Supporting Information

Probing Multiscale Transport and Inhomogeneity in A Lithium-ion Pouch Cell Using In-situ Neutron Methods

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Experimental Methods

**In-situ Neutron Radiography and Pouch Cell Fabrication**

Neutron imaging was performed at the High Flux Isotope Reactor (HFIR) CG-1D beamline at Oak Ridge National Laboratory (ORNL)$^1$. For polychromatic neutron imaging, apertures with variable diameters, D, (pinhole geometry) can be used at the entrance of the He-filled flight path with a maximum length, L, of 5.5 m. For this experiment, l, the sample-to-detector distance, D and L are 38 mm, 10 mm and 5 m, respectively, resulting in an L/D of 550 and spatial resolution of about 75 µm at the detector. The facility provides neutron wavelengths approximately between 0.8 ~ 6.0 Å (with center around 2.6 Å).$^2$ The detector consists of a 50 µm thick LiF/ZnS scintillator and a DW936 IkonL ANDOR™ charge coupled device (CCD) camera coupled with an optical lens. In order to reduce dark current, the CCD camera is equipped with a Peltier cooling system and is routinely cooled down to -60 °C.

The neutron imaging experimental setup is shown in Figure 1, where a collimated incident neutron beam enters the pouch cell placed as close as possible to a neutron sensitive detector, which digitally records the changes in neutron transmission. The planar pouch cell construction has a unique advantage for neutron radiography. Because the optical axis is parallel to the plane of the separator, it is easy to identify the anode and cathode by measuring the transmission of each electrode before the first discharge. The carbon electrode is transparent to the neutron beam whereas the Li metal strongly attenuates the beam. Furthermore, the lithium ion migration
between the anode and cathode during charge and discharge can be observed in this orientation. The neutron beam is attenuated as it passed through the cell to reach the detector, producing a 2D projection of the cell on the detector plane. The electrode width, $\delta$, along the beam path can be tailored to optimize beam transmission. Increasing $\delta$ decreases neutron transmission due to the change in lithium concentration. However, if $\delta$ is too large, neutrons transmit less, which increases the measurement uncertainty. In this study, the electrode width $\delta$ is approximately 2.5 cm. For the radiography measurements, the pouch cell was sandwiched between two silicon (Si) discs and fixed on the sample stage with a steel binder clip in front of the detector so that the neutron beam path travels through the cell along the Z-axis parallel to the plane of the electrode and separator. We call this the “edge” configuration (see Fig. 1(a)), where one can monitor the contrast changes along the electrode thickness rather than in the in-plane configuration.

The configuration of the pouch cell is shown in Figure 1(b) of supplemental section, where the cathode (graphite) and anode (Li metal) were spaced by the separator, and then sealed with the pouch film. The copper (Cu) and nickel (Ni) tabs were respectively used to connect the cathode and anode to the outside cycler. Two layers of graphite electrode were specially used to enhance the signal, which were calendared and have the thickness of around 100 µm each. The electrode consists of 92% graphite powder (ConocoPhillips, A12), 6% PVDF (Polyvinylidene Fluoride) binder (Kureha, 9300) and 2% carbon (IMERYS Graphite & Carbon, C-NERGY Super P C65) by weight. The electrolyte is 1.2 M LiPF$_6$ (lithium hexafluorophosphate) dissolved in a mixture solution of EC (ethylene carbonate) and DMC (dimethyl carbonate) (battery grade, BASF, USA) in a volume ratio of 3:7 with HF and H$_2$O impurity less than 50 and 5 ppm respectively; a Celgard 2325 separator (Celgard Inc., USA) is used. A small section of Cu foil was extended as the tab for the graphite cathode while a nickel tab was attached to the lithium anode during pouch cell assembly. The charge-discharge cycling (at 25 °C) is performed between 0.001 ~ 2.0 V. To reduce the strong incoherent scattering of H atoms present in the electrolyte, deuterated electrolyte was specially used, where H was substituted by deuterium (D), which has an incoherent scattering cross-section of ~ 2 barn, compared to ~ 80 barns for H, at 1 Å.

The cell cathode and anode were connected to a multichannel potentiostat (VMP3, Bio-Logic) for cycling purpose. Electrochemical cycling and the acquiring of the neutron radiographs were
started at the same time to establish a precise relationship between the charge/discharge states and the images. The exposure time for each image is 60 s with a 5 s delay between images due to data transfer from the CCD to a Linux computer via USB. Radiographs were normalized using the Lambert-Beer law:

\[ I_{\text{norm}} = \frac{(I_{\text{raw}, t} - I_{\text{DarkField}})}{(I_{\text{raw}, t=0} - I_{\text{DarkField}})} \]

where \( I_{\text{raw}, t} \) is the raw radiograph at time \( t \), \( I_{\text{DarkField}} \) is the dark field radiograph (i.e. electronic noise of the detector without the neutron beam), and \( I_{\text{raw}, t=0} \) is the first radiograph of the discharge or charge process. All image processing and quantitative analyses were performed using in-house iMars\(^3\) tool and ImageJ\(^4\) software.

**In-situ Neutron Diffraction**

Neutron diffraction measurements were performed using the state-of-the-art engineering diffractometer–VULCAN\(^5,6\) located at the Spallation Neutron Source (SNS) of Oak Ridge National Laboratory. VULCAN is a time-of-flight neutron diffractometer where a diffraction pattern over a large range of \( d \)-spacing can be collected simultaneously. The typical setup of the in-situ experiment of cycling batteries can be found in our previous studies\(^7-9\). In brief, the pouch cell was placed with the cell plane at 45 degree from the incident beam and a set of +/-90 degree time-of-flight (TOF) position sensitive static detectors (Bank #1 and Bank #2) were used to collect the diffraction pattern (Figure S3 of supplemental section). While both banks of detectors measure lattice signals in-plane (Q1) and normal (Q2) directions simultaneously, the data collected in the bank #2 shows the cell expansion in the normal direction. A chopper setting of 20 Hz provided a measurable \( d \) spacing range from 0.5~3.5 Å. A beam size of \( 2(W)\times12(H)\times2mm^3 \) was used for the measurement, resulting in a \( 2.82\times12\times0.76 \text{ mm}^3 \) area coverage in the cell. Neutrons were collected continuously over the electrochemical cycle, and then the data was combined in 30 min time windows with the VDRIVE software\(^10\).

**Neutron Imaging: Basic Concepts**

The principal of neutron imaging is based on the attenuation of a neutron beam passing through matter. The attenuation mainly depends on the composition and density of the material being
studied. For a uniformly thick, homogeneous sample, the attenuation is governed by the Beer-Lambert law:

\[ I = I_0 e^{-\mu \delta} \]  

where \( I_0 \) and \( I \) are respectively the intensity of the incident and transmitted neutron beam, \( \mu \) is the attenuation coefficient and \( \delta \) is the thickness of the sample along the direction of the neutron beam. The attenuation coefficient, \( \mu \), is given by

\[ \mu = \frac{\sigma N_A}{M} \]  

where \( \sigma \) is the neutron total cross-section of the material, \( \rho \) is the material’s density, \( N_A \) is Avogadro’s number and \( M \) is the molar weight of the material. The neutron cross-section represents the attenuation by the material due to both scattering and absorption. Depending on different elements, the value is distinct (see Figure S1).

For a sample consisting of many components, the total neutron attenuation is the summation of the attenuations due to each component weighted with their molar concentration. In our case, the total measured intensity, \( I(t) \), at one pixel position can be expressed as the sum of two components in the exponent, one is constant and another changes over time (attenuation due to the Li ions):

\[ I(t) = I_0 \exp \left( -\sigma_{Li} c_{Li}(t) N_A \delta - \sum_{i \neq Li} \sigma_i c_i N_A \delta \right) \]  

where \( I(t) \) is the intensity of the neutron beam after attenuation at time \( t \), and \( c \) is the molar concentration, \( \sigma \) is the neutron cross-section of the material.

To correct for background noise, beam inhomogeneities, detector fluctuations, and eliminate the signal from the other components of the cell, the collected raw images of the cell were normalized by the \( t = 0 \) image of the cell and the dark field image. The normalized expression is given by:

\[ I = f_r \frac{I_{(Sample\ Image)} - I_{(Dark\ Field)}}{I_{(t=0)} - I_{(Dark\ Field)}} \]  

where \( f_r \) is the scale factor to correct for beam fluctuations and is based on the differences in the mean intensity values between the selected open beam area in the sample images and the mean
intensity of the same area in the $t = 0$ image. After normalization, all signals but the attenuation from Li ions is removed from the radiograph, which is related to the change of Li concentration (quantity) during an elapsed time $t$ at that position (Equation 5). All image processing and quantitative analyses were performed using in-house iMars$^3$ tool and ImageJ$^{11}$ software.

$$I(t)/I(t_0) = I_0 \exp \left( \sigma_{Li} N_d \delta (c_{Li}(t) - c_{Li}(t_0)) \right)$$

(5)

**Figure S1.** Total (scattering and absorption) thermal neutron cross-sections for different elements.

Compared to the components of the cell, i.e. aluminum (Al), copper (Cu), carbon (C), the much higher neutron cross-sections for Li and H ensure high contrast in the neutron radiograph, where attenuation is mainly caused by Li and H.

The spatial resolution of the neutron imaging is limited by the geometric unsharpness ($U_g$):

$$U_g = \frac{l \cdot D}{L}$$

(6)

where $l$ is the distance between the sample and the detector, $D$ is the aperture diameter and $L$ is the distance between the aperture and the detector. Generally, larger $L/D$ ratios and smaller $l$ (sample is closer to the detector) contribute to a better resolution.

**Normalization and Measurement Uncertainty**
The imaging data inherently constitutes neutron attenuation of the all components of the pouch cell therefore, image normalization is necessary to remove any contribution of the cell and its components, and thus highlighting Li changes and transport through cycling. As shown in Figure 1, the raw radiographs (top) of the cell collected at three different times (t = 0, 1, and 60 minutes) during the lithiation process of the graphite electrode display a very low transmission through the whole cell, which is caused by the neutron attenuation from the H-rich separator, pouch and Li metal anode. From these radiographs, it is difficult to observe the change in transmission due to lithium migration. Comparatively, after the normalization process, the signal from static components, i.e., cell, pouch, separator, etc. are eliminated and the change of attenuation with time can be observed and is due to the changes of Li concentration in the graphite electrodes as illustrated after 60 min in Fig. 1. The color scale indicated here is purely a qualitative guide for the contrast with red indicating more transmission and blue less transmission.

Figure S2. (top) Raw neutron transmission radiographs of the pouch cell as a function of time (t = 0, 1 and 60 minutes). Due to the attenuation from the components, changes in transmission are difficult to see and; (bottom) Neutron transmission radiographs of the pouch cell where data were normalized using the radiograph at t = 0, thus removing the unwanted contributions from cell components such as the electrolyte, pouch itself and Li metal anode. The thin strips are carbon electrodes that separated from Li metal. The decrease of transmission through time is directly related to the increase in Li content during the discharge process. Radiography shows clear inhomogeneity in Li distribution in the graphite cathodes. The color attenuation scale is displayed from 0 to 1.
The measurement uncertainty of neutron radiography mainly comes from the nature of the neutron production (the reactor flux increases slowly and steadily during the reactor cycle) and neutron background in the experimental area and around the detector. In order to minimize the measurement uncertainty or statistical error, the number of measured neutrons needs to be increased, which generally can be achieved by increasing exposure time. However, this will decrease the temporal resolution and may be unsuitable for in-situ kinetic measurements, such as the Li transport during lithiation and delithiation. Another approach is to combine (or bin) pixels together with similar sample coverage. By treating each pixel as an independent measurement and taking a spatial sum, increased counts can be achieved by trading off the in-plane resolution, which is similar to increasing exposure time at the cost of spatial resolution. Therefore, 30-pixel line profiles along the Y-direction of the cell are summed for data analysis.

Inhomogeneity in the contrast color can be seen along the cell height and up to some degree across the electrode thickness as well (see 60 min attenuation-based radiograph in Figure 1), where a larger contrast variation in the bottom half of the cell on the right carbon electrode is noticeable. This requires some careful evaluation of the plausible experimental artifacts as well. Since the spatial resolution of the instrument is close to 75 µm (at the detector, with a pixel size of ~ 36 µm) and our electrode thickness was less than 200 µm it is always a bit challenging to interpret the results unless the spatial resolution is improved to 10 micron or below. Additionally, along the vertical height the analysis of imaging contrast is complicated for a number of reasons such as, (i) pouch cell not being aligned perfectly vertical to the collimated neutron beam, (ii) variation of thickness, bending and pressure variation of individual electrode sandwich layers during cell fabrication etc., (iii) smearing of the soft lithium metal across the edges, and (iv) interference of the liquid electrolyte which permeates across the overall cell thickness. These factors could also contribute to the overall imaging contrast and may not be driven by the actual electrochemical effect of lithium intercalation in graphite. Due to these factors, and to pursue a more quantitative comparison of imaging results with electrochemical transport modelling, we only consider the top electrode region where the contrast variation looks more uniform with less possibility of experimental or design artifacts.
**In-situ Neutron Diffraction**

**Figure S3.** A schematic illustration of the setup of the *in-situ* neutron diffraction. The height of the beam is determined by a set of incident slits while the width of the beam is done by matching the horizontal openings of the incident slits and the radial collimators. The cross-section of the incident beam and irradiated sample (orange strip) determine the sampling volume.

**Electrochemical modeling of lithium transport in graphite:**

The Li/Li$_3$C$_6$ cell sandwich is modeled with galvanostatic discharge boundary conditions. A 3D volume averaged formulation is used to capture the transport of lithium in graphite across the cell. The solid-phase particles are assumed to be spherical with radii much smaller than the thickness of the electrodes. Consistent with this assumption and to reduce computational complexity, Duhamel approximation is used as a solution profile in radial direction of these
spherical particles. The physical domain consists of lithium foil negative electrode, a porous separator and a porous carbon positive electrode with electrolyte. We model the half-cell i.e., two regions of separator and positive electrode. The conservation equation of lithium ion concentration \(c_e\) within the electrolyte solution is given by

\[
\frac{\partial (\varepsilon_c c_e)}{\partial t} - \nabla \cdot (\varepsilon_c D_e^{\text{eff}} (\varepsilon_c) \nabla c_e) = \frac{1 - \Theta_t}{F} j^{Li}
\]

The potential in the solution phase is referenced with the lithium electrode and is defined by conservation of charge

\[
\nabla \cdot (\varepsilon_c \kappa_e^{\text{eff}} (\varepsilon_c) \nabla \phi_e) + \nabla \cdot (\varepsilon_c \kappa_s^{\text{eff}} (\varepsilon_e) \nabla \ln c_e) = - j^{Li}
\]

Similarly, in solid phase we have conservation of solid phase concentration,

\[
\frac{\partial (\varepsilon_s c_{s, \text{avg}})}{\partial t} - \nabla \cdot (\varepsilon_s D_s^{\text{eff}} (\varepsilon_s) \nabla c_{s, \text{avg}}) = - \frac{j^{Li}}{F}
\]

and conservation of charge,

\[
\nabla \cdot (\varepsilon_s \sigma_s^{\text{eff}} (\varepsilon_s) \nabla \phi_s) = j^{Li}
\]

and the chemical kinetics at the electrode/electrolyte interface is given by Butler-Volmer equation

\[
i_{nj} = i_0 \left[ \exp \left( \frac{\alpha_{nj} F}{RT} \eta_j \right) - \exp \left( - \frac{\alpha_{nj} F}{RT} \eta_j \right) \right]
\]

To computationally well pose this half-cell simulation without the anode region three boundary conditions are necessary.

\[
D_e^{\text{eff}} \frac{\partial c_e}{\partial x} \bigg|_{x=0} = \frac{i_{\text{app}}}{F}
\]

\[
\sigma_{e}^{\text{eff}} \frac{\partial \phi_s}{\partial x} \bigg|_{x=L} = i_{\text{app}}
\]

\[
\phi_e \big|_{x=0} = 0
\]

The meanings of the parameters mentioned in the equations are explained as follows:
\( c_e \) Concentration of lithium salt in liquid electrolyte phase
\( c_s \) Surface concentration of lithium in solid phase
\( c_{s,avg} \) Average concentration of lithium in solid phase
\( D_e \) Diffusion coefficient of lithium salt in the solution
\( D_e^{\text{eff}} \) Effective diffusivity of electrolyte
\( D_s \) Diffusion coefficient of lithium in solid phase
\( D_s^{\text{eff}} \) Effective diffusivity of solid electrode matrix
\( F \) Faraday’s constant (96485 C mol\(^{-1}\))
\( i_0 \) Exchange current density
\( j^{\text{Li}} \) Pore wall Li flux across interface
\( R \) Universal gas constant (8.3143 J mol\(^{-1}\) K\(^{-1}\))
\( t \) Time
\( T \) Temperature
\( t_0 \) Lithium cation transference number
\( \alpha_a \) Anodic transfer coefficient
\( \alpha_c \) Cathodic transfer coefficient
\( \varepsilon_e \) Volume fraction of electrolyte
\( \varepsilon_s \) Volume fraction of solid phase
\( \varphi_e \) Potential of liquid phase
\( \varphi_s \) Potential of solid phase
\( \eta \) Surface overpotential
\( \kappa \) Ionic conductivity of electrolyte
$\kappa_{\text{eff}}$ Effective ionic conductivity of liquid phase in solid matrix

$\kappa_D^{\text{eff}}$ Effective diffusional conductivity of electrolyte

$\sigma$ Electric conductivity of solid electrode material

$\sigma^{\text{eff}}$ Effective electric conductivity of electrode

$i_{\text{app}}$ Applied discharge current density

In line profiles of Fig S4, we observe that as the discharge continues the lithium concentration gradually increases with formation of peaks near the separator/electrode interface and then shift towards the bulk of the electrode towards the end of discharge. This is in agreement with the experimental study as the peak of transmission gradually decreases and shifts towards the bulk of the electrode. Also, there appears to be a good qualitative agreement of the color contrast at various discharge times obtained from neutron imaging and electrochemical modeling, since both vary with local lithium concentration per unit volume of graphite.

**Figure S4** Calculated discharge profile (line and 2D surface) showing lithium concentration as a function of electrode thickness. The profiles are modeled based on the pouch cell shown in Figure S1. The color maps of the cell sandwich shown in left is not to scale.
problem setup, the modeling capability still serves as a good tool to quantify the lithium concentration distribution and understand the staging process across the entire electrode thickness.

References


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