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Electrochemical effect and mechanism of adiponitrile additive for high-voltage electrolyte

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ABSTRACT

To satisfy the need of 5 V high-voltage cathode materials, lithium difluoro(oxalato)borate (LiDFOB) with excellent film-forming property has been chosen as lithium salt, and adiponitrile (ADN) with stable electrochemical performance has been evaluated as functional additive. An electrochemical investigation of this novel electrolyte solution shows a wide electrochemical oxidation window of nearly 6.0 V vs Li^+/Li. Due to the positive effect of ADN on the cathode/electrolyte interface, $LiNi_{0.5}Mn_{1.5}O_4$/Li half-cell with ADN-adding electrolyte exhibits prominent rate capability and cyclability. It is believed that the improvement of electrochemical performances has benefitted greatly from interfacial impedance reducing. Two modeling hypotheses have been used to explain interfacial interaction between ADN and $LiNi_{0.5}Mn_{1.5}O_4$, by the means of analysis of X-ray photoelectron spectroscopy and theoretical calculation. Results show that ADN can enrich the surface of cathode material to hinder the further decomposition of the electrolyte, and contribute to the formation of a cathode-electrolyte interface passivation film with protective and conductive properties.

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1. Introduction

With the incremental improvements of the lithium-ion battery (LIB) market over the past four decades, which can provide sufficient energy densities to sustain a significant mobile electronic device industry, people have begun to expect better electrochemical performance materials applied to electric vehicles (EVs) and hybrid electric vehicles (HEVs). Nevertheless, the evolution of higher energies and power densities in LIBs is suffering some technical bottlenecks during this phase.

Studies have shown that cathode and electrolyte materials developed with wide electrochemical window has been of great importance for power battery applications. Among the various cathodes, spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LMNO) is appealing due to its ability to supply high power/energy densities and high lithiation/delithiation voltage of around 4.7 V, together with the merits of low cost and toxicity [1–3].

However, the electrodes charged to a high voltage lead to a significant deterioration of cycle performance. The origin of the capacity fading mainly relates to the increase in surface reactivity between the highly oxidized cathode and the electrolyte solution. Consequently, the bottleneck effect of electrolyte becomes especially conspicuous in the efforts of developing a coveted “5 V” class Li-ion chemistry.

At present, the commercial 5 V electrolyte usually consists of a fluorine-containing lithium salt ($LiPF_6$, for example) and alkyl carbonate solvents. However, in LMNO/Li half cells, it has been found that these preferred electrolyte systems show limited stability as they undergo oxidative decomposition at high voltage. That is, the formed cathode-electrolyte interface (CEI) passivation film on the surface of LMNO cathode, which is composed of organic and inorganic species such as carbonates, ($ROCO_2Li$), polyethers (-(CH_2O)n-), LiF and Li_xPF_y, do not completely protect the electrolyte solution under prolonged cycling conditions [4–7]. And that will then result in the negative effect on the long-term stability of the battery, such as rapid capacity fading and dramatic impedance increase. Solutions to this problem are centered on finding new optimized electrolyte formulations that can properly passivate the cathode surface in the same way as they do to change the anode electrode [8].

One of the most promising methods to improve high-voltage tolerance of electrolyte is the use of novel salts, including lithium bis(oxalato)borate (LiBOB) and lithium difluoro(oxalato)borate (LiDFOB). Each of these salts has particular film-forming property, accompanied by the generation of cross-link borate radicals to form a passivating surface film on electrode surface. It is worth

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mentioning that $LiPF_6$ replaced with LiBOB and LiDFOB can offer significant improvements in the performance of LMNO-based cells, which relates to a combination of forming cathode surface film and the inhibition of Mn dissolution [9]. However, there are some drawbacks lying in carbonate-based conventional electrolytes with LiBOB and LiDFOB, namely, whether LiBOB or LiDFOB has low solubility in linear carbonates and shows high interface impedance at ambient temperature.

In order to satisfy the strict requirement of "5 V" class electrolyte formulations, in addition to the electrolyte salt, solvent is the most important factor affecting the stability and high-voltage tolerance of electrolyte [10]. Nowadays, these "5 V" class solvents mainly include sulfone, ionic liquids and nitriles. Sulfone, however, is not stable against graphitic carbon anodes. In addition, melting point (i.e. 25 °C for sulfolane) and viscosity for sulfone are generally relatively high [11], limiting low-temperature and high-rate performances of LIBs.

As for ionic liquids, they not only show low high-rate battery performance due to the high viscosity, but also are expensive to make in large quantities [10]. Moreover, nitrile solvents are relatively considered as promising "5 V" class solvents owing to their balanced unique characteristics. In generally, they have wide electrochemical stability windows of 7–8 V (vs. Li/Li^+), and high flash points that surpassed those of carbonate solvents to mitigate electrolyte solutions flamed without the need for flame-retardant additives [12–15]. Besides, nitriles solvents could improve electrochemical performance by positive effects on electrode/electrolyte interface. For example, it has been reported that 3-methoxypropionitrile could improve charge-transfer process at the electrode/electrolyte interface, by decreasing the interfacial reaction between solvent and electrode as well as accelerating desolvation of Li^+ ions [16]. In addition, it has been reported that adiponitrile (ADN) is in favor of capacity retention by forming stable and effective films on surfaces of anode and cathode electrodes [12,17,18]. About the toxicity of nitriles, general remarks have been put forward as follows. The toxicity of nitrile-containing compounds lies in their ease of releasing the highly toxic CN- cyanide ion that can happen easily during the hydrolysis of inorganic compounds like metal cyanides (i.e., HCN, KCN) [19]. However, this does not take place in organic nitriles because their hydrolysis (under certain conditions) leads to the formation of the corresponding carboxelates or aldehydes, and their reduction product is most likely their corresponding amines [20].This reflects in the LD_{50} value of ADN, which is 155 mg kg^{-1} that is 31 times less toxic than KCN ($LD_{50} \sim 5$).

In this work, we introduced LiDFOB as lithium salt, which combined advantages of LiBOB and $LiBF_4$ to build new electrolyte formulation for LMNO-based cells [21]. To remedy the defects of LiDFOB itself, we adopted ADN as electrolyte additive, with the expectation of not only increase stability against oxidative decomposition but also decrease interface impedance. Besides, to rate the newly built electrolyte formulations, electrochemical performances of LiDFOB-DEC/EC with and without ADN additive were studied. Finally, to clarify the mechanism of ADN additive on improvement of high-voltage tolerance for electrolyte, we propose and discuss two kinds of research hypotheses.

2. Experimental

2.1. Electrolyte preparation

LiDFOB was synthesized in our laboratory with an improved method as described previously [22]. ADN was purchased from Aladdin Industrial Co., ethylene carbonate (EC) and diethyl carbonate (DEC) were purchased from Chaoyang Yongheng Chemical Co., Ltd. Each kind of solvents was dried by 0.4 nm molecular sieves and alkali metal for at least two days until the water content was typically less than 20 ppm determined by Karl Fischer titration.

To strike a balance between conductivity and high-voltage tolerance, the additive amount of ADN was selected as 10%. And electrolytes of 0.7 mol L^{-1} LiDFOB-DEC/EC/ADN (4.5:4.5:1, by volume, the same as follows) and 0.7 mol L^{-1} LiDFOB-DEC/EC (1:1) were prepared in argon gas protection glove box. To ease the discussion, LiDFOB-DEC/EC/ADN and LiDFOB-DEC/EC electrolytes are marked as ADN-adding and ADN-absent.

2.2. Cell preparation

LMNO was purchased from Sichuan XingNeng New Materials Co., Ltd. The cathode electrode sheet was based on an aluminum foil coated by a mixture of 84 wt. % LMNO, 8 wt. % carbon black, and 8 wt. % polyvinylidene fluoride (PVDF) on a single side of the substrate. The thickness of the composite cathode and mass loading of active material is 30 μm and 2.78 mg cm^{-2}.

CR2032 coin cells were assembled in an argon atmosphere glove box using the thus-fabricated cathode, lithium foil anode, Celgard porous polypropylene separator (2400) and one of the above mentioned electrolytes.

2.3. Measurements

Ionic conductivities of the electrolytes were measured by DDSJ-308A conductivity meter (Shanghai, China) in a temperature range of 253.15-343.15 K.

Electrochemical windows of the electrolytes were measured in a three-electrode system (a Pt sheet was used as the working electrode, and lithium sheets were used both as the counter electrode and the reference electrode, respectively) for the linear sweep voltammetry (LSV). The test was through a CHI660C Electrochemical Workstation (Shanghai, China) at the scan rate of 2.0 mV s^{-1} in the voltage range of OCP-7.0 V.

Electrochemical impedance spectroscopy (EIS) tests of the LMNO/Li cells with different electrolytes were measured on the same electrochemical station, in a three-electrode cell system (the cathode electrode was used as the working electrode with a reaction area of 1 cm^2, and lithium sheets were used both as the counter electrode and the reference electrode, respectively). All cells were tested at the fully delithiated state of 5.0 V at room temperature. A sinusoidal AC perturbation of 5.0 mV was applied to the electrode over the frequency range of 100 kHz to 10 mHz.

Electrochemical property tests of cells were carried out on a Land cell tester CT2001A (Wuhan, China) in the voltage range of 3.5 to 5.0 V for the LMNO/Li test. Cathode materials of the experimental cells were stripped off from LMNO-based electrodes in an Ar glove box after 10 cycles. Prior to surface analysis, the cathode materials were rinsed with DEC three times to remove adsorbed substances, and then dried in a vacuum drying even for 12 h at 120 °C to remove the residual solvent of DEC. The surface element analysis was performed by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos Analytical Ltd.).

2.4. Theoretical calculations

Quantum chemical calculations were performed by Gaussian 09 package [23]. Density functional theory (DFT) was the method used for geometry optimization with B3LYP along with the 6–311 + G (d, p) basis set (C, H, O, N, B, F, Li) and lanl2dz pseudopotential basis set (Ni). In order to investigate the effect of solvents, the structures were optimized by using the polarized continuum model (PCM), with a dielectric constant of 46.83, which was calculated for the ADN-adding system mentioned above.

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