Real-time investigation of the structural evolution of electrodes in a commercial lithium-ion battery containing a V-added LiFePO4 cathode using *in-situ* neutron powder diffraction

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**Abstract**

*In-situ* neutron powder diffraction was employed to investigate the structural evolution of the electrode materials in a commercial lithium-ion battery used for electric buses in Taiwan. The battery, containing a vanadium-added LiFePO4 cathode, does not exhibit a delayed phase transition between LiFePO4 (triphylite) and FePO4 (heterosite) suggesting that the delayed phase transition can be suppressed through the use of vanadium-added LiFePO4 cathodes, which also enhances the capacity and prolongs the cycle life of these batteries. Furthermore, we characterize the readily reversible structural change of the anode (Li$_x$C$_6$ where 0 $\leq$ x $\leq$ 1) and correlate this to battery voltage.

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**Highlights**

- *In-situ* neutron powder diffraction was used to study a commercial lithium ion battery.
- The phenomenon of delayed phase transition was not observed in vanadium-added LiFePO4.
- The structural changes of lithium-intercalated graphite are reported.

**Graphical Abstract**

**1. Introduction**

Phase transitions of electrode materials occur as Li ions are inserted and extracted from both the cathode and the anode within a lithium-ion battery (LIB) during charging and discharging.
Previous work shows that an understanding of the phase transitions [1–4] is crucial to progressing research aimed at prolonging LIB cycle life and enhancing the LIB rate-capability. Currently, most commercial electrode materials are based on layered rock-salt type crystal structures, composed of Li and transition metal oxides, such as LiMnO2, LiCoO2, ... etc. for cathodes [5], and graphitic carbon or LiTiO2 for anodes [6]. For application in electric vehicles [7,8], the olivine-type LiFePO4 (LFP) cathode-based LIB is the most promising commercial battery. This is because LFP shows superior safety characteristics relative to other cathode materials. In this work, we study the phase changes of the cathode and the anode of a commercial battery used in electric buses. The cathode material is based on LFP and the anode is made of graphite. Since we are investigating a LIB with a thickness greater than 8 mm which includes several layers of cathodes, anodes, separators, and interconnects, X-rays cannot easily penetrate the LIB pack. Additionally, X-rays are also relatively insensitive to the low Z elements such as carbon and lithium. Therefore, in this study we take an unmodified bus battery and probe the structural evolution of the electrode materials during conventional battery use by in-situ neutron powder diffraction (NPD).

For a LFP battery, Padhi et al. reported a reversible theoretical specific capacity of 170 mAh g−1 [9] and a flat potential plateau at 3.4 V versus Li/Li+. However, the rate capability is restricted by the intrinsically low electronic conductivity and poor ionic transport properties exhibited by pristine LFP. In order to achieve better performance for electric bus applications, the electrochemical properties need to be improved, especially at the higher C-rates (>5 C). Supervalent-cation addition in the LFP cathode material is a viable method to improve the performance of a LFP cathode [10–13]. Vanadium has been shown to readily substitute into LFP [14,15]. Evidence of vanadium enhanced capacity in LIBs was found by Omenya et al. [16], however, this approach features the addition of relatively high amounts of vanadium and their results show no phase segregation. A distinct peak shift in the X-ray diffraction of the V-added LiFePO4, relative to pure LiFePO4, was also noted. In the present work, we employ a different fabrication process (large-scale manufacturing to optimize performance and minimize cost), and obtain slightly different results, particularly regarding the small amount of V-addition required to improve commercial performance. In this work, the cathode material is vanadium-added LFP and is denoted LFPV. For this system, previous work [17] showed that the capacity and conductivity of LFPV is improved relative to the pristine LFP by 14% and by a factor of 40, respectively. Reliable and reproducible capacity, including relatively small capacity changes at high current, with continuous cycling is also demonstrated, and a less than 10% capacity reduction upon cycling at 20 C relative to 0.1 C. These results are seemingly different to other reports [18–21]. Therefore, a detailed time-dependent study of the LFPV cathode material is carried out to provide further insight into the consequences of the vanadium addition. In particular, a non-destructive real-time study of the relationship between the electrode’s structural response and the battery performance in a full-scale commercial LIB is required and directly relevant to practical applications.

Previous X-ray-based reports [2,22,23], found evidence of a delayed phase transition, which is a phenomenon related to the non-synchronization between the phase evolution (phase fraction) and the percentage of Li-ions transferred during electrochemical cycles. For example, the phase fractions of LFP (triphylite) and FP (heterosite) under low charging and discharging currents are expected to undergo a linearly-varying relation at room temperature. However, the phase fractions lag behind the amount of Li-ions inserted or extracted, as calculated electrochemically. For practical applications, an understanding of the mechanism of the delayed phase transition in LFPV as a function of the battery state-of-charge is needed. The delayed phase transition is important because it may be the key to understanding the cycling life-time of LIBs, especially at high C-rates.

On the anode side, although new emerging materials are being developed [6], graphite is still the most popular commercial LIB material, because of its low cost and high capacity [24]. However, the graphite anode still features several problems, such as the formation of solid electrolyte interface (SEI) layers [25]. These problems cause irreversible capacity loss and poor cycling life [26]. An in-situ study of the phase evolution of the anode material during electrochemical cycling is important to provide a complete picture of the Li+ transfer that occurs during battery use.

2. Experimental

The commercial LIB featuring a nominal capacity of 10 Ah with dimensions, 8.2 mm thick × 128 mm wide × 155 mm high, were obtained from Advanced Lithium Electrochemistry Co. Ltd. (ALEEES), Taiwan. The battery consists of a graphite anode, LiPF6 containing electrolyte, and a carbon coated LFPV cathode. The information provided by the manufacturer states 1% vanadium is added to form LFPV, with the cathode made using a mixture of LFPV and polyvinyl difluoride (PVDF) binder coated onto aluminum foil and containing 75.83 g of the active material. The graphite anode paste is coated onto copper foil with an active material mass of 40.45 g. Copper and aluminum act as current collectors. The electrolyte consists of LiPF6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The in-situ neutron powder diffraction (NPD) experiment was performed on Wombat, the high-intensity powder diffractometer at the OPAL reactor facility in the Australian Nuclear Science and Technology Organisation (ANSTO) [27]. The NPD patterns were measured using a wavelength of 2.4086 Å which was determined using the NIST Al₂O₃ SRM 676 standard. Similar in-situ experiments have been conducted on this instrument in the past [28–33]. Here, we use a relatively large battery for these experiments and the neutron beam only impinges on 40 × 20 mm of the whole battery. In order to collect the NPD patterns, the neutron beam was aligned centrally with respect to the height of the battery and one edge of the battery was exposed to the neutron beam. The angle between the battery and incoming neutron beam was adjusted to maximize the signal from the electrodes. During the data collection, the battery was operated between 2.0 and 3.8 V at a constant current (CC) of 1 A which corresponds to 0.1 C. NPD patterns were collected at room temperature in the 2θ range from 15° to 135° with an exposure time of 5 min per pattern. NPD data is collected using Wombat’s continuous 2D detector and each pattern is normalized with respect to incident beam intensity. Single peak fits were undertaken using the Large Array Manipulation Program (LAMP) [34] with a Gaussian peak-shape and an adjustable flat background.

3. Results and discussion

Fig. 1 shows the in-situ 3-dimensional NPD patterns of the as-made LIB during the 1st to 4th charging and discharging cycles between 2.0 and 3.8 V at 0.1 C. The vertical axis going into the page in Fig. 1(a) is time, where each pattern represents 5 min. The time progression correlates to the charging and discharging cycles as shown in Fig. 1(b). This battery was found to have a specific capacity of about 11.3 Ah. From Fig. 1(a), the structural transformation between triphylite and heterosite at the cathode can be observed and the lattice contraction and expansion as a result of lithium fluctuations in LiₓC₆ at the anode can be seen via the 002 graphite peak at 2θ ~ 42°. Each NPD pattern in Fig. 1(a) can be represented as shown...
in Fig. 2. Although the background in the NPD pattern is high due to the use of hydrogenated electrolyte, the signal-to-noise ratio is sufficient for meaningful data interpretation and analysis. In addition, since the sample geometry is non-annular, the differences in neutron path-lengths may affect the background in the NPD pattern. We discuss our results from the diffraction data for the anode and cathode in separate sections below.

3.1. Anode

Lithium ions are inserted into and extracted from the graphite lattice during the charging and discharging processes, respectively. Fig. 3 shows the electrochemical response of the battery along with the identified charge products: Dilute stage I, stage VI (whose composition is not well defined), stage III (LiC₁₂₄), liquid-type stage II (LiC₁₈), stage II (LiC₁₂), and stage I (LiC₆) [35].

With increasing Li concentration, the LiC₆ intercalation occurs in stages, where the stage number n contains n empty layers between each Li-filled layer [36]. For a range of x in LiₓC₆ from 0 to 1, the theoretical calculation of the capacity of graphite is 15.05 Ah (372 mAh g⁻¹ [37] × 40.45 g), which is greater than the specific capacity of 11.3 Ah that we obtained during cycling. This is related to the ratio of active cathode and anode materials and the amount of lithium that can be extracted/inserted from the electrodes at the C-rate used. In-situ NPD data also illustrate this, as not all the LiₓC₆ anode is converted to the fully lithiated LiC₆ compound during charge. Approximately 75% lithium insertion/extraction occurs in the LiC₆ anode. In order to approximate the x values in LiₓC₆ we assume x = 0 at 0 Ah and x = 1 at 15.05 Ah with the x values increasing linearly with respect to electrochemical cycling process. Fig. 4 shows the evolution of the in-situ NPD patterns during charging (Fig. 4(a)) and discharging (Fig. 4(b)). The numbers marked beside the NPD diffraction patterns are the pattern numbers (time evolution). The diffraction pattern marked “1” is collected at the beginning of charging process with the numbers increasing as charging proceeds. Changes of the LiₓC₆ (0 < x < 1) 002 and LiC₆ 001 reflections were observed. At the initial stage of charging, lithium ions occupy the available sites between the graphite layers, dilute stage I, causing the 2θ value of the 002 reflection to shift to slightly lower angles (larger d-spacings). During charging, the anode material is a compound of nominal composition LiC₁₈, the liquid-type stage II product, whose 002 reflection shifts to approach 2θ = 40.2° at x ~ 0.32 in LiₓC₆. At this
point, lithium atoms feature no long-range ordering within the layers [38]. After ~50% charging, LiC12 (Li0.5C6) forms with the lithium arranging in a highly ordered hexagonal structure. As x (in Li1-xC6) increases to ~0.61, the stage I (LiC6) 001 reflection is observed and the stage II (LiC12) 002 reflection does not shift continuously in 2θ value toward lower angles. Instead, the reflection abruptly transitions or “jumps” from a position corresponding to LiC12 to one corresponding to LiC6, indicating a two-phase reaction. As x in Li1-xC6 increases from 0.61 to the end of charge, the intensity of the LiC12 002 reflection decreases while the intensity of the LiC6 001 reflection increases, as similar to previous reports [29,39]. The LiC6 phase is approximately 26.3% of the final anode composition at the charged state.

Fig. 4(b) shows that the changes in the diffraction peaks vary in the opposite direction as the battery is discharged which corresponds to the average interlayer spacing shifting back toward the initial graphite composition of the anode. This result at the anode shows a reversible process during electrochemical cycling.

3.2. Cathode

Typical structural transformations between triphylite and heterosite phases at the cathode are presented in Fig. 5. Here, the selected NPD pattern numbers correspond to those shown in Fig. 1(b) alongside the charging and discharging curves. The lithium content, y in Li1-yFePO4V was calculated by assuming y = 0 at 0 Ah and y = 1 at 11.3 Ah with a linear combination of these two phases upon electrochemical cycling.

During the charging process, the amount of the triphylite phase reduces and the heterosite phase increases as expected. This phase evolution indicates the extraction of lithium ions from the triphylite phase. In the literature [2,22,23], reflections of pristine LFP cathodes can be indexed to triphylite and heterosite phases up to ~60% state-of-charge during the charging cycle, even at 0.1 C at room temperature. During the discharging process, a substantial amount of heterosite remains in the electrode until near the end of discharging and then rapidly transforms to triphylite. Studies by Wang et al. [22] using ex-situ soft X-ray absorption at Fe LIII edges show that the Li content in the bulk cathode material changes more slowly than that calculated from the charging rates, but at the cathode surface, the Li content is linearly correlated to the charging rate. These results are characteristic of the delayed phase transition phenomenon. However, in our in-situ NPD data, the delayed phase transition was not observed. The percentage of triphylite and heterosite at each y value in Li1-yFePO4V (charging cycle) and Li1-yFePO4V (discharging cycle) are shown in Fig. 6, as derived from single-peak fits of the triphylite and heterosite 401 reflections. Fig. 6 shows an almost linear behavior of the phase composition of the cathode (dashed lines), indicating that the structural changes in Li1-yFePO4V are effectively synchronized with the electrochemical cycling process (voltage profile).

A possible explanation of the suppressed delayed phase phenomenon may be the vanadium in our sample. In order to quantify the influence of V-addition into LFP on the delayed reaction mechanism we undertook in-situ X-ray powder diffraction measurements on pristine and V-added LFP cells (Figure S1 in the Electronic Supplementary Information). We find a significant suppression of the delay in the phase transition, by about 20%, when a vanadium-added LFP cathode is used. This result indicates that vanadium is playing a part in the kinetics of the charge/discharge processes. According to the suggestions from Chang et al. [2], the delayed phase transition results from the slow nucleation kinetics...
of the resulting phase and disturbing the linear conversion of triphylite to heterosite during the charging–discharging cycling.

Previous studies of the delayed phase transition [2,22,23] use in-situ X-ray experiments with a half-cell sample to overcome the small penetration depth of X-rays. Furthermore, the X-ray beam is less than 0.5 mm, much smaller than the size of the detector. Without a correction for the non-uniformity of the sample, the specific location of X-ray beam in conjunction with its small penetration depth mean that the details concerning the delayed phase reaction are location-biased and not representative of the bulk cathode behavior. Additionally, Christian Masquelier suggested in a recent unpublished finding, that the delayed phase transformation might arise from insufficient contacts between components in the LIB during X-ray powder diffraction experiments. The additional windows and spacers used to allow the X-ray beam to access the cathode in X-ray experiments published on the phase delay issue, factors such as charge/discharge rates, type of electrolytes, cycling history of the battery, operating temperature and voltage ranges, and vanadium ordering must be comparable.

4. Conclusions

Structural phase transitions of a vanadium-added LFP cathode and a graphite anode in a commercial Li-battery were investigated by in-situ NPD. At the anode, we characterize the phase evolution of Li$_x$C$_6$ for $0 < x \leq 1$. At the cathode, a delayed phase transition was not observed, which we show to be, at least in part, a result of the vanadium-addition.

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Appendix A. Supplementary materials

Supplementary materials related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2013.02.074.

References
