

Tris (trimethylsilyl) Phosphate as Electrolyte Additive for Lithium - Ion Batteries with Graphite Anode at Elevated Temperature

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In this work, the tris(trimethylsilyl) phosphite (TMSP) was used as an electrolyte additive to improve the cycling performance of graphite anode at elevated temperature (60°C). The electrochemical properties were characterized by CV, galvanostatic cycling and EIS. The CV and galvanostatic cycling results showed as the concentration of TMSP added in the electrolyte was 5 vol. %, the graphite had good cycle stability to reach 332.27 mAh/g at 60°C, with a capacity retention of 96.1% after 70 cycles. SEM and EIS revealed that the TMSP additives effectively suppress the electrolyte decomposition and stabilized the SEI of the graphite at elevated temperature. In addition, the TMSP can drastically decrease the resistances of SEI and charge transfer at elevated temperature.

Keywords: lithium ion battery, electrolyte additive, tris(trimethylsilyl) phosphite, cycling performance, Electrochemical impedance spectroscopy

1. INTRODUCTION

Lithium-ion batteries (LIBs) are one of the most promising energy storage devices because of their high power and energy densities, long service life, and environmental friendliness, and thus have wide application in the area of consumer electronics, as well as well-suited for electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1, 2]. Automotive LIBs must operate within the safe and reliable operating area restricted by temperature and voltage windows. Great majority of automotive LIBs work at the temperature range from 55 to minus 20°C. However, LIBs would suffer poor cycling and capacity decaying because of decomposition of electrolyte at elevated temperature of 55°C or over, which is unstable thermodynamically at the high temperature [2]. Moreover, the electrolyte

decomposition is usually accompanied by the electrode destruction and SEI (solid electrolyte interface) film crack. So, the suppression of the electrolyte decomposition is vital to the electrochemical performance of LIBs at elevated temperature.

To date, several approaches toward the development of electrolytes for high temperature in LIBs have been explored. One way is to explore the high thermally stable lithium salts, for example LiBOB [3]/LiTFSI [4], flame retardant solvents, such as sulfone-based solvents [5, 6], dinitrile solvents [7, 8], ionic liquids [9-11] and so on. Unfortunately, these lithium salts and solvents suffer from high intrinsic viscosity and high resistance of the SEI, and severe reductive decomposition on carbonaceous anode materials [12-14]. The other is the use of functional electrolyte additive which is one of the most economic and most effective methods to improve electrochemical performance of LIBs at high temperature [15, 16]. Hung-Chun Wu *et al.* [15] reported that addition of vinylene carbonate (VC) in electrolyte solution has been found to greatly improve the high-temperature (55 °C) cycling performance of LIBs. Tae-Heum Nam *et al.* [16] confirmed the promising potential of DPOF as a flame-retardant additive for improving the electrochemical performance of Li-ion batteries. Recently, tris(trimethylsilyl) phosphite (TMSP) is a promising high-temperature/high-voltage additive garnered attention from researchers. Young-Kyu Han *et al.* [17, 18] found that TMSP is oxidized more readily than electrolyte solvent, is more difficult to be reduced, and exhibits high reactivity with HF, so improving the electrochemical performance of LIBs. Haibo Rong *et al.* [19] reported that TMSP as an electrolyte additive can improve the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode not only at high voltage, 4.9 V vs. Li/Li^+ at room temperature, but also at elevated temperature (55 °C) by forming a more stable and more conductive cathode layer. Similarly to those for the graphite anode, other electrolyte additives also show noteworthy results [20]. Nevertheless, detail knowledge of TMSP additive effects on the graphite anode at elevated temperature, especially, the underlying mechanism responsible for their outstanding performance at elevated temperature has still remained elusive.

Electrochemical impedance spectroscopy (EIS) is a commonly used technique to analyze electrochemical processes occurring at electrode/ electrolyte interfaces, and has been widely used for the studies of electrochemical lithium intercalation into electrode materials [21,22]. Herein, the effects of TMSP as electrolyte additive on the electrochemical performance of graphite anode at elevated temperature (60 °C) were investigated thoroughly, in particular, the properties of electronic and ionic transports as well as the charge transfer reaction at the electrode/electrolyte interface by EIS.

2. EXPERIMENTAL

2.1 Preparation of the graphite working electrode

The battery-grade fiber graphite as anode was purchased from Shenzhen BRT Co. Ltd., China. Tris (trimethylsilyl) phosphate ($\text{C}_9\text{H}_{27}\text{O}_4\text{PSi}_3$, TMSP) was from Sigma-Aldrich Co., directly used without further purification. The blank electrolyte was composed of commercially available 1.0 M lithium hexafluorophosphate (LiPF_6) dissolved in a solvent mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) in a 1 : 1 : 1 volume ratio, and the electrolyte

with various contents of TMSP additive (0.5, 1.0, 3.0, 5.0 and 10 vol. %) in the above blank electrolyte was prepared in a high argon-filled box (SSuper 1220/750), in which the water and oxygen content were less than 0.1 ppm. To prepare the anode, the graphite, acetylene black and polyvinylidene fluoride (PVdF) binder were mixed in 90 : 5 : 5 weight ratio in *N*-methyl-2-pyrrolidone (NMP) to form a viscous slurry which was cast onto Cu foil current collector and then dried at 120 °C for 12 h under vacuum before to use.

2.2 Characterization of the graphite anode

In the study, cyclic voltammogram (CV) and EIS were carried out at an electrochemical work station (CHI 660C) with three-electrode cell, using lithium metal as the reference electrode and counter electrode. The CV was taken at a scan rate of 0.5 mV/s in the potential range from 0.0 to 3.0 V, and EIS was measured by applying an ac-amplitude of 5 mV over the frequency ranging from 10^{-2} to 10^5 Hz, and the electrode was equilibrated for 1 h before the EIS measurements to attain steady-state conditions. Galvanostatic cycling was performed on battery testing equipment (2XZ-2B, Neware) in the range of 0.0-1.5 V at 1C with 2032 coin type half cell, using lithium metal as the second electrode. All cells were assembled under argon atmosphere in the glove box.

The morphology of the anode electrodes cycled was taken by scanning electron microscopy (SEM, Oxford LEO 1530). After cycling at different temperature, the 2032 cells were disassemble in the glove box, and dried overnight under vacuum at room temperature before examine.

3. RESULTS AND DISCUSSION

3.1 Electrochemical behavior of the graphite in the CV study

Fig. 1 gives the CV curves of graphite anode for the first ten cycles in the blank electrolyte at different temperatures (25, 50, 55 and 60°C). In the first cycle, there are three cathodic peaks (marked as α , β and γ , respectively) at about 0.90, 0.55 and 0.00 V at 25°C in Fig. 1 a. The two weak cathodic peaks (α and β) disappearing in subsequent cycle were related to the formation of the SEI at the electrode-electrolyte interface, corresponding to the formation of Li_2CO_3 at about 0.90 V and ROCO_2Li ($\text{R}=\text{CH}_2$, $-\text{CH}_2\text{CH}_2\dots$) at 0.55 V due to the decomposition reactions of EC in the electrolyte, separately, which was the same as our previous study [23]. Obviously, another strong cathodic peak (γ) at about 0 V was attributed to the reversible insertion/extraction of lithium ions into/from the graphite layers.

In Fig. 1, it can be found that the redox current of the graphite anode at over 50°C is bigger than that at 25°C in Fig. 1, proving faster kinetics of lithium ions removal/insertion from /into the graphite anode at elevated temperature. Moreover, a small new peak (δ) appears at about 1.5 V, which maybe related to the decomposition of electrolyte at high temperature of above 50°C. In Fig. 1 a and b, the reversible duplication of CV is better at the temperature range from 25 to 50°C, indicating the graphite anode has excellent cycling performance below 50°C.

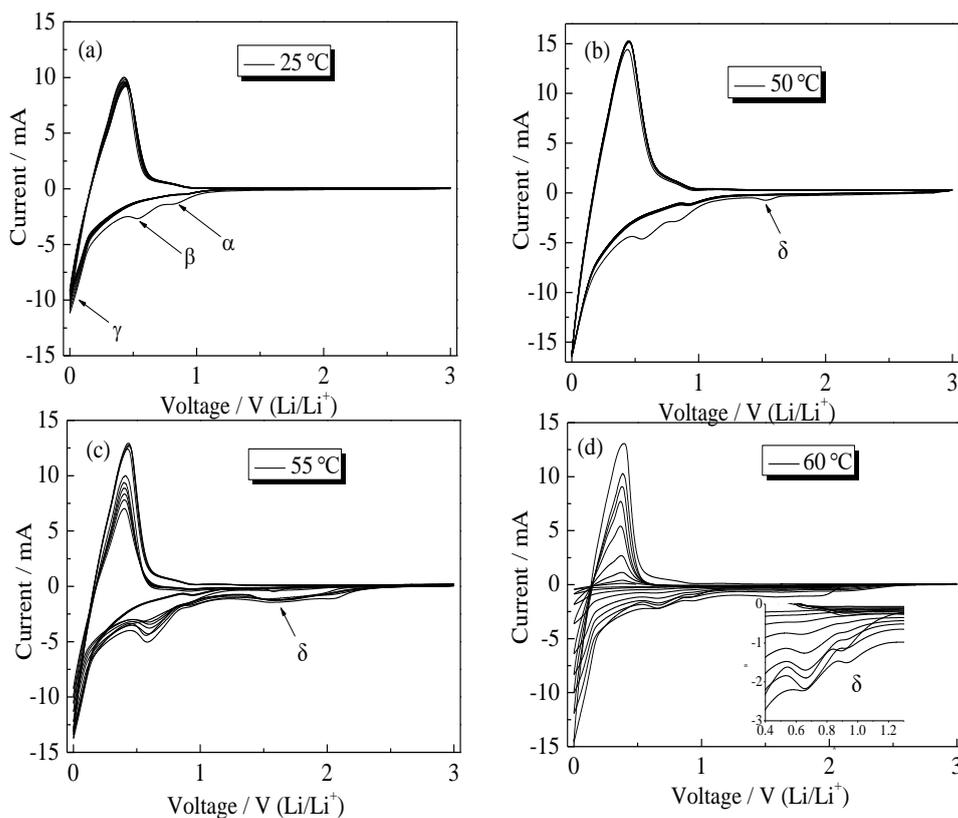


Figure 1. CV curves recorded on graphite anode in the blank electrolyte for the first ten cycles at various temperature (a) 25 °C, (b) 50 °C, (c) 55 °C, and (d) 60 °C

However, as the temperature increases to above 55 °C, the two weak cathodic peaks (α and β) merge into a large one in Fig. 1 c and d, which would not disappear in subsequent cycle, suggesting the decomposition of EC of the electrolyte is aggravated continuously and the stability of SEI is gradually destroyed. As the temperature to 60 °C, the stability of CV dramatically deteriorates, indicating that the conventional electrolyte of 1 mol/ L LiPF_6 EC+DEC+DMC is outside its thermodynamic stability region. Thus, the choice for increasing the high-temperature performance of the conventional electrolyte is to add stabilizer, for which is one of the most economical methods.

Fig. 2 shows CVs of graphite anode at elevated temperature for the first ten cycles in the electrolyte added various concentrations of TMSP additive (0.5, 1, 3, 5 and 10 vol. %). It can be observed that compared with the blank electrolyte, the cycling stability of graphite anode is significantly improved in the above 3% TMSP additive electrolyte at 60 °C, and the graphite anode with 5 vol.% TMSP containing electrolyte has superior cycling performance than those for any other concentrations of TMSP added, in addition, the small peak (δ) attributed to the decomposition of electrolyte disappear or much smaller than that in the blank electrolyte at elevated temperature. These suggest that the incorporation of TMSP additive can drastically improve the cycling stability of the anode and stability of the conventional electrolyte at elevated temperature. Therefore, the present study for the electrochemical performance of graphite at 60 °C uses the 5 vol.% TMSP containing electrolyte.

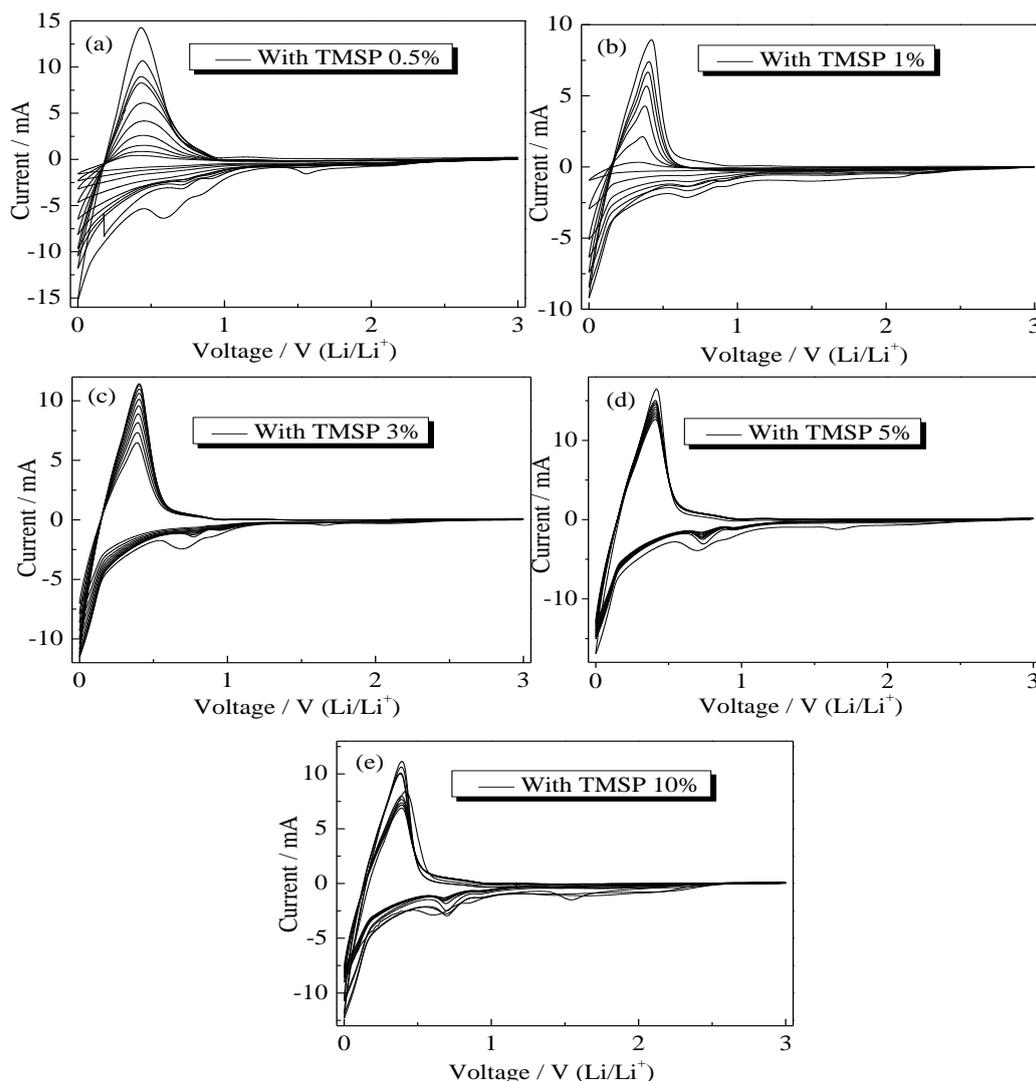


Figure 2. CV curves recorded on graphite electrode at 60°C for the first ten cycles in the electrolyte added by (a) 0.5 vol. % TMSP, (b) 1 vol. % TMSP, (c) 3 vol. % TMSP, (d) 5 vol. % TMSP, (e) 10 vol. % TMSP

3.2 Cycling performance of the graphite in the electrolyte added TMSP additive

The cycling performance of graphite anode in the electrolyte with and without 5 vol. % TMSP added at room temperature (25°C) and elevated temperature (60°C) was employed, as shown in Fig. 3. It can be seen that at room temperature, the initial discharge capacity of graphite anode is 333.64 mAh/g in the blank electrolyte, after the first 45 cycles, fading to 321.61 mAh/g with capacity retention of 96.4%. In contrast, the graphite anode in the 5 vol.% TMSP electrolyte presents 348.41mAh/g of initial discharge capacity, the capacity retention of 94.5% after 45 cycles, indicating that the TMSP has almost no effects on the electrochemical performance of graphite anode at room temperature. However, when the temperature is elevated to 60°C, the discharge capacity of graphite anode without TMSP drastically fades from 332.27 mAh/g for the 46th cycle down to the minimum

247.40 mAh/g for the 54th cycle, then slowly increases, to attain maximum capacity of 353.12 mAh/g at the 91th cycle, then rapidly decreases to only 181.43 mAh/g at the 160th cycle with 54.60% capacity retention of the 46th cycle discharge capacity.

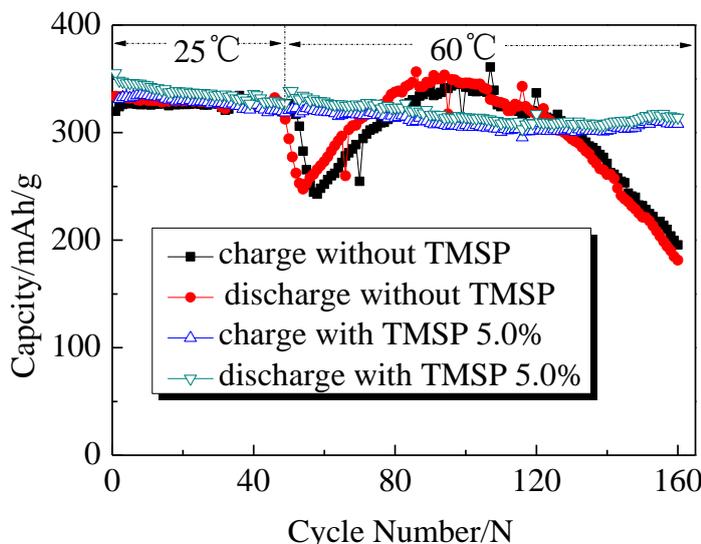


Figure 3. Cyclic performance of graphite anode in the electrolyte with and without TMSP at room temperature (25°C) and elevated temperature (60°C)

Table 1. the comparison of the electrodes with different electrolyte additives for LIBs

Electrode or cell	Electrolyte additive	The capacity retention		Condition
		Without additive	With additive	
LiFePO ₄	vinylene carbonate (VC)	81%	97%	after 200 cycles at 1-3 C at 55°C [15]
LiNi _{0.5} Mn _{1.5} O ₄	tris (trimethylsilyl) phosphate (TMSP)	70%	94.9%	after 70 cycles at 0.5C at 55°C [19]
LiMn ₂ O ₄	3, 3'-sulfonyldipropio nitril (SDPN)	56.7%	70.3%	after 200 cycles at 1.0C at 55°C [24]
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	Tris(trimethylsilyl) phosphite (TMSPi)	75.2%	91.2%	after 100 cycles at 0.5C at 25°C [18]
LiCoO ₂ / (MCMB)	diphenyloctyl phosphate (DPOF)	66%	68%	after 100 cycles at 25°C at a constant rate of 1C [16]
Graphite	tris(trimethylsilyl) phosphite (TMSP)	96.4%	94.5%	after 45 cycles at 1C at 25°C
Graphite	tris(trimethylsilyl) phosphite (TMSP)	54.60%	96.1%	after 70 cycles at 1C at 60°C

The drastic capacity increasing for the 54th cycle to the 91th cycle may be related to the extensive decomposition of the blank electrolyte at high temperature, and with time, more and more electrolytes decompose at 60°C, thus cause the electrochemical performance of graphite anode to faster deteriorate.

The discharge capacity of graphite anode is 320.48 mAh/g for the 46th cycle in the 5 vol. % TMSP-containing electrolyte at 60°C, and with time, the cycling performance is more stable than that in the blank electrolyte. After 115 cycles, the discharge capacity fades to 308.02 mAh/g with 96.1% capacity retention of the 46th cycle discharge capacity. Obviously the 5 vol.% TMSP can significantly improve cyclic stability of graphite anode, which is in good agreement with the CV results as discussed above.

Table 1 gives the comparison of the electrodes with different electrolyte additives for LIBs. It can be seen that in Table 1, the capacity retention of the cathode electrode improved significantly with different electrolyte additives at elevated temperature, for example, the LiNi_{0.5}Mn_{1.5}O₄ cathode with 1.0% TMSP has a capacity retention of 94.9% after 70 cycles at 55°C, while it is only 70% without additive [19]. Compared to these cathode electrode, in the study the graphite anode with TMSP additive has still superior cycling ability at elevated temperature of 60°C, while it is almost no change or even decline at 25°C, indicating that the TMSP additive can dramatically improve the cycling ability of graphite anode at elevated temperature.

3.3 The dynamics mechanism of graphite anode at elevated temperature

SEM analyses for cycled electrodes support the electrochemical behaviors of each cycled half cell. Fig. 4 shows the SEM images of the graphite anode cycled after 160 cycles in the electrolyte with and without TMSP at 60°C, with a comparison of the pristine electrode without cycle. Clean graphite bar with diameter of about 10µm can be identified in the pristine electrode, as shown in Fig. 4 a and b, which surface is smooth without SEI film. After 160 cycles the graphite bar is not found in the blank electrolyte at 60°C in Fig. 4 c, d. This observation suggests that at high temperature the electrolyte decomposition proceeds dramatically and its products almost covered with the graphite bar, which shroud the graphite bar.

Kristina Edstrom [25] reported that the general structural of the SEI is one of a dense inorganic matrix consisting mainly of LiF and Li₂CO₃ close to the electrode surface and a porous organic or polymeric layer extending further out from the electrode surface, and large crystals of LiF are also exist in this matrix. Obviously, in Fig. 4 c, d, no porous organic or polymeric layer on the surface of the graphite was found, which may be decomposed at elevated temperature, only some cracks are observed on the surface of the graphite anode. All these would be adverse for alleviating the volume expansion during lithium ion intercalation/ de-intercalation from/into the graphite anode, which agree well with those in the cycling performance of graphite anode in the blank electrolyte at 60°C in Fig. 3.

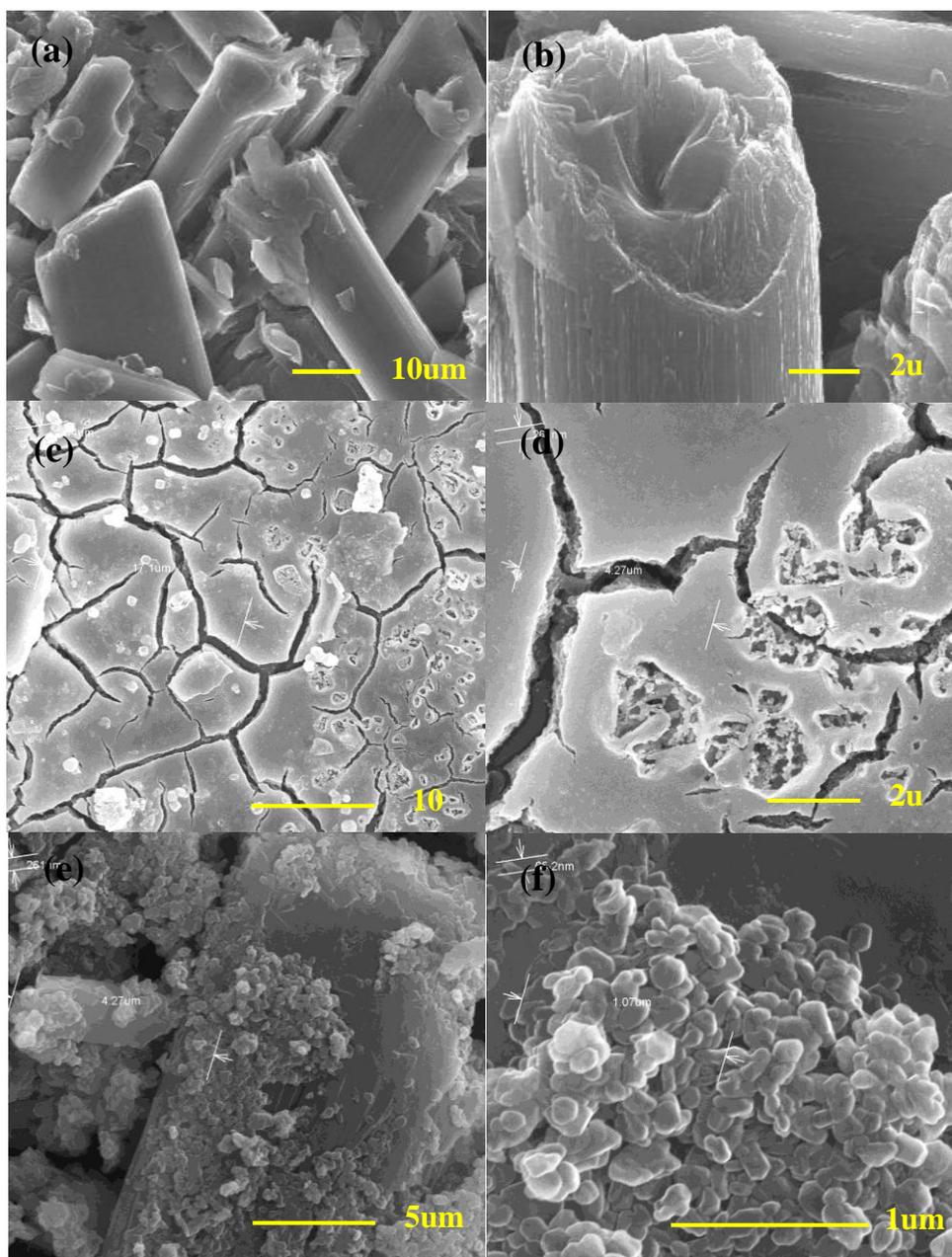


Figure 4. SEM images of pristine (a, b) and cycled graphite electrode in bare (c, d) and 5 vol.% TMSP-containing (e, f) electrolytes at 60 °C

Compared to the baseline electrolyte, the graphite bar in the 5 vol.% TMSP-containing electrolyte still can be found after 160 cycles at 60 °C in Fig. 4 e, f, which is virtually identical to the blank electrode case. The surface of the graphite bar is covered with thick deposits due to the formation of the protective SEI film without gaps. The organic or polymeric layer of SEI has still porous mesh structure, indicating that the TMSP additive can effectively suppress the decomposition of SEI at elevated temperature, and to further effectively stabilize the electrolyte, which would improve the electrochemical performance of the cell.

To further investigation the TMSP additive effect on lithium ion insertion/deinsertion mechanism at the electrode/electrolyte interface at elevated temperature, the EIS was employed. Fig. 5

shows EIS of graphite anode at 0.6V in blank electrolyte and 5 vol.% TMSP-containing electrolyte at 60°C, respectively. For comparison, the EIS of graphite anode was also carried out in blank electrolyte at 25°C. In our previous study [22], the EIS of electrode for lithium ion battery were usually made up of three parts at room temperature, namely a high frequency arc (HFA), a middle frequency arc (MFA), and an inclined line in the low-frequency region (LFL), as shown in Fig. 5. According to Aurbach and his coworkers' opinions [26, 27], the HFA is related to lithium ion migration through SEI film of graphite, the MFA is attributed to charge-transfer through the electrode/electrolyte interface, and the LFL is assigned to solid state diffusion of Lithium ion in the graphite matrix. Similarly, the EIS of graphite anode consists of HFA, HFA and LFL in blank electrolyte at 25°C in Fig. 5.

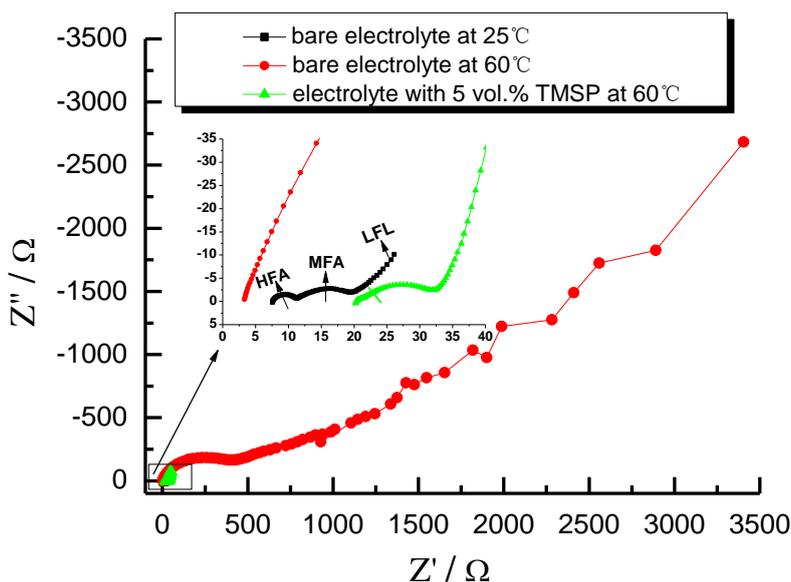


Figure 5. Nyquist plots of graphite anode at different conditions

Due to good conductivity of graphite, the sizes of the two arcs are small, indicating the resistances of the SEI and the charge transfer reaction are accordingly small. However, at elevated temperature (60°C) the EIS has only two parts, and obviously, the only large arc is attributed to charge-transfer through the electrode/electrolyte interface, indicating that No HFA in the EIS is found because of decomposition of SEI film at 60°C, which is unable to protect negative carbon from side reactions with the organic electrolyte [28], and so lead to bad cycling performance of electrode. Moreover, the MFA is much bigger at 60°C than that at 25°C, corresponding to higher charge-transfer resistance, resulting in lithium ion intercalation/de-intercalation more difficulty. However, in the electrolyte with 5 vol. % TMSP the EIS has three parts at 60°C, that is HFA, MFA, and LFL, which is the same as that in the blank electrolyte at 25°C, indicating that incorporation of TMSP can keep the stability of SEI film at elevated temperature, as well as that at room temperature. In addition, it can be find that the size of the MFA is much smaller than that in the bare electrolyte at the same high temperature, corresponding to the smaller resistance of charge transfer. So the incorporation of TMSP

in the electrolyte is favorable for the electrochemical performance of graphite anode at elevated temperature.

4. CONCLUSION

The tris(trimethylsilyl) phosphite (TMSP) is used as an electrolyte additive to improve the cycling performance of graphite anode at 60°C. The graphite anode with 5 vol.% TMSP containing electrolyte exhibits excellent cycle stability at elevated temperature, with a capacity retention of 96.1% after 70 cycles at 60°C. The TMSP can drastically decrease the resistances of SEI and charge transfer at elevated temperature.

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