Journal of Power Sources 270 (2014) 53–58

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

A composite membrane based on a biocompatible cellulose as a host of gel polymer electrolyte for lithium ion batteries

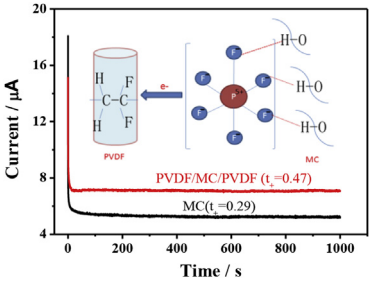
S.Y. Xiao [a], Y.Q. Yang [a], M.X. Li [a], F.X. Wang [a], Z. Chang [a], Y.P. Wu [a, b, *], X. Liu [b, *]

[a] New Energy and Materials Laboratory (NEML), Department of Chemistry & Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China
[b] Institute of Energy Engineering, Nanjing University of Technology, Nanjing, China

HIGHLIGHTS

- Methyl cellulose (MC) is environmentally friendly and cheap.
- A composite polymer membrane is prepared by coating PVDF on the surface of a membrane from MC.
- The composite membrane is used as the separator and the host of a gel polymer electrolyte.
- The prepared gel polymer electrolyte shows excellent electrochemical performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 March 2014
Received in revised form
10 July 2014
Accepted 11 July 2014
Available online 18 July 2014

Keywords:
Polymer membrane
Separator
Polymer electrolyte
Lithium ion batteries

ABSTRACT

A composite polymer membrane is prepared by coating poly(vinylidene fluoride) (PVDF) on the surface of a membrane based on methyl cellulose (MC) which is environmentally friendly and cheap. Its characteristics are investigated by scanning electron microscopy, FT-IR, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The outer PVDF layers are porous which results in high electrolyte uptake and the lithium ion transference number is much larger than that of the pure MC. Moreover, the cell based on Li//$LiFePO_4$ delivers high discharge capacity and good rate behavior in the range of 4.2–2.5 V when the composite membrane is used as the separator and the host of a gel polymer electrolyte, lithium as the counter and reference electrode, and $LiFePO_4$ as cathode. The obtained results suggest that this unique composite membrane shows great attraction in the lithium ion batteries with high safety and low cost.

1. Introduction

Rechargeable lithium ion batteries have become a commercial reality in recent years. They are widely used in mobile electronic equipment, such as computers, cell phones and so on [1–3]. Conventional lithium ion batteries used liquid electrolyte, which made the batteries unsafe because of electrolyte leakage. Now this problem has been suggested to solve by polymer electrolytes. Until now, polymer electrolytes based on polyacrylonitrile (PAN) [4–6], poly(ethylene oxide) (PEO) [7–9], poly esters [10–12] and poly(-vinylidene fluoride) (PVDF) [13–15] have been widely studied. Recently, the poly(vinylidene fluoride) (PVDF) has been identified as a potential host for lithium polymer batteries because of its appealing properties. This polymer host is expected to be more anodically stable because of the strong electron-withdrawing functional group (–C–F) [16–20]. However, its practical

* Corresponding author. Institute of Energy Engineering, Nanjing University of Technology, Nanjing, China. Tel./fax: +86 21 5566 4223.
E-mail addresses: wuyp@fudan.edu.cn, wuyuping99@yahoo.com (Y.P. Wu).

http://dx.doi.org/10.1016/j.jpowsour.2014.07.058
0378-7753/

application is still not realized due to its high cost, which greatly limits the commercialization of electric vehicles.

Formerly we reported its composites with nonwoven fabrics and glass fiber mats, which can sharply decrease the cost together with excellent electrochemical performance [21,22]. However, both nonwoven fabrics and glass fiber mats are too thick and too heavy, and will lead to a decrease of volumetric and gravimetric energy densities of the prepared lithium ion batteries. Recently, we found that methyl cellulose (MC) can be a host of gel polymer electrolyte for lithium ion batteries leading to higher ionic conductivity and higher lithium ion transference number than the commercial separator [23]. However, due to the existence of the remaining hydroxyl groups in MC, the difference between charge and discharge voltages is larger than that for the commercial separators, and the rate capability of lithium ion batteries could not be improved.

Cellulose is the most abundant polysaccharide, and occurs mainly within the cell wall of higher plants as a structural material. Cellulose is a linear macromolecule consisting of (1–4) linked b-D-glucopyranosyl monomers, and this b-(1–4) configuration contributes to its rigid structure and to the formation of aggregates through intra- or inter-molecular hydrogen bonds via hydroxyl groups [24]. When some or even all of the hydrogen atom in the hydroxyl group were replaced by methyl group, the cellulose becomes MC, which is widely used in construction, food, cosmetics industry as an environmentally friendly and economic polymers. These results suggest great promise for its application as a host of gel polymer electrolytes for lithium ion batteries.

In order to overcome the problems of MC, here we reported a composite membrane which consists of sandwiched structure of PVDF/MC/PVDF. The composite membrane has good mechanical property and relatively high ionic conductivity. Moreover, it produces no pollutant during the preparation because MC is nontoxic and the solvent water is harmless, which made our work very significant. It can meet the great demand for highly efficient and mobile energy storage, which furthermore is sustainable from an economic and environmental point of view.

2. Experimental

MC (100 mg, Aldrich) was dissolved in distilled water (40 mL) at room temperature with constant stirring, then the solution was casted on a glass plate. After the solvent was vaporized at 80 °C, a thin MC membrane with the thickness of 20 μm was obtained. For comparison, a sandwiched membrane PVDF/MC/PVDF was prepared as follows: a home-made PVDF membrane from electrospinning (30 kV at a GVR-200 Instrument of Fuerma Company, Beijing, with diameter of the spinhole of 0.06 mm) was coated on a piece of glass, then a little water was added on the upper surface of the PVDF membrane. After that, the prepared MC membrane was rolled onto the PVDF membrane. Later another layer of PVDF was coated on the MC layer in the same way. After vaporizing the water, a sandwiched membrane PVDF/MC/PVDF with thickness of 60 μm was obtained. The membrane was further dried under vacuum at 80 °C for 24 h to remove the residual solvent prior to measurement and use.

The surface morphology of the prepared membranes was examined by means of scanning electron microscope (SEM, Philip XL30). The specimens for the SEM micrographs of the cross-section of the membranes were prepared by fracturing them in liquid nitrogen. FT-IR measurement was carried out on a BRUKER VECTOR-22 spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the membranes were carried out by utilizing a Perkin–Elmer TGA7/DSC7. The thickness of the membranes was measured with a micrometer (SM & CTW, Shanghai). Stress–strain tests were conducted by using a Sansi YG832 tensile testing machine with a crosshead speed of 1 mm min^{-1}.

The calculation of the amount of liquid electrolyte uptake is referred to the equation: $\eta = (w_t - w_o)/w_o \times 100\%$, where w_o and w_t

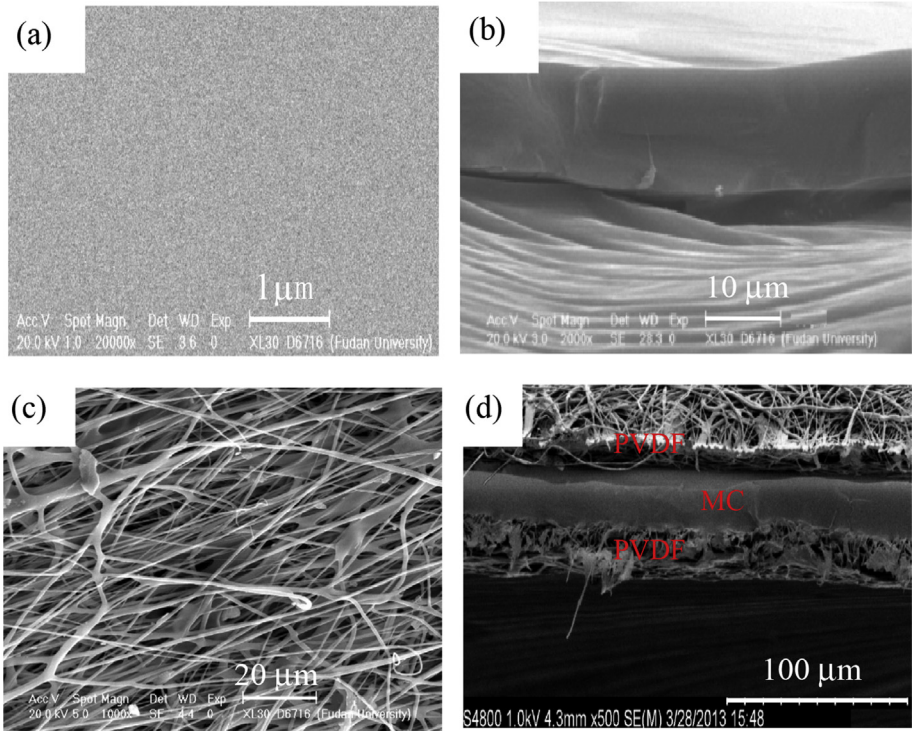


Fig. 1. SEM micrographs of (a) the surface and (b) cross section of MC, (c) the surface of PVDF and (d) the cross section of the sandwiched membrane PVDF/MC/PVDF.