



Tris(pentafluorophenyl) borane as an electrolyte additive for LiFePO₄ battery

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ABSTRACT

The effects of tris(pentafluorophenyl) borane (TPFPB) additive in electrolyte at the LiFePO₄ cathode on the high temperature capacity fading were investigated by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), cyclability, SEM and Fourier transform infrared (FTIR). According to the study results, tris(pentafluorophenyl) borane has the ability to improve the cycle performance of LiFePO₄ at high temperature. LiFePO₄ electrodes cycled in the electrolyte without the TPFPB additive show a significant increase in charge transfer resistance by EIS analysis. SEM and FTIR disclose evidence of surface morphology change and solid electrolyte interface (SEI) formation. FTIR investigation shows various functional groups are found on the cathode material surface after high temperature cycling tests. The results showed an obvious improvement of high temperature cycle performance for LiFePO₄ cathode material due to the TPFPB additive. The observed improved cycling performance and improved lithium ion transport are attributed to decreased LiF content in the SEI film.

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1. Introduction

The battery is the heart of the mobile applications. It is now popularly considered that LiFePO₄ cathode material has the most suitable characteristics for application as middle/large-size electric vehicle (EV) and hybrid electric vehicle (HEV) batteries in terms of cost and stability. LiFePO₄ with an olivine structure as cathode material for lithium-ion secondary batteries has been studied extensively due to advantages such as low cost, good cycling performance at room temperature, high safety, non-toxicity and environmental friendliness. On the other hand, a major issue of the LiFePO₄ material is its low intrinsic electrical conductivity [1]. Moreover, olivine LiFePO₄ exhibits such undesirable features as capacity fading during cycling at elevated temperature due to the olivine undergoing iron dissolution [2,3]. The dissolution of iron in LiFePO₄ material has been shown to be caused by the impurities of LiFePO₄ materials during the preparation process [4,5] as well as the presence of HF and H₂O in the cell [6].

Solid electrolyte interface (SEI) films are formed on LiMO₂ cathodes in LiPF₆ carbonate solutions (M = V, Co, Mn, etc.) [7], with strong effect on cathode performance [8]. LiPF₆ itself always brings with it HF contamination, which is detrimental to the performance of both negative and positive electrodes [9]. For instance, HF reacts with the LiMO₂ cathode materials to form surface LiF, and some of the cathode materials (e.g. LiNiO₂) are nucleophilic and attack

the electrolytic alkyl carbonate molecules, thus forming –OCO₂Li surface groups and/or inducing polymeric species such as polycarbonates [10,11]. In general, both the solvent molecules and the PF₆[−] anions are reduced on the Li-graphite anodes to form surface films composed of ROCO₂Li, ROLi, Li₂CO₃, species containing Li–C bonds, polymeric species (e.g. polycarbonate, polyethylene), LiF, Li_xPF_y, and Li_xPOF_y species [12]. It should be noted that the capacity fading found for both Li–C and LiMO₂ electrodes in Li-ion batteries is largely due to surface phenomena related to the above reactions. Surface film formation may increase the electrode's impedance and pronounced surface-rated capacity fading of Li-ion electrodes can be observed [13].

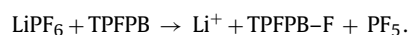
Some work has replaced the graphite carbon anode with a Li₄Ti₅O₁₂ anode, which operates at a potential above the reduction to iron metal. As a result, only the test cells with a graphite anode experienced significant capacity fading even though some Fe dissolution was reported in both cases at 37 and 55 °C [3]. The iron dissolution was connected to the presence of HF in the LiPF₆. The use of solutions containing lithium bisoxalato-borate (LiBOB) and LiClO₄ resulted in reduced capacity fading, although some fading was still observed [3,6,14]. High crystallinity LiFePO₄ cathodes prepared by hydrothermal synthesis exhibited no substantial iron dissolution during cycling at elevated temperatures when the solution contained no acidic or protic contaminants [4,6].

Wu et al. [15] reported that addition of vinylene carbonate (VC) in electrolyte solution greatly improved the high-temperature (55 °C) cycling performance of LiFePO₄-based Li-ion batteries, reportedly because the VC additive significantly reduced formation of solid-electrolyte interface layers on both the LiFePO₄ cathode

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and the mesocarbon microbead (MCMB) anode. Recently, several researchers have investigated anion receptors as a new additive for lithium secondary battery electrolytes [16–19]. Anion receptors can form complexes with anions, thereby inhibiting the decomposition reaction of anions. Tris(pentafluorophenyl) borane (TPFPB) additive is one of the anion receptors. It is able to increase the dissociation of LiPF_6 in electrolytes. Adding a tris(pentafluorophenyl) borane compound in an electrolyte can reduce production of electrolyte decomposition residues, while washing the LiMn_2O_4 cathode with solvent can partially restore lost capacity in subsequent cycling, showing the importance of electrolyte decomposition in capacity fading behavior [20,21]. TPFPB additive can improve the thermal stability of LiPF_6 -based electrolyte. Sun et al. [22] reported that a $\text{Li}/\text{LiMn}_2\text{O}_4$ cell with a composite LiPF_6 -based electrolyte containing 0.1 mol dm^{-3} TPFPB additive exhibited superior capacity retention and cycling efficiency at 55°C than a cell with an electrolyte without additive. The improvement is attributed to the dissolution of LiF out of the SEI. A negative impact of TPFPB is that it captures LiF from LiPF_6 to release highly reactive PF_5 , which accelerates deterioration of the electrolyte solvents, i.e. [23]



Therefore, the amount of TPFPB added to the electrolytes should be strictly controlled. In this paper, we investigate the effect of a boron-based anion receptor, TPFPB, in LiPF_6 in a mixture of ethylcarbonate (EC) and dimethylcarbonate (DMC) (1:1 by weight) on the electrochemical performance and the cycling performance at high temperature (60°C) of LiFePO_4 cathodes. The electrochemical performance is investigated by galvanostatic cycling. The solid electrolyte interface is characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and X-ray diffraction (XRD).

2. Experimental

LiFePO_4 cathode materials with carbon treatment were purchased from Changes Ascending Ent., Taiwan. Cathode electrodes were prepared by slurring the LiFePO_4 material power (91%) with 6% polyvinylidene fluoride (PVDF, Solef 6020, Solvy), and 3% Super S (MMM Carbon, Belgium) in an *N*-methylpyrrolidone (NMP, ISP) solvent. The mixed slurry was then coated onto aluminum foil ($20 \mu\text{m}$, Nippon Foil Co., Japan). The dried electrode was compressed by a roller at room temperature to make a smooth and compact film structure. After vacuum drying at 100°C for 12 h, the electrode disks (1.368 cm^2) were punched out of the larger coated foil sheets and weighed. Disks of similar surface area, thickness and weight were selected for further testing. Finally, to remove residual water content and standardize the level of hydration, the selected electrodes were stored in a glove box with oxygen and humidity content maintained below 5 ppm for more than 24 h before electrochemical characterization. The cathodes were incorporated into coin type cells with a Li foil (FMC) anode electrode and Celgard separator (Celgard 2300). The electrolyte was a commercially available 1.2 mol dm^{-3} LiPF_6 in a 1:1 EC/DMC solvent (Ferro Corp.). In studying the effects of the electrolyte additive, the same batch of 1.2 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte with $0.028 \text{ mol dm}^{-3}$ tris(pentafluorophenyl) borane (TPFPB, Strem Chemical) was used as an additive in all the cells. Cycle life tests were conducted at both room temperature and at 60°C using an oven thermostat. Experimental cells were tested for charge/discharge behavior at the constant current mode, cycled galvanostatically at 1.0 C (3.25 mA cm^{-2}) over the range of 2.5–4.2 V. After and before cycled galvanostatic measurement, electrochemical impedance spectroscopy (EIS) was observed immediately at open circuit voltage conditions. EIS was performed in the coin cell

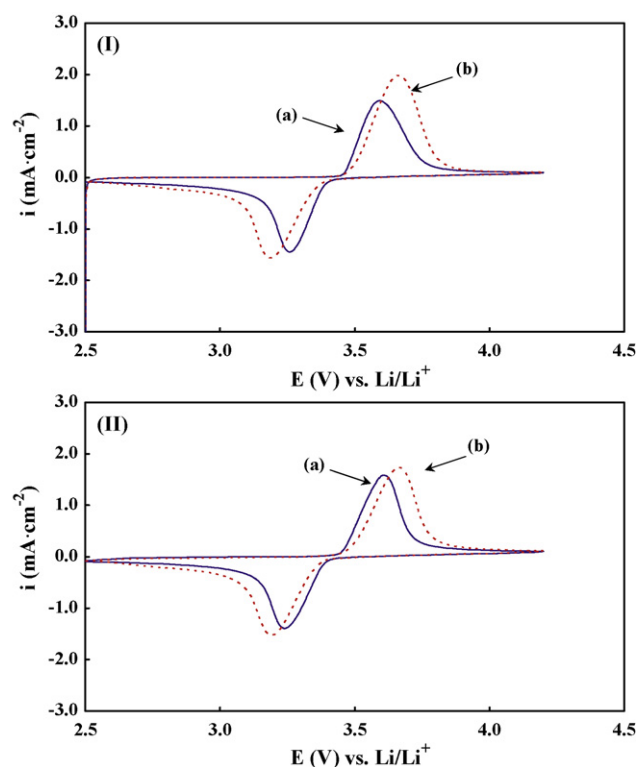


Fig. 1. The cyclic voltammograms of LiFePO_4 electrodes at (I) 1st and (II) 2nd cycles in 1.2 mol dm^{-3} LiPF_6 EC-DMC (1:1) solutions (a) without and (b) with $0.028 \text{ mol dm}^{-3}$ TPFPB. Scan rate: 0.1 mV s^{-1} ; potential range: 2.5–4.2 V.

by coupling the potentiostat with an Autolab frequency response analyzer locked in an amplifier and an impedance phase analyzer. A sinusoidal amplitude modulation of $\pm 10 \text{ mV}$ was used over a frequency range from 0.01 Hz to 1 MHz.

Cyclic voltammetry (CV) measurements were carried out with an Autolab electrochemical analyzer (Autolab PGSTAT30, Eco Chemie) with a current sensitivity of 1 nA. A one-compartment three-electrode polypropylene cell was used and the whole apparatus was set in a glove box. The working electrode was the LiFePO_4 cathode electrodes prepared by the above procedure with a dimension of $1 \times 1 \text{ cm}^2$. Both the counter and reference electrodes were lithium metal. The electrolyte was 1.2 mol dm^{-3} LiPF_6 dissolved in weight ratio 1:1 of EC and DMC solvents.

Infrared absorption spectra were recorded ex-situ, with a PerkinElmer Spectrum 100 FTIR system inside a nitrogen-purged

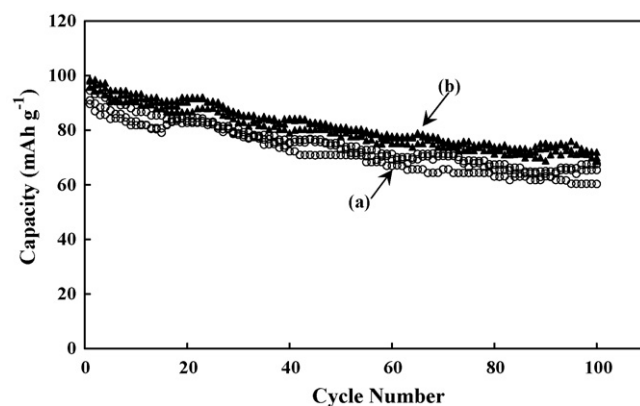


Fig. 2. Cycling performance of LiFePO_4 electrodes at room temperature in 1.2 mol dm^{-3} LiPF_6 EC-DMC (1:1) solution (a) without and (b) with $0.028 \text{ mol dm}^{-3}$ TPFPB. Charge/discharge at 1 C rate. Voltage range: 2.5–4.2 V.

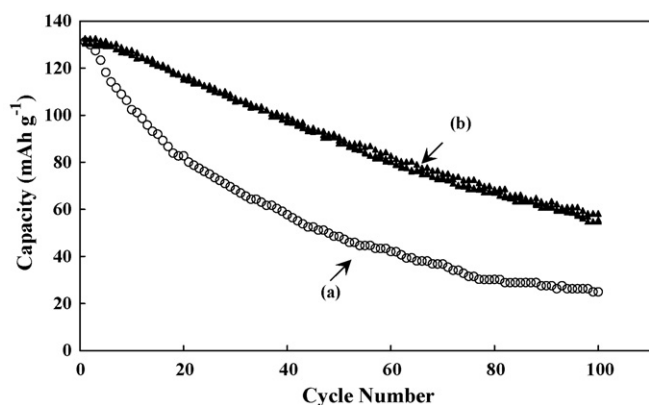


Fig. 3. Cycling performance of LiFePO₄ electrodes at 60 °C in 1.2 mol dm⁻³ LiPF₆ EC-DMC (1:1) solution (a) without and (b) with 0.028 mol dm⁻³ TFPFB. Charge/discharge at 1 C rate. Voltage range: 2.5–4.2 V.

glove bag. The samples were cycled for 100 cycles. Working inside of the glove box, the cell was disassembled from the coin cell and the electrode was rinsed with DMC to remove the salts. The electrode was dried under vacuum at room temperature for 24 h. All spectra were recorded at room temperature using an attenuated total reflectance (ATR) mode with a resolution of 2 cm⁻¹ and a total of 128 scans. Surface morphology of the LiFePO₄ electrodes were evaluated by scanning electron microscope (SEM, JEOL JSM35 operating at 20 kV). X-ray diffraction patterns of the samples were recorded using a CuK_{α1} beam ($\lambda = 0.15406$ nm) with a Rigaku Dmax-2400 automobile diffractometer. The diffraction data were collected for 3 s at each 0.02° step width over a 2 θ range from 20° to 60°.

3. Results and discussion

The effects of the TFPFB additive on the electrochemical behaviors of the LiFePO₄ electrode in the LiPF₆-based electrolyte were obtained by cyclic voltammetry. Typical first and second consecutive CVs of the LiFePO₄ electrode in the 1.2 mol dm⁻³ LiPF₆ EC/DMC electrolyte with and without 0.028 mol dm⁻³ TFPFB are shown in Fig. 1(I) and (II), respectively. There is only one peak pair, consisting of one anodic peak (charge) and one cathodic peak (discharge), which corresponds to the two-phase charge/discharge reaction of the Fe³⁺/Fe²⁺ redox couple. The fact that the first and second anodic peaks do not overlap may relate to the improvement in the impregnation of the solution into the composite (porous) electrode from the first to the second anodic polarization. The non-overlap may also relate to fractures in the carbon coating that occur during the first delithiation of the material, which implies that electrode reactivity is improved during the initial cycling. These results are in good agreement with what has been reported [24]. The reproducibility of the peaks in the CV plots confirms the good reversibility of lithium extraction/insertion reactions in the LiFePO₄ electrodes. Examination of Fig. 1(II) shows that oxidation peaks at 3.61 and 3.67 V and reduction peaks at 3.23 and 3.18 V of LiFePO₄ electrodes are clearly resolved in the electrolyte without and with 0.028 mol dm⁻³ TFPFB additives, respectively. During the initial two cycles, the cathodic peak of the LiFePO₄ electrodes in the electrolyte with TFPFB additives has a shift to a higher voltage and the anodic peak has a shift to a lower voltage, suggesting an increase in the redox potential separation. We believe this peak shift is related to the participation of TFPFB. More specifically, this result suggests that the addition of the anion receptor (TFPFB) can affect the lithium ion transfer rate and the interfacial properties of the passivation films. It is demonstrated that TFPFB is involved in the passivation reactions of the LiFePO₄ electrode during the initial charge process.

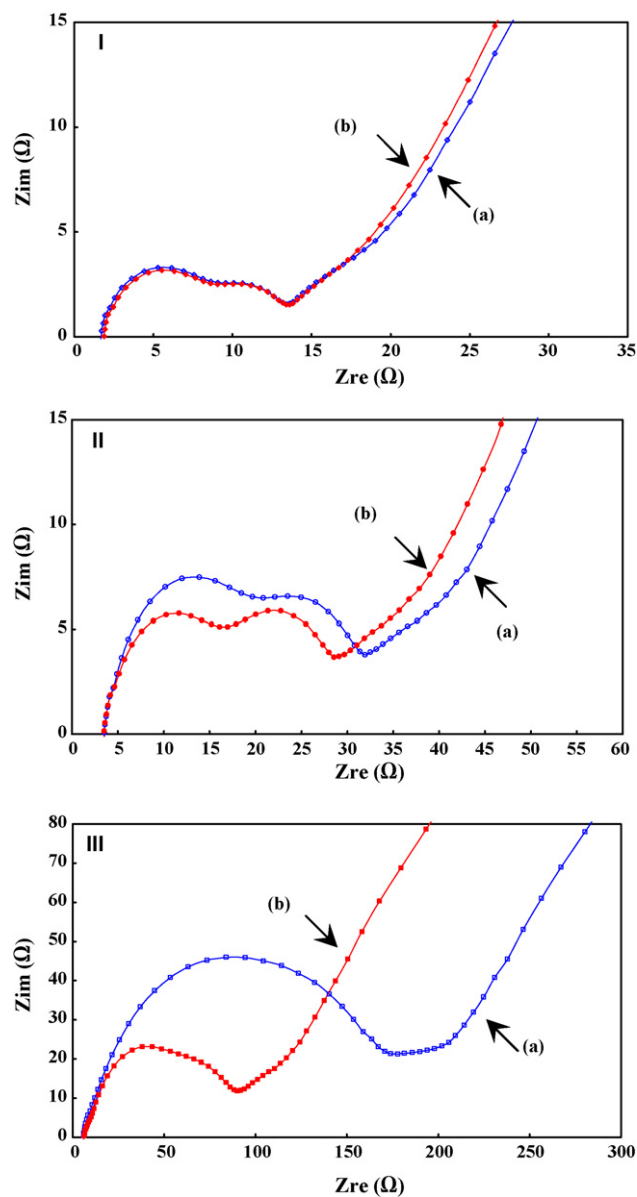


Fig. 4. Impedance spectra of fully charged LiFePO₄ electrodes ((I) after 1st 0.1 C charge/discharge cell, (II) after 100 cycles 1.0 C charge/discharge cell at room temperature, (III) after 100 cycles 1.0 C charge/discharge cell at 60 °C) in 1.2 mol dm⁻³ LiPF₆ EC-DMC (1:1) solution (a) without and (b) with 0.028 mol dm⁻³ TFPFB. Frequency range: 0.01 Hz and 10⁶ MHz.

To further confirm the effect of the TFPFB on improving the cycling performance of the LiPF₆-based electrolyte at elevated temperatures, Li/LiFePO₄ cells with the 1.2 mol dm⁻³ LiPF₆ EC/DMC electrolyte and the composite electrolyte containing 0.028 mol dm⁻³ TFPFB were cycled at 1 C rate under constant current conditions. The experiments were run at both room temperature and 60 °C. Fig. 2 shows the capacity variation of the Li/LiFePO₄ cells cycled at room temperature. The cell with the composite LiPF₆-based electrolyte displays around 20% capacity loss at the 100th cycle, which is identical to that obtained from the cell with the 1.2 mol dm⁻³ LiPF₆ EC/DMC electrolyte. This indicates that the presence of TFPFB additive does not have any adverse effect at room temperature on either electrochemical stability of the electrolyte or compatibility with the LiFePO₄ cathode. Fig. 3 compares the variation of capacity vs. cycle number obtained from Li/LiFePO₄ cells with the 1.2 mol dm⁻³ LiPF₆ EC/DMC electrolyte and the composite electrolyte with 0.028 mol dm⁻³ TFPFB when cycled at 60 °C.

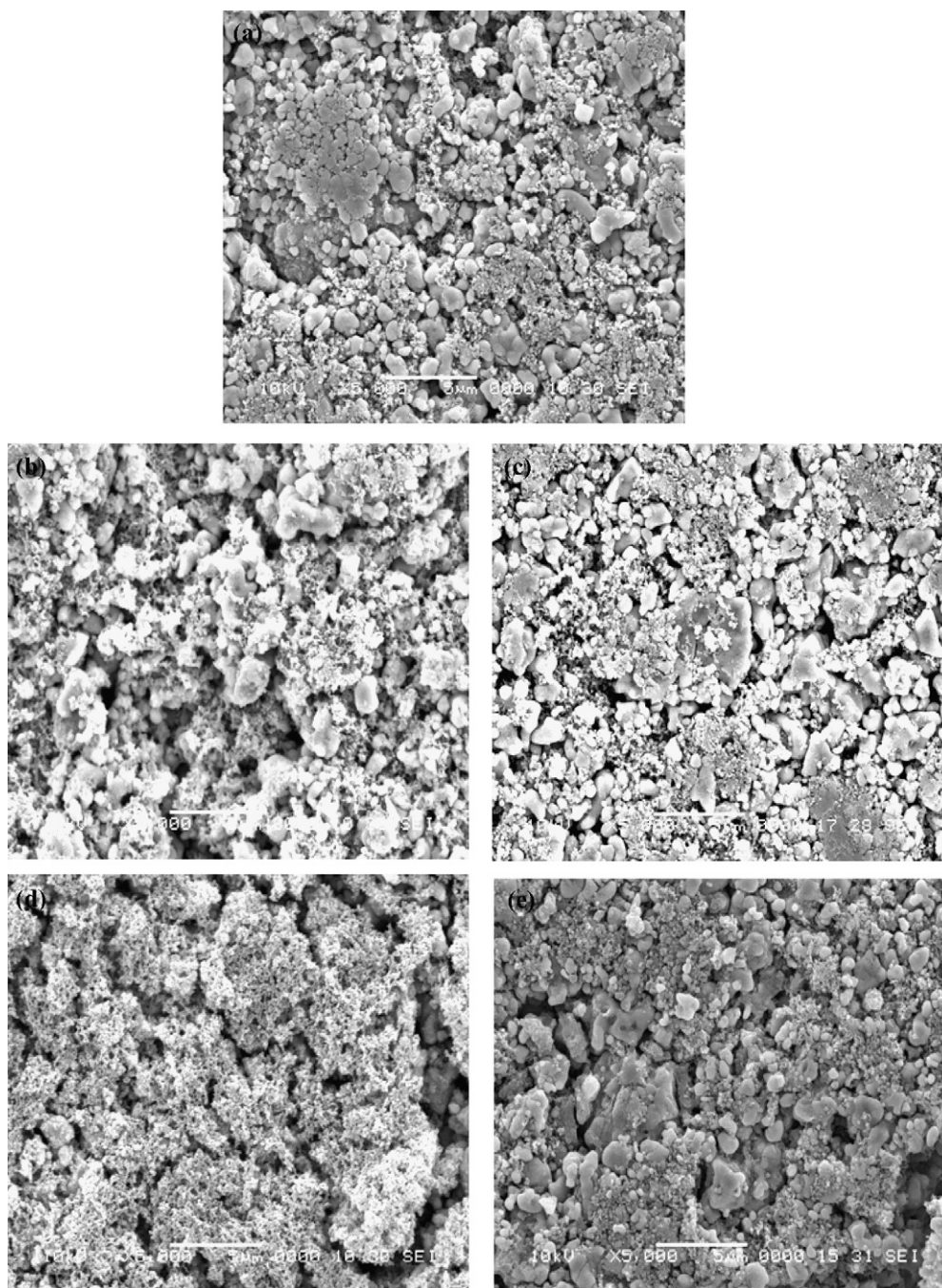


Fig. 5. SEM micrographs of the LiFePO_4 electrode: (a) pristine, (b) after 100 cycles at room temperature in 1.2 mol dm^{-3} LiPF_6 EC-DMC (1:1) solution, (c) after 100 cycles at room temperature in 1.2 mol dm^{-3} LiPF_6 EC-DMC (1:1) solutions with $0.028 \text{ mol dm}^{-3}$ TFPFB, (d) after 100 cycles at 60°C in 1.2 mol dm^{-3} LiPF_6 EC-DMC (1:1) solution, (e) after 100 cycles at 60°C in 1.2 mol dm^{-3} LiPF_6 EC-DMC (1:1) solution with $0.028 \text{ mol dm}^{-3}$ TFPFB. The magnification is $\times 5000$.

The cell with the composite electrolyte containing $0.028 \text{ mol dm}^{-3}$ TFPFB lost only 53.8% capacity in 100 cycles, while the cell with the 1.2 mol dm^{-3} LiPF_6 EC/DMC electrolyte lost 76.9% capacity. This result clearly shows that the TFPFB additive maintained excellent electrochemical stability of the LiPF_6 -based electrolyte at 60°C . Apparently, the capacity retention of the Li/LiFePO₄ cells was improved by the addition of TFPFB. The improvement in capacity retention may be related to a new passivation film composition comprising less LiF because of the participation of TFPFB.

Our results show that when TFPFB is combined with the 1.2 mol dm^{-3} LiPF_6 in EC:DMC (1:1 by weight) electrolyte, the capacity fading at the end of discharge is reduced. Chung et al. [20] reported observing that for a LiMn_2O_4 cathode obtained

from a disassembled cell where significant fading had occurred through multiple cycling at 55°C , the lost capacity could be partially restored after solvent washing. This suggests the possibility that electrolyte decomposition leads to LiF precipitation on the surface of the cathode. Thus stabilizing the electrolyte with additives may be an effective way to reduce LiF precipitation and resulting capacity loss on cycling. Chen and Amine [25] reported that a small amount (1.0 wt%) of TFPFB additive did not influence the differential capacity profile on a graphite anode, but Chen's interpretation assumed that the added TFPFB was just enough to dissolve the LiF in the SEI layer on the graphite, and hence had no direct impact on the decomposition of the salt anion. Decreased LiF concentration in the SEI layer as a result of TFPFB addition was also

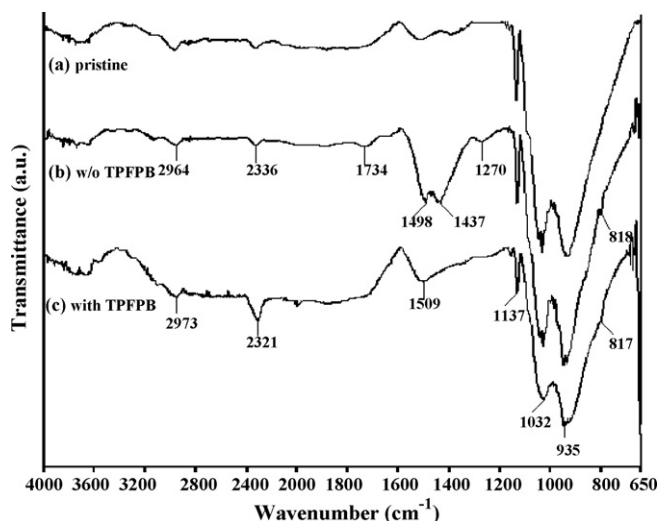


Fig. 6. FTIR spectra of (a) pristine LiFePO₄, (b) LiFePO₄ electrode after 100 cycles at RT in 1.2 mol dm⁻³ LiPF₆ EC-DMC (1:1) solution, (c) LiFePO₄ electrode after 100 cycles at RT in 1.2 mol dm⁻³ LiPF₆ EC-DMC (1:1) solutions with 0.028 mol dm⁻³ TFPFB.

reported by Herstedt et al. [18]. Herstedt further reported that, with 0.2 mol dm⁻³ TFPFB in 0.8 mol dm⁻³ LiBF₄ EC:DEC (2:1) electrolyte, the SEI layer formed on the graphite anode consisted of: (i) less LiF; (ii) more solvent reduction products; (iii) no Li₂CO₃. These results show that 0.2 mol dm⁻³ TFPFB is able to lower LiF formation. The absence of Li₂CO₃ further suggests that the capture of F⁻ ions by TFPFB provides an environment which stabilizes lithium alkyl carbonates [18]. However, excess TFPFB can facilitate the decomposition of lithium salt (LiPF₆) and generate PF₅ [23], which is well known to have negative consequences to both cathode and anode materials.

AC impedance data for the Li/LiFePO₄ cells with and without anion receptor (TFPFB) after one cycle at room temperature, after 100 cycles at room temperature and after 100 cycles at 60 °C are shown in Fig. 4(I)–(III), respectively. The AC impedance was measured after the cells were constant-current (0.1 C) charged to 4.2 V. Clearly, the interfacial impedances of the cells were not changed for the cells with/without TFPFB after the formation cycles at 25 °C. However, the cell impedance after 100 cycles at room temperature in electrolyte with TFPFB additive was smaller than without additive. The increase in cell impedance after 100 cycles at 60 °C was significantly greater than after 100 cycles at room temperature. Specifically, the SEI resistance at room temperature after 100 cycles was 18.84 Ω without additive and 18.00 Ω with TFPFB. In contrast, the SEI resistance at 60 °C after 100 cycles was 143.4 Ω without additive and 67.6 Ω with TFPFB. We believe that the added TFPFB participates in the formation of passivation films, dissolves LiF formed during SEI formation on the LiFePO₄ surface when cycled at both room temperature and 60 °C, and that TFPFB assists in transportation of lithium ions through passivation films on the LiFePO₄ surface. As is well known that LiF is a nonconductor for both electrons and lithium ions. Therefore, the dissolution of LiF from the passivation films can result in lower interfacial impedance. However, it seems that TFPFB has a dual role in the formation of the passivation film.

Surface analysis of the LiFePO₄ electrodes was obtained after the cycling test of the coin-type cells. Fig. 5 shows SEM micrographs of a pristine LiFePO₄ electrode and also of electrodes after cycling in the electrolyte with/without TFPFB additive at room temperature and at 60 °C as indicated. SEM imaging of the pristine electrode clearly shows LiFePO₄ particles with an average size of a few μm and also nano-size conductive carbon. The SEM micrographs in Fig. 5(b) and (d) of the LiFePO₄ electrodes with electrolyte

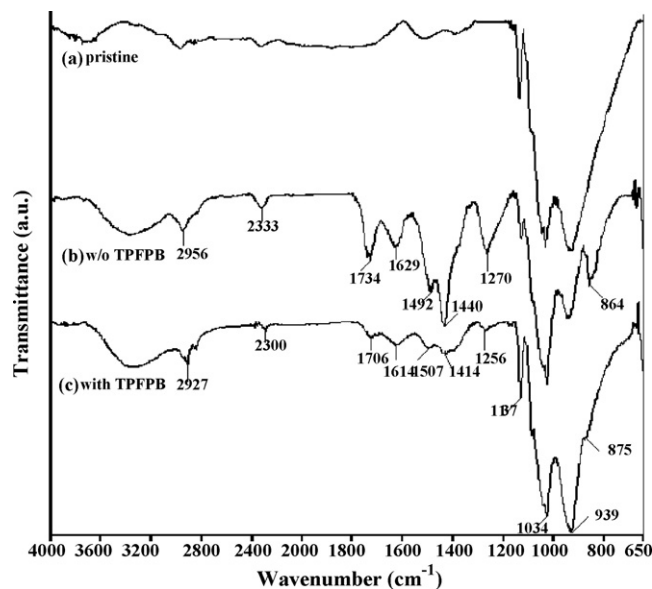


Fig. 7. FTIR spectra of (a) pristine LiFePO₄, (b) LiFePO₄ electrode after 100 cycles at 60 °C in 1.2 mol dm⁻³ LiPF₆ EC-DMC (1:1) solution, (c) LiFePO₄ electrode after 100 cycles at 60 °C in 1.2 mol dm⁻³ LiPF₆ EC-DMC (1:1) solution with 0.028 mol dm⁻³ TFPFB.

without TFPFB additive have fluff-like material on the electrode surface. The fluff-like material is seen to increase with increasing cycling temperature. The fluff-like material on the electrode surface may be a kind of SEI which is produced from electrolyte decomposition on LiFePO₄ electrode surface, forming thick residue films. The morphologies of the LiFePO₄ electrodes as seen in Fig. 5(c) and (e) result from cycling at 60 °C in electrolyte with TFPFB and appear similar to the morphology of the pristine electrode in Fig. 5(a).

We then compared the electrode surfaces by FTIR spectroscopy, using the diffuse reflectance mode. FTIR is a useful tool to probe the local composition of the surface layer because the vibrations of the molecular units of the LiFePO₄ lattice are responsible for absorption bands in the spectrum even when the material is disordered [26]. Fig. 6 displays the FTIR patterns of the LiFePO₄ cathodes for the following conditions: pristine, after 100 cycles at room temperature in LiPF₆-based EC/DMC electrolyte, after 100 cycles at room temperature in LiPF₆-based EC/DMC electrolyte with 0.028 mol dm⁻³ TFPFB, being shown, respectively, as Fig. 6 curves (a)–(c). FTIR spectrum (Fig. 6 curve (a)) for olivine FePO₄ exhibits a broad maximum between 900 and 1200 cm⁻¹ which can be assigned to P–O vibrations of the PO₄³⁻ polyanion [27,28]. The absorption at 1137 cm⁻¹ originates from symmetric and anti-symmetric stretching vibrations of O–P–O. Because the difference of the two vibrations is extremely small, there is only one peak at 1137 cm⁻¹ [27,29]. The absorption at 1034–1096 cm⁻¹ originates from symmetric stretching vibration of P–O [27,29]. The absorption at 939 cm⁻¹ originates from P–O stretching vibration [27,29]. These data suggest that the post-run cell's (FePO₄) olivine is still at the same position, but a little distortion has occurred due to the interaction between LiFePO₄ and electrolyte. The FTIR patterns of Li₂CO₃ groups around 1500–1420 cm⁻¹ agree well with the results of Aurbach [7,30]. The spectrum shown in Fig. 6(b) is for the electrode cycled without TFPFB at room temperature and, unlike the other obtained spectra, contains peaks around 1500–1420 cm⁻¹.

Whereas Fig. 6 showed the room-temperature FTIR curves, Fig. 7 displays the 60 °C FTIR curves, again for cathodes of the conditions: pristine, after 100 cycles at 60 °C in LiPF₆-based EC/DMC

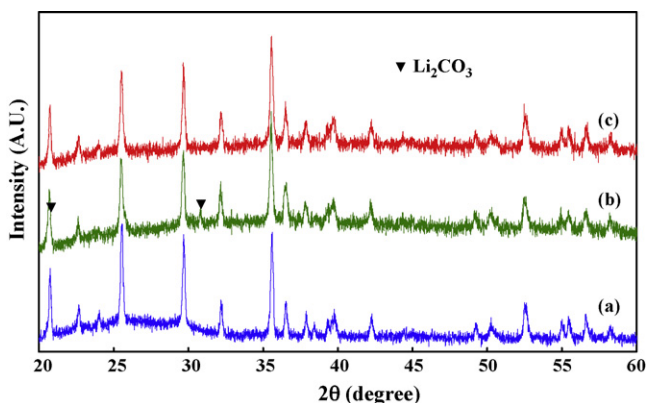


Fig. 8. X-ray diffraction patterns LiFePO₄ electrodes. (a) Pristine LiFePO₄, (b) LiFePO₄ electrode after 100 cycles at 60 °C in 1.2 mol dm⁻³ LiPF₆ EC-DMC (1:1) solution, (c) LiFePO₄ electrode after 100 cycles at 60 °C in 1.2 mol dm⁻³ LiPF₆ EC-DMC (1:1) solution with 0.028 mol dm⁻³ TFPFB.

electrolyte, after 100 cycles at 60 °C in LiPF₆-based EC/DMC electrolyte with 0.028 mol dm⁻³ TFPFB, respectively, as Fig. 7 curves (a)–(c). The intensity of absorption at 939 cm⁻¹ on the LiFePO₄ electrode cycled at 60 °C was reduced for the without-TFPFB case, whereas the with-TFPFB case under cycling at either room temperature or 60 °C showed essentially the same absorption intensity. The reduction may be due to surface P–O bonds resulting from LiFePO₄ reaction with electrolyte components such as LiPF₆, EC, etc., forming PO_yF_z or P–F. Electrolyte LiPF₆-based EC/DMC has been shown to react with the specimen after cycling, giving rise to stretching mode C=O around 1700–1600 cm⁻¹, bending mode Li_xPO_yF_z around 1300–1100 cm⁻¹ and LiF around 1300–1100 cm⁻¹ [31]. The peaks around 885–850 cm⁻¹ may be attributed the species with P–F bonds [11]. The FTIR pattern of Fig. 7(b) contains significant peaks indicating Li₂CO₃ groups around 1500–1420 cm⁻¹ in consequence of 60 °C cycling in the LiPF₆-based EC/DMC electrolyte without TFPFB additive.

Fig. 8 shows the XRD patterns of the LiFePO₄ cathode specimens for the conditions: (a) pristine; (b) after 100 cycles at 60 °C in LiPF₆-based EC/DMC electrolyte; (c) after 100 cycles at 60 °C in LiPF₆-based EC/DMC electrolyte with 0.028 mol dm⁻³ TFPFB. This figure shows no pronounced changes in the bulk structure of the LiFePO₄ electrode after cycling at elevated temperature (60 °C) with/without TFPFB additive in the electrolyte. The XRD data of Fig. 8 curve (b) shows that some smaller Li₂CO₃ peaks are present. We conclude then that the LiFePO₄ reaction with the electrolyte that causes the P–O bond changes observed from the FTIR data (Fig. 7 curve (b)) does not affect the bulk electrodes and thus probably relates to surface phenomena.

Upon cycling, the cathode materials reacted with the electrolyte and, according to the FTIR data, formed different functional groups such as C=O, Li₂CO₃, CO, CH₂, CH₃, OCO₂⁻, etc. These FTIR spectra may reflect polymerization of the solvent molecules to derivatives of polyethylene oxide and polycarbonates on LiFePO₄ electrode surface. The impedance of the LiFePO₄ cells increased after cycling in the electrolyte with/without TFPFB additive at elevated temperature (60 °C), but the impedance increase was significantly more serious. SEI resistance after 100 cycles at room temperature was 18.84 Ω without additive and 18.00 Ω with TFPFB, whereas SEI resistance after 100 cycles at 60 °C was 143.4 Ω without additive and 67.6 Ω with TFPFB additive. It is concluded that TFPFB additive can reduce the polymerization reaction and LiF precipitation on LiFePO₄ electrode surfaces.

4. Conclusion

It is demonstrated that TFPFB can be an effective electrolyte additive to improve the cycle life and power capabilities of LiFePO₄ cathodes. When 0.028 mol dm⁻³ tris(pentafluorophenyl) borane compound is added to the 1.2 mol dm⁻³ LiPF₆ in EC:DMC (1:1 by weight) electrolyte, the capacity fading at the end of discharge is reduced. A Li/LiFePO₄ cell with a composite LiPF₆-based electrolyte containing 0.028 mol dm⁻³ TFPFB additive also exhibits much higher capacity retention and cycling efficiency at 60 °C than the same cell under the same conditions but without the additive. The LiFePO₄ electrode cycled at 60 °C in 1.2 mol dm⁻³ LiPF₆ EC/DMC electrolyte forms a fluff-like material on the electrode surface, causing capacity fading in the LiFePO₄/Li cell. The fluff-like material is formed by electrolyte decomposition on the LiFePO₄ surface, producing compounds like Li₂CO₃, LiF, etc., as confirmed by XRD and FTIR. TFPFB presence in electrolyte eliminates the fluff-like material and reduces the resistance of SEI films in the LiFePO₄/Li cell. TFPFB is believed to participate in the formation of passivation films on LiFePO₄ electrode surface and in the dissolution of LiF in the films during cycling. TFPFB is also believed to improve the transport of lithium ions through the passivation films. TFPFB is an effective electrolyte additive to improve the high temperature performance of LiFePO₄ cells.

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