

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

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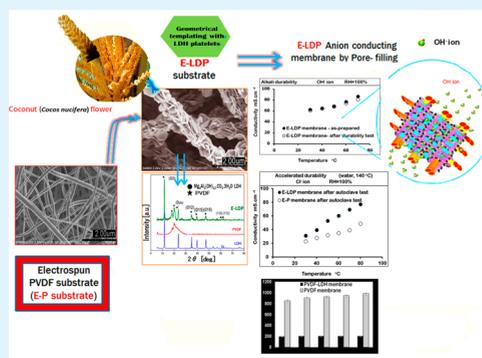
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S Supporting Information

ABSTRACT: A bioinspired geometric templating of an electrospun PVDF substrate with hexagonal platelets of Mg–Al layered double hydroxide (LDH), an intrinsic anion conductor, is presented. The distinctive morphology restructures the internal pore geometry and modulates the dynamic wetting profile of PVDF, transforming it into a highly functional substrate for SAFC anion conducting membranes. The membrane fabricated with PVDF-LDH substrate exhibited exceptionally high durability (>140 °C), high anionic conductivity, ion exchange capacity (IEC), restricted swelling, and improved tensile strength, overcoming critical challenges associated with PVDF electrospun substrates and validating its immense potential as a high-temperature-stable and durable substrate for advanced fuel cell membrane applications.

KEYWORDS: PVDF-LDH substrate, electrospinning, geometric templating, pore-filling anion conducting membrane, solid-state alkaline fuel cell



Organic–inorganic hybrid porous substrates have recently been used in a number of applications, including as separators in batteries,^{1,2} fuel cell electrolyte membrane substrates,³ and electrode materials for supercapacitors.⁴ Among the several fabrication methods adopted including phase-inversion and template-assisted techniques, electrospinning has acquired remarkable interest because of its superior 3D interconnecting configurations, high surface area, and rich variety of morphology.⁵ Nevertheless, their special nonwoven structure, larger pore size (~2 μm), and poor wettability of certain nanofibers remain as unresolved challenges, restricting their applications to mainly milder environments.⁶

The poly(vinylidene fluoride) (PVDF) electrospun substrate, a widely explored partially fluorinated polymer with superior electrochemical and thermal stability, is hindered from advanced applications due to its poor wettability/adhesion properties in addition to its weak nonwoven structure.⁷ Conventional strategies aiming to resolve this problem often altered its surface, thermo-mechanical properties or internal porous structure.^{8–10} Herein, we have envisioned a comprehensive bioinspired approach and designed a micropatterned PVDF electrospun substrate with distinctive geometrically templated hexagonal platelets of hydrotalcite-like (naturally occurring anionic clay) Mg–Al layered double hydroxide (LDH) having a structural formula of $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$. With its unique cationic and brucite-like layered $[M^{2+}_{1-x}M^{3+}_x(OH)_2] [A^{n-}_{x/n} \cdot mH_2O]$ structure, neutralized by anions and water molecules at the interlayer, LDH finds diverse

application as an anion conducting/exchange material and adsorbent as well as in drug delivery.^{11–14} The PVDF-LDH hybrid substrate presented here is morphologically analogous to the *Cocos nucifera* (coconut) flower. The internal pore geometry of the as-prepared PVDF substrate is controlled with a positively contributing template and regulating the dynamic wetting behavior, thereby improving its mechanical properties without compromising any of its favorable functional properties. This unique design and its cumulative functional properties is the first of its kind reported, imparting a synergistic solution to prevailing challenges of electrospun substrates. The design concomitantly overcomes the intrinsic limitations of PVDF, qualifying it for diverse applications that might include its function as a flexible supercapacitor substrate, separators for batteries, and a durable substrate for anion conducting membranes.

As an illustrative application, an anion conducting membrane (ACM) was fabricated with LDH-templated PVDF electrospun substrate (referred to as the PVDF-LDH substrate) for solid-state alkaline fuel cells (SAFCs), a superior source of power generation in the present century. SAFCs have a higher energy density and are more convenient with the specific advantages of employing non-noble metal based catalysts and liquid fuels.^{15–17} Nevertheless, the paramount commercial prospects

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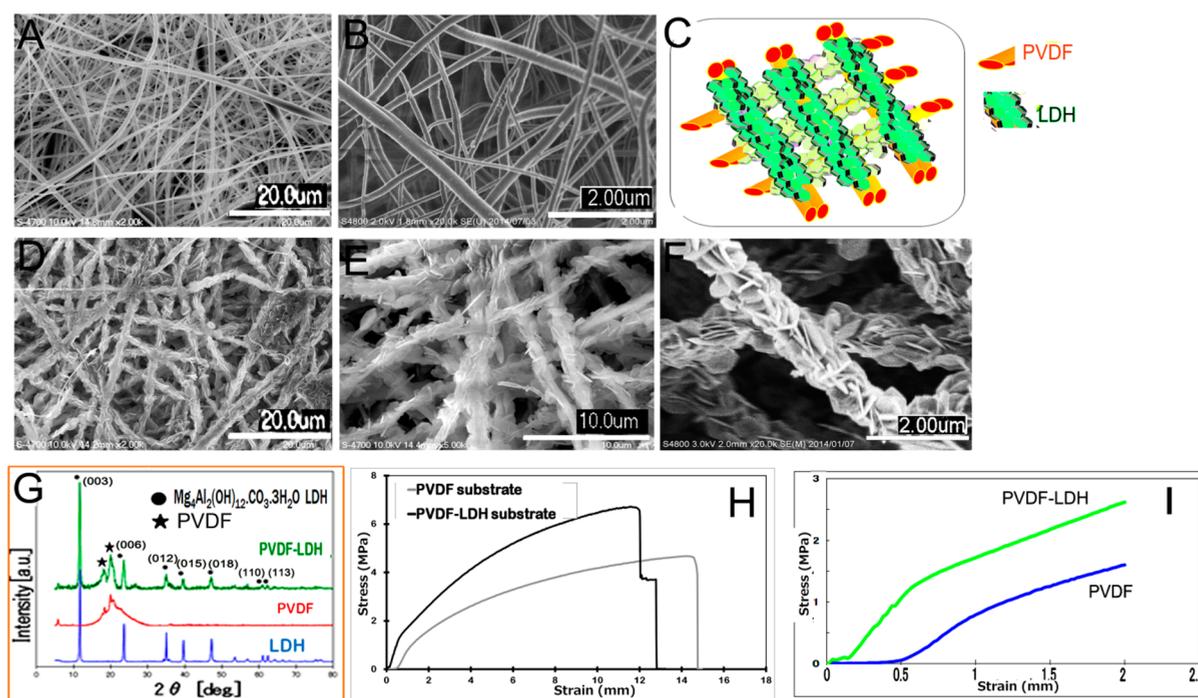


Figure 1. Morphological and functional properties of the LDH-templated PVDF electrospun substrate. (A, B) FESEM images of the as-prepared PVDF electrospun substrate. (C) Illustration of the geometric templating of LDH on the PVDF substrate. (D–F) FESEM images of the PVDF electrospun substrate after geometrical templating with LDH platelets (PVDF-LDH substrate). (G) XRD spectra of the PVDF-LDH substrate demonstrating templated LDH on PVDF. (H) Tensile strength comparison of the as-prepared PVDF electrospun substrate and the substrate after LDH templating. (I) Tensile strength comparison of the as-prepared PVDF electrospun substrate and the substrate after LDH templating at initial phase.

anticipated for SAFCs could be fully realized only by employing a high functional ACM with good durability, the vital component of SAFC that determines hydroxide ion transport. ACMs with higher ionic conductivity and ion exchange capacity (IEC) often elicit high water uptake/swelling, leading to prominent loss of mechanical properties, deteriorating its durability.^{18–20} However, by employing our original “pore-filling concept”, where an inert and thermally stable porous substrate is employed to fill the polyelectrolyte, better dimensional stability, uniformity, mechanical strength, and swelling suppression could be achieved.^{21–25} Conventional porous substrates, such as polyethylene, have a relatively lower temperature stability of <120 °C, highlighting the need for durable, high-temperature-stable, and porous substrates for ACM applications.

Exceptionally high ionic conductivity can be accomplished for fuel cell membranes when electrospun substrates are employed because of a higher amount of polyelectrolyte available in the pores. Nevertheless, redesigning and controlling the pore structure is inevitable in order to transform it into a durable supportive framework. Here, the special pore geometry, unique micropatterning, and intrinsic properties of LDH positively contribute to the hybrid substrate as a durable ACM substrate for SAFC; this is evidenced by the retention of its functional properties after an accelerated durability evaluation at 140 °C in water, improved tensile strength and swelling suppression. Good anionic conductivity is maintained even at a lower relative humidity (RH) of 50%. The PVDF-LDH substrate presented here validates its immense potential as a high-temperature-stable and durable substrate for advanced fuel cell membrane application and simultaneously allows for new opportunities for fabricating several innovative highly

functional products through versatile combinations of filling constituents.

Images A and B in Figure 1 present the morphology and internal structure of the as-prepared PVDF substrate harvested with field emission scanning electron microscopy (FESEM), and Figure 1C presents a schematic illustration of the unique PVDF-LDH substrate micropatterning. Figure 1D–F presents FESEM images demonstrating the anisotropic organization of LDH along the nanofibers of PVDF, corroborated by XRD spectra (Figure 1G), validating the crystal structure of templated $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$ (JCPDS 22–0700) on the PVDF-LDH substrate. The optimized structure of the PVDF-LDH substrate presented in Figure 1D–F was obtained by systematically modulating the templating procedure and altering various parameters, such as the precursor concentration, temperature and duration of the hydrothermal treatment. The variation in morphology as a function of the LDH precursor concentration is provided in Figure S1 in the Supporting Information, and the amount of LDH present in each of these compositions determined by X-ray fluorescence analysis is provided in Table S1 in the Supporting Information. The mechanical property is a fundamental aspect that dictates dimensional stability of the ACM and thus the durability of the membrane electrode assembly (MEA) in a fuel cell. The restructuring of the internal pore-geometry and anisotropic organization of LDH has increased the tensile strength of the PVDF-LDH substrate by nearly 2-fold (7.0 ± 1.0 MPa) when compared to as-prepared PVDF substrate, as shown in Figure 1H,I.

ACMs were fabricated with vinylbenzyltrimethylammonium chloride (VBTAAC),^{26,27} a widely explored and highly conducting anionic electrolyte. The confocal-Raman spectra along the

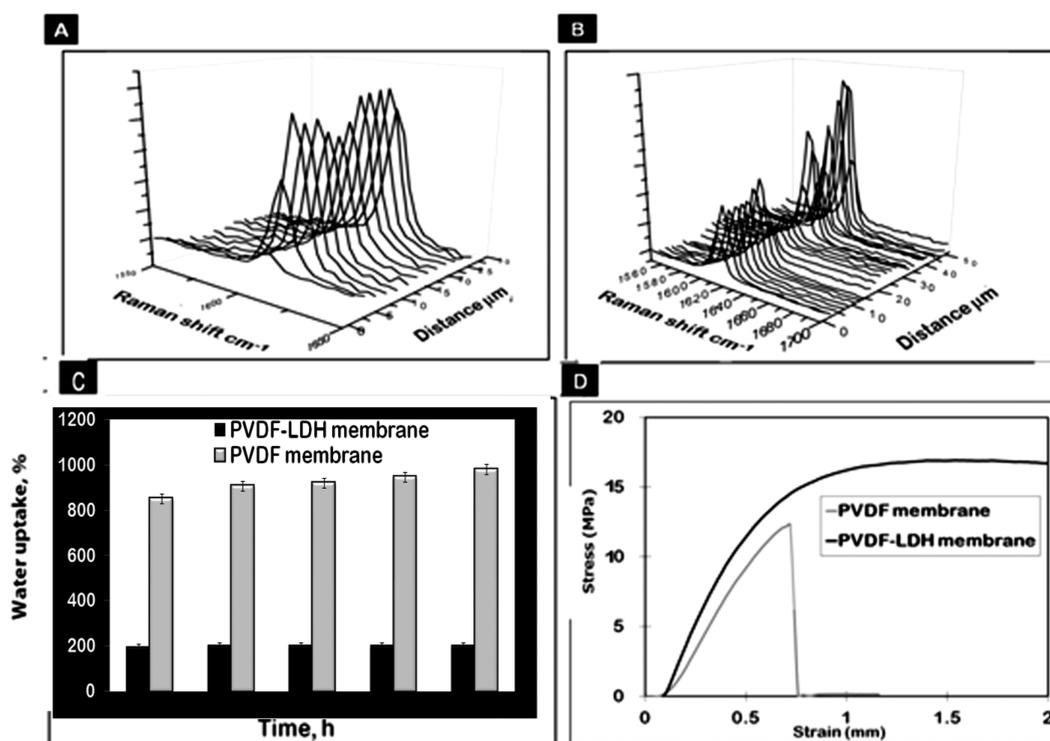


Figure 2. Physical properties of anion conducting membranes fabricated from PVDF and PVDF-LDH substrates. Confocal-Raman spectra of (A) PVDF and (B) PVDF-LDH pore-filling membranes, ensuring pore-filling of VBTAAC. (C) Water uptake comparison of PVDF and PVDF-LDH pore-filling membranes. (D) Tensile strength comparison of PVDF and PVDF-LDH pore-filling membranes.

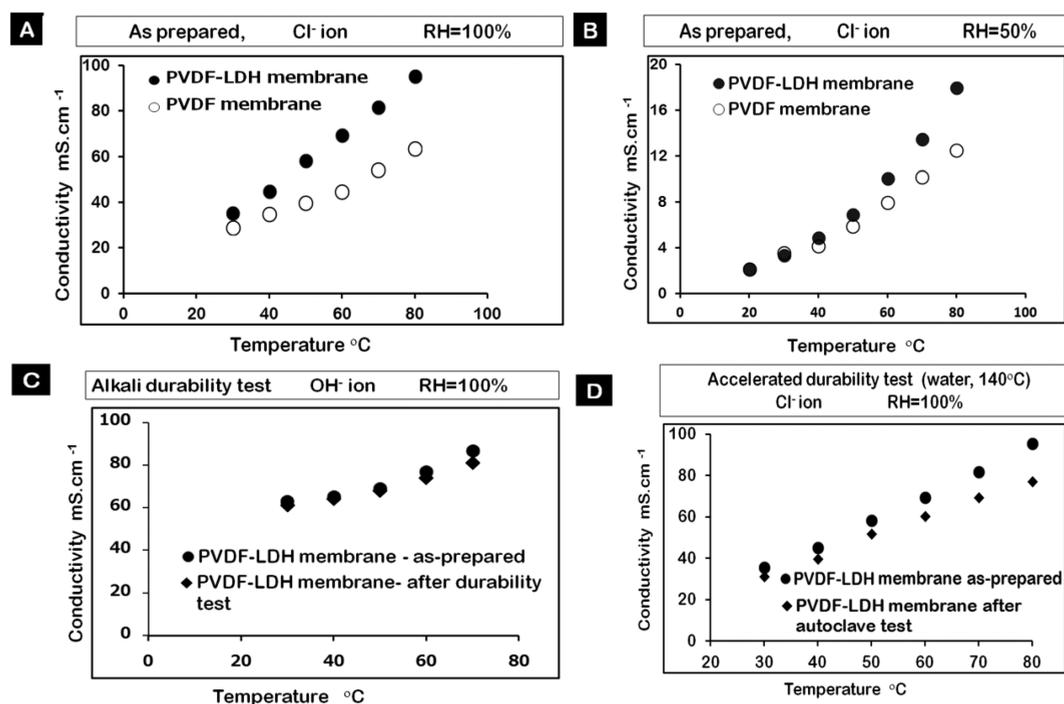


Figure 3. Ionic conductivity and durability profile of PVDF and PVDF-LDH membranes. (A) Cl⁻ ion conductivity of the as-prepared PVDF and PVDF-LDH membranes at 100% RH. (B) Comparison of the Cl⁻ ion conductivities of as-prepared PVDF and PVDF-LDH membranes at 50% RH. (C) OH⁻ ion conductivity of the PVDF-LDH membrane after durability evaluation in a hot alkaline environment (1 M KOH; 60 °C) for 100 h at 100% RH. (D) Ionic conductivity (Cl⁻ ion) of PVDF-LDH membranes at 100% RH before and after the accelerated durability test at 140 °C in water, illustrating the high durability of the membranes.

cross-section of PVDF (Figure 2A) and PVDF-LDH (Figure 2B) pore-filling membranes in the region of 1500 cm⁻¹ to 1700 cm⁻¹ confirm the pore-filling by VBTAAC. The Raman shift at

1610 cm⁻¹, derived from aromatic domains of VBTAAC, confirms the presence of VBTAAC in the pores of the porous substrates, and the uniformity of the relative intensity in the

depth profile is correlated with its filling uniformity. The reaction scheme is provided in the Supporting Information (Scheme S1). The uniform topography for the PVDF-LDH membrane viewed by FESEM micrographs further demonstrates efficient pore-filling (Figure S2A in the Supporting Information). An inhomogeneous surface micro texture was observed for the PVDF membrane (Figure S2B in the Supporting Information), which was attributed to the poor wetting characteristics and larger pore size of the as-prepared PVDF substrate. The PVDF substrate is demonstrated to have a profoundly hydrophobic behavior with a contact angle of 136° , which was lowered significantly to $28\text{--}54^\circ$ by LDH templating and leads to a deep wettability modulation without losing the fundamental thermomechanical properties of PVDF. Increased water uptake adversely affects the durability of the membrane, eventually leading to physical disintegration and loss of mechanical properties. The secondary structure imparted by LDH templating has restricted the water uptake of PVDF-LDH ACM to 1/5 of that of PVDF-VBTAC ACM (Figure 2C), and this remarkable swelling suppression is made possible through effective control of pore-geometry. The LDH templating has also reinforced the tensile strength of the PVDF-LDH membrane by two-fold (14.0 ± 1 MPa), and interestingly exhibits a tougher structure when compared to the PVDF membrane's more brittle nature (Figure 2E). The special functional properties and rich structural diversity of natural organisms are not intrinsically evolved; rather, they are governed by smart micronano topographical features that account for their desirable characteristics.^{28,29} One example of this is the PVDF-LDH microtexture.

The ionic conductivity value of as-prepared PVDF-LDH electrospun mat was measured as 1.2×10^{-6} S/cm at 80°C , at R.H. = 80%, whereas the intrinsic ionic conductivity value of LDH (measured as solid pellet) is 1.9×10^{-4} S/cm at the same condition.¹³ It is to be envisaged that LDH-templated PVDF electrospun mat is characterized by intrinsic micropores and hence unable to function as a continuous conducting channel by itself, reflected as its very low ionic conductivity when compared to LDH pellet.

The ion exchange capacities of PVDF and PVDF-LDH ACMs were experimentally determined to be 2.68 and 2.91 mequiv g^{-1} , respectively, using an autotitrating machine. The high IEC value demonstrates the high anionic conductivity of the PVDF-LDH membrane at both high (100%) and low (50%) RH, illustrated by a Cl^- ion conductivity of 92 mS cm^{-1} at 80°C at 100% RH (Figure 3A) and 18 mS cm^{-1} at 50% RH (Figure 3B). The high OH^- ion conductivity value of the PVDF-LDH membrane, 87 mS cm^{-1} at 70°C (100% RH), was retained in the alkaline environment (1 M KOH; 60°C) for 100 h (Figure 3C); however, the PVDF membrane could not retain its physical integrity after the alkali durability test; thus, its ionic conductivity could not be measured. More significantly, the PVDF-LDH membrane retained its functional properties after an accelerated aging test performed in an autoclave at 140°C for 6 h in an aqueous environment (Figure 3D). The slight decrease in ionic conductivity after the accelerated durability test could be attributed to the decomposition of the VBTAC quaternary ammonium groups occurring at the elevated temperature (140°C). The retention of the physicochemical integrity of the PVDF-LDH membrane, along with the absence of any significant morphological variation (Figure S4A in the Supporting Information), clearly demonstrates its exceptional durability even under harsh

conditions, whereas the larger pore size and inhomogeneous filling of the PVDF membrane leads to severe erosion of the polyelectrolyte as a result of the accelerated durability test (Figure S4B in the Supporting Information).

Poly(vinylbenzyl trimethylammonium chloride) (PVBtAC), the well-known anionic electrolyte, conducts OH^- ions typically through its quaternary ammonium groups.^{26,27,30} In the case of LDH, its intrinsic cationic layered structure has inherent potential to transport OH^- ions through their interlayer channels.¹³ When anion conducting membrane is fabricated by pore-filling PVDF-LDH with PVBtAC, the LDH templating provides an additional channel for movement of OH^- ions through their interlayer spaces in addition to the electrolyte derived ion transport, thereby offering a synergistic ionic conductivity that is absent when conventional PVDF substrate is used. This is well-reflected in the conductivity results.

In conclusion, we have developed a highly functional electrospun PVDF-LDH substrate by modulating the pore geometry and dynamic wetting profile of a nonwoven PVDF substrate with a positively contributing template of Mg–Al layered double hydroxide. The inimitable bioinspired design realized here addresses several prevailing challenges of conventional electrospun substrates with special reference to PVDF, which is validated by the outstanding durability of the PVDF-LDH substrate at 140°C compared to conventional substrates, such as polyethylene. The enhanced mechanical properties, restricted swelling and remarkable anion conductivity even at lower RH (50%) were accomplished without compromising any of the favorable properties of the PVDF electrospun substrate and demonstrate its commercial prospects as a highly functional anion conducting membrane substrate for SAFCs. The enriched versatility and remarkable features of the PVDF-LDH substrate along with its feasibility for easy scale-up is anticipated to provide exceptional functionality as a flexible substrate for supercapacitor use, for battery separators and as durable substrates for filtration/adsorption through the advantageous qualities of the filling constituents.

■ ASSOCIATED CONTENT

📄 Supporting Information

The experimental section, reaction scheme illustrating the in situ polymerization of vinyl benzyl trimethylammonium chloride (VBTAC) inside the pores of PVDF and PVDF-LDH substrates, 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, path of optimization of the PVDF-LDH substrate microstructure, FESEM images of the surface topography of (A) PVDF-LDH, (B) PVDF anion conducting membranes, 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, FESEM images of the surface topography of (A) PVDF-LDH, (B) PVDF anion conducting membrane after the autoclave test. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

Poly(vinylidene fluoride), PVDF
Layered double hydroxide, LDH
Ion exchange capacity, IEC
Solid-state alkaline fuel cell, SAFC

REFERENCES

- (1) Cao, X. C.; Ma, J.; Shi, X. H.; Ren, Z. Effect of TiO₂ Nanoparticle Size on the Performance of PVDF Membrane. *J. Appl. Surf. Sci.* **2006**, *253*, 2003–2010.
- (2) Song, J. Y.; Wang, Y. Y.; Wan, C. C. Review of Gel-type Polymer Electrolytes for Lithium-ion Batteries. *J. Power Sources* **1999**, *77*, 183–197.
- (3) Zhao, Y. H.; Zhu, B. K.; Kong, L.; Xu, Y. Y. Improving Hydrophilicity and Protein Resistance of Poly (vinylidene fluoride) Membranes by Blending with Amphiphilic Hyperbranched-star Polymer. *Langmuir* **2007**, *23*, 5779–5786.
- (4) Bottino, A.; Capannelli, G.; Comite, A. Preparation and Characterization of Novel Porous PVDF-ZrO₂ Composite Membranes. *Desalination* **2002**, *146*, 35–40.
- (5) Cavaliere, S.; Savych, S. S. I.; Jones, D. J.; Roziere, J. Electrospinning: Designed Architectures for Energy Conversion and Storage Devices. *Energy. Environ. Sci.* **2011**, *4*, 4761–4785.
- (6) Asazawa, K.; Yamada, K.; Tanaka, H.; Oka, A.; Taniguchi, M.; Kobayashi, T. A Platinum-Free Zero-Carbon-Emission Easy Fuelling Direct Hydrazine Fuel Cell for Vehicles. *Angew. Chem., Int. Ed.* **2007**, *46*, 8024–8027.
- (7) Hietala, S.; Skou, E.; Sundholm, F. Gas Permeation properties of Radiation Grafted and Sulfonated Poly-(vinylidene fluoride) Membranes. *Polymer* **1999**, *40*, 5567–5573.
- (8) Duca, M. D.; Plosceanu, C. L.; Pop, T. Surface modifications of Polyvinylidene Fluoride (PVDF) under Ar Plasma. *Polym. Degrad. Stab.* **1998**, *61* (1), 65–72.
- (9) Ying, L.; Wang, P.; Kang, E. T.; Neoh, K. G. Synthesis and Characterization of Poly(acrylic acid)-graft-poly(vinylidene fluoride) Copolymers and pH-Sensitive Membranes. *Macromolecules* **2002**, *35*, 673–679.
- (10) Ross, G. J.; Watts, J. F.; Hill, M. P.; Morrissey, P. Surface modification of poly(vinylidene fluoride) by alkaline treatment. *degradation mechanism polymer* **2000**, *41* (5), 1685–1696.
- (11) Williams, G. R.; O'Hare, D. Towards understanding, Control and Application of Layered Double Hydroxide Chemistry. *J. Mater. Chem.* **2006**, *16*, 3065–3074.
- (12) Evans, D. G.; Duan, X. Preparation of Layered Double Hydroxides and their Applications as Additives in polymers, as Precursors to Magnetic Materials and in Biology and Medicine. *Chem. Commun.* **2006**, 485–496.
- (13) Zhang, P.; Sago, S.; Yamaguchi, T.; Anilkumar, G. M. Mg–Al Layered Double Hydroxides Containing Glycine Betaine as Low humidity-Dependent Anion Conducting Electrolyte Material for Solid State Alkaline Fuel Cell (SAFC). *J. Power Sources* **2013**, *230*, 225–229.
- (14) Zhang, P.; Yamaguchi, T.; Nair, B. N.; Miyajima, K.; Anilkumar, G. M. Mg–Al layered Double Hydroxides: a Correlation Between Synthesis-Structure and Ionic Conductivity. *RSC Adv.* **2014**, *4*, 41051–58.
- (15) Varcoe, J. R.; Slade, R. C. T. Prospects for Alkaline Anion-Exchange Membranes in Low Temperature. *Fuel Cells* **2005**, *5*, 187.
- (16) Poynton, S. D.; Kizewski, J. P.; Slade, R. C. T.; Varcoe, J. R. Novel Electrolyte Membranes and Non-Pt Catalysts for Low Temperature Fuel Cells. *Solid State Ionics* **2010**, *181*, 219–222.
- (17) Merle, G.; Wessling, M.; Nijmeijer, K. Anion Exchange Membranes for Alkaline Fuel Cells: a Review. *J. Membr. Sci.* **2011**, *377*, 1–35.
- (18) Luo, Y.; Guo, J.; Wang, C.; Chu, D. Fuel Cell Durability Enhancement by Crosslinking Alkaline Anion Exchange Membrane Electrolyte. *Electrochem. Commun.* **2012**, *16*, 65–68.
- (19) Clark, T. J.; Robertson, N. J.; Kostalik, H. A., IV; Lobkovsky, E. B.; Mutolo, P. F.; Abruna, H. D.; Coates, G. W. A Ring-Opening Metathesis Polymerization Route to Alkaline Anion Exchange Membranes: Development of Hydroxide-Conducting Thin Films from an Ammonium-Functionalized Monomer. *J. Am. Chem. Soc.* **2009**, *131*, 12888–12889.
- (20) Duan, Q.; Ge, S.; Wang, C. Y. Water Uptake, Ionic Conductivity and Swelling Properties of Anion-Exchange Membrane. *J. Power Sources* **2013**, *243*, 773–778.
- (21) Yamaguchi, T.; Miyata, F.; Nakao, S. Polymer Electrolyte Membranes with Pore-filling Structure for a Direct Methanol Fuel Cell. *Adv. Mater.* **2003**, *15* (14), 1198–1201.
- (22) Yamaguchi, T.; Nakao, S.; Kimura, S. Plasma-graft Filling Polymerization: Preparation of a New Type of Pervaporation Membrane for Organic Liquid Mixtures. *Macromolecules* **1991**, *24* (20), 5522–5527.
- (23) Yamaguchi, T.; Hua, Z.; Nakazawa, T.; Hara, N. An Extremely Low Methanol Crossover and Highly Durable Aromatic Pore-Filling Electrolyte Membrane for Direct Methanol Fuel Cells. *Adv. Mater.* **2007**, *19* (4), 592–596.
- (24) Yamaguchi, T.; Kuroki, H.; Miyata, F. DMFC Performances Using a Pore-Filling Polymer Electrolyte Membrane for Portable Usages. *Electrochem. Commun.* **2005**, *7* (7), 730–734.
- (25) Jung, H.; Fujii, K.; Tamaki, T.; Ohashi, H.; Ito, T.; Yamaguchi, T. Low Fuel Crossover Anion Exchange Pore-Filling Membrane for Solid-State Alkaline Fuel Cells. *J. Membr. Sci.* **2011**, *373* (1–2), 107–111.
- (26) Kwak, N. S.; Koo, J. S.; Hwang, T. S. Synthesis and Characterization of EFFE-g-(VBTA-co-HEMA) Anion Exchange Membranes Prepared by a ⁶⁰Co Radiation-Induced Graft Copolymerization for Redox-Flow Battery Applications. *Macromol. Res.* **2012**, *20*, 205–211.
- (27) Lee, M. S.; Kim, T.; Park, S. H.; Kim, C. S.; Choi, Y. W. A Highly Durable Cross-Linked Hydroxide Ion Conducting Pore-Filling membrane. *J. Mater. Chem.* **2012**, *22*, 13928–13931.
- (28) Sun, T.; Feng, L.; Gao, X.; Jiang, L. Bioinspired Surfaces with Special Wettability. *Acc. Chem. Res.* **2005**, *38*, 8–12.
- (29) Barthaott, W.; Neinhuis, C. Self-Cleaning of Biological Surfaces. *Planta* **1997**, *202*, 1–8.
- (30) Grew, K.; Chiu, W. K. S. A dusty fluid model for predicting hydroxyl anion conductivity in alkaline anion exchange membranes. *J. Electrochem. Soc.* **2010**, *157* (3), 327–337.