Electrochimica Acta 110 (2013) 181–190

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Charge–discharge behavior of graphite negative electrodes in bis(fluorosulfonyl)imide-based ionic liquid and structural aspects of their electrode/electrolyte interfaces☆

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ARTICLE INFO

Article history:
Received 30 November 2012
Received in revised form 23 February 2013
Accepted 4 March 2013
Available online 20 March 2013

Keywords:
Ionic liquids
Bis(fluorosulfonyl)imide
Double layer structure
Lithium-ion battery
Graphite negative electrode

ABSTRACT

We evaluated the charge–discharge behavior of four types of graphite electrode, including raw synthetic graphite (SG), shaped natural graphite (NG), soft carbon-coated natural graphite (SCNG), and hard carbon-coated natural graphite (HCNG), in a 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMImFSI) ionic liquid. Based on the charge–discharge curves for the first cycle in LiTFSI/EMImFSI, capacity loss arising from an irreversible reaction on the graphite anodes was clearly observed for the cells consisting of SG and SCNG, whereas the capacity loss for the cells containing NG and HCNG was relatively low. The coulombic efficiency during cell cycling also confirmed that the charge–discharge behavior of graphite in LiTFSI/EMImFSI is strongly affected by the surface structure of the graphite and that basal-plane-oriented graphite, such as NG and HCNG, can reduce the primary charge capacity loss. The advantages of the stable charge–discharge behavior provided by FSI-based ionic liquids for lithium ion batteries are also discussed based on the application of voltammetric and electrochemical impedance techniques to model carbon electrodes in ionic liquids. Based on these analyses, a mechanism involving a double-layer-based interface (not a solid electrolyte interface (SEI)) is proposed to stabilize the surface of graphite negative electrodes.

1. Introduction

Recent growth and demand for portable electronics and large-scale applications, such as plug-in hybrid or electric vehicles, aircraft, and renewable energy storage devices, require advanced lithium ion batteries that have high power, high storage capacity, and safe performance. Room-temperature ionic liquids, such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI), are attractive candidates for use as the electrolyte in lithium-ion batteries due to their various properties, such as a wide electrochemical potential window, acceptable ionic conductivity, high thermal stability, and negligible vapor pressure. In particular, such ionic liquids have been investigated to improve the safety of lithium-ion batteries because they have lower flammability and lower reactivity than conventional organic electrolytes [1–6]. However, lithium-ion batteries composed of ionic liquid electrolytes have considerable drawbacks associated with their charge–discharge performance, partly because of the significant decomposition of the ionic liquids, especially the imidazolium-based ionic liquids, on the negative electrode, which can lead to a complete lack of reversibility at the anode. Another problem is the low ionic conductivity of typical ionic liquids, including both aromatic and aliphatic cations, which results in a lower rate capability [7,8].

Certain organic additives, such as ethylene carbonate (EC) and vinylene carbonate, have been introduced into ionic liquid electrolytes to stabilize and protect the interface between the negative carbon electrode and the ionic liquid phase from the undesirable, irreversible reactions of the ionic liquid components [9–12]. However, despite considerable research into this strategy, there have been few reports of room-temperature ionic liquids that can provide the reversibility of a graphitized negative electrode in the absence of additives.

☆ This paper was presented at the 63rd Annual Meeting of ISE, Prague, Czech Republic, August 19-24, 2012.

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http://dx.doi.org/10.1016/j.electacta.2013.03.018

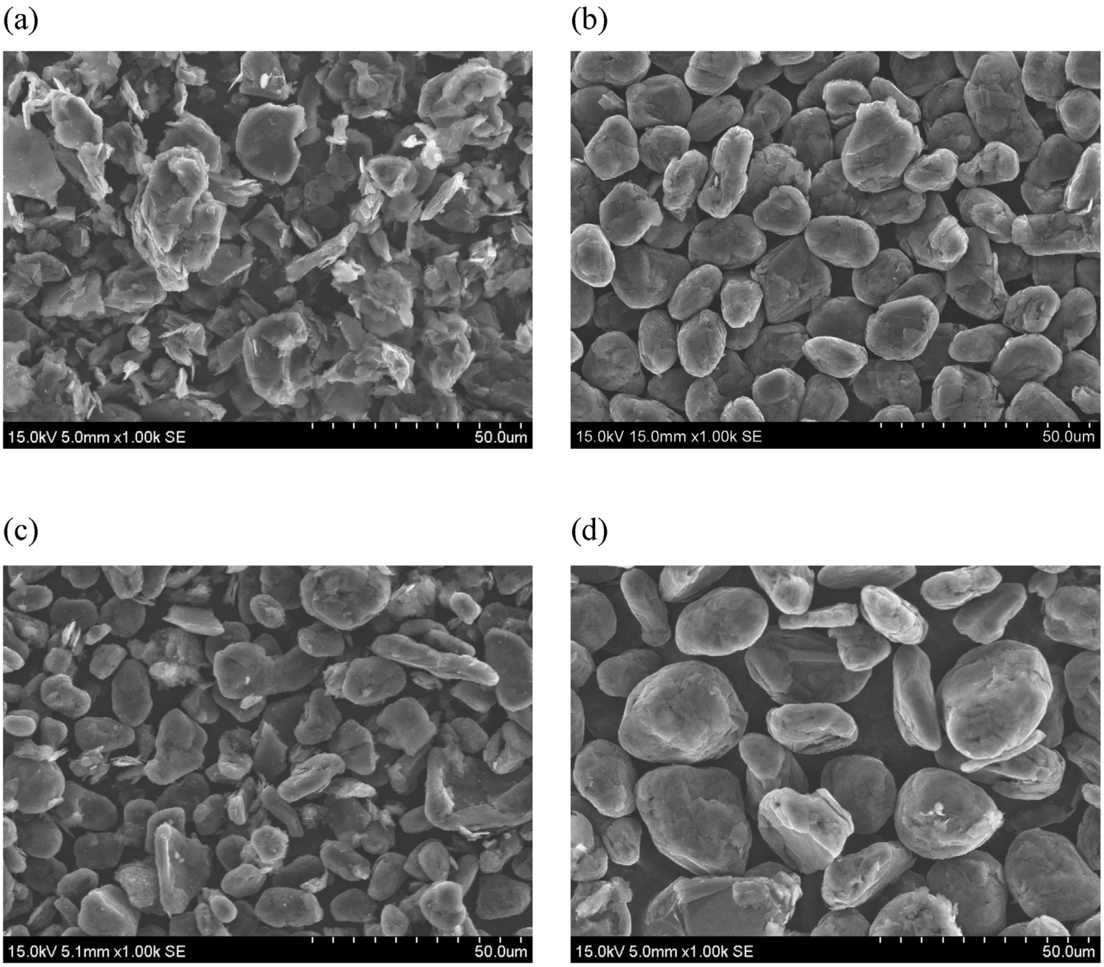

Fig. 1. SEM images of the graphite powders employed in this study. (a) Synthetic graphite (SG), (b) natural graphite (NG), (c) soft-carbon-coated natural graphite (SCNG), (d) hard-carbon-coated natural graphite (HCNG).

We successfully developed a reversible lithium insertion/extraction method for a negative graphite electrode in a promising ionic liquid containing bis(fluorosulfonyl)imide (FSI^-) in the absence of additives [13]. This liquid dissolving LiTFSI offers low electrode/electrolyte interfacial resistance, which leads to high-rate charge–discharge characteristics for the graphite electrode relative to a typical organic solution-based electrolyte [14,15]. In addition, we investigated the electrochemical behavior of a high-capacitive Si–C composite negative electrode in an FSI-based ionic liquid electrolyte in which the galvanostatic cycling of the electrode in the ionic liquid with a charge limitation of 800 mAh g^{-1} is stable for 50 cycles [16]. Seki et al. and Usui et al. also confirmed that reversible and stable charge–discharge behavior of graphite and Si negative electrodes can be achieved through the use of an FSI-based ionic liquid with a pyrrolidinium cation [17–19]. In our previous work mentioned above, it is important to note that the electrolyte can contain an $EMIm^+$ cation, which typically causes irreversible decomposition at the negatively polarized graphite and Si electrode.

We also found that the charge–discharge performance of an attractive cathode, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC), improves in the FSI-based ionic liquid. The rate capability of the NMC cathode in LiTFSI/EMImFSI clearly exceeds that in conventional $LiPF_6$/EC + DMC (DMC = dimethyl carbonate), most likely because of the stable and low-resistivity layer on the NMC [20]. Many studies, such as those of Matsumoto et al. [21,22], Passerini et al. [23–25] and Guerfi et al. [26], have also reported the advantages of FSI-based ionic liquids for lithium-metal or lithium-ion batteries [27–31].

Regarding the graphite anode, the practical application of FSI-based ionic liquids requires a clarification of the effects of graphite-based active materials on their charge–discharge behavior. Herein, we report results from a charge–discharge cycle test, focusing on the initial cycle, of several graphite anodes in an FSI-based ionic liquid. In addition, we clarify the origin of the benefit provided by the ionic liquids from the standpoint of the electrode/electrolyte interface structure in the ionic liquid electrolyte using voltammetric and AC impedance measurements with several model carbon electrodes.

2. Experimental

EMImFSI was produced by Dai-ichi Kogyo Seiyaku Co. Ltd. (Kyoto, Japan). The ionic liquid contains less than 10 ppm (w/w) of moisture and less than 2 ppm (w/w) of halides and alkali metal ion impurities. The ionic liquid was dried under vacuum for more than 24 h and preserved in an argon-filled glove box (less than 1.0 ppm of oxygen and moisture). LiTFSI was purchased from Kanto Kagaku Co. Ltd. and was used after drying under vacuum. We used four graphite powders, including raw synthetic graphite (SG), shaped natural graphite (NG), soft carbon-coated natural graphite (SCNG), and hard carbon-coated natural graphite (HCNG), as the active materials. Figs. 1 and 2 show SEM and TEM images, respectively. The surface of the SG was rough, whereas that of the NG, SCNG, and HCNG was very smooth, which indicates that the latter three graphite particles are spherically shaped. From the TEM measurements, a portion of the edge-plane surface was observed for the SG