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Short communication

Effect of an inorganic additive on the cycling performances of lithium-ion polymer cells assembled with polymer-coated separators

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ABSTRACT

Gel polymer electrolytes were prepared by immersing a porous poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VdF-*co*-HFP))-coated separator in an electrolyte solution containing small amount of inorganic additive. Four kinds of inorganic compounds, aluminum fluoride, aluminum iodide, lithium fluoride and lithium iodide were used as inorganic additives. By using the gel polymer electrolytes containing different inorganic additives, lithium-ion polymer cells composed of carbon anode and $LiCoO_2$ cathode were assembled and their cycling performance evaluated. Adding small amount of an inorganic additive led to less capacity fade and better high rate performance. Good cycling performances in the cell with these additives could be ascribed to the formation of a protective layer to cover active material in the electrode during cycling, which reduces the electrolyte decomposition.

1. Introduction

There has been an increasing need for high energy density rechargeable batteries for portable electronic devices, electric vehicles and load leveling systems. Among them, lithium-ion batteries are now being widely developed and produced, because they exhibit high energy density and good cycling properties [1–4]. In the commercialized lithium-ion batteries, high amounts of organic solvents are being usually used. The organic solvents used in the lithium-ion 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 [5–10], metal oxide coating on the surface of cathode active materials [11–15] and so on. Recently, Abe et al. have investigated several organic additives to form a conductive polymer film on the cathode in lithium-ion batteries [9]. They reported that electrode surface modification by organic additives exerted a significant influence on the cycling performance of lithium-ion batteries. Our group has reported that the addition of an inorganic additive to the electrolyte could reduce the interfacial resistance of the Li/V_2O_5 polymer cell and thus the cells exhibited a less capacity fading and better high rate performances [16]. However, the effect of these inorganic additives on the cycling performance of lithium-ion polymer cells has not been reported to date. In our study, we introduced four kinds of inorganic additives (AlF_3, AlI_3, LiF, LiI) to the gel polymer electrolyte. In order to make highly conductive gel polymer electrolyte that can be handled like conventional separator, gel polymer electrolyte was prepared from a porous polymer-coated separator. The electrochemical performances of lithium-ion polymer cells assembled with gel polymer electrolyte containing different inorganic additive will be presented and discussed.

2. Experimental

2.1. Preparation of the gel polymer electrolyte

The polymer coated on polyethylene (PE) separator was poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VdF-*co*-HFP), Kynar 2801). To prepare the polymer-coated separator, P(VdF-*co*-HFP) copolymer was dissolved in an anhydrous dimethylformamide (DMF). A microporous PE separator (thickness: 25 μm, porosity: 40%) was then immersed in the polymer solution for 3 h. The separator was taken out and immersed in a water bath for 5 h to induce phase inversion. After the exchange of DMF and water by phase inversion, a substantial number of pores were formed in

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the polymer layer coated on PE separator. The resulting polymer-coated separator was washed with deionized water and vacuum dried at 100 °C for 24 h. Gel polymer electrolyte was prepared by soaking the polymer-coated separator in 1 M $LiClO_4$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume, Samsung Cheil Industries, battery grade) containing 0.1 wt.% inorganic additive for 1 h. Anhydrous AlF_3, AlI_3, LiF, LiI (Aldrich) were chosen as the inorganic additives in this study.

2.2. Electrode preparation and cell assembly

The cathode was prepared by coating the *N*-methyl pyrrolidone (NMP)-based slurry containing $LiCoO_2$ (Japan Chemical), PVdF and super-P carbon (MMM Co.) on an aluminum foil. The carbon anode was also prepared by coating the NMP-based slurry of mesocarbon microbeads (MCMB, Osaka gas), 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 $LiCoO_2$ 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.

2.3. Measurements

The surface morphology of polymer-coated separator was examined using a scanning electron microscope (JEOL, JSM-6300). 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 mV s^{-1}. The charge and discharge cycling tests of lithium-ion polymer cells were conducted over a voltage range of 2.8–4.3 V galvanostatically with Toyo battery test equipment (TOSCAT-3000U).

3. Results and discussion

A scanning electron micrograph of the polymer-coated separator is presented in Fig. 1. As the P(VdF-*co*-HFP) copolymer was coated on the PE separator by dip coating and phase inversion, a lot of micropores were formed in the coating layer. The presence of micropores on the surface of the polymer-coated separator could lead to efficient uptake of the liquid electrolyte when it was soaked in an electrolyte solution, which finally results in gelation of the coated polymer. In the polymer-coated separator, PE separator can give mechanical integrity to the electrolyte system and offers the enhanced safety of exhibiting thermal shutdown under severe abuse condition, while gel-forming polymer coated on both sides of the separator is adapted to encapsulate an electrolyte solution in the porous PE separator and to further assist in adhering the electrodes to the separator. Thickness of polymer layer coated on both sides of PE separator was about 5 μm. The polymer-coated separator was soaked in $LiClO_4$–EC/DMC containing small amount of an inorganic additive for 1 h. The polymer coated on both sides of PE separator was gelled in contact with the electrolyte solution. Ionic conductivity after soaking in the electrolyte solution ranged from 0.8×10^{-3} to 1.2×10^{-3} S cm^{-1} at room temperature and the values were found to be little dependent on type of an inorganic additive.

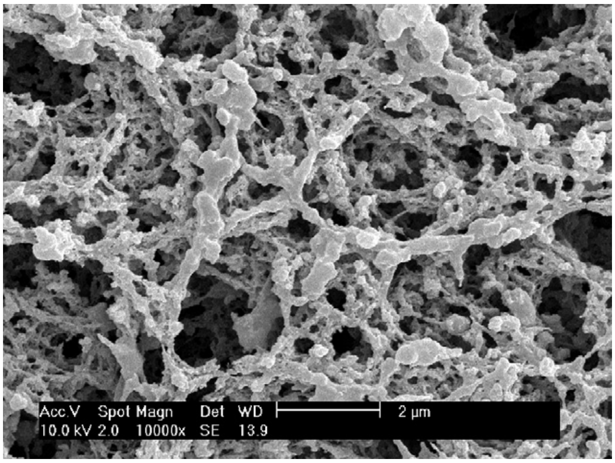

Fig. 1. Scanning electron micrograph of porous polymer-coated separator.

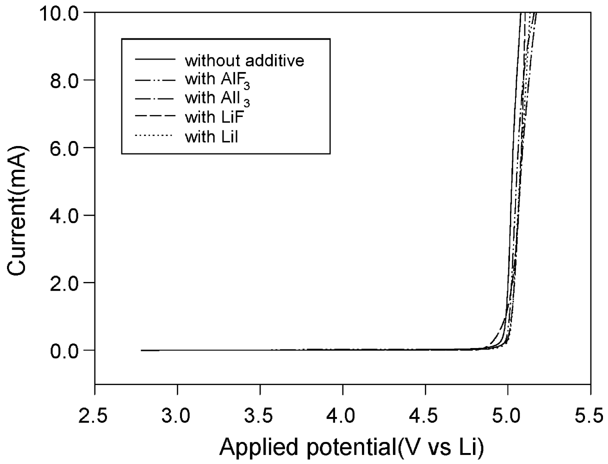

Fig. 2. Linear sweep voltammetry curves of the cells prepared with gel polymer electrolytes containing different inorganic additives. (scan rate: 1 mV s^{-1}).

Linear sweep voltammetry curves of the cells prepared with gel polymer electrolyte containing different inorganic additive are presented in Fig. 2. A rapid rise in current was observed around 5.0 V *vs* Li/Li^+ and continued to increase as the potential was swept, which was associated with the oxidative decomposition of the gel polymer electrolyte. In case of using AlI_3 and LiI as an electrolyte additive, it can be expected that oxidative current occur below 5.0 V *vs* Li/Li^+, since the oxidation potential of iodide ion is lower than decomposition voltage. However, we could not observe the oxidative current peak of iodide ion, which may be due to the use of small amount of iodide compound. It appears that the oxidative stability of the gel polymer electrolyte is not influenced by type of inorganic additives. From these results, it is understood that adding small amount of inorganic additive does not affect the electrochemical stability of gel polymer electrolyte in this study.

Electrochemical performance of lithium-ion polymer cells prepared with gel polymer electrolyte containing different inorganic 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 2.8 V for discharge at a constant current of 0.145 mAh cm^{-2} (*C*/20 rate). Fig. 3 shows the preconditioning charge-discharge curves of the lithium-ion polymer cells prepared with gel polymer electrolytes containing different inorganic additive. The voltage drop in passing from charge to discharge is observed to be relatively small for all the cells, which means a low overall resistance of the cells. It can be seen that the initial discharge capacities of the cells containing an inorganic additive are lower than that of the cell without an inorganic additive. The cell without an additive shows an initial discharge capacity of

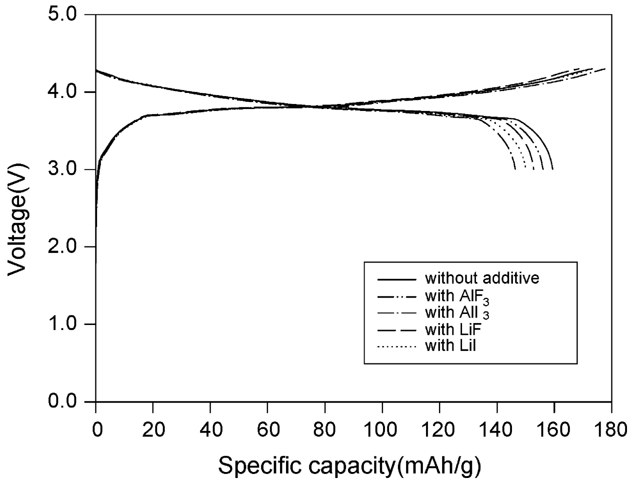

Fig. 3. First preconditioning cycle of lithium-ion polymer cells prepared with gel polymer electrolytes containing different inorganic additives. (0.05*C*, cut-off: 3.0–4.3 V).

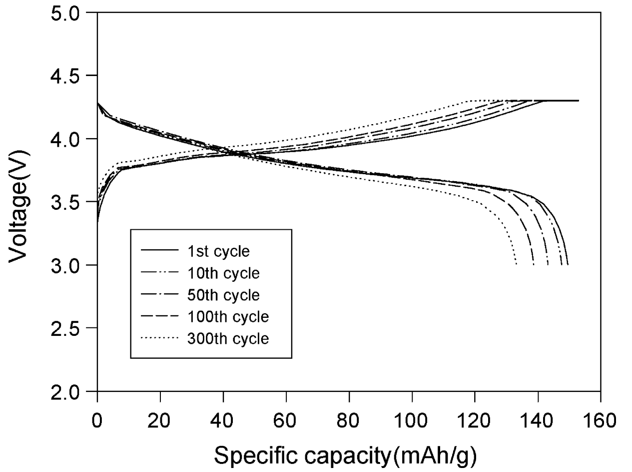

Fig. 4. Charge and discharge curves of the lithium-ion polymer cell prepared with gel polymer electrolyte containing AlF_3. (0.5*C* CC and CV charge, 0.5*C* CC discharge, cut-off: 3.0–4.3 V).

159 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. Initial discharge capacities of the cells containing an inorganic additive are 156, 146, 153, 152 mAh g^{-1} for AlF_3, AlI_3, LiF, LiI, respectively. When comparing the coulombic efficiency of the pre-conditioning cycle, the cell without an inorganic additive has the highest value (92.0%). The coulombic efficiency of the cell containing an inorganic additive ranged from 82.4% to 90.6%. Low coulombic efficiency of the cell containing an inorganic additive may be associated with an irreversible electrochemical reaction of an inorganic additive on the electrodes during the first charging cycle. In the gel polymer electrolyte containing AlF_3 or AlI_3, Al^{3+} ions dissolved in the electrolyte can form a thin layer of Li-Al alloy on the electrode surface during pre-conditioning cycle, which causes an irreversible capacity. The formation of a Li-Al alloy in the presence of AlI_3 has been previously reported by other workers [17–19]. Furthermore, the reaction between the halide (iodide or fluoride) anion and lithium on the electrode may form a lithium halide layer on the electrode.

After preconditioning cycle, three cycles were performed in the voltage range of 2.8–4.3 V at constant current of 0.1*C*, 0.2*C* and 0.5*C* rate. After three cycles, the cells were charged at a current density of 1.45 mA cm^{-2} (0.5*C* 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 2.8 V at the same current density (0.5*C* rate). Fig. 4 compares the charge-discharge curves of the 1st, 10th, 50th, 100th and 300th cycle of the lithium-ion polymer cell assembled with gel polymer electrolyte containing AlF_3. The cell has a first discharge capacity of 149.5 mAh g^{-1}. The discharge capacity of the cell declines to 133.1 mAh g^{-1} after 300 charge/discharge cycles, which corresponds to 89.0% of initial discharge capacity. As can be seen in the figure, the voltage profiles remain almost unchanged 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.

Fig. 5 compares the effect of the different additives on the discharge capacities as a function of cycle number. Initial discharge capacities of the cells ranges from 144 to 152 mAh g^{-1} and cycling characteristics of the cells are found to depend on the type of the inorganic additive. The addition of inorganic compound to the gel polymer electrolyte leads to improved cycling characteristics. The cell without an additive has a discharge capacity of 118 mAh g^{-1} at 300th cycle, which corresponds to 77.9% of initial discharge capacity. On the other hand, the capacity retentions of the cells containing an inorganic additive were from 82.6% to 89.0% at 300th cycle. AlF_3-added cell exhibited the best capacity retention (89.0%) among the cells containing an inorganic additive. Good capacity retention even at high charging cut-off voltage in the cell with these additives may be ascribed to the formation of a protective layer to cover active material in the electrode during cycling, as discussed above. The formation of a protective layer on active material reduces the electrolyte decomposition so that the structural stability of active material can be enhanced. It should be noted that the improvement of capacity retention in the cell containing AlF_3 is consistent with the previous work by Sun et.al. [15]. They reported that AlF_3-coated $LiCoO_2$ cathode exhibited better capacity retention and rate capability than those of pristine $LiCoO_2$. Without any additives, the decomposition products of the electrolyte may cover the electrode surface with a highly resistive layer as cycling progresses at high charging potential. Fig. 6 shows the coulombic efficiency of the

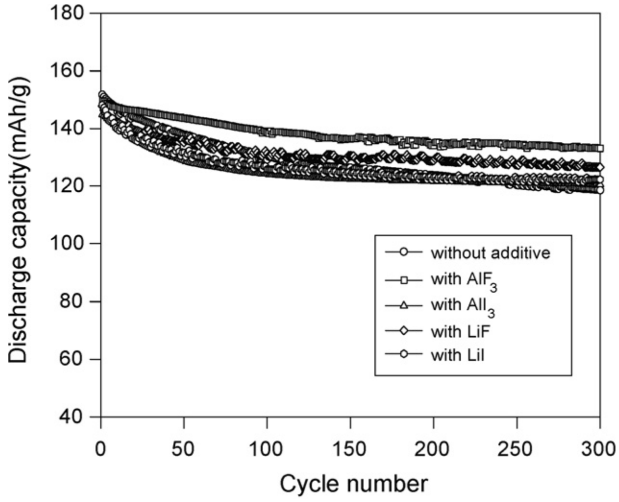

Fig. 5. Discharge capacities of the lithium-ion polymer cells prepared with gel polymer electrolytes containing different inorganic additives as a function cycle number. (0.5*C* CC and CV charge, 0.5 V CC discharge, cut-off: 3.0–4.3 V).

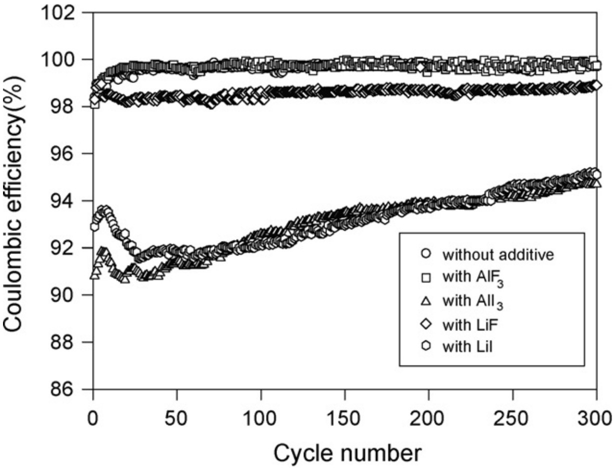

Fig. 6. Coulombic efficiency of the lithium-ion polymer cells prepared with gel polymer electrolytes containing different inorganic additives as a function cycle number. (0.5*C* CC and CV charge, 0.5 V CC discharge, cut-off: 3.0–4.3 V).

lithium-ion polymer cells containing different inorganic additives, as a function of cycle number. The coulombic efficiency was calculated from the ratio of the discharge capacity to the charge capacity. It should be noted that the low coulombic efficiency is observed in the cells containing AlI_3 or LiI as an additive. As mentioned earlier, the oxidation potential of iodide ion is lower than cell voltage, and oxidized product (I_3^-) is highly soluble in electrolyte solution. Thus, a shuttle–redox reaction ($3I^- \leftrightarrow I_3^- + 2e^-$) may occur between the graphite anode and the $LiCoO_2$ cathode, which is the main reason for the low coulombic efficiency observed in the cells containing iodide-based additive. As can be seen in the figure, AlF_3-added cell exhibited the highest coulombic efficiency through cycling, among the cells containing an inorganic additive, which is well consistent with results for comparing capacity retention shown in Fig. 5.

Rate capability of the lithium-ion polymer cell prepared with gel polymer electrolyte containing an inorganic additive was evaluated. In order to distinguish the effect of additives clearly, the cells were initially cycled five 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 0.2*C* and discharged at different current rate from 0.2 to 2.0*C*. The discharge curves of the lithium-ion polymer cell assembled with gel polymer electrolyte containing AlF_3 at different *C* rate are given in Fig. 7.

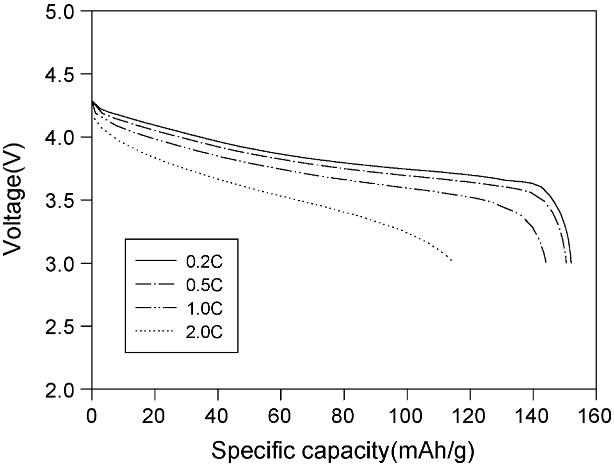

Fig. 7. Discharge profiles of lithium-ion polymer cell prepared with gel polymer electrolyte containing AlF_3, as function of *C* rate. Charge rate is 0.2*C* with 4.3 V cut-off.

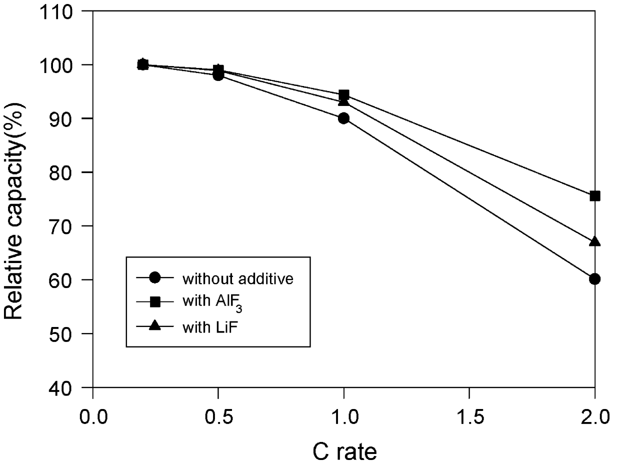

Fig. 8. Relative capacities of lithium-ion polymer cells prepared with gel polymer electrolytes containing different inorganic additives, as a function of *C* rate.

Both the voltage and the capacity are found to decrease gradually with increasing current rate. The cell delivered a relatively high discharge capacity (144 mAh g^{-1}) at a current density of 2.9 mA cm^{-2} (1.0*C* rate), whose discharge capacity was 95% compared to that obtained at 0.2*C* rate. However, the discharge capacity was shown to drop to 115 mAh g^{-1} at 5.8 mA cm^{-2} (2.0*C* rate). Fig. 8 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 0.2*C* rate. With increasing current density to 5.8 mA cm^{-2} (2.0*C* rate), the effect of additives on rate performance of the cell becomes noticeable. It is clear that the addition of inorganic compound to the gel polymer electrolyte leads to higher capacity at high current rate. High rate performance of the cell prepared with gel polymer electrolyte containing an inorganic additive may be related to the formation of less resistive film on electrode, which results in faster kinetics of the charge transfer reaction. Furthermore, 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. In order to confirm this presumption, we need to analyze the chemical composition of surface layer formed on active materials, which are in progress.

4. Conclusions

We have shown that improved capacity retention and cycling performances at higher rates could be achieved by adding a small amount of an inorganic additive to the gel polymer electrolyte based on polymer-coated separator. Lithium-ion polymer cells assembled with the gel polymer electrolyte containing an inorganic additive exhibited high initial discharge capacity of ~152 mAh g^{-1} at 0.5*C* and good capacity retention even at high charging cut-off voltage. Good cycling performances in the cell with these additives could be ascribed to the formation of a protective layer to cover active material in the electrode during cycling, which reduces the electrolyte decomposition so that the structural stability of active material can be enhanced.

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