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RESEARCH PAPER

Effect of Butyl Sultone on the Li-ion Battery Performance and Interface of Graphite Electrode

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Abstract: The effect of butyl sultone (BS) on the graphite interface of a lithium ion battery in carbonate-based electrolytes was studied by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), as well as density functional theory (DFT) calculation. The results indicate that BS has a lower LUMO energy than the solvents and is reduced prior to solvent compositions of the electrolyte on a graphite electrode, forming a stable solid electrolyte interface (SEI) film during the first cycle. The SEI film resistance and the charge-transfer resistance of the graphite electrode in BS containing solution changed little after storage at 70 ℃ for 24 h, while those in BS free solution increased significantly. The influence of BS on the electrochemical performance was also discussed. It was found that the discharge capacities were significantly improved at room temperature, low temperature, and after high temperature storage, on account of the presence of BS.

Key Words: Li-ion battery; Butyl sultone; Discharge capacity; Cycling stability; SEI film

On account of their high discharge voltage, high energy density, and small environmental harm, lithium ion batteries have become the research focus of new power sources. With the ever-changing development of mobile electronic products and hybrid electric vehicles, the need to improve the cycling capacity, performance at high/low temperature, and safety properties has become more and more popular[1–5]. The performance of the batteries is closely related to the solvent composition of the electrolyte and the utilization of additives[6–9]. The current electrolytes used in the lithium ion battery are prepared by dissolving $LiPF_6$ in EC-based solvents. Nevertheless, ethylene carbonate (EC) has a poor low-temperature performance because of its high melting point (about 36 ℃), which confines the utilization of the lithium ion battery[10]. Propylene carbonate (PC) has a similar structure and properties with EC, a lower melting point (about –49.2 ℃), can effectively suppress the crystallization of EC at low temperature, and improve the performance of lithium ion batteries at low temperature[11–13]. Unfortunately, PC is not widely used as a solvent in lithium ion batteries, as PC can easily insert into the graphite with Li-ion, which causes the cycling performance of the Li-ion battery to decrease significantly. The co-intercalation behavior of PC could be eliminated when an additive is used[14–16]. In this paper, butyl sultone (BS) as an additive for the formation of SEI film on graphite is considered, and the effects of BS on the graphite interface of a Li-ion battery in carbonate-based electrolytes have been studied by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), as well as density functional theory (DFT) calculation.

1 Experimental

1.1 Electrolyte preparation

$LiPF_6$ (Stella Chemical, Osaka Japanese), carbonate solvents of EC, PC and EMC(ethyl(methyl) carbonate) were purified

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by distilling and adsorption with a molecular sieve till the purity was higher than 99.9% (GC-14C, SHIMADZU). Electrolyte solutions were prepared by dissolving $LiPF_6$ in the mixture solvents. The concentration of $LiPF_6$ in all the electrolytes was 1 $mol \cdot L^{-1}$. The preparation of the electrolyte was carried out in a dry glove box ($w_{H_2O} < 10^{-6}$) filled with argon of high purity. Water and free acid (HF) contents in the electrolyte were controlled below 20×10^{-6}. These were determined by Karl-Fisher 831 Coulometer (Metrohm) and Karl-Fisher 798 GPT Titrino (Metrohm).

1.2 Lithium ion battery performance

Electrochemical performances of batteries with and without BS were evaluated in 053048-size batteries, with lithium cobalt oxide ($LiCoO_2$) as cathode and graphite as anode. 1 $mol \cdot L^{-1}$ $LiPF_6$ in a mixture of 1:1:3 (mass ratio) EC, PC, and EMC as a base electrolyte was selected. A BS-9300R type battery charger (Guangzhou Qingtian Industrial Co., Ltd., China) was used. The temperature was controlled with a WD4003 oven (Chongqing Yinhe experimental equipment Co. Ltd., China). The batteries were charged at a constant current of 1*C* rate to 4.2 V, kept at 4.2 V till the current decreased to 20 mA at room temperature. Then the following steps were taken: (1) the batteries were discharged at 1*C* rate to 3.0 V to measure the cycling and discharge performance at room temperature; (2) the charged batteries were stored for 24 h under 70 ℃ and discharged at 1*C* rate to 3.0 V at room temperature; (3) the charged batteries were stored for 4 h under –20 ℃ and then discharged at 0.2*C* rate to 2.7 V.

1.3 Electrochemical measurements

A three-electrode battery was used for CV measurements, with graphite as the working electrode (the graphite electrodes were prepared as follows: a carbonaceous mesophase sphere (CMS) was slurried with 8% (*w*) polyvinylidene fluoride (PVDF), and the mixture was rolled onto a copper foil, pressed and dried at 120 ℃ for 14 h), with Li foils as counter and reference electrodes, respectively. 2016 coin-type batteries were used for EIS measurements, with graphite as the working electrode and Li foils as counter and reference electrodes. The impedance measurements were performed at OCV (open circuit voltage) potentials after stabilizing the electrodes by five charge-discharge cycles with a constant current of 0.1 $mA \cdot cm^{-2}$. The AC frequency range was from 100 kHz to 10 mHz, with an amplitude of 5 mV. Electrochemical measurements were carried out on Autolab (PGSTAT30, ECO Echemie B.V.Company).

1.4 DFT calculation

All calculations were performed using the Gaussian 03 programs package. The equilibrium and transition structures were fully optimized by the B3LYP method using a 6-31+G (*d*, *p*) basis set.

1.5 Electrode's surface chemistry analysis

The morphology of the graphite was observed on an S-520 SEM (Hitachi) equipped with an EDS detector (Oxford, INCA), accelerative voltage 20 kV.

2 Results and discussion

2.1 Cycling performance at room temperature

Fig.1 presents the cycling performance of lithium ion batteries with and without BS at room temperature. From Fig.1, it can be seen that the performance of the battery with BS far surpasses the performance of the battery without BS. The initial capacity of a lithium ion battery with BS electrolyte is 623.8 mAh, much larger than that of the battery without BS, which is only 594.4 mAh. The cycling stability of the battery with BS is also improved. The capacity of the battery with BS keeps at 605.6 mAh (97.1% of the initial capacity) after 100 cycles, while that of the battery without BS keeps at 568.8 mAh (95.7% of the initial capacity).

2.2 Discharge performance at room temperature, low temperature and after high temperature storage

Fig.2(a) shows discharge curves of the lithium ion batteries with or without BS at room temperature. It can be seen from Fig.2(a) that the battery with BS shows higher discharge voltage and capacity than the battery without BS. Fig.2(b) shows discharge curves of the lithium ion battery with and without BS at –20 ℃. It can be seen from Fig.2(b) that the battery with BS shows better discharge performance than the battery without BS. The discharge capacity of the battery with BS is 539.7 mAh at –20 ℃, but the discharge capacity of the battery without BS is only 517.1 mAh at –20 ℃. Besides, the

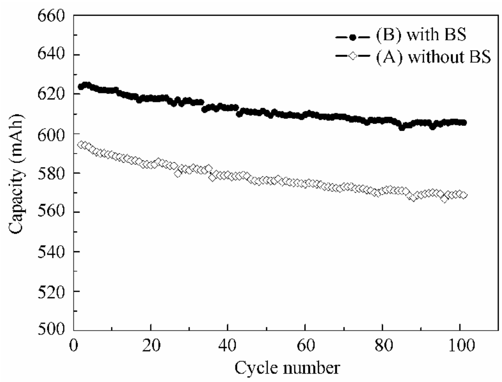

Fig.1 Cycling performance of Li-ion batteries at room temperature

(A) *c* ($LiPF_6$) =1 $mol \cdot L^{-1}$, *m* (EC): *m* (PC): *m* (EMC)=1:1:3;
(B) A with BS (*w*=1%)