

Study on the Cycling Performances of Lithium-Ion Polymer Cells Containing Polymerizable Additives

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Gel polymer electrolytes were prepared by immersing a porous poly(vinylidene fluoride-*co*-hexafluoropropylene) membrane in an electrolyte solution containing small amounts of polymerizable additive (3,4-ethylenedioxythiophene, thiophene, biphenyl). The organic additives were electrochemically oxidized to form conductive polymer films on the electrode at high potential. With the gel polymer electrolytes containing different organic additive, lithium-ion polymer cells composed of carbon anode and LiCoO₂ cathode were assembled and their cycling performances were evaluated. Adding small amounts of thiophene or 3,4-ethylenedioxythiophene to the gel polymer electrolyte was found to reduce the charge transfer resistance in the cell and it thus exhibited less capacity fading and better high rate performance.

Key Words: Cycling performance, Electrochemical oxidation, Gel polymer electrolyte, Lithium-ion polymer cell, Polymerizable additive

Introduction

There has been an increasing need for high energy density rechargeable batteries for portable electronic devices, hybrid electric vehicles and load leveling systems. Among them, lithium-ion polymer batteries have been widely developed and produced, because they exhibit high energy density, good cycling characteristics and enhanced safety. In the commercialized lithium-ion polymer batteries, high amounts of organic solvents are usually used. The organic solvents used in the lithium-ion polymer batteries tend to decompose on the electrode surface, leaving a poorly conductive surface film on the electrodes. It can lead to the gradual deterioration of the cell performance upon cycling. To solve this problem, a number of alternatives have been investigated such as the addition of various inorganic and organic additives to the electrolyte,¹⁻⁷ metal oxide coating on the surface of cathode active materials⁸⁻¹⁴ and so on. Our group has previously reported that cathode surface modification by organic additives exerted a significant influence on the performance of lithium metal polymer cells.¹⁵ 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.^{16,17}

In this work, the gel polymer electrolytes containing these polymerizable additives are applied to the lithium-ion polymer cells composed of carbon anode and LiCoO₂ cathode. Three kinds of monomeric additives (3,4-ethylenedioxythiophene, thiophene and biphenyl) are introduced to the gel polymer electrolyte. The influence of these organic additives on cycling performances of the rechargeable lithium-ion polymer cells will be discussed.

Experimental

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 μm using a doctor blade. After 30 min, the membranes were immersed in methanol to remove DBP. Then the membranes were vacuum dried at 80 °C for 12 h. The gel polymer electrolyte was prepared by immersing the membrane in 1 M LiClO₄ in ethylene carbonate(EC)/dimethyl carbonate(DMC) (1:1 by volume, Samsung Cheil Industries, battery grade) containing 0.1 wt.% organic additive for 5 min. Thiophene, 3,4-ethylenedioxythiophene (EDOT) and biphenyl were chosen as the organic additives. Linear sweep voltammetry (LSV) was performed on a stainless steel (SS) working electrode, with counter and reference electrodes of lithium, at a scanning rate of 1.0 mV s⁻¹.

The cathode was prepared by coating the N-methyl pyrrolidone (NMP)-based slurry containing LiCoO₂, PVdF and super-P carbon on an aluminum foil. The carbon anode was also prepared by coating the NMP-based slurry of mesocarbon microbeads (MCMB), PVdF and super-P carbon on a copper foil. All the electrodes were roll pressed to enhance particulate contact and adhesion to foils. The thickness of electrodes ranged from 55 to 70 μm after roll pressing, and their active mass loading corresponded to capacity of about 2.9 mAh cm⁻². Lithium-ion polymer cells were assembled by sandwiching the gel polymer electrolyte between the carbon anode and the LiCoO₂ cathode. The cell was then enclosed in a pouch bag and vacuum-sealed. All assemblies of the cells were carried out in a dry box filled with argon gas. The charge and discharge cycling tests of lithium-ion polymer cells were conducted over a voltage range of 3.0–4.3 V galvanostatically with Toyo battery test equipment (TOSCAT-3000U). In order to measure the interfacial resistances of lithium-ion polymer cells, ac impedance measurements were performed using an impedance analyzer over the frequency range of 1 mHz to 100 kHz with an amplitude of 10 mV.

Results and Discussion

In the previous study, it was shown that monomeric additives oxidized prior to the decomposition (4.90 V vs Li/Li^+) of the liquid electrolyte.¹⁵ That is, two small oxidative current peaks are observed for the gel polymer electrolyte containing EDOT (4.06, 4.55 V) and thiophene (4.11, 4.55 V), respectively, and single oxidative current is observed at around 4.62 V for the gel polymer electrolyte containing biphenyl. The electrochemical oxidation of monomeric 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.^{17,18} It should be also noted that EDOT and thiophene are polymerized at lower potentials than biphenyl.

Cycling performance of lithium-ion polymer cells prepared with gel polymer electrolyte containing different organic additive has been evaluated. The assembled cells were initially subjected to a preconditioning cycle with cut-off voltages of 4.3 V for charge and 3.0 V for discharge at a constant current of 0.145 mAh cm^{-2} (C/20 rate). On such a high charging cut-off voltage, the oxidative polymerization of monomeric additives is liable to occur so that we can distinguish clearly the effect of additives on cycling characteristics. Figure 1 shows the preconditioning charge-discharge curves of the lithium-ion polymer cells prepared with gel polymer electrolytes containing different organic additive. It can be seen that the initial discharge capacities of the cells containing an organic additive are lower than that of the cell without an organic additive. The cell without an additive shows an initial discharge capacity of 157 mAh g^{-1} based on LiCoO_2 active material in the cathode. High initial discharge capacity of the cell is due to the higher charging cut-off voltage (4.3 V). Initial discharge capacities of the cells containing an organic additive are 149, 149, 154 mAh g^{-1} for EDOT, thiophene, biphenyl, respectively. When comparing the coulombic efficiency of the pre-conditioning cycle, the cell without an organic additive has the highest value (91.2 %). The coulombic efficiency of the cell containing an organic additive

ranged from 85.7 to 89.4 %. Low coulombic efficiency of the cell containing an organic additive may be associated with an irreversible electrochemical oxidation of an organic additive on the electrode during the charging cycle.

After preconditioning cycle, three cycles were performed in the voltage range of 3.0 - 4.3 V at constant current of 0.1C, 0.2C and 0.5C rate. After three cycles, the cells were charged at a current density of 1.45 mA cm^{-2} (0.5C rate) up to a target voltage of 4.3 V. This was followed by a constant voltage charge with a decline of current until the final current was reached to 20% of charging current and then it was discharged down to a cut-off voltage of 3.0 V at the same current density (0.5C rate). Figure 2 compares the charge-discharge curves of the 1st, 10th, 50th, 100th, 200th and 300th cycle of the lithium-ion polymer cell assembled with gel polymer electrolyte containing thiophene. The cell has a first discharge capacity of 147.0 mAh g^{-1} . The discharge capacity of the cell declines to 128.1 mAh g^{-1} after 300 charge/discharge cycles, which corresponds to 87.1% of initial discharge capacity. As can be seen in the figure, the voltage profiles remain almost unch-

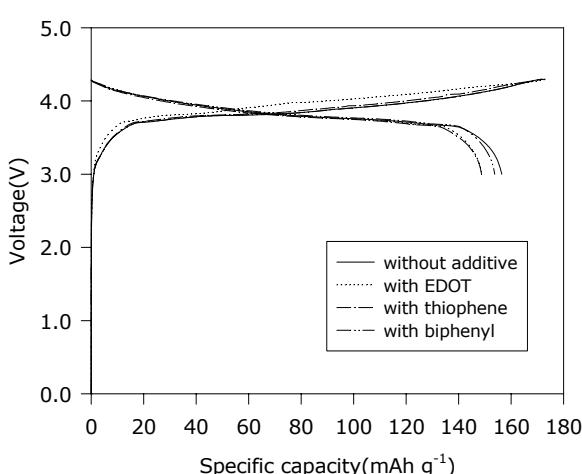


Figure 1. First preconditioning cycle of lithium-ion polymer cells prepared with gel polymer electrolytes containing different organic additives. (0.05C, cut-off : 3.0 - 4.3 V).

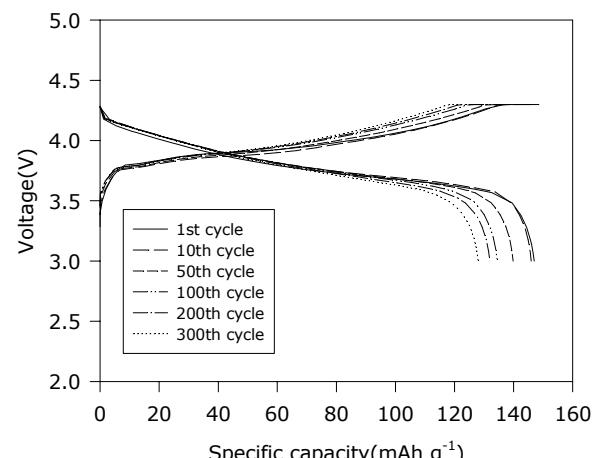


Figure 2. Charge and discharge curves of the lithium-ion polymer cell prepared with gel polymer electrolyte containing thiophene. (0.5C CC & CV charge, 0.5C CC discharge, cut-off : 3.0 - 4.3 V).

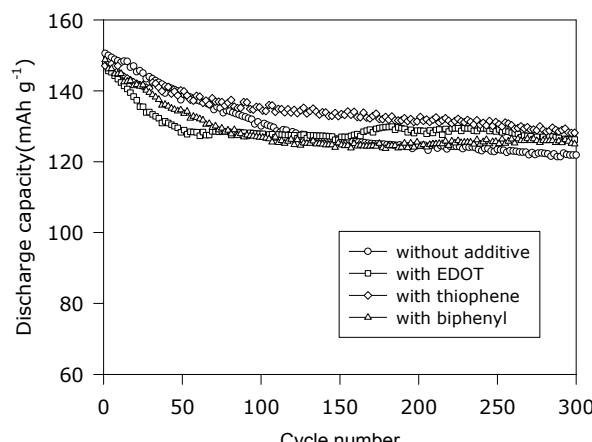


Figure 3. Discharge capacities of the lithium-ion polymer cells prepared with gel polymer electrolytes containing different organic additives a function cycle number. (0.5C CC & CV charge, 0.5C CC discharge, cut-off : 3.0 - 4.3 V).

anged on increasing the cycle number, although both average discharge voltage and discharge capacity are slightly decreased. Coulombic efficiency is steadily increased and stabilized with cycle number, and it is maintained to be higher than 99.0% through cycling after the initial few cycles.

Figure 3 presents the effect of an additive on the discharge capacities as a function of cycle number. Initial discharge capacities of the cells ranges from 147 to 151 mAh g⁻¹ and cycling characteristics of the cells are found to depend on the type of the organic additive. The addition of organic compound to the gel polymer electrolyte leads to improved cycling characteristics. The cell without an additive has a discharge capacity of 122 mAh g⁻¹ at 300th cycle, which corresponds to 80.8 % of initial discharge capacity. On the other hand, the capacity retentions of the cells containing an organic additive were from 83.2 to 87.1% at 300th cycle. Thiophene-added cell exhibited the best capacity retention among the cells containing an organic additive. Good capacity retention in the cell with this additive 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 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 oxidative potential needed to electrochemically polymerize this monomer.

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 (300 cycles) was measured in the fully discharged state, and the resultant ac impedance spectra are shown in Figure 4. At open circuit potential before cycling, there are no semicircles in the high frequency region. Almost identical ac 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, two overlapped semicircles are found, as observed in Figure 4(b). According to the previous studies of ac impedance analysis,^{19,20} the semicircle in the high frequency range can be attributed to the resistance due to 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. It is found that the surface film resistance observed in the high frequency region is little affected by the presence of the organic additives in the gel polymer electrolyte. On the other hand, the charge transfer resistance is found to be lower in the cells containing an organic additive ; the highest resistance is observed in the absence of any additive whilst the cell assembled with EDOT or thiophene has the lowest charge transfer resistance after cycling. This would support the notion that, in the presence of EDOT or thiophene, a protective conductive film is formed on the cathode during cycling, which limits the growth of a resistive layer due to electrolyte

breakdown. When a conductive layer does form on the surface of active material, this would also produce a good electrical contact between less conductive oxides, which facilitates electron transfer. The value of charge transfer resistance in the biphenyl-added cell is the almost same to that of the cell without additives. This result suggests that the conductive polymer film can be hardly formed on cathode in the biphenyl-added cell due to its higher oxidation potential than charging cut-off voltage.

Rate capability of the lithium-ion polymer cell prepared with gel polymer electrolyte containing different organic additive was evaluated. In order to distinguish the effect of additives clearly, the cells were initially cycled 5 times at a constant current of 0.58 mA cm⁻² (0.2 rate) before the execution of rate capability tests. The cells were then charged to 4.3 V at a constant current of 0.2C and discharged at different current rate from 0.2C to 2.0C. The discharge curves of the lithium-ion polymer cell assembled with gel polymer electrolyte containing thiophene at different C rate are given in Figure 5. Both the voltage and the capacity are found to decrease gradually with increasing current rate. The cell delivered a relatively high discharge capacity (137 mAh g⁻¹) at a current density of 2.9 mA cm⁻² (1.0C rate), whose discharge

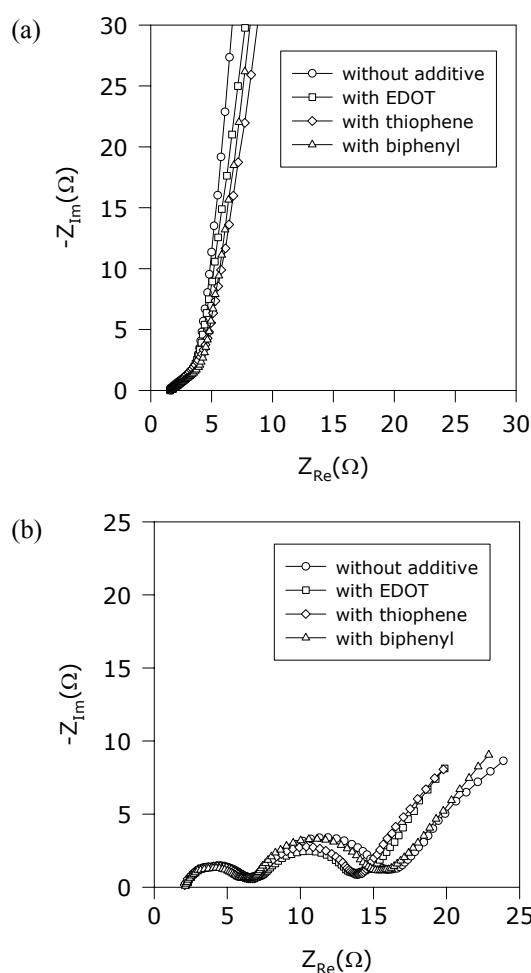


Figure 4. AC impedance spectra of the lithium-ion polymer cells prepared with gel polymer electrolytes containing different organic additives (a) before and (b) after charge-discharge cycling.

capacity was 93% compared to that obtained at 0.2C rate. However, the discharge capacity was shown to drop to 110 mAh g⁻¹ at 2.0C rate. Figure 6 compares the relative discharge capacities of lithium-ion polymer cells prepared with gel polymer electrolyte containing different additives, as a function of current density. The relative capacity is defined as the ratio of the discharge capacity at a specific C rate to the discharge delivered at 0.2C rate. With increasing current density to 5.8 mA cm⁻² (2.0C rate), the effect of additives on rate performance of the cell becomes noticeable. It is clear that the addition of thiophene or EDOT to the gel polymer electrolyte leads to higher capacity at high current rate. 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 or EDOT is related to the formation of conductive film on electrode, which results in faster kinetics of the charge transfer reaction, as explained in Figure 4.

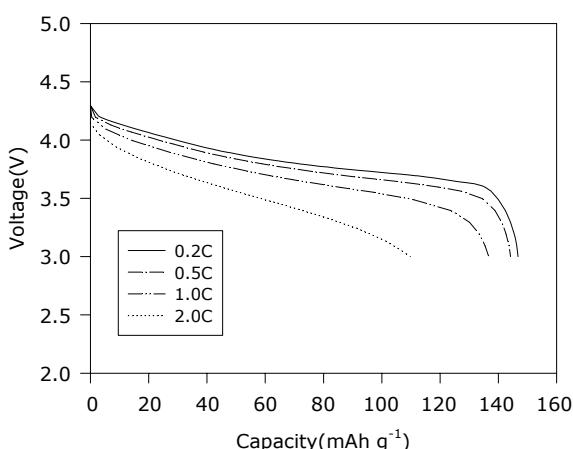


Figure 5. Discharge profiles of the lithium-ion polymer cell assembled with gel polymer electrolyte containing thiophene at different current density.

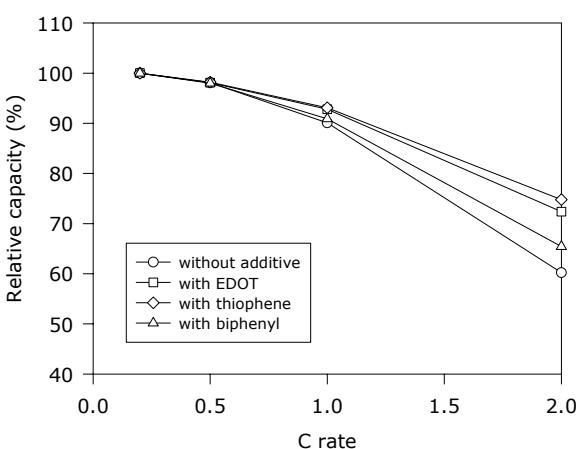


Figure 6. Relative discharge capacities of lithium-ion polymer cells prepared with gel polymer electrolyte containing different additive, as function of C rate.

Conclusions

Cycling performances of lithium-ion polymer cells could be improved by adding a small amount of an electrochemically polymerizable additive to the gel polymer electrolyte based on P(VdF-co-HFP) membrane. Lithium-ion polymer cells containing thiophene or EDOT exhibited good capacity retention even at high charging cut-off voltage and good high rate performances. Good cycling performances with these additives in the cell could be ascribed the formation of a conductive film to suppress the electrolyte decomposition on cathode active sites, which reduces the electrolyte decomposition so that the structural stability of active material can be enhanced.

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