Short communication

Electrolyte additive to improve performance of MCMB/LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Li-ion cell

Yan Qin, Zonghai Chen, Wenquan Lu, Khalil Amine*

Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

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ABSTRACT

The electrolyte additive, 3,9-divinyl-2,4,8,10-tetraoxaspiro[5,5] undecane (TOS), was investigated as a means to improve the life of mesocarbon microbead (MCMB)/Li$_{1.1}$[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]$_{0.9}$O$_2$ (NCM) cells for high-power applications. With the addition of an appropriate amount of TOS (no more than 1 wt%) to MCMB/NCM cells, the capacity retention was significantly improved at 55 °C compared with cells containing pristine electrolyte. Aging tests at 55 °C indicated that the capacity retention of the negative electrode had benefited as a result of the formation of a stable passivation film at the surface of the carbon electrode due to TOS reduction. Electrochemical impedance spectroscopy showed that a TOS addition of more than 0.5 wt% increased the cell interfacial impedance. Differential scanning calorimetry showed that the thermal stability of lithiated MCMB was also improved with the TOS addition.

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1. Introduction

Currently, lithium-ion batteries are being developed as the power source for hybrid and plug-in hybrid electric vehicles [1–4], which generally require a 15-year battery life. This requirement is a significant challenge for the current technology of lithium-ion batteries, and much effort is being devoted to extend the battery calendar and cycle life. The most promising approach is to develop functional electrolyte additives that limit the degradation of electrodes during cycling by stabilizing the electrode/electrolyte interface. The state-of-the-art nonaqueous electrolyte for lithium-ion batteries is LiPF$_6$ in carbonates, but LiPF$_6$ is sensitive to moisture. A tiny amount of moisture will trigger the decomposition of LiPF$_6$ to produce PF$_5$, LiF, POF$_3$, and HF [5]. The HF will, in turn, attack the cathode materials to release metal ions. Amine et al. [2] reported that a trace amount of reaction byproducts, such as HF, LiF, POF$_3$, and Mn^{2+}, can attack the battery electrodes (in particular, the negative electrode) and dramatically shorten the life of the battery. To overcome this problem, researchers have developed several passivation additives that can polymerize and form a stable passivation film at the electrode surface during the formation cycles. Example of these additives are vinyl ethylene carbonate [6–8], vinylene carbonate [8–11], lithium bis(oxalato)borate [12,13], lithium tetrafluoro oxalato phosphate [14], and vinyl pyridine [15]. In this paper, we report on a new TOS additive that improve significantly the cycle life performance of mesocarbon microbeads (MCMB)/Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ cells, especially when operating or aging the cell at high temperature.

2. Experimental

The TOS additive was purchased from Sigma–Aldrich and was used as-received without further purification.

The positive electrode was prepared by casting a slurry of 84 wt% NCM, 8 wt% carbon black (TB5500), and 8 wt% poly(vinylidene fluoride) (PVDF) (Kureha 7208) dispersed in N-methyl-2-pyrrolidone on an aluminum foil. The active loading is 10 mg cm^{-2}. The negative electrode was made by casting a slurry of 90 wt% mesocarbon microbeads (MCMB-1028), 2 wt% vapor-grown carbon fiber, and 8 wt% PVDF (Kureha 1100) dispersed in N-methyl-2-pyrrolidone on a copper foil and the active loading is 7 mg cm^{-2}. Then the electrodes were dried completely in a vacuum oven at 75 °C for overnight. The capacity ratio between anode and cathode is about 1.2 taking into account of 15% irreversible capacity loss for NCM [16] and 18% for MCMB.

The performance of the MCMB/NCM cells was evaluated in 2032-type coin cells. The cell was configured with a negative electrode (MCMB), a microporous polypropylene separator (Celgard 3501), a positive electrode (NCM), and an appropriate amount of electrolyte. The electrolyte was 1.2 M LiPF$_6$ dissolved in the mixture solvent of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with a ratio of 3:7 by volume, with or without TOS additive.

The concentrations of TOS tested were 0, 0.25, 0.5, 0.75, 1, and 2 wt%. The cells were first subjected to three formation cycles at the C/10 rate, and then cycled under the following conditions: 1C rate, temperature of 55 °C, and voltage between 3 and 4.0 V. The upper cut-off voltage of 4 V was chosen because according to the previous study, the best capacity retention was achieved when cycled between 3 and 4.0 V [16]. Before and after 400 cycles, the cells were constant-voltage charged to 3.8 V and then taken out of the oven and cooled down to room temperature for AC impedance investigation using a BAS-Zahner IM6 Impedance Analyzer (Zahner Electric). The frequency window was between 1 MHz and 0.01 Hz, with voltage amplitude of 5 mV.

In other tests, Li metal foil was used as the counter electrode to prepare Li/MCMB and Li/NCM cells, respectively, with addition of different amounts of TOS. The cells were subjected to three formation cycles at the C/10 rate, and then charged to 0.001 V for the Li/MCMB and 4.1 V for the Li/NCM, respectively. After about 4 weeks of aging at 55 °C, the cells were taken out of the oven to measure their capacity at room temperature. The Li/MCMB cells were cycled at the C/10 rate, while the Li/NCM cells were cycled at the 1 C rate. The low charge rate of C/10 was chosen for the Li/MCMB cells because the capacity of those cells only recovered about 10% of their initial capacity at the 1C rate after aging due to increase in the cell impedance. After the capacity measurement, the cells in good condition (capacity retention >30%) were subjected to the aging test at 55 °C for another 2–4 weeks.

To study the impact of TOS on thermal stability of electrode materials, cells of Li/MCMB and Li/NCM with/without 1 wt% TOS were charged to 0.1 V and 4.1 V respectively. The cells were then disassembled in the glove box; the recovered MCMB and NCM electrode material were peeled off from the current collector. Then, about 3 mg materials was transferred to the stainless steel pan with addition of 3 μL electrolyte and tightly sealed. The prepared samples were then subjected to differential scanning calorimetry (DSC) (Perkin-Elmer, Pyrix1) in the temperature range of 25–375 °C at a scan rate of 10 °C/min.

3. Results and discussion

3.1. Effect of TOS additive on capacity retention

Fig. 1 shows the normalized discharge capacity retention of the MCMB/NCM cells with different amounts of TOS in the electrolyte.
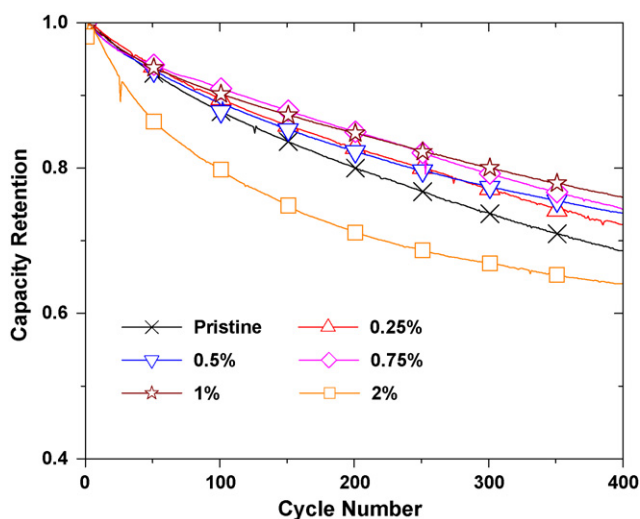

Fig. 1. Capacity retention of MCMB/NCM cells cycled between 3 and 4 V at 55 °C in electrolyte of 1.2 M LiPF$_6$-EC:DEC (3:7 volume ratio) with and without TOS. The weight percentage of the TOS is indicated in the plot.
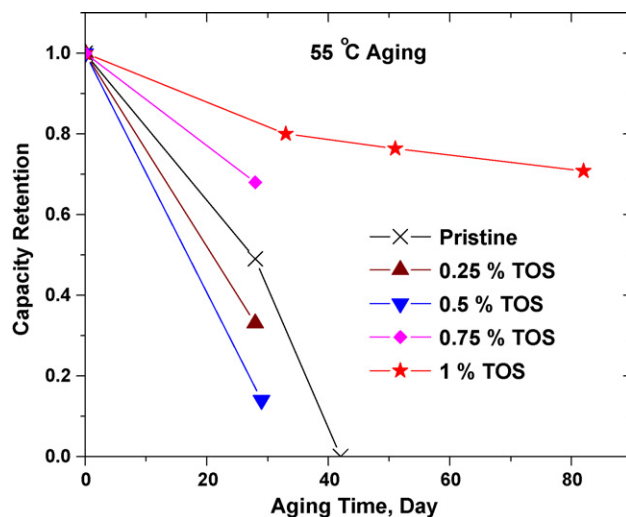

Fig. 2. Capacity retention of Li/MCMB half cells with and without various amounts of TOS after aging at 55 °C.

The initial specific capacity of these cells was about 130 mAh g^{-1}, based on the weight of positive electrode material (NCM). As the concentration of TOS increased from 0 to 1 wt%, the cell capacity retention increased. However, as the concentration increased from 1 to 2 wt%, the capacity retention decreased and was even worse than that of the cell without TOS. After 400 cycles at 55 °C, the capacity retention of the pristine cell was less than 68%, while that of the 1 wt% TOS cell was above 76%.

Fig. 1 confirms that the addition of TOS as an electrolyte additive can improve the capacity retention of the full cell. However, the mechanism of this improvement is not understood. To that end, a series of Li/MCMB half cells were prepared with different TOS contents. These cells were initially cycled at 25 °C with a constant current of C/10 (0.3 mA) to check the initial capacity before being constant-voltage discharged to 1 mV. The fully discharged cells (1 mV) were then aged at 55 °C before being cooled to 25 °C for capacity check (with a constant current of C/10 or 0.3 mA). Fig. 2 shows the normalized reversible capacity of the negative electrodes at 25 °C with different TOS concentrations in the electrolyte after cell aging at 55 °C. After being aged for 42 days at 55 °C, the cell with pristine electrolyte had no reversible capacity left. The cells with 0.75 and 1 wt% TOS showed excellent capacity retention of 70% and 80%, respectively after 28 days of aging. However, after extensive aging for over 80 days, only cells with 1 wt% TOS survived with about 70% capacity retention. Further increases of the concentration of TOS to 2 wt%, did not improve the capacity retention above that of the cell using pristine electrolyte, i.e., almost no capacity was left after only 30 days of aging (not shown in Fig. 2).

The same aging experiments were carried out with Li/NCM half cells. Fig. 3 shows the normalized discharge capacity of the positive electrodes as a function of both the aging time and the concentration of TOS added. The cells with and without TOS showed similar capacity retention, and the performance of the cell without TOS was slightly better than that of the cells with TOS. Similar to well-studied additive VC [17], TOS has obvious beneficial effect on graphite anodes and no adverse effect on cathode. Therefore, we concluded that the added TOS benefited the negative electrode and hence improved the capacity retention of full cells and significantly improved the aging characteristics of the negative-electrode half cells, especially at 55 °C.

Fig. 4 shows the partial dQ/dV curve of the first charge-discharge cycle (at C/10) from the Li/MCMB half cell. The insert shows the whole cycle profile. Although no extra peak was observed with
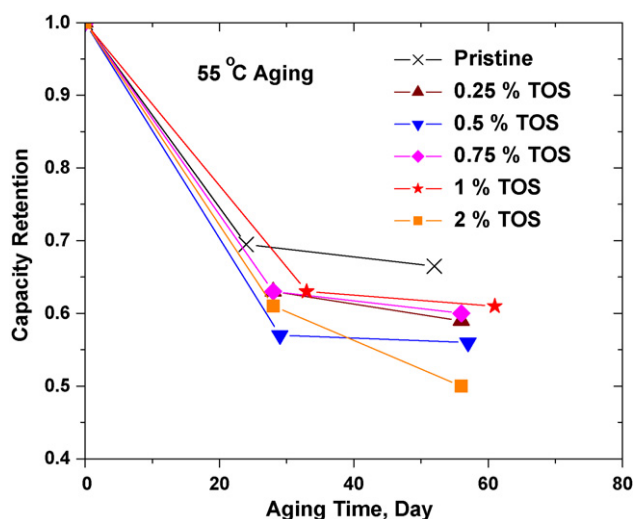
Fig. 3. Capacity retention of Li/NCM half cells with and without various amounts of TOS after aging at 55 °C.

Fig. 5. Voltage response at constant charge current of (a) 2 mA and (b) 0.2 mA for MCMB/NCM cells with 2 wt% TOS in the electrolyte at room temperature.

addition of 1 wt% TOS in the electrolyte, considering the positive effect of TOS on cycling and aging performance, we still believe that TOS can form polymerized SEI film on the electrode surface. There are two possible pathways for the polymerization. One is the proton induced condensation polymerization. For instance, 3,9-diethylidene-2,4,8,10-tetraoxaspiro[5.5] undecane (DETOSU), which has very similar structure as TOS, can convert to poly(ortho esters) (POE) through proton induced condensation polymerization, which has been intensively studied due to its biodegradability by hydrolysis [18,19]. In those cases, DETOSU reacted with a variety of diols to produce the POE backbone with acid as the trigger agent. However, in the electrolyte of the lithium ion battery, the concentration of proton in non-aqueous electrolyte is very low, besides, no diols are presented in the lithium ion cell. Hence, we lean to another possible pathway, electrochemically induced free radical polymerization. Monomers with double bonds, such as styrene [20] and methylenebisacrylamide [21], followed such polymerization pathway. We hypothesized that the unsaturated bonds on TOS could be electrochemically reduced, and that the generated radical initiates the radical polymerization at a low potential during the initial discharge, when lithium is inserted into the graphite. The amount of current needed to initiate the free radicals could be too small to be
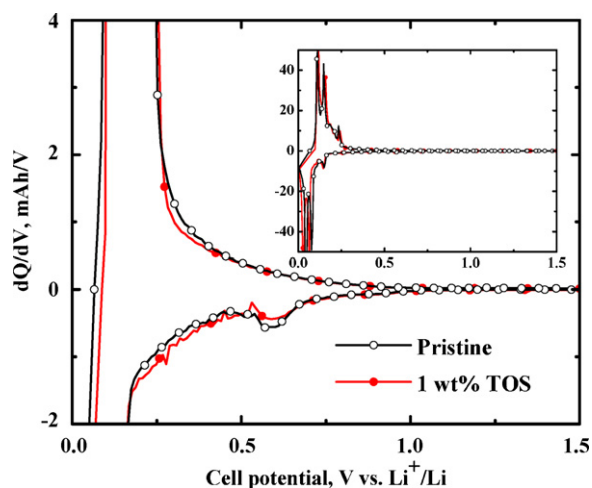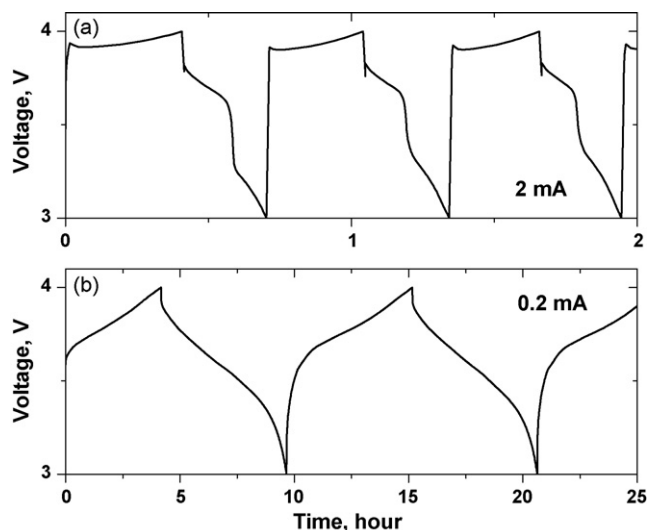

Fig. 4. Partial dQ/dV curve of the first charge–discharge cycle (at C/10) from the Li/MCMB half cell with the insert showing the whole curve.

detected by our equipments, which emphasize on stability and relatively high current application. The resulting polymer then covers the surface of the negative electrode, forming an artificial solid-electrolyte interface (SEI) to protect the negative electrode from attack by the electrolyte. According to this mechanism, we expect that the interfacial impedance of lithium-ion cells will increase with TOS concentration.

As stated earlier, the capacity retention of the cell with 2 wt% TOS was worse than that of the cell without TOS. Fig. 5a shows the voltage profile of the cell with 2 wt% TOS after being cycled at 55 °C for 400 cycles. These data were collected at 25 °C with a constant current of 1C (2 mA). Fig. 5a shows that the voltage jumped considerably at the beginning of each charge and then decayed slightly with the charge time. This unusual behavior can only be explained by large internal cell impedance that is sensitive to temperature. At the beginning of each charge, the cell was "cold" and the cell impedance was high. These conditions led to a large initial polarization (∼0.9 V), as shown in Fig. 5a. The large voltage drop on the resistive component was then converted to electric heat, which increased the working temperature of the resistive component and decreased the cell impedance. As the cell impedance decreased, the initial large polarization also decreased, resulting in the slight voltage decay following the initial voltage jump.

This high impedance at room temperature can be attributed to the thick film formed by the TOS additive polymerization. It was reported that the glass transition temperature of POE film will vary as a function of the proportion of two diols used in the synthesis [18]. The glass transition temperature will be higher when more rigid diols take part in the reaction. With the different diols, the highest glass transition temperature of polymerized DETOSU is about 100 °C [18]. Since TOS has the similar structure as DETOSU, the polymerized TOS may be more flexible due to the location of the double bonds on the structure. Therefore, the glass transition temperature might be lower than 100 °C. At room temperature or when the cell temperature was cold, the film on the electrode was rigid, which hindered or slowed down the diffusion of lithium ion from the electrode surface to the electrolyte. Therefore, the cell impedance increased, and no or little capacity could be obtained, especially at rates higher than 1C. The film became flexible when the cell temperature increased, which could facilitate the transportation of Li-ion through the film, and all the cell capacity was recovered. Based on the preliminary results above, we expect that cell performance maybe improved if the film is less rigid at room
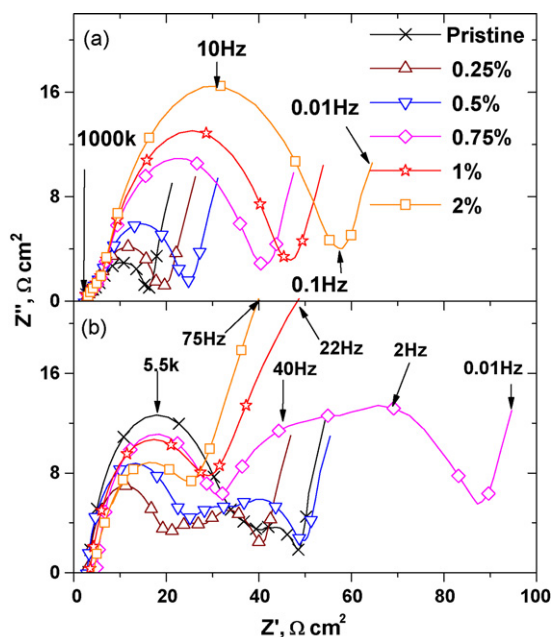
Fig. 6. Nyquist plots of cells (a) before cycling, (b) after 400 cycles, and (c) after 800 cycles at 55 °C in electrolyte of 1.2 M LiPF$_6$-EC:DEC (3:7 volume ratio) with and without various amounts of additive TOS.

temperature, meaning that the glass transition temperature should be lower than or close to room temperature. Therefore, physical characterization of the film with various precursors, such as DETOSU and diols, should be studied in the future to verify the cell performance and the modified SEI film property relation.

To test our speculation, we cycled the 2 wt% TOS cell at 25 °C with a very low constant current of C/10 (0.2 mA). The voltage profile of the cell is shown in Fig. 5b. As expected, the high polarization and voltage drop shown in Fig. 4a were not observed with low-rate cycling. This confirmed that an excess amount of TOS caused a significant increase of the cell impedance and deterioration of the capacity retention as shown in Figs. 1 and 2 (with 2 wt% TOS).

3.2. Effect of TOS additive on electrochemical impedance

The above results indicate that the TOS electrolyte additive can improve capacity retention of lithium-ion cells, but there is an upper concentration of 1 wt% that should not be exceeded. Electrochemical impedance spectroscopy (EIS) was carried out to investigate the effect of TOS content on the cell impedance. Before and after 400 cycles at 55 °C, the cells were constant-voltage charged to 3.8 V before EIS measurement at 25 °C.

Fig. 6a shows the EIS measurements for fresh cells with different amounts of TOS. For fresh cells with or without TOS in the electrolyte, the high-frequency semicircle (5–10 kHz) did not stand out well from the middle-frequency semicircle (tens of Hz). After 400 cycles (Fig. 6b), the high-frequency semicircles became more obvious and bigger. However, the high-frequency semicircles for the TOS additive electrolyte were all smaller than those for pristine electrolyte. With an increase in TOS additive, these high-frequency semicircles first increase, then decrease when 0.75–1 wt% was reached. The mid-frequency semicircles were clearly visible at the beginning of cycling, but became depressed and less obvious after prolonged cycling. Following the mid-frequency semicircle, a depressed low-frequency (few Hz) semicircle developed, and the low-frequency semicircle grew dramatically when the TOS concentration was larger than 0.5 wt%. Compared to the pristine electrolyte cell, the cells with TOS consistently had a smaller high-
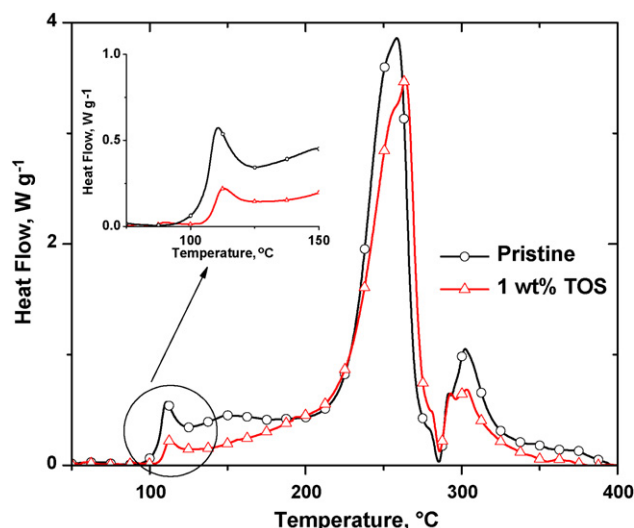
frequency semicircle after cycling (see Fig. 6b). The fresh cells (Fig. 6a) had very small high-frequency semicircles, and the effect of TOS on the high-frequency semicircle was not clearly shown in Fig. 6a. Moreover, when the TOS additive was no more than 0.5 wt%, the growth rate of the mid- and low-frequency semicircles was equivalent to that of the cell without TOS. When more than 1.0 wt% TOS was added, the low-frequency semicircle grew dramatically for the cycled cells. This impedance behavior may be the cause of the poor performance of cells with 2 wt% TOS. This result corroborates with the cycling result shown in Fig. 1 where up to 1 wt% TOS additive resulted in cell cycling improvement due to limited increase of cell impedance compared to pristine cell.

3.3. DSC thermal stability studies

Fig. 7 shows the DSC results for the fully charged MCMB-1028 in electrolyte with and without 1 wt% TOS. Without TOS, the onset of SEI breakdown begins around 90 °C. However, with 1 wt% TOS, the onset of SEI layer breakdown takes place after 110 °C. The amount of heat generated by the SEI layer breakdown on the anode is the key factor that triggers the thermal runaway [22]. The data clearly show that with addition of TOS, the modified SEI layer has high thermal resistance, which leads to the observed delay in the onset of the breakdown temperature, and reduces the heat generated after the breakdown until 200 °C. Above 200 °C, the cathode material will react with electrolyte to induce thermal runaway. The additive effect could be explained in two ways. First, if the additive improves the stability of SEI layer on the anode, it could delay the onset of the SEI layer breakdown and reduce the rate of the heat increase in the cell. Secondly, the reduction of the heat rate increase, will delay the onset temperature of the cathode reaction with the electrolyte which is the cause of the thermal runaway in the cell.

4. Conclusions

The effect of TOS additive on MCMB/NCM cells has been studied. The addition of no more than 1 wt% TOS to the electrolyte improved the cell capacity retention. This benefit was demonstrated on MCMB carbon electrodes aged at 55 °C. Especially when 1% TOS was added, the capacity retention significantly improved. Without TOS, the MCMB/Li cells lost all the reversible capacity after 40 days of aging; however, with 1% TOS, the cells retained about 70% capacity after more than 80 days of aging at 55 °C.

Fig. 7. DSC curves of fully lithiated MCMB with and without 1 wt% TOS.

Although TOS has a positive effect on the cell cycleability, EIS indicated that the addition of TOS increased the cell resistance at room temperature. With only 0.5% TOS, the cell impedance only slightly increased. However, with more than 0.5% TOS, the cell impedance dramatically increased. Considering the overall performance of the lithium ion cells, no more than 1 wt% TOS addition is recommended.

Addition of TOS in the electrolyte improved the thermal stability of the negative electrodes by delaying the SEI breakdown onset temperature and decreasing the heat accumulation to reduce the rate of the heat increase in the cell and delay the onset temperature of the reactivity of the cathode with electrolyte which is known to cause the thermal runaway of the cell.

Acknowledgments

References

[1] K. Amine, J. Liu, I. Belharouak, S.H. Kang, I. Bloom, D. Vissers, G. Henriksen, J. Power Sources 146 (2005) 111–115.
[2] K. Amine, J. Liu, S. Kang, I. Belharouak, Y. Hyung, D. Vissers, G. Henriksen, J. Power Sources 129 (2004) 14–19.
[3] Z. Chen, K. Amine, J. Electrochem. Soc. 153 (2006) A1221–A1225.
[4] T.R. Jow, K. Xu, M.S. Ding, S.S. Zhang, J.L. Allen, K. Amine, J. Electrochem. Soc. 151 (2004) A1702–A1706.
[5] D. Aurbach, B. Markovsky, A. Shechter, Y. Ein-Eli, H. Cohen, J. Electrochem. Soc. 143 (1996) 3809–3820.
[6] G. Chen, G.V. Zhuang, T.J. Richardson, G. Liu, J. Philip, J Ross Jr., Electrochem. Solid-State Lett. 8 (2005) A344–A347.
[7] Y. Hu, W. Kong, Z. Wang, H. Li, X. Huang, L. Chen, Electrochem. Solid-State Lett. 7 (2004) A442–A446.
[8] J.M. Vollmer, L.A. Curtiss, D.R. Vissers, K. Amine, J. Electrochem. Soc. 151 (2004) A178–A183.
[9] D. Aurbach, J.S. Gnanaraj, W. Geissler, M. Schmidt, J. Electrochem. Soc. 151 (2004) A23–A30.
[10] H. Ota, Y. Sakata, A. Inoue, S. Yamaguchi, J. Electrochem. Soc. 151 (2004) A1659–A1669.
[11] H. Ota, Y. Sakata, Y. Otake, K. Shima, M. Ue, J.-I. Yamaki, J. Electrochem. Soc. 151 (2004) A1778–A1788.
[12] Z.H. Chen, W.Q. Lu, J. Liu, K. Amine, Electrochim. Acta 51 (2006) 3322–3326.
[13] K. Xu, S. Zhang, T.R. Jow, Electrochem. Solid-State Lett. 8 (2005) A365–A368.
[14] Y. Qin, Z. Chen, J. Liu, K. Amine, Electrochem. Solid-State Lett. 13 (2010) A11–A14.
[15] S. Komaba, T. Itabashi, T. Ohtsuka, H. Groult, N. Kumagai, B. Kaplan, H. Yashiro, J. Electrochem. Soc. 152 (2005) A937–A946.
[16] Z. Chen, Y.K. Sun, K. Amine, J. Electrochem. Soc. 153 (2006) A1818–A1822.
[17] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, Electrochim. Acta 47 (2002) 1423–1439.
[18] J. Heller, J. BArr, S. Ng, H. Shen, Drug Deliv. Technol. 2 (2002).
[19] C. Wang, Q. Ge, D. Ting, D. Ngugen, H. Shen, J. Chen, H.N. Eisen, J. Heller, R. Langer, D. Putnam, Nat. Mater. 3 (2004) 190–196.
[20] C.U. Lee, D. Roy, B.S. Sumerlin, M.D. Dadmun, Polymer 51 (2010) 1244–1251.
[21] J. Bünsow, D. Johannsmann, Macromol. Symp. 248 (2007) 207–212.
[22] H. Yang, H. Bang, K. Amine, J. Prakash, J. Electrochem. Soc. 152 (2005) A73–A79.