

Short communication

## Effect of organic additives on the cycling performances of lithium metal polymer cells

Ji-Ae Choi<sup>a</sup>, Seung-Min Eo<sup>a</sup>, Douglas R. MacFarlane<sup>b</sup>,  
Maria Forsyth<sup>c</sup>, Eunhee Cha<sup>d</sup>, Dong-Won Kim<sup>a,\*</sup>

<sup>a</sup> Department of Applied Chemistry, Hanbat National University, Yuseong-Gu, Daejeon 305-719, Republic of Korea

<sup>b</sup> School of Chemistry, Monash University, Wellington Road, Clayton, Victoria 3800, Australia

<sup>c</sup> Department of Materials Engineering, Monash University, Wellington Road, Clayton, Victoria 3800, Australia

<sup>d</sup> Department of Art and Literature, Hoseo University, Baebang-Myun, Asan, Chungnam 336-795, Republic of Korea

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### Abstract

Gel polymer electrolytes were prepared by immersing a porous poly(vinylidene fluoride-co-hexafluoropropylene) membrane in an electrolyte solution containing small amounts of organic additive. Three kinds of organic compounds, thiophene, 3,4-ethylenedioxythiophene and biphenyl, were used as a polymerizable monomeric additive. The organic additives were found to be electrochemically oxidized to form conductive polymer films on the electrode at high potential. By using the gel polymer electrolytes containing different organic additive, lithium metal polymer cells, composed of lithium anode and LiCoO<sub>2</sub> cathode, were assembled and their cycling performance evaluated. Adding small amounts of a suitable polymerizable additive to the gel polymer electrolyte was found to reduce the interfacial resistance in the cell during cycling, and it thus exhibited less capacity fade and better high rate performance. Differential scanning calorimetric studies showed that the thermal stability of the fully charged LiCoO<sub>2</sub> cathode was improved in the cell containing an organic additive.

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### 1. Introduction

Rechargeable lithium batteries employing lithium metal as an anode are widely considered to be one of the most important prospects for next-generation power sources for portable electronic devices and electric vehicles [1]. The major problems that prevent the successful development of lithium metal batteries are their poor cycle life due to the deleterious dendrite formation of lithium and safety concern. To solve these problems, a number of alternatives have been investigated such as the addition of various inorganic and organic additives to the electrolyte [2–6], use of polymer electrolyte and ionic liquid as a replacement of the liquid electrolyte [7–12], metal oxide coating on the surface of cathode active materials [13–16] and so on. Most of the studies related to additives have focused on

the chemical modification of the lithium surface. At high cell voltage, the electrolytes used in the lithium batteries tend to decompose on the cathode surface, leaving a poorly conductive surface film on the cathode. This can also lead to the deterioration of the cell performance upon cycling. Recently, Abe et al. [17] have investigated several organic additives to form a conductive polymer film on the cathode in lithium ion batteries. They reported that cathode surface modification by polymerizable additives exerted a significant influence on the performance of lithium ion batteries. The use of these monomeric additives has been based on the concept that they could be electrochemically polymerized at the potential region just above 4.2 V and quite below 5.0 V, resulting in the formation of a thin conductive polymer film on the cathode during charging [17–19]. However, to our knowledge, their influence on the cycling performance of lithium metal polymer batteries has not been reported to date. It is our interest to investigate the electrochemical performance of the lithium metal polymer cells assembled with gel polymer electrolytes containing organic additives. In our study, we

\* Corresponding author. Tel.: +82 42 821 1550; fax: +82 42 822 1562.

E-mail address: [dwkim@hanbat.ac.kr](mailto:dwkim@hanbat.ac.kr) (D.-W. Kim).

introduced three kinds of polymerizable monomeric additives (3,4-ethylenedioxythiophene, thiophene and biphenyl) to the gel polymer electrolyte. We have investigated the influence of these organic additives on cycling performances of the rechargeable lithium metal polymer cells.

## 2. Experimental

### 2.1. Preparation of the gel polymer electrolyte

A porous poly(vinylidene fluoride-*co*-hexafluoropropylene), P(VdF-*co*-HFP) membrane was prepared as follows. P(VdF-*co*-HFP)(Kynar 2801), fumed silica, dibutyl phthalate (DBP) and acetone were mixed together and ball milled for 48 h and then cast to the thickness of 500  $\mu\text{m}$  using a doctor blade. Fumed silica was added to enhance the electrolyte uptake and the physical strength of the membrane, and DBP was used as a plasticizer for formation of pores in the polymer membrane when immersing in methanol, as previously described [20]. After 30 min, the membranes were immersed in methanol to remove DBP. Then the membranes were vacuum dried at 80  $^{\circ}\text{C}$  for 12 h. The gel polymer electrolyte was prepared by immersing the membrane in 1 M  $\text{LiClO}_4$  in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v, Samsung Cheil Industries, battery grade) containing 0.1 wt.% organic additive for 5 min. Thiophene, 3,4-ethylenedioxythiophene (EDOT) and biphenyl (Aldrich) were chosen as the organic additives in this study.

### 2.2. Cell assembly

The cathode was prepared by coating the *N*-methyl pyrrolidone (NMP)-based slurry containing 94 wt.%  $\text{LiCoO}_2$  (Japan Chemical), 3 wt.% PVdF and 3 wt.% super-P carbon (MMM Co.) on an aluminum foil. The thickness of the cathode was about 56  $\mu\text{m}$  after roll-pressing, and its active mass loading corresponded to the capacity of about 2.84  $\text{mAh cm}^{-2}$ . The anode consisted of 50  $\mu\text{m}$  thick Li foil (Cyprus Foote Mineral Co.) pressed onto a copper current collector. Lithium metal polymer cells were assembled by sandwiching the gel polymer electrolyte between the lithium anode and  $\text{LiCoO}_2$  cathode. The cell was then enclosed in a metallized plastic bag and vacuum-sealed. All assemblies of the cells were carried out in a dry box filled with argon gas.

### 2.3. Measurements

Linear sweep voltammetry was performed on a stainless steel (SS) working electrode, with counter and reference electrodes of lithium, at a scanning rate of 1.0  $\text{mV s}^{-1}$ . In order to measure the interfacial resistances of lithium metal polymer cells, ac impedance measurements were performed using an impedance analyzer over the frequency range of 1 mHz–100 kHz with an amplitude of 10 mV. The charge and discharge cycling tests of lithium metal polymer cells were conducted over a voltage range of 2.8–4.3 V galvanostatically with Toyo battery test equipment (TOSCAT-3000 U). For differential scanning calorimetry (DSC) measurements, fresh cells were initially cycled for five times

in the voltage range of 2.8–4.3 V at 0.28  $\text{mA cm}^{-2}$ . They were recharged to 4.3 V at the same current density and held at that voltage for 2 h. After disassembling the cells in a glove box, the cathode composite was gently scraped from the current collector. Approximately 5 mg of the cathode was hermetically sealed in an aluminum pan and measurements were carried out using TA instrument (DSC 2010) at a heating rate of 2  $^{\circ}\text{C min}^{-1}$ .

## 3. Results and discussion

Linear sweep voltammetry curves of the cells prepared with gel polymer electrolyte containing different organic additives are presented in Fig. 1. As shown in the figure, the gel polymer electrolytes containing an organic additive exhibited small oxidation currents prior to the solvent decomposition. On sweeping from open circuit potential towards more anodic value until a large current due to the electrolyte decomposition occurred, two small oxidative current peaks are observed for the gel polymer electrolyte containing EDOT (4.06, 4.55 V versus  $\text{Li/Li}^+$ ) and thiophene (4.11, 4.55 V), respectively, before decomposition of the liquid electrolyte (4.90 V). For the gel polymer electrolyte containing biphenyl, the oxidative current is observed at around 4.62 V. The oxidation potential of biphenyl is almost identical to the value (4.54–4.75 V) reported previously [18]. It is well known that compounds with a high HOMO (the highest occupied molecular orbital) energy tend to easily decompose [17,21], since they are good electron donors. Because all the additives used in this study have higher HOMO energies than those of solvents (EC, DMC) in liquid electrolyte, they can oxidize prior to the solvent decomposition. The electro-oxidation of monomeric additives used here may thus result in the formation of a conductive polymer film on the electrode, because their polymerization products are electronically conductive in their oxidized states [22]. The reaction mechanism of electrochemical polymerization for the aromatic compounds with  $\pi$ -electron conjugated systems on the positive electrode has been previously investigated in detail by Shima et al. [19]. From the results in Fig. 1, it

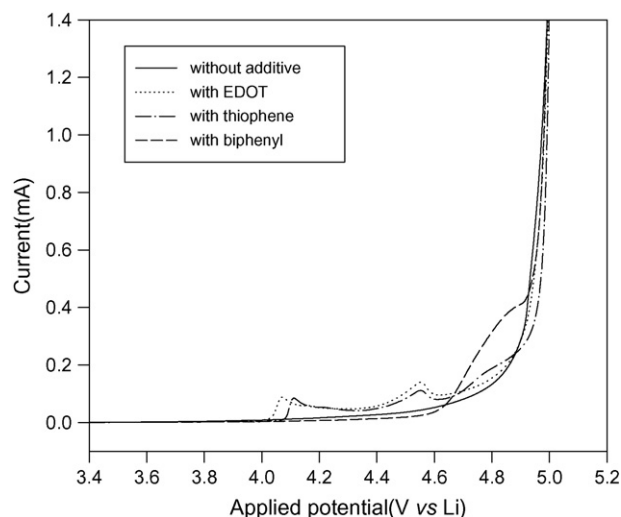


Fig. 1. Linear sweep voltammetry curves of the cells prepared with gel polymer electrolytes containing different additives (scan rate: 1  $\text{mV s}^{-1}$ ).

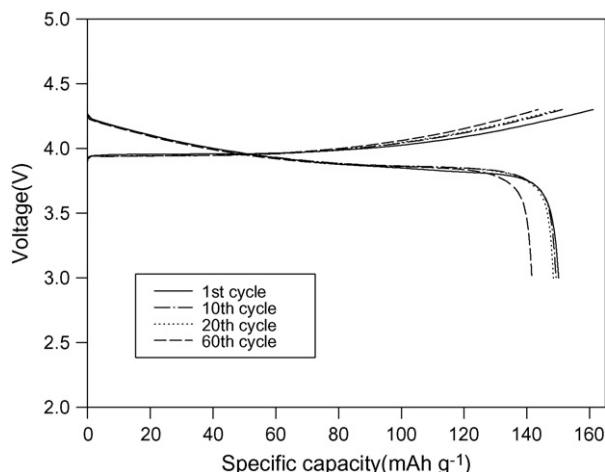


Fig. 2. Charge and discharge curves of the lithium metal polymer cell prepared with gel polymer electrolyte containing thiophene. Cycling was carried out at constant current density of  $0.28 \text{ mA cm}^{-2}$  between 3.0 and 4.3 V.

could be understood that EDOT and thiophene are oxidized at lower potentials than biphenyl, thereby resulting in the formation of an electronically conductive layer on the electrode quite below the decomposition potential of liquid electrolyte.

Fig. 2 shows the typical charge–discharge curves of the lithium metal polymer cell assembled with the gel polymer electrolyte containing thiophene, which are obtained at constant current of  $0.28 \text{ mA cm}^{-2}$ . Cut-off voltage for charging was set to 4.3 V, because oxidative decomposition of the organic additive was likely to occur at higher voltages. This figure shows that reversible charge and discharge is favorably occurring in the lithium metal polymer cell containing the additive. The voltage drop in passing from charge to discharge is observed to be relatively small, which means a low overall resistance of the cell. These results indicate that the addition of a small amount (0.1 wt.%) of thiophene does not show any harmful influence on cycling behavior of the cell. The cell has an initial discharge capacity of  $150 \text{ mAh g}^{-1}$  based on  $\text{LiCoO}_2$  active material in the cathode. High initial discharge capacity of the cell was due to the higher charging cut-off voltage. The coulombic efficiency of the first cycle is calculated to be 93.2%. This low coulombic efficiency of the cell may be associated with a high irreversible capacity due to the electrochemical oxidation of thiophene during the first charging cycle. After the initial few cycles, the coulombic efficiencies gradually approached 99.0%.

Fig. 3 compares the effect of the different additives on the discharge capacities as a function of cycle number. Initial discharge capacities of the cells range from 148 to  $150 \text{ mAh g}^{-1}$ , and the values show little dependence on gel polymer electrolyte composition, however, cycling characteristics of the cells are found to depend on the nature of the additive. The addition of EDOT or thiophene to the gel polymer electrolyte leads to improved cycling characteristics. 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, which functions as a protective layer to cover the active cathode sites and reduces the electrolyte decomposition so that the structural stability of cathode material

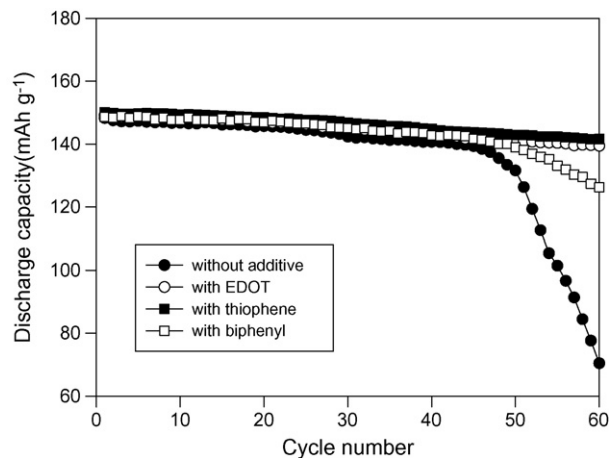


Fig. 3. Discharge capacities of the lithium metal polymer cells prepared with gel polymer electrolytes containing different additives as function cycle number.

can be enhanced. Without additives, the decomposition products of the electrolyte may cover the cathode surface with a highly resistive layer as cycling progresses. It should be noted that the cycling characteristics of the cell containing the biphenyl additive were less favorable and this may be due to the higher potential needed to electrochemically polymerize this monomer, as shown in Fig. 1. Thus, the formation of conductive polymer layer on  $\text{LiCoO}_2$  cathode during charging may not be sufficient to provide effective hindrance of the electrochemical degradation of cathode material and electrolyte in the biphenyl case, when the cell is charged up to 4.3 V. These results suggest that the monomeric additive should have a low enough oxidation potential to be electrochemically polymerized on the cathode surface during charging.

In order to understand the effect of the organic additives on cell cycling performance, the ac impedance of the cells before and after the repeated cycles (60 cycles) was measured in the fully discharged state (Fig. 4). According to the previous studies of ac impedance analysis [23,24], the semicircle in the high frequency range can be attributed to the resistance due to  $\text{Li}^+$  ion migration through the surface film on the electrode and the semicircle in the medium-to-low frequency range is due to charge transfer resistance between the electrode and electrolyte. At open circuit potential before cycling, one semicircle appeared in the high frequency region, as shown in Fig. 4(a). Almost identical impedance spectra for all the cells indicate that adding a small amount of organic additive to the gel polymer electrolyte has little effect on the interfacial resistance in the cell before cycling. After charge and discharge cycling, the semicircle due to charge transfer resistance was separated from that of the surface film resistance, as observed in Fig. 4(b). It is clear that the surface film resistance observed in the high frequency region is affected by the presence of the additives in the gel polymer electrolyte; the highest resistance is observed in the absence of any additive whilst the cell assembled with thiophene has the lowest film resistance and charge transfer resistance after cycling. These results are consistent with the cycling behavior of the cells shown in Fig. 3. This would support the notion that, in the presence of EDOT or thiophene, a protective film is formed on

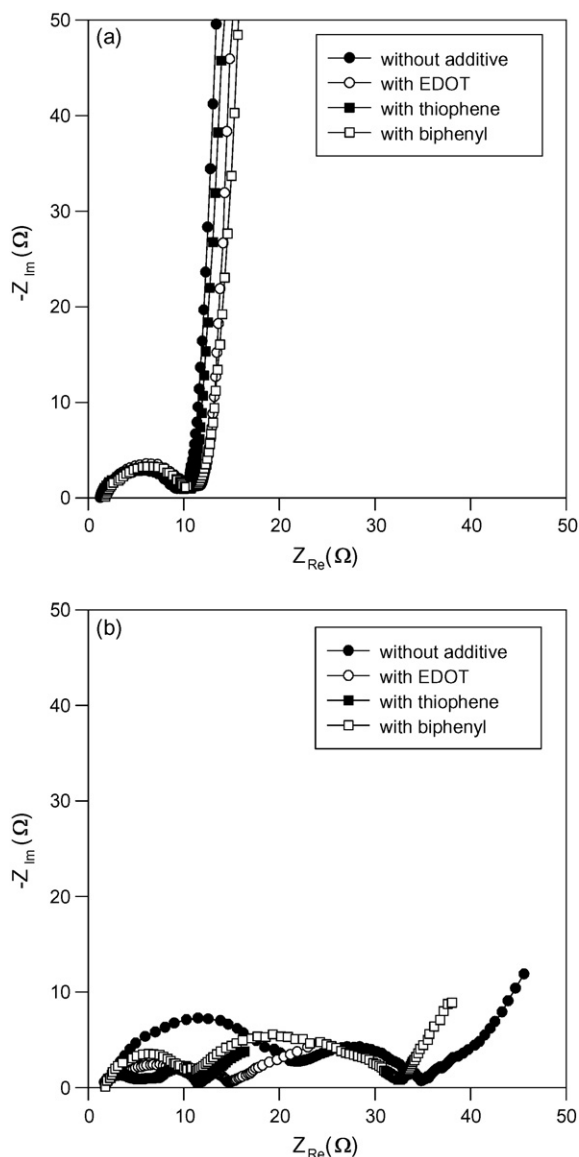


Fig. 4. ac impedance spectra of the lithium metal polymer cells (a) before and (b) after charge–discharge cycling.

the cathode, which limits the growth of a resistive layer due to electrolyte breakdown.

The rate capability of the lithium metal polymer cell prepared with gel polymer 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 initially cycled for five times at a constant current of  $0.28 \text{ mA cm}^{-2}$  before the execution of rate capability tests. The discharge curves of the lithium metal polymer cell assembled with gel polymer electrolyte containing thiophene at different current rates are given in Fig. 5. Both the voltage and the capacity are found to decrease gradually with increasing current. The cell delivered a relatively high discharge capacity ( $136 \text{ mAh g}^{-1}$ ) at a current density of  $2.84 \text{ mA cm}^{-2}$ , but the discharge capacity was shown to drop to  $96 \text{ mAh g}^{-1}$  at  $5.68 \text{ mA cm}^{-2}$ . Fig. 6 compares the discharge capacities of lithium metal polymer cells prepared with gel polymer elec-

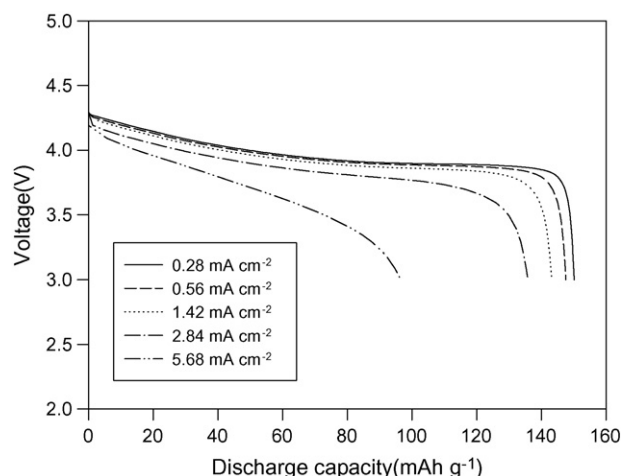


Fig. 5. Discharge profiles of the lithium metal polymer cell assembled with gel polymer electrolyte containing thiophene at different current density.

trolyte containing different additives, as a function of current density. It is found that the discharge capacities are almost the same at low current density in all the cells, regardless of the addition of organic additive. This may be due to the fact that the current rates tested are not high enough to reflect the difference in the interfacial resistances. However, with increasing current density to  $5.68 \text{ mA cm}^{-2}$  ( $2.0 \text{ C}$  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 prepared with gel polymer electrolyte containing thiophene may be encouraged by the faster kinetics of the charge transfer reaction and the less resistive film on  $\text{LiCoO}_2$  cathode, as explained in Fig. 4. Furthermore, when a conductive layer does form on the surface of  $\text{LiCoO}_2$  particles due to electrochemical polymerization of the thiophene additive, this would also produce a good electrical contact between less conductive oxides, which facilitates electron transfer. In order to verify the improvement of cycling performances is really due to the conductive polymer formed on cathode surface, not the monomer

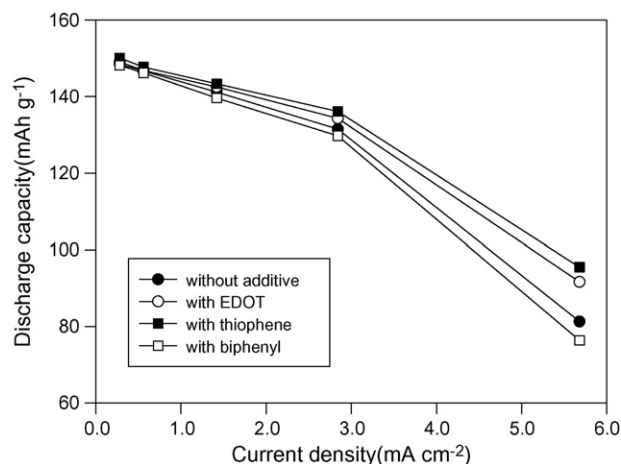


Fig. 6. Discharge capacities of lithium metal polymer cells prepared with gel polymer electrolyte containing different additive, as function of current density.

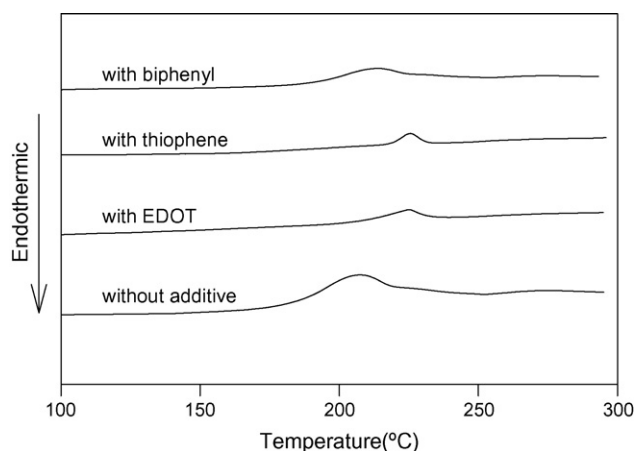


Fig. 7. DSC profiles of the charged cathodes containing different additive in the lithium metal polymer cells.

in the electrolyte, we need to do the comparative studies using different cut-off voltages for their formation cycle, which are in progress.

DSC measurements were performed in order to evaluate the thermal stability of the cathode material in charged state. Fig. 7 shows the DSC profiles of the cathode materials charged to 4.3 V, which are obtained after five cycling. In this figure, the DSC trace of  $\text{LiCoO}_2$  in the cell without additive has an exothermic peak with the reaction heat of  $133.7 \text{ J g}^{-1}$  at about  $207^\circ\text{C}$ . On the other hand, the  $\text{LiCoO}_2$  material in the cell containing an organic additive has much smaller exothermic reaction peak at higher temperature. The heat of reaction for the  $\text{LiCoO}_2$  material in the cell containing EDOT, thiophene, biphenyl was measured to be 21.8, 18.7 and  $53.2 \text{ J g}^{-1}$  based on weight of  $\text{LiCoO}_2$ , respectively. These results suggest that the conductive polymer layer formed on  $\text{LiCoO}_2$  renders the cathode material less reactive towards the liquid electrolyte, leading to an improvement of the thermal stability.

#### 4. Conclusions

We have shown that improved cycling performances and capacity retention at higher rates could be achieved by using a gel polymer electrolyte based on an  $\text{LiClO}_4\text{-EC/DMC}$  imbibed P(VdF-co-HFP) membrane containing a small amount of an organic additive which is capable of being electrochemically polymerized during the charging cycle of the cell. Lithium metal polymer cells composed of a lithium anode and  $\text{LiCoO}_2$  cathode exhibited a high initial discharge capacity of  $150 \text{ mAh g}^{-1}$  and their cycling performances were found to be improved by addition of organic additive. Good capacity retention even at high charging cut-off voltage may be ascribed to the formation of a conducting film to suppress the electrolyte decomposition on cathode active sites. The thiophene additive led to the best results

with good capacity retention during cycling and an attractive discharge capacity of  $136 \text{ mAh g}^{-1}$  at  $2.84 \text{ mA cm}^{-2}$ . The thermal stability of the fully charged  $\text{LiCoO}_2$  cathode was proved to be significantly improved in the cell containing an organic additive. Further studies are being conducted in order to improve the cycling performance of the lithium metal polymer cells by optimizing the type and quantity of organic additive.

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