Effects of TiO₂ coating on high-temperature cycle performance of LiFePO₄-based lithium-ion batteries

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1. Introduction

Lithium-ion secondary batteries have extensively been applied in electronic devices. LiCoO₂ is by far the most successful commercial cathode material. However, there has been constant effort made to find cheaper, less toxic, and more available cathode materials to replace the Co-based ones. LiFePO₄ [1] was firstly demonstrated by Padhi et al. [2] as a potential cathode material for Li-ion secondary batteries, and it has lately drawn considerable attention not only for its properties matching the needs mentioned above but also for its high safety and theoretical capacity (170 mAh g⁻¹). LiFePO₄ has the drawback of poor electronic conductivity, and mainly two methods have been adopted to circumvent this drawback, including carbon coating [3–5] and cation doping [6–8]. By these modifications, LiFePO₄ cathode has been demonstrated to possess good cycle stability at room temperature.

Electrochemical properties of the LiFePO₄-based Li-ion secondary batteries at elevated temperatures are foreseen to be important for electric-vehicles applications. Amine et al. [9] revealed that, while the LiFePO₄/mesocarbon microbead (MCMB) cell was cycled with essentially no capacity fading up to 100 cycles at room temperature, the cells cycled at 37 and 55 °C showed significant fading. The accelerated fading at the high temperatures was attributed to the dissolution of Fe from the cathode (LiFePO₄) side and subsequent deposition of the Fe ions on the MCMB anode, where the metal deposit catalyzed the formation of the solid/electrolyte interphase (SEI) layer. The formation of the SEI layer consumes Li ions and imposes high surface resistance. Both lead to capacity fading.

Metal oxide coating has often been used to improve the performance of cathode materials [10–20]. Researchers have reported that these oxides, such as Al₂O₃, ZrO₂, MgO, ZnO, and TiO₂, can give multi-functional improvements in cycle performance by, for example, preventing direct contact between the cathode material and the electrolyte, improving the structural stability and so on. However, to our knowledge, similar approach has not yet been tested on LiFePO₄.

In this work, TiO₂ was coated onto the surface of LiFePO₄ particles by a sol–gel process, and the effects of the oxide coating on the high-temperature (55 °C) cycle performance of the LiFePO₄-based cells were studied. The coated LiFePO₄ was cycled against either a Li or a C (MCMB) anode. It is demonstrated that, while the employment of the oxide coating indeed reduces capacity fading of...
the LiFePO4/Li cell, it imposes an opposite effect on the LiFePO4/C one. The causes to such improvement and deterioration have been investigated.

2. Experimental

The LiFePO4 powder (Phostech Lithium Inc.) employed has an average particle size of \( \sim 5.0 \mu m \) and a carbon content of 1.9% by weight. Surface coating of TiO2 on the LiFePO4 powder was conducted as follows. Firstly, Ti(C2H7O)4 (Aldrich, 97%) in ethanol was mixed with the LiFePO4 powder in a molar ratio of Ti(C2H7O)4/LiFePO4 = 0.03:1, and the slurry was heated to \( \sim 70^\circ C \) in ambient until totally dried. The as-prepared powder was then fired in a horizontal oven at 750 \(^\circ C\) for 0.5 h under 1% H2/N2 atmosphere. X-ray diffraction (XRD) was carried out on a Philips X'pert diffractometer with Cu Kα radiation.

For electrochemical tests, the LiFePO4 electrode contains on a dry basis 86% the LiFePO4 powder either with or without TiO2 coating, 5% graphitic flakes (KS6, Timcal), 1% nano-sized carbon black (Super P, Timcal), and 8% poly(vinylidene fluoride) (PVdF, Solvay Singapore Pte. Ltd.). Al foil is used as the current collector, and the thickness of the LiFePO4 overlay is \( \sim 55 \mu m \). In the LiFePO4/Li cell, a Li foil was used as the counter-electrode; while in the LiFePO4/C cell, a C electrode was used. The C electrode contains 93% MCMB (Osaka Gas) and 7% PVdF. The electrolyte is 1 M LiPF6 in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with a volume ratio of 1:2. The electrodes were assembled into CR2032 coin cells for testing. The cells were cycled at 1C-rate between 2.5 and 4.3 V for the LiFePO4/Li cells and between 2.5 and 3.65 V for the LiFePO4/C cells at 55 \(^\circ C\) with a charge-discharge tester (Arbin, model: MCN6410). Cyclic voltammetry (CV) analysis was performed at 5 mV min \(^{-1}\). Both the CV and electrochemical impedance spectroscopy (EIS) measurements were obtained using AUTOLAB, Eco Chenie PGSTAT30.

To prepare samples for surface analyses, the cycled coin cells were dissembled in a glove box under Ar atmosphere, and the electrodes were rinsed with diethyl carbonate (DEC) and dried and stored in the glove box before analysis. Surface and particle morphology were examined by scanning electron microscopy (SEM; LEO1530 and JOEL JSM-6700F). Energy dispersive X-ray spectroscopy (EDS, Oxford Instrument, model: 6587) and X-ray photoelectron spectroscopy (XPS, VG MICROTECH, MT-500) were used to analyze the surface compositions of electrodes.

In one experiment, Fe and Ti films were, respectively, deposited onto different C electrodes, and the deposited C anodes were then cycled against LiFePO4 cathode in order to evaluate the effects of the metal deposit on capacity fading rate. The metal films were deposited by vacuum sputtering under an atmosphere of 5 mtorr Ar with the power condition of 60 mA and 280 V and designated deposition periods that produce films of \( \sim 40 \) nm thick.

3. Results and discussion

For brevity, the TiO2-coated LiFePO4 powder will hereafter be abbreviated as c-LFPO, while the un-coated powder as u-LFPO. Fig. 1 compares the XRD patterns of the u- and c-LFPO powders. For both patterns, only LiFePO4 was detected. The olivine phase in these two patterns show essentially the same lattice constants (\( a = 1.025 \pm 0.001 \text{ nm}, b = 0.597 \pm 0.001 \text{ nm} \) and \( c = 0.466 \pm 0.001 \text{ nm} \)), suggesting absence of solid solution, which would otherwise cause change in lattice constants. Being inaccessible to direct observation of the TiO2/LiFePO4 interface by, for instance, high-resolution transmission electron microscopy, the presence of the TiO2 coating was ascertained by the following analyses. Firstly, a c-LFPO/Li cell was subjected to CV test between 1.0 and 4.3 V. As shown in Fig. 2, in addition to the lithiation/de-lithiation pair of LiFePO4 centered at 3.44 V, there is an additional redox pair centered at 1.84 V. This low-voltage redox pair can be attributed to lithiation/de-lithiation of anatase TiO2 [21]. Indeed, all the strong reflections of the anatase phase overlapped with the reflections of LiFePO4, and this explains why its presence has not been detected by XRD. Secondly, as shown in Fig. 3a and b, EDS mapping of Ti on individual c-LFPO particles gives fairly uniform Ti distribution. These combined results give unequivocal evidence to the presence of anatase TiO2 coating on the LiFePO4 particles. Unfortunately the thickness of the coating cannot be determined.

Discharge capacity data for the LiFePO4/Li cells were summarized in Fig. 4. The c-LFPO/Li cell showed a maximum capacity of 145 mAh g \(^{-1}\), and the capacity faded gradually with continuous cycling, retaining 140 mAh g \(^{-1}\) after 90 cycles. The u-LFPO/Li cell also exhibited a maximum capacity of 145 mAh g \(^{-1}\) but its capacity faded faster, to 132 mAh g \(^{-1}\) in totally 90 cycles (open symbols in Fig. 4). The beneficial effect of the TiO2-coating in reducing capacity fading of the LiFePO4/Li type of cells is clear. Fig. 5 compares the discharge potential curves of the maximum-capacity cycles for the two cells. The curves match perfectly with each other. The coa-
Fig. 3. (a) SEM micrograph of a TiO₂-coated LiFePO₄; and (b) the corresponding EDS mapping of Ti.

Fig. 4. Specific capacity versus cycle number (■: c-LFPO/Li; □: u-LFPO/Li). The cells were cycled at 55°C at 1C–1C rate between 2.5 and 4.3 V.

Fig. 5. Comparison of discharge potential curves of the maximum-capacity cycles (solid line: c-LFPO/Li; dashed line: u-LFPO/Li).

Fig. 5. Nyquist plots of the cells discharged to 2.5 V after selected cycles for (a) the c-LFPO/Li cell and (b) u-LFPO/Li.

Fig. 6 compares the EIS profiles of these two cells at selected cycles. All the EIS measurements were carried out at the lower terminal voltage, 2.5 V, i.e., at the fully discharged state, at room temperature. The curves show basically the same characteristics, including a depressed semi-circle within the high-to-middle frequency range and an inclined line within the low frequency range. The curve profile is typical of the electrochemical reaction associated with Li-ion intercalation. The resistance of the semi-circle can be considered as the total interfacial resistance that is equal to
the sum of the resistance of Li$^+$ migration through the SEI film and the resistance of charge transfer at the solid-film interface [see, for instance, Ref. #22]. This attribution holds for LiFePO$_4$ electrode at the fully discharged or charged state, which falls within the two terminal solid-solution regions of LiFePO$_4$-FePO$_4$ phase diagram [23,24]. As shown in Fig. 6, the interfacial resistance of the u-LFPO/Li cell, 7.0 $\Omega$, is initially lower than that, $\sim 10$ $\Omega$, of the c-LFPO/Li cell. However, the former increases more rapidly with cycle number than the latter. After 90 cycles, the u-LFPO/Li cell shows an interfacial resistance of 32 $\Omega$, while the c-LFPO/Li cell 26 $\Omega$. The trend shown by the interfacial resistance coincides with the capacity data. That is, as the interfacial resistance of the u-LFPO/Li cell increases faster with cycling, the cell also exhibits faster capacity fading.

The TiO$_2$-coating on LiFePO$_4$ particles, however, was found to have an opposite effect on the cycle performance of the LiFePO$_4$/C type of cells, including u-LFPO/C and c-LFPO/C, as show in Fig. 7. When cycled between 3.65 and 2.5 V, both cells exhibited initial maximum discharge capacities near 1.0 mAh, suggesting that they have similar initial properties. Two features are worth noting upon prolonged cycling. Firstly, for both cells, the capacity fades at a faster pace than their LiFePO$_4$/Li counterparts. For instance, the u-LFPO/C cell lost 29% capacity after 90 cycles, while the u-LFPO/Li cell lost only 9.7% (Fig. 4a). The difference is even more dramatic for the TiO$_2$-coated LiFePO$_4$ electrode; the c-LFPO/C cell lost 39%, in contrast to 3.5% for the u-LFPO/Li. Secondly, for the LiFePO$_4$/C configuration, the u-LFPO/C cell shows a slower fading rate than the c-LFPO/C cell. This is opposite to the trend shown by the LiFePO$_4$/Li cells.

SEM study on the cycled C anodes of both the u- and c-LFPO/C cells showed that the surfaces of the anodes were found to be covered with nodules of SEI materials (Fig. 8a and b). There is apparently a much greater amount of the nodules for the c-LFPO/C cell. While they give similar intensities of the C and O peaks (Fig. 9a and b), the anode of the c-LFPO/C cell shows distinctly higher intensities of the F and P peaks (Fig. 9c and d). The F peak has a binding energy (b and e) characteristic of LiF [25], suggesting that a greater amount of LiF is deposited on the C anode of the TiO$_2$-coated LiFePO$_4$ cell. This is consistent with the SEM and EDS results described above, which showed a greater amount of F-rich nodules formed on the surface of the C anode of the c-LFPO/C cell.

XPS analysis detected Fe signal on both anodes. Fig. 10 plots the Fe XPS signal intensity as a function of sputtering depth. The data confirmed the occurrence of Fe deposition on both C anodes. Furthermore, it is shown that there is less amount of Fe deposited on the C anode of the c-LFPO/C cell than on the anode of the u-LFPO/C cell. On the other hand, the former additionally showed Ti signal but the latter did not (Fig. 11). The Ti appearing on the C anode of the c-LFPO/C cell must have come from the TiO$_2$ coating on the cathode side. The results indicate that Ti ions were dissolved from the cathode side and subsequently reduced on the C anode in the c-LFPO/C cell during the cycling process. Possible dissolution of Ti ions has not been addressed in the earlier studies concerning the TiO$_2$-coated cathodes [17–20].

The capacity data of the LiFePO$_4$/Li cells in Fig. 4 have demonstrated reduced capacity fading rate as a result of the TiO$_2$-coating on the LiFePO$_4$ powder. This is in agreement with the general trend that has been reported in several other TiO$_2$-coated cathode materials, such as LiCoO$_2$ [17,18], LiMn$_2$O$_4$ [18,19], and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ [20]. In all these studies, the TiO$_2$-coated cathodes have been cycled against Li metal electrode. Taking into account all the analysis results presented above, we infer that the fading improvement is largely because the presence of the TiO$_2$ coating helps to prevent direct contact between the LiFePO$_4$ particles and the electrolyte, and hence it reduces erosion of LiFePO$_4$ upon cycling. As pointed out by Amatucci et al. [26] in their study on LiMn$_2$O$_4$, dissolution of metal ions may lead to the formation
of passivating surface layer of high charge-resistance on cathode, which, along with material loss, contributes to capacity fading. This is consistent with the observation that the c-LFPO/Li cell has a lower increasing rate in interfacial resistance than the u-LFPO/Li cell upon cycling (Fig. 6). Furthermore, the XPS data (Fig. 9) also confirmed that, in the case of the LiFePO4/C type of cells, there is less Fe deposition on the C anode cycled against c-LFPO than against u-LFPO.

The LiFePO4/C type of cells exhibited a completely opposite trend in cycling stability to the LiFePO4/Li cells. That is, the c-LFPO/C cell showed a faster capacity fading rate than the u-LFPO/C cell (Fig. 7). Different from the LiFePO4/Li cells, the LiFePO4/C cells have only limited amount of Li ions. As the SEI formation consumes Li, the cell that exhibits more SEI materials formation is expected to show a faster capacity fading. This is consistent with the SEM and XPS results (Figs. 8 and 9), which show that there has indeed been more SEI formation on the C anode of the c-LFPO/C cell. The question is now why the cell, c-LFPO/C, showing less Fe deposition at anode turns out to have a greater amount of SEI materials.

As shown by XPS, in addition to Fe, there was also Ti deposition on the C anode of the c-LFPO/C cell. The effect of Ti deposit on the cycling performance of the olivine cathode has never been determined in the literature. To evaluate such effects, the following experiment was conducted. Ti and Fe layers were, respectively, deposited onto different C electrodes by vacuum deposition, and the electrodes were then cycled against u-LFPO cathode. Fig. 12 compares the capacity data between these two cells. Data of the cell without any pre-deposited metal film are also shown. It was found that the cell containing the Ti-coated anode shows the fastest...
capacity fading than the rest cells. As shown by SEM analysis (Fig. 13), the SEI layer on the Ti-coated C anode is very thick, showing uniformly covered film morphology. On the other hand, the granular nature of the MCMB particles can still be seen on the Fe-coated anode. The pre-deposited Ti layer apparently has a much greater catalytic activity in accelerating SEI formation than the Fe layer. Therefore, one may anticipate that Ti deposited on the C anode causes more pronounced deteriorating effect on capacity performance than the Fe deposit. This result explains why the c-LFP/C cell, which shows Ti deposition on the C anode, exhibits faster capacity fading than the u-LFP/C cell.

It is worth noting that large majority of the past studies concerning metal-oxide coating on cathodes have been using Li as the counter electrode. The results of the present study point out the need to re-evaluate those coating materials for their chemical stability under cycling as well as for their potential deteriorating effect on the anode side.

4. Conclusions

The effects of TiO₂ coating on the cycling performance at 55 °C of the LiFePO₄ cathode against either a Li or a C anode have been studied. It has been demonstrated that, while the presence of the oxide coating helps to reduce capacity fading for the LiFePO₄/Li cell, it imposes an adverse effect on the LiFePO₄/C cell. The analysis results indicate that the presence of the TiO₂ coating helps to reduce the Fe dissolution problem at the cathode. However, the coating itself is not stable and partially dissolved upon cycling, causing redeposition of Ti at the C anode. Ti deposit has been shown to be more active than Fe in causing SEI layer formation at the anode, leading to accelerated capacity fading.

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