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Functionalized 1,3-dialkylimidazolium bis(fluorosulfonyl)imide as neat ionic liquid electrolytes for lithium-ion batteries

Guojun Wang [a], Shaohua Fang [a,c,*], Dong Luo [a], Li Yang [a,b,c,**], Shin-ichi Hirano [b]

[a] School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China
[b] Hirano Institute for Materials Innovation, Shanghai Jiaotong University, Shanghai 200240, China
[c] Shanghai Electrochemical Energy Devices Research Center, Shanghai 200240, China

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ABSTRACT

Neat ionic liquid electrolytes based on functionalized 1,3-dialkylimidazolium cation and bis(fluorosulfonyl)imide anion were investigated in MCMB/$LiFePO_4$ full cells with commercial electrodes for the first time. Ether functionalization could bring the prominent improvement of initial efficiency and the comparable cycle performance to a conventional carbonate-based electrolyte. In view of full cells, it was inferred that the further oxidation on cathode of the reduction products on anode during the charge process might result in the serious capacity loss of initial cycle.

1. Introduction

Ionic liquids (ILs), composed of organic cations and various anions, are regarded as novel safe electrolytes for lithium-ion batteries because of their superior characteristics, including non-flammability, negligible volatility, high thermal stability and wide electrochemical window [1,2]. However, IL electrolytes usually cannot provide the effective solid electrolyte interphase (SEI) film on graphite anode [3–5]. As a result, the reductive decomposition of IL electrolytes on graphite anode or the intercalation of IL cation into graphite is inevitable [6–8]. Therefore, the nonideal compatibility with graphite anode restricts the commercial application of IL electrolytes in lithium-ion batteries.

In order to enhance the compatibility with graphite anode, some organic additives, typically vinylene carbonate (VC) and ethylene carbonate (EC), have been introduced into IL electrolytes to optimize the surface between graphite anode and ionic liquid phase [9–11]. Besides, organic co-solvents, such as ethyl methyl carbonate (EMC) and diethyl carbonate (DEC), are also added to improve viscosity and conductivity of electrolyte. This kind of mixed electrolytes, for example, IL + EC/DEC/VC [12], IL + EC/DEC [13], IL + EC/DMC/EMC [14], exhibit better rate performance than neat IL electrolytes. Nevertheless, addition of organic additives and co-solvents will make neat IL electrolytes lose their inherent characteristics of negligible volatility and high thermal stability [15–17], and weaken high safety of neat IL electrolytes [18].

Recently, much attention has focused on ILs based on bis(fluorosulfonyl)imide (FSI) anion. Compared with bis(trifluoromethanesulfonyl)imide (TFSI) counterparts, FSI-based ILs own lower viscosity and higher conductivity [19]. More importantly, FSI anion can participate in the formation of SEI on graphite and improve the compatibility of IL electrolytes with graphite, evidenced by Li/natural graphite half cells using neat 1-ethyl-3-methylimidazolium FSI (EMI-FSI) [20,21], *N*-methyl-N-propylpyrrolidinium FSI (P13-FSI) [20,22] and *N*-methyl-N-propylpiperidinium FSI (PP13-FSI) [23] electrolytes. Unfortunately, natural graphite is not adopted in commercial lithium-ion batteries due to low initial coulombic efficiency and poor cycle performance [24]. So researchers still need to seek suitable FSI-based IL electrolytes to support graphite materials used in commercial lithium-ion batteries.

The properties of ILs can be modified easily by diverse structural variation of cation and anion. And ether or alkenyl functionalization of cation is favorable to obtain low-viscous and high-conductive ILs [25–29]. In this article, two ether- or alkenyl-functionalized 1,3-dialkylimidazolium ILs based on FSI anion were proposed as new electrolytes for lithium-ion batteries, and compared with EMI-FSI electrolyte. The structures of these ILs were illustrated in the insets of Fig. 1. Mesocarbon microbeads (MCMB)/$LiFePO_4$ full cells with commercial electrodes were used to evaluate the performance of neat IL electrolytes for the first time. It was proved that ether functionalization could bring the prominent improvement of performance. The mechanism of initial capacity loss was also explored deeply in view of full cells. We inferred

* Correspondence to: S.H. Fang, School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China.
** Correspondence to: L. Yang, Hirano Institute for Materials Innovation, Shanghai Jiaotong University, Shanghai 200240, China.
E-mail addresses: housefang@sjtu.edu.cn (S. Fang), liyangce@sjtu.edu.cn (L. Yang).

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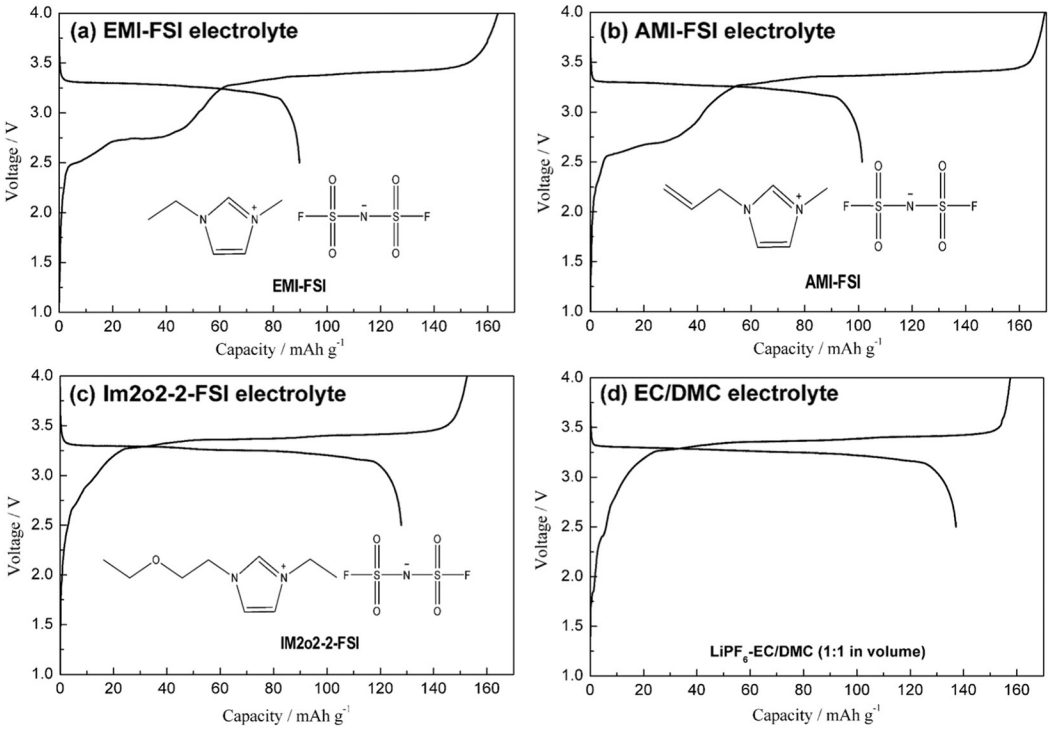

Fig. 1. Voltage profiles for the first cycle of MCMB/$LiFePO_4$ cells at 0.02C.

that the further oxidation on cathode of the reduction products on anode during the charge process might result in the serious capacity loss.

2. Experimental

EMI-FSI, 1-allyl-3-methylimidazolium bis(fluorosulfonyl)imide (AMI-FSI) and 1-ethoxyethyl-3-ethylimidazolium bis(fluorosulfonyl)imide (Im2o2–2-FSI) were synthesized following the previous method [30]. Lithium bis(fluorosulfonyl)imide (LiFSI) was kindly provided by Morita Chemical Industries Co., Ltd. A conventional electrolyte, 1 M $LiPF_6$-EC/DMC (1:1 volume), was purchased from Zhangjiagang Guotai-Huarong Co., Ltd. IL electrolytes were prepared by dissolving 0.8 M LiFSI into ILs in an argon-filled glove box ($H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm). The water content of IL electrolytes was detected by a moisture titrator (Metrohm 73KF coulometer) based on the Karl-Fischer method, and the value was <50 ppm.

Electrochemical performances were measured by using CR-2016 coin cells on a CT2001A test instrument. The commercial $LiFePO_4$ cathode and MCMB anode were kindly supplied by Jiangsu Litian New

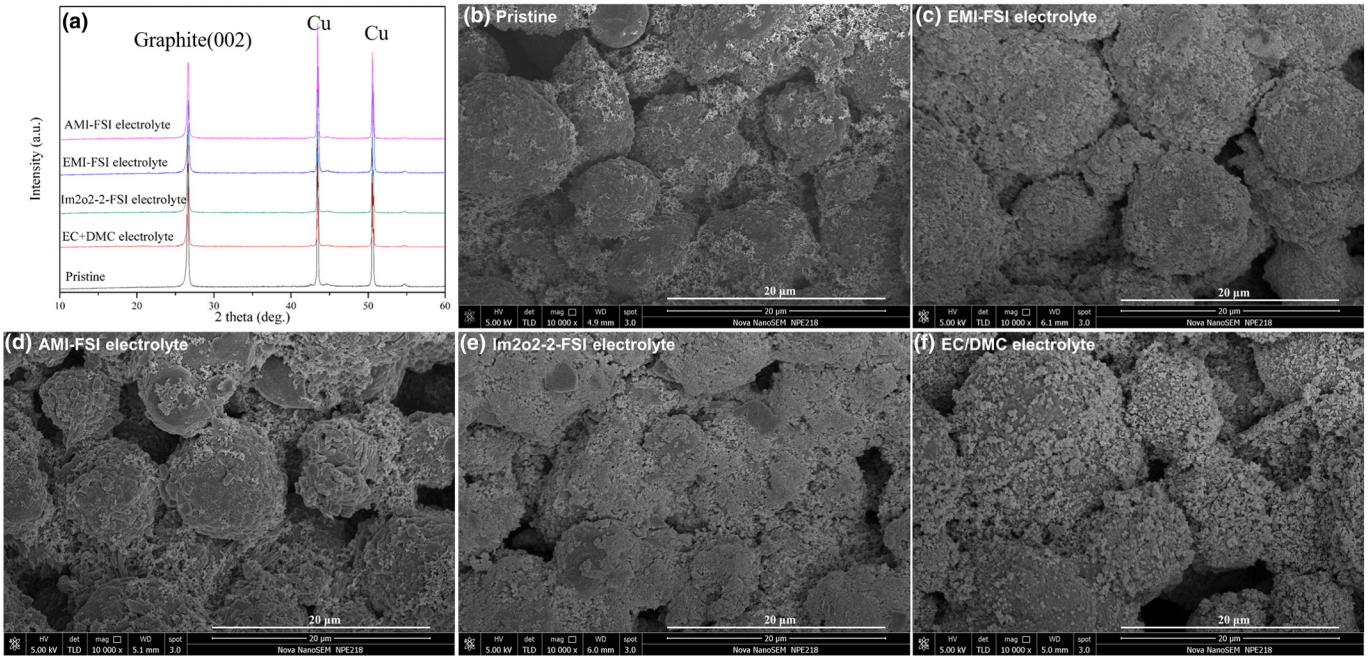

Fig. 2. (a) XRD patterns of pristine and cycled MCMB anode, (b-f) SEM image of pristine and cycled MCMB anode.