



Triethoxysilane with oligo(ethylene oxide) substituent as film forming additive for graphite anode*

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Abstract: {3-[2-(2-methoxyethoxy) ethoxy]-propyl} triethoxysilane (TESM2) was synthesized and used as an electrolyte additive to improve the performances of lithium-ion batteries (LIBs). The electrochemical properties of the electrolyte (1 mol/L lithium hexafluorophosphate (LiPF₆)/ethylene carbonate (EC):diethylene carbonate (DEC):dimethyl carbonate (DMC), 1:1:1) with different contents of TSM2 were characterized by ionic conductivity measurement, galvanostatic charge/discharge test of graphite/Li half cells, and electrochemical impedance spectroscopy. Both the cycling performances and C-rate capabilities of graphite/Li half cells were significantly improved with an optimized content of 15% TSM2 in the electrolyte. The graphite/Li half cell delivered a very high specific capacity of 370 mAh/g at 0.2C rate without any capacity loss for 60 cycles, and retained a capacity of 292 mAh/g at 2C rate. The solid electrolyte interphase (SEI) film on the surface of the graphite anode was investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), indicating that TSM2 was effectively involved in the formation of SEI film on the surface of graphite.

Key words: Triethoxysilane, Electrolyte additive, Solid electrolyte interphase, Graphite anode, Lithium-ion batteries (LIBs)

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1 Introduction

Lithium-ion batteries (LIBs) have attracted great interest since the 1990s because of their unique properties such as high energy density, high voltage, and long cycling life. With the increasing demand for electric vehicles (EVs), much effort has been devoted to developing LIBs with long cycling life and high rate capacity (Hao *et al.*, 2010; Li *et al.*, 2011).

The electrolyte is an important component in LIBs and plays a key role in the electrochemical

performances of LIBs by forming a solid electrolyte interphase (SEI) film on the surface of a graphite anode during the initial charging/discharging process. The structure and components of the SEI film critically determine the stability of SEI film, and thus have great impact on the performance of LIBs (Zhang, 2006; Walkowiak *et al.*, 2010). Therefore, a large number of additives have been reported to improve the interfacial properties of LIBs, such as reduction-type additives vinylene carbonate (VC) (Aurbach *et al.*, 2002; 2004; Contestabile *et al.*, 2003), vinyl ethylene carbonate (VEC) (Hu *et al.*, 2004), reaction-type additives CO₂ (Sakamoto *et al.*, 2001), and lithium bis(oxalato) borate (LiBOB) (Xu *et al.*, 2002).

Recently, organosilicon compounds have been reported as electrolyte solvents for LIBs because of their unique properties, such as nonflammability,

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biocompatibility, and thermal and electrochemical stability (Zhang *et al.*, 2008). Some organosilicon compounds have already been developed as functional electrolyte additives such as film forming (Markovsky *et al.*, 2004; Schroeder *et al.*, 2006a; 2006b; Ryu *et al.*, 2008; Xia *et al.*, 2008; Song and Baek, 2009; Walkowiak *et al.*, 2008; 2010; Li *et al.*, 2011), and flame retardant (Zhang *et al.*, 2009; Li *et al.*, 2011) additives. To date, phenyl-functionalized silane (Xia *et al.*, 2008; Li *et al.*, 2011), polyether-functionalized disiloxanes (Walkowiak *et al.*, 2008; 2010) and silicon tripodands (Schroeder *et al.*, 2006a; 2006b) have been reported as additives in propylene carbonate (PC)-based electrolytes for graphite anodes to prevent exfoliation of the graphite.

In this work, we synthesized a triethoxysilane with oligo(ethylene oxide) substituent, {3-[2-(2-methoxyethoxy) ethoxy]-propyl} triethoxysilane (TESM2), and used it as a film forming additive in the electrolyte of 1 mol/L lithium hexafluorophosphate (LiPF₆)/ethylene carbonate (EC):diethylene carbonate (DEC):dimethyl carbonate (DMC) (1:1:1, defined as LB303) for a graphite anode. The film forming capability was characterized by the electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) analyses. The electrochemical performances of the electrolytes with different contents of TESM2 were investigated in graphite/Li half cells.

2 Experimental

2.1 Materials

2-(2-methoxyethoxy) ethanol (99%), triethoxysilane (97%), and allyl bromide (97%) were obtained (Aladdin Co., China). The triethoxysilane was dried with molecular sieves before use. Potassium hydroxide (KOH, 85%) was purchased from the Guangzhou Maolin Co. (China). The platinum(IV) oxide (PtO₂, metal content 84.65%) was purchased from the Shaanxi Kaida Chemical Engineering Co. (China). Graphite was obtained from the Amperex Technology Ltd. (China). The electrolyte of LB303 (with water content below 20 ppm) was commercially available from the Zhangjiagang Guotai-Huarong Co. (China).

2.2 Apparatus

¹H NMR (nuclear magnetic resonance) and ¹³C NMR spectra were taken on a Bruker avence 600 spectrophotometer. Ionic conductivity of electrolytes (LB303) with different contents of TESM2 at room temperature were measured using a YSI 3200 conductivity instrument equipped with an YSI 3253 conductivity cell (conductivity meter DDS-310). The water content of electrolytes was measured by the Karl-Fischer coulometric moisture titrator (831 KF). All the cells were assembled under a dry argon atmosphere in glove box (Mikrouna, H₂O and O₂ < 1 ppm). The constant discharge and charge measurements of the graphite/Li cells were carried out with a multi-channel battery test system (Neware BTS-610) using 2032 coin cells at room temperature. The EIS was measured on an electrochemical analyzer (BAS-ZAHNER IM6) with 5 mV AC amplitude applied in the frequency range of 0.01 Hz to 100 kHz. SEM and EDS were performed on the Hitachi S4800 to inspect the surface morphology of the graphite electrode. Before SEM and EDS, the cycled graphite electrode was washed three times with pure DEC followed by vacuum drying overnight at room temperature.

2.3 Cell preparation and electrochemical measurements

The graphite electrode was prepared by coating a mixture of graphite, carbon black, and poly(vinylidene) difluoride (PVDF) with weight ratio 90:5:5 on copper foil. The separator was purchased from Celgard Co. (Celgard 2400, USA). The electrolytes were prepared by adding 0, 5%, 10%, 15%, and 20% TESM2 to the electrolyte of LB303. The cycling performance tests of the cells were operated at a constant current density of 0.2C (74.4 mA/g) under 0.005–3 V. The C-rate performance tests of the cells were operated at a constant current density of 0.2C (10 cycles), 0.5C (10 cycles), 1C (10 cycles), 2C (10 cycles), 4C (10 cycles), and 0.2C (2 cycles) under 0.005–3 V. All cell tests were conducted at a constant temperature of 25 °C.

2.4 Synthesis of TESM2

Firstly, allyl bromide (0.8 mol, 96.8 g) was added to a mixture of KOH (0.8 mol, 44.8 g) and

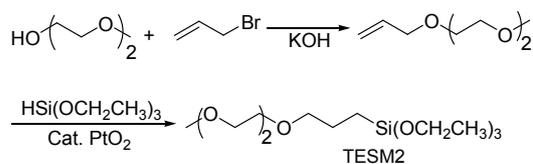
2-(2-methoxyethoxy) ethanol (0.7 mol, 84 g) in a two-necked flask at 0 °C, then the mixture was stirred at 55 °C overnight. After completion of the reaction, the product was extracted with toluene/water (1:1), and dried with MgSO₄. After pumping off the solvent, the allyl substituted oligo(ethylene oxide) ether was purified through repeated vacuum distillation in the presence of CaH₂ to remove trace water, giving the purity of 99% characterized by gas chromatography. TESM2 was produced by hydrosilylation reaction of allyl substituted oligo(ethylene oxide) ether (0.3 mol, 48 g) and triethoxysilane (0.3 mol, 49.2 g) with 1% (in weight) PtO₂ as a catalyst in the condition of 80 °C for 12 h. Upon reaction completion, TESM2 was purified by repeated vacuum distillation giving a yield of 80% with a purity of 99.6%. The TESM2 was dried over molecular sieves to ensure water content below 20 ppm prior to use for electrochemical tests. The chemical structure of TESM2 was confirmed by NMR: ¹H NMR (600 MHz, CDCl₃): 0.62 (m, 2H), 1.21 (t, J=7 Hz, 9H), 1.69 (m, 2H), 3.38 (s, 3H), 3.42 (t, J=7 Hz, 2H), 3.54 (m, 2H), 3.58 (m, 2H), 3.63 (m, 4H), 3.80 (q, J=7 Hz, 6H); ¹³C NMR (109 MHz, CDCl₃): 6.41, 18.25, 22.87, 58.30, 58.97, 69.97, 70.51, 70.63, 71.93, 73.60.

3 Results and discussion

3.1 Synthesis and characterization

The TESM2 was synthesized through a hydrosilylation reaction of triethoxysilane with oligo(ethylene oxide) allyl methyl ether using PtO₂ as a catalyst to yield 80% (Scheme 1) (Ghosh *et al.*, 2005). Its chemical structure was confirmed by NMR (Section 2). The basic physical properties of TESM2 at room temperature were collected, showing a low viscosity (3.26 mPa·s), moderate dielectric constant (4.88) and ionic conductivity (1.14 mS/cm doped with 1 mol/L LiTFSI).

The dependence of ionic conductivity of the electrolytes with different doping content of TESM2 is plotted in Fig. 1. The ionic conductivity of the electrolytes decreased with increasing TESM2 content, reducing from 9.4 mS/cm without additive to 7.4 mS/cm with 20% addition of TESM2 in the electrolyte of LB303.



Scheme 1 Synthesis of silane-based compound TESM2

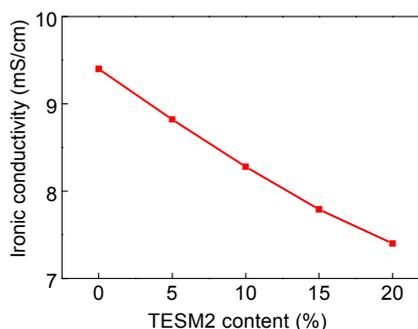


Fig. 1 Relationship between the ionic conductivity and doping content of TESM2 in LB303

3.2 Cycle performance test

Fig. 2 shows the cycling and C-rate performances of graphite/Li half cells with different contents of TESM2 in LB303 electrolyte. All the cycling performances of the cells were improved with 5%, 10%, 15%, and 20% additions of TESM2 without sacrificing the initial coulombic efficiency (the initial coulombic efficiencies of the cells with 0, 5%, 10%, 15%, and 20% addition of TESM2 are 82.0%, 79.5%, 81.1%, 81.6%, and 81.1%, respectively), as compared with the control cell without additive (Fig. 2a). The cell with 20% addition exhibited the highest capacity of 370 mAh/g and showed no capacity loss after 60 cycles. Furthermore, the C-rate performances of the cells (with charge/discharge rates of 1C, 2C, and 4C) were also improved with 5%, 10%, and 15% additions of TESM2, but not with 20% addition (Fig. 2b). The graphite/Li cell with 15% addition displayed the best C-rate performance at 4C rate. Moreover, the higher doping content of TESM2 deteriorated the rate performances as seen in the case of 20% addition, probably due to its low ionic conductivity (Fig. 1).

3.3 Impedance analysis

The EIS and surface analysis of these graphite electrodes were carried out to investigate the underlying impact of the doping content of TESM2 on the cycling and C-rate performance. The impedance of graphite/Li cells with different contents of TESM2

in LB303 after 4 cycles are shown in Fig. 3. In the Nyquist plots, the semicircles at high frequency are related to the SEI film resistance and the impedance of lithium ion transport through the interphase of electrolyte and electrode (Hao *et al.*, 2010; Li *et al.*, 2011). The SEI film resistances of the cells with 5%, 10%, and 15% additions were 14.0 Ω , 15.0 Ω , and 15.5 Ω , respectively, as compared with higher values of 18.0 Ω and 17.7 Ω for the cell without and with 20% addition in the electrolyte, respectively. This decrease of the resistance with proper doping content implies a higher lithium ion migration rate and better kinetic characters, thus the C-rate performance of the cells was improved.

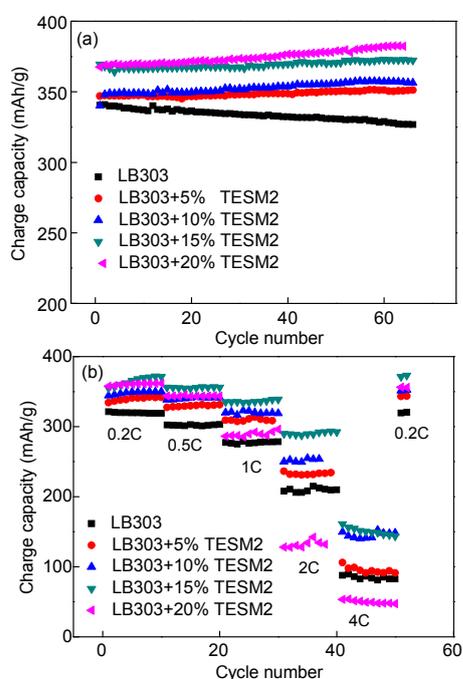


Fig. 2 Cycling performance at 0.2C rate (a) and C-rate performance (b) of graphite/Li batteries with different doping contents of TSM2 in LB303

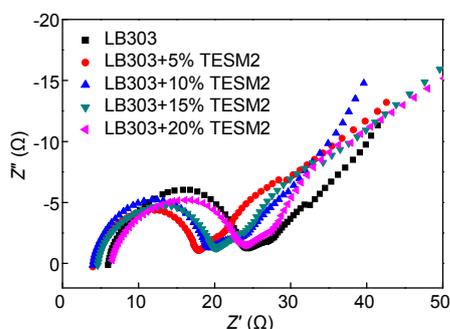


Fig. 3 Impedance of graphite/Li batteries with different doping contents of TSM2 added in LB303 after 4 cycles

3.4 Analyses of graphite anode surface

To further study the effect of TSM2 on the surface modification of graphite anode, SEM analysis was conducted to characterize the surface morphologies of graphite electrodes. For the cell without additive (Fig. 4a), there was more fluff-like and particle-like materials covered on the surface of graphite; while the surface of graphite with 10% additive became smoother and had large-sized particles (Fig. 4b).

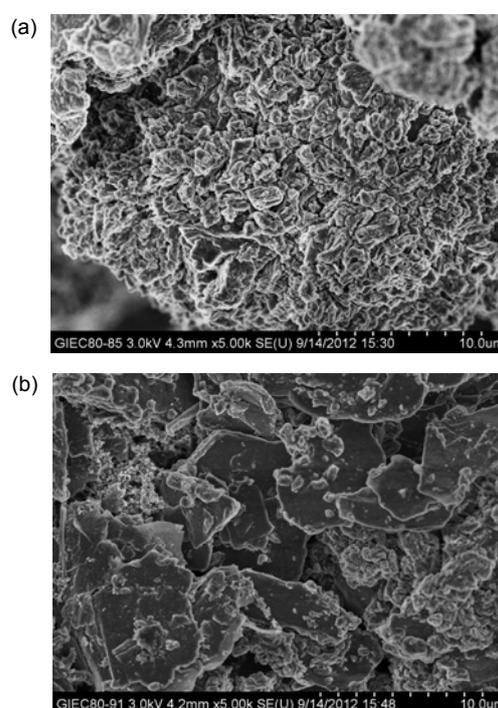


Fig. 4 SEM micrographs of graphite electrode without TSM2 (a) and with 10% TSM2 after 3 cycles (b)

The surface film components of the graphite anode without and with 10% TSM2 addition in LB303 were further studied by EDS (Fig. 5). A silicon peak at 1.8 keV was detected for the sample of the latter cell, indicating that TSM2 was obviously involved in the formation of SEI film on graphite anode. No silicon signal was observed for the sample of the cell without additive. On the other hand, the increase of the carbon signal in the EDS spectrum of the sample with TSM2 addition further evidenced that TSM2 was involved in the formation of SEI film, as the carbon content relative to oxygen of TSM2 was higher than EC. Apparently, TSM2 participated in the formation of SEI film on graphite

anode, and thus improved the cycling and C-rate performance.

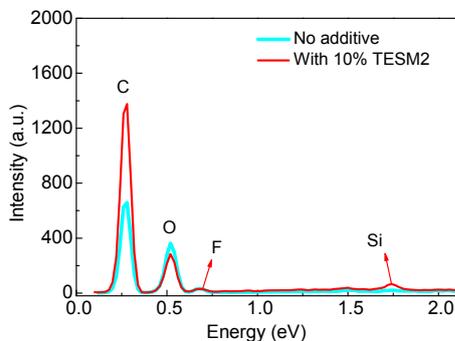


Fig. 5 EDS spectrum of graphite electrode without and with 10% TESM2 after 3 cycles

4 Conclusions

Oligo(ethylene oxide) functionalized triethoxysilane (TESM2) was synthesized as film forming additive for graphite anode in lithium-ion batteries. In an electrolyte of 1 mol/L LiPF₆/EC:DEC: DMC with an optimized content of triethoxysilane compound (15%), both the cycling performances and C-rate capabilities of graphite/Li half cells are significantly improved. The graphite/Li half cells delivered a very high specific capacity of 370 mAh/g at 0.2C without any capacity loss for 60 cycles, and retained a capacity of 292 mAh/g at 2C rate. EIS, SEM, and EDS analyses disclosed that the TESM2 participated in the formation of stable and effective SEI film on the surface of graphite electrode, thus improved the performance of graphite half cells. Therefore, triethoxysilane compound with oligo(ethylene oxide) substituent is a promising additive candidate to be used for improving the performances of LIBs.

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