



# Methyl phenyl bis-methoxydiethoxysilane as bi-functional additive to propylene carbonate-based electrolyte for lithium ion batteries

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## ABSTRACT

Methyl phenyl bis-methoxydiethoxysilane (MPBMDS) was prepared and its effects were investigated as an additive in 1.0 mol dm<sup>-3</sup> LiPF<sub>6</sub>-propylene carbonate (PC)/dimethyl carbonate (DMC) (1:1, v/v) electrolyte for lithium ion batteries. The electrochemical properties of the electrolyte with MPBMDS were characterized by discharge/charge tests, cyclic voltammetry, electrochemical impedance spectroscopy, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The addition of MPBMDS can effectively prevent the decomposition and the co-intercalation of PC. In addition, burning tests showed that the addition of 4–13 wt.% MPBMDS to the bare PC-based electrolyte effectively reduces the flammability. This eco-friendly compound provides a new promising direction for the development of bi- or multi-functional additives for lithium ion batteries.

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## 1. Introduction

Lithium ion batteries have experienced growing acceptance in the consumer market since they were commercialized by Sony in the early 1990s, because of their favorable properties such as their high voltage, high energy density, and low self-discharge [1]. Their application in developing fields such as the space industry, polar research and electric vehicles results in a higher demand for low- and high-temperature performance lithium ion batteries. Use of these batteries, in conjunction with fuel cell and supercapacitor technology can contribute significantly to reduction of CO<sub>2</sub> emissions and protecting the environment. However, safety concerns are still challenging when scaled-up lithium-ion batteries are considered, especially at the overcharged state of the batteries. This is because the strongly oxidized cathodes may take part in a series of hazardous chemical reactions, leading to thermal runaway, fire or explosion [2–8]. The solvent of the electrolyte used in lithium ion batteries is a crucial factor influencing the low-temperature performance. Ethylene carbonate (EC)-based electrolytes are extensively used in current commercial lithium ion batteries, but they can only work well at above –20 °C because of the high melting point of

EC (about 36 °C) [9,10]. In contrast, with such excellent properties as low melting point (–49 °C), high flash point (132 °C), high dielectric constant and wide electrochemical window, propylene carbonate (PC) is an attractive candidate as a solvent for nonaqueous electrolytes in lithium ion batteries at low temperatures and is also helpful in improving the safety of lithium ion batteries [11,12]. However, PC has been shown to have the tendency to co-intercalate together with lithium cations into the crystal structure of graphite, followed by its decomposition [12–14].

To improve safety and reliability, self-actuating overcharge protection, such as positive temperature coefficient resistors and integrated circuits, has been introduced. However, these methods are not completely reliable. The electropolymerization or coating of monomer additives on electrode surfaces is another possible protection mechanism for lithium-ion batteries [15–21]. In the case of PC, several ways have been explored to modify the surface of the graphite by means such as coating to prevent the direct contact of PC with the graphitic structure [22,23].

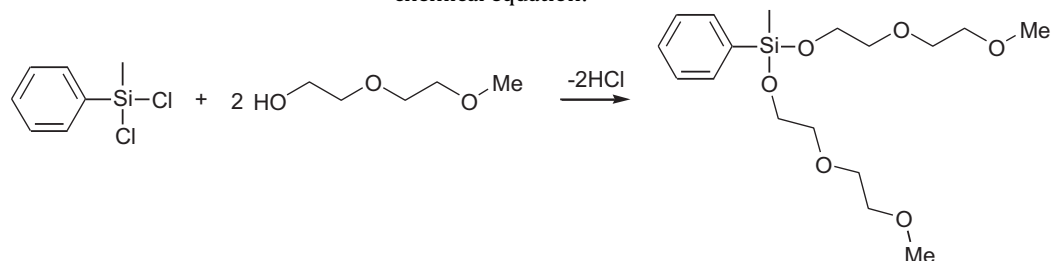
Several anode materials are currently pursued, such as titania-C [24], silicon-C [25], silicon-silica [26], SnO<sub>2</sub>-CNT [27], and MoO<sub>2</sub> [28] nanocomposites, but graphite is still the first choice for use in commercial batteries. However, graphite suffers extensive surface structural disordering upon prolonged cycling, especially at high charging rates and elevated temperatures [29]. When certain substances are added to PC-based electrolytes [30,31], an effective solid electrolyte interface (SEI) film is formed prior to the decomposition of PC and intercalation of Li<sup>+</sup> into the graphite so

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that  $\text{Li}^+$  can reversibly intercalate and de-intercalate [32–36]. For example, substances such as allyl ethyl carbonate [37], acrylonitrile [38], tetrachloroethylene [39], ethylene sulfites [40], vinylene carbonate (VC) [41], propylene sulfite [10], chloroethylene carbonate [42], silanes [10,43], triethyl orthoformate [44], 2-phenylimidazole (PID) [45] and *N*-phenylmaleimide (NPM) [46] have been used. Silanes seem to behave similarly to crown ethers and cryptands as far as formation of complexes with metal cations is concerned [47–49]. Apparently, a unique component of the protective effect of polyoxasilanes, aside from electropolymerization, is condensation (polymerization) of podand molecules *via* silicon atoms, leading to the formation of a protective network on the graphite surface. In our own experience, phenyl tris-2-methoxydiethoxysilane (PTMS)



suppresses the co-intercalation of PC by formation of a cross-polymerized network of Si–O–Si bonds on the graphite surface, thus restraining PC molecules from co-intercalating with lithium ions into graphite electrodes [30]. A specific capacity above  $275 \text{ mAh g}^{-1}$  is maintained using CMS electrode in  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6/\text{PC}:\text{DMC}$  (1:1, v/v) electrolyte. In addition, silanes can act as fire-retardant to improve the safety performance of lithium-ion batteries. When we added 3 wt.% PID to  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6/\text{PC}:\text{DMC}$  (1:1, v/v) electrolyte the co-intercalation of PC was suppressed and the decomposition of electrolyte during the first lithium intercalation was inhibited by formation of a favorable solid electrolyte interface (SEI) on the CMS graphite electrode, reaching a reversible capacity of  $300 \text{ mAh g}^{-1}$  [45]. NPM can electrochemically polymerize at the overcharge potential of 3.8–4.2 V (vs.  $\text{Li}/\text{Li}^+$ ) and form a thin polymer film on the surface of the cathode, thus preventing voltage runaway. On the other hand, the use of 3–5% NPM as an overcharge protection electrolyte additive does not influence the normal performance of lithium-ion batteries, providing a specific capacity above  $70 \text{ mAh g}^{-1}$  for the  $\text{LiFePO}_4$  electrode over many cycles [46].

One of the problems hindering the commercial application of large capacity lithium-ion batteries needed in the developing hybrid electric vehicle market is indeed the safety concerns arising from the use of volatile and flammable liquid electrolytes [50]. One promising strategy to address this safety issue is to employ solid electrolytes such as gelled polymer electrolytes as alternatives to the currently used organic carbonate electrolytes [51]. However, the improved flame retardation of these electrolytes is accompanied by reduced battery performance including significantly lower conductivity, especially at low temperature [52]. An alternative and popular approach is to add additives as flame retardants to increase the thermal stability of the electrodes and decrease the flammability of the electrolytes. In that case, the low temperature performance of lithium ion batteries can be maintained [53,54]. Burning tests showed that the addition of up to 10 vol% vinyl-tris-(methoxydiethoxy)silane (VTMS) to the currently used electrolyte could effectively reduce the flammability. As long as the added amount was kept below 10%, electrochemical performance such as reversible capacity and cycling showed little change [51].

In this paper, methyl phenyl bis-methoxydiethoxysilane (MPBMDS), a new film-forming additive, is examined for non-aqueous

electrolytes-based lithium-ion batteries with graphite anodes. The performance of graphitic anodes was remarkably improved in PC-based electrolytes after adding MPBMDS. At the same time, MPBMDS is an environmental friendly flame retardant with high thermal stability and low viscosity. Here we report the performance of MPBMDS as a bi-functional additive: preventing the exfoliation of graphite for PC-based electrolyte and acting as a flame retardant.

## 2. Experimental

Methyl phenyl bis-methoxydiethoxysilane (MPBMDS) was prepared by reaction of methyl phenyl dichlorosilane with anhydrous diethylene glycol monomethyl ether, according to the following chemical equation:

Methyl phenyl dichlorosilane (15.02 g of 98% purity, 0.077 mol, 12.79 ml) in 15 ml anhydrous dichloromethane was added dropwise (under argon) over 4 h to a solution of anhydrous diethylene glycol monomethyl ether (18.44 g of 99% purity, 0.152 mol) in 15 ml anhydrous dichloromethane cooled to  $0^\circ\text{C}$ , with continuous stirring. After warming to room temperature, the solvent was removed by evaporation and the mixture was heated at  $90^\circ\text{C}$  under vacuum (15–20 mmHg) for about 6 h to remove gaseous HCl. The obtained product was purified by vacuum distillation ( $240^\circ\text{C}$  at 1 mmHg to remove the reactants) and the identity of the obtained compound was verified by FTIR and NMR spectroscopy. IR (neat): 3450, 3030, 2878, 1593, 1456, 1354, 1199–1108, 1083,  $967 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 0.23$  (3H, s, Si–Me), 3.19 (6H, s, O–Me), 3.3–3.6 (16H, m,  $8 \times -\text{CH}_2-$ ), 7.20 (3H, m, *arom.*), 7.47 (2H, m, *arom.*).

The bare PC-based electrolyte,  $1.0 \text{ mol dm}^{-3}$   $\text{LiPF}_6\text{-PC}/\text{DMC}$  (1:1, v/v), was supplied by Guotai Huarong Co. Ltd., China, and used as the electrolyte without further treatment. Due to strong Van der Waals forces, the viscosity of pure PC is high. DMC was therefore added to reduce the viscosity of the electrolyte so that  $\text{Li}^+$  can move faster. Different amounts of MPBMDS were added to the above bare electrolyte in an argon-filled glove box (water content less than 10 ppm). The bare EC-based electrolyte,  $1.0 \text{ mol dm}^{-3}$   $\text{LiPF}_6\text{-EC}/\text{EMC}/\text{DMC}$  (1:1:1, v/v/v) (Guotai Huarong Co. Ltd., China) was used as the control.

Model cells were fabricated in an argon-filled glove box to investigate the effects of the additive on the electrochemical performance of graphite anodes. The anode was prepared by coating a mixture of CMS (an artificial spherical graphite, C content  $\geq 99.0\%$ , Shanshan Co. Ltd., Shanghai, China), PVDF (C.P.), and carbon black (with weight ratio = 80:10:10) on a piece of copper foil. After drying under ambient conditions, round discs of 1 cm diameter and  $170 \mu\text{m}$  thickness were cut off and further dried under vacuum at  $120^\circ\text{C}$  for 12 h. The amount of active material was about 5 mg. Lithium foil was employed as the counter and reference electrode, and Celgard 2400 as the separator.

Cyclic voltammetry (CV) curves were recorded on a CHI604C Electrochemical Work Station. The scan rate was  $0.3 \text{ mV/s}$  in the potential range 1.8–0 V. Cycling performance was tested on a Land battery tester (Land Co. Ltd., China) at  $90 \text{ mA g}^{-1}$  in the potential range 0.01–2 V vs.  $\text{Li}/\text{Li}^+$ .

The AC impedance measurements were taken by means of the CHI604C Electrochemical Work Station. Scanning frequencies

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