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Enhanced High-Temperature Cycle Life of $LiFePO_4$-Based Li-Ion Batteries by Vinylene Carbonate as Electrolyte Additive

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Addition of vinylene carbonate (VC) in electrolyte solution has been found to greatly improve the high-temperature (55°C) cycling performance of $LiFePO_4$-based Li-ion batteries. It has been established that the VC additive remarkably suppresses Fe dissolution from $LiFePO_4$ cathode and hence, subsequent Fe deposition on the anode side. Furthermore, the VC additive also significantly reduces formation of solid-electrolyte interface layers on both $LiFePO_4$ cathodes and mesocarbon microbead (MCMB) anodes. With VC addition, a 18650-type $LiFePO_4$/MCMB cell has been shown to retain ~80% capacity after 980 cycles at 55°C under 1–3 C charge–discharge rates. This is in contrast with more than 25% capacity loss after merely 100 cycles when no VC is added.

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Orthorhombic olivine compound $LiFePO_4$ has drawn considerable attention for its application as a cathode material for lithium ion batteries.[1] This compound has a theoretical capacity of 170 mAh g^{-1} and is environmentally benign. In addition, compared with other cathode oxide materials, such as $LiCoO_2$ and $LiNi_{1-x-y}Co_xMn_yO_2$, $LiFePO_4$ possesses greater thermal stability and is suitable for large-scale rechargeable Li-ion battery applications. Li-ion batteries for hybrid electric vehicle (HEV) or electric vehicle (EV) use are exposed to much more severe temperature environments than those for 3 C products, such as mobile phones or notebooks.[2] Therefore, charge–discharge cyclability and durability against high temperature should always be big challenges to the HEV and EV applications of Li-ion batteries.

The issue of metal dissolution from the cathode active materials has been in focus[3-7] because there is a general consensus that it is one major cause to the observed poor high-temperature performance of several Li-ion battery systems. In particular, Amine et al.[3] reported that the capacity of a $LiFePO_4$/graphite cell with $LiPF_6$ electrolyte fades rapidly at high temperature (55°C) due to Fe dissolution from cathode and subsequent deposition of the Fe ions on the graphite anode to form an unfavorable superficial layer. In studying the influence of metal ions, including divalent Mn, Co, and Ni, in electrolyte on the performance of graphite anodes, Komaba et al.[4] showed that the metal ions were electroreduced on the graphite anode on discharge and that the metal deposits hinder intercalation of Li ions into graphite and, in some cases, accelerate decomposition of electrolyte, resulting in thick solid-electrolyte interface (SEI) layer. Both effects cause capacity fading upon cycling. Similar effects are expected for Fe ion dissolved in electrolyte. To amend the adverse effect by Fe dissolution, Amine et al.[3] have shown that the high-temperature cycle performance of a $LiFePO_4$/graphite cell can be improved by using lithium bis(oxalato)borate (LiBOB) electrolyte and/or $Li_4Ti_5O_{12}$ as the anode material. Presumably the use of non-F-containing electrolyte helps to avoid Fe dissolution. From the viewpoint of commercial application, however, replacement with either a completely new electrolyte salt or anode material requires elaborate modifications of existing manufacturing processes and recipes. The modifications would be greatly simplified, however, if only additives in either electrode or electrolyte solution are involved.

In this paper, it is reported that dissolution of Fe in the $LiFePO_4$-based cells has been greatly suppressed by introducing vinylene carbonate (VC) as an electrolyte additive, and the cycling performance at 55°C of the cells was greatly enhanced. For instance, with VC addition, a $LiFePO_4$ mesocarbon microbead (MCMB) cell retains ~80% capacity after 980 cycles at 55°C. This is in contrast with more than 25% capacity loss after only 100 cycles when no VC is added.

Experimental

Sample preparation.— For electrochemical characterization, the $LiFePO_4$ electrode was made of 86 wt % $LiFePO_4$ powder (D_{50} = 3 μm, 1.2 wt % coated carbon content, from Phostech Lithium), 5 wt % graphite (KS6, Timcal), 1 wt % carbon black (Super P, Timcal), and 8 wt % poly(vinylidine difluoride) (PVdF) binder on an Al current collector. The anode electrode was made of 93 wt % MCMB (D_{50} = 10 μm, from Osaka Gas) and 7 wt % PVdF binder on a Cu current collector. The coin-type half-cell sample consists of a $LiFePO_4$ disk electrode, PP separator (Celgard 2400), and Li foil disk as the counter electrode. The 18650-type full-cell Li-ion batteries consist of $LiFePO_4$ as cathode, PP separator (Celgard 2400), and MCMB as anode. The cells were all assembly in a dry room with dew point of −40°C.

Electrochemical measurements.— The cycling tests on the Li–$LiFePO_4$ coin cells were performed within the potential window from 2.5 to 4.3 V with charge–discharge currents of 1 C–1 C rates at 55°C, while the tests on the 18650-type $LiFePO_4$-MCMB cells were between 2.5 and 3.65 V at 1–3 C charge–discharge rates. For the 18650 cell, the cell was charged to 3.65 V at 1 C rate, held for 25 min at charge state, discharged to 2.5 V at 3 C rate, and then held again for another 25 min before the next cycle. The electrolyte (Samsung) was 1 M $LiPF_6$ in ethylene carbonate (EC)/methyl ethyl carbonate (MEC) 1:2 by volume mixture either with 2 wt %VC or without. The water content in the electrolytes was measured by a Karl Fischer moisture titrator (Kyoto, MKC-510), and the H_2O contents were 30 and 28 ppm in the electrolytes with or without VC additive, respectively.

Compositional and microstructural analyses.— To analyze the compositions and microstructures of the electrodes after charge-discharge cycling, the cells were disassembled in a glove box under Ar atmosphere. The electrodes were extracted and washed in dimethyl carbonate (DMC) and then dried under vacuum, in order to remove the salt and solvent on the electrode.[8] A scanning electron microscope (SEM; JEOL JSM-6500F) was used to investigate the morphology of the electrodes. Surface composition was analyzed by X-ray photoelectron spectroscopy (XPS) on an Escalab 250 system (Thermo VG Scientific) using a monochromatized Al Kα ray as the X-ray source ($h\upsilon$ = 1486.6 eV). Core peaks and valence-band spec-

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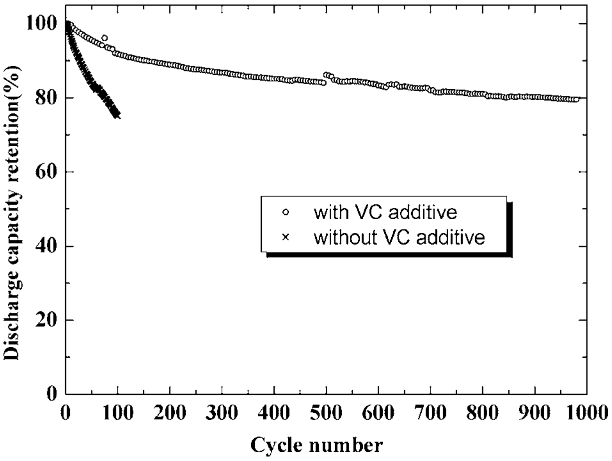

Figure 1. Cycle life test of $LiFePO_4$/graphite full cells at 55°C.

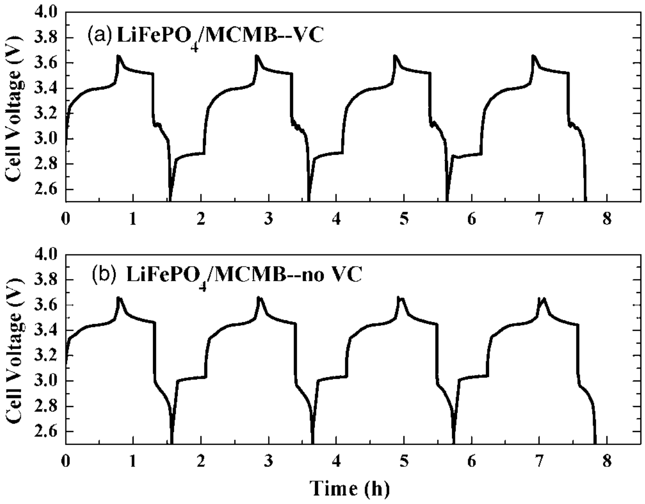

Figure 2. Charge–discharge potential curves of $LiFePO_4$/graphite full cells (a) with VC additive and (b) without VC cycled at 55°C.

tra were recorded with 20 eV constant pass energy and the energy step was 0.1 eV. The pressure in the chamber was $<6 \times 10^{-9}$ Torr. The etching of the samples for the depth profile was carried out with Ar ion sputtering. The sputtering rate was equivalent to 1 nm/min on SiO_2.

To determine the extent of Fe dissolution, the following procedure was followed. After dissembly from a cell, the anode electrode, along with the electrolyte left within the pores, was dried at 60°C. The dried electrode layer was then scratched off from the surface of the current collector (Cu) and dissolved in aqueous HCl solution. The solution was finally subjected to measurement by inductively coupled plasma–atomic emission spectrometry (ICP-AES) (Jarrell-Ash, ICAP 9000) to determine its Fe content. Accordingly, the amount of Fe detected herein is the sum of the solid Fe deposits on the anode surface and Fe ions in the residue electrolyte, and it is expressed in terms of weight ratio (in parts per million) with respect to the electrode layer.

Results and Discussion

The design capacity of the present $LiFePO_4$/MCMB 18650-type cell is 430 mAh. The actual discharge capacity was found to be 410 mAh at 3 C discharge rate at 55°C for the first cycle. The results of cycling test of the 18650 cell either with or without VC additive were shown in Fig. 1. The capacity of the cell not containing VC in the electrolyte solution decreased to 75% of the initial capacity after 100 cycles. The capacity fading problem was significantly improved by adding VC in the electrolyte solution, and the cell containing VC retained around 80% of the initial capacity after 980 cycles. Figure 2 shows some of the corresponding charge–discharge potential curves. It was found that the cells either with or without VC showed a similar charge plateau at ~3.4 V. However, the cell with VC exhibited a significantly higher discharge plateau than the cell without VC. That is, the former showed a discharge plateau between 3.2 and 3.0 V, while the latter below 3.0 V. This indicates that the resistance of the cell without VC is much higher than the cell containing VC. Higher resistance results in a greater potential drop during discharge.

The beneficial effect of VC on the cell cycling life was also observed on the Li/$LiFePO_4$ half-cell, as shown in Fig. 3. The half-cell containing VC shows only 3% capacity fading after 200 cycles, in contrast with the half-cell without VC additive, which exhibited 19% capacity fading after 200 cycles. That is, the VC additive can significantly enhance the cycling performance of the $LiFePO_4$ cathode at high temperature.

ICP analysis (Table I) on the compositions of the cycled MCMB anodes showed that in the cells containing VC, the anodes contain 50 and 240 ppm of Fe after 100 and 980 cycles, respectively. The Fe content remarkably increased to 1807 ppm after merely 100 cycles when no VC was used.

Scanning electron microscopy (SEM) images of the cycled MCMB anodes are shown in Fig. 4. The anode from the cell not containing VC (Fig. 4a) showed the presence of a thick film on the electrode surface, and as a result the granular nature of MCMB particles can no longer be seen. On the contrary, the anode from the cell containing VC shows no deposited film on the surface, and the granular morphology of MCMB particles, which are of a few tens of micrometers in diameter, are vividly seen even after 100 cycles. The results indicate that the presence of VC in electrolyte significantly reduces decomposition of electrolyte on MCMB anodes and hence the thickness of SEI layers. Furthermore, XPS analysis detected an Fe signal on both MCMB anodes (Fig. 5); however, the anode of the cell without VC exhibited much stronger Fe signals (712 and 725 eV) than that with VC after 20 min sputtering, suggesting that the former contains more Fe surface deposits. The result is consistent with the ICP data.

SEM images of the cathode sides after cycling are shown in Fig. 6. For cathodes from the cell not containing VC, paste-like deposited films were observed on the surface of the particles (Fig. 6a). No deposited film was observed on the cathode from the cell containing

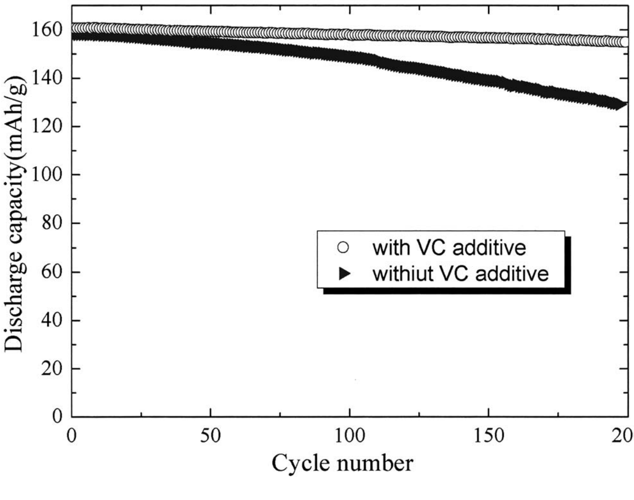

Figure 3. Cycle life test of $LiFePO_4$/Li cells at 55°C.

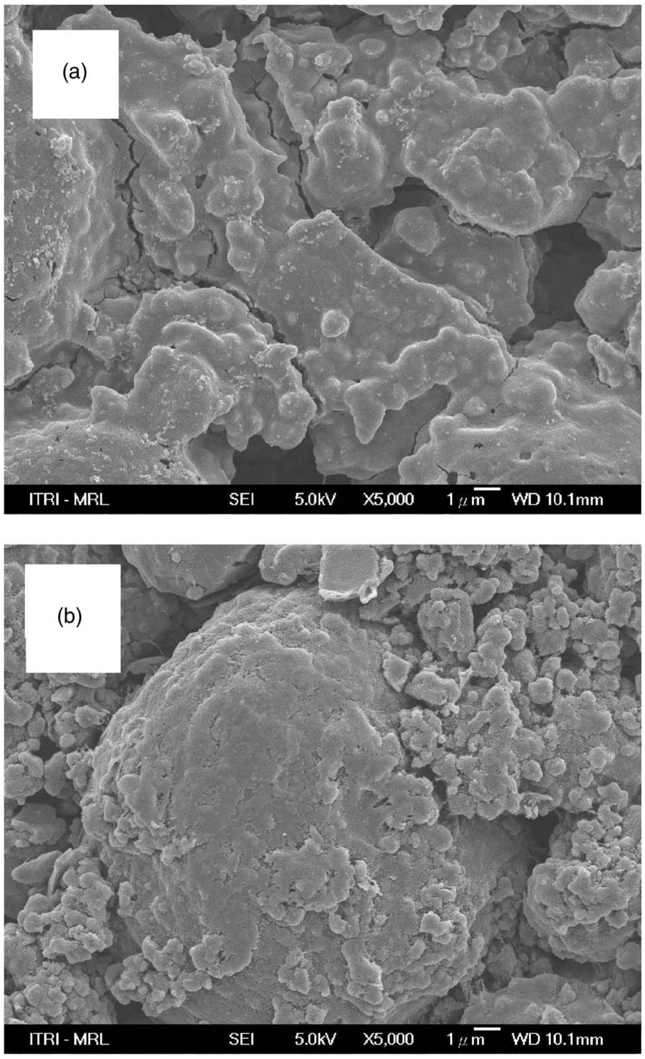

Figure 4. SEM micrographs of the anodes in the cells (a) without VC and (b) with VC after 100 cycles at 55°C.

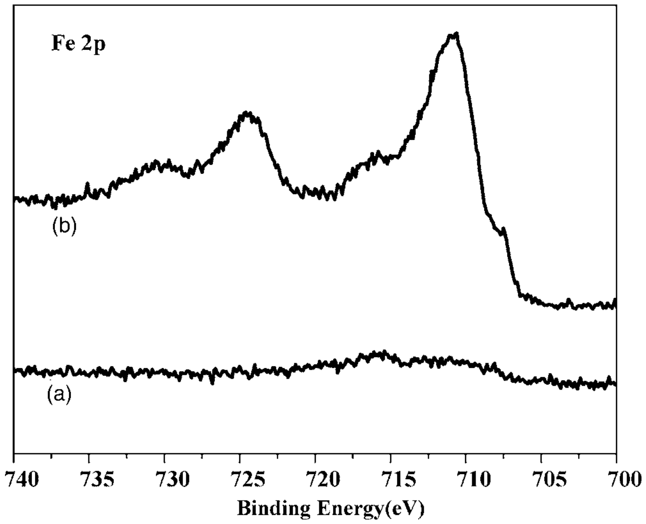

Figure 5. Fe (2p) XPS spectra at 20 min sputtering of the MCMB anodes that are cycled (a) with VC and (b) without VC in the electrolyte solution (100 cycles; 55°C).

Table I. Data of Fe dissolution determined by the ICP analysis.

	100 cycles 55°C	980 cycles 55°C	6-day storage[a] 25°C	Formation 1[b] 25°C	Formation 2[c] 25°C
Cell without VC (ppm)	1807	NA	27	102	144
Cell with VC (ppm)	50	240	29	37	40

[a] Fresh cells without formation and storage at 25°C for 6 days after assembly.

[b] Formation no. 1 process consists of the the steps ofcharge to 3.65 V, storage at 25°C for 8 h, and discharge to 2.5 V.

[c] Formation no. 2 is basically the same as formation no. 1, except that the storage period at 3.65 V is increased from 8 h to 6 days.

VC (Fig. 6b), and the morphology of $LiFePO_4$ particles is very clear after 100 cycles. This result is consistent with the XPS data, as described in the following. Figure 7 shows the Fe (2p) and P (2p) XPS spectra acquired from three different cathodes, including (a) a fresh electrode before cell assembly, (b) the cathode in the cell containing VC after 100 cycles at 55°C, and (c) that in the cell not

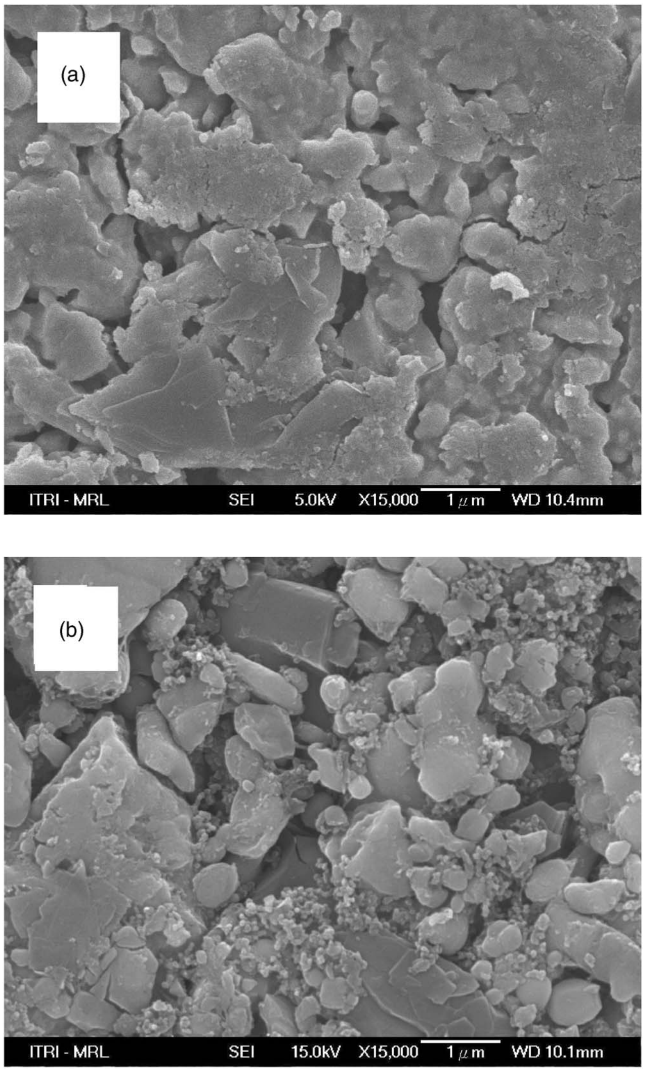

Figure 6. SEM micrographs of the cathodes that have been cycled (a) without VC and (b) with VC in the electrolyte solution (100 cycles; 55°C).

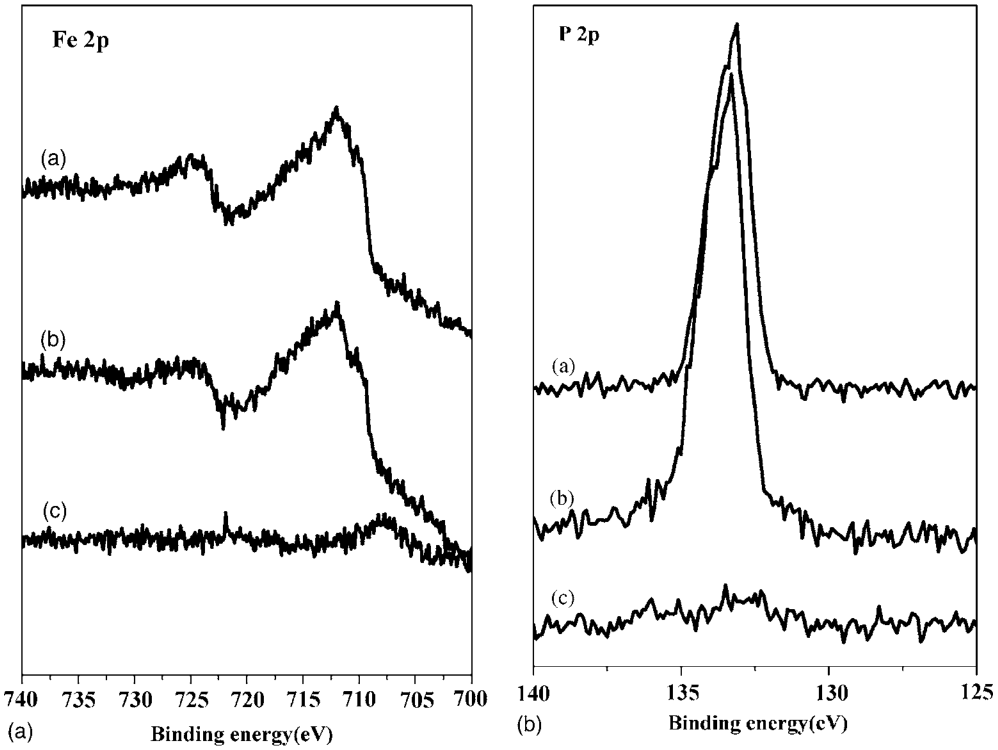

Figure 7. Fe (2p) and P (2p) XPS spectra of three different cathodes: (a) fresh electrode before cell assembling, (b) with VC in the electrolyte solution after 100 cycles at 55°C, and (c) without VC under the same cycling conditions as (b).

containing VC under the same cycling conditions as (b). The Fe and P signals are mainly from the components of $LiFePO_4$. Both cathodes a and b show strong Fe (2p) and P (2p) XPS peak intensities, confirming that the surface of the cathode cycled with the presence of VC additive is nearly as "clean" as the surface of a fresh cathode. In contrast, the Fe and P signals were not observed on cathode c, suggesting that the electrode surface is in general covered with thick deposited layers that do not contain $LiFePO_4$.

Figure 8 shows the C (1s) XPS signals acquired from the cathodes b and c described above at different etched depths. For cathode

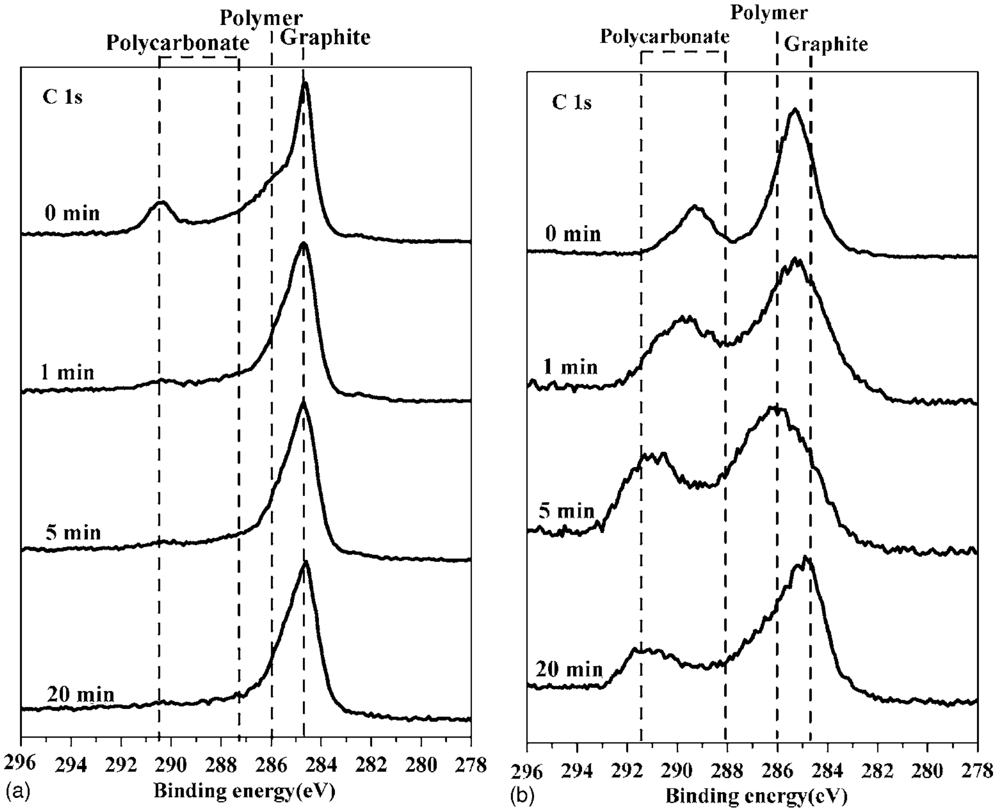

Figure 8. C (1s) XPS spectra at different etched depths of two cathodes: (a) with VC in the electrolyte solution after 100 cycles at 55°C and (b) without VC under the same cycling conditions as (a).

b, which was cycled with the presence of VC, three C (1s) peaks were observed at the very outer surface. The peak at 284.6 eV can be attributed to the graphitic additive. A shoulder peak at around 286 eV can be assigned to polymeric hydrocarbons, while the peak at 291 eV is associated with either polycarbonates or Li_2CO_3, which typically have C (1s) binding energies within the range between 288 and 292 eV.[9-11] The polymer and carbonate species are believed to arise from electrolyte decomposition. As shown, the C (1s) peaks associated with the polymer and carbonate species quickly disappear and can barely be detected after etching for 5 min.

The C (1s) spectra of the cathode c (Fig. 8b) are very different from those of cathode b, suggesting that the SEI layers on these two cathodes have markedly different structures/compositions. In addition, the C (1s) peaks of cathode c shifted in a complex manner with sputtering depth, suggesting complicated distribution in structure/composition with depth. While the detailed structure of the SEI layer has yet to be determined, it is sufficient to note that the C (1s) peaks of the polymer and carbonate species persist even after 20 min of etching. This is in great contrast with cathode b (Fig. 8a). Overall, the XPS analysis on the cathodes clearly indicates that VC is also effective in suppressing electrolyte decomposition and hence, in reducing SEI formation on the $LiFePO_4$ cathode when cycled at 55°C.

The ICP (Table I) and XPS (Fig. 5) data on the MCMB anodes described above have unequivocally established that the addition of VC in electrolyte has effectively reduced dissolution of Fe from $LiFePO_4$. The XPS data on $LiFePO_4$ cathode (Fig. 8) further indicates the cathode surface appears "pacified" due to the presence of VC and becomes relatively "inert" toward electrolyte decomposition, as it was covered by a much thinner SEI layer. The observed reduction in SEI formation on cathode by VC is accordance with the finding of Aurbach et al.,[12] who reported that VC additive decreased the interfacial impedance of the positive electrodes, including $LiMn_2O_4$ and $LiNiO_2$. However, no pronounced effect on cycling behavior due to VC was observed in their study for either of the cathode materials. Thus, the significant reduction in metal-ion dissolution accompanied by improved cathode cyclability by VC appears unique to $LiFePO_4$ cathode. Combination of the reduced Fe dissolution and suppressed SEI formation is believed to contribute mostly to the enhanced high-temperature cyclability of $LiFePO_4$ cathode as observed here (Fig. 2).

Table I compares additional ICP data of the $LiFePO_4$-MCMB cells subjected to different treatments. Two facts are noticed. First, from the data of the cell without VC, it can be deduced that the charge–discharge action has a much greater impact than storage in causing Fe dissolution. That is, the Fe dissolution process is to a great extent electrochemically driven. This result is consistent with the finding of Iltchev et al.,[5] which indicates negligible Fe dissolution for storage at 60°C. Second, in the cell containing VC, the $LiFePO_4$ cathode was found to be effectively pacified and became very resistant against Fe dissolution/deposition upon completion of the charging phase of the first cycle (the formation process).

The dissolution of Fe from $LiFePO_4$ has previously been linked to the presence of Fe_2P impurity.[13] However, no Fe_2P impurity in the pristine $LiFePO_4$ powders or cathode electrode after cycling was detected by X-ray diffraction (the spectra are not shown). The amount of Fe_2P impurity, if any, will be too small to account for the amount of Fe deposit found on the MCMB anode, particularly for the cell without VC after 100 cycles (Table I). Therefore, the dissolution of Fe ion in the present cell has to result from the reaction of $LiFePO_4$ and electrolyte.

In concurrence with reduced SEI formation on the cathode side, the thickness of the SEI layer on MCMB anode has apparently been greatly reduced due to the presence of VC in electrolyte (Fig. 4). Two factors have to be considered in accounting for this phenomenon. First, as shown by Komaba et al.,[4] deposited metal films, such as Mn and Co, on the graphite anode surface can accelerate decomposition of electrolyte, leading to thickening of the SEI layer. Accordingly, reduced Fe deposition by VC in the present case can reduce SEI formation on the MCMB anode. Second, it has been well established[12] that VC can react on graphite anode upon discharge to form thin layers of polycarbonate species, which suppress solvent and salt anion reduction. Thus, the reduced SEI formation on MCMB anode may result from the combination of these two beneficial factors due to VC. To what extent each of these two factors contributes remains to be investigated.

In summary, VC additive in electrolyte has been found to exert several beneficial effects which dramatically improve the high-temperature cycling performance of $LiFePO_4$-based Li-ion cells. These effects include suppressed Fe dissolution and SEI formation on the cathode side and, in the case MCMB anode, reduced Fe deposition and SEI formation on the anode side.

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