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Electrochemical performances of inorganic membrane coated electrodes for li-ion batteries

Min Kim · Young-Chang Nho · Jong Hyeok Park

Abstract In the present study, we prepared new Li-ion batteries with inorganic membrane-coated electrodes fabricated by the direct coating of a 400-nm-sized Al_2O_3 particles onto the anodes and studied their charge–discharge characteristics for the first time. Being made of 94 wt.% Al_2O_3 powder and 6 wt.% polymeric binder, the membranes on the anodes showed excellent wettability with the liquid electrolytes, due to their high porosity and capillarity. The Li-ion batteries prepared by the assembly of the inorganic membrane-coated electrodes showed excellent charge–discharge behavior compared to conventional Li-ion batteries with a polymeric separator. However, their high-rate performance was affected by the binder contents in the inorganic membranes. The thermal properties of the Li-ion battery with the inorganic membrane-coated electrodes were compared with those of a conventional one with a polymeric separator.

Keywords Inorganic membrane · Li-ion battery · Safety

Introduction

Since the successful introduction of rechargeable nickel-cadmium and nickel-metal hydride batteries, the search for

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lighter, smaller, and more potent power sources has inevitably led to the development of lithium-ion battery technology [1–4]. Li-ion batteries have been studied as a potential power source for hybrid electric and fuel cell vehicles [5, 6]. However, their high cost and safety concerns still place restrictions on their general application. Microporous (polypropylene (PP) or polyethylene (PE)) polymer membranes have been used as a physical separator between the cathode and anode in Li-ion batteries. It is well known that polymer membranes soften or melt when the temperature reaches 130 °C or higher [7], owing to the dimensional instability of the polymer-based separators, which may cause internal short circuiting or lead to thermal runaway [5]. Therefore, it is necessary to design an alternative separator, which has dimensional stability at high temperature. The current gel materials with inorganic nanoparticles might perform well from an electrochemical point of view, but they have several drawbacks from the viewpoint of their safety and handling [8].

Recently, a new type of separator for use in rechargeable Li and Li-ion batteries was introduced [6, 9–11]. The films were made of inorganic nanoparticles and a small amount of polymer binder. These inorganic particle-based separators showed excellent thermal stability as well as wettability. However, they do not have sufficient mechanical strength to withstand the handling procedures used during cell winding assembly [10]. Kritzer et al. introduced nonwoven support materials to improve the mechanical strength of inorganic-based separators [8]. However, the mechanical strength of these inorganic-based membranes with nonwoven supports is still insufficient for the roll-to-roll process.

To overcome this drawback, densely packed inorganic sub-micron-sized particles were directly coated onto the

electrode for the first time. In this paper, we discuss the cell performance of Li-ion batteries prepared by the assembly of an inorganic membrane-coated anode and cathode without any additional polymer separator.

Experimental

Preparation of inorganic particle-coated anodes based on Al_2O_3 and PVdF-HFP

The inorganic particle-based membrane was directly coated on the anode as follows: The weighed Al_2O_3 powder (~400 nm) and PVdF-HFP (Kynar 2801, Arkema) were dispersed in acetone solvent and ground for 30 min using a homogenizer (Fluko, F25). The particle size of Al2O3 powder in the suspension was ~600 nm after the grinding (Brookhaven, 90 plus). In this work, the typical compositions of the membrane were 90:10 and 94:6 (by weight) Al2O3/PVdF-HFP. Then, the anode with 55 μm thickness and 19.3 mg/cm^2 density was dipped into the solution for 1 s and dried in a chamber for 5 min. The thickness of the inorganic membrane was controlled in the range of 8~25 μm by adjusting the solid contents in the suspension.
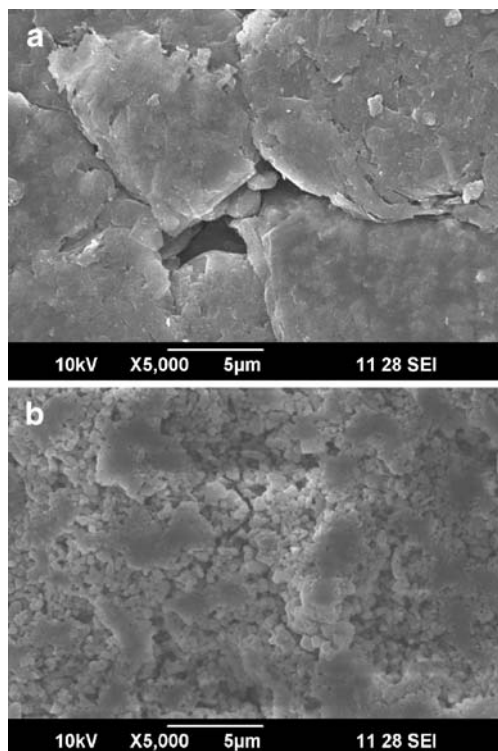

Fig. 1 SEM image of anode (**a**) and after (**b**) it was coated with the inorganic membrane (90 wt.% inorganic content)
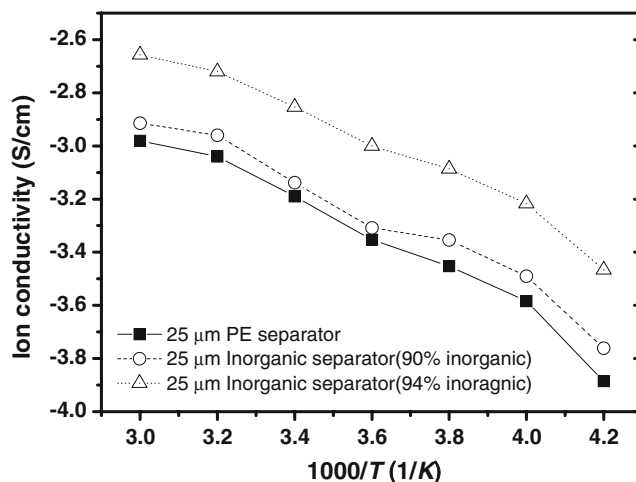
Fig. 2 Temperature dependence of ionic conductivity of inorganic particle based separator and PE separator

Preparation of electrodes

The anode has a composition of 94 wt.% graphitized mesocarbon microbeads (MCBM2528) and 6 wt.% Kynar741 as a polymeric binder. The cathode was composed of 90 wt.% $LiCoO_2$, 6 wt.% super-p, and 4 wt.% Kynar741.

Cell assembly and electrochemical measurements

Various types of cells with different inorganic coating layers were prepared (10 μm on anode+uncoated cathode, 20 μm on anode+uncoated cathode, and 25 μm on anode+ uncoated cathode). In the case of the cells with the composition [10 μm on anode+uncoated cathode], inorganic membranes with thicknesses of 10 μm were coated on the anode. The cells with the composition [10 μm on
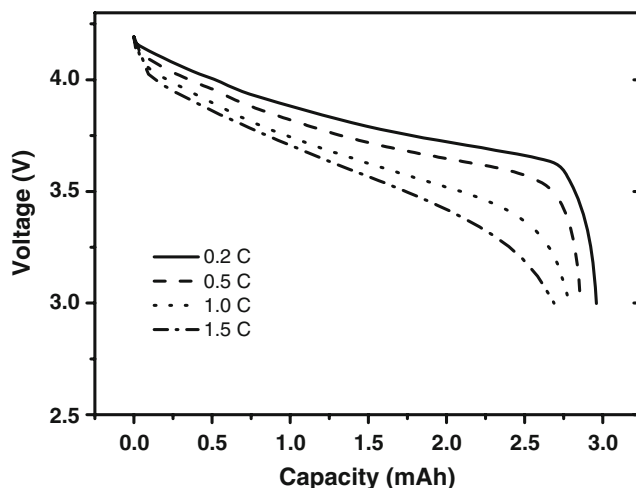

Fig. 3 Discharge capacity of unit cell (25 μm on anode+uncoated cathode (90 wt.% inorganic content)) at various discharge rates after charging at 0.2 C
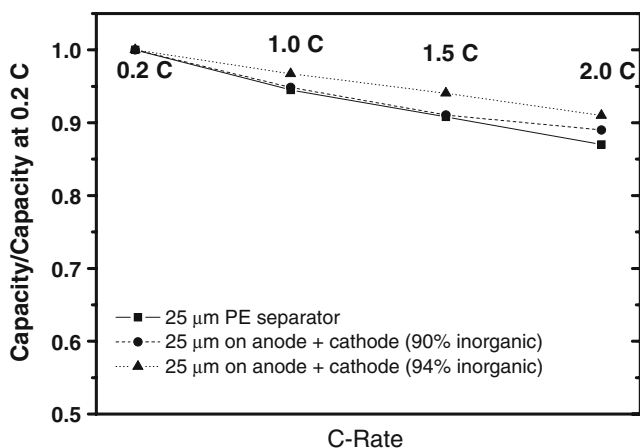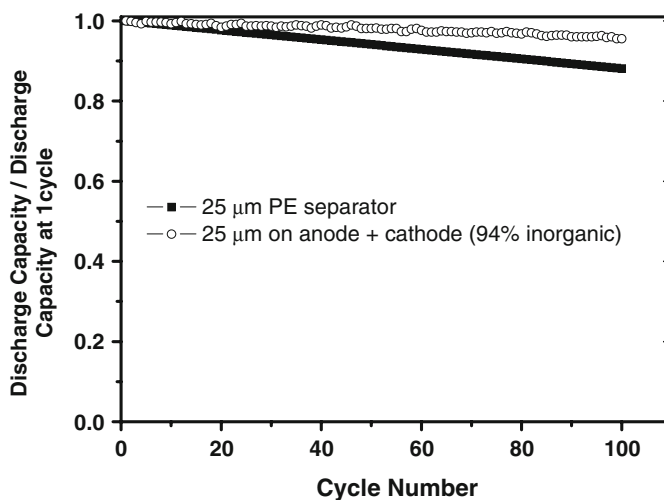
Fig. 4 Rate performance of cells at various discharge rates

anode+uncoated cathode] were not suitable for the charge–discharge test, because some of them had internal shorts. For the charge–discharge tests, 2,032 coin-type cells with an electrode area of 1.4 cm^2 were used. The inorganic membrane-coated anode and neat cathode were punched into disks and dried at 80 °C in a vacuum for 24 h before use. The electrolyte consisted of 1 M $LiPF_6$ dissolved in ethylene-methylcarbonate (EC-EMC; 3:7v/v). In an argon filled glove box, the coin cells were assembled and filled with the electrolyte. The charge–discharge cycling tests of the cells were performed using a TOSCAT-3000U (Toyo System). The cells were charged up to 4.2 V at a 0.2 C rate then discharged to 3.0 V with various C-rates. The charge process was cut-off at 20% of the initial constant current.

Ionic conductivity measurements

The ionic conductivity of free-standing inorganic membranes with nonwoven support materials was determined by ac impedance spectroscopy (CHI-660 impedance analyzer).

Sample films were sandwiched between two parallel stainless steel disks. The frequency ranged from 1 MHz to 1 Hz at a perturbation voltage of 5 mV. The ion conductivity was calculated from below equation.

$$\sigma = 1/R_b \times \lambda/A \qquad (1)$$

where R_b is the bulk resistance obtained from the ac impedance, λ the film thickness, and A is the surface area of the electrode.

Results and discussion

In the present study, an inorganic-based separator was directly coated onto the anode. This material consists of sub-micron-sized Al_2O_3 and a small amount of PVdF-HFP binder. Recently, many researchers have studied the surface treatment of electrode active materials with Al_2O_3 to improve both their cycle stability and rate capability at room and high temperature [12–14]. However, these mixed solid solution materials do not possess a separator function.

Figure 1 shows the SEM micrographs of the MCMB electrodes before and after they were coated with the inorganic membrane. The anode was well-covered with the inorganic particle/PVdF-HFP membranes with no significant defects. Because the electrode/membrane composite is flexible and electrically isolating, Li-ion batteries can be prepared without the need for an additional polymer separator. As can be seen in Fig. 1, the membranes on the anode have no macro pores. However, we found that they had excellent wettability with all of the liquid electrolytes tested, due to the good capillarity of the Al_2O_3 particle surface. Therefore, the membranes can be easily endowed with ion conductivity.

It was impossible to check the ion conductivity of the inorganic membrane itself because it could not be separated

Fig. 5 Discharge capacity as a function of cycle number of the unit cells (25 μm on anode+ uncoated cathode (94 wt.% inorganic content) and 25 μm-thick PE separator) at room temperature

Fig. 6 Photographs of the inorganic membrane-coated anode (before (**a**) and after (**c**) thermal annealing at 150 °C for 30 min) and PE separator on anode (before (**b**) and after (**d**) thermal annealing at 150 °C for 30 min)
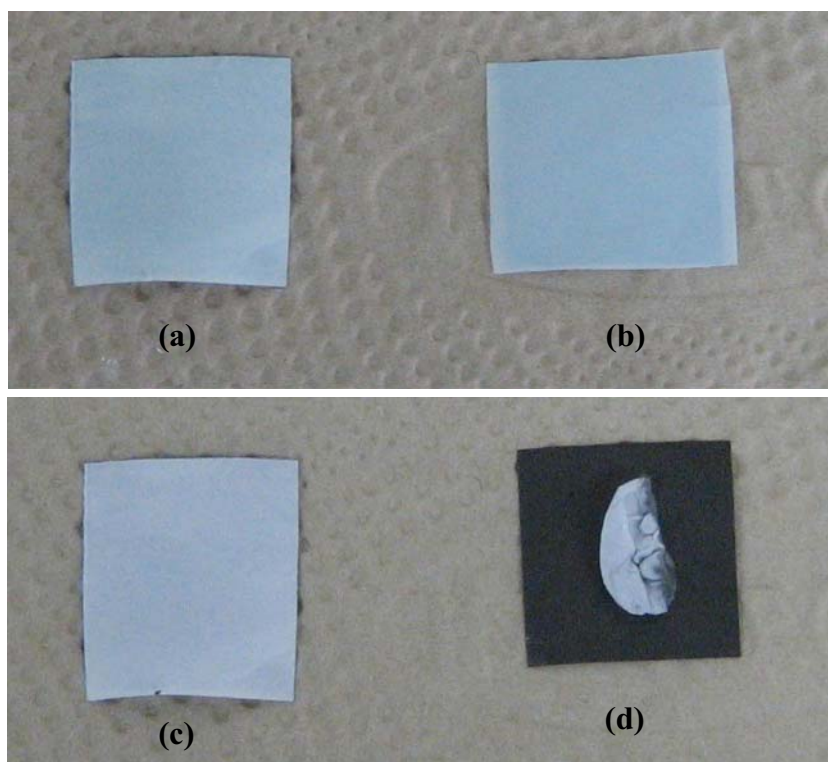
from the electrode/membrane assembly. Hence, free-standing inorganic membranes with nonwoven support materials were prepared and their ionic conductivities were tested. Figure 2 shows the Arrhenius plots of the ionic conductivities of the electrolyte-wetted membranes with different binder contents and that of a PE-based membrane (25 μm, Asahi Kasei, Japan). The electrolyte-wetted inorganic membrane with a thickness of 25 μm showed more enhanced ionic conductivity compared with the PE-based membrane. From these results, it can be seen that the ion conductivities of the membranes vary with the temperature in a very similar manner. This means that the ionic conductivity in the inorganic-based membranes originates from the liquid electrolyte impregnated in their voids [6].

The rate characteristics of the Li-ion battery were evaluated by charging the cell at a constant current of 0.2 C and discharging it at various current densities. The charging profiles of all of the cells were almost the same. Figure 3 shows the effect of the discharge current on the voltage-capacity profile (25 μm on anode+uncoated cathode). It is observed that both the capacity and voltage decreased with increasing discharge current density. This can be explained by the electrical polarization caused by the increase in the serial resistance. To observe the rate performance, the relative capacity of the cell was plotted against the discharge current in Fig. 4. The 1.0 unit in Fig. 4 represents 2.96 mAh/g. As can be seen, all of the separators show a linear capacity drop with increasing in C-rate. It was

observed that the capacity of the cell with the PE-based separator remained at about 87% of the relative capacity even when the discharge current was increased to 2.0 C. In the case of the [25 μm on anode+uncoated cathode] cell with a binder content of 10 wt.%, however, the cell capacity was almost the same at a low-discharge current density as that of the cell with the PE-based separator, even though the ionic conductivity of the 25-μm-thick inorganic membrane
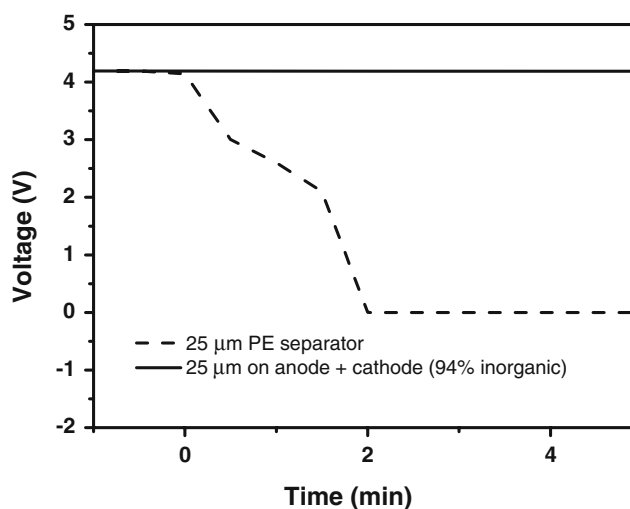

Fig. 7 Voltage profiles of the unit cells (25 μm on anode+uncoated cathode (94 wt.% inorganic content) and 25 μm-thick PE separator) at 150 °C (Park et al.)

is higher than that of the 25-μm-thick PE separator. This can be easily explained by the increase in the cell resistance owing to the PVdF-HFP coating deposited on the surface of the electrodes materials during the dipping process When the electrodes were dipped in acetone containing Al_2O_3 and PVdF-HFP for the preparation of the inorganic membrane, the PVdF-HFP dissolved in the acetone can penetrate into the pores of the electrodes, resulting in the formation of a polymer coating on the surface of the active materials or an additional polymer film in the pore of the anode after solvent evaporation. This polymer material can hinder the migration of the ions and increase the total cell resistance.

The [25 μm on anode+uncoated cathode (6 wt.% binder content) and PE separator] cells were cycled in constant current mode at 0.5 C rate and their discharge capacities were measured as a function of the cycle number (Fig. 5). Initial capacity of the cell was 2.86 mAh/g. The cell with the inorganic separator showed much higher discharge capacity retention than the one with the PE separator. The discharge capacities of the cells with the PE membrane and [25 μm on anode+uncoated cathode] coatings at the 100th cycle were 88% and 95% of the initial discharge capacity, respectively.

It is well known that internal shorts at high temperature may cause thermal runaway [5]. To compare the thermal stability of the cell introduced herein with that of a cell with a general PE-based separator, coin-type cells were prepared without an electrolyte and annealed at 150 °C for 30 min. Then, the cell resistances were measured before and after thermal annealing using a Hioki 3540. The resistance of the cell with the PE-based separator was of the order of several ohms after the thermal annealing process because of the development of internal shorts. However, the cell with the [25 μm on anode+uncoated cathode] with 6 wt.% binder content retained 100% of its initial resistance. Figure 6 shows the photographs of the cells with the [25 μm on anode] with 6 wt.% binder content and PE separator on the anode after the thermal annealing process. As can be seen in Fig. 6, there is no dimensional change in the case of the inorganic membrane-coated anode. Secondly, coin-type cells were prepared with an electrolyte and charged to 4.2 V. Then, these cells were annealed at 150 °C for 30 min and the voltage changes were monitored. As can be seen in Fig. 7, the initial voltage of the cell with the inorganic particle-coated anode was not influenced by thermal annealing at 150 °C. However, the cell with the PE separator showed internal short behavior immediately after being exposed to high temperature.

Conclusions

New Li-ion batteries with inorganic membrane-coated electrodes were easily prepared by directly coating the inorganic membrane onto the anode. The cells showed good capacity retention with increasing cycle number. In these batteries, the inorganic particle-based membrane on the electrode acts as a microporous separator, physically isolating the anode from the cathode, without the need for an additional polymer separator. In addition, because these inorganic particles have excellent thermal stability, the problem of the dimensional instability of polymer-based separators, which may cause internal short circuiting or lead to thermal runaway, can be solved.

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