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Influences of trace water on electrochemical performances for lithium hexafluoro phosphate- and lithium Bis(oxalato)borate-based electrolytes

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ABSTRACT

Water has a fatal influence on the performance of lithium ion batteries. In this work, Lithium hexafluoro phosphate($LiPF_6$)-ethylene carbonate (EC)/diethyl carbonate (DEC) and lithium bis(oxalato)borate (LiBOB)-tetramethylene sulfone (SL)/DEC are taken as examples to investigate the influences of water concentration for electrochemical window, acidity, impedance and cycling performance for lithium ion batteries by adjusting water concentrations in the electrolytes. Results show that LiBOB-based electrolyte has better water tolerance compared with $LiPF_6$-based system, due to the formation of $LiBOB{\cdot}xH_2O$ compounds by consuming the additive trace water. Besides, inductively coupled plasma test result shows that Mn ion dissolution in $LiPF_6$ systems is extremely severe, which is mainly caused by the corrosive reaction between $LiMn_2O_4$ and by-product HF acid. And we believe that Mn ion dissolution and the following deposition should be responsible for failure work of $LiPF_6$-based cells. But for LiBOB-based cells, stable SEI layers and good electrochemical performances have been obtained, benefitting from the synergistic effect between LiBOB salt and SL solvent. And the presence of high-resistance $B(C_2O_4)(OH)$ and $LiB(C_2O_4)(OH)_2$ products on surface of graphite electrode is the main reason for a small number of capacity fading.

1. Introduction

Lithium ion batteries (LIBs) are expected to be large-scale applications in electric cars and solar energy reserves. It is well known that trace water will lead to loss of irreversible capacity, increase of internal resistance for battery, damage for the so-called solid electrolyte interphase (SEI) layer, and corrosion for cathode materials [1–4]. Burns et al. [2] reported that cells that containing either 200 or 1000 ppm water in the electrolyte that were stored for one week before formation showed no difference in performance when compared to the cells that were formed immediately after being filled. However, the cells containing 2000 ppm water at elevated temperature (>50 °C) begin to have detrimental impact to cell performance for LCO/LTO cells. A corresponding increase in first cycle irreversible capacity with increasing water content was observed. Adding up to 2000 ppm water resulted in change to measure coulombic efficiency, charge end point slippage, voltage drop during storage and average charge voltage increase. Cheng et al. [5] studied the impact of maleimide as an additive with cells containing 100 ppm water in the electrolyte and suggested that the use of this additive can help mitigate the poor performance that would be caused by water in the electrolyte. These negative impacts are detrimental to the performance of battery and would lead to safety hazards [6,7]. Thus, water should be strictly controlled for LIB in production process. However, trace water impurities are inevitably introduced through the production process of LIBs, mainly coming from environment humidity, non-absolute drying electrode and electrolyte materials.

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At present, $LiPF_6$ is the commercial electrolyte lithium salts for LIBs. However, in addition to the poor thermal stability of $LiPF_6$, unstable P–F bond is sensitive to trace water in $LiPF_6$ electrolyte. Preliminary studies suggest that traces of water will react with $LiPF_6$ to generate the POF_3 and HF substances, which have corrosion effect on electrode materials, and result in the decrease of LIB electrochemical performance as well as the deterioration in security [8]. That is, $LiPF_6$ electrolyte is very sensitive for high temperature and trace water, which leads to some limitations in the application of advanced lithium ion battery. Therefore, it is necessary to find new salt substitutes to promote the tolerance for high temperature and moisture. A few years ago, bis(oxalato)borate (LiBOB) has been reported as an attractive new type of lithium salt. Compared with $LiPF_6$, LiBOB salt has many advantages including superior thermal stability, increased safety, and a more stable SEI layer [9–12]. However, there are some drawbacks lying in LiBOB-based conventional electrolytes, namely, LiBOB has low solubility in linear carbonates and shows high interface impedance at ambient temperature. Functional additives have been used to manage drawbacks of LiBOB. For example, we had attempted to use tetramethylene sulfone (SL) solvent tailored for LiBOB with success [13]. This combination circumvented two issues that had been troubling LiBOB and SL respectively, that is, (1) the less-than-ideal solubility of the former in carbonate-based solvents and (2) the inability of the latter to form protective SEI on graphite anodes. The two components complemented each other and formed an electrolyte that supports full lithium ion cells consisting of mesophase carbon microbeads (MCMB) and $LiFePO_4$ with superior reversibility.

During the past period of time, very few people have devoted to study the effect of water concentration on the cell electrochemical performance, whether on the preferred conventional electrolyte as $LiPF_6$-ethylene carbonate/diethyl carbonate (EC/DEC) or on the promising novel system as LiBOB-SL/DEC.

In this paper, we project to investigate the influences of water concentration on comprehensive performance for LIBs by adjusting the water concentration in these electrolytes. To magnify the influence of water on performance of battery, on the one hand, spinel $LiMn_2O_4$ is chosen as cathode material, due to the inferior compatibility between Mn(III)-containing electrode and acid-containing electrolyte. It has already been established that $LiMn_2O_4$ electrodes suffer from severe capacity fading during charge-discharge cycles, mainly caused by inevitable trace water with dissolution and corrosion behaviors. On the one hand, water concentrations are extended to about 550 ppm and 850 ppm for $LiPF_6$ and LiBOB-based electrolytes, respectively. Besides, the compatibilities of $LiPF_6$ and LiBOB-based electrolytes with graphite cathodes are studied.

2. Experimental

2.1. Cell preparation

A slurry mixed by 92 wt% of MCMB and 8 wt% of polyvinylidene fluoride (PVDF) in N-methyl pyrrolidinone solvent was used to prepare negative electrode. The positive electrode was composed of $LiMn_2O_4$ (84 wt%), acetylene black (8 wt%) and PVDF (8 wt%). The mass density of the $LiMn_2O_4$ and MCMB that loaded on Al and Cu foil was approximately 3.1 mg cm^{-2} and 2.51 mg cm^{-2} 1 mol L^{-1} $LiPF_6$-EC/DEC (1:1, by volume, the same below) electrolyte was produced by Chaoyang Yongheng Chemical Co. Ltd. LiBOB was synthesized in our laboratory by employing a solid state reaction [13]. SL and DEC were produced by Chaoyang Yongheng Chemical Co. Ltd. 0.7 mol L^{-1} LiBOB-SL/DEC (1:1) electrolyte was prepared in an argon atmosphere glove box.

A little water was added into the fresh $LiPF_6$ and LiBOB-based electrolytes, respectively. Water concentrations of these as-prepared electrolytes are 82.8 ppm (w-a-1),129.1 ppm (w-b-1), 211.3 ppm (w-c-1), 299.2 ppm (w-d-1), 412.1 ppm (w-e–1) and 525.5 ppm (w-f-1) for $LiPF_6$-based systems, and 143.6 ppm (w-a-2), 295.8 ppm (w-b-2), 412.3 ppm (w-c-2), 539.1 ppm (w-d-2), 671.2 ppm (w-e-2) and 821.5 ppm (w-f-2) for LiBOB-based systems, respectively.

Experimental CR2032 coin cells were assembled in an argon atmosphere glove box (O_2, $H_2O < 1$ ppm) using one of the above prepared electrodes as the cathode, a lithium sheet as the anode, one of the above prepared hydrous systems as the electrolyte, and a Celgard (2400) porous polypropylene as the separator dried at 65 °C for 2 h before use.

2.2. Measurements

Water and acid concentrations were tested by Karl Fischer Moisture Titrator (KF756) and acidity meter PHS-3G (Shanghai, China), respectively. Electrochemical measurements of Li/MCMB and $LiMn_2O_4$/Li half-cells were performed on a LAND CT2001A tester (Wuhan, China) in the voltage range of 0.01–2 V and 3.5–4.3 V, respectively.

Electrochemical windows were measured in a three electrode system through a CHI 660C electrochemical analyzer (Shanghai, China), at the scan rate of 2 mV s^{-1} in the voltage range of 4.0–7.0 V. The three electrode system includes the following parts, working $LiMn_2O_4$ electrode with the reaction area of 1 cm^2, and counter and reference electrodes using lithium sheets.

Electrochemical impedance spectroscopies (EIS) were carried out on the CHI 660C electrochemical analyzer at a fully lithiated state of 0.01 V for Li/MCMB half-cell and a fully delithiated state of 4.3 V for $LiMn_2O_4$/Li half-cells. A sinusoidal AC perturbation of 5 mV was applied to the electrode over the frequency range of 100 kHz to 10 mHz.

Before cycling $LiMn_2O_4$ electrodes before cycle were put into 4.0 mL sealed polyethylene plastic vials filled with $LiPF_6$- and LiBOB-based hydrous electrolytes, respectively. After being placed in atmospheric environment for two weeks at room temperature, the concentrations of Mn ions were obtained by an IRIS Advantage Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) measurement (United States).

The morphologies of SEI layer was measured though a JSM-5600 scanning electron microscope (SEM, Japan). The chemical composition of materials on surface of graphite electrodes in Li/MCMB cells were characterized by Fourier transform infrared spectroscopy (FTIR) (FTIR-650, China). Prior to these surface analyses, electrode of the experimental cells were stripped off from electrodes in an Ar glove box, rinsed with dimethyl carbonate (DMC) solvent five times to remove electrolyte from electrode, then dried in Ar atmosphere drying even for 12 h at room temperature to remove the residual solvent of DMC.

The calculations of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies were carried out by density functional theory (DFT) calculation with the Gaussian 03, B3LYP/6-311 + G(d,p).

3. Results and discussion

3.1. Electrochemical windows and acidities

Fig. 1 shows the electrochemical windows of $LiPF_6$ and LiBOB-based electrolytes with different water concentrations. As has been recently reported, the novel designed LiBOB-based system is able to improve the stability of electrolyte against oxidative