Multi Length Scale Microstructural Investigations of a Commercially Available Li-Ion Battery Electrode

P. R. Shearing, N. P. Brandon, J. Gelb, R. Bradley, P. J. Withers, A. J. Marquis, S. Cooper and S. J. Harris


Receive free email alerts when new articles cite this article - sign up in the box at the top right corner of the article or click here

To subscribe to Journal of The Electrochemical Society go to: http://jes.ecsdl.org/subscriptions

© 2012 The Electrochemical Society
Reactions in lithium ion batteries are supported by porous electrode microstructures, which are expected to support a range of physical phenomena; in common with all functional materials, there is a direct link between the electrode microstructure and its performance. The microstructure of the electrodes can influence battery energy and power density, electrical conductivity and charge times – furthermore, as these microstructures can evolve over time and with state of charge, microstructural degradation is intimately linked with device lifetime. In spite of the clear importance of lithium ion battery electrode microstructure, there is currently only a limited understanding of these structures and how they change during processing, operation and failure. For example, in operation, graphite anodes are known to expand as Li enters intercalated during cell discharge with volume changes of ca. 10%. For alloying type electrodes, such as Sn or Si based structures and how they change during processing, operation and failure, for example, in operation, graphite anodes are known to expand as Li enters intercalated during cell discharge with volume changes of ca. 10%. For alloying type electrodes, such as Sn or Si based compounds, volume changes of up to 400% have been observed. Over the past 20 years, a large number of microstructural investigations of Li-ion battery electrodes have been performed using a suite of microscopy techniques such as optical microscopy, scanning electron microscopy, TEM and AFM, alongside techniques such as TOF-SIMS and NMR. Techniques including TEM, AFM and optical microscopy have also been used to explore microstructural evolution processes associated with charge cycling in a variety of battery materials. The extent and quality of these papers illustrates the success of these conventional 2D techniques. For example, Figure 1 shows a series of scanning electron micrographs at increasing magnification, for the commercially available cathode material studied here. The micrographs reveal a wealth of qualitative information regarding the structure, which has a characteristically bi-modal particle size distribution. However some phenomena, such as percolation, are inherently three-dimensional and as such stereological interpretations from 2D data sets can prove ambiguous.

With increasing magnification, the micrographs reveal a highly complex composite structure; however, this two-dimensional data reveals little quantitative information, as the geometrical properties of these materials are inherently three-dimensional. Battery performance will be dictated by the ability of Li\(^+\) ions to move through porous structures and into electrically connected solids. Understanding the transport behavior of these electrode microstructures in three dimensions is key to understanding their performance.

Historically, attempts to model the effects of battery microstructure have made assumptions regarding heterogeneity – for example the models of Newman and co-workers have provided a valuable tool for battery design. However, the restricted ability of such models to account for microstructural heterogeneity has limited their use in studies of electrode aging and failure, as microstructural heterogeneities often predicate failure.

Recent advances in 3D imaging techniques have enabled three-dimensional microstructural characterization of a wide range of materials with unprecedented resolution. A range of techniques of varying resolution are now available including: atom probe tomography, electron tomography, X-ray computed tomography (CT) and focused ion beam (FIB) tomography. Two recent reviews of state-of-the-art nano-tomography systems provide a thorough introduction to FIB and electron techniques; provides a summary of the latest developments in X-ray techniques and Miller and Forbes review the status of atom probe tomography. The authors have also reviewed the application of tomography and spectroscopic techniques to electrochemical devices.

Of these techniques, the suite of X-ray techniques is particularly versatile, not only providing multiple length scale characterization options but also a non-destructive imaging platform. For studies of microstructural evolution (for example degradation, aging and failure), this is a significant advantage over destructive techniques, such as focused ion beams. The two X-ray microscopy systems used in this study utilize unique optics architectures to achieve 700nm and 50nm spatial resolution respectively.

The battery community has recently begun to recognize the power of 3-dimensional techniques to characterize battery structures: a number of recent studies have successfully reconstructed graphite, LiFePO\(_4\) and LiCoO\(_2\) at the electrode and particle length scales. Meier et al. have recently published proof-of-concept for combined X-ray tomography with coupled chemical phase analysis (TXM-XANES) for battery materials, signposting an exciting direction for multi-probe spectroscopic techniques. In addition, developments in microstructurally faithful modeling tools also allow researchers to effectively combine experimentally derived microstructural data to explore battery performance in silico.

The effective diffusivity of a porous medium is commonly related to the tortuosity of the pore structures, which, in its simplest definition, describes the geometrical limitation to a diffusing species as a result of pore curvature, “twistedness” or additional pore length. Whilst a number of empirical relationships linking tortuosity and porosity exist (such as the widely used Bruggeman relationship), there remains no robust, geometrical definition of tortuosity and as such it is commonly treated as a fitting parameter.
Modern X-ray microscopes can now routinely provide access to intricate geometrical descriptions of real-life pore geometries using the computed tomography technique; in spite of this, there remains no universal agreement in quantification method. Gostovic et al. were amongst the first to utilize a commercially available implementation for geometric tortuosity, using an algorithm to track the path length through the center of mass of each pore divided by the Euclidian distance across the electrode thickness.

An alternative definition of tortuosity considers the relationship between the absolute and effective diffusivity of a diffusing species in a porous media. The measurement of diffusion through complex pore geometries has been traditionally achieved by the use of a diffusion cell (e.g. Kalyvas). Recent advances in high-resolution tomography techniques and improvements in meshing capabilities for computational fluid dynamics (CFD) and finite element (FE) software afford the opportunity to investigate the geometrical limitations to diffusion in porous structures. In diffusion media, the sub-micron pore geometries are of particular interest, at the length scales where wall-interactions (Knudsen type diffusion) do not play a significant role in the bulk diffusion but where the geometrical complexity of the pore structure can impact the diffusion process.

Owing to the range of microstructural phenomena occurring in Li-ion batteries — from SEI growth at the nanometre length scale to catastrophic failure by short circuiting which has implications for pack designs — it is essential to characterize these materials at the multiple length scales relevant to the various physical processes.

Here we present microstructural investigations of a commercial manganese-based Li-ion battery cathode (E-One Moli Energy) by multi-modal X-ray tomography using both laboratory and synchrotron radiation. Tomographs have been obtained with spatial resolutions spanning more than an order of magnitude, and with analysis volumes varying over 4 orders of magnitude from around 250 μm³ to over 10 million μm³. Geometrical data is extracted from each of the data sets providing the first comprehensive multi-length scale investigation of a commercial Li battery material known to the authors. Finally, these data sets are combined with relevant simulations in order to predict the tortuosity based on an analog predicting the limitation to mass transport.

### Experimental

A commercial cathode from E-One Moli Energy was used: fragments of the electrode were easily separated from the aluminium foil without the requirement for chemical dissolution (as in Shearing et al.). The X-ray diffraction of the electrode structure shown in Figure 2 is matched by the ICDD database to LiMn₂O₄.

Microstructural analysis of the electrode layer was conducted using three X-ray microscopy platforms: laboratory X-ray micro-focus tomography, laboratory nano-XRM and synchrotron nano-XRM. Results from each platform are presented here in order of increasing spatial resolution with the imaging parameters summarized in Table I.

### Table I. Tomograph acquisition details.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Pixel size (nm)</th>
<th>Radiograph Exposure Time (sec)</th>
<th>Rotation range (°)</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MicroXCT-200</td>
<td>597</td>
<td>20</td>
<td>[−91, 91]</td>
<td>&lt;100</td>
</tr>
<tr>
<td>UltraXRM-L200</td>
<td>65</td>
<td>75</td>
<td>[−90, 90]</td>
<td>&lt;8</td>
</tr>
<tr>
<td>nanoXCT-S100 (SSRL)</td>
<td>15</td>
<td>3</td>
<td>[−90, 90]</td>
<td>6.5</td>
</tr>
</tbody>
</table>

**Figure 1.** Scanning electron micrographs of the commercially available manganese-based Li-ion battery cathode materials at progressively higher magnifications (top to bottom) all recorded using a Zeiss-Gemini FEG-SEM @ 10kV, SE2 Detector.

**Figure 2.** XRD Pattern matched to the ICDD database to LiMn₂O₄.
that a reduction in porosity could improve cell capacity without compromising power (pore connectivity), a full investigation of which is reserved for future experiments.

With increasing resolution, the most notable difference is the change in volume specific surface area: the normalized pore surface area measured by the nano-XRM scan was more than twice that measured for the micro-XRM. This effect was first identified by Mandelbrot who had noted that a coastline’s length depends on the resolution of the map. A similar analogy can be applied to surface area calculation as discussed by Coppens.

The agreement in calculation of bulk porosity and tortuosity between micro and nano-XRM scans is in support of fractal-like arguments in that, while the perimeter increases with spatial resolution, the enclosed volume does not. This suggests that the resolution requirement to characterize these properties is not as stringent as for surface area studies. In this instance, lower resolution can be tolerated without sacrificing data quality whilst simultaneously leveraging the statistical advantages of larger analysis volumes. Surface area calculations, which are sensitive to small variations in surface roughness, require some serious consideration as to the length scale of relevance to the phenomena being considered.

Clearly the resolution requirements will vary not only by physical parameter, but also by the material under investigation, the capacity for multi-length scale characterization is therefore also desirable to explore the range of commercially available electrode materials which may have notably different microstructures.

At the highest resolution using synchrotron radiation there is a large apparent discrepancy in the porosity because the sampled volume (See Figure 5) is so small that the entire volume of the image appears to lie within a single particle. Thus, the porosity revealed in this image volume represents internal defects in the solid structure (see Fig. 5a) rather than the bulk interconnected porosity measured with the lower resolution instruments. No connection between the bulk interconnected pores and these closed “nano-pores” is observed – therefore no penetration of electrolyte into the solid structure is achieved, and across this limited field of view 4.5% of the analysis volume is electrochemically inactive. In the analyzed volume of 263 μm³, nearly 6000 independent and isolated pores were resolved; the average volume of these individual “defect” pores is 0.02 μm³ (corresponding to a sphere with diameter about 430 nm).

In addition to these geometrical calculations, the data sets obtained using the laboratory X-ray instruments have been combined with Star CCM+ (CD-Adapco, London, UK) a commercial CFD simulation tool in order to calculate the tortuosity of the porous media evaluated from a mass transport perspective, as illustrated in Figure 6. The analog between Fick’s law for mass transport driven by a concentration gradient and Fourier’s Law for heat transfer across a temperature gradient is well documented (e.g.) The mathematical (and physical) similarities of the heat and mass transport calculations allow us to effectively utilize a heat-transfer simulation in order to predict the tortuosity of a pore network – providing the same tortuosity value but with easily implementable boundary conditions.
Table II. Microstructural analysis of multi length scale tomography data sets.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Total Volume (µm³)</th>
<th>Vol% Solid</th>
<th>Vol% Porosity</th>
<th>% Pore Connectivity</th>
<th>Geometrical Tortuosity</th>
<th>Vol. Specific Surface Area (µm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MicroXCT 200</td>
<td>10,434,731</td>
<td>63.7</td>
<td>36.3</td>
<td>99.7</td>
<td>2.0</td>
<td>0.6</td>
</tr>
<tr>
<td>nanoXCT-100</td>
<td>75,164</td>
<td>62.0</td>
<td>38.0</td>
<td>100.0</td>
<td>1.9</td>
<td>1.3</td>
</tr>
<tr>
<td>nanoXCT-S100 (SSRL)</td>
<td>263</td>
<td>95.5</td>
<td>4.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Further information on this method and implementation will be provided in a forthcoming paper.

Table III shows the results of these calculations; Figure 5 shows the analyzed volume alongside detail of the polyhedral mesh:

For the samples investigated, the tortuosity was found to vary in all three directions. In Table III, the y-dimension corresponds to the electrode “thickness” with the x and z dimension arbitrarily prescribed. The tortuosity calculated in the y-dimension, shows good agreement between the micro and nano-scan. The three-dimensional averaged calculated tortuosity was seen to decrease with increasing scan resolution, (from 2.21 to 2.01) a trend consistent with the geometrical tortuosity calculations.

Iwai et al.38 have observed similar directional tortuosity phenomena for studies of solid oxide fuel cell materials where pore phase tortuosities were shown to vary by ca. 15% and solid phase tortuosities by a value in excess of 320%. Comparison of the calculated tortuosity for these LiMnO4 electrodes with recently published data for an LiFePO4 electrode (Ender et al.22) show that the (pore) presented structures have a higher tortuosity, this is consistent with the higher bulk porosity observed for the LiFePO4 material.

Further investigations on cathode structures (not presented here) suggest that the directional dependence of tortuosity is a common feature for many cathode materials and, as expected, this directional dependence becomes increasingly marked with diminishing sample volume. In addition, it is conceivable that processing steps, such as calandering, will give rise to directional anisotropy, although such effects cannot be qualified for these commercially sourced samples. For the samples studied here, it is not yet established whether the directional dependence of tortuosity is principally linked with the sample investigation volume or the true nature of the microstructure. This will be the subject of future investigations.

Conclusions and Future Work

Multi modal characterization of a commercially available Li-ion battery cathode material has been conducted, providing unique insight into these highly complex materials across a range of length scales. A range of microstructural data has been extracted from these experiments at different length scales, confirming the requirement for different resolution depending on the physical parameters under investigation. As expected, volume specific surface area was significantly more sensitive to resolution changes than bulk porosity calculation. The techniques demonstrated here will also be valuable for post mortem analysis of battery structures.

The results demonstrate the importance of a multi-length scale tomography approach, revealing important (3-dimensional) microstructural information at each length scale and confirm the authors’ previous hypothesis that the resolution (and representative volume element)

Table III. Tortuosity calculation results based on the micro and nano-XRM data sets.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Mesh Dimensions (µm)</th>
<th>Total Mesh Elements</th>
<th>Calculated Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X Y Z</td>
<td></td>
<td>X Y Z</td>
</tr>
<tr>
<td>MicroXCT 200</td>
<td>238.8 59.7 238.8</td>
<td>407,064</td>
<td>2.88 1.52 2.23</td>
</tr>
<tr>
<td>nanoXCT-100</td>
<td>25.8 25.8 25.8</td>
<td>1,320,604</td>
<td>2.55 1.49 1.99</td>
</tr>
</tbody>
</table>

The tomography data sets were imported into Avizo and converted into stereolithography (*.stl) files, which describe the interface between the solid and pore phases. Star-CCM+ was then used to generate adaptive polyhedral volume meshes from these stl files. Using this microstructurally faithful modeling framework, simulations were run by applying boundary conditions suitable for the heat transfer analog, with nominal values for the thermal conductivity and temperature difference. The simulations were run on the largest volume fully bounded by the sample data, to try and negate the effect of small scale heterogeneities. To measure the tortuosity in all three directions, three separate simulations were run. For each simulation, the two parallel faces normal to the direction being investigated were set to fixed temperatures, while all other faces were set as adiabatic. The heat transfer measured could then be input into a modified form of the heat transfer equation, and the tortuosity determined:

\[
\tau_x = \phi \frac{Q}{Q_p}
\]

Where: \(Q = \) heat transferred through a solid block (W), \(Q_p = \) heat transferred through a porous media (W), \(\tau_x = \) Tortuosity, \(\phi = \) Porosity. 

\[
\tau_{y z} = \phi \frac{Q}{Q_p}
\]

\[
\tau_x = \frac{\left(1 - \frac{\phi}{\phi_{bulk}}\right)}{\phi_{bulk}}
\]

\[
\tau_{y z} = \frac{\left(1 - \frac{\phi}{\phi_{bulk}}\right)}{\phi_{bulk}}
\]

\[
\tau_{x y z} = \frac{\left(1 - \frac{\phi}{\phi_{bulk}}\right)}{\phi_{bulk}}
\]

Further investigation into these highly complex materials across a range of length scales is needed, confirming the requirement for different resolution depending on the physical parameters under investigation. As expected, volume specific surface area was significantly more sensitive to resolution changes than bulk porosity calculation. The techniques demonstrated here will also be valuable for post mortem analysis of battery structures.

The results demonstrate the importance of a multi-length scale tomography approach, revealing important (3-dimensional) microstructural information at each length scale and confirm the authors’ previous hypothesis that the resolution (and representative volume element)
requirement for a 3D image varies depending on the physical parameter that is under investigation.\textsuperscript{21} The analysis suggests that unless 3D data are collected at more than one length scale there is a danger that the results may not be quantitatively correct.

The increase in surface area recorded with increasing spatial resolution is not unexpected but does prompt the question as to what measure of the surface area is most representative in terms of understanding electrode performance? This will of course depend on the physical processes that are of paramount interest and the modeling tools we are using to explore them - for example, for electrochemical activity, the appropriate phase scale is most likely the one we use to normalize the exchange current per unit length of interface; for mass transport it is the length scale we use for the diffusion path lengths in solid or pore phase, and should also reflect the size of the finest mesh elements used in the analysis.

Work is underway to extend these techniques to more battery materials and to widen the capability to include techniques across a broader range of length scales, including industrial CT for cell and pack analysis (see e.g. Yufit et al.\textsuperscript{35}) and electron microscopy and surface analysis techniques for near atomic resolution studies. In addition significant effort is being devoted to effectively combine all of these structures with relevant simulations – to explore transport in these porous media, SEI growth and battery performance. The availability of phase contrast imaging modes for both the micro- and nano- XRM platforms further allow the reliable imaging of carbon-based materials. This suggests the possibility of additional studies on, for example, graphite electrodes, utilizing similar analysis protocols to understand the 3D microstructure of Li-ion battery anode materials as well as cathodes.\textsuperscript{30}

Acknowledgments

The authors acknowledge financial support from the EPSRC (under grants under EP/F007906 and EP/I02249X) and University of Manchester funding for the establishment of the Henry Moseley X-ray Imaging Facility at Manchester. PS is grateful to the Royal Academy of Engineering for financial support. The support and expertise of Xradia, Visualization Sciences Group and CD-Adapco is also acknowledged. Synchrotron data was collected at beamline 6–2 at the Stanford Synchrotron Radiation Lightsource supported by the Dept. of Energy Office of Basic Energy Science and we thank the beamline scientists for their support. Finally, we also acknowledge Ryan Bayliss at Imperial College for collection of XRD data.

References