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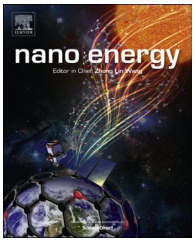

RAPID COMMUNICATION

Ionic liquid electrolytes with protective lithium difluoro(oxalate)borate for high voltage lithium-ion batteries

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Abstract

The electrolyte based on ionic liquid and sulfone with lithium difluoro(oxalate)borate (LiODFB) was prepared for high voltage lithium-ion battery because of its high conductivity, wide electrochemical window and non-flammability. High voltage cathodes and carbonaceous anodes were used as electrodes to evaluate the electrochemical properties of cells with the electrolyte. $Li/Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ and Li/MCMB cells with LiODFB-PP14TFSI/TMS exhibit good cycling performance, which retain capacities of above 220 mA h g^{-1} and 338.6 mA h g^{-1} after 50 cycles, respectively. The solid-electrolyte interphase (SEI) formation were characterized by ab initio simulations and X-ray photoelectron spectroscopy. The results indicate that LiODFB can be preferably oxidized during charging and reduced during discharging process. The nano reaction products pile up to form the SEI layers on the surfaces of electrodes. The SEI layers which prevent the electrolyte and electrode materials ensure the good electrochemical performance of the cells.

Introduction

Substantial efforts have been focused on lithium-ion batteries for their high energy density and long cycle life as one of the most promising energy for electric cars and mobile electronics. However, the adoption of lithium-ion battery still faces major challenges because the batteries cannot meet the

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increasingly demand of the consuming electronic devices. It is particularly crucial to develop the lithium-ion battery with high energy density, which must satisfy several requirements such as: (1) a nonaqueous electrolyte with wide electrolyte window; (2) a cathode with high electrochemical potentials (μ_C) value and (3) an anode with low electrochemical potentials (μ_A) value as well as each allowing cycles of large reversible capacity. At present, many new cathode materials with potentials beyond 4.5 V (vs. Li/Li^+) have been developed, such as Li-rich cathode material [1,2] and spinel $LiNi_{0.5}Mn_{1.5}O_4$ [3,4]. Carbonaceous anode materials are generally used because of their merits of low potentials, high specific energy, inexpensive and resource abundance. Nevertheless, the conventional carbonate/$LiPF_6$ electrolytes suffer from the limit electrochemical window and tend to react with the high-potential cathode material leading to deteriorating cycle performance [5,6].

The use of ionic liquid has been worldwide launched [7-10] as an alternative to the traditional carbonates electrolyte for lithium-ion battery due to its high electrochemical stability and non-flammable nature. In particular, the ionic liquid/organic solvent binary electrolyte systems, which combine the high electrochemical stability of ionic liquid and low viscosity of organic solvent, have attracted much attention [11-13]. Piperidium-based ionic liquids possess high oxidation potential and low reduction potential [14–17]. However, the graphitic anodes remained the insurmountable hurdle for piperidium cations, unless an additive of solid-electrolyte interphase (SEI) formation was used.

Novel boron based materials have been reported as lithium salts [18–26] or electrolyte additives [27-32] in lithium batteries because it can be decomposed to form SEI on the surface of electrodes improving the battery performance. Inspired by these studies, we have reported ionic liquid/sulfone mixed electrolytes based on *N*-butyl-methyl piperidinium bis(trifluoromethylsulfonyl)imide (PP14TFSI) and tetramethylene sulfone (TMS) with lithium difluoro(oxalate)borate (LiODFB) as wide electrochemical window and safe electrolytes [33]. In this work, we studied the compatibilities of the LiODFB–PP14TFSI/TMS electrolyte with both high voltage cathodes ($Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ and $LiNi_{0.5}Mn_{1.5}O_4$) and carbonaceous anodes. Both computational and experimental methods were used to confirm the SEI formation on the surface of electrodes and the consequent good cycle performance.

Experimental

The electrolyte was prepared with 60 wt% PP14TFSI (99%, Shanghai Chengjie Chemical Co. LTD) and 40 wt% TMS (>99%, Acros) after dehydration for 12 h. 0.4 M LiODFB was dissolved in the mixed electrolytes in an argon-filled glove box. The flammability of the electrolyte was tested by immersing a glass fibre ball into the electrolyte and then exposing it to a butane blowtorch flame which was judged to be non-flammable after it failed to ignite within 60 s. The ionic conductivity of the electrolyte was measured using a CHI660D electrochemical workstation over the test frequency range of 10^5–10 Hz. The oxidation potential and reduction potential were determined by cyclic voltammetry (CV) in the voltage range of -0.5 V to 6.0 V at a scan rate of 0.1 mV s^{-1} using a sealed glass cell with a platinum wire as the working electrode and Li foil as the reference and counter electrodes.

$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ and $LiNi_{0.5}Mn_{1.5}O_4$ were obtained by coprecipitation according to the previous work [2,4]. The carbonaceous materials such as mesocarbon microbead (MCMB), graphite, hard carbon and soft carbon were purchased from Shenzhen BTR New Energy materials INC, China. The electrodes consisted of 80 wt% active material, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF) with *N*-methyl-2-pyrrolidone (NMP) as the solvent. The obtained slurry was coated onto the current collector and dried at 70 °C under vacuum. Coin cells were fabricated using a Celgard® 2300 separator and with the prepared electrolytes in the argon-filled glove box. Electrochemical performances of the coin cells were recorded by CV curves at a scan rate of 0.1 mV s^{-1} to characterize the reversible behavior on a CHI660D electrochemical workstation. The constant current charge–discharge experiments with the coin cells were carried out to test their cycling stability (Wuhan LAND electronics, China). The electrochemical impedance spectra (EIS) were measured using a CHI660D electrochemical workstation over the test frequency range of 10^5-10^{-2} Hz.

The cycled cells were disassembled to obtain the electrodes. After washed with excess TMS, the morphology and the chemical element distribution of the surface of the cycled electrodes were investigated. The morphology was characterized by scanning electron microscopy (SEM, HITACHI S-3500N, Japan). X-ray photoelectron spectroscopy (XPS) measurements were employed to investigate the chemical element distribution on the surface of the cycled electrodes at room temperature by means of an electron spectroscopy for chemical analysis (ESCA) spectrometer (PHI-1600, USA) with a monochromatic Al-K_α (1486.6 eV) source. The calculations were performed with the DMol3 module of the Materials Studio 5.5 program. The solvent molecules and ion structures with sizes were optimized and calculated employing nonlocal density functional theory (DFT) with the BLYP functional based on a DNP group.

Results and discussion

Figure 1 presented the electrochemical characteristics and flammability of the LiODFB–PP14TFSI/TMS electrolyte and the molecular structures of the components. The cationic and anionic sizes of the ionic liquid (calculated along the longest expansion) are 0.91 nm and 0.79 nm (Figure 1(b)). The heterocycle in the cation of the ionic liquid shows a diameter on average 0.3 nm. The oxidation potential and reduction potential of the electrolyte are 5.1 V and 0.05 V (as compared to Li/Li+), respectively. The room temperature ionic conductivity of the electrolyte is 1.62×10^{-3} S cm^{-1}. Furthermore, the electrolyte is judged to be non-flammable after it failed to ignite when exposed to a flame of 1300 °C for 60 s. Its non-flammability can be attributed to two factors: (1) the non-flammable nature of the ionic liquid, (2) addition of an appropriate amount of TMS which does not take a heavy toll on the non-flammability of the bulk electrolyte. All the above good performance makes the LiODFB–PP14TFSI/TMS electrolyte a promising choice for use in safe high voltage lithium-ion batteries.