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Effect of polydopamine surface coating on polyethylene separators as a function of their porosity for high-power Li-ion batteries

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ABSTRACT

This study demonstrates the effect of polydopamine coating on separator membranes used in liquid electrolyte batteries as a function of membrane porosity. We select two typical separators that differed only in porosity. High-porosity (16H) and low-porosity (16L) separators are coated with polydopamine by simple dip-coating. Their properties are evaluated via scanning electronic microscopy (SEM) and determining the water contact angle, Gurley number, ionic conductivity, and uptake volume of liquid electrolyte. In addition, the effect of polydopamine coating on electrochemical properties is tested using CR2032 coin-type half-cells ($LiMn_2O_4$/Li metal). With enhanced hydrophilic properties of surfaces as keeping pore structures, both of polydopamine coated high and low porous separators show enhanced rate capability and cell performance compared to uncoated versions. The effect of polydopamine coating is greatly enhanced in the low-porosity separators, with up to 40% increase in power capability (at 5 *C* rate) and a 290% increase in cycle performance (after 500 cycles, at *C*/2 rate), compared to the high-porosity type (13% increase in power capability, 43% increase in cycle performance).

1. Introduction

Due to high energy density and long cycle life, lithium-ion batteries (LIBs) have been the dominant power source for portable electronic devices during the past twenty years. LIBs are presently the focus of considerable attention in the scientific and industrial communities targeting new large-scale battery applications such as electric vehicles and energy storage systems (ESSs) [1–6]. For such applications, they require higher standards in terms of the cycle life, energy density, power capability, safety, and price. In general, LIBs are comprised of anodes, cathodes, electrolytes, and separators, and each component needs to be studied in parallel in order to realize optimal battery performance [7,8]. Nevertheless, recent studies tend to place considerable emphasis on active materials, including anode and cathode materials with high energy density, and they focus on manipulating the crystalline structure and developing nanostructures [7].

Essentially, separators offer protection against internal short circuits as physically placed between anode and cathode electrodes, and provide a lithium ion pathway through the pores of the separator material as well [9,10]. Despite the widespread adoption of micro-porous polyolefin separators in commercialized LIBs, the properties of separators require improvement for large-scale LIB applications, especially with regard to power capability and safety issues [10–14].

Polyolefin-based separators are inherently hydrophobic with a low melting point (polyethylene ≈130 °C, polypropylene ≈165 °C), and thus suffer from poor wettability, resulting in poor electrolyte uptake and low thermal stability [9,13,14]. To overcome these limitations, we introduced a technique based on mussel-inspired polydopamine to modify the surface of polyolefin separators [7,11,15]. This technique very effectively resolves the mentioned performance issues.

The physical properties of separators, especially their permeability, which is affected by the type of pore generation process used and by porosity, are important factors that determine the power capability and safety. In general, there are two different approaches to pore generation in separators: the wet process and the dry process. The dry process forms pores entirely by the stretching of semi-crystalline polyolefin films, whereas the wet process involves solvent extraction and the stretching of polyolefin films [9,16]. As a result, separators made by the wet process have significantly greater tortuosity, which makes them better suited to applications requiring a long battery life compared to those produced via the dry process [16,17]. In addition, it is clear that the adequate porosity of separators is necessary for ensuring a high power capability of LIBs, as this helps them retain a sufficient volume of liquid electrolyte. Nevertheless, excessive porosity is detrimental to the safety function of separators because the membrane shrinks or softens rather

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than effectively closing the pores and thereby shutting down the battery as intended [18].

In line with our previous results that demonstrate the importance of high hydrophilicity of separator surfaces for good cell performance, we investigate herein the effect of polydopamine coating on polyolefin separators as a function of porosity, which is the most important parameter in separators [7,15,19,20]. In order to achieve this objective clearly, we controlled other variables that influence separator properties, namely, the thickness of the material (polyethylene, PE) and the process of pore generation (wet process).

2. Experimental

2.1. Materials

$LiMn_2O_4$ (LMO, Kyushu Ceramics, Japan), polyvinylidene fluoride (PVDF, KF-1300, Kureha, Japan), conductive carbon (Super-P, Timcal, Switzerland), and Li metal foil (450 μm, Honjo Metal, Japan) were used. A mixture of 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/DEC = 1/2 by vol.) was purchased from PANAX ETEC (Korea) and used without further purification. Deionized (DI) water from a Milli-Q system (Millipore Co., USA, 18.2 MΩ cm) was used. *N*-methyl-2-pyrrolidone (NMP), Trizma® base (99.9%), Trizma® hydrochloride (99%), 2-(3,4-dihydroxyphenyl)ethylamine hydrochloride (dopamine hydrochloride, 98%), and methanol (CH_3OH) were purchased from Aldrich and used without further purification. Two types of micro-porous PE separators with different permeability were supplied from W-SCOPE Korea Co. (thickness: 16 μm, porosity: 41% and 47%, respectively).

2.2. Polydopamine surface coating

Separators were surface-coated via a simple polydopamine coating method used by Ryou et al. [7,15]. Dopamine solution (2 mg mL^{-1}) was prepared using a mixture of tris buffer solution (pH 8.5, 10 mM) and methanol (CH_3OH/buffer = 1/1 in wt%) as a co-solvent.

2.3. Characterization of separators

The morphology of separators associated with polydopamine coating was monitored using a scanning electron microscope (SEM, JSM-6390, JEOL, Japan). The porosity of separators was evaluated by a simple liquid absorption test (in our case, we used hexadecane) according to ASTM D2873, using Eq. (1) [9,19]:

$$\text{Porosity}(\%) = \frac{V_{\text{occupied by hexadecane}}}{V_{\text{polymer}} + V_{\text{occupied by hexadecane}}} \times 100 \quad (1)$$

As described in ASTM-D726, the Gurley number of the separators was determined using a densometer (4110N, Thwing-Albert, USA). In general, the Gurley number indicates the time required for a specific volume of air (100 mL) at a given pressure (6.52 psi) to pass through a specific area of the separator [9,19].

The uptake of electrolyte solution was determined using Eq. (2), where W_1 and W_2 indicate the weights of the samples before and after immersion in the liquid electrolyte for 10 h [21]:

$$\text{Uptake amount}(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (2)$$

2.4. Electrode preparation

A mixture of slurry containing 90 wt% LMO, 5 wt% conductive carbon, and 5 wt% PVDF in NMP was prepared, and cast on aluminum foil (15 μm, Sam-A Aluminum, Korea) using a doctor blade for the cathode electrode. The cast slurry was dried in air at 130 °C for 1 h, and then roll-pressed with a gap-control-type roll-pressing machine (CLP-2025, CIS, Korea). The cathode electrode (density: 1.67 g cm^{-3}, loading amount: 7.35 mg cm^{-2}, thickness: 44 μm) was punched into a disk shape (radius: 12 mm) and dried at 60 °C for 12 h under vacuum before use.

2.5. Electrochemical measurements

The ionic conductivity of separators impregnated with liquid electrolyte was evaluated by sandwiching between two stainless steel electrodes. To evaluate the cell performance, CR2032 half-cell units (LMO/Li metal) were assembled in a glove box filled with argon. The unit cells were aged for 12 h and cycled between 3.0 and 4.5 V vs. Li/Li^+ at a *C*/10 rate (0.088 mA cm^{-2}, constant current for both charging and discharging processes) at 25 °C using a charge/discharge cycle tester (PNE Solutions, Korea). The unit cells were also stabilized in three subsequent cycles between 3.0 and 4.5 V vs. Li/Li^+ at a *C*/5 rate (0.44 mA cm^{-2} constant current for both charging and discharging processes) and at 25 °C. After stabilization, the AC impedance of the cells was measured using an impedance analyzer (VSP, Bio-Logic, USA) across a frequency range of 1 MHz–0.01 Hz.

In order to evaluate rate capability, the cells were cycled at several discharging current densities varying from 1 to 30 *C* (1, 5, 10, 15, 20, 25, and 30 *C*) while maintaining the charging current density at a rate of *C*/2 (constant current–constant voltage mode for charging and constant current mode for discharging between 3.0 and 4.5 V vs. Li/Li^+ at 25 °C).

After rate capability tests, the unit cells were subsequently cycled at a rate of *C*/2 for 500 cycles at 25 °C to examine cycle retention performance (constant current–constant voltage mode for charging and constant current mode for discharging between 3.0 and 4.5 V vs. Li/Li^+).

3. Results and discussion

In order to investigate the effect of polydopamine surface-coating on battery separators as a function of their permeability, we selected two control cases to facilitate easy comparison, which were matched in terms of the material (polyethylene, PE), thickness (16 μm), and pore generation method (wet process) used, but differed in porosity. Hereafter, 16H denotes a separator with higher porosity (thickness: 16 μm, porosity: 47%) and 16L denotes that with lower porosity (thickness: 16 μm, porosity: 41%).

As described in Fig. 1(a), polydopamine-coated separators are prepared by a simple immersion process of dipping the separators in an aqueous-based dopamine solution [7,15]. Beginning with the self-oxidization of dopamine to yield dopaquinone, a series of complex intra- and inter-molecular reactions occurs that finally results in polydopamine, a melanin-like high molecular weight heterogeneous polymer [22–25]. Consequently, as shown in Fig. 1(b), the solution color gradually changes over time, from transparent to brown-black. It is known that polydopamine can coat immersed samples, irrespective of their material, and therefore, the coated separators also revealed the same color as the solution [26,27]. We characterized the surface-coated separators via X-ray photoelectron spectroscopy (XPS) and FT-IR using the same procedure as reported in previous studies, and confirmed that polydopamine was coated well on both the separators [7,15].

In order to investigate effect of the polydopamine coating on the morphology of the separators, we observed the surface morphologies of the separators via a scanning electron microscope (SEM). As indicated in Fig. 2(a) and (b), both bare separators, 16H and 16L have the similar pore structures because the same pore generation