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Preparation of hydrophilic polyethylene/methylcellulose blend microporous membranes for separator of lithium-ion batteries

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ABSTRACT

Hydrophilic high density polyethylene/methylcellulose (HDPE/MC) blend microporous membranes were prepared via the thermally induced phase separation process. The effect of MC on the HDPE membranes was investigated by examining the morphology and determining the phase diagram, hydrophilicity, crystallinity, and mechanical properties. In addition, the electrochemical properties were evaluated from button cells consisting of the pure HDPE membrane and HDPE/MC blended microporous membranes as separators saturated by the $LiPF_6$ electrolyte. The obtained results indicated that the cloud point temperature and the surface morphology of the membranes was shifted to high values and changed from dense to porous, respectively, with increasing MC content. The blended membranes also had a higher electrical uptake than the pure HDPE membrane. Moreover, the maximum ionic conductivity (1.01×10^{-3} S/cm) and minimum activation energy (Ea) value (10.48 kJ/mol) were obtained at an MC content of 2 wt%. Furthermore, compared to those consisting of the pure HDPE membrane, button cells consisting of the HDPE/MC blend microporous membranes exhibited higher charge-discharge capacity and better discharge performance at various current densities.

1. Introduction

Lithium ion batteries (LIBs) have become the primary energy storage device of portable devices such as cell phones, laptop computers, etc. [1–4]. The high capacity of LIBs renders them suitable candidates as power sources for electric vehicles, hybrid electric vehicles, and plug-in hybrid electric vehicles. LIBs are composed of an anode, a cathode, and a separator, which constitutes an essential barrier that ensures the safety of the batteries. Most LIB separators have a porous morphology, which favors the transmission of lithium (Li) ions [5].

Porous membranes have been prepared using several methods including melt-spinning and cold-stretching (MSCS) [6] and non-solvent-induced phase separation (NIPS) [7]. The NIPS and MSCS produce membranes that are multi-morphological and have excellent mechanical properties, respectively. There are, however, drawbacks associated with each method. For example, membranes fabricated via the MSCS typically have an average pore diameter of only 0.09 μm that is not conducive for ion transmission [8]. The NIPS suffers from the drawback of being only applicable to soluble polymers [9]. In contrast, the thermally induced phase separation (TIPS) process is facile [10,11], uses easily controlled parameters, is effective in controlling the final pore size, and can generate both isotropic and anisotropic structures [12–17]. During this process, the polymer and diluents are heated above the melting temperature of the polymer in order to form a homogenous solution, and then cooled to induce a phase separation. An extraction agent is used to remove the diluents after the polymer solidifies via crystallization or a glass transition [18,19]. Owing to low cost, ease of processing, and electrochemical stability, microporous polyethylene (PE) membranes are typically used as separators for commercial LIBs [20,21]. However, PE is intrinsically hydrophobic, and hence exhibits poor liquid-electrolyte retention and low absorption of electrolytes. Therefore, PE porous membranes need to be modified in order to be used as separators in LIBs [22].

Extensive studies have been conducted with the aim of endowing hydrophilic properties to hydrophobic PE membranes, through surface coating and blending with hydrophilic monomers. For example, Xiong et al. [23] reported that an ethylcellulose-coated polyolefin separator improved the hydrophilic properties, thereby leading to increased absorption of electrolytes. Zhang et al. [24] reported that the hydrophilic properties of high density polyethylene (HDPE) were significantly improved with the addition of a PE-b-PEG amphiphilic copolymer. Compared to surface coating, blending is a simpler method that results in enhanced

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hydrophilicity of the PE, and the formation of a hydrophilic membrane in a single step. Blending is only performed, however, on inorganic particles and polymers. Moreover, the effect of blending natural polymers with PE has scarcely been investigated. Methylcellulose (MC) is an easily obtained, bio-compatible, highly hydrophilic cellulose derivative that contains many polar groups such as hydroxyl and ether groups, which exhibit a high affinity for electrolytes [25,26]; blending MC therefore constitutes an effective and economical means of modifying the hydrophilicity of the HDPE.

As such, this paper describes the first-ever blending of MC with HDPE for the fabrication of microporous membranes via the TIPS process. The effect of MC on the membrane morphology and properties are investigated. Furthermore, the electrochemical properties of an assembled button cell that uses the HDPE/MC membrane as a separator are discussed. The results indicate that the MC can be used as a structure and performance regulator (of the membranes) that leads to improved hydrophilicity and electrochemical properties of the HDPE porous membranes.

2. Experimental

2.1. Materials

HDPE (5000S), which was purchased from Sinopec Beijing Yanshan Corporation, was dried at 60 °C under vacuum for 4 h in order to remove the moisture. The MC powder (AR.) was supplied by Tianjin Fuchen Chemical Reagent Co. Ltd. In addition, dioctyl phthalate (DOP, industrial grade, purity > 99%) was obtained from Guangzhou Chuangjingxing Chemical Reagent Co. Ltd and used as the latent diluent; ethanol was used as the extractant without further purification. The $LiPF_6$ electrolyte dissolved in the EC/DEM/EMC in a weight ratio of 1:1:1, was provided by Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.

2.2. Preparation of the HDPE/MC blend microporous membranes

A portion of the MC powder was dissolved in 12% NaOH solution, stirred for 1 h at room temperature, and then filtered [27,28]. The dried HDPE and pretreated MC powder were dissolved in the DOP and then stirred at 180 °C for 3 h in a glass vessel, in order to form a homogeneous solution (20 wt%); this stirring was performed under nitrogen and the resulting membranes with *n* wt% of MC were referred to as MC-*n*. Furthermore, a pie-shaped sheet was formed by pouring samples of the HDPE/DOP/MC blend onto the mirror-polished stainless steel that was covered with a polyester film. Another polyester film was quickly laid on the sheet (Fig. 1), in order to prevent solvent volatilization. The sample was subsequently pre-heated at 200 °C for 5 min on a flat vulcanizing machine and compressed until the pressure reached 10 MPa. Afterwards, the stainless steel plate containing the membrane was removed and quenched at room temperature for 10 min. The membrane was then immersed in ethanol for 24 h in order to extract the diluent and subsequently dried at ambient temperature.

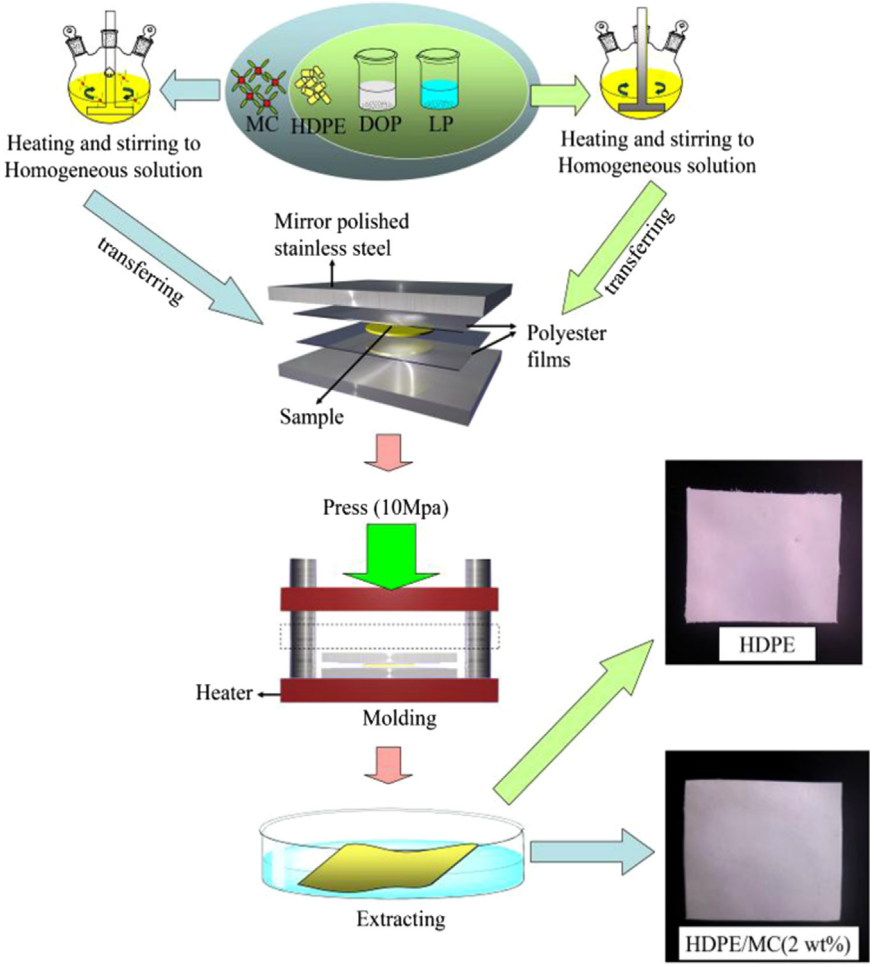

Fig. 1. Schematic showing the preparation of the HDPE microporous membrane and the hydrophilic HDPE/MC (2 wt%) blend microporous membranes.