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Short communication

Improving the electrochemical properties of graphite/$LiCoO_2$ cells in ionic liquid-containing electrolytes

Nam-Soon Choi [a,*], Yongbeom Lee [a], Sung-Soo Kim [a], Soon-Cheol Shin [a], Yong-Mook Kang [b,**]

[a] Corporate R&D Center, Samsung SDI Co. Ltd., 428-5, Gonse-dong, Giheung-gu, Yongin-si, Gyeonggi-do 446-577, Republic of Korea
[b] Division of Advanced Materials Engineering, Kongju National University, 275 Budae-dong, Cheonan, Chungnam 330-717, Republic of Korea

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ABSTRACT

The electrochemical performance of graphite/lithium cobalt oxide ($LiCoO_2$) cells in *N*-methoxymethyl-*N,N*-dimethylethylammonium bis(trifluoromethane-sulfonyl) imide (MMDMEA-TFSI)-containing electrolytes is significantly enhanced by the formation of a fluoroethylene carbonate (FEC)-derived protective film on an anode during the first cycle. The electrochemical intercalation of MMDMEA cations into the graphene layer is readily visualized by ex situ transmission electron microscopy (TEM). Moreover, differences in the X-ray diffraction (XRD) patterns of graphite electrodes in cells charged with and without FEC in dimethyl carbonate (DMC)/MMDMEA-TFSI are clearly discernible. Conclusively, the presence of FEC in MMDMEA-TFSI-containing electrolytes leads to a remarkable enhancement of discharge capacity retention for graphite/$LiCoO_2$ cells as compared with ethylene carbonate (EC) and vinylene carbonate (VC).

1. Introduction

Lithium-ion batteries (LIBs) with high specific energy or high specific power should also possess good thermal stability, which is essential for their safety and reliable performance. Unfortunately, organic solvents commercially used in LIBs generally have low boiling and flash points. Because major problems in battery safety, such as venting or explosion, arise from the volatility and flammability of the electrolyte solution vapours, the unique properties of ionic liquids, simultaneously meeting the desired parameters of negligible vapour pressure, low flammability, and high thermal stability, have stimulated interest in the use of these materials for improving battery safety [1–3]. Recently, the Aurbach and co-workers reported that quaternary ammonium, pyrrolidinium, and piperidinium-based ionic liquids exhibit good anodic stability up to 5 V vs. Li/Li^+ on Pt and glassy carbon as working electrodes [4]. Unfortunately, however, the low cathodic stability of ionic liquids induces the formation of an unstable solid electrolyte interphase (SEI) on graphite anodes and thereby extremely restricts their application in LIBs [2,5]. One of the most efficient ways to form an electrochemically stable SEI is to use reducible compounds, which tend to decompose on the graphite surface before the reduction of main organic solvents during charging [6,7]. Ionic liquids containing 1-ethyl-3-methylimidazolium (EMI) cations have been intensively studied for LIBs applications due to their low viscosity. Nevertheless, the use of imidazolium-based ionic liquids would seem problematic because imidazolium cations are significantly reduced at the graphite/electrolyte interface during charging [8,9]. While there has been growing interest in tetraalkyl ammonium [2,10,11], pyrrolidinium [2] and piperidinium [12]-based ionic liquids with wide electrochemical stability windows, their insufficient cathodic stability would still be a main barrier to their application in graphite anodes charged to a potential of 0.01 V vs. Li/Li^+. From this point of view, the Lewandowski and Świderska-Mocek [12] and Sato et al. [13] found that vinylene carbonate, a representative functional additive forming a stable SEI, facilitates the reversible charge and discharge of graphite anodes in electrolyte solutions based on *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bis(trifluoro-methylsulfonyl) imide and *N*-methyl-*N*-propylpiperidinium bis(trifluoro-methylsulfonyl) imide [12,13].

This study presents an investigation of the electrochemical properties of graphite/$LiCoO_2$ cells cycled in *N*-methoxymethyl-*N,N*-dimethylethyl-ammonium bis(trifluoromethane-sulfonyl) imide (MMDMEA-TFSI)-containing electrolyte solutions with and without fluoroethylene carbonate (FEC), a representative stable SEI-forming additive.

* Corresponding author. Tel.: +82 16 257 9051; fax: +82 41 568 5776.
** Corresponding author.
E-mail addresses: ns75.choi@samsung.com (N.-S. Choi), dake1234@kongju.ac.kr (Y.-M. Kang).

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2. Experimental

To evaluate the electrochemical properties of graphite anodes, a slurry was prepared by mixing 97 wt.% graphite particles and a 3 wt.% polyvinylidene fluoride (PVdF) binder dissolved in anhydrous *N*-methyl-2-pyrrolidinone (NMP). The resulting slurry was cast on a copper foil. The composite electrode was then dried in a convection oven at 110 °C for 2 h. The cathode had a composition of 92 wt.% lithium cobalt oxide ($LiCoO_2$), 4 wt.% carbon black, and a 4 wt.% PVdF binder. The loading of active materials in the cathode corresponded to a capacity of 2.54 mAh cm^{-2}.

N-Methoxymethyl-*N*,*N*-dimethylethylammonium bis(trifluoro-methanesulfonyl) imide (MMDMEA-TFSI) (Otsuka-Stella Co. Ltd.) has a melting point of −21 °C and a viscosity of 75 mPa s at 25 °C. Fluoroethylene carbonate (FEC), vinylene carbonate (VC), and ethylene carbonate (EC) at 10 vol% were used as solid/electrolyte interphase (SEI)-formers and separately added into a mixture of dimethyl carbonate (DMC) and MMDMEA-TFSI at a (6/3) volume ratio. $LiPF_6$ at a concentration of 1 M was then dissolved in the resulting solution. The non-flammability of the MMDMEA-TFSI-based electrolyte solutions was confirmed by means of a flammability test.

Transmission electron microscope (TEM) images were taken with a Tecnai G2 FE-TEM microscope. The crystal structure of the graphite anodes was obtained using a Philips X'pert Pro X-ray diffractometer that was equipped with a Cu Kα source at 40 kV and 30 mA. 2032-Type coin cells were assembled in a dry room. Cycling tests were performed galvanostatically between 2.75 and 4.2 V using a computer-controlled battery-measurement system (TOSCAT 3000 U).

3. Results and discussion

Fig. 1(a) displays the electrochemical performance of graphite/lithium cobalt oxide ($LiCoO_2$) cells with a *N*-methoxymethyl-*N*,*N*-dimethylethyl-ammonium bis(trifluoro-methanesulfonyl) imide (MMDMEA-TSI)-based electrolyte solution. As shown in Fig. 1(a), there are clear disparities in the initial charge–discharge profiles depending on whether or not FEC is incorporated into the electrolyte. A cell including 1 M $LiPF_6$ dissolved in dimethyl carbonate (DMC)/MMDMEA-TFSI (7/3) exhibits an extraordinarily low discharge capacity of 59 mAh g^{-1}, whereas DMC/MMDMEA-TFSI/FEC (6/3/1) with 1 M $LiPF_6$ gives a much higher discharge capacity of 318 mAh g^{-1} during Li^+ extraction. The low reversible capacity of cells where 1 M $LiPF_6$ in DMC/MMDMEA-TFSI (7/3) is used as the electrolyte seems to be related to the preferential reduction of MMDMEA-TFSI on a graphite anode. Because DMC cannot form a suitable protective layer on the graphite surface, a large capacity loss is inevitably generated by the irreversible reduction of MMDMEA-TFSI. This point is clearly exemplified by the d*Q*/d*V* results in Fig. 1(b). DMC/1 M $LiPF_6$ only evolves a peak around 3.5 V, while the addition of MMDMEA-TFSI to DMC/1 M $LiPF_6$ produces three apparent reductive peaks at 3, 3.3, and 3.5 V. The peaks at 3 and 3.3 V originate from the irreversible reduction of the MMDMEA-TFSI ionic liquid, whereas the peak at 3.5 V is attributed to DMC reduction. By contrast, the evolution of two reductive peaks at 3 and 3.3 V is significantly restrained by the additional use of FEC (Fig. 1(b)). This result may indicate that FEC forms a protective layer on the graphite surface, suppressing the electrochemical reduction of MMDMEA-TFSI.

In order to clarify the significant role of FEC in inhibiting the electrochemical reduction of MMDMEA-TFSI, high-resolution transmission electron microscopy (HR-TEM) analysis was conducted on the charged graphite anodes. Graphite anodes were

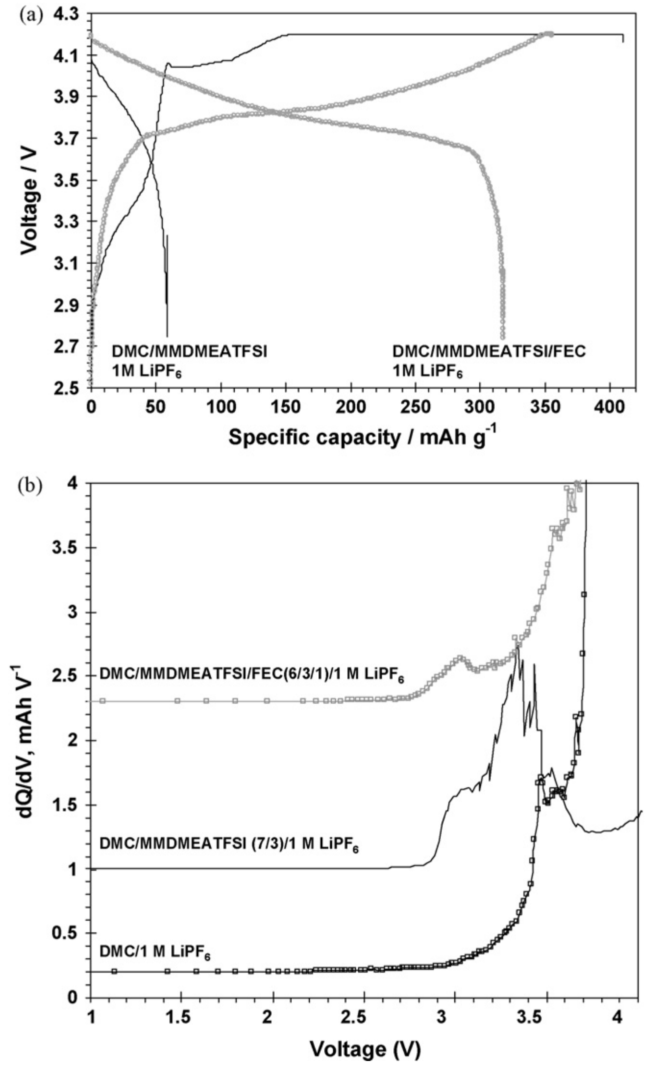

Fig. 1. (a) Voltage profiles of graphite/$LiCoO_2$ cells and (b) d*Q*/d*V* graph of graphite/$LiCoO_2$ cells cycled at a 0.1 C rate during the first cycle.

charged in DMC/MMDMEA-TFSI (7/3) without $LiPF_6$ to facilitate the intercalation of MMDMEA cations into the graphene layers. The images presented in Fig. 2(a) show that the graphene layers are highly disordered in DMC/MMDMEA-TFSI (7/3) when the graphite anode is charged to 0.01 V vs. Li/Li^+. It is thought that the fringes of the (0 0 2) plane of the graphite crystal are broken by the intercalation of MMDMEA cations into the graphene layer. This is in good agreement with a previous study [8], which indicated that trimethyl-*N*-hexylammonium cations intercalate into graphene layers. Meanwhile, the existence of FEC in the electrolyte solution apparently helps to maintain the (0 0 2) plane of the graphite crystal structure. Since FEC has a much lower unoccupied molecular orbital (LUMO) energy (0.983 eV) than that of DMC (1.137 eV), FEC tends to undergo electrochemical reduction during charging before DMC [14]. This implies that FEC easily supplies a stable SEI layer and thereby prohibits MMDMEA cations from being intercalated into graphene layers.

X-ray diffraction (XRD) patterns of graphite anodes cycled in DMC/MMDMEA-TFSI/1 M $LiPF_6$ with and without FEC are shown in Fig. 3. When charged in DMC/MMDMEA-TFSI/1 M $LiPF_6$, the peak related to the (0 0 2) graphitic plane (located at 26.5°) almost disappears, and peaks assigned to LiC_6 or LiC_{12} (located at 24° and 25.2°, respectively) are not observed. This indicates that the

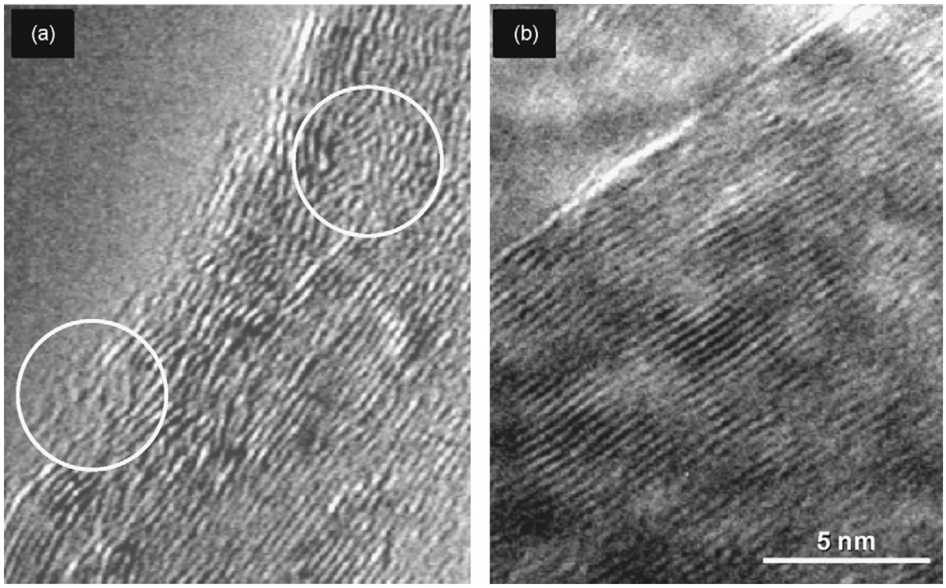

Fig. 2. TEM images of graphite anodes charged in (a) DMC/MMDMEA-TFSI (7/3) and (b) DMC/MMDMEA-TFSI/FEC (6/3/1).

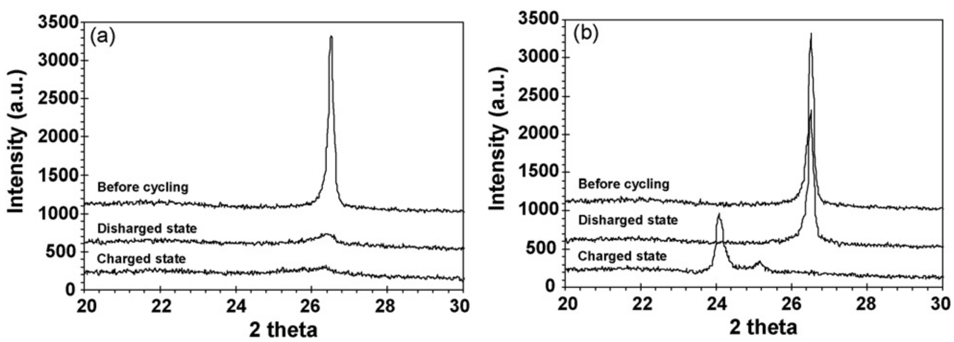

Fig. 3. XRD patterns of graphite anodes cycled in 1 M $LiPF_6$ dissolved in (a) DMC/MMDMEA-TFSI (7/3) and (b) DMC/MMDMEA-TFSI/FEC (6/3/1).

crystal structure of graphite is significantly disordered and an amorphous phase is generated by the intercalation of MMDMEA cations, which are much larger than Li cations. The X-ray patterns given in Fig. 3(a) clearly show that when the graphite anode is discharged in DMC/MMDMEA-TFSI/1 M $LiPF_6$ without FEC, the (0 0 2) graphite crystal plane is not recovered. By comparison, a graphite anode charged in DMC/MMDMEA-TFSI/FEC (6/3/1) with 1 M $LiPF_6$ displays a clear phase transition to LiC_6 and LiC_{12}. In addition, the peak attributed to the (0 0 2) graphite crystal plane is nearly recovered at a fully-discharged state (Fig. 3(b)).

The discharge capacity retention of $LiCoO_2$/graphite cells over 100 cycles is shown in Fig. 4. A cell including DMC/MMDMEA-TFSI/1 M $LiPF_6$ yields the worst cycling performance. Even when vinylene carbonate (VC) and ethylene carbonate (EC) are used as a solid/electrolyte interphase (SEI)-former, the electrochemical properties of cells with MMDMEA-TFSI-containing electrolytes are not sufficient to meet the requirements of practical application in lithium-ion batteries. This indicates that an SEI-based on polymer-like components [15] from VC-reduction and lithium alkyl carbonates [16] from EC is inappropriate to suppress the reduction of the MMDMEA-TFSI ionic liquid on a graphite anode. Contrarily, the addition of FEC to DMC/MMDMEA-TFSI/1 M $LiPF_6$ results in an apparent leap in the cycling performance. This is because FEC-derived SEI consisting of LiF [17] permits the reversible electrochemical reaction of lithium in the presence of the MMDMEA-TFSI ionic liquid.

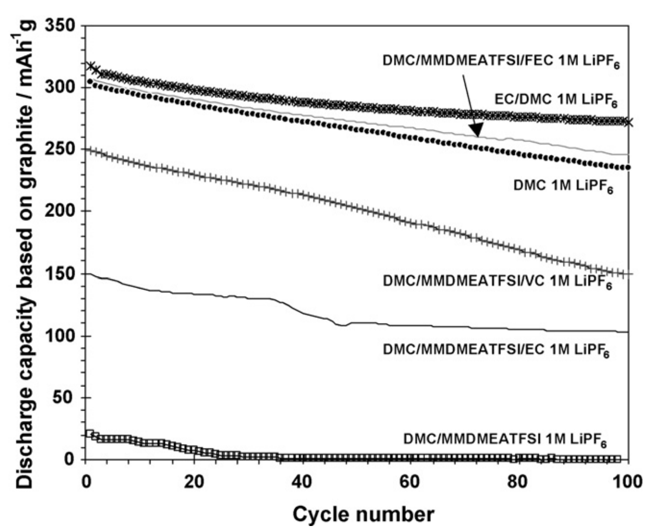

Fig. 4. Specific discharge capacity retention of graphite/$LiCoO_2$ cells cycled at a 0.5 C rate during 100 cycles.

4. Conclusions

Several structural analyses have confirmed that MMDMEA cations tend to intercalate into graphene layers prior to lithium intercalation and there by make the crystal structure of graphite highly disordered. The FEC-derived SEI layer effectively restrains the exfoliation of graphene layers induced by the destructive intercalation of MMDMEA cations and thus contributes to the enhancement of cycling performance in graphite/$LiCoO_2$ cells with DMC/MMDMEA-TFSI/1 M $LiPF_6$. This result indicates the effectiveness of FEC as a novel additive as well as the feasibility of applying ionic liquids to lithium-ion batteries.

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