Short communication

Triethyl 2-(1,3-oxazolidin-3-yl)ethyl orthosilicate as a new type electrolyte additive for lithium-ion batteries with graphite anodes

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Abstract

Triethyl 2-(1,3-oxazolidin-3-yl)ethyl orthosilicate (OZOS) has been studied as an additive to the 1 M $LiPF_6$/EC:EMC:DMC:PC (3:6:1:1) electrolyte of lithium-ion battery with graphite anode by cyclic voltammetry and chronopotentiometry. The above additive in amounts of 0.25, 0.5, and 1.0 wt.% increases the first cycle efficiency (ratio of charge to discharge capacity) by 0.4–1.0% as compared to the base electrolyte. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Propylene carbonate (PC) is known to be an important component of lithium-ion batteries electrolytes [1–6]. It increases the solubility of lithium salts, extends the battery working temperature interval (due to its own low freezing point), insures better discharge–charge characteristics. Also, known are the problems preventing a wider application of PC as the electrolytes component for lithium-ion batteries.

One of them is a practically coincidence of reduction potential of PC (0.48 ± 0.03 V) and intercalation potential of Li^+ ions to the graphite anode which results in co-intercalation of PC. The PC solvated Li^+ ions intercalate into carbon until the solid electrolyte interface (SEI) is formed. The bulky $PC \cdot Li^+$ solvate and the products of its reduction (CO_2 and propylene) cause detrimental graphite exfoliation [1–3].

Modification of electrolyte with additives, which form a quality SEI before co-intercalation of PC can occur, is a viable approach for the use of PC-based electrolytes in Li-ion batteries with graphite anodes [5–7].

In the recent review [4] the efficiency of vinylene carbonate and methyl cinnamate as electrolyte additives improving the SEI structure is mentioned. Butyrolactone derivatives were tested as additives to $LiClO_4$/PC electrolyte for lithium-ion batteries with graphite anodes [5]: it was shown that 0.3 M and higher concentrations of 2-acetoxy-4,4-dimethyl-4-butanolide suppresses exfolation of graphite, co-intercalation and decomposition of PC, while lithium insertion and extraction into/from graphite anode proceeded. Acrylonitrile was also found to be a useful SEI film-forming electrolyte additive for lithium-ion batteries with graphitic anodes [6]: PC co-intercalation into graphite is suppressed in the presence of even small amounts of acrylonitrile. The addition of Li_2CO_3 to a solution of 1 M $LiPF_6$/ethylene carbonate (EC):diethyl carbonate (DEC) (1:1, v/v) results in a decrease in the initial irreversible capacity caused by solvent decomposition [7]. Nevertheless, vinylene carbonate [8] still remains most promising among perspective additives.

In spite of numerous additives of different chemical nature tested as the PC-based electrolyte improving agents, no explicit correlations between their structure and effect on the SEI properties have as yet been established. The mechanism of the additives action still stands under discussion and the-

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oretical basis of the search for tailor-made additives keeps being developed. Among the existing rationalizations, the most general and common is that a "good" additive should be capable of reducing and polymerizing to form a perfect SEI prior to the PC·Li$^+$ solvate intercalation into the graphite anode occurs.

In fact, as expected, the SEI-forming process and the morphology of the protective membrane are extremely complex and involve not only the additives but all components of the base electrolyte, including its salt [1–4,6,7] and depend on the type of charge procedure in the first cycle [5–7].

Another prerequisite for preventing the PC·Li$^+$ intercalation is that the additive should be a stronger ligand than PC towards the Li$^+$ ion thus minimizing the PC·Li$^+$ solvate concentration.

All these deliberations are accounted for while our systematic search for new type of additives to improve the PC-based electrolytes for lithium-ion batteries with graphite anodes.

In this paper, we briefly report on the synthesis and performance of a representative of a new type multifunctional additives, namely triethyl 2-(1,3-oxazolidin-3-yl)ethyl orthosilicate (OZOS), which has been design to meet the above requirements. Indeed, OZOS consists of 1,3-oxazolidine cycle that is more basic than PC owing to its tertiary amino nitrogen and potential chelating ability with participation of oxygen and additionally capable of ring-opening anodic polymerization.

Accordingly, the orthosilicate moiety due to its low-lying LUMO is to be reduced at more positive potential than that at which the PC·Li$^+$ intercalation starts thus contributing to the SEI membrane with lithium silicate film possessing the Li$^+$-ion conductivity. The (CH$_2$)$_2$ spacer is appropriate to isolate electronically the two functions, but short enough to ensure trough-space cooperative interaction in radical-ion species during the SEI forming process.

2. Experimental

Synthesis of triethyl 2-(1,3-oxazolidin-3-yl)ethyl orthosilicate (OZOS) was carried out according to the following scheme:
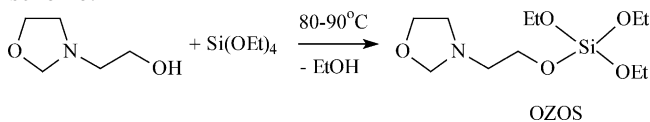
A mixture of 2-(1,3-oxazolidin-3-yl)-1-ethanol (14.6 g, 0.125 mol) and tetraethyl orthosilicate (62.4 g, 0.300 mol) was heated upon stirring at 80–90 °C for 5 h. The reaction mixture was distilled under vacuum to give 11.3 g (32%) of OZOS, a transparent, movable liquid, bp 118–120 °C (5 mmHg), n_D^{20} 1.4248, soluble in the electrolyte components: ethylene carbonate (EC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), PC and in the electrolyte composed from these solvents, as well in diethyl ether, acetone, benzene, dioxane, THF, DMSO, HMPA.

^{1}H NMR (CDCl$_3$), δ, ppm: 4.30 s (2H, ^{2}CH$_2$), 3.89 t (2H, OCH$_2$, ^3J 6.1 Hz), 3.84 q (6H, CH$_2$O, ^3J 7.0 Hz), 3.75 t (2H, ^{5}CH$_2$, ^3J 6.7 Hz), 3.00 t (2H, ^{4}CH$_2$, ^3J 6.7 Hz), 2.73 t (2H, NCH$_2$, ^3J 6.1 Hz), 1.22 t (9H, Me, ^3J 7.0 Hz).

IR (neat, cm^{-1}): 2976 s, 2929 s, 2888 s, 2819 shld (ν, CH$_2$, Me); 2730 m (ring vibrations); 1490, 1454, 1428, 1391, 1369 m (δ, CH$_2$, Me); 1296, 1251 m, 1168 s, 1105 s, 1085 s (ν, C–O, Si–O, C–N; ring vibrations); 970 s, 915 m, 890 m, 804 s, 680 (δ, CH$_2$).

Found, %: C, 47.12; H, 9.30; N, 5.27; Si, 10.16. C$_{11}$H$_{25}$NO$_5$Si. Calcd., %: C, 47.28; H, 9.02; N, 5.01; Si, 10.03.

Dielectric constant of OZOS is 4.9 and kinematic viscosity is 2.04 mm^2/s (for PC – 60.9 and 2.00 mm^2/s, respectively).

The electrolyte solutions were prepared by adding various amounts (0.25, 0.5 and 1.0 wt.%) of OZOS to the 1 M LiPF$_6$/EC:EMC:DMC:PC (3:6:1:1) electrolyte composition.

Electrochemical experiments were carried out in model coin cells. The working electrode was a mixture of graphite powder and PVdF deposited onto foamed Cu sheet. Lithium metal was used as counter electrode. The electrodes were separated with a Celgard polypropylene separator. Electrolyte preparation and cell assembly were accomplished under dry argon atmosphere in a glow-box.

Cyclic voltammetry and chronopotentiometry were used to study the initial irreversible capacities (IIC) and coulombic efficiency. The graphite electrode were potentiostatically and galvanostatically charged and discharged between 3.0–0.0 and 1.5–0.001 V, respectively.

3. Results and discussion

Fig. 1(a) shows a typical cyclic voltammogram for the graphite anode in 1 M LiPF$_6$/EC:EMC:DMC:PC (3:6:1:1) electrolyte with 1 wt.% of OZOS added. Coulombic efficiency of the cycling calculated from these voltammograms is represented in Fig. 1(b), where, for the comparison, the cycling efficiency of the graphite anode in the above electrolyte without the additive is given. As it is seen from the Fig. 1(b), the cycling efficiency in the electrolyte with the additive is 73% at the first cycle and 99% at the following cycles. The cycling efficiency in the electrolyte without the additive is much lower: 64% at the first, 88% at the second, 92% at the third and 94% at the following cycles.

Charge–discharge curves of the first cycle obtained under conditions of the galvanostatically charged and discharged graphite anode in the electrolyte in the potential range of 1.5–0.001 V are presented in Fig. 2. The initial irreversible capacity (IIC), which was calculated by subtracting the initial de-intercalation capacity from the initial intercalation capacity, equals 28 mAh/g in case of the graphite anode cycling in the additive-free electrolyte. Addition to the electrolyte OZOS in amounts of 0.25, 0.5 and 1 wt.% decreases the ini-
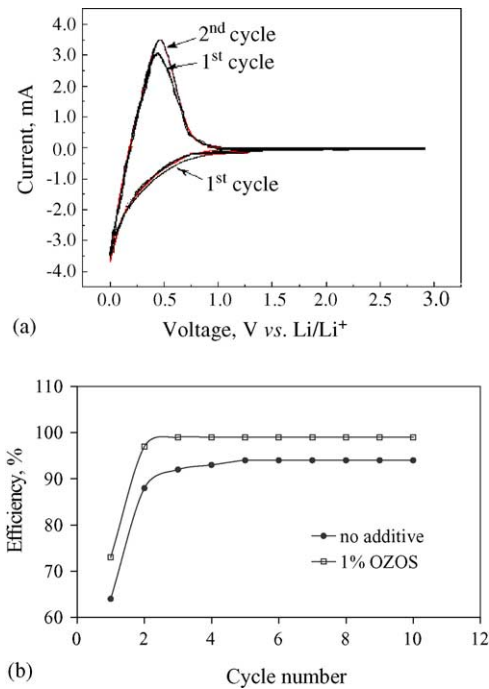
Fig. 1. Cyclic voltammograms (a) of the graphite electrode in the 1 M LiPF$_6$/EC:EMC:DMC:PC (3:6:1:1) electrolyte with 1 wt.% of OZOS added, scan rate is 1 mV/s and its coulombic efficiency, (b) compared with the same electrolyte without additive.

Fig. 3. Constant current charge-discharge cycling of the graphite electrode in the 1 M LiPF$_6$/EC:EMC:DMC:PC (3:6:1:1) electrolyte without additive and with 0.25, 0.5, and 1.0 wt.% of OZOS. Current density is 60 mA/g (0.2 °C).

Fig. 4. The coulombic efficiency vs. cycle number of the graphite electrode in the 1 M LiPF$_6$/EC:EMC:DMC:PC (3:6:1:1) electrolyte without additive and with 0.25, 0.5, and 1.0 wt.% of OZOS added.

tial irreversible capacity value to 24, 24, and 25 mAh/g, respectively.

The specific charge capacity values from the second to tenth cycles upon the graphite anode cycling with 0.5 and 1 wt.% of OZOS are higher compared to the capacity values upon cycling without additive (Fig. 3(a)). The specific discharge capacity values of the graphite electrode obtained with 0.25, 0.5, and 1 wt.% of OZOS are higher at all 10 cycles than those without additive (Fig. 3(b)). Using these date the coulombic efficiency of cycling have been calculated, which
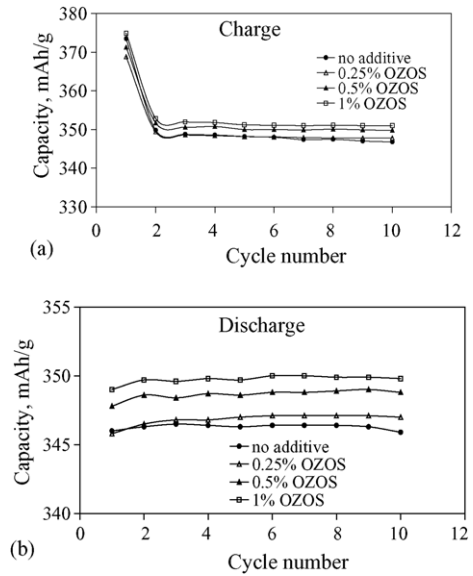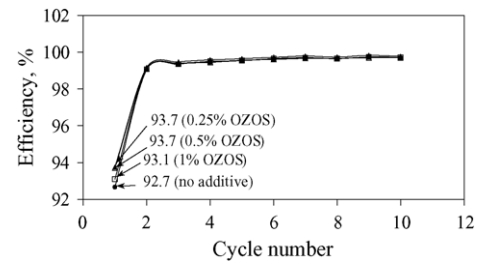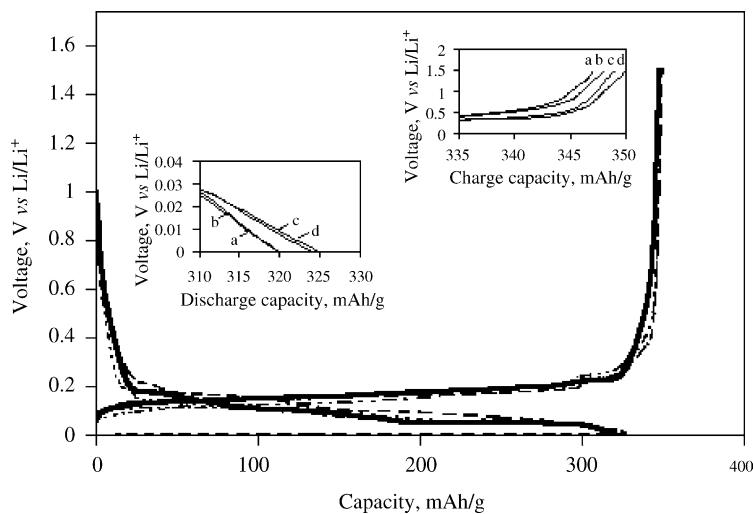

Fig. 2. First charge–discharge curves of the graphite electrode in the 1 M LiPF$_6$/EC:EMC:DMC:PC (3:6:1:1) electrolyte without additive (a) and with 0.25 (b), 0.5 (c), and 1.0 (d) wt.% of OZOS. Current density is 60 mA/g (0.2 °C).

values are presented in Fig. 4. It follows, that addition of OZOS to the electrolyte in the amounts specified, enhances the coulombic efficiency of the graphite electrode cycling at the first cycle by 0.4–1.0%.

4. Conclusions

Thus, a new multifunctional compound, triethyl 2-(1,3-oxazolidin-3-yl)ethyl orthosilicate (OZOS), a representative of the oxazolidine family, combining 1,3-oxazolidine (Lewis base) and orthosilicate (Lewis acid) functions in the same molecule has been synthesized. It has been demonstrated that OZOS is a prospective additive to the PC-based electrolytes for lithium-ion batteries with graphite anodes improving their first cycle coulombic efficiency upon cycling and decreasing initial irreversible capacity.

The preliminary results obtained allow one to conclude that the alkoxysilane-functionalized oxazolidines represent a new promising family of multifunctional compounds for the further systematic search for additives improving performance of PC-based electrolytes.

Acknowledgement

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