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Neutron radiography, tomography, and diffraction of commercial lithium-ion polymer batteries

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Abstract

Imaging an intact, commercial battery as it cycles and wears is proved possible with neutron imaging. The wavelength range of imaging neutrons corresponds nicely with crystallographic dimensions of the electrochemically active species and the metal electrodes are relatively transparent. The time scale of charge/discharge cycling is well matched to dynamic tomography as performed with a golden ratio based projection angle ordering. The hydrogen content does create scatter which tends to blur internal structure. In this report, three neutron experiments will be described: 3D images of charged and discharged batteries were obtained with monochromatic neutrons at the FRM II reactor. 2D images (PSI) of fresh and worn batteries as a function of charge state may show a new wear pattern. In situ neutron diffraction (SNS) of the intact battery provides more information about the concentrations of electrochemical species within the battery as a function of charge state and wear. The combination of 2D imaging, 3D imaging, and diffraction data show how neutron imaging can contribute to battery development and wear monitoring.

Keywords: lithium-ion battery; wear; imaging; tomography; diffraction

1. Imaging an Intact Battery

Imaging an intact, commercial battery is the goal of this project, and is considered to be important for the progress of battery technology, but is recognized to be subject to compromises as one performs the neutron imaging experiment. The hydrogen content of the electrolyte causes significant neutron scattering and image degradation. The lithium content of even a small battery generates more absorption than is optimal for tomography.

Imaging an intact battery provides unique information not otherwise available. Typical components and materials are: (a) a copper negative electrode, (b) lithium ions intercalated into graphite, (c) an electrolyte barrier for electron insulation, but permitting rapid lithium ion diffusion, (d) metal oxide such as Li\textsubscript{x}CoO\textsubscript{2}, and (e) aluminum positive electrode [1]. For the process of battery discharge, electrochemists label the electrodes as anode (negative) and cathode (positive). The solid state chemist formulates a high Fermi level anode material, such as the LiC\textsubscript{6}, and a low Fermi level cathode material, such as Li\textsubscript{x}CoO\textsubscript{2}, (x = 0.2, battery charged). The range of Fermi levels in the charged battery challenge the stability of the organic electrolyte; decomposition of a small amount of electrolyte at the surface of the electrode material creates a solid/electrolyte-interface (SEI) layer. The stability of the SEI layer is
very important for the long term performance of the battery. A wide range of hydrogen-containing organics are used for the electrolyte, ranging from ethylene carbonate and/or polyethylene oxide to ionic liquids.

There are alternatives to neutron imaging, for example, solid-state NMR spectroscopy and NMR imaging, provided the battery cells are specially constructed for NMR compatibility with allowance for factors such as RF skin depth and magnetic field homogeneity [2]. Then, an extensive array of battery features can be examined, including lithium dendritic structures, lithium-ion mobility, polyelectrolyte decomposition, and metal oxide structure [3, 4, 5]. Of course, a disassembled battery can be inspected by electron microscopy, X-ray spectroscopy, and other classical methods. We note several significant recent works using neutron imaging and diffraction: lithium concentrations and mobilities have been imaged in lithium-ion batteries [6, 7]; neutron diffraction has been reported for several commercial batteries [8]; and 3D maps of a lithium-air cathode have been correlated with a transport model [9]. Herein, we briefly discuss our experiences with neutron-based battery imaging, survey recent neutron imaging reports, and speculate upon the future of this field, particularly with respect to the possibilities of time-of-flight beamline imaging, hydrogen scattering, and grating-based phase contrast 2D imaging.

2. Battery Preparation, Imaging, and Diffraction

Commercial single-cell lithium-ion prismatic pouch batteries, Kokam SLB452128, with LiCoO2 cathode were purchased and cycled from 2.7 to 4.2 V with an Agilent U2722A power supply (±0.12 A, triple output). A LabVIEW program logged V, I data which was then integrated into stored coulombs for each discharge cycle. Up to two weeks were required to precondition batteries with up to 400 charge/discharge cycles at 0.8 C (constant current at 80% of the labeled value in ampere hours). Batteries were cycled at ambient temperature and were not held in any confining structure. Under these conditions, battery wear was observed as a reduction of capacity, to as low as 16% of initial capacity. The small power supply was easily installed in tight beamline conditions and controlled by a long USB cable to an external laptop; however, the maximum 0.12 A power supply output limits the usage of this model to small batteries, ≤150 mAhr.

Detailed specifications of commercial batteries is not freely available. Given the known electrochemical cycle of lithium intercalated graphite negative electrode material, cycling between LiC6 to graphite, and the Li1xCoO2 positive electrode, the battery capacity defines the minimal mass quantities: 145 mAhr = 522 C = 5.41 mmol LiC6 = 0.427 g LiC6 = 0.53 g Li1xCoO2. In practice, the mass quantities are greater. For example, the Li1xCoO2 cathode is used over the range of x = 0 (battery charged) to x = 0.8 (battery discharged [1]; attempting to overcharge to x < 0.2 risks the decomposition of CoO2, liberating O2 gas and leading to subsequent battery destruction.

The nominal stored electrical energy is calculated as 3.7 V x 145 mAhr = 1.9 kJ. For reference, consider a chemistry classroom demonstration of a hydrogen balloon explosion, say 19 cm diameter; the change in enthalpy is 39 kJ. That is, a battery driven to destruction at the beamline may be somewhat entertaining; this calculation does not include the heat of combustion of the components.

Imaging experiments were done at FRMII Antares and at PSI ICON beamlines. Both used 6LiF/ZnS scintillators with thicknesses of 50 to 100 μm, Andor CCD camera, and L/D was typically set at 100 to 200. Pixel resolution was 54 μm (Antares) and 137 μm (ICON). The Antares experiments employed a double graphite crystal monochromator and a turbine velocity selector was used at ICON. Neutron powder diffraction was done at ORNL SNS VULCAN beamline with intensity and wavelength corrections done with samples of vanadium and cerium oxide [10].

3. Results and Discussions

In these exploratory experiments, the objective has been development of the most productive experimental protocols for the study of fresh and worn, intact, commercial batteries.

3.1. 2D Imaging at FRM II

We started with the observation of the LiC6 Bragg edge as an indicator of state-of-charge as well as a testing a new data acquisition method for dynamic tomography [11, 12, 13]. We noted the LiC6 Bragg edge was observable
in the intact battery in 2D imaging with monochromatic neutrons (BW=3%) in 0.1 Å steps from 3 to 4 Å; the edge diminished as the battery slowly discharged. Difference images of the discharged versus charged battery showed no structure; this was taken as evidence of a fresh battery, performing well.

3.2. 2D Imaging at PSI

Next, fresh and worn batteries were examined with 2D imaging and a velocity selector (BW=15%) while undergoing in situ continuous charge/discharge cycling. A 2x2 grid of batteries (Fig. 1) was mounted on an aluminum plate; a fresh, never charged battery was used as a reference for the batteries preconditioned to 92%, 56%, and 35% of initial capacity. Wavelengths were stepped over the range of 3 to 4.6 Å with 1 to 2 hr of observation at each wavelength (see Fig. 2). In retrospect, charge-and-hold-and-image followed by discharge-and-hold-and-image would have simplified data processing with no addition cost in beamtime; the time at each wavelength was dictated by the time spent charging/discharging the highest capacity battery. The 35% worn battery showed a transient structure that changed with state-of-charge and was observed at all wavelengths (Fig. 3a); this feature was interpreted as a dynamic wrinkle inside the battery formed due to the change in volume with state-of-charge. Both the 56% and 35% batteries have difference images that are visually not as smooth, with more speckle or salt-and-pepper noise, than the reference battery or the 92% initial capacity battery (Fig. 3b). This may be a sign of electrode degradation at a distance scale near that of the imaging system, 137 μm. The image structure near terminals does not appear any different than the rest of the battery. The image structure at the folds of this prismatic pouch battery was difficult to assess in the difference images due to battery volume changes; this indicates the need for battery holder with a confinement as used in real applications.

3.3. 3D Imaging at FRM II

Then, in a 7-day run, tomography data were collected for two batteries at three states-of-charge across the LiC₆ Bragg edge. The tomography data were reconstructed with filtered back-projection reconstruction. Electrode structure is partially observed at battery corners, but not in the interior, even with the small battery size, the opacity and scattering degrade the projection data. Per suggestions from a colleague, alternative reconstruction algorithms will be tested; the SNARK09 software provides access to a number of current algorithms [14]. With the tomography results, we had hoped to calculate a 3D difference image showing the LiC₆ concentration through the battery; 3D LiC₆ distribution has the potential to address a variety of battery wear questions: Is battery wear uniform across all electrode surfaces or does electrochemical cycling fail first near the terminals or, for prismatic batteries, at the electrode folds? Also, when electrochemical cycling fails, is the failure in the limit of (i) high LiC₆/low LiₓCoO₂, (ii)
low LiC_6/high Li_1CoO_2, or (iii) low LiC_6/low Li_1CoO_2 and Li dendrites? 3D Bragg edge imaging is, in principle, a beautiful technique for these questions.

3.4. Neutron Diffraction at VULCAN

For comparison to the imaging work, we tested time-of-flight neutron diffraction at two gauge volumes, 20 mm^3 and 250 mm^3. The small gauge volume yielded insufficient signal-to-noise for mapping areas near the terminals and folds. Thus, the large gauge volume was used so as to track battery chemistry throughout a controlled discharge. Significant differences were noted between fresh and worn batteries, as shown in Fig. 4. The diffraction experiment provides useful battery chemistry information, especially when combined with imaging data. Serious consideration should be given to the development of beamlines with simultaneous imaging and diffraction capabilities.

4. Comments about the Future of Intact Battery Imaging

Based on these exploratory experiments, we are now in a position to suggest a set of the most efficient battery experiments, when the constraint is to study an intact, commercial battery. First, the high value of the 3D Bragg edge tomography experiment is seductive, but as yet, is a very difficult experiment. We recommend consideration
Fig. 4. Neutron diffraction from the VULCAN time-of-flight diffractometer. The two traces clearly show battery chemistry in this intact battery with peaks due to graphite, lithiated graphite, and a metal oxide similar to LiCoO$_2$. The baseline has not been corrected for hydrogen scatter. The signal fall off at 2.5 Å is due to lack of flux at long wavelengths from this water moderated beamline. The d-spacings in Angstroms for diffraction peaks that change with state-of-charge are noted with blue (charged) and black (discharged) text.

...of alternative reconstruction methods; limited angle tomography and discrete tomography are two options. Second, 2D Bragg edge imaging at 3 Å to 4.5 Å is already seen to be a productive experiment; increasing the spatial and energy resolution, as well as the energy range of this experiment is highly recommended. To observe the Li$_x$CoO$_2$ cathode structure will require extension to wavelengths near 5 Å [11, 15]; some other cathode materials have even larger crystallographic unit cells. Here is a case where time-of-flight instruments, with their wide bandwidths, can be especially useful. Third, the option of simultaneous acquisition of diffraction data appears to be very useful. However, this is just one possible role for secondary detector system at an imaging beamline.

...Secondary detector systems should be considered for the observation of hydrogen scattering from within the battery. In some batteries, all hydrogen atoms are initially contained in the polymer electrolyte in a chemical functional group known as a methyl rotor. As the battery degrades forming hydrogen gas bubbles and lithium dendrites, these methyl groups are consumed. Given the specific and high cross section interaction between methyl groups and cold neutrons, observation of this inelastic scattering may be one route to the earliest detection of battery degradation. Other batteries will have hydrogen in similarly distinctive functional groups such as methylene units and aromatic rings [1].

We propose the consideration of grating-based phase contrast imaging as a 2D method with a balance of high information content and low exposure time, hence minimal activation. We note that US Department of Transportation regulations for radioactive samples have an exemption limit of 1 microCurie (37 kBq = 2500 bananas equivalent activity [16]). We are curious if a protocol of image, car testing, and then re-imaging can be performed while limiting sample activation to well below the DOT exempt limit. A leading manufacturer of transportation batteries, Dow Kokam, is continuing to use a battery cathode containing cobalt [17].
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References

[1] J. B. Goodenough, Y. Kim, Challenges for rechargeable li batteries, Chem. Mater. 22 (3) (2010) 587–603.
[2] N. M. Trease, L. Zhou, H. J. Chang, B. Y. Zhu, C. P. Grey, In situ nmr of lithium ion batteries: Bulk susceptibility effects and practical considerations, Solid State NMR 42 (2012) 62–70.
[3] R. Bhattacharyya, B. Key, H. Chen, A. S. Best, A. F. Hollenkamp, C. P. Grey, In situ nmr observation of the formation of metallic lithium microstructures in lithium batteries, Nature Materials 9 (6) (2010) 504–510.
[4] S. Chandrashekar, N. M. Trease, H. J. Chang, L.-S. Du, C. P. Grey, A. Jerschow, Li-7 mri of li batteries reveals location of microstructural lithium, Nature Materials 11 (4) (2012) 311–315.
[5] I. Hung, L. Zhou, F. Pourpoint, C. P. Grey, Z. Gan, Isotropic high field nmr spectra of li-ion battery materials with anisotropy 1 mhz, J. Amer. Chem. Soc. 134 (4) (2012) 1898–1901.
[6] J. B. Siegel, X. Lin, A. G. Stefanopoulou, D. S. Hussey, D. L. Jacobson, D. Gorsich, Neutron imaging of lithium concentration in lfp pouch cell battery, J. Electrochem. Soc. 158 (5) (2011) A523–A529.
[7] J. P. Owejan, J. J. Gagliardo, S. J. Harris, H. Wang, D. S. Hussey, D. L. Jacobson, Direct measurement of lithium transport in graphite electrodes using neutrons, Electrochimica Acta 66 (2012) 94–99.
[8] N. Sharma, V. K. Peterson, In situ neutron powder diffraction studies of lithium-ion batteries, J. Solid State. Electrochem. 16 (5) (2012) 1849–1856.
[9] J. Nanda, H. Bilheux, S. Voisin, G. M. Veith, R. Archibald, L. Walker, S. Allu, N. J. Dudney, S. Pannala, Anomalous discharge product distribution in lithium-air cathodes, J. Phys. Chem. C 116 (15) (2012) 8401–8408.
[10] X. L. Wang, T. M. Holden, G. Q. Rennich, A. D. Stoica, P. K. Liaw, H. Choo, C. R. Hubbard, Vulcan - the engineering diffractometer at the sns, Physica B 385 (2006) 673–675.
[11] A. Steuwer, P. J. Withers, J. R. Santisteban, L. Edwards, Using pulsed neutron transmission for crystalline phase imaging and analysis, J. Appl. Phys. 97 (7) (2005) art. no. 074903.
[12] L. G. Butler, B. Schilling, K. Ham, T. Dobbins, P. Liu, J. J. Vajo, Neutron imaging of a commercial li-ion battery during discharge: Application of monochromatic imaging and polychromatic dynamic tomography, Nucl. Instrum. Methods A 651 (2011) 320–328.
[13] A. Kaestner, B. Muench, P. Trtik, L. Butler, Spatiotemporal computed tomography of dynamic processes, Optical Engineering 50 (12).
[14] Website, R. Davidi, G. Herman, J. Klukowska, Snark09: A programming system for the reconstruction of 2d images from 1d projections, http://www.dig.cs.gc.cuny.edu/software/snark09 (2012).
[15] Y. Shao-Horn, L. Croguennec, C. Delmas, E. C. Nelson, M. A. O’Keefe, Atomic resolution of lithium ions in licoo2, Nature Materials 2 (7) (2003) 464–467.
[16] Website, Banana equivalent dose, http://en.wikipedia.org/wiki/Banana_equivalent_dose (2012).
[17] Website, Dow Kokam, http://www.dowkokam.com/ (2012).