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Short communication

Close-packed poly(methyl methacrylate) nanoparticle arrays-coated polyethylene separators for high-power lithium-ion polymer batteries

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ABSTRACT

In an endeavor to improve the discharge C-rate performance of lithium-ion polymer batteries targeting high-power applications, we develop a novel gel polymer electrolyte-coated separator, which is based on introduction of close-packed poly(methyl methacrylate) (PMMA) nanoparticle arrays onto a polyethylene (PE) separator. In contrast to a conventional PMMA dense coating layer, a noticeable feature of the PMMA nanoparticle array coating layer is its highly ordered nanoporous structure, i.e. well-connected interstitial voids formed between the close-packed PMMA nanoparticles. This unique morphology allows for not only favorable liquid electrolyte wettability but also facile ionic conduction of the PMMA nanoparticle arrays-coated separator, both of which play crucial roles in improving the discharge C-rate performance of cells assembled with the separator.

1. Introduction

Owing to the superior design flexibility and low rates of safety failures, lithium-ion polymer batteries incorporating gel polymer electrolytes have attracted great attention as promising next-generation batteries [1,2], where the gel polymer electrolytes consist of liquid electrolytes and polymer matrixes. Among various efforts to the development of lithium-ion polymer batteries, an approach based on coating polyolefin separators with gel polymer electrolytes is highly recommended owing to the simplicity of the process [3] and improved electrochemical stability at interfaces with electrodes [4]. Representative gel polymer electrolytes include poly(vinylidene fluoride) [5], poly(methyl methacrylate) [6], and poly(acrylonitrile) [7]. Recently, as lithium-ion polymer batteries expand to new applications such as electric vehicles and power tools that strongly demand high-power density, the importance of C-rate performance of these batteries is rapidly growing.

However, when we target the aforementioned high-power applications of batteries, the gel polymer electrolyte-coated separators may face serious problems concerning the C-rate performance. In general, gel polymer electrolytes are known to exhibit lower ionic conductivity as compared to liquid electrolytes [1–4]. This implies that introducing gel polymer electrolytes onto polyolefin separators may cause drawbacks for ionic conduction, which becomes more serious at higher charge/discharge current densities.

In this study, in an effort to overcome these limitations of the gel polymer electrolyte-coated separators and facilitate their applicability to high-power batteries, we demonstrate a novel approach, which is based on introduction of well-ordered, close-packed polymer nanoparticle arrays. The well-controlled nanoparticle arrangement driven by self-assembly has attracted much attention as an ideal starting template [8–10] for preparing porous materials that could be used in various applications ranging from sensors to catalysts. Exploiting the concept of these unique colloidal templates, we apply close-packed PMMA nanoparticle array coating layers onto both sides of a PE separator, instead of conventional PMMA dense coating layers, where PMMA is selected as a representative example of gel polymer electrolytes. A major objective of this study is to evaluate the performance benefits of the PMMA nanoparticle array coating layer in terms of liquid electrolyte wettability, ionic conductivity, and more importantly discharge C-rate performance of cells.

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2. Experimental

A colloidal solution (inset in Fig. 1(b)) of PMMA nanoparticles (average particle size = approximately 490 nm) was prepared by conventional emulsion polymerization. The detailed synthesis procedure has been described in previous publications [11,12]. For a PMMA dense coating layer (as a control sample), the PMMA solution (inset in Fig. 1(f)) was prepared by dissolving PMMA powders in acetone. The PMMA powders were obtained by evaporating water from the PMMA colloidal solution. Unlike the transparent PMMA solution, the PMMA colloidal solution was white in color due to the light scattering by the PMMA nanoparticles dispersed in water. As a coating substrate, a PE separator (thickness = 20 μm, gurley value = 240 s 100 cc^{-1}, porosity = 45%, Tonen) was chosen. The PMMA colloidal solution or the PMMA/acetone solution was applied onto both sides of the PE separator by a dip-coating process. The separator was then dried at room temperature to evaporate the solvent and was further vacuum dried at 50 °C for 12 h. The final thickness of the PMMA-coated separators was determined to be around 25 μm.

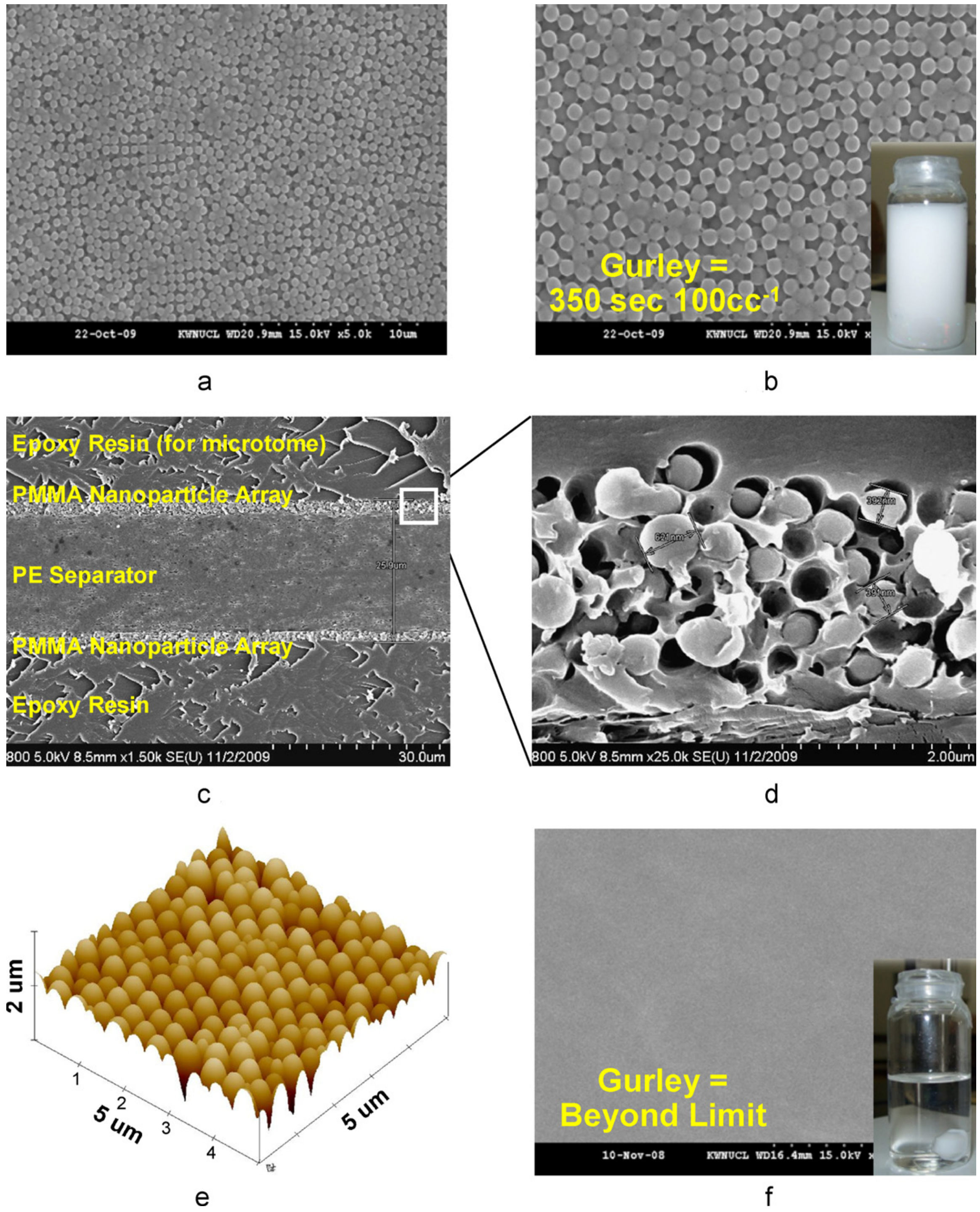

Fig. 1. Morphological characterization of PMMA nanoparticle arrays-coated separator: (a) and (b) FE-SEM photographs (surface); (c) and (d) FE-SEM photographs (cross-section); (e) an AFM photograph. (f) A FE-SEM photograph (surface) of PMMA dense layer-coated separator. Insets demonstrate PMMA nanoparticle colloidal solution and PMMA/acetone solution, respectively.

The air permeability of the separators was measured using a Gurley densometer (Gurley). The surface and cross-sectional (epoxy-molded) morphologies of the coating layers were investigated by field emission scanning electron microscopy (Hitachi) and tapping mode-atomic force microscopy (scan range = 5 μm × 5 μm, Digital Instruments). The electrolyte wettability was examined by measuring electrolyte uptake as a function of wetting time. For evaluating the electrochemical performance, a liquid electrolyte of 1 M $LiPF_6$ in EC/DEC (1/1 v/v, Techno Semichem) was used. The ionic conductivity of the separators was measured by carrying out an AC impedance analysis using a VSP classic (Bio-Logic) over a frequency range of 1 to 10^6 Hz. Lithium half-cells (2032-type coin) were assembled by sandwiching the separator between a lithium-metal anode and a $LiCoO_2$ cathode, and then activated by filling the liquid electrolyte. The discharge capacities of cells were examined as a function of discharge current density using a cycle tester (PNE solution). Discharge current densities between 0.2 C (=0.68 mA cm^{-2}) and 2.0 C (=6.80 mA cm^{-2}) were employed at a constant charge current density of 0.2 C under a voltage range of 3.0–4.3 V.

3. Results and discussion

Fig. 1(a) and (b) shows that the self-assembly of PMMA nanoparticles provides the well-ordered, close-packed nanoparticle arrays on the PE separator. This demonstrates that the highly connected interstitial voids are formed between the PMMA nanoparticles. In contrast, the PMMA dense layer (Fig. 1(f)) exhibits neither pores nor interstitial voids. The cross-sectional morphologies shown in Fig. 1(c) and (d) reveal that the coating thickness is around 2–3 μm on each side of the separator and approximately five PMMA nanoparticles are deposited. This novel morphology of the PMMA nanoparticle coating layer was further investigated by carrying out AFM measurements. Fig. 1(e) confirms the formation of the well-connected interstitial voids between the close-packed PMMA nanoparticles. These nanosized interstitial voids are expected to play a key role in improving the electrolyte wettability and ionic conduction. This unique porous structure of PMMA nanoparticle coating layer was quantitatively characterized by measuring the air permeability, i.e. the gurley value, of the separators. The gurley value of the PMMA nanoparticle arrays-coated separator was found to be 350 s 100 cc^{-1}, which is slightly higher than that (=240 s 100 cc^{-1}) of the pristine PE separator. Meanwhile, the gurley value of the PMMA dense layer-coated separator was too high to be determined, i.e. it was beyond the measuring limit of the instrument. The air permeability represented by the gurley value is considered to be a useful property for quantitatively characterizing the porous structure of separators, where a low gurley value indicates high air permeability, reflecting a highly developed porous structure [1,2]. Thus, the low gurley value of the PMMA nanoparticle arrays-coated separator confirms the successful formation of the porous structure in the PMMA nanoparticle coating layer.

The electrolyte uptake of the PMMA nanoparticle arrays-coated separator was compared with that of the PMMA dense layer-coated separator as well as the pristine PE separator as a function of wetting time. Fig. 2(a) shows that similar to the pristine PE separator, the PMMA nanoparticle arrays-coated separator is quickly wetted by the liquid electrolyte and its electrolyte uptake becomes saturated in a very short wetting time. On the other hand, the PMMA dense layer-coated separator requires relatively long time, which is measured to be about 60 s to reach the saturated level of electrolyte uptake. This improvement in the liquid electrolyte wettability of the PMMA nanoparticle arrays-coated separator was further confirmed by observing the surface immediately after dropping liquid electrolyte onto the separator. Fig. 2(b) clearly shows that the PMMA nanoparticle coating layer is highly effective in absorbing the liquid electrolyte as compared to the PMMA dense coating layer. This fast and facile electrolyte uptake of the PMMA nanoparticle coating layer is attributed to its unique nanosized porous structure, i.e. the well-connected interstitial voids. In the case of the PMMA dense layer, its electrolyte wetting proceeds through the free volume of PMMA [2,3,6]. In contrast, in the PMMA nanoparticle coating layer, the electrolyte can be soaked preferentially through the well-connected interstitial voids, possibly driven by the capillary force of the nanosized pores. Another interesting finding is that the PMMA nanoparticle arrays-coated separator shows larger amount of electrolyte uptake (~200%), as compared to the PMMA dense layer-coated separator (~140%) as well as the pristine PE separator (~120%). This difference in the electrolyte uptake is also attributed to the well-developed porous structure of the PMMA nanoparticle coating layer, because a porous structure of gel polymer electrolytes can generally absorb larger amounts of liquid than a dense structure [13,14]. As lithium-ion polymer batteries rapidly expand to new applications such as electric vehicles and power tools that generally necessitate large-sized batteries, fast and uniform wetting of liquid electrolyte over the whole separators poses a major challenge. In this regard, this unique porous structure of the nanoparticle coating layer can be a promising solution to improve the liquid electrolyte wettability of gel polymer electrolyte-coated separators.

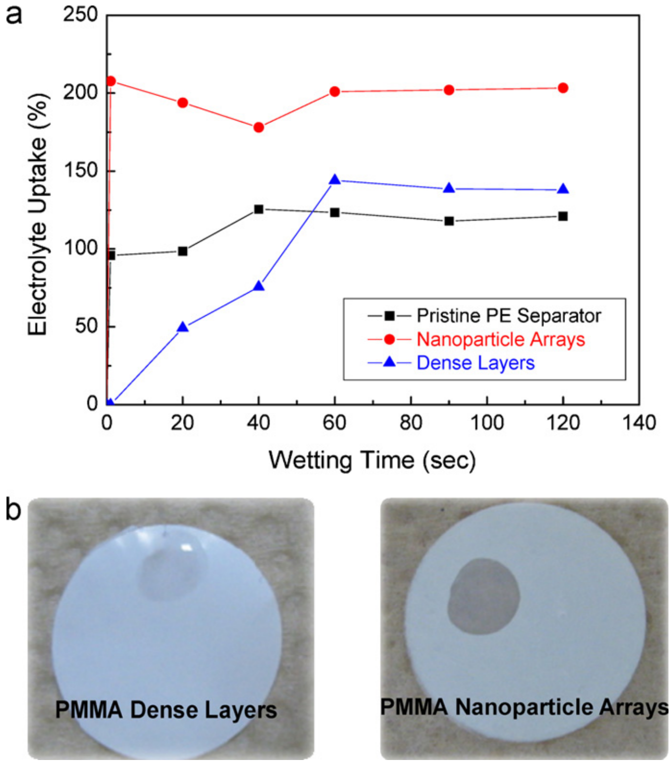

Fig. 2. (a) Liquid electrolyte uptake of pristine PE separator, PMMA nanoparticle arrays-coated separator, and PMMA dense layer-coated separator as a function of wetting time. (b) Comparison of liquid electrolyte wetting behavior between the different separators.

Finally, we investigated the effect of the morphological difference between the coating layers on the electrochemical performance of cells. Fig. 3 shows that the discharge capacities of the PMMA-nanoparticle arrays-coated separator seem to be comparable to those of the pristine PE separator. This indicates that the PMMA-nanoparticle array coating layer hardly hinders the ionic conduction, owing to its well-developed nanoporous structure. An intriguing finding is that the PMMA nanoparticle arrays-coated separator presents higher discharge capacities than the PMMA dense layer-coated separator. This difference in the discharge capacity between the two separators becomes larger with the increase of discharge current density where the influence of ionic transport on the ohmic polarization (i.e., IR drop) of cells is more significant. This improvement in the discharge C-rate performance could be explained by examining the ionic conductivity of the separators. The ionic conductivities for the two different separators are respectively observed to be 0.52 mS cm^{-1} for the PMMA nanoparticle arrays-coated separator and 0.31 mS cm^{-1} for the PMMA dense layer-coated separator. The schematic representations illustrating the structure and ionic transport of the separators are also given in the insets of Fig. 3. The well-developed interstitial voids of the PMMA nanoparticle array coating layer are believed to allow for the higher ionic conductivity, which thus contributes to improving the discharge performance of cells.

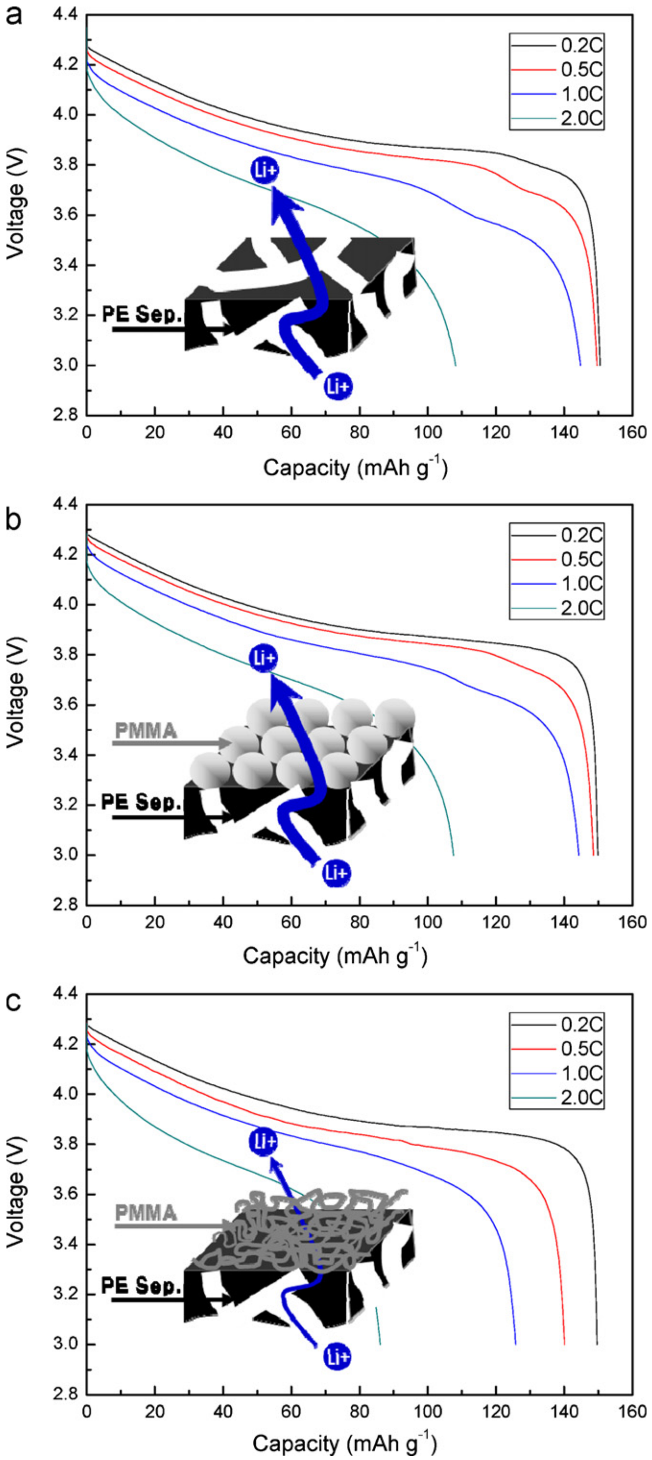

Fig. 3. Discharge profiles of cells assembled with: (a) pristine PE separator, (b) PMMA nanoparticle arrays-coated separator, and (c) PMMA dense layer-coated separator, where insets show the schematic representation illustrating the structure and ionic transport of the separators (bold arrows signify more facile ionic transport).

4. Conclusion

The close-packed PMMA nanoparticle arrays-coated separators have noticeably improved the discharge C-rate performance of cells, as compared to the conventional PMMA dense layer-coated separators. The PMMA nanoparticle coating layer was featured with the highly ordered nanoporous structure, i.e. well-connected interstitial voids. This unique morphology afforded the favorable liquid electrolyte wettability and facile ionic conduction, both of which were considered key factors in improving the discharge C-rate performance of cells. A noteworthy achievement of this study was to provide a new insight into the nanostructure control of gel polymer electrolytes for lithium-ion polymer batteries demanding high-power density.

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References

[1] P. Arora, Z. Zhang, Chem. Rev. 104 (2004) 4419.
[2] A.M. Stephan, Eur. Polym. J. 42 (2006) 21.
[3] J.Y. Kim, S.K. Kim, S.J. Lee, S.Y. Lee, H.M. Lee, S. Ahn, Electrochim. Acta 50 (2004) 363.
[4] T. Yamamoto, T. Hara, K. Segawa, K. Honda, H. Akashi, J. Power Sources 174 (2007) 1036.
[5] Y.M. Lee, J.W. Kim, N.S. Choi, J.A. Lee, W.H. Seol, J.K. Park, J. Power Sources 139 (2005) 235.
[6] M.M. Rao, J.S. Liu, W.S. Li, Y. Liang, D.Y. Zhou, J. Membr. Sci. 322 (2008) 314.
[7] J.Y. Kim, Y. Lee, D.Y. Lim, Electrochim. Acta 54 (2009) 3714.
[8] K.E. Mueggenburg, X.M. Lin, R.H. Godsmith, H.M. Jaeger, Nat. Mater. 6 (2007) 656.
[9] K.M. Kulinowski, P. Jaing, H. Vaswani, V.L. Colvin, Adv. Mater. 12 (2000) 833.
[10] Jiang, S. Markusya, Y. Pikus, V.V. Tsukuruk, Nat. Mater. 3 (2004) 721.
[11] X. Du, J. He, J. Appl. Polym. Sci. 108 (2008) 1755.
[12] F. Bai, X. Yang, W. Huang, J. Appl. Polym. Sci. 100 (2006) 1776.
[13] J.H. Cao, B.K. Zhu, Y.Y. Xu, J. Membr. Sci. 281 (2006) 446.
[14] Z. Tian, X. He, W. Pu, C. Wan, C. Jiang, Electrochim. Acta 52 (2006) 688.