



Electrochemical performance of $0.5\text{Li}_2\text{MnO}_3-0.5\text{Li}(\text{Mn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25})\text{O}_2$ composite cathode in pyrrolidinium-based ionic liquid electrolytes

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HIGHLIGHTS

- High-energy-density cathodes are synthesized using an auto-combustion method.
- ILs have high thermal stability and are thus ideal for high-safety applications.
- Li^+ /PMP-TFSI IL (rather than Li^+ /BMP-TFSI IL) exhibits high ionic conductivity.
- At 50 °C, a high capacity of 304 mAh g^{-1} is obtained for the Li^+ /PMP-TFSI cell.
- ILs (instead of organic electrolyte) increase the electrode cyclability at 50 °C.

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ABSTRACT

High-energy-density $0.5\text{Li}_2\text{MnO}_3-0.5\text{Li}(\text{Mn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25})\text{O}_2$ composite cathodes for lithium rechargeable batteries are synthesized using an auto-combustion method. The electrode charge–discharge properties are studied at 25 and 50 °C in Li^+ -containing N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (BMP-TFSI) and N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PMP-TFSI) ionic liquid (IL) electrolytes. The IL electrolytes have a high decomposition temperature (~400 °C) and thus are ideal for high-safety applications. Compared to Li^+ /BMP-TFSI IL, Li^+ /PMP-TFSI IL exhibits higher ionic conductivity and lower viscosity. As a result, the composite cathode shows superior electrochemical performance in Li^+ /PMP-TFSI IL electrolyte. With the increase in cell temperature from 25 to 50 °C, the maximum capacities and rate capabilities of both IL cells improve significantly. Thus at 50 °C, discharge capacities of 304 mAh g^{-1} (@10 mA g^{-1}) and 223 mAh g^{-1} (@100 mA g^{-1}) are obtained for the Li^+ /PMP-TFSI cell. These capacities are superior to those for a control cell made with the same composite cathode and a conventional organic electrolyte. At elevated temperature, the cyclability of the composite cathode in the IL electrolytes is markedly higher than that obtained in a conventional organic electrolyte.

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) are attractive power sources for a variety of applications, such as portable electronic devices, electric vehicles, and smart grids [1–3]. To endow batteries with higher energy and power densities, novel high-voltage and high-capacity cathode materials need to be developed [4]. Recently,

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it has been demonstrated that lithium-rich $\text{Li}(\text{Li}_x\text{Mn}_a\text{Ni}_b\text{Co}_z)\text{O}_2$ (or $\text{Li}_2\text{MnO}_3\text{--LiMO}_2$ ($M = \text{Ni, Co, Mn}$)) layered oxide cathodes are promising due to their high capacity ($\sim 250\text{--}280 \text{ mAh g}^{-1}$) in the operating voltage window of 2.0–4.8 V [5,6]. It is interesting to note that unlike conventional cathode materials, in these lithium-rich cathodes, lithium is also present at transition metal sites and eventually the lithium ions create super-lattice ordering with manganese ions to form Li_2MnO_3 -type domains [6]. When charged beyond 4.5 V, lithium ions are extracted from inactive Li_2MnO_3 domains with a concomitant release of lattice oxygen, forming electro-active manganese oxide. Upon discharge, lithium ions are intercalated into the manganese oxide and Mn ions are reduced to a +3 state [7,8]. These Mn ions are oxidized to +4 valence in subsequent charging cycle. The capacity is increased (compared to that of conventional layer oxides) due to the occurrence of this extra $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple along with the usual $\text{Ni}^{2+}/\text{Ni}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ redox transitions. However, despite the high capacity, these composite cathodes suffer from poor stability at elevated temperature and unsatisfactory rate capability [5]. Further investigation of the electrode/electrolyte interactions is thus needed.

For these composite cathodes, the typical cutoff charge voltage is as high as 4.8 V, which is outside the electrochemical stability window of the conventional organic electrolyte that consists of carbonate esters and LiPF_6 salt [9,10]. Decomposition of the organic electrolyte causes (i) the formation of a thick solid–electrolyte interface layer, which leads to high initial irreversible capacity loss and a barrier for lithium intercalation/de-intercalation into/from the cathode material; and (ii) gas evolution, which results in build-up of the cell internal pressure [11]. These phenomena are intensified when the cell operation temperature is increased. Other limitations of conventional organic electrolytes are high volatility and high flammability; consequently, these electrolytes pose serious safety and environmental concerns. Thus, an alternative electrolyte with a wide electrochemical stability window and high thermal stability is highly desired to improve the electrochemical properties of composite cathodes.

To overcome the aforementioned problems, ionic liquid (IL) electrolytes are promising candidates as they are characterized by large electrochemical windows, excellent chemical and thermal stability, non-volatility, and non-flammability [12–14]. Importantly, the physicochemical properties of ILs can be tuned by designing various cation/anion combinations [15], leading to optimal LIB performance. Imidazolium, pyridinium, pyrrolidinium, sulfonium, ammonium, and phosphonium cations together with BF_4 , PF_6 , CF_3SO_3 , and $(\text{CF}_3\text{SO}_2)_2\text{N}$ anions have been used to form ILs for LIB applications [16]. An electrochemical window of up to 6 V and a wide operation temperature range of -90 to 350°C have been reported for these ILs [17,18]. Despite the potential of IL electrolytes, their use for composite cathodes has rarely been investigated [11,19,20]. As reported in these studies [19,20], pyrrolidinium-based cations (i.e., N-butyl-N-methylpyrrolidinium (BMP^+)) seemed to be superior to piperidinium-based cations (i.e., N-propyl-N-methylpiperidinium) for the IL electrolytes. It has been elsewhere reported that shortening the chain length on BMP^+ can increase the ionic mobility without significantly affecting the potential stability window of the electrolyte [21]. In view to this, we felt that the use of N-propyl-N-methylpyrrolidinium (PMP^+) in the IL electrolyte should improve the electrochemical performance of composite cathodes, despite this has never been attempted. This topic is thus addressed in this work.

In the present study, a $0.5\text{Li}_2\text{MnO}_3\text{--}0.5\text{Li}(\text{Mn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25})\text{O}_2$ composite cathode material is prepared using a facile and scalable auto-combustion method. BMP –bis(trifluoromethanesulfonyl)imide (TFSI) and PMP –TFSI IL electrolytes are synthesized and used to investigate the effects of IL cations on

the electrochemical properties (in terms of capacity, rate capability, and cyclability) of the composite cathode. To the best of our knowledge, this is the first attempt to conduct such a comparison for any type of LIB electrode. A conventional organic electrolyte, which consists of ethylene carbonate (EC), diethyl carbonate (DEC), and LiPF_6 salt, is also adopted in this work. The temperature-dependent cell performance with various electrolytes is systematically investigated.

2. Experimental procedure

2.1. Synthesis of $0.5\text{Li}_2\text{MnO}_3\text{--}0.5\text{Li}(\text{Mn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25})\text{O}_2$ composite powder

Stoichiometric amounts of lithium, manganese, nickel, and cobalt acetates were dissolved separately in warm distilled water (60°C). The acetate solutions were mixed together under continuous stirring for 15 min. This solution was subsequently mixed with citric acid solution, with the citrate-to-metal ion ratio maintained at 1:1. Upon heating at $\sim 120^\circ\text{C}$ (with constant stirring), the solution turned into a viscous gel. With further heating, the gel was auto-ignited, forming a black fluffy powder. The resultant powder was first calcined at 450°C for 3 h for organic removal and then pressed into pellets and calcined again at 800°C for 8 h. The obtained pellets were manually crushed into fine powder and used for electrode preparation.

2.2. Synthesis of electrolytes

BMP –TFSI and PMP –TFSI ILs were prepared and purified by following a published method [22]. TFSI anions were used in this study since they are highly stable and can withstand a potential of $>5.5 \text{ V}$ (vs. Li) [21]. The ILs were washed with dichloromethane (99%, SHOWA), filtered to remove precipitates, and then vacuum-dried at 100°C for 12 h before use. Their water contents, measured using a Karl Fisher titrator, were below 100 ppm. 1 M LiTFSI (98%, Tokyo Chemical Industry Co. Ltd.) was dissolved into the ILs to allow Li^+ transport. Each mixture was continuously stirred by a magnetic paddle for 24 h to ensure uniformity. A conventional organic electrolyte, consisting of 1:1 (by volume) EC (99%, Alfa Aesar) and DEC (99%, Alfa Aesar) as co-solvents and 1 M LiPF_6 salt, was also prepared for comparison. All the chemicals were handled and stored in an argon-filled glove box (Innovation Technology Co. Ltd.), where both the moisture content and oxygen content were maintained at below 1 ppm.

2.3. Cell assembly

A cathode slurry was prepared by mixing 80 wt.% synthesized $0.5\text{Li}_2\text{MnO}_3\text{--}0.5\text{Li}(\text{Mn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25})\text{O}_2$ powder, 15 wt.% carbon black, and 5 wt.% poly(vinylidene fluoride) in N-methyl-2-pyrrolidone solution. The slurry was cast onto Al foil and vacuum-dried at 110°C for 2 h. The active material loading amount was $4(\pm 0.3) \text{ mg cm}^{-2}$. Then, the cathode electrode was roll-pressed and punched to match the required dimensions of a CR2032 coin cell. Li foil and a Celgard polypropylene membrane were used as the anode and the separator, respectively. The assembly of coin cells was conducted in the argon-filled glove box.

2.4. Material and electrochemical characterizations

The crystallinity of the calcined powder was characterized using an X-ray diffractometer (Bruker, D8 Advance). X-ray diffractograms were recorded at a scanning speed of $1.2^\circ \text{ min}^{-1}$ in a 2θ range of $10\text{--}75^\circ$ using $\text{Cu-K}\alpha$ radiation. The diffraction data were refined

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