3D mapping of lithium in battery electrodes using neutron activation

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ABSTRACT

The neutron depth profiling technique based on the neutron activation reaction, ${}^6\text{Li} (n, \alpha) {}^3\text{H}$, was applied with two dimensional (2D) pinhole aperture scans to spatially map lithium in 3D. The technique was used to study model LiFePO_4 electrodes of rechargeable batteries for spatial heterogeneities of lithium in two cathode films that had undergone different electrochemical cycling histories. The method is useful for better understanding the functioning and failure of batteries using lithium as the active element.

Keywords: Neutron depth profiling, 3D mapping, Lithium iron phosphate electrode, Lithium distribution

1. Introduction

Rechargeable Li-ion batteries (LIBs) are an indispensable technology in modern life for efficient energy storage; they are deployed in large numbers and operate close to their electrochemical stability limits [1-4]. Detrimental reactions at battery electrodes can cause capacity fade and occasionally catastrophic failures, hindering the widespread use of LIBs, particularly in mobile power energy solutions such as all-electric vehicles [1-4]. It is valuable to visualize the distribution and flow of the active element, lithium, in electrodes for better diagnosis of battery functioning and failure. While the electron energy loss spectroscopy in transmission electron microscope is able to image Li in a specimen volume of the order of Å to 10's of nm [5, 6], which is suitable for lattice structure analysis of active materials, and magnetic resonance imaging [7] and neutron imaging [8] can map Li over length scales from 10's of μm to millimeters, relevant for battery assembly and packaging, an imaging method for 3D Li mapping to cover the length scales of the interest for electrode design, *i.e.*, over 10's of nm for the particle size of active materials to 10's of μm for the electrode film thickness to 10's of mm for electrode lateral dimensions, has not been previously applied. A promising candidate to fill this gap is 3D tomographic neutron depth profiling (NDP), which has depth resolution in 10's nm and covers thickness range in 10's μm, while scanning across an area larger than 10 mm × 10 mm.

NDP is a neutron activation analysis method developed in the early 1970s and used to quantitatively measure the abundance and depth distribution of several technologically important elements (Li, B, N, He, Na, etc) [9, 10]. The technique has been used to measure the Li distribution in modern battery technologies [11-16], based on the nuclear reaction, ${}^6\text{Li} + n \rightarrow \alpha$

(2055 keV) + ^3H (2727 keV). Charged α and triton (^3H) particles lose kinetic energy during transport through the specimen media, which is measured to determine the depth of the activation reaction. The normalized counts of activation events are recorded to determine the abundance of Li at the corresponding depth. Typical NDP setup and measurement principles have been described previously [10, 17]. Recently, *in situ* NDP has been applied to observing the 1D Li distribution and transport in working LIBs during charge/discharge cycles [17-19].

While there were several prior efforts in taking NDP to 3D mapping [10, 20-24], thus far, the application of NDP to battery studies has focused on probing only the Li depth profiles averaged over lateral areas of several millimeters square. Here, we report the application of the 3D NDP Li mapping method implemented by combining the traditional NDP and a 2D pinhole scan to demonstrate its applicability to imaging the variation of Li distribution in LiFePO_4 (LFP) electrodes that have undergone different electrochemical cycling histories. Commercial LFP materials were used to construct model electrodes in this study because of their technological significance. Since the initial proposal by Padhi *et al.* in 1997 [25], LFP has become the cathode of choice in many energy storage applications due largely to its safety, low cost, excellent cyclability, and remarkable rate capability [26-29]. The NDP mapping results reveal that the Li concentration is significantly less and spatial distribution much more heterogeneous in the heavily and abusively cycled electrode than in the lightly cycled one.

2. Experimental

Details of electrode fabrication are described in the supporting information. Although the

preparation of specimens mostly followed conventional methods, special arrangement of the anode has been employed in this study. Because NDP is sensitive only to the ^6Li isotope of Li, which has a natural isotope abundance of 7.5 at%, isotope enrichment of LFP was used to greatly improve mapping efficiency. In this work, the LFP electrodes of approximately 25 μm in thickness were initially electrochemically delithiated to remove most of the natural Li and recovered from the first battery assembly, they were subsequently lithiated with ^6Li by charge/discharge cycling against the ^6Li metal as the counter electrode. Two electrodes were prepared, one with a single charge/discharge cycle and the other with 5532 cycles, denoted as LFP1 and LFP5k, respectively. LFP1 is lithiated with ^6Li at 0.1 mA (~ 0.2 C) to 1.0 V, and held at 1.0 V for hours till no electric current flow was measurable before disassembly (Supplemental Fig. S1). LFP5k has been cycled at high rates, primarily at 0.5 mA, between 0 V and 4.2 V, and held at 0 V for hours before the current diminished at the final discharge (Supplemental Fig. S2). In this study we discharge batteries to a lower potential in order to accelerate the degradation of the cathode electrodes for the demonstration of 3D NDP Li mapping. Each ^6Li -enriched LFP electrode was supported on a 127 μm thick Kapton substrate. The assembly was capped with a 7.6 μm Kapton film for mounting in NDP vacuum chamber.

NDP spectra were acquired at the NG1 Cold Neutron Depth Profiling station at the NIST Center for Neutron Research (NCNR) [10, 17], where two high precision stepper motors (730 steps/mm) were used to control the translational motion of specimen [10] with regard to a stationary pinhole mask placed in front of the specimen to define the area and position for lateral mapping, as schematically shown in Fig. 1. The entire specimen was irradiated at a constant

fluence rate of cold neutrons, with wavelengths in the range of 0.4 nm – 2 nm. Both nuclear reaction products, α and ^3H particles, are emitted from the electrode film, although only triton particles are able to pass through the 7.6 μm Kapton cover. Reaction products from within the 1 mm $\times$ 1 mm area facing the mask aperture were permitted to reach the silicon surface barrier detector. While the NDP spectra were recorded every 60 s, the aperture moved across the specimen surface at a step length of 1 mm and the dwell time of 540 s at each position to allow for 9 spectra to be captured at each location. The 9 spectra were later integrated to yield one spectrum for each position. A square area of 7 mm $\times$ 7 mm was scanned and the corresponding 49 spectra analyzed.

3. Results and discussion

Each individual spectrum carries the Li depth information at the corresponding sample location. To illustrate the 1D features of Li distribution, Fig. 2 shows the NDP spectra of both LFP1 (blue curves) and LFP5k (red curves), which were obtained by averaging the spectra of four neighboring 1 mm $\times$ 1 mm locations and smoothed using multiple-channel fast Fourier transform (FFT) filtering. Figure 2a shows the per channel integrated count of ^3H particles, which is proportional to the abundance of ^6Li , as a function of its energy, or its linearly correlated channel number in the multichannel energy analyzer, which yields the depth information. In 1D NDP spectra, the high energy regime (2450 – 2727 keV) shows only background signals, and is highlighted with yellow shade. This corresponds to the thickness of the 7.6 μm Kapton cover film. The immediate adjacent range (1440 – 2450 keV) corresponds to the thickness of the LFP

electrodes. The peaks around 1440 keV, highlighted blue, is due to a slight boron contamination on the pinhole mask; whereas signals at even lower energies are almost entirely dominated by electronic noise inherent from the detection system.

Using the Stopping and Range of Ions in Matter (SRIM) program [30], the energy loss of triton particles during the transport through the electrode and the Kapton film could be calculated to yield the depth of their originating location. By normalizing against a pure ${}^6\text{Li}$ film as a standard, the ${}^3\text{H}$ counts were converted to elemental Li composition x in Li_xFePO_4 ($0 \leq x \leq 1$, here x is the atomic ratio of ${}^6\text{Li}$ to Fe), as shown in Fig. 2b, where the Li depth profiles expand the shaded zones of LFP and Kapton in Fig. 2a. The location of the surface of LFP electrodes, in contact with the separator in electrochemical cycling and facing the barrier detector in measurements, is set to be the origin (surface). A depth of 20 μm for the LFP electrode was plotted, below which variations in the film thickness, errors in the stopping power, and electronic noises make accurate quantification impractical.

A comparison of the two spectra reveals their common features and major differences. Both spectra show a surface Li enrichment followed by a depletion zone, while the concentration difference between the two zones is more pronounced in LFP5k than in LFP1. Two main differences: (1) The Li composition is lower in LFP5k ($x \approx 0.38$, in the depth range of 2.5 μm – 20.0 μm) than in LFP1 ($x \approx 0.65$), even with the former cycled to a deeper discharge. (2) Li is distributed more uniformly in LFP1 than in LFP5k in the depth range of 2.5 μm – 20.0 μm (Fig. 2b), which is the regime of interest and further elucidated in this study by 2D and 3D mapping.

As a typical NDP depth profile gives Li distribution over a single location, averaging the

spectra from 4 locations smears lateral information. To clearly illustrate the variation in lateral distribution of Li in both electrodes, 2D maps of Li composition were constructed for sequential depth increments of 2.5 μm . Figure 3 shows the 2D color maps of each layer at the specified depth, for the entire area of 7 mm $\times$ 7 mm at an aerial resolution of 1 mm for LFP1 (upper row) and LFP5k (lower row) respectively. The same color concentration scale is applied across all Li distribution maps in Fig. 3. As anticipated from 1D profiles, the overall color contrasts distinctly between LFP1 and LFP5k, indicating significant discrepancies in the average Li content between the two electrodes, clearly exceeding the degree of lateral variations of Li in each depth slice of the electrodes.

Importantly, lateral Li heterogeneity exists as shown in the variation of colors according to the scale bar placed to the right of the Fig. 3. Variations in Li content for LFP1 are mostly red and yellow, with $x = 0.65 \pm 0.06$ and Li concentration variation of 9%, while those of LFP5k vary over yellow, green, blue to purple, with $x = 0.38 \pm 0.05$ and Li concentration variation of 13%. The 9% variation in LFP1 is statistically significant and marginally higher than the statistical counting error of *ca.* 7%, the lateral Li variation of 13% in LFP5k, however, is much higher than that of LFP1. This level of heterogeneity is rather prominent in presumably highly uniform commercial LFP electrodes, particularly considering that each pixel is integrated over the Li distributed over a lateral area of 1 mm $\times$ 1 mm and to a depth of 2.5 μm . Furthermore, it is clear from comparing the Li maps near the two surfaces of electrodes (maps 1 & 7) to those in the bulk, the variation of LFP5k is much larger although both the film thickness and initial preparation are identical. Such large lateral variations within each layer and among different

layers reveals very heterogeneous Li distribution in the heavily cycled LFP5k while it is relatively homogeneous in the electrode after only a single cycle of delithiation and lithiation.

The 3D Li maps were constructed by stacking equal thickness layers of 2D maps to display the total sample volume of $7\text{ mm} \times 7\text{ mm} \times 17.5\text{ }\mu\text{m}$ at a voxel resolution of $1\text{ mm} \times 1\text{ mm} \times 2.5\text{ }\mu\text{m}$. To better illustrate the spatial distribution of Li heterogeneity, the 3D maps are shown in Fig. 4 highlighting only the distribution of highest and lowest Li concentration spots in the electrodes while leaving voxels of intermediate composition voids. Threshold values, x_H , are set to define high concentration regions, above which the voxels are marked red for LFP1 and green for LFP5k, respectively; similarly, x_L defined low concentration regions, below which voxels are marked yellow for LFP1 and blue for LFP5k, respectively, while other voxels with composition values in between are not shown for clearer visualization. x_H and x_L are set to maintain the same numbers of high and low regions in the 3D maps. By setting $x_H = 0.70$ and $x_L = 0.60$ in LFP1, while $x_H = 0.43$ and $x_L = 0.34$ in LFP5k, respectively, 60 each of high and low Li regions are labeled out of 343 ($= 7 \times 7 \times 7$) total voxels in each electrode. Note that the threshold concentration values are much lower in LFP5k than in LFP1. Figure 4 shows representative 3D images, as viewed from different perspectives, which were produced by varying the rotation angle, α , and the tilt angle, β . Additional details of the 3D maps as well as rotation animation videos are supplied in the supporting information. The 180° difference in azimuthal angle ($\alpha = 45^\circ, 225^\circ$) allows for observing the opposing front and back sides of Li distribution within the volume of electrode in this imaging study, while two tilt angles, $\beta = \pm 20^\circ$, offer two different views angles. The 3D image data show that the red and yellow spots are more evenly distributed

in LFP1 (Fig. 4a) than in LFP5k (Fig. 4b), whose green and blue spots are more preferentially segregated to the top and bottom layers respectively, implying there is more Li near the electrode surface and less Li deep beneath the surface. Regional segregations also exist in the bulk of the electrode, indicating a more heterogeneous distribution of Li in LFP5k.

The observations of severe Li depletion and rather heterogeneous Li distribution in heavily cycled LFP electrode offer new insights in the behavior and failure of intercalation cathodes. Since the primary cause of the significant capacity loss is due to the inaccessible sites for Li intercalation, as opposed to a scenario of trapped Li in isolated electrode particles, it is more likely that there are losses of transport paths occurring during the discharge. Since LFP5k was cycled between 4.2 and 0 V at higher rates, large amounts of solid electrolyte interface (SEI) layers could form on the surface of LFP particles during deep discharge, partially blocking the paths for Li insertion. The situation is the most severe at the current collector side of the electrode, which is at the forefront of electron injection during discharge. SEI may also cause large over- and under-potentials in charge/discharge, further distorting the local electric field and electrochemical processes, which is possibly related to the large heterogeneity found in LFP5k. Although SEI products generally immobilize Li, loose components and organic ones could be rinsed off during the acetonitrile wash for electrode recovery, they are not present in the NDP specimens. Although we assume that detected signals are mostly due to LFP cathode, details on the influences of process conditions are beyond the scope of this work and will be topics for future studies.

4. Conclusions

In summary, a 3D Li mapping method based on NDP has been applied to imaging Li in battery electrodes by using a 1 mm $\times$ 1 mm aperture 2D pinhole scan. The method has been successfully applied to measuring the spatial distribution of Li in two LiFePO₄ electrode films cycled through electrochemical delithiation/lithiation for 1 and 5532 cycles each. It was shown that the Li concentration is significantly less and spatial distribution much more heterogeneous in the heavily and abusively cycled electrode. The significant capacity decay in LFP5k is discussed in the context of structural changes in electrode materials due to electrochemical processes. The method of 3D Li mapping by NDP will find useful application in future development of battery technology, including material and processes innovation, system optimization, safety analysis, failure diagnosis, and lifetime prediction. To better reach this goal, both spatial resolution and measurement efficiency of the technique should be improved.

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Figure captions:

Fig. 1. Schematics of the NDP set up to rastering a $1\text{ mm} \times 1\text{ mm}$ aperture over the sample surface in 1 mm steps so as to capture the Li depth profile in 3D for the entire sample.

Fig. 2. Typical 1D depth profiles of Li distribution in ^6Li -enriched LiFePO_4 electrodes undergone different cycling histories. (a) The overall NDP spectra vs. both channel and energy. (b) The Li composition vs. depth profiles of $20\text{ }\mu\text{m}$ thick electrodes.

Fig. 3. The 2D maps of Li distribution in two electrodes, (a) LFP1 and (b) LFP5k, at different depth ranges.

Fig. 4. The 3D reconstructions of high and low regions of Li concentration in two electrodes: (a) LFP1, high Li regions in red and low Li regions spots in yellow; (b) LFP5k, high Li regions in green and low Li regions in blue, as viewed from two azimuthal angles, $\alpha = 45^\circ$ and $\alpha = 225^\circ$, and two tilt angles, $\beta = \pm 20^\circ$, respectively.

Fig. 1.

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