Electronic Supplementary Information for:

A facile method for construction of a functionalized multi-layered separator to enhance cycle performance of lithium manganese oxide

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Experimental

1. Preparation and characterization of multi-layered separator

Silica (SiO_2, Evonic) coated poly(ethylene) (PE, Ashahi Kasei) separator was prepared by dip-coating method in a acetone solution consisting with SiO_2 and PVdF-HFP (kynar 2801, MW: 470,000) with 1:1 ratio (The total solid contents is 2.5 wt.%). 1g of PVdF-HFP was dissolved in 80ml of acetone then 1g of SiO_2 is finely dispersed by Filmix (Primix). Then, the bare PE separator was dipped in a coating solution and dried at room temperature for 24 h. The TEOS-coated separator was prepared by dip-coating in a tetraorthosilicate (TEOS, Aldrich, 98%). Coating solution was prepared by addition of 40ml TEOS and then the SiO_2-coated PE separator was immersed for 24 h to proceed condensation reaction sufficiently. Then, the separator was dried at room temperature for 12 h to remove residual chemicals such as TEOS and alcohol (side product). The morphology of separators was observed by field-emission-scanning electron microscope (FE-SEM, Thermo keytex) after PT coating. For characterization of surface functionalities, separators were analyzed by Fourier Transform Infrared (FT-IR, Bruker-Vertex70) by transmittance mode. The electrolyte uptake was obtained by measuring the weight of separators with a certain area before and after liquid electrolyte soaking for 1 h and then calculated using an Eq. (1):

$$\text{Electrolyte uptake (\%)} = [\ (W_f - W_i) - 1\ ] \text{ X } 100 \qquad (1)$$

where W_i and W_f are the weight of the PE separators before and after soaking, respectively. The Gurley number of separators were measured by a Gurley-type densometer (Toyoseiki). The ionic conductivity of separators were obtained using a symmetry cell consisting with two Li-metal electrodes by measurement for electrolyte resistance (AC impedance technique using Solatron 1280C over frequency range from 0.1 Hz to 20,000 Hz with an amplitude of 10 mV). Then, the ionic conductivity was calculated by the relation $\sigma = d/RA$, where d and A are thickness and area of the separator, respectively, and R is electrolyte resistance obtained from the AC impedance test.

2. *Electrochemical experiments and analysis*

For preparation of anodes, a mixture of the graphite, super P, carboxymethyl cellulose (CMC (Cellogen), DKS) and styrene-butadiene rubber (SBR (BM 400B), Zeon) (96:1:1:2, weight ratio) was dispersed in distilled water. Then, the slurry was coated on a piece of copper foil, and the resulting electrode plates were dried in a vacuum oven at 120 °C for 12 h. For preparation of cathodes, a mixture of the $LiMn_2O_4$, PVdF (KF1100, Kureha) and Super P (92:4:4, weight ratio) was dispersed in N-methyl-2-pyrrolidone (NMP). Then, the slurry was coated on a piece of aluminum foil, and the resulting electrode plates were dried in a vacuum oven at 120 °C for 12 h.

Galvanostatic discharge-charge cycling was performed with a pouch-type cell (34 mm X 50 mm size) assembled with anode, cathode, electrolyte (EC:EMC=1:2 (volume %) with 1M $LiPF_6$) with a variation of separator (bare PE, PE-SiO_2 and PE-TEOS separator). To confirm an action of HF scavenger on separator, additional water was added to the electrolyte at a level of 1000 ppm to stimulate generation of HF in electrolyte. They were galvanostatically charged to 4.2 V vs. Li/Li+ and discharged to 3.0 V vs. Li/Li^+ repeatedly with a constant current of 0.5 C. After galvanostatic cyclings were completed, the cells were dismantled in an argon-filled glove box with < 0.5 ppm of H_2O and <1 ppm of O_2 then electrodes and separators were washed with fresh dimethyl carbonate (DMC). The surface morphologies of separator was analyzed by FE-SEM and their chemical functionality was characterized by FT-IR by transmittance mode under N_2 atmosphere in a dry room where dew points were less than -60 ^{o}C. The quantitation of Mn-ion for anode and separator was performed by ICP-MS (Bruker).

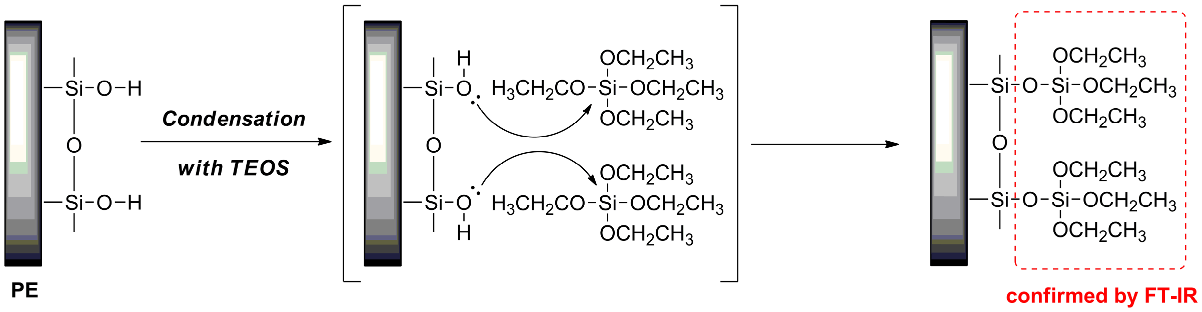


Fig. S1: Mechanism for condensation reaction of alcohol (in interlayer) with TEOS.

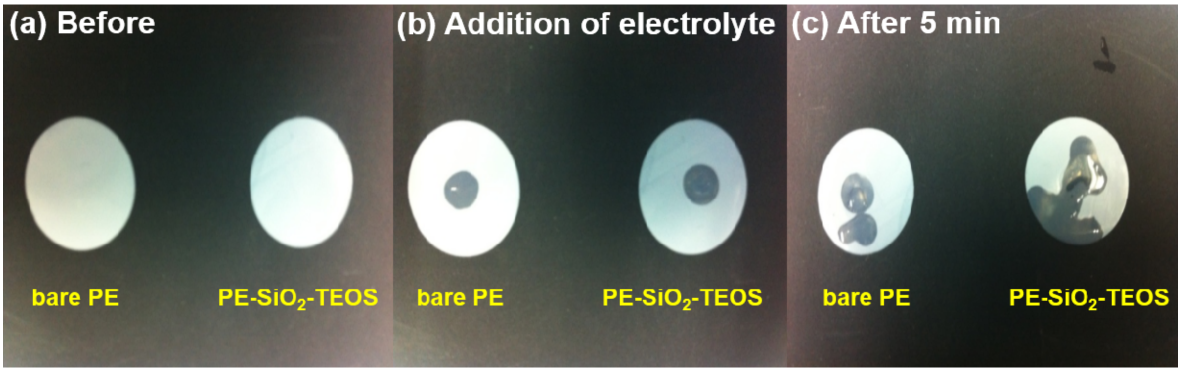


Fig. S2: Wettability test for bare PE (left) and PE-SiO_2-TEOS separator with electrolyte (EC:EMC=1:2 + 1M $LiPF_6$) (a) before electrolyte addition (b) addition of electrolyte (c) after 5 min.

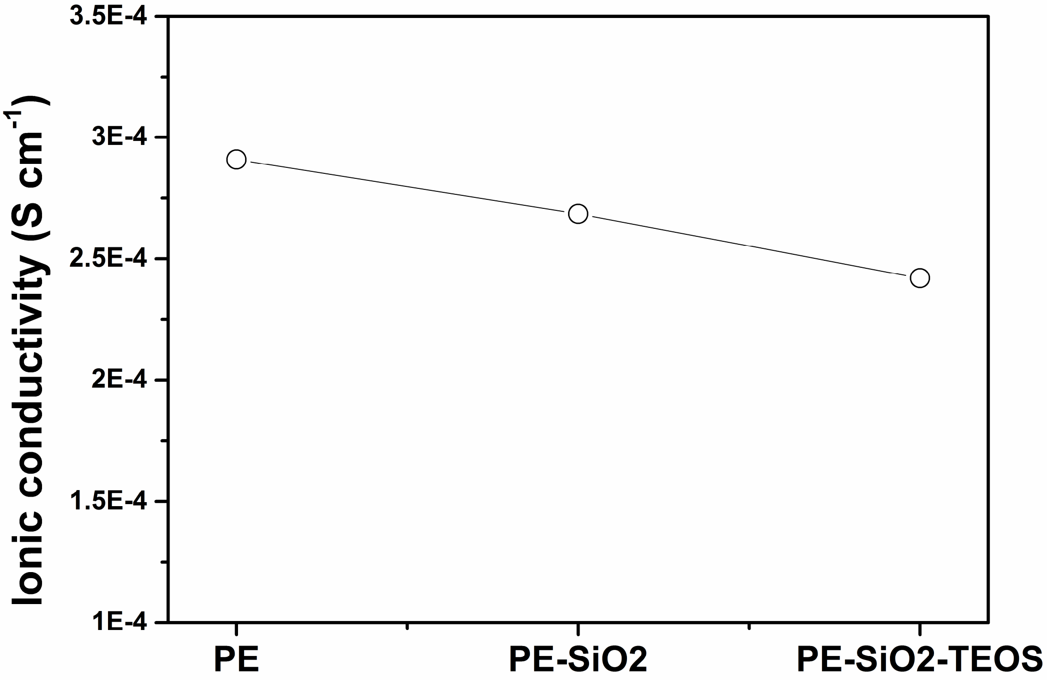


Fig. S3: Ionic conductivity for bare PE, PE-SiO_2 and PE-SiO_2-TEOS.

The ionic conductivity of separators were obtained using a symmetry cell consisting with two Li-metal electrodes by measurement for electrolyte resistance (AC impedance technique using Solatron 1280C over frequency range from 0.1 Hz to 20,000 Hz with an amplitude of 10 mV). According to results, the ionic conductivity was calculated by the relation σ = d/RA, where d and A are thickness and area of the separator, respectively, and R is electrolyte resistance obtained from the AC impedance test.

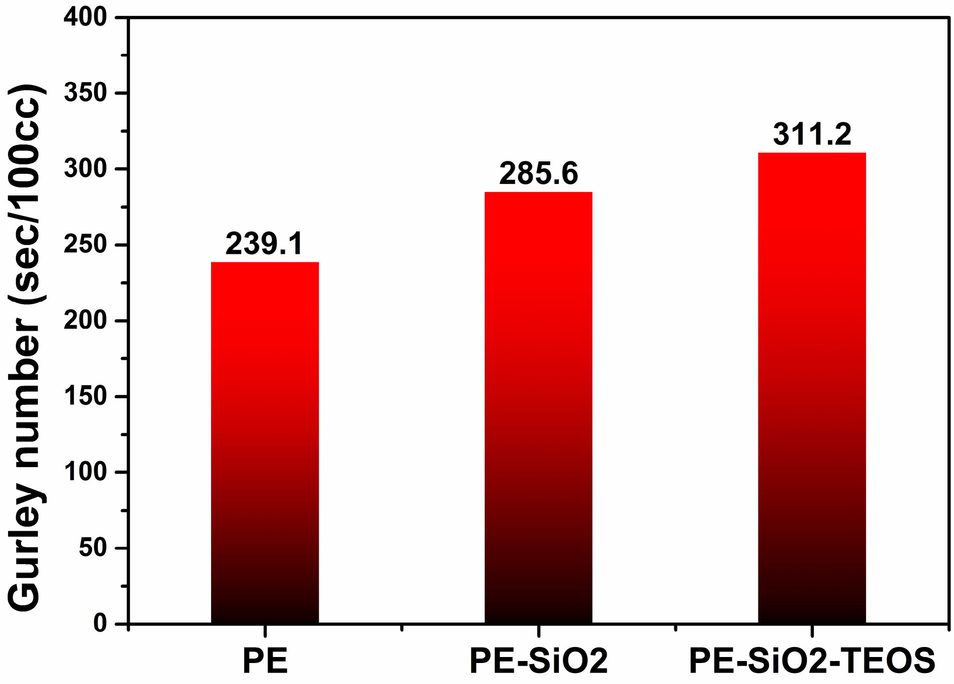
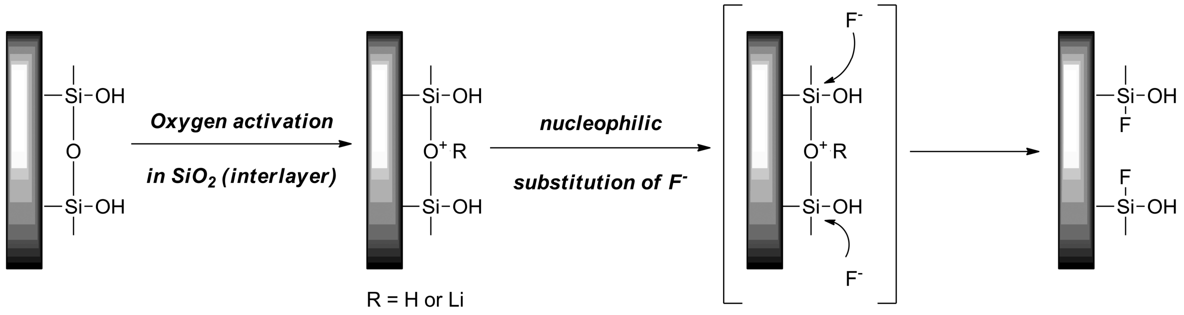


Fig. S4: The results for Gurley numbers of separators (air permeability tests). The Gurley numbers were estimated by measurement of the times required for 100 cc air to pass through a specific area of a separator.

a) Mechanism for HF scavenging



b) Undesired reaction with $LiPF_6$

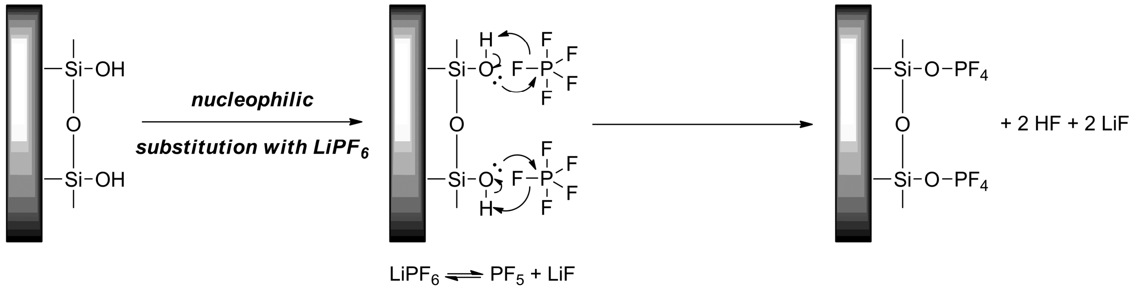


Fig. S5: (a) Desired mechanism for chemical reaction between SiO_2 and HF, (b) Undesired reaction mechanism between SiO_2 and $LiPF_6$.