Tracking inhomogeneity in high-capacity lithium iron phosphate batteries

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HIGHLIGHTS

- *In-situ* and *operando* profiling of a real-world 8 Ah lithium iron phosphate cell.
- Spatial tracking of inhomogeneity in three dimensions is achieved while discharging.
- Strong correlation between inhomogeneity evolution and cell overpotential is observed.
- Results suggests that particles contribute sequentially in order of connectivity.

GRAPHICAL ABSTRACT
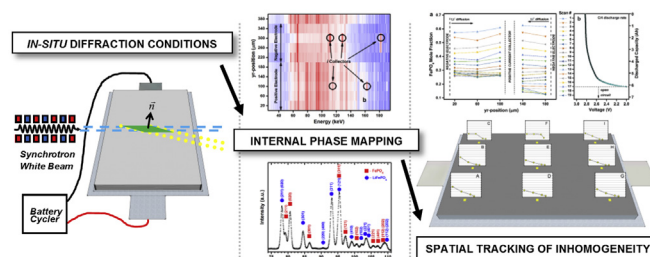
ABSTRACT

Energy-dispersive x-ray diffraction (EDXRD) is one of the few techniques that can internally probe a sealed battery under operating conditions. In this paper, we use EDXRD with ultrahigh energy synchrotron radiation to track inhomogeneity in a cycled high-capacity lithium iron phosphate cell under *in-situ* and operando conditions. A sequence of depth-profile x-ray diffraction spectra are collected with 40 μm resolution as the cell is discharged. Additionally, nine different locations of the cell are tracked independently throughout a second discharge process. In each case, a two-peak reference intensity ratio analysis (RIR) was used on the LiFePO4 311 and the FePO4 020 reflections to estimate the relative phase abundance of the lithiated and non-lithiated phases. The data provide a first-time look at the dynamics of electrochemical inhomogeneity in a real-world battery. We observe a strong correlation between inhomogeneity and overpotential in the galvanic response of the cell. Additionally, the data closely follow the behavior that is predicted by the resistive-reactant model originally proposed by Thomas-Alyea. Despite a non-linear response in the independently measured locations, the behavior of the ensemble is strikingly linear. This suggests that effects of inhomogeneity can be elusive and highlights the power of the EDXRD technique.

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1. Introduction

The commercial introduction of lithium-ion batteries has enabled a worldwide portable-electronics revolution. More recently they are being used in much larger portable devices: hybrid gas/electric and electric vehicles. Lithium-ion batteries offer competitive properties (i.e. energy density, cycle life, and low self-discharge rates) which have proved advantageous for the

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development of portable electronics [1]. However, for successful implementation in electric vehicle applications the current technological state of lithium-ion batteries needs improvement. Specifically, fire susceptibility and limited driving ranges of electric vehicles are pushing researchers and engineers to improve the durability, safety, and energy density of lithium-ion batteries [2].

Lithium iron phosphate ($LiFePO_4$) is an electrode material which offers a high cycle life, excellent thermal stability, and is composed of relatively earth abundant materials [3]. For these reasons, it is welcomed as the next-generation lithium-ion battery for electric vehicles. Structurally, $FePO_6$ octahedra combine with PO_4 tetrahedra to form a crystalline framework which can accommodate lithium intercalation. While the exact nature of lithium intercalation remains elusive, it is generally known lithium diffusion is one-dimensional and the transformation is biphasic, evident in its flat voltage profile [3].

Following its discovery by Padhi et al. 1997, lithium iron phosphate was regarded as a low-power material due to its poor intrinsic electronic and ionic conductivity [4]. Recently however, researchers have found that high-rate performance is possible with a reduction particle size and modification of surface chemistry [5,6]. Synthesizing nano-sized particles can reduce the bulk diffusion distances and adding a conductive surface coating improves intra-particle conductivity. With high-rate capability now achievable, lithium iron phosphate is a prime contender for use in electric vehicle batteries. However, with a theoretical energy density that is 30% less than well-established oxide electrodes (NCA) a formidable challenge for adoption remains.

For electric vehicles, theoretical energy density is still only one factor which influences driving range. A more applicable indicator of driving range would be the effective energy density of an entire battery pack. One strategy to improve effective energy density is to scale up the capacity of the electrochemical cell from which a battery is composed. By a simple calculation done in our lab, the energy density of an 8 Ah polymer pouch cell is 25% greater than that of an 18650 equivalent. Thus, cells produced with higher capacities (up to 100 Ah) could be advantageous to the electric vehicle industry allowing for simpler manufacturing, reduced battery-management overhead, and increased driving ranges.

Challenges still exist for high-capacity lithium ion cells, however. Specifically, the increase in size contributes to the complexity of their inner-working and behavior. Large cells are typically composed of multiple thin layers of current collectors, separators, electrodes, and electrolyte materials. When particulate electrodes exhibit large volume expansions from lithiation, electrochemical shock and fracture can occur [7]. Distributed across large areas and multiple layers, this can cause erratic and unpredictable current pathways which lead to cell inhomogeneity. Inhomogeneity is undesirable because it can cause under-utilization of electrode materials and create local areas of overcharge and overdischarge. This can ultimately reduce effective energy density and compromise cell safety and lifetime.

Past modeling efforts have predicted inhomogeneity in high capacity cells using multi-scale multi-dimensional modeling [8]. Additionally, numerous attempts have also been made to accurately model the phase transformation and voltage behavior for lithium iron phosphate batteries [9–16]. However, such modeling efforts should be met with experimental validation. Different attempts have been made to measure spatial variation and inhomogeneity in lithium ion batteries. Nanda et al. used Raman spectroscopy to map the state of charge of battery electrodes *ex situ* [17]. Liu et al. measured a large distribution of state of charge in a prismatic cell *ex situ* by synchrotron micro-diffraction [18]. Maire et al. provided state of charge mapping using an *in-situ* colorimetry method [19]. Zhang et al. developed a cell with multiple electrode tabs in an

attempt to track *in-situ* current distribution in a lithium ion cell [20]. Within the last year, X-ray absorption spectroscopy measurements carried out by Ouvrard et al. and Katayama et al. have shown inhomogeneous reaction distributions [21,22]. Their results point towards variance in conductive networks as the origin of inhomogeneity observed. However, the measurements aren't made in real-world cells and don't provide resolution required for correlation to the voltage profile of the cell.

In this paper, we use a synchrotron white beam to conduct energy-dispersive x-ray diffraction (EDXRD) experiments in order to observe inhomogeneity in real-world high-capacity cells. EDXRD has proven to be a valuable tool for *in-situ* battery characterization [23–25]. Aided by ultrahigh photon energies, we are able to internally probe large lithium iron phosphate cells and collect diffraction spectra while discharging. By determining the relative amounts of non-lithiated and lithiated phases, we reveal the evolution of inhomogeneity with spatial and temporal resolution.

2. Experimental

2.1. Electrochemical cells

Two 8 Ah lithium iron phosphate polymer cells were chosen for this study. The cells were constructed in a prismatic layout consisting of multiple repeating units of electrodes, current collectors, and separator materials. The positive electrodes were comprised of nano-sized lithium iron phosphate and were treated with a carbonaceous coating. The negative electrodes were composed of graphitic carbon. Both cells were cycled approximately 1500 times with a 2C discharge rate and a 1C charge rate and were rested two days before the experiment.

2.2. Energy-dispersive x-ray diffraction

The energy-dispersive X-ray diffraction experiments were carried out at the superconducting wiggler beamline X17B1 of The National Synchrotron Light Source at Brookhaven National Laboratory in Upton, NY. The beamline provides a spectral flux with high brilliance across a range of energies up to 200 keV. The ultrahigh photon energies specifically allow for deep penetration in to the battery and minimal sample preparation; cells can be probed as-is. The cell was connected to a battery cycler (Arbin), and mounted to the sample stage. A germanium energy detector was fixed at $3°$ from the transmitted beam path. Bragg diffraction was measured in transmission (Laue) geometry, resulting in a fixed volume in space where diffraction occurs. A schematic is provided in Fig. 1 and the details of the beamline have been covered in this journal previously [24].

The incident and detector collimating slits were arranged such to form a gauge volume with dimensions of approximately 3 mm × 3 mm × 40 μm. The height of the gauge volume is commensurate with that of the individual layers in the cell and allows for a proper resolution across the electrochemical interface.

2.3. Stoichiometric determination

In order to determine the relative amounts of $FePO_4$ and $LiFePO_4$ present in the gauge volume, a semi-quantitative peak-fitting routine was employed. The $FePO_4$ (020) and the $LiFePO_4$ (311) reflections were chosen for their high intensities and minimal overlap with other reflections. For each diffraction spectra, the aforementioned peaks, and surrounding peaks, were fit with a Gaussian function and their integrated intensity was determined. The formula used to estimate the weight fraction for each phase is given below: