



Short communication

Tris(trimethylsilyl) borate as electrolyte additive to improve performance of lithium-ion batteries

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ABSTRACT

Tris(trimethylsilyl) borate (TMSB) used as new electrolyte additive to improve performance of LiFePO₄ based lithium-ion battery is investigated in this paper. The effects of the TMSB on the LiFePO₄ electrode are investigated via a combination of electrochemical impedance spectroscopy (EIS), cyclability, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). It is found that the LiFePO₄ battery with a composite LiPF₆-based electrolyte containing 1 wt% TMSB additive exhibits higher discharge retention and better cycling performance than the battery without TMSB additive at both 30 °C and 55 °C. SEM and XPS measurements show the changes of surface morphology and formation of solid electrolyte interface (SEI). EIS results indicate that the interfacial impedances of the batteries after cycled at 55 °C with the electrolyte containing TMSB additive are significantly smaller than the batteries without additive. The improved performances are ascribed to the enhancement of the thermal stability of the electrolyte and the modification of SEI component on the LiFePO₄ electrode.

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1. Introduction

With the increasing demands for portable electronic devices, electric vehicles (EVs) and hybrid EVs applications, numerous studies have been done to develop lithium-ion battery (LIB) with high rate capacity and long cycle life [1,2]. However, most of the works were under the strategy of improving Li⁺ ions moving in the electrode materials [3,4]. Actually, the electrolyte used in the LIB is a crucial factor influencing the performance of the batteries. Since the first commercialization of LIB by Sony in 1990, most of the current commercial electrolytes are based on dissolving lithium hexafluorophosphate (LiPF₆) salt into some alkyl carbonate solvents, such as ethylene carbonate, dimethyl carbonate and diethyl carbonate. However, the thermal and hydrolytic stability of LiPF₆ is very poor. It is more sensitive to even trace amount of moisture, which will lead to the decomposition of the LiPF₆ into the electrolyte: LiPF₆ (sol) → LiF (s) + PF₅ (sol) [5–7]. The generated LiF will reduce both conductivity and numbers of free Li⁺ ions, and the PF₅ produced from both the thermal and hydrolytic decompositions will easily cause the alkyl carbonate solvents to be polymerized, which then will reduce the performance of the LIBs [8,9]. Although many salts such as LiAsF₆ [10], LiClO₄ [11] and LiBF₄ [12] have been synthesized in recent years, none of them

can surpass LiPF₆ due to its superior combination of high conductivity in various organic solvents, a wide electrochemical stability window, and its ability to passivate Al and prevent current collect corrosion of the cathode [13,14]. Therefore, it is important to improve the stability of LiPF₆-based electrolyte for lithium batteries.

Use of electrolyte additives is one of the most economic and effective methods to improve the performance of LIB with LiPF₆-based electrolyte. Tasaki and Nakamura suggested that promotion of ion pair dissociation of LiPF₆ may prevent thermal decomposition of LiPF₆ [15]. From their molecular dynamic simulations, it was found that the average distance between Li⁺ cation and F atom in the PF₆⁻ anion in the presence of anion receptor was much larger than the absence of the anion receptor. This enlarged distance will suppress the reactivity of the Li⁺ cation and F atom. Therefore, the anion receptor used as the electrolyte additive is a more attractive approach to improve the stability of the LiPF₆-based electrolyte [14–18]. Sun et al. synthesized tris(pentafluorophenyl)borane (TPFPB) as an anion receptor additive for LIB electrolytes [14]. Due to the electron deficient characteristic of fluorinated boron of TPFPB, the boron-based anion receptor additive improved the thermal stability of the LiPF₆-based electrolyte. The LiMn₂O₄/Li cell with the LiPF₆-based electrolyte containing 0.1 mol dm⁻³ TPFPB additive exhibited superior capacity retention and cycling efficiency at 55 °C than the cell without additive. Recently, some researchers found that TPFPB as electrolyte additive into the LiPF₆-based electrolyte also improved the

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power capability [16,17] and high rate performances of the LIBs [18].

In this paper, a new boron-based anion receptor, tris(trimethylsilyl)borate (TMSB), was used as electrolyte additive to improve the performance of LiFePO_4 based lithium-ion battery with the LiPF_6 -based electrolyte. The effects of the TMSB on the improvement of electrolyte thermal stability and cycle life of the LiFePO_4 based lithium-ion battery were investigated via a combination of electrochemical impedance spectroscopy (EIS), cyclability, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

Battery-grade TMSB was obtained from Fujian Chuangxin Science and Technology Develops Co., Ltd., China, and used without further purification. Battery-grade EC, DMC and LiPF_6 were purchased from Shenzhen Capchem Chemicals Co., Ltd., China, and used without further purification. The electrolytes of 1 mol dm^{-3} LiPF_6 in a 1:1 (weight ratio) EC/DMC with and without 1 wt% TMSB additive were prepared in an argon-filled glove box, in which the oxygen and water content were less than 1 ppm.

LiFePO_4 electrode materials with carbon treatment were purchased from Pylon Technologies Co., Ltd., China. The LiFePO_4 electrodes were prepared by mixing the LiFePO_4 powder (90 wt%), 5 wt% carbon black and 5 wt% poly(vinylidene fluoride) (PVDF) in N-methylpyrrolidone (NMP) solvent. The mixed slurry was then coated onto aluminum foil collector and vacuum dried at 120°C for 2 h. The dried electrode was compressed by a roller at room temperature to make a smooth and compact film structure. Then the electrode disks (1.5386 cm^2) were punched out of the larger coated foil sheets and weighted. $\text{LiFePO}_4/\text{Li}$ half cells were fabricated with 2016-coin type cells in the argon-filled glove box using Celgard 2400 as separator. The charge–discharge behavior of the cells was tested on Land CT2001A tester (Wuhan, China) at the constant current mode over the range of 2.5–4.2 V. The constant current modes of 1.0 C and 0.5 C were carried out at 30°C and 55°C , respectively. At the initial and last cycled galvanostatic measurement, electrochemical impedance spectroscopy (EIS) was observed immediately at the full charged condition. EIS was investigated 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 0.1 Hz to 1 MHz.

To analyze the composition and microstructure of the electrodes after charge–discharge cycling measurements, the cells were disassembled in a glove box under Ar atmosphere. The LiFePO_4 electrodes were washed with anhydrous DME solvent 5 times to remove residual EC and LiPF_6 followed by vacuum drying for 2 h at room temperature. Scanning electron microscope (SEM, Ultra 55, Carl Zeiss) was used to investigate the morphology of the electrodes. X-ray photoelectron spectroscopy (XPS) tests were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). The X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54° . The pass energy was fixed at 93.90 eV to ensure sufficient resolution and sensitivity. Binding energies were calibrated by using the containment carbon ($\text{C}1s = 284.6 \text{ eV}$). Peak assignment was made based on detailed curve fitting of the recorded spectra using Gaussian–Gauss2 peak shapes and a Shirley function background correction, together with reference measurements.

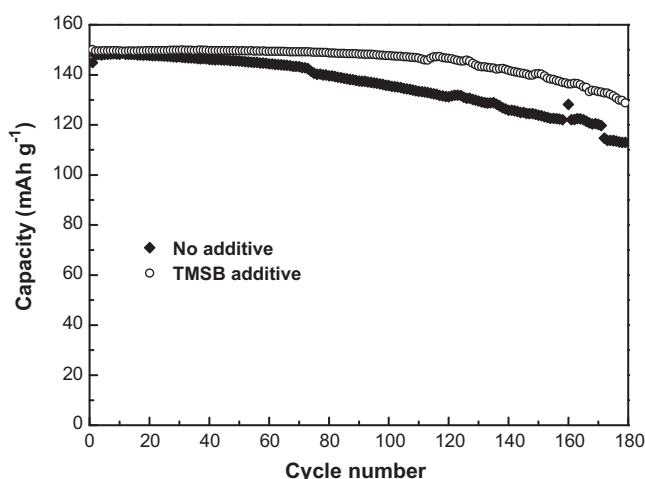


Fig. 1. Cycling performance of $\text{LiFePO}_4/\text{Li}$ cells using 1 mol dm^{-3} LiPF_6 in EC/DMC (1:1, w w^{-1}) as electrolyte with and without 1 wt% TMSB additive at 30°C . Charge–discharge rate was 1 C in the potential range of 2.5–4.2 V.

3. Results and discussion

The $\text{LiFePO}_4/\text{Li}$ half cells were constructed containing 1 mol dm^{-3} LiPF_6 in EC/DMC (1:1, w w^{-1}) composite electrolytes without or with the presence of 1 wt% TMSB additive. Fig. 1 shows the cycling performance of the cells at 30°C with the different electrolytes. The cells were tested by constant current mode of 1.0 C over the range of 2.5–4.2 V. The cell with the LiPF_6 -based composite electrolyte without additive displayed around 25% capacity loss at the 180th cycle, while the cell containing TMSB additive showed only 14% capacity loss at the same cycle number. Fig. 2 shows the cycling performance of the cells with the different electrolytes at 55°C . The cells were tested by constant current of 0.5 C during 2.5–4.2 V. The capacity fading of the cell without TMSB additive decreased to 76% of the initial capacity after 80th cycle, while the cell containing TMSB additive showed high capacity retention as 94% at the same cycle number. The cells with the composite electrolyte containing TMSB additive exhibit much more stable cycling performance than that the cells without additive, especially at elevated temperature. It indicates that TMSB additive will effectively improve the cycling performance of the cells. AC

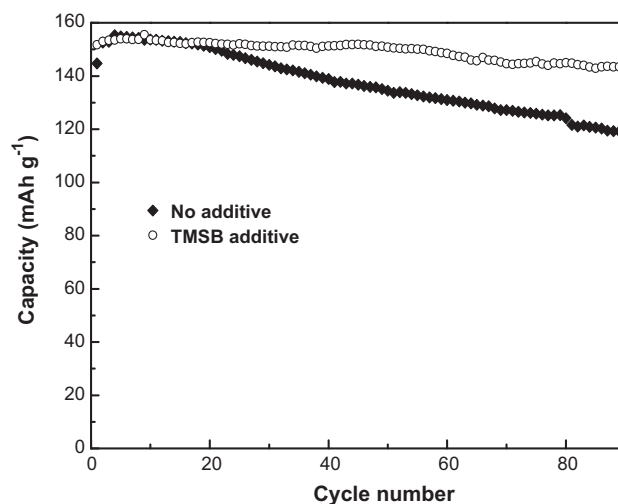


Fig. 2. Cycling performance of $\text{LiFePO}_4/\text{Li}$ cells using 1 mol dm^{-3} LiPF_6 in EC/DMC (1:1, w w^{-1}) as electrolyte with and without 1 wt% TMSB additive at 55°C . Charge–discharge rate was 0.5 C in the potential range of 2.5–4.2 V.

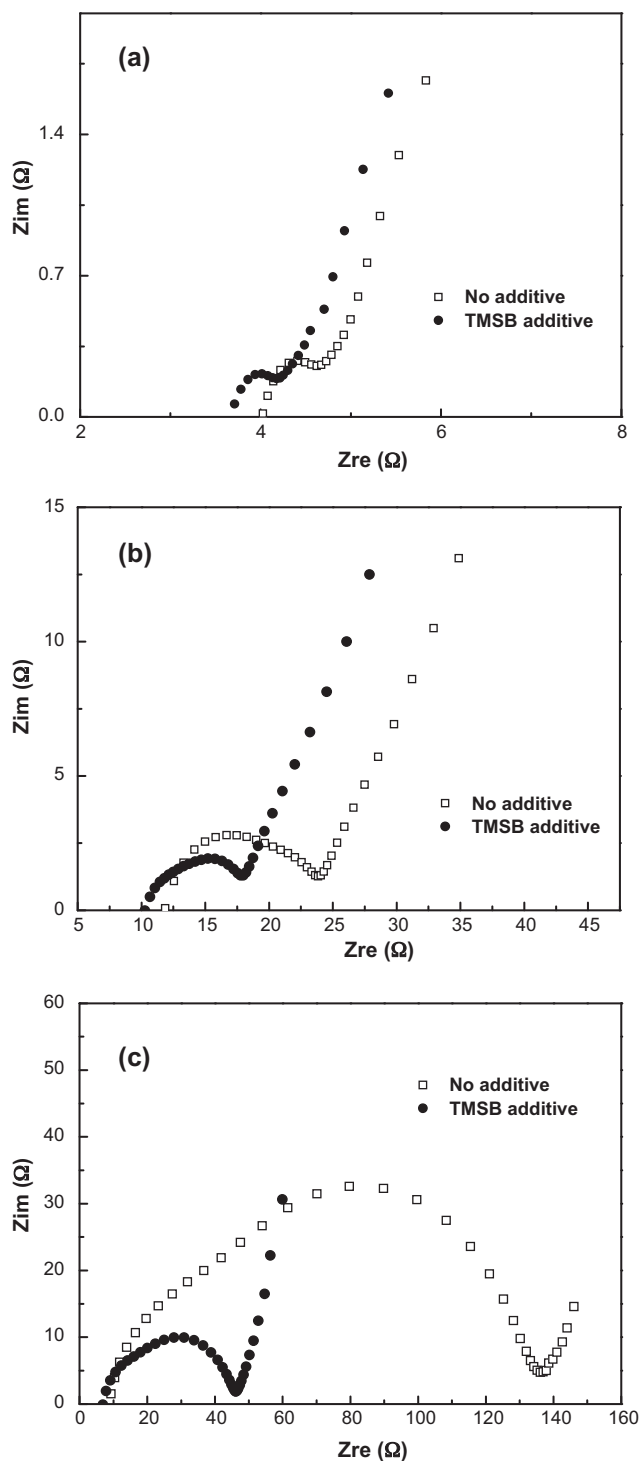


Fig. 3. Impedance spectra of full charged LiFePO₄/Li cells using 1.0 mol dm⁻³ LiPF₆ in EC/DMC (1:1, w w⁻¹) as electrolyte with and without 1 wt% TMSB additive: (a) after first 1.0C charged cell at 30 °C, (b) after 180 cycles 1.0C charged-discharged cell at 30 °C, (c) after 80 cycles 0.5C charged-discharged cell at 55 °C. Frequency range: 0.1–10⁶ Hz.

impedance, charge-discharge curves analyses and surface analyses of LiFePO₄ electrodes of the cells with the different composite electrolytes, as described below, provided insight into the sources of the difference in capacity retention.

AC impedance data of the LiFePO₄/Li cells with the different composite electrolytes are shown in Fig. 3. The impedance was measured after the cells were full charged and the

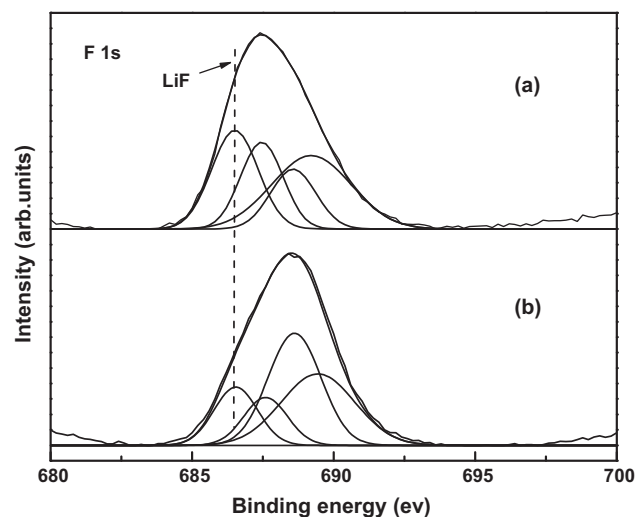


Fig. 4. F 1s spectra of LiFePO₄ electrodes after 80 cycles at 55 °C using 1.0 mol dm⁻³ LiPF₆ in EC/DMC (1:1, w w⁻¹) electrolyte (a) without and (b) with 1 wt% TMSB additive.

voltage was about 4.2 V. The interfacial impedances of the cells after the formation cycle at 30 °C with and without TMSB additive are 0.51 Ω and 0.63 Ω, respectively. It indicates that the interfacial impedances with different electrolyte are nearly same after the first charged condition at 30 °C. After 180 cycles at 30 °C, the interfacial impedance of the cell with TMSB additive (7.82 Ω) was smaller than the cell without the additive (12.10 Ω). Clearly, the increase of the cell impedance after 80 cycles at 55 °C was significant than the cell after 180 cycles at 30 °C. As shown in Fig. 3(c), after 80 cycles at 55 °C, the interfacial impedance of the cell with TMSB (39.26 Ω) is greatly smaller than the cell without additive (127.72 Ω). Lee et al. reported that the additive based on electron deficient borate or borate compounds with alkyl groups would coordinate with anion, which would suppress the thermal decomposition of LiPF₆ [14]. Chang and Chen found that the defined amount of TFPFB could dissolve the LiF from the SEI on the LiFePO₄ and then lower the interfacial impedance of the LiFePO₄/Li half cell at high temperature [16]. Both F1s spectra of the LiFePO₄ electrodes after 80 cycles at 55 °C with the different composite electrolytes are shown in Fig. 4. There are four peaks in both spectra. One peak at 686.50 eV is corresponding to LiF [19], the other three peaks at 687.45 eV, 688.50 eV and 689.92 eV may attribute to the salt and salt residues such as Li_xPF_y [20,21], Li_xPF_yO_z [22] and the C–F of PVDF [21], respectively. From Fig. 4, it is easily found that the intensity of the LiF (686.5 eV) peak of the LiFePO₄ electrode without TMSB additive is very higher than that of the electrode containing TMSB additive. It indicates that more LiF produced from the reaction were covered onto the surface of the LiFePO₄ electrode in the additive-free electrolyte. It is well known that the LiF is a nonconductor for both electrons and lithium ions. Therefore, the LiF covered onto the electrode would increase the interfacial impedance. This is the reason why the interfacial impedance of the cells with TMSB additive was smaller than that the cells without TMSB in our experiments. Therefore, we believe that the added TMSB may participate in the formation of the passivation films on the LiFePO₄ electrode, dissolve the LiF formed during the SEI formation of the cell, and assists in the transportation of the lithium ions through the passivation films.

The charge-discharge curves of the LiFePO₄/Li cells cycled at 30 °C and 55 °C are shown in Fig. 5 and Fig. 6, respectively. In Fig. 5, it is clearly found that capacity of the cell without additive faded more quickly than that the cell containing TMSB additive. Since both the resistances of the cells cycled at 30 °C are almost same, (see Fig. 3 (b)), the charge-discharge profiles of the cells with

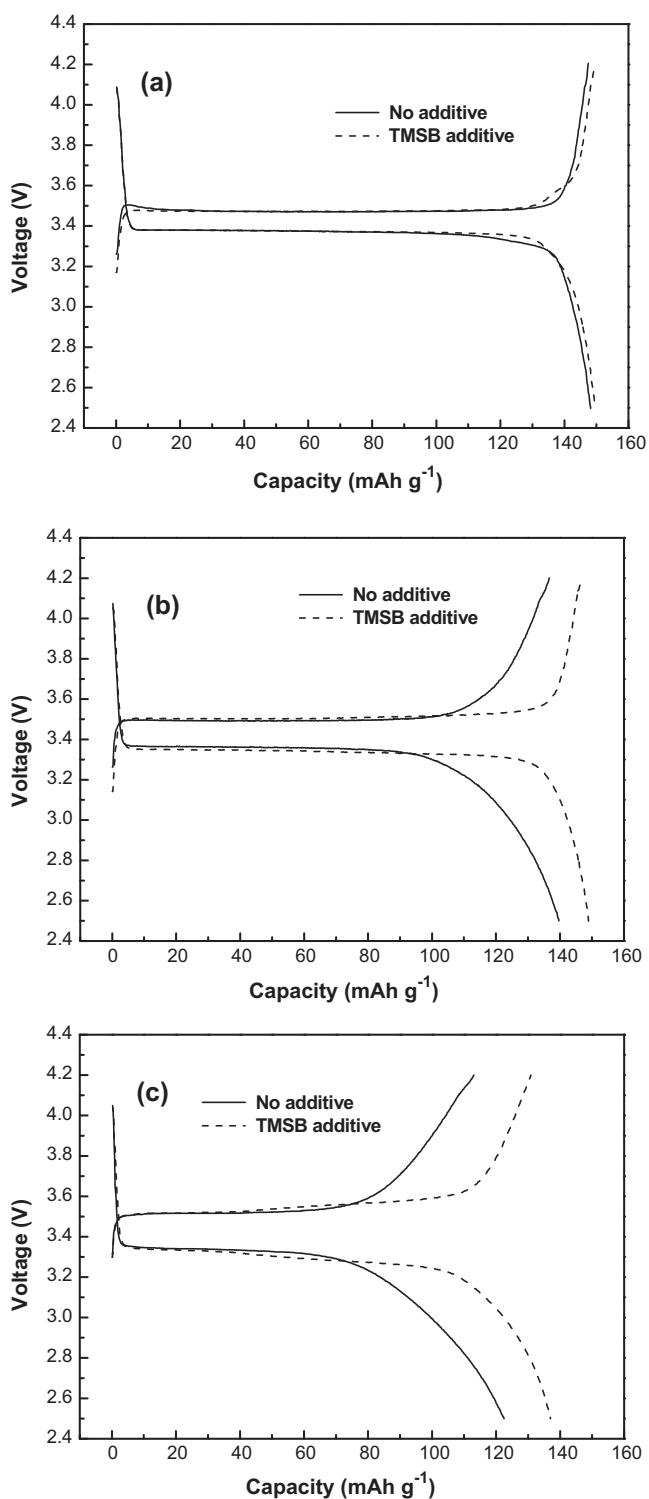


Fig. 5. Charge–discharge curves at 30 °C of LiFePO₄/Li cells using 1.0 mol dm⁻³ LiPF₆ in EC/DMC (1:1, w w⁻¹) electrolyte with and without 1 wt% TMSB additive: (a) 5th cycle, (b) 80th cycle and (c) 160th cycle.

the different composite electrolytes show nearly same. Compared with the cell cycled at 30 °C, there were significant changes of the charge–discharge profiles of the cells cycled at 55 °C. The change of charge–discharge platform of the cell without additive was larger than the cell containing TMSB additive (see Fig. 6). Unlike the cell with the composite electrolyte without additive, the cell with the

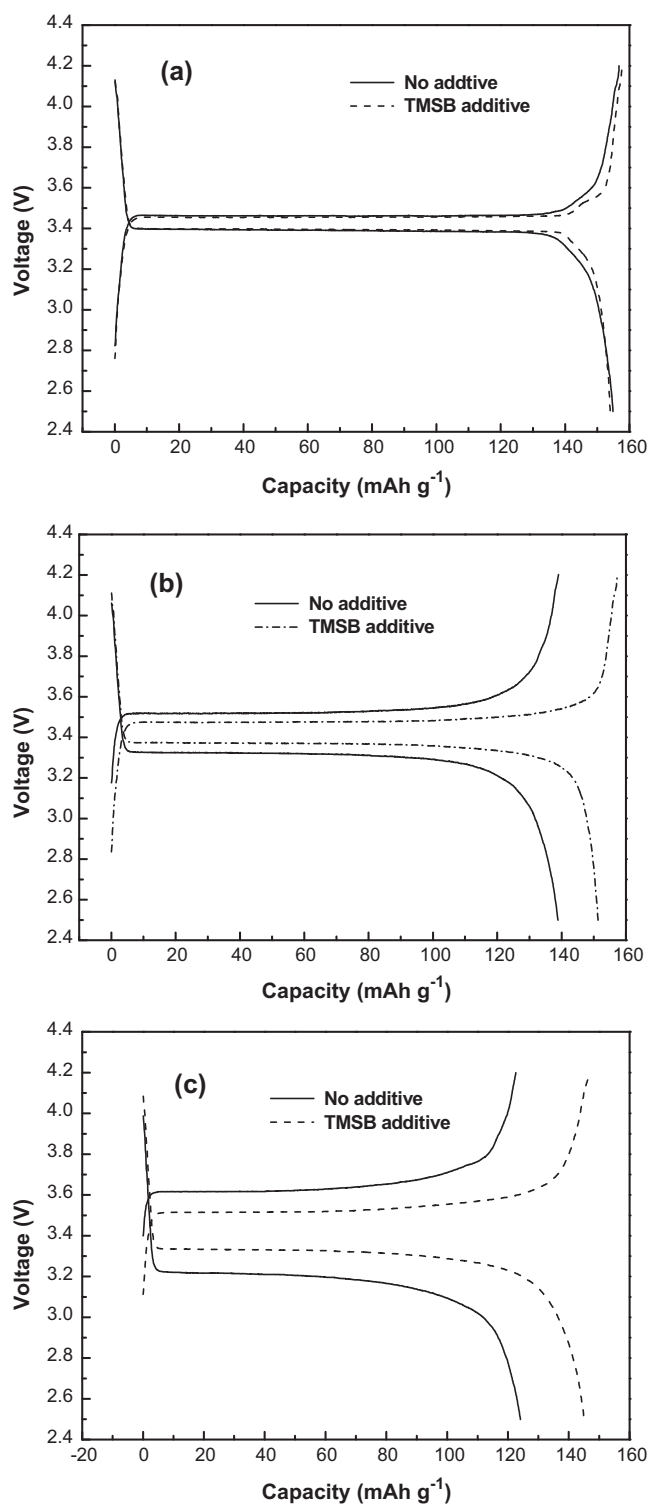


Fig. 6. Charge–discharge curves at 55 °C of LiFePO₄/Li cells using 1.0 mol dm⁻³ LiPF₆ in EC/DMC (1:1, w w⁻¹) electrolyte with and without 1 wt% TMSB additive: (a) 5th cycle, (b) 40th cycle and (c) 80th cycle.

composite electrolyte containing TMSB additive exhibited negligible polarization and smooth charge–discharge profiles.

To further investigate the effect of the TMSB on the LiFePO₄ electrode, surface analysis of the electrodes was obtained after the cycling test of the coin-type cells. Fig. 7 shows SEM micro-graphs of a pristine LiFePO₄ electrode and the electrodes after cycled with the different electrolytes at 55 °C. From the SEM measurements,

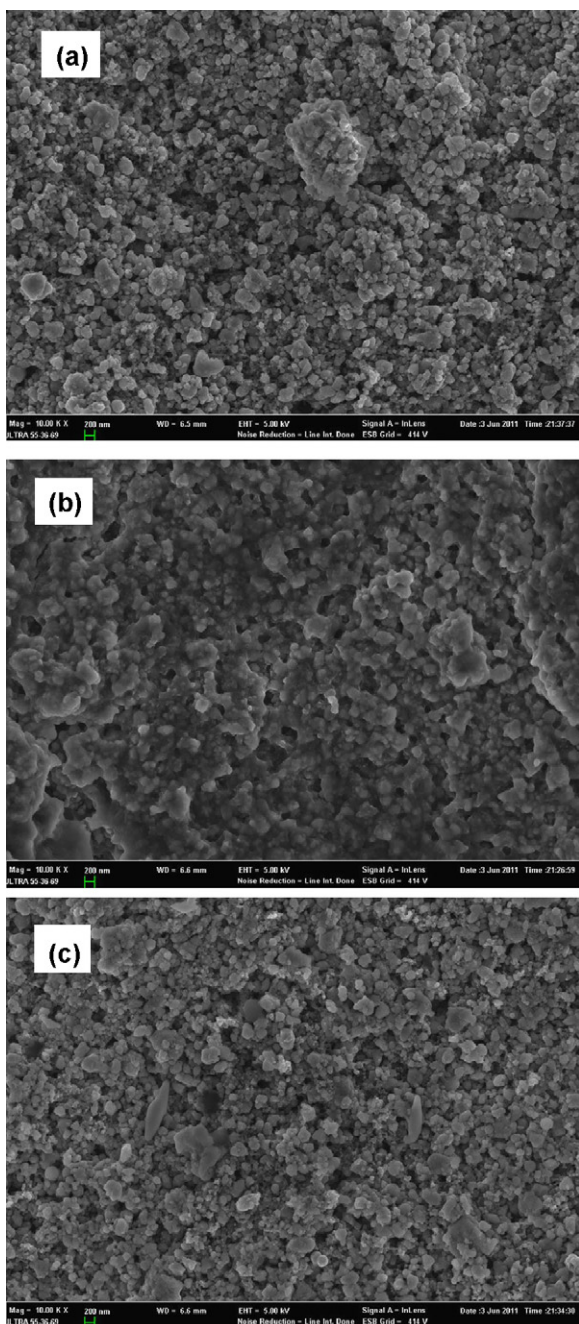


Fig. 7. SEM micrographs of LiFePO₄ electrode: (a) pristine, (b) after 80 cycles at 55 °C in 1.0 mol dm⁻³ LiPF₆ EC/DMC (1:1, w w⁻¹) electrolyte, (c) after 80 cycles at 55 °C in 1.0 mol dm⁻³ LiPF₆ EC/DMC (1:1, w w⁻¹) electrolyte containing 1 wt% TMSB additive.

it can be found that there were LiFePO₄ particles with an average size of a few μm and nano-sized conductive carbon into the pristine LiFePO₄ electrode. Compared with the pristine electrode, the morphology of the LiFePO₄ electrodes without TMSB after 80 cycles at 55 °C shows a significant change. There are many film materials covered onto the surface of the electrode. These film materials on the electrode surface may be a kind of SEI which was produced from electrolyte decomposition on the electrode surface, forming thick residue films. These thick film materials would increase the interfacial resistance of the cells, and thus result in lower the performance of the cells. The morphology of the LiFePO₄ electrodes with TMSB after 80 cycles at 55 °C as shown in Fig. 7 (c) appears similar to the morphology of the pristine electrode. These SEM

micro-graphs indicate that TMSB will effectively prevent the LiPF₆ composite electrolyte from decomposing onto the surface of the LiFePO₄ electrode, which resulted in improving performance of the cells.

In our experiments, we think there are two main functions of TMSB additive to improve performance of the cells. Since TMSB is an electron-deficient boron compound, it will easily combine with electron-rich materials such as PF₆⁻ and F⁻. The combination of TMSB-PF₆⁻ will enhance the ion pair dissociation of Li⁺ and PF₆⁻, which then will improve the thermal stability of LiPF₆ salts. In addition, it is well known that the LiPF₆ will be easily thermal or hydrolytic decompositions to the LiF and PF₅. The generated LiF salt would reduce both the conductivity and numbers of free Li⁺ ions, which then increase the resistance of the cell and bring about the fading of the cell capacity. The combination of the TMSB-F⁻ will improve the dissolvability of the LiF in the electrolyte, which will result in lower the interfacial impedance and improving the performance of the lithium battery.

4. Conclusion

It is demonstrated that TMSB can be an effective electrolyte additive to improve the cycling performance of LiFePO₄ based lithium battery with the LiPF₆-based electrolyte. When 1 wt% TMSB was added to the 1.0 mol dm⁻³ LiPF₆ in EC/DMC (1:1, w w⁻¹) electrolyte, the capacity fading of the cycled cells is obviously reduced, especially at elevated temperature. EIS show the interfacial impedance of the cycled LiFePO₄/Li cell with TMSB is lower than the cell without additive, especially cycled at 55 °C. The charge–discharge curves indicated that TMSB can effectively suppress the polarization of charge–discharge platform at 55 °C. One of the reasons is that TMSB will improve the dissolvability of the LiF in the electrolyte, which result in lower interfacial impedance. Another reason is the combination of TMSB-PF₆⁻ will not only enhance the ion pair dissociation of Li⁺ and PF₆⁻, but also improve the thermal stability of LiPF₆ salt. Therefore, TMSB would be a promising additive in improving cycling performance of lithium-ion battery.

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