Electronic Supplementary Information

Highly Lithium-ion Conductive Battery Separators from Thermally Rearranged Polybenzoxazole[†]

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1. Materials

Hydroxyl copolyimide was synthesized from three monomers: 4,4'-oxydiphthalic anhydride (ODPA, Shanghai Resin factory Co. Ltd., China), 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB, Central Glass Co. Ltd., Japan) and 4,4'-oxydianiline (ODA, Central Glass Co. Ltd., Japan). N-Methyl-2-pyrrolidinone (NMP) and o-xylene (Sigma-Aldrich Chemical Co. Milwaukee, WI, USA) were used as solvents for polymer synthesis. For particle production, NMP was used as solvent, while methanol, ethanol and isopropanol (Sigma-Aldrich) and deionized water (DI water) were used as non-solvents. Poly(vinyl pyrrolidone) (PVP, Sigma-Aldrich) with average molecular weight (Mw) of 40,000, was used as a surfactant.

2. Synthesis of polymer
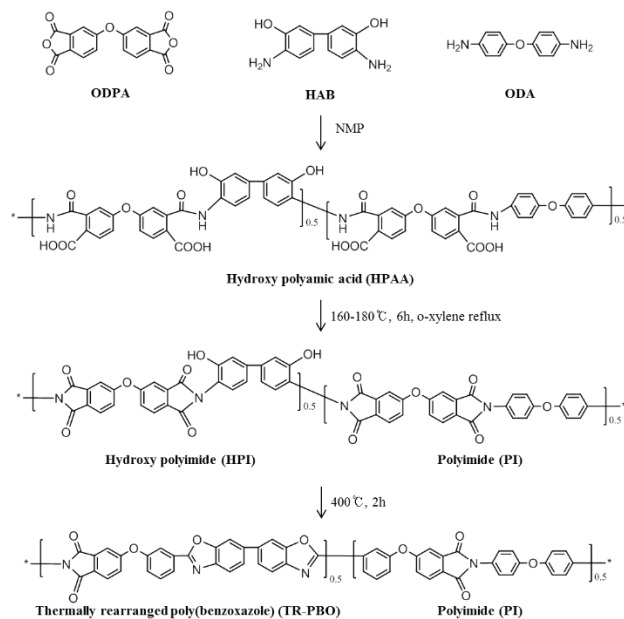
Scheme S1 Schematic diagram of the synthesis for thermally rearranged polybenzoxazole-co-imide

2.1 Hydroxyl copolyamic acid (HPAA) synthesis

HPAAs were synthesized by polycondensation as previously described.[10] Monomers (ODPA, HAB, and ODA) were vacuum dried overnight. 15 mmol of diamines (ODA and HAB) were poured into a four-neck-round-bottomed flask under a nitrogen atmosphere and then anhydrous NMP was added to dissolve the diamines. The resulting diamine solution was cooled and maintained below 10 °C using a chiller. 30 mmol of ODPA monomer was added into the flask to react with the diamines with additional NMP (a total of 60 mL). The solution was stirred for 12 h and it finally became a viscous yellowish HPAA solution.

2.2 Hydroxyl copolyimide (HPI) synthesis

Azeotropic imidization converts the HPAA solution to HPI solution by the following procedure. 60 mL of o-xylene was poured into the HPAA solution, while the temperature was maintained between 160-180 °C for 6 h to fully convert the amic acid groups into imide groups. After removing eliminated water, the solution became a viscous brownish HPI solution, which was precipitated in a 3:1 ratio of water/methanol solution by using a mechanical mixer to effectively remove solvents. After washing the precipitated HPI polymer overnight, it was washed again in fresh water/methanol solution for 4 h, and then subsequently in deionized water several times. The HPI polymer was vacuum dried at 150 °C for 12 h. Average molecular weights (Mw) of two batches of synthesized polymer measured by gel permeation chromatography (GPC) in tetrahydrofuran (THF) were 250,000 and 210,000 Da.

3. Fabrication of electrospun HPI copolymer membrane

A 10 wt% of HPI, prepared in Section 2.2 above, in dimethyl acetamide (DMAc, Sigma-Aldrich Chemical Co. Milwaukee, WI, USA) solution was stirred overnight at 50 °C to obtain a homogeneous state, then filtered through a 11 μm nylon net filter (Millipore) in a pressure holder (Millipore, USA) using N_2 gas. A commercial multi-needle electrospinning device (M-tek, Korea) was set with 16 needles (23 gauge), with a 15 cm tip-to-collector distance, drum-type collector covered with PET non-woven fabric. The HPI copolymer solution was electrospun at 28 kV and -4 kV

charged to needles and collector, respectively, with 4.0 mL/h of total flow rate of the HPI solution using a syringe pump. To obtain uniform electrospun membrane (referred to as ESM), the needles were moved in a cycle with 10 mm/min in a 25 cm range of rail. The total volume of HPI solution for electrospinning was 40 mL and total area of collector is 2100 cm^2. After electrospinning, the HPI copolymer membrane was air dried overnight to remove residual solvents. Dried membrane was detached very carefully from the PET nonwoven support and pressed with Teflon and rubber sheets both sides at 130 °C with 150 bar for 2~3 s.

4. Synthesis of HPI copolymer nanoparticles

HPI copolymer prepared in Section 2.2 above were fabricated to prepare nanoparticles by a reprecipitaion method as previously described.[17] HPI copolymer powders were dispersed into NMP at a concentration of 2 wt% with mechanical stirring. After dissolution in NMP, the HPI copolymer solution was filtered using a 0.5 μm PTFE syringe filter. For the surfactant-free microspheres, no additional surfactant was needed. However, to prepare microspheres using surfactant, PVP was added into the prepared solution at the same weight percent of polymers. Water was injected into the polymer solution at a speed of 0.05 mL/min, using a syringe pump (LB-200, Longer pump, China) into the four-neck-bottomed flask with no purge gas, pre-heated at 70 °C by an oil bath and with mechanical stirring at 300 rpm. Depending on the total volume of the final solution, additional stirring was required. After particle formation was completed and stabilized, the flask was quenched in ice water to prevent any aggregation of particles. The particle solution was filtered with pressurized paper filter and centrifuged to wash off the residual solvent and non-solvents. The particles were obtained after freeze drying at 0 °C for 30 h.

5. Fabrication of TR-PBOI composite membrane

The preformed HPI particles (prepared in Section 4 above) were coated onto the electrospun membranes (prepared in Section 3 above) by a spraying method. By thermal treatment, the nano-composite membranes were transformed into thermally rearranged poly(benzoxazole-co-imide) as follows. First, the temperature was increased at a rate of 10 °C/min up to 300 °C and equilibrated for 1 h in a furnace under argon atmosphere to remove residual solvent. The thermal rearrangement step to form poly(benzoxazole) was accomplished at a ramp rate of 10 °C /min to a temperature of 400 °C for 2 h. The conversion procedure was optimized and described in our previous studies[1-2] and in section S6, ESI†.

6. Characterization of membrane
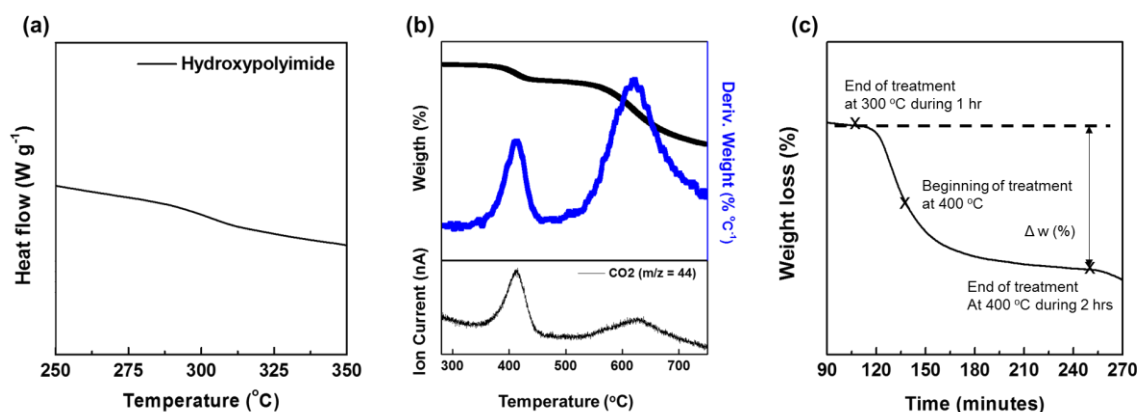
Fig. S1 (a) Differential scanning calorimetry (DSC), (b) thermogravimetry analysis (TGA) and differential thermograms (DTG) curves for HPI precursor which is used in this study with mass curve of CO_2 on the bottom.

To investigate the thermal rearrangement from HPI to PBOI, we used differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) - mass spectroscopy (mass) using 5 mg samples of HPI nanofibrous membranes which was the precursor to TR-PBOI membranes used in this study. DSC curve was obtained at the second heating cycle of two heating-cooling cycles in a range of 50 to 350 °C with a heating rate of 10 °C/min under a nitrogen atmosphere using TA Instruments Q-20 calorimeter. TGA-mass (TA Q-50, TA Instruments, DE, USA and ThermoStar™ GSD 301T, Pfeiffer Vacuum GmbH, Asslar, Germany) was used and heated from 50 °C to 800 °C at 10 °C/min in a TGA furnace under a nitrogen atmosphere. To prove the optimized condition for thermal rearrangement, the HPI pristine membrane was measured at 300 °C for 1 h and 400 °C for 2 h with a 10 °C/min heating rate using TG Q-50. Fig. S1a, ESI† shows HPI has a T_g of around 300 °C which is below the thermal rearrangement temperature (400 °C) selected. To confirm the optimized temperature for thermal conversion, we investigated HPI membrane with TGA-mass analysis. In Fig. S1b, ESI†, the maximum weight loss of sample is occurred at around 400 °C and a CO_2 peak also indicated that the maximum thermal rearrangement rate is around 400

°C, because CO_2 is generated during the process (see Scheme S1, ESI†). Therefore, we carefully determined that the optimized procedure for thermal rearrangement is 300 °C for 1 h to ensure complete removal of residual solvent and heated to 400 °C for 2h to confirm 100 % conversion of HPI to PBO segment. In Fig. S1c, ESI†, we could confirm almost complete TR conversion by comparing weight loss and theoretical calculation using equation (S1);

$$C\ (\%) = \frac{W_{exp.}}{W_{theo.}} \times 100 \tag{S1}$$

where C (%) is the percentage of conversion into the TR-PBO portion, $W_{exp.}$ (%) is the experimental weight loss in the TGA, and $W_{theo.}$ (%) is the theoretical weight loss. The theoretical weight loss of CO_2 is 8.95 % in this study and we obtained 8.78 % weight loss experimentally (Fig. S1c). Therefore, we believe that this evidence supports the thermal conversion of the HPI segment to TR-PBOI.

The porosity of membranes was evaluated by measuring weight changes of membranes in n-hexadecane (Alfa Aesar, MA, USA). Remaining solvent on the surface of the membranes was wiped using filter paper before measuring weight. Porosity values were obtained by averaging at least 5 samples. The porosity was obtained using the following Equation,

$$Porosity\ (\%) = \frac{W_1 - W_0}{\rho \times V_0} \times 100 \tag{S2}$$

where W_1 and W_0 are the weights of polymer membranes before and after soaking in electrolyte, respectively, ρ is the density of n-hexadecane.

The thermal characteristics of TR-PBOI membranes were investigated using thermogravimetric anaylsis (TGA, TA instruments, DE, USA) from 30 °C to 800 °C with a thermal ramp of 10 °C min^{-1} and differential scanning calorimetry (DSC, Q20, TA instruments, DE, USA) from 30 °C to 250 °C and from 250 °C to 30 °C with a ramp of 10 °C min^{-1} under a nitrogen atmosphere.

Surface morphology and roughness of the membranes were characterized with atomic force microscopy (AFM) consisting of a digital instruments Multimode 8 (Veeco, NY, USA) and diNanoScope V controller (Veeco). Before measurement, all membranes samples were dried in a vacuum oven at 120 °C to remove residual water and solvent. The membrane morphology was measured through the tapping mode using a silicon probe (Nanosensors, Switzerland) with a force constant of 1.2 – 20 Nm^{-1}. Surface roughness was measured by Nanoscope 8.10 program and each sample was measured at three different regions of the surface.

The wettability of the separators was measured by a contact angle analyzer (Phoenix 300, S.E.O, Ansung, Korea) by dropping a liquid electrolyte on the separators and comparing pictures taken 0.5 s after the droplet had fallen.

The electrolyte uptake was determined by weight changes of the membranes having an area of 16 cm^2 before (W_0) and after (W_1) immersing membrane into 1.15 M $LiPF_6$ (dissolved in ethylene carbonate (EC) / diethyl carbonate (DEC) (3/7 v/v) solution containing vinyl chloride (VC) for 1 h. The excess electrolyte on the surface of membranes was wiped with filter paper. The electrolyte uptake was then measured using the following Equation,

$$Electrolyte\ uptake(\%) = \frac{W_1 - W_0}{W_0} \times 100 \tag{S3}$$

The solubility parameter was calculated by the Hildebrand method using the following equation;

$$\delta = (\Delta E_v / V)^{1/2} \tag{S4}$$

Also, for calculating the TR-PBOI, correction factors were considered.

Membranes morphologies of TR-PBOI membranes (P1 and P2) were verified with field emission scanning electron microscope (FE-SEM, JEOL JSM-6330F). Membrane morphologies were changed during thermal rearrangement. As seen in Fig. S2, not only membrane color, but also morphological changes were observed. Both the nanofibers and nanoparticles were interconnected each other.
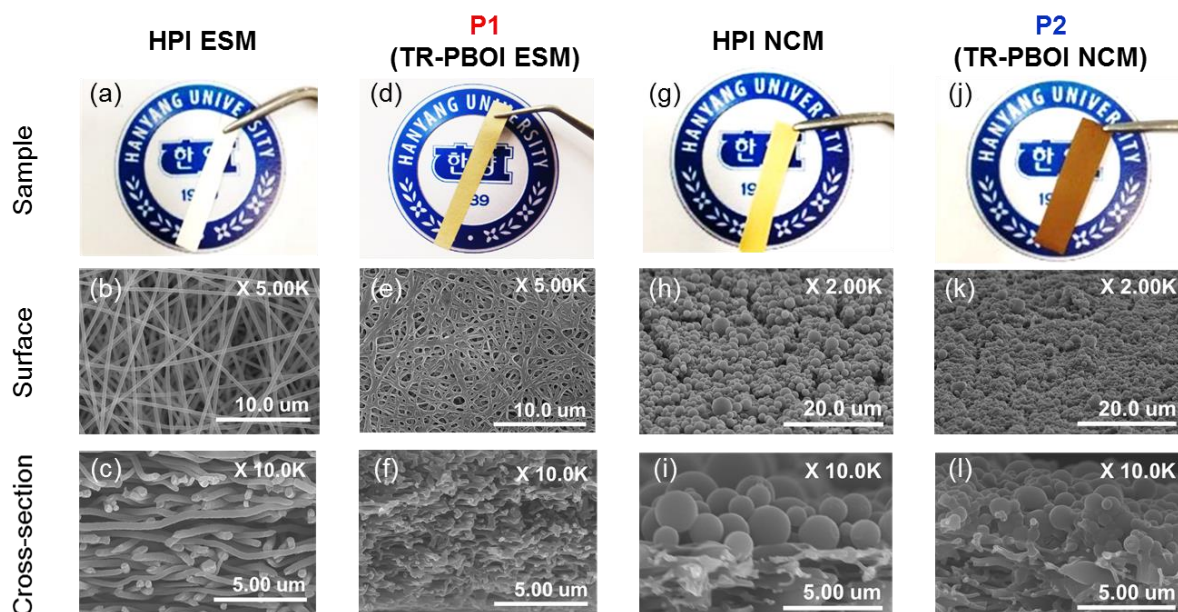
Fig. S2 SEM images of HPI ESM ((b) and (c)), TR-PBOI ESM (P1) ((e) and (f)), HPI NCM ((h) and (i)) and TR-PBOI NCM (P2) ((k) and (l)). After thermal-rearrangement, (e) and (f), nanofibers were interconnected and evolved into TR-PBOI. Similarly, (k) and (l), nanoparticles and nanofibers were merged together and converted into TR-PBOI during thermal treatment. The TR-PBOI nano-composite membrane (P2) was fabricated without binder.

Thermal conversion of TR-PBOI membranes were determined by attenuated total reflectance infrared spectroscopy (ATR-IR, Nicolet 6700, Thermo Scientific, MA, USA). First of all, as seen in Fig. S3, there was no discernable broad and strong band between 3200 cm^{-1} and 3600 cm^{-1} in the spectra of P1 and P2, because the hydroxyl group in HPI copolymer was had previously been converted into polybenzoxazole. Secondly, two imide bands (-C-O) which appeared at 1777 cm^{-1} and 1718 cm^{-1} were observed in all samples. On the other hand, imide bands of P1 and P2 decreased. ODPA-HAB5-ODA5 is a co-polymer of polybenzoxazole (ODPA-HAB) and polyimide (ODPA-ODA). In addition, the characteristic benzoxazole bands appeared at 1052 cm^{-1} and 1475 cm^{-1}.
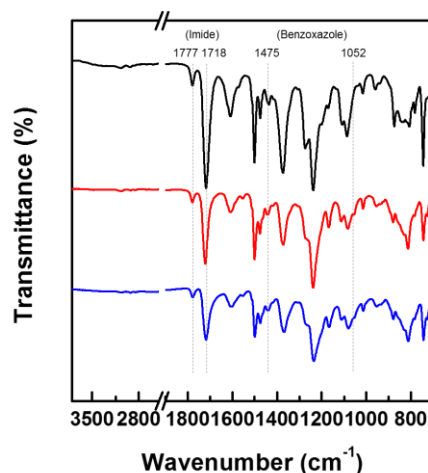

Fig. S3 ATR-FTIR spectra of HPI electrospun membrane (ESM) and TR-PBOI membranes. The black, red and blue lines indicate HPI ESM, P1 and P2 membrane, respectively. (— HPI ESM, — P1 and NCM — P2)

Thermal shrinkage of separators was evaluated by measuring dimensional changes of membranes by inserting them in a pre-heated oven at 90, 110, 130, and 150 °C for 1 h, consecutively. Thermal shrinkage was calculated using the following Equation;

$$\text{Thermal shrinkage (\%)} = \frac{A_0 - A_1}{A_0} \times 100 \qquad \text{(S5)}$$

where A_0 and A_1 is the area before and after heat treatment, respectively.

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The mechanical properties of the membranes were obtained using a testing machine, AGS-J (Shimadzu, Japan), at ambient conditions. ASTM D638-5 was used for testing and each of the samples was measured 5 times following the directions of collector, which are named as machine direction (MD) and transverse direction (TD). When a lithium ion battery cell is manufactured by winding and assembling, the separators which have weak tensile strength should be wound with the electrode mechanically. Therefore, high mechanical strength of separator is required with an adequate elongation property. This is because a separator which has high elongation shows contraction of the width. This implies that high Young's modulus is a key parameter. Furthermore, the mean porosity of the separators was measured by using a capillary flow porometer (CFP-1500-AE, Porous Materials Inc., Ithaca, NY, US).
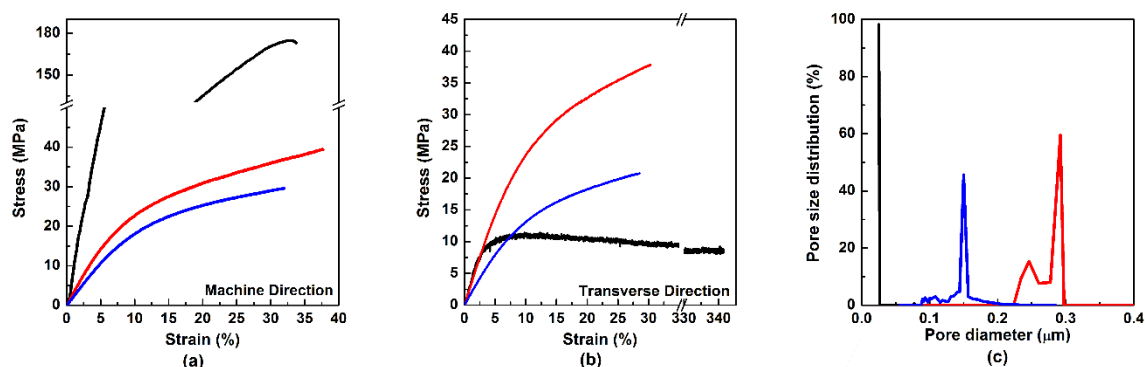

Fig. S4 Mechanical properties and pore size distribution of commercial olefin, TR nanofibrous and nanocomposite membranes. (— Celgard® 2400, — P1 and — P2): (a) mechanical direction, (b) transverse direction and (c) pore size distribution

7. Test for electrochemical performance

For electrochemical testing, PP separator (Celgard® 2400, Charlotte, NC, USA) was used as a reference separator for the non-coated TR-PBOI electrospun membrane (P1) and nanoparticle-coated nano-composite membrane (P2) separators the electrodes and the separators were dried at 100 °C for 20 min before assembly. Coin-type full-cells (CR 2032) were employed to test electrochemical measurement, natural graphite (Welcos, Japan) for the anode, LiCoO$_2$ (LCO, Welcos, Japan) for the cathode, and 1.15 M LiPF$_6$ in EC:DEC (3:7, v/v%, Techno Semichem Co. Ltd., Korea) was applied for the liquid electrolyte. Vinyl chloride (VC) was added to the liquid electrolyte (1.0 wt%) as a solid electrolyte interphase (SEI) forming agent. The mass loading of the active materials was 8.12 mg cm^{-2} and N/P capacity ratio was 1.15.

Charge and discharge cycling tests of the lithium-ion cells were conducted at a constant current of 0.5 C-rate over a voltage range of 3.0-4.2 V using battery test equipment (WBCS 3000, WonATech, Korea).

Electrochemical stability window of the separators was measured using a stainless steel electrode as working electrode and lithium piece as counter and reference electrode and 1.15 M LiPF$_6$ in EC:DEC (3:7, v/v%) as electrolyte in a potential range of 2.0 to 5.5 V at 0.1 mV s^{-1} of scan rate by linear sweep voltammetry (LSV, VMP3, Bio-Logic, France).
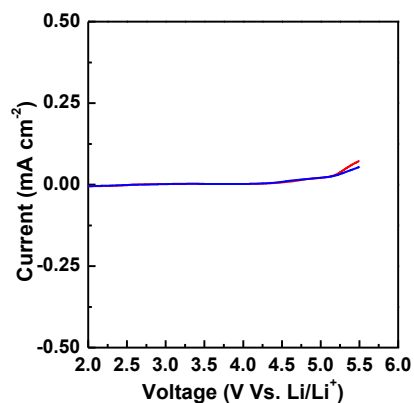
Fig. S5 The electrochemical stability windows of the — P1 and — P2 membranes.

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In Fig. S5, the current flows of P1 and P2 were very small when the voltage was below 5.0 V (vs. Li/Li$^+$), indicating that no decompositions of polymer and electrolyte occurs below this potential. Above 5.0 V (vs. Li/Li+), oxidation occurs because of electrolyte stability[3].

The wetted separator was sandwiched between two stainless steel electrodes for conductivity measurements. AC impedance measurements were performed to measure the ionic conductivity using an impedance analyzer over the frequency range of 10 Hz-100 kHz with amplitude of 10 mV. The ionic conductivities of the separators were determined using the following equation;

Ion conductivity (S/cm) $= l/(R_b \times S)$ (S6)

Here, R_b is the bulk resistance, l and S are the thickness and area of the separator, respectively.

References

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