

## Supporting Information (SI)

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### **Anisotropically Organized LDH on PVDF: A Geometrically Templated Electrospun Substrate for Advanced Anion Conducting Membranes**

*G. S. Sailaja<sup>a</sup>, Peilin Zhang<sup>b</sup>, Gopinathan M. Anilkumar<sup>b</sup>, Takeo Yamaguchi<sup>a\*</sup>*

<sup>a</sup>Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama, Kanagawa 226-8503, Japan

<sup>b</sup> Research & Development Center, Noritake, Co., Ltd., 300 Higashiyama, Miyoshi cho, Miyoshi, Aichi 470-0293, Japan

### **Experimental Section**

*E1. Materials:* All reagents were procured from Wako Pure Chemicals Industries Ltd. (Tokyo, Japan) and used as received unless otherwise stated. PVDF with a molecular weight of 270,000 was purchased from Kureha Corporation (Japan).

*E2. Electrospinning:* PVDF electrospun nanofiber substrates were fabricated from a solution of 20 wt.% PVDF in a mixed solvent. The DMF: acetone weight ratio was maintained as 7:3 using a 'Nanofiber system' (NANON-01A, MECC, Japan). The distance between the needle tip and collecting drum was optimized to 15 cm with an applied current potential of 20 kV to obtain the optimal morphological features. The fibrous substrate formed on the drum collector was dried under vacuum at 130°C for 5 h.

*E3. Geometrical templating of Mg-Al layered double hydroxide (LDH) on electrospun PVDF substrates (Referred to as the PVDF-LDH substrate):* In the optimized procedure, the PVDF electrospun nanofibrous substrate was immersed in a precursor solution composed of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and urea in RO water in the ratio  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} : \text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} = 2.0$  and urea:  $[\text{NO}_3^-] = 4.0$  in a Teflon-lined autoclave reactor, facilitating the organized nucleation and growth of LDH nanocrystals, and allowed to react in an electric oven at  $120^\circ\text{C}$  for 24 h. The LDH-coated PVDF electrospun substrates were recovered, washed by ultrasonication with RO water three times, dried at  $80^\circ\text{C}$  for 2 h and characterized.

*E4. Fabrication of the Anion exchange membrane:* Anion exchange membranes were fabricated by filling poly (vinyl benzyl) trimethylammonium chloride (VBTAC) polyelectrolyte on PVDF as well as PVDF-LDH substrates through ‘impregnation polymerization’ technique. Approximately 24.91 mM of VBTAC monomer was dissolved in 5.27 g of ethanol, and 0.80 g of 10 wt% 2, 2'-Azobis (2-methylpropionamide) dihydrochloride (V 50) was used as an initiator along with 0.4 mM divinyl benzene (1 wt.% cross-linking based on monomer weight). After measuring their dimensions, the substrates were preconditioned by ultrasonication for 30 min in ethanol, followed by impregnation in the monomer recipe for 2 h at  $4^\circ\text{C}$ . They were then carefully placed on Teflon sheets supported by glass plates using binder clips. Polymerization was allowed to take place at  $60^\circ\text{C}$  for 16 h. The fabricated membranes were washed several times using RO water to remove any unreacted monomer and/or excess polyelectrolyte, dried at  $50^\circ\text{C}$  and characterized. The membranes ( $\text{Cl}^-$  form) were converted to their  $\text{OH}^-$  form by treating with  $\text{KOH}_{\text{aq}}$  ( $1 \text{ Mol L}^{-1}$ ), followed by washing in RO water for several hours inside the glove box

to avoid CO<sub>2</sub> poisoning; then, the OH<sup>-</sup> ion conductivity was measured. The pore-filling ratio  $\Phi_f(\%)$  was calculated from Equation (i) below.

$$\Phi_f = \frac{W_{mem} - W_{sub}}{W_{sub}} \times 100$$

where  $W_{mem}$  and  $W_{sub}$  are the dry-weight membrane and substrate (g), respectively.

*E5. Characterization:* The morphological features of PVDF and PVDF-LDH substrates and their corresponding ACMs were acquired using a Hitachi S-4200 scanning electron microscope (SEM) after Osmium coating. The tensile properties were characterized under ambient conditions using a micro tensile testing instrument, Tensile Tester (RTC-1210, Orientec, Okabe, Japan). Contact angle measurement: the surface hydrophilicities of PVDF and PVDF-LDH were measured based on the water contact angle using a NRL contact angle goniometer (CA-DT, Kyowa Interface Science Co., Ltd., Japan) at 25°C and 60% RH.

*E6. Ion-Exchange Capacity measurements:* IEC was measured by an auto-titration method. The Cl<sup>-</sup> forms of the AEMs were converted into their OH<sup>-</sup> form by immersion in a 1 Mol L<sup>-1</sup> KOH solution for 3 h under stirring. The membrane was removed from the solution, and the pH of solution adjusted to 2 (using HNO<sub>3</sub>). Then, the solution was titrated against 0.01 Mol L<sup>-1</sup> AgNO<sub>3</sub> using a potentiometric titrator (COM-1700, Hiranuma Sangyo, Japan).

$$IEC = \frac{\text{mmol of quaternary ammonium groups}}{\text{Molecular weight of unit polymer}}$$

*E7. Ionic conductivity measurement:* The ionic conductivity of AEMs were measured using two-probe AC electrochemical impedance spectroscopy (Solartron 1260, TOYO Corporation, Japan) at a temperature of 30-80°C at RHs of 50% and 100% within the frequency range of 0.01-10<sup>6</sup> Hz. The membrane was clamped between a two-probe cell consisting of two platinum plate electrodes kept 1 cm apart that was mounted on a glass plate. The cell was placed in a thermally controlled humidity chamber (SH-241, ESPEC, Japan) to attain the prescribed temperature and humidity conditions when measurements were performed. The ionic conductivity of the membrane was calculated according to the following equation:

$$\sigma = \frac{d}{R_{\text{bulk}} \cdot l \cdot w}$$

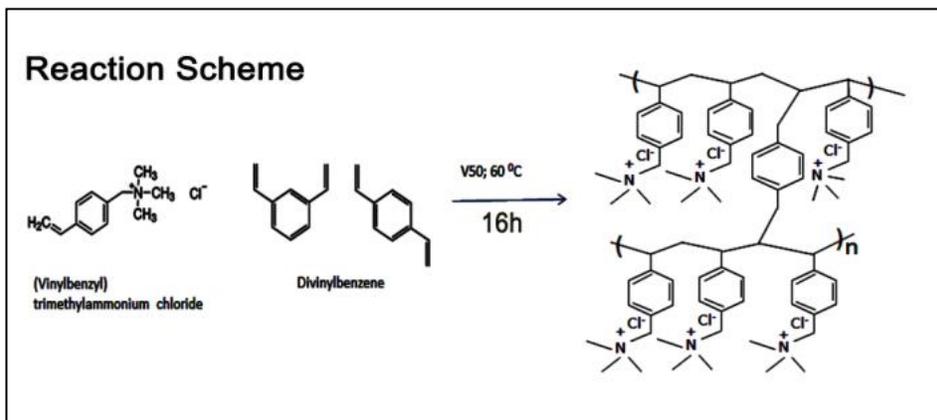
Where  $\sigma$  is the ion conductivity (S·cm<sup>-1</sup>),  $R_{\text{bulk}}$  is the membrane resistance ( $\Omega$ ),  $d$  is the length between two Pt electrodes (cm), and is equal to 1 cm here. ' $l$ ' and ' $w$ ' denote the thickness and width of the membrane (cm), respectively.

*E8. Water uptake measurements:* The amount of water uptake (WU) by the membranes at various time points were measured as follows:

$$\text{WU} = \frac{W_{\text{hyd}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

where,  $W_{\text{hyd}}$  is the hydrated weight of the membrane and  $W_{\text{dry}}$  is the dry weight. The water uptakes were calculated as the average of three replicate membrane samples for each membrane.

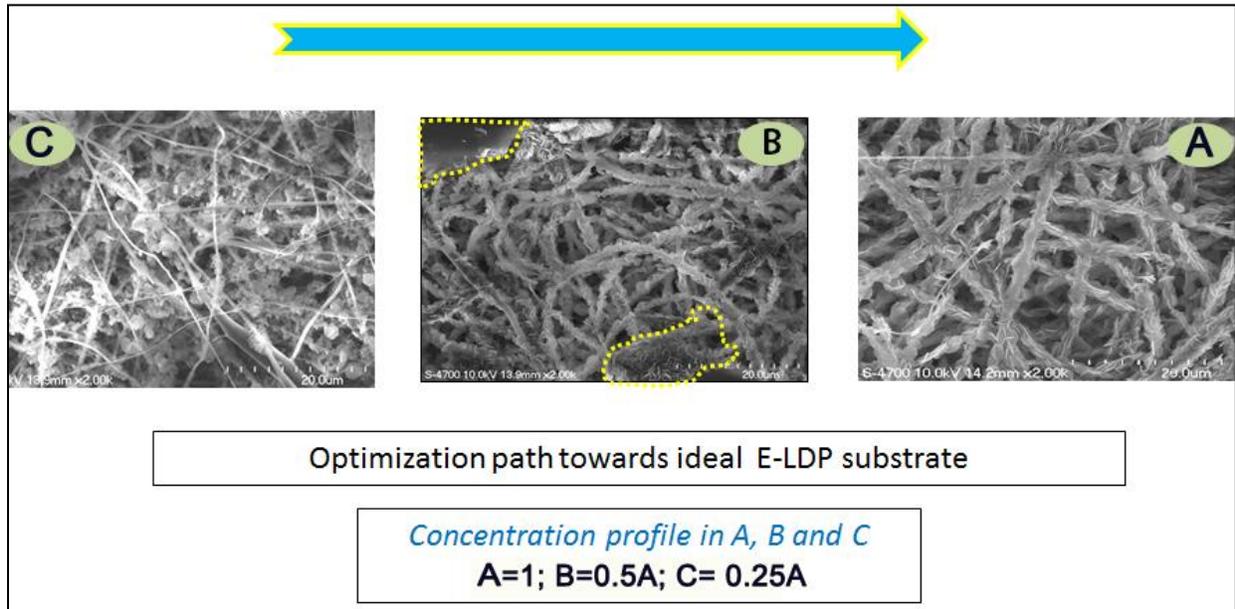
*E9. Accelerated durability evaluation (autoclave test):* The test was performed by treating PVDF and PVDF-LDH substrates and the corresponding anion exchange membranes at 140°C in water in an autoclave for 6 h. Then, their morphological and functional properties were evaluated.



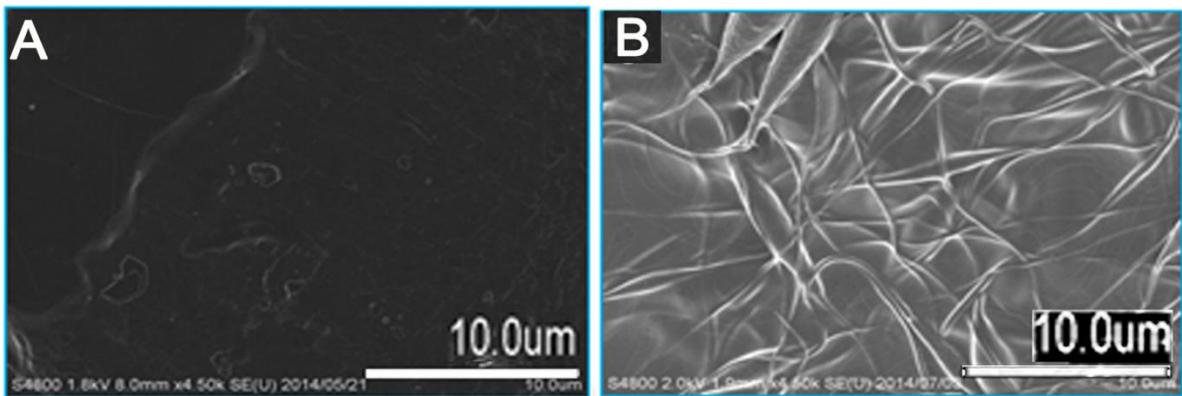
**Scheme S1** Reaction scheme illustrating the *in situ* polymerization of vinyl benzyl trimethylammonium chloride (VBTA) inside the pores of PVDF and PVDF-LDH substrates.

	Component	Type A	Type B	Type C
<b>PVDF</b>	<b>CO<sub>2</sub></b>	59.6	65.4	66.6
	<b>F</b>	25.5	28.3	30.3
<b>LDH</b>	<b>MgO</b>	8.76	3.87	1.27
	<b>Al<sub>2</sub>O<sub>3</sub></b>	6.13	2.47	1.74

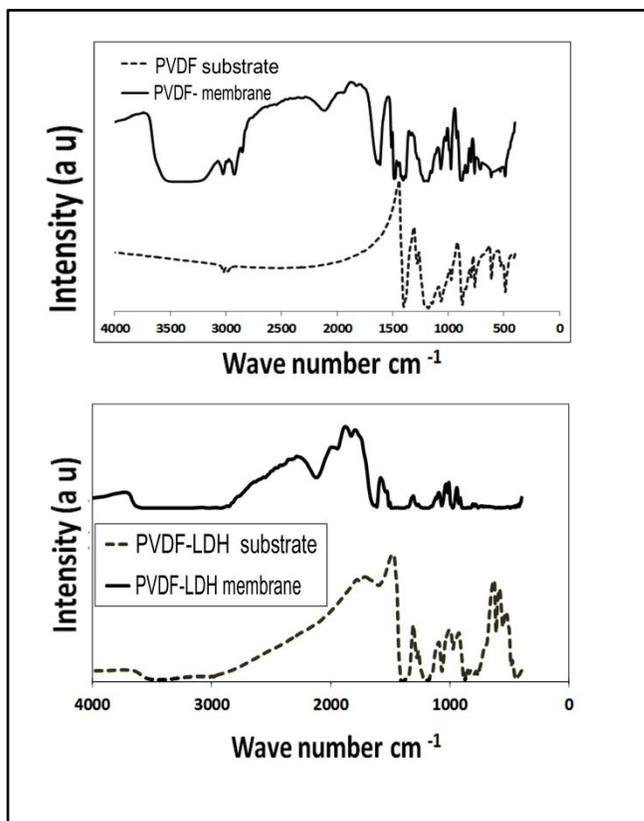
**Table S1:** Component analysis of PVDF-LDH substrates with different compositions (A, B and C) indicating the amount of LDH present as a function of composition, determined by X-ray fluorescence spectrometry.



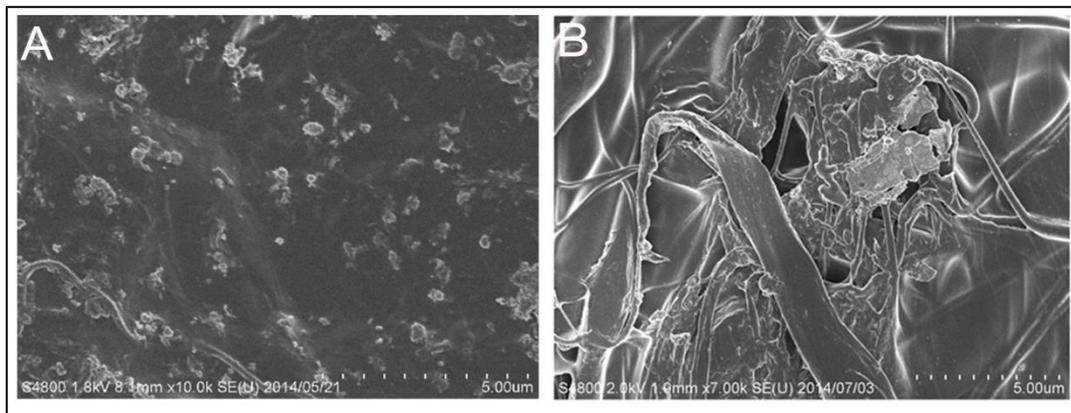
**Figure S1:** Path of optimization of the PVDF-LDH substrate microstructure



**Figure S2:** FESEM images of the surface topography of (A): PVDF-LDH (B): PVDF anion conducting membranes



**Figure S3:** ATR spectra of PVDF and PVDF-LDH substrates and the corresponding pore-filling ACMs with VBTAC polyelectrolyte confirming the presence of VBTAC inside the pores



**Figure S4:** FESEM images of the surface topography of (A): PVDF-LDH (B): PVDF anion conducting membrane after the autoclave test