Electrode Behavior of Iron Oxide/Carbon Nanotube Composite in Ionic Liquid Electrolyte

Minato EGASHIRA,^{a,b,*} Yohei TSUBOUCHI,^a Nobuko YOSHIMOTO,^a and Masayuki MORITA^a

^a Graduate School of Science and Engineering, Yamaguchi University,
2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

^b Present address: College of Bioresource Sciences, Nihon University,
1866 Kameino, Fujisawa, Kanagawa 252-0880, Japan

* Corresponding author: egashira.minato@nihon-u.ac.jp

ABSTRACT

Composite electrode of iron oxide Fe_2O_3 and carbon nanotube has been prepared for the negative electrode of lithium batteries with ionic liquid electrolyte. The composite containing 29 wt% of Fe_2O_3 exhibits as large as 300 mAh g^{-1} of specific capacity in the electrolyte based on 1-ethyl-3-methyl imidazolium bis(fluorosulfonyl)amide (EMIFSA) as well as in a conventional alkylcarbonate electrolyte. When the loading of Fe_2O_3 is at as low extent as 29 wt%, cross-linking morphology created by carbon nanotube substrate provides nano-spaces in the composite and assures mass transfer beneath electrode and thus rate capability even in viscous ionic liquid electrolyte.

© The Electrochemical Society of Japan, All rights reserved.

Keywords : Lithium Batteries, Ionic Liquid, Iron Oxide, Carbon Nanotube

1. Introduction

Ionic liquids, defined as molten salts at ambient temperature, have been attracted as novel candidates of non-flammable electrolyte component for the improvement of safety of lithium batteries.^{1–3} To date a number of ionic liquids have been proposed and investigated for the use in electrolyte component.² According to great development during this decade, 1-ethyl-3-methyl imidazolium bis(fluoro-sulfonyl)amide (EMIFSA) appear to be attractive for practical viewpoint.^{4,5} The authors recognize that the main problems at present are the high cost of ionic liquid materials and the rate capability at ambient temperature of the cells containing ionic liquid electrolyte.^{4–9} The cost may depend somewhat on the scale of production, and the cost of a cell can be reduced by the selection of low cost material for other parts such as electrode active mass. The high viscosity of ionic liquids, inhibiting mass transfer around electrode/electrolyte interface, is frequently assumed as low rate capability of the resulted cells. The concept of porous active material has been reported to be effective for the reduction of mass transfer resistance.¹⁰ In addition, the charge transfer process is expected to affect somewhat to the rate capability, as Cheng et al. indicates high-rate performance of radical electrode even in ionic liquid electrolyte.¹¹ The authors previously estimated the contribution of charge transfer process,¹² and found that the careful selection of electrode material is important to reduce charge-transfer resistance. According to this assumption, attempts to combine various electrode materials with ionic liquid electrolyte are meaningful.

In the present study, the authors have concerned on iron oxide, Fe_2O_3 , as a negative active electrode to combine ionic liquid electrolyte. Fe_2O_3 has been known to exhibit unique conversion reaction during charge-discharge process.^{13–19} The high theoretical specific capacity 1007 mAh g^{-1} of this electrode is also attractive for practical usage. However, Fe_2O_3 itself is an insulator and the compositing with a conductive agent is necessary for the high utilization of this active material. The authors have assumed that fibrous carbon substrates are suitable for the conductive agents, because of their high conductivity along fiber axis, high surface area providing large interface between electrode active mass/electrolyte, high chemical and mechanical stabilities. Here carbon nanotube

(CNT) is selected as compositing substrate with Fe_2O_3 . Indeed, the similar iron/nano-carbon composites have been investigated for negative electrodes in aqueous alkaline batteries, and the optimization of preparation of this composite, including the selection of CNT as substrate, has been conducted.²⁰ Here the preliminary study has been conducted in order to compare the electrode behavior of Fe_2O_3 composite in ionic liquid electrolytes with conventional alkyl carbonate electrolyte. It has been highlighted whether ionic liquid electrolyte provides similar electrode performance even under high-rate condition to conventional electrolyte, and what charge-discharge characteristics are different.

2. Experimental

2.1 Preparation of iron oxide/carbon nanotube composite

CNT (Nanocyl Inc., Belgium) was irradiated by ultrasonic in ethanol before in order to loosen aggregation, and then dispersed in 1 mol dm^{-3} HCl aq. containing FeCl_3 (Wako Pure Chemical Co., Japan) with prescribed ratio of FeCl_3 with CNT. The resulted suspension was neutralized by the titration of 1 mol dm^{-3} NaOH aq. to pH = 8, and filtrated by using filter paper (Toyo Roshi Co., Japan, No. 2) in order to collect CNT on which $\text{Fe}(\text{OH})_x$ was impregnated. The collected precipitation was dried under atmospheric condition, and calcined at 773 K under Ar flow. The actual iron contents in the final products are checked to be similar in most cases to those expected from initial FeCl_3 and CNT ratios by using inductive couple plasma spectroscopy (ICP; ICPE-9000, Shimadzu Co., Japan). The structures of these composites were characterized by X-ray diffraction (XD-D1, Shimadzu Co.), and their morphologies were observed by scanning electron microscope (SEM, VE-8800, Keyence Co., Japan).

2.2 Ionic liquid electrolyte

EMIFSA (Kanto Chemical Co., Japan) and N,N-methylpropyl piperidinium bis(trifluoromethane sulfonyl)amide (PP13TFSA; Kanto) are used as electrolyte solvents. Each ionic liquid was used as received. The electrolytes were prepared by dissolving LiTFSA (Kanto) at the molar ratio of 0.20. The dissolving procedure was conducted in a glove box filled with argon.

Figure 1. X-ray diffraction patterns of $\text{Fe}_2\text{O}_3/\text{CNT}$ composites. (a) Fe_2O_3 29% (b) Fe_2O_3 60%. Character: $\blacklozenge$ maghemite Fe_2O_3 ∇ hematite Fe_2O_3 $\times$ carbon (CNT).

2.3 Charge-discharge test

The electrode properties of prepared $\text{Fe}_2\text{O}_3/\text{CNT}$ composites were evaluated by constant-current charge-discharge tests. The test cell was 2032 stainless-steel sealed 2-electrode coin cell, which consisted of working electrode, lithium metal (Honjo metal Co., Japan) counter electrode, ca. 2 cm^3 of electrolyte, a polypropylene separator (Celgard 2500). In most cases poly(vinylidene difluoride) (PVDF) was used as binder. The $\text{Fe}_2\text{O}_3/\text{CNT}$ composite was suspended in N-methylpyrrolidinone (Kanto Chemical, Japan) with 5 wt% of PVDF (Kureha Chemical Co., Japan) followed by the processes that the suspension was spread onto copper mesh and dried under vacuum. The disk (10 mm diameter) cut out from the pasted mesh was used as the working electrode. The approximate $\text{Fe}_2\text{O}_3/\text{CNT}$ active mass on the working electrode was ca. $5 \times 10^{-3}\text{ g}$. In addition to the ionic liquid electrolytes, electrolytic solution of 1 mol dm^{-3} LiPF_6 (battery grade, Kishida Chemicals Co., Japan) in mixed solvent of ethylene carbonate (EC; Kishida) with dimethyl carbonate (DMC; Kishida) was also used as comparison. After the assembly of coin cells containing the ionic liquid electrolyte, the cells were stored overnight at 338 K.

The charge-discharge tests for the coin cell were conducted using a constant-current cycler (BTS-2004, Nagano Co., Japan) under prescribed current densities. The cut-off voltages were from 2.0 V to 0.2 V in order to avoid the lithium intercalation in CNT. These charge-discharge tests were conducted at ambient temperature, roughly controlled at 298 K.

3. Results and Discussion

3.1 Characterization of $\text{Fe}_2\text{O}_3/\text{CNT}$ composites

The X-ray diffraction patterns of the $\text{Fe}_2\text{O}_3/\text{CNT}$ composites with the Fe_2O_3 content of (a) 29 wt% and (b) 60 wt% are shown in Fig. 1.

Figure 2. SEM and TEM images of $\text{Fe}_2\text{O}_3/\text{CNT}$ composites. (a) SEM, Fe_2O_3 29% (b) SEM, Fe_2O_3 60% (c) TEM, Fe_2O_3 29%.

Both composites show sharp peaks at 30° , 36° assigned to maghemite Fe_2O_3 [JCPDS No. 39-1346], peaks at 24° and 34° assigned to hematite Fe_2O_3 [JCPDS No. 33-0664], in addition to a broad band around 26° assigned to (002) of CNT. The SEM images of the $\text{Fe}_2\text{O}_3/\text{CNT}$ composites containing 29 wt% and 60 wt% are shown in Figs. 2(a) and 2(b), respectively. While Fig. 2(a) is not clear due to the lack of resolution, it is obvious that the morphologies of these two composite is markedly different. Some sub-micron scale features may be dominated in the former SEM image. In order to help to clarify structural image of the former composite, its typical TEM image is shown in Fig. 2(c). The image indicates that particles with 2–50 nanometers are dispersed on CNT surface. In contrast, the latter SEM image provides the coverage of Fe_2O_3 on entangled CNT.

3.2 Electrode behavior of $\text{Fe}_2\text{O}_3/\text{CNT}$ composites

The constant-current charge-discharge profiles of $\text{Fe}_2\text{O}_3/\text{CNT}$ composite with 29 wt% Fe_2O_3 in (a) 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$, (b) EMIFSA, and (c) PP13TFSA electrolytes under the current density of 0.05 mA cm^{-2} (approximately corresponding to $0.08C$) are shown in Fig. 3. In all cases reversible capacities between 200 and 600 mAh g^{-1} are exhibited after initial irreversible capacities of $1000\text{--}2000\text{ mAh g}^{-1}$. The initial irreversible plateau can be assigned to be the SEI formation with the reductive decomposition of electrolyte, as frequently observed in conventional electrolyte/negative electrode interface. The plateau potential thus varies depending on the kind of electrolyte. The ionic liquid electrolytes provide plateau around 1.5 V, higher than 1.0 V for $\text{LiPF}_6/\text{EC-DMC}$,

Figure 3. Charge-discharge profiles of (a-c) $\text{Fe}_2\text{O}_3/\text{CNT}$ electrode (with 29% of Fe_2O_3) in various ionic liquid electrolytes and (d) CNT electrode in $\text{LiPF}_6/\text{EC-DMC}$. Current density: 0.05 mA cm^{-2} . Electrolyte: (a) $\text{LiPF}_6/\text{EC-DMC}$ (b) $\text{LiTFSA}/\text{EMIFSA}$ (c) $\text{LiTFSA}/\text{PP13TFSA}$.

suggesting that the ionic liquids intrinsically decompose at higher potential compared with $\text{LiPF}_6/\text{EC-DMC}$.

In the all composite electrode, the plateaus are observable around 1.0 V vs. Li at charging (lithium insertion) process, and then leveled slopes around 0.5 to 2.0 V at the discharging process. The reversible capacities are based on the conversion reaction of Fe_2O_3 with lithium because such capacity is not observable when the electrode includes only CNT [Fig. 3(d)]. Bare CNT electrode having large surface area shows similarly large initial irreversible capacity.

The value of reversible capacity is larger than the expected one from the assumption of 6Li into Fe_2O_3 (460 mAh g^{-1}), probably due to the excess capacity (140 mAh g^{-1}) by the lithium insertion in CNT and the contribution of double-layer discharging process. The compatibility of Fe_2O_3 active material in ionic liquid electrolytes can clearly be indicated, while the capacities are varied with the kind of ionic liquid. Such electrolyte dependence on the capacity may be mainly due to the electrolyte conductivity, wettability of electrode surface and the accessibility of viscous electrolyte in the nanopores created by nanoparticles of Fe_2O_3 and CNT. As reported previously,^{4,6} ionic liquids have similar conductivities (ca. 18 mS cm^{-1} for EMIFSA and ca. 1.5 mS cm^{-1} for PP13TFSA) and higher viscosities (20 mPas for EMIFSA and 165 mPas for PP13TFSA) compared with $\text{LiPF}_6/\text{EC-DMC}$. Indeed, the lowest rate, 0.05 mA cm^{-2} corresponding to 0.08C, can minimize the influence of the bulk resistances of PP13TFSA electrolyte. The wetting patterns of electrolyte spots on the composite electrode sheet containing Fe_2O_3 (29 wt%)/CNT (spread on aluminum foil) are shown in Fig. 4 as the indicator of the macroscopic wettability of the electrolytes. The drops of similar amounts of electrolytes provides different patterns, indicating that $\text{LiPF}_6/\text{EC-DMC}$ and EMIFSA have immersed in the composite electrode more than PP13TFSA. The macroscopic wettability may mainly provide influences on the rate capabilities of $\text{Li}/\text{Fe}_2\text{O}_3/\text{CNT}$ cells.

Figure 4. Photographs of wetting patterns of various electrolytes on Fe_2O_3 (29%)/CNT electrode sheet. Electrolyte: (a) $\text{LiPF}_6/\text{EC-DMC}$ (b) EMIFSA (c) PP13TFSA. Circle by broken line: mark of initial spot.

Figure 5. Dependence of specific capacity of Fe₂O₃/CNT electrode on current density in various electrolytes. *discharge capacity at 1st cycle. Electrolyte: x LiPF₆/EC-DMC ▲ LiTFSA/EMIFSA ■ LiTFSA/PP13TFSA.

Figure 6. Dependence of Fe₂O₃ loading amount on the specific capacity of Fe₂O₃/CNT electrode in various electrolytes. (Black bar): in LiPF₆/EC-DMC, (Grey bar): in LiTFSA/EMIFSA.

The discharge (lithium de-insertion) capacities of Fe₂O₃/CNT composite with 29% Fe₂O₃ in various electrolytes are plotted toward the current density in Fig. 5. The Fe₂O₃/CNT electrode exhibit slight capacity loss in LiPF₆/EC-DMC electrolyte even by the highest current density in this figure. Similarly, EMIFSA-based electrolyte provides excellent capacity maintenance, ca. 200 mAh g⁻¹ under high current condition. This electrode exhibits abrupt capacity decrease in the PP13TFSA electrolyte. It sounds reasonable that the PP13TFSA electrolyte having high viscosity provides severe capacity decrease at high rate. The rate capability of this composite electrode exhibits significant electrolyte dependence even among ionic liquid electrolytes, and EMIFSA provides rather good properties compared with PP13TFSA. The lower viscosity of EMIFSA compared with PP13TFSA may assure better mass transport in interfibrillar spaces, and also the SEI forming in EMIFSA-based electrolyte may be more compact than that in PP13TFSA-based electrolyte as suggested by the previous reports.⁴

The dependences of the specific capacity (on the basis of the mass of composite) on Fe₂O₃ loading amount of Fe₂O₃/CNT electrode in LiPF₆/EC-DMC and the EMIFSA-based electrolyte are summarized in Fig. 6. Here the applied current density was 1.0 mA cm⁻², thus the capacity values involve the influence of the cell resistances. In the conventional electrolyte, the capacity increases by the increase of the Fe₂O₃ amount. The capacity is approximately proportional to the Fe₂O₃ amount. Thus, the loaded

Fe₂O₃ works in the electrolyte regardless of the morphology of composite electrode. In contrast, the specific capacities in the EMIFSA-based electrolyte are almost similar by the increase of Fe₂O₃ content. The utility of Fe₂O₃ clearly decreases in this sequence. The capacity of the composite with 29% of Fe₂O₃ indicates that Fe₂O₃ itself works even in the ionic liquid media. Therefore, such low utility of Fe₂O₃ in the composites with high loading amount is considered to be caused by the lack of the contact between Fe₂O₃ and the ionic liquid electrolyte. From Figs. 2(a) and 2(b), the pores created by intertubular spaces of CNT remains in the composite with 29% of Fe₂O₃, while Fe₂O₃ covers such pores in the one with 60% Fe₂O₃. Such intertubular spaces may facilitate the immersion of viscous ionic liquids and provide large extent of the interface between Fe₂O₃ and the ionic liquid electrolyte in the composite with 29% Fe₂O₃. As the loading amount increases, the intertubular spaces decreases and the creation of interface may be inhibited. From this result, it is clearly indicated that the cross-linking morphology by CNT is necessary for immersing viscous ionic liquid-based electrolyte with sufficient mass transport.

The present study has indicated that the composite electrode of iron oxide with carbon nanotube exhibiting significant capacity in ionic liquid electrolyte when the kind of ionic liquid is carefully chosen and the morphology of the composite is properly designed. The conversion reaction of Fe₂O₃ appears to be compatible in EMIFSA-based electrolyte, with sufficient rate. Indeed, the substance and the preparation method of the Fe₂O₃/CNT composite are not optimized yet, while the preparation process providing small Fe₂O₃ particles with dispersed feature has been investigated at some extent.²⁰ The cross-linking morphology of the CNT appears to be favorable, and the discharge capacities of Fe₂O₃(29 wt%)/CNT in the EMIFSA-based electrolyte is close to the theoretical capacity of this composite under the assumption of only Fe₂O₃ acts as active mass. It is expected that the overall capacity of the composite electrode in the ionic liquid electrolyte can be improved by the increase of the loading amount of Fe₂O₃ with further modification of Fe₂O₃ dispersion on CNT. Further efforts will also be conducted to reduce initial irreversible capacity by the improvement of the coverage over CNT surface by nano-sized Fe₂O₃ more effectively.

4. Conclusion

The Fe₂O₃/CNT composite, prepared by the sol-gel precipitation and containing 29 wt% of Fe₂O₃, exhibits as high as 300 mAh g⁻¹ of specific capacity under conventional charge-discharge rate even in LiTFSA/EMIFSA ionic liquid electrolyte. In this composite, Fe₂O₃ is compatible under such reaction rate in this ionic liquid electrolyte. Presently the capacity of the Fe₂O₃/CNT composite in this electrolyte does not increase even when the loading amount of Fe₂O₃ increases, due to the decrease of intertubular spaces which assure electrolyte mass transport. Further optimization of nano-structure of electrode can provide sufficient performance in ionic liquid electrolyte.

Acknowledgment

The authors thank Nanocyl Japan Inc. to provide carbon nanotube used in the present study. The TEM observation of Fe₂O₃/CNT composite has been conducted by Ms. Yumiko Kimura, JFE Techno-research Inc., Japan.

References

1. A. Femicola, B. Scrisati, and H. Ohno, *Ionics*, **12**, 95 (2006).
2. A. Lewandowski and A. Świdorska-Mocek, *J. Power Sources*, **194**, 601 (2009).
3. H. Nakagawa, Y. Fujino, S. Kozono, Y. Katayama, T. Nukuda, H. Sakaebe, H. Matsumoto, and K. Tatsumi, *J. Power Sources*, **174**, 1021 (2007).

4. M. Ishikawa, T. Sugimoto, M. Kikuta, E. Ishiko, and M. Kono, *J. Power Sources*, **162**, 658 (2006).
5. T. Sugimoto, Y. Atsumi, M. Kikuta, E. Ishiko, M. Kono, and M. Ishikawa, *J. Power Sources*, **189**, 802 (2009).
6. H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, and M. Kono, *J. Power Sources*, **160**, 1308 (2006).
7. C. S. Stefan, D. Lemordant, B. Claude-Montigny, and D. Violleau, *J. Power Sources*, **189**, 1174 (2009).
8. N. Tachikawa, J.-W. Park, K. Yoshida, T. Tamura, K. Dokko, and M. Watanabe, *Electrochemistry*, **78**, 349 (2010).
9. S. Fang, Y. Jin, L. Yang, S. Hirano, K. Tachibana, and S. Katayama, *Electrochim. Acta*, **56**, 4663 (2011).
10. L. Zhao, Y.-S. Hu, H. Li, Z. Wang, and L. Chen, *Adv. Mater.*, **23**, 1385 (2011).
11. Y.-Y. Cheng, C.-C. Li, and J.-T. Lee, *Electrochim. Acta*, **66**, 332 (2012).
12. M. Egashira, A. Kanetomo, N. Yoshimoto, and M. Morita, *J. Power Sources*, **196**, 6419 (2011).
13. B. Di Pietro, M. Patriarca, and B. Scrosati, *J. Power Sources*, **8**, 289 (1982).
14. M. M. Thackeray, W. I. F. David, and J. B. Goodenough, *Mater. Res. Bull.*, **17**, 785 (1982).
15. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, and J.-M. Tarascon, *Nature*, **407**, 496 (2000).
16. D. Larcher, D. Bonnin, R. Cortes, I. Rivals, L. Personnaz, and J.-M. Tarascon, *J. Electrochem. Soc.*, **150**, A1643 (2003).
17. C. Wu, P. Yin, X. Zhu, C. OuYang, and Y. Xie, *J. Phys. Chem. B*, **110**, 17806 (2006).
18. B. T. Hang, T. Doi, S. Okada, and J. Yamaki, *J. Power Sources*, **174**, 493 (2007).
19. M. V. Reddy, T. Yu, C.-H. Sow, Z. X. Shen, C. T. Lim, G. V. Subba Rao, and B. V. R. Chowdari, *Adv. Funct. Mater.*, **17**, 2792 (2007).
20. M. Egashira, S. Nakayama, N. Yoshimoto, and M. Morita, *Electrochemistry*, **81**, 473 (2014).