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Performance of through-hole anodic aluminum oxide membrane as a separator for lithium-ion battery

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ABSTRACT

A high porosity through-hole anodic aluminum oxide (AAO) membrane has been prepared by a two-step anodization procedure. The as-prepared AAO membrane is around 60 μm thick with a uniform pore size of about 80 nm. Moreover, we also found that the AAO membrane not only has a good mechanical strength but also shows better performances on electrolyte infiltration and retention compared with the commercial polymer separator. The $LiFePO_4$/graphite battery using the AAO separator exhibits better cycling stability, rate capability and low-temperature performance than those using the polymer separators. The excellent electrochemical performances can be attributed to good hydrophilic characteristic, high porosity and through-pore structure of the AAO separators used. Therefore, the AAO separator is very promising to be applied in lithium-ion batteries.

1. Introduction

Lithium ion batteries (LIBs) are electrochemical energy storage devices with unique ability to deliver the stored chemical energy as electric energy efficiently without any kind of gaseous exhaust [1–5]. So far, LIBs have monopolized the portable electronic market (used in mobile phones and laptop computers), but their applications in high power equipments are mostly restricted by safety [6]. The separator plays very important roles and is crucial to the safety and durability of LIBs [7–10]. The most commercially used microporous polymer separators are made of polyethylene (PE) or/and polypropylene (PP) which have low melting points and poor mechanical strengths. Thus, the polymer separators could easily be punctured by lithium dendrite generated at high rate or long cycling test. Besides, the polymer separators usually show poor wettability with organic electrolyte due to their inherent hydrophobic property and low porosity ($\sim$45%) [11–18]. The above-mentioned defects would induce safety issues and affect the overall electrochemical performance, which would severely hinder the high safety and high power applications of LIBs, such as HEVs and EVs [19–21]. In order to overcome these drawbacks, many strategies have been proposed, such as non-woven fabric mats [22], microporous membranes based on PVdF [8,23–24] and polymer incorporated with the ceramic fillers (such as SiO_2 and Al_2O_3) [16,25–26]. But the presence of organic materials still affects the thermal stability of the separators at higher temperature ($>$140 °C) and does not solve the safety problems [11]. In our previous work, inorganic membranes such as porous Al_2O_3 membranes and porous SiO_2 membranes, prepared by a high-temperature sintering process, have been investigated as the separators for high safety LIBs [27,28]. However, the thickness of the Al_2O_3 and the SiO_2 separators are as high as 200 μm, limiting the volume energy density of the batteries. Furthermore, the curving and irregular pores in these separators prolong the diffusion path of lithium ions in the separators and reduce the rate capabilities of batteries. Therefore, a thinner inorganic separator with through-hole structure is an optimal choice to solve the above issues in LIBs.

Herein, we proposed a through-hole porous anodic aluminum oxide (AAO) membrane as a separator for LIB. The prepared AAO membrane is around 60 μm thick and its mechanical strength is sufficient for battery assembly. The through-hole AAO membrane also has a high porosity of 72% for adsorbing enough electrolytes to get high ionic conductivity. The electrochemical performances of the $LiFePO_4$/graphite batteries using the AAO separator have been investigated in detail. For comparison, the commercial polymer separator (Celgard 2400) was tested under the same conditions.

2. Experimental section

2.1. Preparation of AAO membranes

AAO membranes used in this work were fabricated using a two-step anodization process [29,30]. High-purity aluminum foil

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(99.999%, 0.30 mm thick) was cut into discs (⌀16 mm) with tailing end of 50 × 5 mm^2 and pressed with a tablet machine, followed by annealing at 500 °C for 5 h under Ar atmosphere. The as-prepared Al specimens were degreased in acetone and etched in 0.1 M NaOH aqueous solution to remove the surface oxide layer. The specimens were then electropolished in a mixture of perchloric acid and ethanol ($HClO_4$:C_2H_5OH=1:4, v/v) at a constant voltage of 15 V for 3 min to remove surface irregularities. The first-step anodization was carried out in a 0.3 M oxalic acid solution for 6 h, and the solution temperature was keep at 0 °C in an ice-water bath. Next, the AAO layer was removed by immersing the specimens in a mixture solution of 6 wt% H_3PO_4 and 1.8 wt% H_2CrO_4 at 80 °C for 6 h. Highly ordered porous AAO was prepared by second anodization of the textured Al surface, and the reaction time was extend to 24 h. Through-hole AAO membranes were obtained by voltage pulse detachment method in a mixture of perchloric acid and ethanol ($HClO_4$:C_2H_5OH=1:1, v/v) by applying voltage of 45 V. The constant voltage was applied by a DC regulated power supply (Digital, Manson SDP 2603). At last, the AAO membranes was immersed in 5 wt% H_3PO_4 for 30 min to enlarge the pores and then treated at 400 °C for 5 h to remove any impurities. The as-prepared AAO membranes were ultrasonically cleaned with acetone and deionized water, and then vacuum dried at 80 °C for 12 h.

2.2. Characterization of the AAO membranes

The morphology and microstructure of the AAO membrane were characterized by scanning electron microscopy (SEM, LEO 1530 VP). The contact angles of the separators with organic electrolyte of 1 M $LiPF_6$/EC+DEC (1:1, w/w) were tested by the contact angle tester (Dataphysics OCA40 Micro). The porosity of the AAO separator was calculated using the following equation [27]:

$$\text{Porosity} = \left(1 - \frac{m}{\rho V}\right) \times 100\% \tag{1}$$

where m is the mass of the AAO separator, ρ is the density of Al_2O_3 (3.98 g cm^{-3}) and V is the volume of the AAO separator.

Electrolyte infiltration and retention of the separators were evaluated as described in Ref. [27]:

$$\text{Electrolyte uptake} = \frac{W_1 - W_0}{W_0} \times 100\% \tag{2}$$

$$\text{Electrolyte retention} = \frac{W_x - W_0}{W_1 - W_0} \times 100\% \tag{3}$$

where W_0 is the weight of separator, W_1 is the initial weight of the separator after absorbing the electrolyte (1 M $LiPF_6$/EC+DEC (1:1, w/w)) for 1 h, W_x is the equilibrium weight of the electrolyte-infiltrated separator stored at 50 °C after x min. Two parallel measurements were carried out for both separators under the same conditions.

The batteries for ionic conductivity tests were fabricated by sandwiching the electrolyte-infiltrated separators between two stainless steel (SS) discs, and the electrochemical impedance spectroscopy (EIS) was measured on an electrochemical workstation (Zahner IM6ex) with the potential perturbation of 10 mV over a frequency range from 1 MHz to 0.01 Hz. Each measurement was carried out after the electrolyte or the testing batteries were held at a certain temperature for 1 h to reach full thermal equilibration. The ionic conductivity (σ) was calculated according to the following equation [10, 28]:

$$\sigma = \frac{l}{RS} \tag{4}$$

where l is the thickness of the separator, R is the bulk electrolyte resistance and S is the area of the separator.

2.3. Electrochemical measurements

A graphite electrode consisting of 85 wt% graphite (Hitachi Powdered Metals Co. Ltd.), 5 wt% acetylene black and 10 wt% PVdF and a positive electrode consisting of 75 wt% $LiFePO_4$ (Tianjin STL Co. Ltd.), 15 wt% acetylene black and 10 wt% PVdF were made on copper foil and aluminum foil, respectively. The specific capacity of the $LiFePO_4$/graphite battery was calculated based on the mass of $LiFePO_4$. The electrolyte was 1 M $LiPF_6$/EC+DEC (1:1, w/w). CR2032 coin-type cells were assembled in an argon-filled glove box (Mikrouna). The batteries were cycled over the voltage range of 2.4–4.0 V using a NEWARE Battery Testing System. For the low temperature tests, all the batteries were cycled three times and charged to 4.0 V at the rate of 0.5 C at room temperature, then transferred into the low temperature chamber and held for 1 h for equilibrium, followed by being discharged to 2.4 V at 0.5 C. The impedances of the $LiFePO_4$/graphite batteries were measured on the Zahner IM6ex electrochemical workstation. The frequency range was set from 0.01 Hz to 1 MHz with the potential amplitude of 5 mV. Before the impedance measurement, the batteries were cycled three times at 0.5 C and subsequently charged to 50% of overall state of charge (SoC=50%).

3. Results and discussion

Fig. 1 shows the SEM images of the as-prepared AAO membrane. As displayed in Fig. 1, the open-hole structure is successfully fabricated. Well-ordered nanopore arrays are observed in the cross-section view of the AAO membrane (Fig. 1(b)); the diameter of the pores is about 80 nm and the interpore distance is about 105 nm. The porosity of the AAO membrane is 72% calculated by Eq. (1), which is much higher than that of the commercial polymer separator (~45%) [14–16]. Large pores and through-hole structure of the AAO separator can shorten the diffusion path of lithium ion and minimize the ionic resistance, resulting in the improvement of

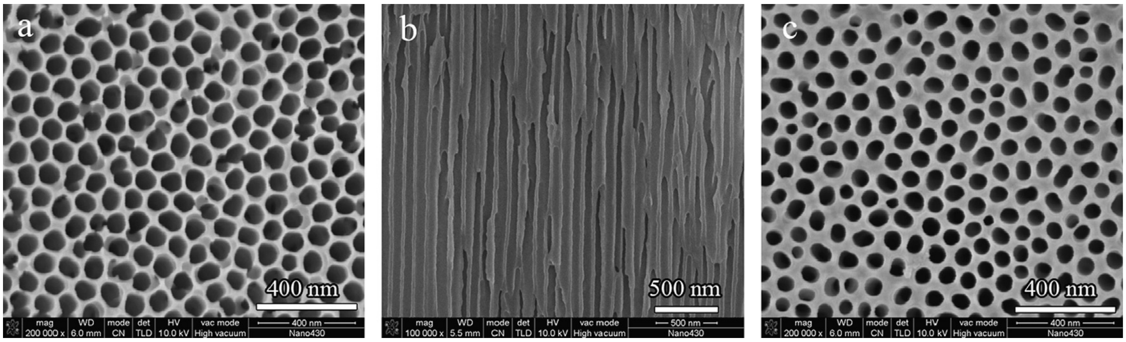

Fig. 1. SEM images of AAO membrane (a) top view, (b) cross-section view and (c) bottom view.