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Electrochemical and structural characterization of Mg ion intercalation into Co_3O_4 using ionic liquid electrolytes

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ABSTRACT

The electrochemical behavior of magnesium perchlorate in ionic liquids is characterized using Co_3O_4 as the working electrode and Mg foil as the anode material. The cations of the ionic liquids were 1,2-dimethyl-3-*R*-imidazolium with R = butyl (MMBI) or octyl (MMOI), and the anion was bis(trifluoromethanesulfonyl)imide (TFSI). The TFSI ionic liquids exhibited large electrochemical windows, with MMOITFSI possessing an electrochemical window of 5 V. Ionic conductivity studies indicated a higher ionic conductivity of 3.67 mS/cm for 1.0 M $Mg(ClO_4)_2$ in MMBITFSI when compared to 2.16 mS/cm for 1.0 M $Mg(ClO_4)_2$. MMOITFSI was selected as the electrolyte for the electrochemical characterizations of Co_3O_4, due to its larger electrochemical window and its inability to intercalate, and therefore degrade, graphitic material added to the Co_3O_4 electrode. Electrochemical results indicated that the maximum attainable value for x in $Mg_xCo_3O_4$ was 0.33, with an initial capacity of only 78 mAh/g. X-ray diffraction studies of the Mg intercalated Co_3O_4 indicated a 20% expansion of the unit cell and a decrease in the symmetry of the metal oxide from cubic to orthorhombic symmetry. Charge/discharge experiments at a C/3 rate were performed vs. Mg metal. Results indicated that after 10 cycles, the capacity decreased linearly with cycling, most likely due to the inability to deintercalate the more strongly interacting Mg^{++}.

1. Introduction

In answer to the growing demand for compact, high energy density power sources and micro power sources, one exciting avenue to be explored is the use of multivalent ion batteries. One possibility is the Mg^{++} ion system, in which the Mg^{++} cation would replace the monovalent Li^+ cation in common lithium ion batteries. Although such a system would operate at a lower voltage (2.3 V for Mg vs. 3.0 V for Li), the higher valence of the Mg^{++} ion could significantly increase the capacity and current output of such a battery [1–3].

One crucial requirement for such a device would be an electrolyte that demonstrates high ionic conductivity of the Mg^{++} ion [4–8]. Researchers have investigated a number of non-aqueous solvents as potential electrolytes for Mg^{++} batteries, such as tertiary amines or ethers, or mixtures of THF and Lewis-acid complexes [9,10]. Ionic liquids, specifically those containing the positively charged imidazolium ring, have been extensively studied as electrolytes due to their numerous unique physical and electrochemical properties [11–14]. Ionic liquids have also demonstrated their ability to function as electrolytes in lithium batteries, which greatly enhances the safety of these batteries without compromising their function [15–18]. Additionally, the ionic liquids 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and 1-butyl-3-methylimidazolium tetrafluoroborate have been studied as potential electrolytes in Mg^{++} batteries [19–21]. We have chosen to investigate two different ionic liquids: 1,2-dimethyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide (MMBITFSI) and 1,2-dimethyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide (MMOITFSI). The cations MMBI and MMOI are displayed in Fig. 1a and b, respectively, while the anion TFSI is shown in Fig. 1c. Our efforts focus on using ionic liquids with a tri-substituted imidazolium ring because these compounds display greater electrochemical stability and the TFSI anion has previously performed exceedingly well in Li-ion systems [15–17]. We also chose to utilize magnesium perchlorate, $Mg(ClO_4)_2$, as the source of the Mg^{++} because, although it is a very powerful oxidizer, the salt was found to have better solubility in ionic liquids than other magnesium salts.

One issue that effects the behavior of ionic liquids in these batteries is that, unlike most common electrolytes, ionic liquids are composed of a cationic and anionic species. Studies have shown that short chain systems, such as 1,2-dimethyl-3-*R*-imidazolium, where R = ethyl, propyl or butyl, can readily intercalate graphite.

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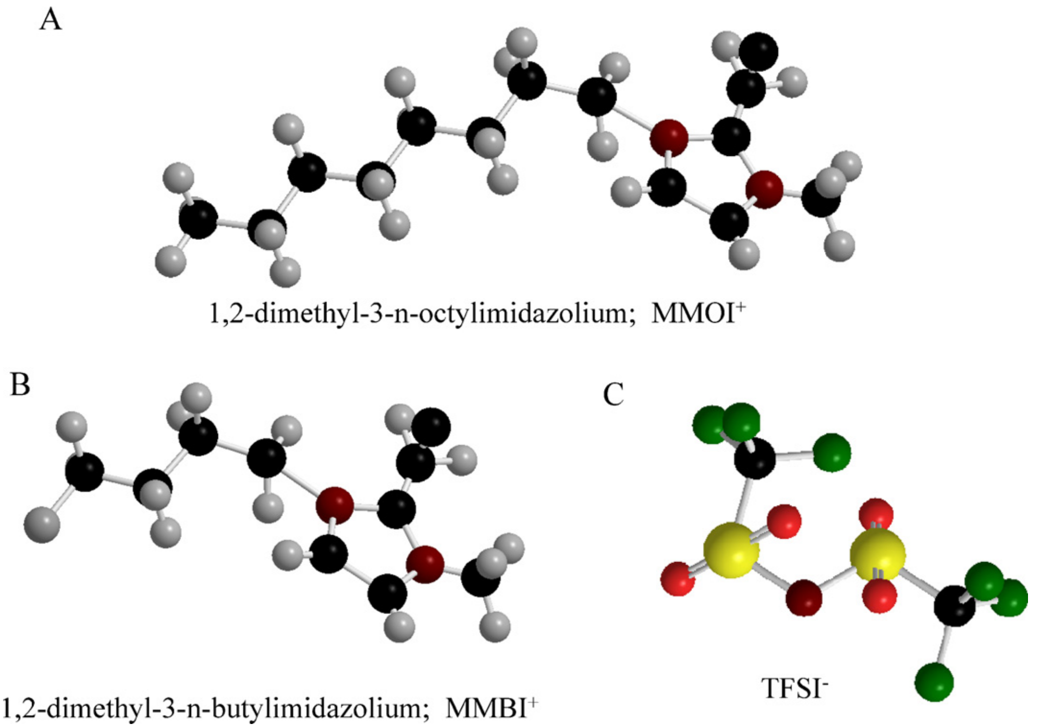

Fig. 1. (A) Structure of the 1,2-dimethyl-3-n-octylimidazolium cation (MMOI$^+$). (B) Structure of the 1,2-dimethyl-3-butylimidazolium cation (MMBI$^+$). (C) Structure of the bis(trifluoromethanesulfonyl)imide anion (TFSI$^-$). Carbon is represented by black, hydrogen by gray, nitrogen by red, boron by purple, fluorine by green, oxygen by pink, and sulfur by yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Unfortunately, this can cause degradation in ion power systems because graphite is a common additive to improve metallic conduction in the cathode and anode materials [22,23]. The long chain octyl-substituted imidazolium was used in the electrochemical characterization of the Co_3O_4 since, with its longer chain, it is less likely to intercalate graphite. The different Mg^{++} solutions are characterized by electrochemical impedance, cyclic voltammetry, and charge discharge experiments. Additionally, the Mg^{++} intercalated Co_3O_4 is characterized by X-ray powder diffraction studies.

2. Experimental

2.1. Preparation of the imidazolium salts

1,2-Dimethyl-3-*R*-imidazolium chloride (MM*R*ICl) was prepared by the reaction of 1,2-dimethylimidazole (Aldrich, 98%) and either 1-chlorobutane (Aldrich, 99%) or 1-chlorooctane (Aldrich, 98%) in a 1:1.15 molar ratio. The method utilized has previously been reported [24].

2.2. Preparation of the TFSI ionic liquids

The TFSI salts were synthesized as previously reported [24]. The resulting MM*R*ITFSI were both clear and colorless.

2.3. Electrochemical measurements

Temperature dependent impedance measurements were made in an argon filled glovebox with a Solartron Si 1260 Gain Phase Analyzer at frequencies from 3 mHz to 1 Hz, using AC amplitude of 5 mV. The sample holder was a 5.0 cm long section of Tygon tubing filled with either MMBITFSI, MMOITFSI, 1.0 M $Mg(ClO_4)_2$/MMBITFSI, or 1.0 M $Mg(ClO_4)_2$/MMOITFSI. The tube was sealed at each end by 0.2 mm thick Pt electrodes. Temperature dependence of the ionic conductivity was measured from 273 to 353 K at temperature intervals of approximately 20 K, with 1-h temperature equilibrium. The ionic conductivity is calculated from the measured resistance when the imaginary component at high frequency fell to zero.

All electrochemical characterizations of the ionic liquids were performed using a VersaSTAT four channel potentiostat wired into an argon-filled glovebox. For three-electrode liquid cell measurements characterizing the electrochemical behavior of the ionic liquids, the counter electrode was a 0.5 cm diameter graphite rod and the working electrode was either a graphite rod or a 2 mm

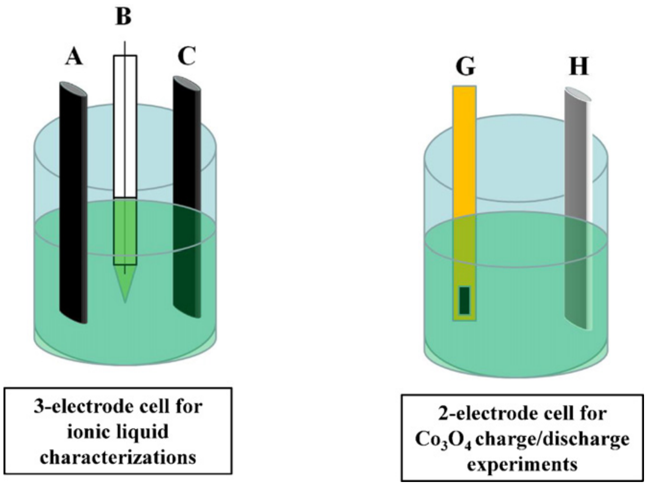

Fig. 2. Schematic of the 3 electrode cell and the 2 electrode cell. (a) The three-electrode cell, shown on the left, was used for characterizing the electrochemical behavior of the ionic liquids, using (A) glassy carbon as the working electrode, (B) Vycor-tipped Ag/Ag$^+$ as the reference electrode, and (C) graphite rod as the counter electrode. (b) The cell on the right was the two electrode cell used for collecting charge/discharge capacities of Co_3O_4, where (D) is again the gold foil with Co_3O_4 pressed into it and (E) was a Mg foil as the anode for the charge/discharge studies.