Neutron depth profiling technique for studying aging in Li-ion batteries

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\textbf{A B S T R A C T}

During operation of a Li-ion cell, lithium diffuses in and out of the solid phase anode and cathode. Measuring the lithium concentration within the electrodes of the cell over its operational life could provide key information for understanding the loss of active lithium and the associated aging mechanisms. Concentration profiles of lithium in a cell are difficult to measure with traditional spectroscopic techniques. Here, neutron depth profiling was used to measure lithium near-surface concentration profiles along the anode and cathode strips in off-the-shelf cylindrical Li-ion batteries as a function of the aging process. A buildup of the surface concentration of lithium was found in graphite anode as well as a general decrease in the intercalation efficiency in lithium iron phosphate cathode material with aging.

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1. Introduction

Demand continues to grow world-wide for environmentally friendly vehicles such as hybrid electric vehicles (HEV), plug-in hybrid electric vehicle (PHEV), and electric vehicles (EV). In part or in whole, each of these vehicles rely on advanced battery technology for clean and transportable energy. Though various battery chemistries such as lead-acid and nickel metal hydride have been commercially used for a period of time, lithium ion battery technology is emerging as the front runner for energy storage systems. Lithium ion batteries deliver high energy and power capacity with minimal maintenance; however, battery performance issues are the focus of much research.

The first lithium ion battery was commercially introduced by Sony in 1990 which had LiCoO\textsubscript{2} as the cathode. Since then there have been several different types of lithium ion batteries based on different cathode materials. These include layered structures such as LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}, LiMn\textsubscript{0.5−x}Ni\textsubscript{x}Co\textsubscript{2}O\textsubscript{4}, Li\textsubscript{1−x}Ni\textsubscript{x}Co\textsubscript{2}O\textsubscript{4}, or spinel structured cathodes such as Li[Mn\textsubscript{1−x}Al\textsubscript{x}]O\textsubscript{2} [1]. However, the more recent olivine structured LiFePO\textsubscript{4} cathode material has shown great potential for applications in EV and PHEV. Apart from being non-toxic and relatively inexpensive, LiFePO\textsubscript{4} has become popular due to its operating potential of 3.4 V and high specific capacity of 160 mAh g\textsuperscript{−1} [2].

In automotive applications, the charging and discharging of the battery is controlled and managed by a battery management system (BMS). The BMS is composed of hardware and software components and is responsible for safe operation of the battery. According to United States Advanced Battery Consortium (USABC), a 42 V battery in a hybrid electric vehicle (HEV) should have a calendar life of 15 years [3]. Electric vehicles (EV) should have a battery system that can last for 10 years [4]. In terms of cycles, 1000 cycles at 80% depth-of-discharge are expected in EV [4], and 300,000 cycles at 50 Wh are expected in a plug-in HEV [5]. Thus, much of the research efforts have been in the area of understanding the aging mechanisms in these batteries.

The capacity (range) and power (performance) capabilities of these batteries decrease when subjected to the charging and discharging cycles in automobiles. This degradation of capacity/power or “aging” is a result of several simultaneous physicochemical processes that occur within the electrode, electrode–electrolyte interface, and within the electrolyte. The aging of these batteries is a very complex phenomenon. Various electrochemical processes, including intercalation of lithium ions into layered graphite anode and cathode materials, as well as mass transport of lithium through the electrolyte, occur simultaneously within the cell. These processes lead to different extent of degradation in materials properties and the subsequent drop in overall performance of batteries. Therefore, it has been scientifically important to track the lithium concentration in the cathode and anode during aging process. The current work pertains to this critical need.

Aging of the LiFePO\textsubscript{4} cathode has been studied by various techniques. Spectroscopy techniques such as energy dispersive X-ray
spectroscopy (EDS) or electron energy loss spectroscopy (EELS) have been used to conduct the elemental analysis of the cathode material. Electron microscopic techniques have been used to analyze phase change, structural changes, etc. Scanning probe microscopy such as conductive atomic force microscopy (AFM) and surface resistance microscopy have been used for analysis of surface electrical properties [6,7]. These techniques deliver some useful information about the changes in the cathode, but they fail to address the issue of lithium transport or lithium concentration within the cathode. The EDS technique is commonly used to identify the atomic percent of the elements in the component. The EDS detectors are very sensitive to impurities. To avoid repeated exposure of the detectors to atmosphere, the detectors are maintained under separate vacuum and separated from the column vacuum in the electron microscope. The thin beryllium window on the EDS detector absorbs low energy X-rays and thus prevents the use of EDS in the detection of elements with an atomic number less than five. Therefore, EDS also fails to detect Li in the component.

Ziegler et al. [15] for first time used the nuclear reaction experiment to determine the concentration of boron impurity in silicon wafers. The sample was bombarded with a well-collimated beam of low energy neutrons in vacuum, and the emitted energized particles were analyzed using a charged-particle spectroscopy for the concentration profile of the boron in the sample. Later, Downing et al. [8] coined the term neutron depth profiling (NDP) for this technique. Since then there have been several applications of this technique to other neutron sensitive light-weight isotopes, some of which are listed by Downing et al. [9]. Biersack and Fink [30] were first to study the implantation of lithium in semiconductors using NDP. Later on Krings et al. [10] studied lithium diffusion in electrochemical WO3 films using NDP. They compared the secondary ion mass spectrometry (SIMS), elastic recoil detection (ERD), and NDP techniques while profiling the lithium concentration along the depth of lithium intercalated thin electrochemical WO3 films. They concluded that the NDP technique has a very good depth resolution with high sensitivity and proves to be very useful over the other techniques because of its non-destructiveness. Lamaze et al. [11] have demonstrated the use of NDP in two thin film battery materials. They profiled the lithium concentration in ion beam assisted deposition (IBAD) thin lithium phosphorus oxynitride films and thin lithium cobalt oxide films. The main advantage was again the non-destructive nature of the NDP technique. The study was limited to the deposited thin films rather than electrodes extracted from actual lithium ion cell.

Most recently, Whitney et al. [12] used NDP to profile the lithium concentration in a cathode of the Li-ion lab cell and an anode of the off-the-shelf Li-ion cells. The lithium transportation was studied for storage of cells at different temperatures and cycling of the cells at different rates. They demonstrated a method to determine the thickness of the solid electrolyte interface on a graphite anode in a LiFePO4 cell when stored for different lengths of time under different temperatures. They also profiled the lithium concentration in LiFePO4 and LiNi1/3Mn1/3Co1/3O2 cathodes after cycling for only 100 cycles. This helped to understand the lithium distribution in initial cycles but did not address the issue of lithium transportation during the end of life of the cells.

In this paper, the NDP technique is applied to study the aging of a commercial off-the-shelf LiFePO4 based Li-ion cell during the aging process, including the end-of-life conditions, which has remained as a challenge until now. A detailed analysis of the lithium concentration in the anode and cathode is carried out. The lithium concentration profiles in the anode and cathode samples unaged and aged at different rates along the depth as well as concentration gradients as a function of cycling current are determined. Further, it is investigated whether the lithium buildup on the surface of the anode or cathode occurred as the battery aged due to cycling.

2. Experimental details

2.1. Sample preparation

Commercial lithium ion cells used in these experiments have a graphite anode and a cathode comprising of LiFePO4 nanoparticles (40 nm–50 nm). Graphite is bonded onto a copper substrate, and layers of LiFePO4 nanoparticles are bonded onto an aluminum substrate using a polyvinylidene difluoride (PVDF) binder. The anode and cathode strips, with a separator in between, are rolled and then packed into a can to form a cylindrical cell. The electrolyte used in this cell is a lithium hexafluorophosphate (LiPF6) salt in 1:1 ethylene carbonate and dimethyl carbonate. The cell has an operating voltage of 3.3 V and a nominal discharge capacity of 2.3 Ah. LiFePO4 has poor electronic conductivity (σ = 2 × 10−9 S cm−1) [13]. To improve the conductivity, the nanoparticles are coated with carbon [14]. Table 1 describes the condition of the cells used in this study. The effect of charging or discharging current rate (C-rate) on the lithium concentration was studied on cells #C1, C3, and C4 cycled from 0% to 10% state of charge (SOC) with a C-rate of 1C, 3C, and 4C, respectively (1C-rate = 2.3 Ah). Two cells were cycled with higher C-rates and at higher SOC to study the effect of the SOC on the lithium concentration profiles. Cell C6 was cycled from 60% to 70% SOC with 6C rate. Cell C16 was cycled with the highest C-rate of 16C from 45% to 55% SOC. All the cells were cycled at 45°C. A cell that underwent only one complete charge–discharge cycle was established as the baseline cell in our studies (C0). The cycling of the cells was terminated when the cells reached ~80% of their rated capacity. This protocol was found to be consistent with the automotive industry standard, which considers a cell to be dead when its capacity drops below 80% of the original rating [5].

The cells are completely discharged after they have reached the ~80% of their rated capacity. The cylindrical cell was then opened in a glove box filled with argon atmosphere. The oxygen level was maintained at ~88 ppm and the dew point was ~34°C. The cell was unrolled, and the long anode and cathode strips were separated. Each electrode strip was then divided into six sections as shown in Fig. 1. Section #1 is near the outer circumference and section #6 is near the center of the cylindrical cell. The NDP measurements were performed on each section of all cells, but for clarity the results of only section #1, 3 and 5 are plotted in the figures below in the paper.

2.2. NDP setup and technique

NDP is a non-destructive analytical technique based on the interaction of an incident beam of neutrons with certain elements, such as lithium, throughout the sample. The cold neutrons are delivered through a neutron guide to the NDP facility. In this work, the “cold” neutrons refer to neutrons with energy less than 5 meV. Since cold neutrons have extremely low energy and momentum, there is no center-of-mass motion in the neutron-lithium reac-

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aging condition</th>
<th>Residual capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>New – no aging</td>
<td>100%</td>
</tr>
<tr>
<td>C1</td>
<td>1C, 0–10% SOC, 45°C</td>
<td>~80%</td>
</tr>
<tr>
<td>C3</td>
<td>3C, 0–10% SOC, 45°C</td>
<td>~80%</td>
</tr>
<tr>
<td>C4</td>
<td>4C, 0–10% SOC, 45°C</td>
<td>~80%</td>
</tr>
<tr>
<td>C6</td>
<td>6C, 60–70% SOC, 45°C</td>
<td>~80%</td>
</tr>
<tr>
<td>C16</td>
<td>16C, 45–55% SOC, 45°C</td>
<td>~80%</td>
</tr>
</tbody>
</table>

SOC, state of charge.
The electrode strip taken from each cell is physically divided into six sections. Section #1 originated farthest from the core and section #6 is nearest to the core of the cell. Furthermore, the neutron event rate is insufficient to cause significant temperature rise in the sample nor is there significant radiation damage to the sample during the measurement period. All NDP experiments were conducted at the NIST Center for Neutron Research (NCNR). A schematic of the NDP facility is shown in Fig. 2.

The sample is attached to an aluminum disk (Figs. 1 and 2) which is held vertically at the center of a vacuum chamber by the grooves provided on the sample mount. The sample mount is oriented such that the sample faces the surface-barrier type charged particle detector. The detector has an active area of 150 mm² and is placed slightly more than 10 cm from the neutron beam-spot on the sample. A ~0.8 cm² area of the sample is illuminated by the cold neutron beam entering the vacuum chamber. Upon the absorption of the neutron by the elemental atom in the sample, monoenergetically charged alpha and triton particles are emitted and travel diametrically opposite from the site of the reaction. More specifically, when the neutron reacts with the ⁶Li atom in this sample, monoenergetically charged alpha (⁴He) and triton (³H) particles emitted are shown in the reaction below:

\[ ^{6}\text{Li} + n \rightarrow ^{4}\text{He}(2055 \text{ keV}) + ^{3}\text{H}(2727 \text{ keV}) \]  

The energy of the ⁴He and ³H particles at the reaction site is known to be at 2055 keV and 2727 keV, respectively [9]. These heavy charged particles lose energy via a stochastic collision with electrons along the path traveling outwards. Both, the count rate and the residual energy are simultaneously measured from all depths for the particle species emerging in the direction of the detector (Fig. 2). The charged particles do not lose any energy after leaving the surface of the sample traveling to the detectors, since the sample chamber is maintained at a vacuum less than 1.33 mPa (10⁻⁶ Torr). Calibration performed prior to the experiment determined the full width half maximum (FWHM) energy resolution of 18 keV for the charged particle detector. The samples were exposed to the neutron beam for various time lengths ranging between 3 and 4h. The exposure time was not fixed so the data was normalized with respect to the run time, but the samples were exposed long enough so that the statistical error in counting of the ⁴He or ³H particles is no higher than 3%.

The reaction center of mass is coincident with the site of the lithium atom. Thus the ⁴He and ³H particles originate from the same location as that of the original lithium atom, and their respective energies are directly related to the location of the lithium atom in the sample. The energy loss of the charged particle per unit length traveled through the sample is given by the stopping power function of the sample. Mathematically, to the first-order approximation, the depth is related to the stopping power by Bragg’s law given as:

\[ x = \int_{E(x)}^{E_0} \frac{1}{S(E)} \, dE \]  

Here \( x \) is the path length traveled by the particle through the material, \( E_0 \) is the initial energy of the particle, \( E(x) \) is the energy of the particle emerging from the surface, and \( S(E) \) is the stopping power of the sample material [15]. The Stopping and Range of Ions in Matter (SRIM) code developed by Ziegler et al. [16] is then used to obtain the stopping power of the LiFePO₄ cathode and the graphite anode and assign the residual energies of the charged particle to the corresponding depth in the sample. The concentration of ⁶Li within the sample is determined by comparing the count rate observed from the sample with that of a well characterized boron concentration standard, labeled as N6 [28]. Since the natural abundance of ⁶Li...
6Li in the sample is only 7.5%, the total Li elemental concentration is obtained by dividing the determined 6Li concentration by 0.075.

3. Results and discussion

The energy spectrum of the 2727 keV 3H particle is used here because of its two advantages over the corresponding energy spectrum of the 2055 keV 4He particle. First, since the 3H particle has higher energy and less mass, the concentration profiles can be obtained to greater depth in the sample. Second, 3H energy spectrum is not overlapped by the 4He energy spectrum, but the 4He energy spectrum is interfered with by the 3H energy spectrum at lower energies, i.e., by the charged particles generated from deeper below the sample surface.

Fig. 3 shows the lithium concentration profile in the anode and cathode of the various cells aged with different C-rates. The lithium profile obtained from cell C0 is established as the baseline for comparison. In the left column the lithium concentration profiles of the anode can be seen changing from section #1 to section #5 at the same C-rate. The surface concentration increases across the different cells with the C-rate. The right column shows the lithium concentration profile in the cathode. The profiles remain identical from sections 1 to 5 at the same C-rate, but the slope of the profile decreases with increasing C-rate.

Fig. 4 shows the effect of the SOC combined with the C-rate on the lithium concentration profile. Fig. a shows the lithium concentration profile in the cell cycled between 60% and 70% SOC with ~6C-rate (C6) for sections #1, 3, and 5. The lithium concentration profile in cell C4 (same as in Fig. 3) is shown again in this figure for comparison. In C6, even though the C-rate is high, the amount of lithium buildup near the surface of the anode is less as compared to C4. The prominent change of lithium concentration profiles in the anode from section #1 to section #5 observed in C4 is also absent in C6 except for minor deviations near the sub-surface. Similar to C4, the lithium concentration profiles in sections #1, 3, and 5 of cell C6 are identical to each other. However, the lithium concentration profile for C6 has dropped below the concentration profile in C4. Thus, the overall lithium concentration in the cathode has dropped significantly in C6 as compared to C4. Thus at a higher SOC and moderate C-rate, the lithium buildup on the surface of the anode is contained, but lithium is lost from the host cathode material. In Fig. b the lithium concentration profile in section #5 of C16 is compared with C0. In this case cell C16 is cycled between 45% and 55% with a very high C-rate of 16C. It should be noted that cells C0 and C16 in this data were chosen from a different batch than the earlier cells. The basic chemistry was the same, but the initial lithium concentration in the cathode was much higher in these cells. The lithium buildup on the surface of the anode was very high in C16 compared to any other cell in this study. The concentration in the anode dropped across its thickness with a steep slope. The lithium concentration profile in the cathodes of cells C0 and C16 are identical, but the concentration of lithium in the cathode was significantly lower than in C0. Thus, at moderate SOC but very high C-rate the process of lithium buildup on the surface of the anode is enhanced while there is significant loss of lithium from the host cathode. These results suggest that a cell operating at high SOC and moderate C-rate has the least amount of lithium build up on the anode surface, and also the least amount of lithium is lost from the host cathode.

Fig. 5 shows the lithium concentration profiles obtained on section #3 of cell C0 and C6 at various locations within the same section. The aim here was to identify any change in the lithium concentration profiles measured at spots away from the center of the given section. The lithium concentration profiles in the anode shown in the left column of Fig. 5 are similar for both cells at various locations on section #3. This indicates that the lithium concentration in the anode does not vary along the height of the anode. The right column shows the lithium concentration profile in the cathode from both cells. The profiles for C0 measured at various locations on section #3 are identical, but the profile measured at the center spot on the front side has a higher surface concentration and shows a higher gradient along the thickness than at any other location on the section #3. The profiles for C6 measured at various locations on section #3 are identical. Since the intensity and change in the lithium concentration in the unaged cell (C0) were greater at the center of the section, the measurements were taken at the center of each section throughout this study.

As expected for a completely discharged unaged cell (C0) (Fig. 3), the lithium concentration in the anode is significantly lower with little buildup of lithium at the surface, while most of the lithium is concentrated in the cathode. The lithium concentration profiles in the anode show higher surface concentration as the C-rate increases. The lithium concentration is at maximum near the surface, and it decays exponentially with the depth (thickness) of the sample. The lithium buildup on the anode surface from a cell cycled at higher SOC is less but increases with increasing C-rate. The lithium concentration drops in the cathode with higher SOC and higher C-rate. The lithium concentration profiles in the cathode show a uniform gradient, but the concentration decreases with increasing C-rate.

The analysis of the surface lithium concentration in the anode is shown in Fig. 6. As seen in Fig. 6a the surface lithium concentration is nearly constant over all the sections for C0 and C1. In the case of C3 and C4 the surface lithium concentration increases from section #1 to section #5. Thus the buildup of lithium on the surface of the anode is greater towards the core of the cylindrical cell than against the outer edge. For example, in the case of cell C4 where the highest change is observed, the concentration increases from 1.36 × 10^20 to 3.74 × 10^20 atoms/cm^2 from edge to core. In Fig. 6b the effect of C-rate on the lithium concentration gradient in anode is shown. The lithium concentration gradient increases with the C-rate. The lithium concentration gradient is very small in the case of cells C0 and C1 and is very prominent in the case of cells C3 and C4. The lithium concentration gradient in all cells exists only for a certain depth from the surface of the anode. The depth up to which the lithium concentration gradient exists in the anode also increases with the C-rate. In the case of cell C4 the lithium concentration gradient exists up to ~1 μm in the anode. Thus with increasing C-rate not only does the lithium buildup on the surface increase, but the lithium build up in the sub-surface area also increases.

It is well known that a solid electrolyte layer (SEI) composed of the decomposition products of the electrolyte salt and the solvent is formed on the surface of the anode [17]. The thickness of the SEI is usually of the order of tens of nanometers [18,19]. This thickness of the SEI on a given type of anode varies depending on the electrolyte components, mode of cycling, overpotential, temperature, etc. [20–23]. The lithium concentration profiles for the anode presented here not only indicate higher lithium content in the SEI layer at higher C-rate, but also show that the lithium concentration in the SEI layer is changing from the outer edge to the core of the cylindrical cell aged at a certain C-rate. This has never been reported before in literature. This study reveals that the anode–electrolyte interphase cannot be assumed to be alike over the length of the anode in a cylindrical cell as is the common practice adapted in Li-ion cell modeling. The analysis of the surface lithium concentration was also conducted and is presented in Fig. 7. A buildup of lithium on the surface as seen in the anode is not observed in cathode samples from different cells. Since there is no buildup it is certain that there is no lithium plating occurring at the cathode surface. The initial expectation was a decrease in the lithium concentration in the aged sample as compared to the unaged sample.
Fig. 3. Effect of C-rate on the lithium concentration in anode and cathode. The profiles were measured in all six sections from C0, C1, C3, and C4; only profiles over section 1, 3 and 5 are shown here. Based on the Li concentration profile in the anode, the lithium tends to build up at the surface of the anode samples aged with higher C-rates, whereas the lithium concentration drops along the thickness of the cathode anode samples. The SOC varies from 0 to 10%.
The decrease in the lithium concentration in the case of cells C1, C3, and C4 (Fig. 3) is not very prominent, but the results in Fig. 4 are in good agreement with this hypothesis. Therefore, there is a critical C-rate beyond which the drop in the lithium concentration from the cathode is noticeable. In Fig. 7, the analysis of the lithium concentration gradient along the depth of the cathode is shown for section #3 of different cells. The lithium concentration gradient observed on a particular section decreases exponentially with the C-rate, as shown by the curve in Fig. 7. For example, in the case of cells C0 and C4 the gradients are $-1.63 \times 10^{18}$ atoms/cm$^3$/μm and $-0.46 \times 10^{18}$ atoms/cm$^3$/μm. For a higher C-rate the concentration gradient is lower, indicating that the flux available for diffusion of lithium into the cathode particles is decreasing. Thus the further cycling of the cells at still higher C-rate will be strongly affected. Since the concentration gradient has a negative slope, it indicates that the lithium diffusion within the LiFePO$_4$ is restricted as the diffusion front moves towards the current collector. No fluctuations were observed in the concentration profile as were observed by Whitney et al. [12]. Thus there is no structural breakdown of the cathode material, unlike that concluded by Whitney et al. [12].

The decrease in the lithium concentration can be explained by a change in the particle size. In previous studies by Nagpure et al. [6,24,7] the effect of LiFePO$_4$ nanoparticles coarsening was reported on the thermal diffusivity and electrical properties. The effects of...
coarsening of the LiFePO$_4$ nanoparticles by sintering were also reported. The sintering of oxide particles usually takes place at high temperatures, but in these nanoparticles, the onset of sintering at relatively low temperatures may be attributed to the high surface energy associated with the nanosize of the LiFePO$_4$ particles. Due to sintering of the nanoparticles, the effective surface area per unit volume decreases, and correspondingly the porosity of the cathode decreases [25]. Also due to the coarsening of the nanoparticles, the diffusion length for the lithium increases within each particle. As a result, the net uptake of lithium during the discharging processes is low. During each charge cycle lithium diffuses out of the LiFePO$_4$, and phase change occurs from LiFePO$_4$ to FePO$_4$. In the discharge cycle the lithium diffuses back in the host FePO$_4$ particle, and the phase changes from FePO$_4$ to LiFePO$_4$. During the early life of the battery the phase change from LiFePO$_4$ to FePO$_4$ and back to LiFePO$_4$ might be complete, but as the particle size increases due to coarsening, the diffusion length changes, and this will affect the phase change. The incomplete phase change continues to occur in subsequent cycles while the particle size tends to increase. Thus the lithium retaining capacity of the particle drops in each subsequent cycle. The loss of active lithium in the cathode is directly related to the drop in capacity of the battery while the increase in the particle size and the subsequent increase in the diffusion length are directly related to the rate capabilities of the battery.

To summarize, based on the results of this study, a schematic of the concentration profiles during the charging/discharging cycle and the concentration profile at the end of life is presented in Fig. 8.

During the assembly of the cell the cathode is rich in lithium, and the graphite anode is without any lithium (Fig. 8a). As the cell is cycled, the phase of the cathode changes from LiFePO$_4$ to FePO$_4$ (Fig. 8b). According to Fuller et al. [26] the concentration profile of lithium in the solid electrodes and the electrolyte is given by:

$$\varepsilon \frac{\partial c_e}{\partial t} = D \frac{\partial^2 c_e}{\partial x^2} + aj(1 - t^+)$$

where $\varepsilon$ is the volume fraction of the phase, $c_e$ is the concentration, $D$ is the diffusion coefficient, $a$ is the specific area of the electrode, $j$ is the reaction rate, $t^+$ is the transference number of Li, and $x$ is the dis-
Fig. 6. (a) Surface lithium concentration of the anode samples taken from cells aged with different C-rate. The surface concentration increases linearly with C-rate. The surface concentration also increases from section #1 to #5 within a cell. (b) Lithium concentration gradient in section #3 of the anode samples taken from cells aged with different C-rate. The concentration gradient increases with C-rate up to a certain depth of the anode. The depth at which concentration gradient disappears increases with C-rate.

Fig. 7. Lithium concentration gradient in section #3 of the cathode samples taken from cells aged with different C-rate. The concentration gradient decreases with C-rate.

Fig. 8. Schematic for the buildup of lithium concentration at the anode surface and simultaneous depletion of lithium concentration in the cathode at the end of life of the cell: (a) start of life, (b) charge/discharge cycle and (c) end of life.

Based on this equation, the concentration gradient is dependent on the diffusion coefficient and reaction rate. These parameters differ for the cathode and anode material.

Fig. 8c shows the schematic of the concentration profiles in the anode and cathode at the end of life. As suggested by Andersson and Thomas [27], during charging/discharging of the cell, trapped, isolated zones of inactive LiFePO₄ are formed resulting in incomplete phase transformation and loss of the active lithium. On discharging of the cell, the lithium from the anode re-enters the major volume of the FePO₄ cathode, and the cathode phase changes to LiFePO₄. During the cycling process the particles appear to coarsen as suggested earlier. The increased size of the particle increases the diffusion resistance for the lithium ions within the LiFePO₄ cathode. Thus the cathode, instead of reaching the LiFePO₄ phase, can only change to Li₁₋ₓFePO₄ phase. The limiting diffusion within the cathode limits the diffusion of the lithium ions from the anode surface and the electrolyte. As the diffusion within the electrolyte solution and the solid phase graphite remains constant, the lithium starts to build up on the surface of the anode. The lithium build up would increase
in each subsequent cycle, consuming the active lithium and leading to the loss of capacity.

The schematic in Fig. 8 is a simple description of the lithium concentration profile during charging/discharging of cells and at the end of life. The schematic needs to be modified by considering the concentration of Li in the electrolyte solution. Only then can the mass balance equation be applied to the schematic, and the net loss of the active Li can be calculated. The schematic also does not help in identifying whether the aging is triggered by inefficiency of lithium ion diffusion in cathode or the coarsening of the cathode. However, the data presented here provides quantitative measure of the lithium concentration profiles in the anode and cathode, which will prove instrumental in calibration of the Li-ion cell models.

4. Conclusions

The NDP technique was successfully applied to the study of the aging of LiFePO$_4$ based lithium-ion batteries. The technique is shown to be efficient in determining the Li concentration to a useful depth of the electrode. Individual cells were aged at different rates to different state of charge. The Li concentration profile across the electrodes of the cells at the end of life is affected by the C-rate of the charge/discharge cycle of the battery. The Li concentration profile is also affected by the state of charge of the cell. The Li concentration profile changes along the length of the electrode from outer edge to the core of the cylindrical cell, but it remains constant along the height of the electrode. In the case of anode, the lithium concentration profile decays exponentially along the thickness of the anode. The Li builds up on the surface of the anode, and the buildup rate increases along the length of the anode and also with the C-rate. This buildup below the surface extends to higher depth in cells cycled at higher C-rate. There is no buildup of lithium near the cathode surface. Beyond a certain critical C-rate the lithium concentration drops with increasing C-rate, and it has a constant gradient along the depth of the cathode. The gradient of the lithium concentration profile in the cathode decreases with increasing C-rate. While the coarsening of the LiFePO$_4$ particles limits the diffusion of the lithium in the cathode, the surface concentration of the lithium on the anode increases with the C-rate. The quantitative measure of the lithium profiles for anode and cathode presented here will prove instrumental in calibrating the diffusion models of the Li-ion cells.

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