Charge-Discharge Characteristics of a $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Cathode in FSI-based Ionic Liquids

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ABSTRACT

We evaluated the charge-discharge behavior of a $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) electrode in a 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMImFSI) ionic liquid. At 163 mAh g^{-1} after 50 cycles, the discharge capacity of the NMC cathode in LiTFSI/EMImFSI ($\text{TFSI}^- = \text{bis}(\text{trifluoromethylsulfonyl})\text{imide}$) at 1.0 C in the voltage range $3.0\text{--}4.5 \text{ V}$ (vs. Li/Li^+) is comparable to that in the conventional electrolyte, $\text{LiPF}_6/\text{EC}+\text{DMC}$. Moreover, the rate capability of the cell with LiTFSI/EMImFSI exceeded that with $\text{LiPF}_6/\text{EC}+\text{DMC}$, especially at high rates, probably owing to the low resistance at the electrode/electrolyte interface. These results suggest that EMImFSI is a suitable electrolyte for lithium-ion batteries utilizing an NMC cathode.

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1. Introduction

Lithium-ion batteries are one of the most promising energy storage devices not only for portable electronics but also for realizing a more convenient and sustainable society based on the use of electric vehicles and solar and wind power. However, to ensure the effective use of lithium-ion batteries for such large-scale applications, further improvements in safety as well as energy and power densities are required mainly because of the flammable-organic-solution-based electrolytes used.

Room temperature ionic liquids (RTILs) are anticipated as a substitute for conventional organic-solvent-based electrolytes because of their diverse properties such as a wide electrochemical potential window, acceptable ionic conductivity, high thermal stability, and negligible vapor pressure. In particular, the use of such ionic liquids in lithium-ion batteries has been considered to improve safety by taking advantage of their lower flammability and lower reactivity compared with conventional organic electrolytes.^{1–5} However, a lithium-ion battery composed of ionic liquid electrolytes has fatal problems in its charge-discharge performance. The greatest problem is the significant decomposition of ionic liquids on the negative electrode, which in most cases leads to a complete lack of reversibility at the anode. Another problem is the low ionic conductivity of such devices, resulting in a lower rate capability.^{6,7}

Some organic additives, typically 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 against the undesirable irreversible reactions of ionic liquid components.^{8–11} 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 without the use of additives.

We have successfully identified a promising ionic liquid containing bis(fluorosulfonyl)imide (FSI^-); this liquid with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) offers reversible charge-discharge properties for negative graphite electrodes without the need for additives, although it contains 1-ethyl-3-methylimidazolium (EMIm^+), which usually causes irreversible decomposition at graphitic anodes.^{12,13} In addition, we have investigated the electrochemical behavior of a high-capacitive Si-C composite anode in an FSI-based ionic liquid electrolyte, in which galvanostatic cycling of the anode in the ionic liquid with a charge limitation of 800 mAh g^{-1} is stable for 50 cycles.¹⁴ Matsumoto et al.,^{15–17} Guerfi et al.,¹⁸ and Seki et al.¹⁹ also reported the advantages of FSI-based ionic liquids for lithium-metal/lithium-ion batteries.

To use FSI-based ionic liquids for practical purposes, it is necessary to clarify the charge-discharge behavior of conventional and novel electrodes in FSI-based ionic liquids. Therefore, we focused on the electrochemical behavior of positive electrodes in FSI-based ionic liquids. In the present study, we employed a mixed transition metal oxide, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC), as the cathode material. The layered compound NMC has attracted attention as a possible next-generation cathode material because it has the potential for higher capacity and energy than cobalt oxide at a lower cost.^{20–24} We report herein the results of a charge-discharge cycle test and an evaluation of the rate characteristics of NMC in combination with an FSI-based ionic liquid.

2. Experimental

EMImFSI was produced by Dai-ichi Kogyo Seiyaku Co. Ltd. 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 RTILs were 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 NMC (Kusaka Rare Metal Products Co. Ltd.) as an active material, acetylene black as a conductive additive, and poly(vinylidene fluoride) (PVdF) as a binder, and prepared the composite electrode according to the following procedure. The slurry consisting of uniformly mixed 85 wt% NMC, 8 wt% acetylene black, and 7 wt% PVdF was cast on an etched aluminum foil and dried overnight under reduced pressure at 100°C. The obtained electrode sheet was punched to 1.13 cm² in size.

All electrochemical measurements were conducted using a two-electrode half cell, which consisted of the obtained NMC sheet electrode, 0.45 mol dm⁻³ LiTFSI/EMImFSI electrolyte, a Li foil (Honjo Metal Co., Ltd.) as a counter electrode, and a ceramic-coated separator. The cell was assembled in the glove box after impregnating both the separator and the NMC electrode with the LiTFSI/EMImFSI electrolyte for 30 min under reduced pressure at -0.1 MPa. For comparison, another cell was constructed with a polypropylene separator and a conventional electrolyte of 1.0 mol dm⁻³ LiPF₆/EC+DMC (v/v = 1/1) (DMC = dimethyl carbonate) purchased from Kishida Chemical Co. Ltd.

The charge-discharge performance of the test cells was measured using a computerized battery analyzer (BTS2400W, Nagano Co. Ltd.) in the constant current-constant-voltage (CC-CV) mode during charging and the CC mode during discharging (the end of the CV mode was defined to be at 1/10 of the set current value) in the voltage range 3.0–4.5 V (vs. Li/Li⁺). The current density was 0.1 C in the first cycle, following an arbitrary C-rate of charge-discharge repeated after the second cycle. AC impedance measurements were run on the test cells after pre-cycling by using an electrochemical measuring unit (SI 1280B, Solartron) in order to evaluate resistive components, especially at the interface between the electrode and electrolyte. The impedance measurements were performed with the typical AC amplitude 10 mV and frequency range from 50 kHz to 10 mHz after maintaining a charged state of 4.5 V in the test cell.

3. Results and Discussion

Figure 1 shows the typical charge-discharge curves of the NMC cathode in LiTFSI/EMImFSI and LiPF₆/EC+DMC at a charge-discharge rate of 1.0/1.0 C (0.1/0.1 C for the first cycle) in the voltage range 3.0–4.5 V. The discharge capacity of the NMC cathode in LiTFSI/EMImFSI at 1.0 C was 165 mAh g⁻¹, which is higher than that in LiPF₆/EC+DMC. In addition, reversible charge-discharge behavior was obtained across 50 cycles, suggesting that the FSI-based ionic liquid allows relatively stable operation of an NMC cathode without the need of additives, electrode surface treatment, or coating. The coulombic efficiency of NMC in LiTFSI/EMImFSI was maintained over 99%. Furthermore, large voltage drops were observed in the organic electrolyte at the transition between charging and discharging probably because of the high resistance derived from the oxidative decomposition products of the electrode. In contrast, the resistance growth at the electrode/electrolyte interface for the FSI-based ionic liquid electrolyte was negligible, indicating that a stable and thin passivation layer was formed.

The cyclability of the test cells with LiTFSI/EMImFSI and LiPF₆/EC+DMC operating in the voltage range 3.0–4.5 V at 1.0/1.0 C (0.1/0.1 C for the first cycle) are represented in Fig. 2. The test cell with LiTFSI/EMImFSI shows a reversible capacity of ca. 160 mAh g⁻¹ at the end of the 50th cycle, which is 97% of its initial discharge capacity, whereas the discharge capacity for LiPF₆/EC+DMC decreases significantly presumably owing to the instability of the delithiated NMC surface²⁴ or electrolyte decomposition.^{25,26} This suggests that the stable cycle characteristics of the

Figure 1. Charge-discharge curves of a LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ cathode in (a) LiTFSI/EMImFSI and (b) LiPF₆/EC+DMC at the first, second, 10th, 30th, and 50th cycles. Charge-discharge C-rate is 1.0/1.0 C, except for the first cycle (0.1/0.1 C).

Figure 2. Discharge capacity of the test cell with LiTFSI/EMImFSI (●) and LiPF₆/EC+DMC (▼). Charge-discharge C-rate is 1.0/1.0 C, except for the first cycle (0.1/0.1 C).

Figure 3. Nyquist plots obtained by AC impedance measurements for the test cells containing (a, c) LiTFSI/EMImFSI and (b, d) LiPF₆/EC+DMC measured at the charged state (4.5 V vs. Li/Li⁺) after the first (○), second (●), 30th (□), and 50th (▲) cycles. Magnifications of plots (a) and (b) are shown in plots (c) and (d), respectively.

FSI-based ionic liquid are attributed to the formation of a stable solid electrolyte interface layer, as mentioned above. It should be noted that no other electrolytes behave in the same way as the FSI-based ionic liquid, which represents a more stable charge-discharge cycling of an NMC cathode than conventional organic electrolytes without any surface coating.

To clarify the low-resistive layer formation in the FSI-based ionic liquid, electrochemical impedance measurements were performed at a charged state of 4.5 V vs. Li/Li⁺. Nyquist plots of the test cells with LiTFSI/EMImFSI and LiPF₆/EC+DMC obtained after the first, second, 30th, and 50th cycles are shown in Fig. 3. Each Nyquist plot for both electrolytes includes two semicircles, which could be attributed to charge transfer resistance and interfacial layer resistance at medium and high frequencies.^{27,28} Regarding the semicircles at high frequency, both test cells showed a decrease in their interfacial layer resistance after the second cycle, which must be caused by stabilization of the interface during the first charge-discharge cycling. On the other hand, the test cell with LiTFSI/EMImFSI showed a stable interface at the NMC/electrolyte because the semicircles at high and medium frequencies did not change across 50 cycles [Figs. 3(a) and 3(c)], whereas the semicircle at medium frequency for the test cell with LiPF₆/EC+DMC became significantly larger after 30 cycles [Figs. 3(b) and 3(d)]. The increase of a large second semicircle for LiPF₆/EC+DMC proves the large charge-discharge resistance presumably due to the instability of the delithiated NMC surface structure,²⁴ resulting in the capacity fading of the NMC cathode in the solution-based electrolyte represented in Fig. 2. Therefore, these AC impedance results suggest that the presence of an FSI-based ionic liquid can stabilize the interface between the electrolyte and NMC cathode surface. Concerning these advantages for the FSI-based ionic liquid, we should discuss why FSI-based ionic liquids can achieve a low resistive and stable interface between the electrolyte/electrode. Consequently, further investigations are required to clarify the role of the FSI anion for a NMC cathode.

Figure 4. Dependence of discharge capacity on discharge C-rate of an NMC cathode in (a) LiTFSI/EMImFSI and (b) LiPF₆/EC+DMC.

Considering the results of the electrochemical impedance measurements, the low-resistive layer formed on the NMC cathode in LiTFSI/EMImFSI can offer the advantages of high C-rate charge-discharge characteristics. Figure 4 shows the electrode potential vs. specific capacity for NMC at a certain charge/discharge C-rate. Regarding the ionic liquid electrolyte, the potential shifts at charge-discharge switching are much smaller than those for the conventional electrolyte. The cell with LiTFSI/EMImFSI was also found to show curves with a smaller polarization and lesser capacity fading than that with LiPF₆/EC+DMC when the charge-discharge C-rate increases. This might be caused by the smaller polarization due to the low-resistive layer at the electrode/electrolyte interface. Figure 5 summarizes the dependence of the discharge capacity of the NMC cathode on the discharge C-rate in both electrolytes. These discharge capacities for both electrolytes monotonically decrease as the discharge C-rate increases. Even after taking it into consideration that the decrease of the specific capacity for LiPF₆/EC+DMC is affected by the continuous capacitive loss during each charge-discharge cycling (~20 mAh g⁻¹ loss at 0.2C re-cycling as shown in Fig. 5), the rate capability of the NMC cathode in LiTFSI/EMImFSI clearly exceeds that in LiPF₆/EC+DMC, especially at high C-rates, probably owing to the low resistance at the electrode/electrolyte interface. Returning toward the low C-rate of 0.2C after 5.0-C cycling, moreover, the cell with LiTFSI/EMImFSI obviously retains its discharge capacity at the level of the corresponding

Figure 5. Rate capability of an NMC cathode in LiTFSI/EMImFSI (●) and LiPF₆/EC+DMC (▼).

capacity at primary 0.2C (sixth cycle), suggesting that no continuous degradation of the NMC cathode or the electrolyte occurs even after the high C-rate charge-discharge cycling.

4. Conclusion

The charge-discharge behavior of an NMC cathode is investigated in an FSI-based ionic liquid as well as a conventional TFSI-based ionic liquid and organic solution-based electrolyte. The NMC cathode shows reversible and stable charge-discharge behavior in the LiTFSI/EMImFSI electrolyte. According to electrochemical impedance analyses, an FSI-based ionic liquid electrolyte can reduce the electrode/electrolyte interfacial resistance compared with a conventional LiPF₆/EC+DMC electrolyte. This is probably because of the formation of a low-resistive layer on the NMC in the FSI-based ionic liquid, which prevents undesirable degradation of the electrode or electrolyte. Nevertheless, the low-resistive layer derived from the ionic liquid results in highly stable cycle performance and high rate capability of the NMC cathode. These advantages suggest that FSI-based ionic liquids are promising electrolytes for lithium-ion batteries.

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