2$. Note that the full field of view, approximately 4 $\mu$m, is several times smaller than the size of a single particle. Scanning electron microscopic images of (c) typical hairline crack propagation in a graphite particle and (d) transgranular crack in a graphite particle.
If \( u \) denotes radial displacement, strain can be given as

\[
\varepsilon_r = \frac{du}{dr}, \quad \varepsilon_\theta = \frac{u}{r}.
\]

We will now assume that there is no stress applied in the \( Z \) direction; i.e., \( \sigma_z = 0 \). Thus the electrode expands freely in the \( z \) direction, and we have plane stress.

For a solid electrode particle, there is no displacement at the center; i.e., \( u(0) = 0 \). For an electrode with a pre-existing void of radius \( a \) at the center, the radial stress on the free surface is zero; i.e., \( \sigma_r(a) = 0 \). For all electrodes, we also have \( \sigma_r(R) = 0 \) at \( r = R \) (radius of the cylinder).

Solving Eq. (6) using the aforementioned conditions, the radial stress distribution inside electrode are:

\[
\sigma_r = \frac{\Omega}{3} E \left[ -\frac{1}{r^2} \int_a^r C(r) rd\!r + \frac{1}{R^2 - a^2} \left( 1 - \frac{a^2}{r^2} \right) \int_a^R C(r) rd\!r \right],
\]

where, when \( a = 0 \), we have the solid electrode case without pre-existing mesopores. The dimensionless stress, radial position, time, and concentration can be represented as

\[
\xi_j = \frac{\sigma_j}{\left[ (\Omega/3)E(C_R - C_0) \right]}, \quad x = \frac{r}{R},
\]

\[
T = \frac{Dt}{R^2}, \quad \text{and} \quad y = \frac{C - C}{C_R - C_0}, \quad \text{respectively}.
\]

Here, \( j \) is \( r \), \( \theta \), or \( z \) depending upon the direction of stress we are looking at. We first determine the dimensionless concentrations at various radial positions and times using the diffusion Eq. (1) and the two sets of boundary conditions, (i) and (ii), listed in Eq. (2). Then, based on the concentration profiles, we compute radial and tangential stresses at different radial positions as a function of time.

The effects of an internal mesopore on the concentration profiles and on the corresponding radial stress field evolution inside particles are shown in Figs. 4(a) and 4(b) for the boundary conditions listed in (i), a solid electrode without any mesopore, and (ii) an electrode with pre-existing coaxial mesopore of radius \( a = 0.01 \), filled with electrolyte. For case (i), the maximum of the radial

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**FIG. 4.** Li concentration profiles and the radial stress distribution inside the particle subject to two different boundary conditions, (a) solid electrode and (b) electrode with a crack filled with electrolyte. (color online)
stress is reached at the center of the cylinder, but even a small hole at the center shifts the maximum stress location away from the center. When we compare Figs. 4(a) and 4(b), we find that not only is there a shift in magnitude and location of the radial stress peak value, but even the sign of the stress changes. Figures 4(a) and 4(b) represent stress distributions for insertion of Li\(^+\) in the electrode. Opposite conclusions would hold for the deinsertion case. Thus, a large region under compression in the homogeneous electrode during deinsertion would be in tension in the presence of a small mesopore (\(\alpha = 0.01\)) when it is filled with electrolyte. These effects are caused primarily by the presence of free surfaces.

As with the radial stress case, the tangential stress \(\sigma_\theta\) and the axial stress \(\sigma_z\) also show differences as a result of the presence of a mesopore, whether or not it is filled with electrolyte. Figure 5 shows tangential stresses for the deinsertion case with and without a mesopore filled with electrolyte. For a mesopore not accessible to the electrolyte, we find that the maximum tensile tangential stress is at the inner surface of the mesopore and has 1.96 times higher magnitude than the maximum stress for the electrode with no mesopore case. Our calculations also show that the maximum tensile tangential stress has only a weak dependence on the mesopore radius.

Following Cheng and Verbrugge, we calculate the bulk strain energy per unit volume, or bulk strain energy density, \(\varepsilon(r)\) accumulated as a result of the elastic deformation for the isotropically deformed cylinder as

\[
W(r) = \frac{1}{2E} \left( \sigma_\theta^2 + \sigma_\theta^2 + \sigma_z^2 \right) - \frac{\nu}{E} \left( \sigma_\theta \sigma_\theta + \sigma_\theta \sigma_z + \sigma_z \sigma_\theta \right) \tag{10}
\]

The total bulk strain energy can be obtained by integrating the strain energy density over the entire volume. Bulk strain energy per unit length of the wire in dimensionless form is

\[
\Pi_{\text{bulk}} = \int\frac{W_{\text{bulk}}}{\pi R^2 E[(\Omega/3)(C_R-C_0)]^2} \left( \sigma_\theta^2 + \sigma_\theta^2 + \sigma_z^2 \right) - 2\nu(\sigma_\theta \sigma_\theta + \sigma_\theta \sigma_z + \sigma_z \sigma_\theta) \right) dx \tag{11}
\]

when \(a = 0\), we have a solid electrode, and when \(a > 0\), we have a mesopore.

Figure 6 shows that the peak dimensionless strain energy for an electrode with a mesopore accessible to the electrolyte is a little more than half that for a homogeneous solid electrode, showing the significant effect that even a single mesopore can have. Based on Griffith’s energy criterion, the large drop in strain energy caused by free surfaces could mean a reduction in the probability of fracture for any given state of lithiation condition. On the other hand, the mesopores will certainly also affect the fracture strength of the particle and increase the stress intensity factor in complex ways. Thus, predictions of both particle strength and internal particle stress levels will have to rely heavily on knowledge of the internal microstructure of the particles for accurate results.
V. DISCUSSION AND CONCLUSIONS

The shrinking core model, which has been widely assumed in battery analysis for calculating transport rates and stress evolution, depends on at least 2 assumptions as it is commonly applied. The first assumption is that the particles are isotropic, at least in terms of Li transport and modulus. It has previously been shown that the shrinking core model is not appropriate for the highly anisotropic single-crystal material LiFePO4. Our results indicate that this same conclusion likely holds also for secondary particles made from highly anisotropic individual grains, such as those seen in Fig. 3, because of unavoidable intraparticle grain boundaries and pores. The second assumption is that transport of Li from the exterior to the interior of electrode particles is controlled by a single process, generally assumed to be bulk diffusion. We believe that the images of Fig. 3, together with analogous results from Zhang et al. also cast doubt on the accuracy of this second assumption, for both positive and negative electrode materials.

If $\xi_{\text{max}}(\text{yield})$ is the yield stress for the electrode material, the stress required to fracture it when there is a pre-existing mesopore is $\xi_{\text{max}}(\text{yield})/K$. Here, $K$ is the stress intensity factor that depends on the geometry of the mesopore and direction of applied stress, but is typically around 2 for small holes. If we define the cracking tendency as the ratio of maximum tensile stress to the yield stress, we find that during insertion the electrode with pre-existing mesopore has 1.96-4 times higher cracking tendency. Our calculations are based on the idealized assumption that the mesopore is cylindrical in nature, but they clearly indicate that the shrinking core model, with its assumption of a flawless solid electrode, would substantially underestimate the cracking tendency.

Similarly, during deinsertion, the isotropic solid electrode model predicts a compressive tangential stress at the center of cylinder and maximum tensile tangential stress at the surface. This indicates that the electrode has a higher cracking tendency at its surface. On the other hand, if the electrode has an electrolyte-accessible pre-existing mesopore, we find that the tangential stress is tensile at both the outer and inner surface of the mesopore inside of the electrode. Depending on the stress intensity factor ($K$ value), the cracking tendency may well be higher at the crack tip. Such an electrode is prone to internal cracking rather than surface cracking, contrary to the prediction of the shrinking core mode.

The presence of SEI in internal mesopores shows that there are processes apart from bulk diffusion—perhaps grain-boundary/pore diffusion—by which Li$^+$ ions can penetrate into the particles. The relative importance of bulk diffusion and grain-boundary/pore diffusion will depend on the particular chemistry/microstructure as well as the local state of lithiation. For example, material swelling from lithiation could deform mesopores and change their effectiveness as a pathway for Li$^+$ ion transport. To the extent that grain-boundary/pore diffusion is significant, the distribution of the various lithiated phases (or stages) within the particles will depend primarily on how the interior surfaces are arranged and may not in general resemble a shell and core. A follow-on step could then be bulk diffusion into individual grains, which might be fast or slow compared with other internal transport mechanisms. Given the extreme anisotropy of the individual grains seen in Fig. 3 it is unlikely that a shrinking core model would be valid for this step either.

Zhang et al. suggested that formation of SEI on interior mesopore surfaces could be sufficiently severe to lead to battery degradation through loss of lithium. The validity of this hypothesis depends on the amount of interior surface area accessible to the electrolyte. Additional analysis of particle microstructure, perhaps best accomplished with additional focused ion beam experiments, will be required to address this suggestion. However, whether or not the internal mesopore/grain boundary surface area is large enough to substantially affect the amount of SEI initially or ultimately formed, our images and analysis suggest that for particles such as those examined here, (i) the internal stress distribution and internal transport can be calculated accurately only with knowledge of the internal particle microstructure; and (ii) the core shell model does not give accurate predictions for either.

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