



Short communication

Effect of an organic additive on the cycling performance and thermal stability of lithium-ion cells assembled with carbon anode and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathodeYoon-Sung Lee^a, Ki-Soo Lee^a, Yang-Kook Sun^b, Yong Min Lee^c, Dong-Won Kim^{a,*}^a Department of Chemical Engineering, Hanyang University, 17 Haengdang-dong, Seungdong-gu, Seoul 133-791, Republic of Korea^b Department of Energy Engineering, Hanyang University, Seungdong-gu, Seoul 133-791, Republic of Korea^c Department of Applied Chemistry, Hanbat National University, Yusung-gu, Daejeon 305-719, Republic of Korea

ARTICLE INFO

Article history:

Received 29 July 2010

Received in revised form 12 October 2010

Accepted 18 October 2010

Available online 26 October 2010

Keywords:

Cycling performance

High voltage

Lithium-ion cells

Organic additive

Thermal stability

ABSTRACT

A small amount of thiophene or ethylene dioxythiophene (EDOT) is introduced into the liquid electrolyte of lithium-ion cells as an additive. These organic additives are electrochemically oxidized to form a thin conductive polymer film on the surface of the cathode at high potential. With the liquid electrolyte containing different additives, the lithium-ion cells composed of carbon anode and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode are assembled, and their cycling performances are evaluated. Adding small amounts of thiophene or EDOT to the liquid electrolyte is found to reduce the interfacial resistance in the cells and thus the cells containing an organic additive exhibit less capacity fading and better high-rate performance. Differential scanning calorimetric studies show that the thermal stability of the charged $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode is also enhanced in the presence of an organic additive.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-ion batteries with high energy density and long cycle life have become important power sources for portable electronic devices, electric vehicles, and load leveling systems. Most of commercialized lithium-ion batteries use LiCoO_2 as a cathode material. However, toxicity and high cost of cobalt pose major obstacles that limit its application in large-scale batteries. Recently, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ has attracted much attention as one of the most promising alternative cathode materials to replace LiCoO_2 for lithium-ion batteries, due to its high capacity, good structural stability and relatively low cost [1–5]. In order to increase the reversible capacity of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material, the charging cut-off voltage could be increased to around 4.5 V. However, the electrodes charged to a high voltage lead to a significant deterioration of the cycle performance [5,6]. The origin of the capacity fade is related to the increase in the surface reactivity between the highly delithiated cathode and the electrolyte solution, resulting in an increase in the interfacial resistance. In addition, operating at high voltage can lead to structural changes in the cathode material [7]. To solve these problems, numerous efforts have been undertaken, such as the addition of various inorganic and organic additives to the electrolyte [8–11] and inorganic coating on the surface of cath-

ode active materials [12–15]. Our group has recently reported that the high voltage (upper cut-off voltage: 4.4 V) cycling performance of lithium-ion cells composed of carbon anode and LiCoO_2 cathode could be improved by adding thiophene [16]. The use of the organic additive was based on the concept that it could be electrochemically polymerized prior to solvent decomposition in the high potential region [17–19].

With the aim of improving the cycling stability of lithium-ion cells with high cut-off voltage, i.e., cells composed of carbon anode and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode, we introduced a small amount of thiophene or ethylene dioxythiophene (EDOT) as an additive to liquid electrolyte. The influences of these organic additives on the cycling performances and the thermal stability of a delithiated $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode were investigated.

2. Experimental

2.1. Electrode preparation and cell assembly

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders were synthesized by the coprecipitation method, as described previously in detail [3]. The cathode was prepared by coating the N-methyl pyrrolidone (NMP)-based slurry containing $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, poly(vinylidene fluoride) (PVdF) and super-P carbon (85:7.5:7.5 by weight) on an aluminum foil. The thickness of the electrodes ranged from 50 to 60 μm after roll pressing, and their active mass loading corresponded to a capacity of about 1 mAh cm^{-2} (geometric electrode

* Corresponding author. Tel.: +82 2 2220 2337; fax: +82 2 2298 4101.

E-mail address: dongwonkim@hanyang.ac.kr (D.-W. Kim).

area: 30 cm²). The carbon anode was also prepared by coating the NMP-based slurry of mesocarbon microbeads (MCMB), PVdF and super-P carbon (88:8:4 by weight) on a copper foil. The liquid electrolyte was 1.15 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (3:7 by volume, battery grade, Techno Semichem Co., Ltd.). Thiophene or EDOT was added to a concentration of 0.05 wt.% as an additive into the liquid electrolyte. The cell composed of carbon anode, a polyethylene separator (Celgard 2400) and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode was assembled with an electrolyte solution containing an organic additive and was enclosed in an aluminum pouch. All cells were assembled in a dry box filled with argon gas.

2.2. Measurements

AC impedance measurements of the lithium-ion cells were performed in the charged state (4.5 V) using a CHI impedance analyzer over the frequency range of 1 mHz to 100 kHz with an amplitude of 10 mV. The surface morphology of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode material was observed using a transmission electron microscope (TEM, JEOL 2010) after the repeated cycling. In order to evaluate the cycling performance, the cells were cycled over 3.0–4.5 V or 3.0–4.6 V at a current rate of 1.0C. For differential scanning calorimetry (DSC) experiments, the cells were fully recharged to 4.5 V after 200 cycles and opened in a dry room. After disassembling the cells, the cathode was gently scraped from the current collector. Approximately 5 mg of the cathode was hermetically sealed in a stainless steel sealed pan, and measurements were performed using a 200 PC (NETZSCH, Germany) differential scanning calorimeter at a heating rate of 1 °C min⁻¹. Before DSC measurements, the amount of cathode active material and electrolyte solution was measured, and heat flow was calculated based on the weight of the cathode active material.

3. Results and discussion

In our previous study, it was shown that EDOT and thiophene oxidized prior to the decomposition (4.90 V vs. Li/Li⁺) of the liquid electrolyte [19]. That is, two additional small oxidative current peaks were observed for the electrolyte solution containing EDOT (4.06 and 4.55 V vs. Li/Li⁺) and thiophene (4.11 and 4.55 V vs. Li/Li⁺), respectively. The electrochemical oxidation of these additives can result in the formation of a conductive polymer film on the electrode because their polymerization products are electronically conductive in their oxidized states [18,20]. Chemical compounds with a high HOMO (highest occupied molecular orbital) energy tend to easily decompose [11,21], since they are good electron donors. Because the HOMO energies of thiophene and EDOT are higher than those of solvents (EC, DEC) in the liquid electrolyte, thiophene and EDOT could be easily oxidized at potentials lower than the decomposition potential of the solvent.

The cycling performance of lithium-ion cells prepared with liquid electrolyte containing an organic additive has been evaluated. For the purpose of comparison, the cell without an additive was also cycled under the same conditions. The assembled cells were initially subjected to a preconditioning cycle over 3.0–4.5 V at a constant current of 0.1 mA cm⁻² (0.1C rate). The preconditioning charge–discharge curves of lithium-ion cells with and without an additive are given in Fig. 1. As shown, the initial discharge capacities of the cells containing an organic additive are slightly lower than that of the cell without an organic additive. The cell without an additive shows an initial discharge capacity of 188.5 mAh g⁻¹ based on the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ active material in the cathode. Initial discharge capacities of the cells containing an organic additive are 185.7 and 185.1 mAh g⁻¹ for EDOT and thiophene, respectively.

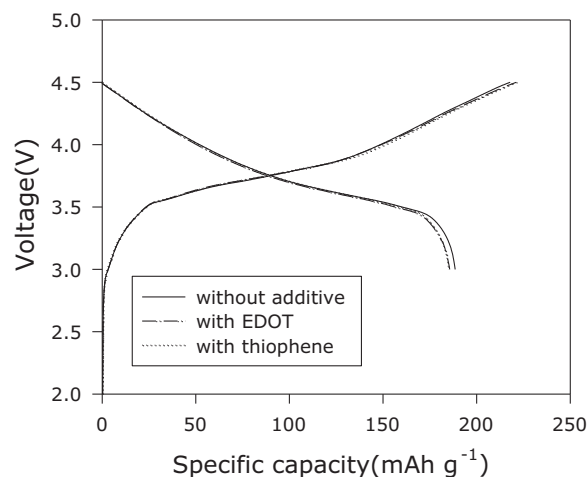


Fig. 1. First preconditioning cycles of lithium-ion cells assembled with liquid electrolyte containing different additives (0.1C, cut-off voltage: 3.0–4.5 V).

When comparing the coulombic efficiency of the pre-conditioning cycle, the cell without an organic additive has a higher value (86.5%) than the cells containing EDOT (84.0%) or thiophene (83.6%). Low coulombic efficiency of the cell containing an organic additive is associated with an irreversible electrochemical oxidation of an organic additive on the electrode during the first preconditioning cycle, as oxidative polymerization of organic additive is liable to irreversibly occur at high voltage during the charging process. It is thus plausible that the oxidative polymerization of an additive consumes part of the capacity, which corresponds to an irreversible capacity loss.

After two cycles at 0.1C rate, the cells were charged to 4.5 V at a constant current of 1.0C rate. This was followed by a constant-voltage charge with a decline of current until the final current reached 10% of the charging current. They were then discharged down to a cut-off voltage of 3.0 V at the same current. Fig. 2 compares the charge–discharge curves of the 1st, 10th, 50th, 100th and 200th cycles of the lithium-ion cell containing thiophene as an additive. The cell has a first discharge capacity of 161.1 mAh g⁻¹, and the discharge capacity of the cell declines to 137.2 mAh g⁻¹ after 200 cycles. Coulombic efficiency steadily increased and stabilized with cycle number, and was higher than 99.5% through cycling after the initial few cycles.

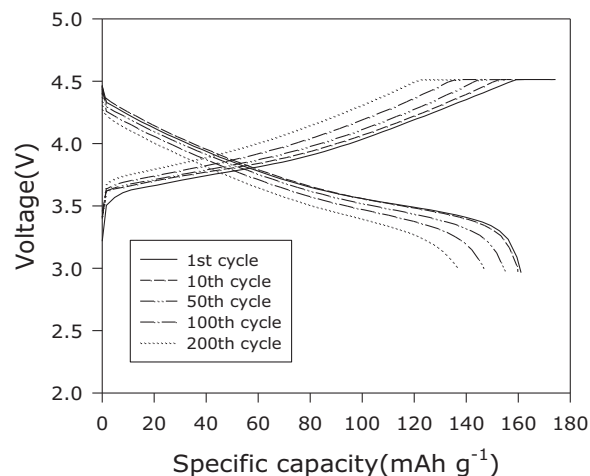


Fig. 2. Charge and discharge curves of the lithium-ion cell assembled with liquid electrolyte containing thiophene. (1.0C CC and CV charge, 1.0C CC discharge, cut-off voltage: 3.0–4.5 V).

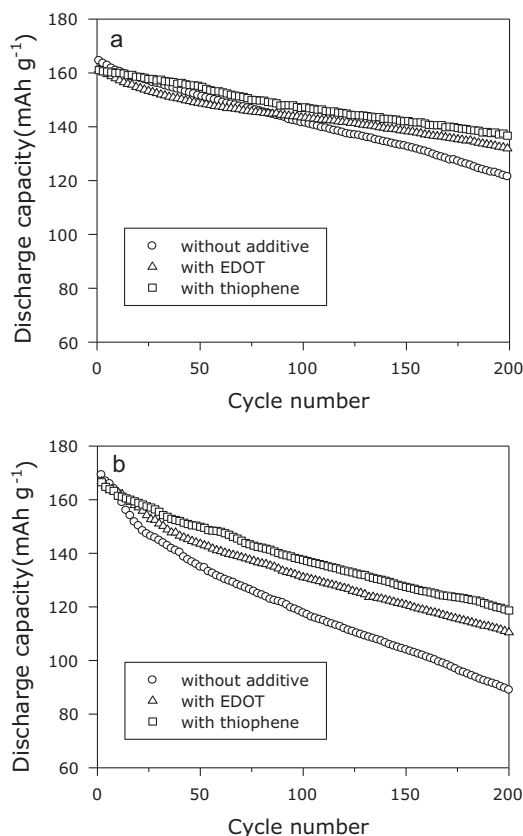


Fig. 3. Discharge capacities of the lithium-ion cells assembled with liquid electrolyte containing different additives, as a function of cycle number. (1.0C CC and CV charge, 1.0C CC discharge). (a) cut-off voltage: 3.0–4.5 V, (b) cut-off voltage: 3.0–4.6 V.

Fig. 3 presents the effect of an additive on the discharge capacities as a function of cycle number. The cells were cycled over 3.0–4.5 V or 3.0–4.6 V at a current rate of 1.0C. It is clear that the addition of an organic compound to the liquid electrolyte leads to improved cycling characteristics. In Fig. 3-(a), the cell without an additive has a discharge capacity of 121.3 mAh g^{-1} at the 200th cycle, which corresponds to 73.7% of initial discharge capacity. On the other hand, the capacity retentions of the cells containing an organic additive are 81.8 and 85.2% at the 200th cycle for EDOT and thiophene, respectively. When the cut-off voltage for charging was increased to 4.6 V, the improvement of capacity retention was more remarkable in the presence of additive, though the cycling stability rather decreased for all the cells, as shown in Fig. 3-(b). Good capacity retention in the cell with these additives can be ascribed to the formation of an electronically conductive polymer film on the active sites of the cathode during charging, as explained above. This conductive polymer film functions as a protective layer to cover the active cathode sites and reduce the electrolyte decomposition at high voltage, so that the structural stability of cathode material can be enhanced.

In order to understand the effect of the organic additives on cell cycling performance, the ac impedance of the cells was measured, and the resultant ac impedance spectra are shown in Fig. 4. It has been known that ac impedance behavior of the cell depends on the state of charge [22]. For a fair comparison, we tried to investigate the ac impedance spectra at charged state of the cell. Fig. 4-(a) was obtained at the charged state after 1 cycle, and Fig. 4-(b) was measured at the charged state after 200 cycles. In both spectra, two overlapping semicircles are observed. According to the previous studies of ac impedance analysis [23,24], the semicircle appeared in the high frequency range can be attributed to

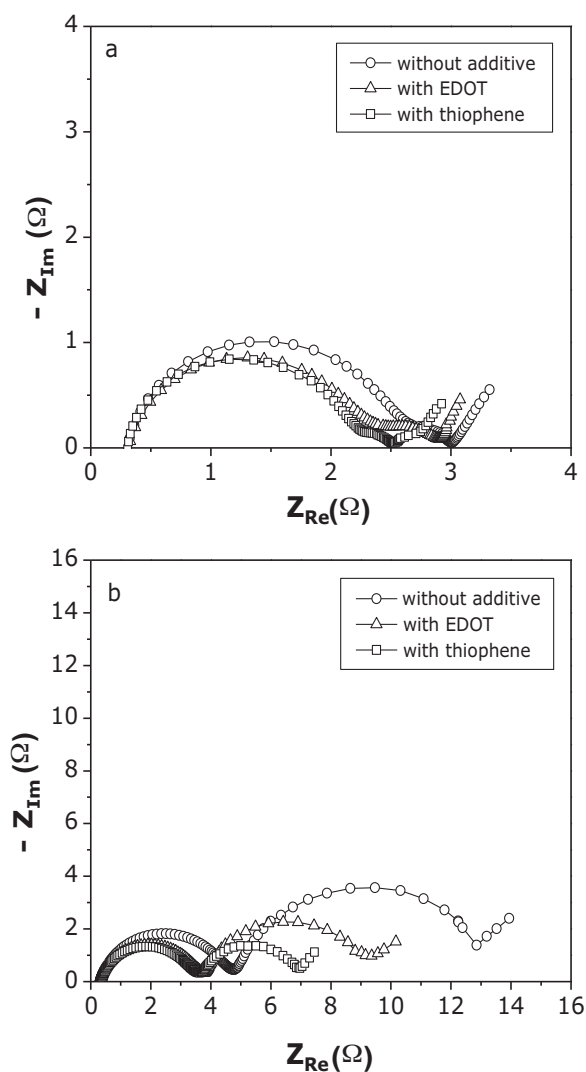


Fig. 4. AC impedance spectra of the lithium-ion cells assembled with liquid electrolyte containing different additives, which are obtained at charged state after (a) 1 cycle and (b) 200 cycles.

the resistance due to Li^+ ion migration through the surface film on the electrode (R_f) and the semicircle observed in the medium-to-low frequency range is due to charge transfer resistance between the electrode and electrolyte (R_{ct}). In Fig. 4-(a), the surface film resistance in the cell without additive is observed to be slightly larger than those of the cells with additive, but there are little differences in the charge transfer resistance. After 200 cycles, the largest increase in charge transfer resistance is observed in the cell without additive. The resistive layer formed on the electrode surface due to electrolyte decomposition may hamper charge transport at the electrode and electrolyte interface, which increases the charge transfer resistance with the repeated cycles. On the other hand, the surface film resistance and charge transfer resistance are lower in the cells containing an organic additive. This would support the notion that, in the presence of an organic additive, a protective conductive film is formed on the cathode during cycling, which limits the growth of a resistive layer due to the electrolyte decomposition. Though the resistances of Li^+ ions through surface film are almost the same in the presence of an organic additive, the charge transfer resistance is shown to be higher in the cell containing EDOT. This result indicates that electronic properties of thin films formed on cathode may be different. When a conductive layer does form on the surface of the active material, this would produce a good electrical

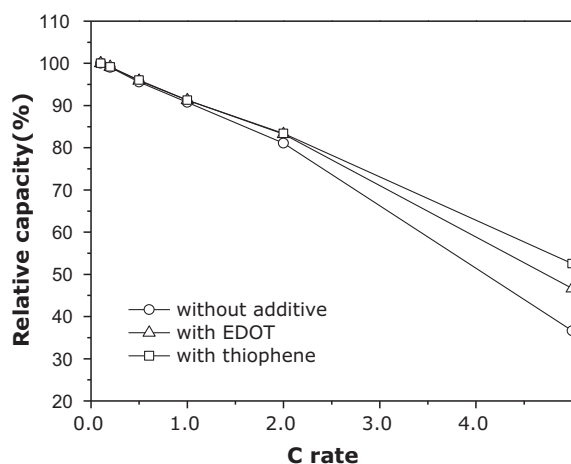


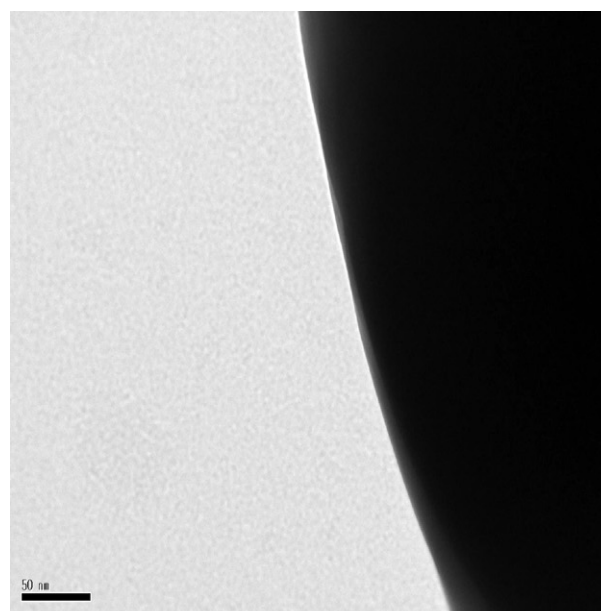
Fig. 5. Relative discharge capacities of the lithium-ion cells assembled with liquid electrolyte containing different additives, as a function of C rate.

contact between less conductive oxides, which facilitates electron transfer. For EDOT, the substitutions at the 3- and 4-positions of thiophene lead to steric interactions that distort the π -conjugated system, lowering the electronic conductivity and thus increasing the charge transfer resistance.

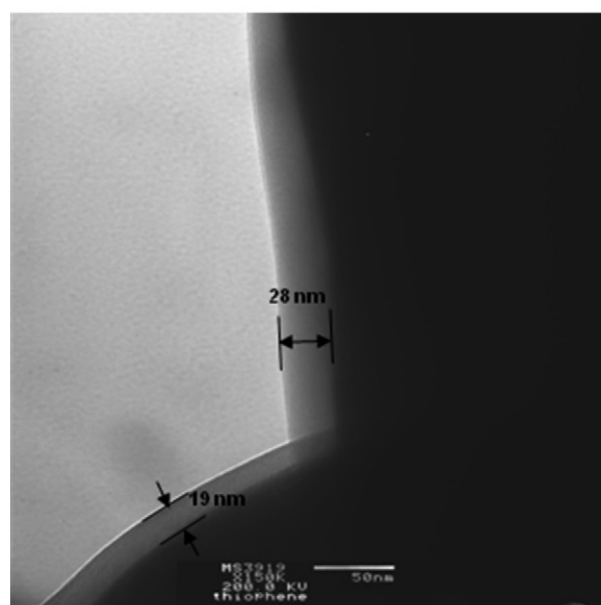
The rate capability of the lithium-ion cell prepared with liquid electrolyte containing an organic additive was evaluated. In order to induce the electrochemical oxidation of additives in the cell and distinguish the effect of additives clearly, the cells were cycled twice at 0.1C rate and then 20 times at 1.0C rate, before the execution of rate capability tests. Fig. 5 compares the relative discharge capacities of lithium-ion cells containing different additives, as a function of current rate. The relative capacity is defined as the ratio of the discharge capacity at a specific C rate to the discharge delivered at 0.1C rate. It was found that the discharge capacities are almost the same at low current density, regardless of the addition of organic additive. However, with increasing current rate to 5.0C rate, the effect of additives on rate performance of the cell becomes more noticeable. It can be seen that, in the presence of thiophene, the highest discharge capacity at high current rates is obtained. High rate performance of the cell containing thiophene may be encouraged by the less resistive surface film on the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode and the faster kinetics of the charge transfer reaction, as explained in the ac impedance spectra of Fig. 4-(b).

Fig. 6 shows the TEM images of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ active materials obtained after 200 cycles of the cells without and with thiophene as an additive. A magnified image around the edge of the primary $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particle cycled in the presence of thiophene additive clearly reveals that it is uniformly coated by the conductive polymer layer, and its thickness ranges from 19 to 28 nm, as shown in Fig. 6-(b). On the contrary, the bright field TEM of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particle cycled in the absence of an additive did not have an extra film on the particle surface. From the auger electron spectroscopy depth profile of the cathode obtained after 200 cycles in the presence of thiophene, the film thickness formed on $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was also measured to be about 23 nm. Thus, these results provide conclusive evidence that the primary $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particle is coated by the thin polymer layer formed by electrochemical oxidation of thiophene.

The thermal stability of cathode materials, especially at the delithiated state, is of great importance for battery safety. DSC measurements were performed in order to evaluate the thermal stability of the delithiated cathode material ($\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) in the presence of additive. The weight ratio of active cathode material to electrolyte solution was almost the same in all the



(a) without additive



(b) with thiophene

Fig. 6. TEM images of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particle obtained after 200 cycles of the cells (a) without and (b) with thiophene.

samples. Fig. 7 shows the DSC profiles of the cathode materials charged to 4.5V, which are obtained after 200 cycles. The DSC profiles of $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ showed two exothermic peaks, one appearing around 243 °C and the other above 255 °C. The first exothermic peak resulted from the decomposition of electrolyte solution due to an active cathode surface, and the second one could be ascribed to the electrolyte oxidation caused by released oxygen from $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, as previously reported by Baba et al. [25]. There is no significant difference in exothermic temperature and heat generation in the first peaks. On the other hand, the $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material in the cell containing an organic additive has a smaller exothermic heat at higher temperature, in the case of the second exothermic peaks. That is, the heat of reaction for the $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material in the cell containing EDOT and thiophene was reduced from 1081.0 to 781.1

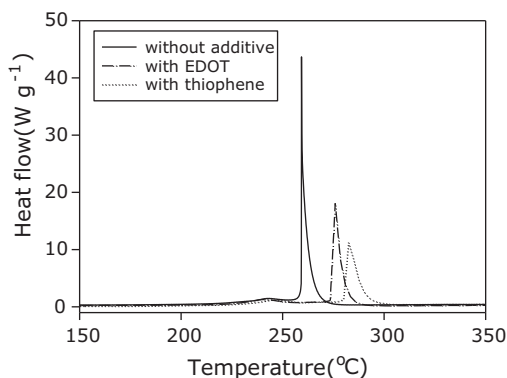


Fig. 7. DSC profiles of $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials charged to 4.5 V after 200 repeated cycles.

and 710.8Jg^{-1} , and their exothermic peaks shifted from 259.3 to 275.4 and 282.3°C, respectively, which indicate the enhanced thermal stability of the delithiated cathode material in the presence of the additive. We believe that the polymer layer coated on active cathode surface may block the oxygen release from $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material and it in turn gives rise to the shift of the exothermic oxidation reaction to higher temperature as well as the reduction of heat generation. These results suggest that more thermally stable cells based on $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode could be assembled by adding a small amount of organic additive into the liquid electrolyte.

4. Conclusions

Cycling performances of lithium-ion cells composed of carbon anode and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode were improved by adding a small amount of an additive to the liquid electrolyte. Lithium-ion cells containing an organic additive exhibited good capacity retention in the voltage range of 3.0–4.5 V and good high rate performance. Good cycling performance with an additive in the cell could be ascribed to the formation of a thin conductive film to suppress the electrolyte decomposition on cathode active sites at high voltage, which reduces the electrolyte decomposition so that the

structural stability of active material can be enhanced. The thermal stability of the charged $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode was also improved in the cell containing an organic additive. It is thus concluded that the addition of an organic additive is very useful for improving cycling performance and thermal stability of high-voltage lithium-ion cells.

Acknowledgement

This work was supported by the National Research Foundation of Korea Grant funded by the Korea Government (MEST) (NRF-2009-0092780 and NRF-2009-C1AAA001-0093360).

References

- [1] T. Ohzuku, Y. Makimura, *Chem. Lett.* (2001) 642.
- [2] Z. Lu, D.D. MacNeil, J.R. Dahn, *Electrochem. Solid State Lett.* 4 (2001) A200.
- [3] M.H. Lee, Y.J. Kang, S.T. Myung, Y.K. Sun, *Electrochim. Acta* 50 (2004) 939.
- [4] W. Lu, Z. Chen, H. Joachin, J. Prakash, J. Liu, K. Amine, *J. Power Sources* 3 (2007) 1074.
- [5] K.M. Shaju, G.V. Subba Rao, B.V.R. Chowdari, *Electrochim. Acta* 48 (2002) 145.
- [6] Y.K. Sun, S.W. Cho, S.W. Lee, C.S. Yoon, K. Amine, *J. Electrochem. Soc.* 154 (2007) A168.
- [7] H. Wang, Y.I. Jang, B. Huang, D.R. Sadoway, Y.M. Chiang, *J. Electrochem. Soc.* 146 (1999) 473.
- [8] R. Mogi, M. Inba, S. Jeong, Y. Iriyama, T. Abe, Z. Ogumi, *J. Electrochem. Soc.* 149 (2002) 1047.
- [9] H. Ota, K. Shima, M. Ue, J. Yamaki, *Electrochim. Acta* 49 (2004) 565.
- [10] Y.K. Han, J. Jung, S. Yu, H. Lee, *J. Power Sources* 187 (2009) 581.
- [11] K. Abe, Y. Ushigoe, H. Yoshitake, M. Yoshio, *J. Power Sources* 153 (2006) 328.
- [12] J. Cho, Y.I. Kim, B. Park, *Angew. Chem. Int. Ed. Engl.* 40 (2001) 3367.
- [13] Z. Chen, J.R. Dahn, *Electrochem. Solid State Lett.* 5 (2002) A213.
- [14] B.C. Park, H.B. Kim, S.T. Myung, K. Amine, I. Belharouak, S.M. Lee, Y.K. Sun, *J. Power Sources* 178 (2008) 826.
- [15] F. Wu, M. Wang, Y. Su, S. Chen, B. Xu, *J. Power Sources* 191 (2009) 628.
- [16] K.S. Lee, Y.K. Sun, J. Noh, K.W. Song, D.W. Kim, *Electrochem. Commun.* 11 (2009) 1900.
- [17] L. Xiao, X. Ai, Y. Cao, H. Yang, *Electrochim. Acta* 49 (2004) 4189.
- [18] K. Shima, K. Shizuka, M. Ue, H. Ota, T. Hatozaki, J. Yamaki, *J. Power Sources* 161 (2006) 1264.
- [19] J.A. Choi, S. Min Eo, D. MacFarlane, M. Forsyth, E. Cha, D.W. Kim, *J. Power Sources* 178 (2008) 832.
- [20] P. Novak, K. Muller, K.S.V. Santhanam, O. Haas, *Chem. Rev.* 97 (1997) 207.
- [21] P. Johansson, P. Jacobsson, *J. Power Sources* 153 (2006) 336.
- [22] S.S. Zhang, K. Xu, J.L. Allen, T.R. Jow, *J. Power Sources* 110 (2002) 216.
- [23] A. Funabiki, M. Inaba, Z. Ogumi, *J. Power Sources* 68 (1997) 227.
- [24] M.D. Levi, G. Salitra, B. Markovsky, H. Teller, D. Aurbach, U. Heider, L. Heider, *J. Electrochem. Soc.* 146 (1999) 1279.
- [25] Y. Baba, S. Okada, J. Yamaki, *Solid State Ionics* 148 (2002) 311.