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Hierarchical structural designs of ion exchange membranes for flow batteries†

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Membranes for flow batteries need to have both high ionic conductivity and selectivity. The selectivity is particularly important for systems involving two different species, such as Fe/Cr, since any crossover is irreversible. However, most membranes suffer from a trade-off between these two properties. We addressed this issue by fabricating a composite cation exchange membrane with a hierarchical structure to ensure mechanical stability, conductivity, and selectivity. The membrane featured a dense, crack-free tungsten oxide coating layer on Nafion that also penetrated into the Nafion's hydrophilic, ionic cluster regions. The oxide inside the polymer was synthesized *in situ* in the hydrophilic regions, while the sol-gel method was used to coat the oxide on the polymer. The oxide inside Nafion reduced water uptake and swelling ratio, which are essential to ensure the adhesion of the top oxide layer on Nafion. The top dense oxide layer served as a highly selective membrane for cation transport. Maintaining comparable conductivities, the membrane showed that the permeabilities for Fe(II) and Cr(III) ions decrease by an order of magnitude as compared to those for Nafion (from $2.66 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $8.84 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ to $2.31 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and $8.34 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, respectively). Noticeably, the oxide coating layer showed three orders of magnitude lower permeability than Nafion. When applied in a lab-scale Fe/Cr flow battery, the cycling stability significantly improved due to the much reduced crossover. This new membrane design can be extended to other polymer membranes and holds promise for applications in a variety of flow batteries.

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Introduction

The utilization of renewable resources, such as wind, solar, and tides, has been growing rapidly. This growth is driven by the increasing energy demand and concerns regarding carbon emissions;^{1–4} however, large-scale energy storage solutions are required due to the intermittent nature of renewable resources.^{5,6} Redox flow batteries (RFBs) are one of the promising candidates due to their low cost, long life, rapid response, high mobility and flexibility.^{5–13} RFBs store energy in two solutions with different redox couples. The positive and negative electrodes are separated by a selective ion exchange membrane (IEM), which prevents the mixing of active species. Most of the leading flow batteries with chemistries such as all-vanadium, all-iron, and iron-chromium utilize cation exchange membranes (CEMs).^{2,5,9–15} Anion exchange membranes (AEMs) have also been used, especially for lowering crossover when cations serve as the active species.^{3,9,10,14,15}

Perfluorinated polysulfonic acid (PFSA) membranes, such as Nafion, are the most widely used CEMs in RFBs due to their

high conductivity and good chemical and thermal stabilities.^{10,14–16} However, Nafion membranes suffer from the crossover of active species, leading to severe self-discharge and decreased energy efficiency.^{2,7,17–19} Various strategies have been proposed to fabricate new composite membranes with reduced crossover.²⁰ Physical blending with inorganic particles,^{21–24} nanotubes,^{25,26} graphene,^{27–29} metal-organic frameworks (MOFs), and polymers has been extensively studied.^{30–33} The crossover rate can be reduced by these added materials *via* reducing mobile water transport and the corresponding leakage of hydrated redox-active ions.¹⁴ Besides the simple mixing method, fillers such as SiO₂ and TiO₂ can also be synthesized during the membrane formation process *via* the sol-gel method to achieve uniform distribution.^{34–37} In the “infiltration method”, fillers are formed *in situ* by infiltrating precursors into an existing polymer membrane, resulting in well-dispersed and extremely small particles inside the hydrophilic ionic cluster regions of phase-segregated polymer membranes.^{20,38–40} Reduced crossover rates can be achieved by the decreased size of the ionic cluster regions. Surface modification, mostly with organic coatings serving as highly selective layers, has been used to reduce the crossover of active species as well.^{41–44}

Inorganic ion conductors are ideal candidates to serve as ion exchange membranes. While perfect selectivity is theoretically possible, most of these conductors tend to be brittle and are difficult to handle and use. This difficulty can be circumvented

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by supporting thin films of ion conductors on porous polymer substrates. Unfortunately, a bilayer inorganic-polymer structure has not been widely adopted due to difficulties in integrating materials with significant differences in mechanical properties. Upon exposure to liquids, the polymer tends to swell, while the inorganic layer does not swell. This mismatch results in cracking, delamination, and failure of the membrane.

Here, we developed a composite cation exchange membrane with a hierarchical structure; it consisted of a polymer membrane with tungsten oxide filling the ionic cluster region and a dense tungsten oxide coating layer on the polymer surface (Fig. 1). This hierarchical structure simultaneously enabled both high selectivity and conductivity during use in a flow battery. Tungsten oxide hydrates ($\text{H}_x\text{WO}_3 \cdot y\text{H}_2\text{O}$) have been reported to show high proton conductivity ($\sim 0.1 \text{ S cm}^{-1}$, 25°C) and are formed *in situ* in the ionic clusters of polymer membranes.^{45–47} By replacing water in the ionic clusters with oxides, we achieve several advantages. (1) Decrease in the permeability of active species: crossover of active species, such as Fe, Cr, and V ions, primarily relies on hydrated ionic clusters, which cannot permeate through the oxide structure. (2) Enhanced mechanical stability of the membrane: interactions between the filled oxide and polymer chains result in denser polymer packing and structural reinforcement. (3) Suppressed swelling of the polymer membrane *via* the interaction between oxide and polymer chain and decreased water uptake: a low swelling ratio is essential for the polymer membrane to be integrated with a rigid oxide coating layer without suffering from delamination and cracking. The dense oxide layer was coated *via* the sol-gel method on the polymer/oxide composite membrane. Tungsten oxide hydrates have been reported to have a layered structure with water molecules bonded between the layers, which can enable efficient proton conduction through

the hydrogen bond network.⁴⁸ Proton insertion/extraction reactions, such as $\text{WO}_3 + x\text{H}^+ + xe^- \leftrightarrow \text{H}_x\text{WO}_3$, convert tungsten oxide into tungsten bronze (H_xWO_3 , $0 < x < 1$). Protons are conducted through the movement of proton vacancies.⁴⁹ Potassium ions are conducted through a similar solid-state ion conduction mechanism. However, multivalent ions, such as Fe, Cr, and V, with high charge densities have strong interactions with water molecules, which make them too bulky to be inserted into the lattice structure of tungsten oxide hydrates. Nafion was used as a test case for the hierarchical structure, and future experiments can allow for further applications of this strategy to other polymer membranes at lower costs. Combining the oxide-in-polymer and oxide-on-polymer structures has promising potential for enhancing the performance of a variety of membranes.

Experimental

Materials

Nafion 117 membrane was purchased from Fuel Cell Store. Tungsten powder ($12 \mu\text{m}$, 99.9% trace metals basis) and bismuth oxide (Bi_2O_3 , $10 \mu\text{m}$, 99.9% trace metals basis) were purchased from Sigma-Aldrich. 3-Hydroxytyramine hydrochloride (dopamine, 99%) was purchased from ACROS Organics. Tris(hydroxymethyl)aminomethane (Tris, 99.8%), hydrogen peroxide solution (H_2O_2 , 30%), sulfuric acid (H_2SO_4 , 95–98%), hydrochloric acid (HCl, 36.5–38%), potassium chloride (KCl, 99%), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99%), and chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 98%) were purchased from Fisher Scientific.

Membrane preparation

Polydopamine was coated onto a Nafion 117 membrane according to a method provided in the literature.⁵⁰ A commercial Nafion 117 membrane was pre-treated by boiling in steps of deionized water, starting from pure to a mixture of 3% H_2O_2 and then 0.5 M H_2SO_4 solutions before being stored in deionized water at room temperature. The membrane was then immersed in 79 mL Tris-HCl buffer (pH 8.5), while 1 mL 160 mg mL^{-1} aqueous dopamine solution was added dropwise under mild stirring to induce spontaneous self-polymerization. The coated Nafion membrane (DNf) was taken out after 90 minutes and rinsed with deionized water.

A tungstic acid solution was prepared by slowly dissolving 2.5 g tungsten powder in 30 mL 30% hydrogen peroxide in a room-temperature water bath while being stirred. Excess hydrogen peroxide was removed by placing a small piece of platinum foil in the solution and putting the solution in an oven at 80°C for 20 minutes. The clear solution turned bright yellow.

DNf was soaked in methanol for 24 hours under room temperature, followed by soaking in tungstic acid solution for another 24 hours. Then, the residues on the membrane were wiped off and it was cured for 1 hour under 100% RH and 80°C ; this environment was created by placing a capped bottle with water in an oven. All the above processes were repeated 3 times to get c-DNf/oxide.

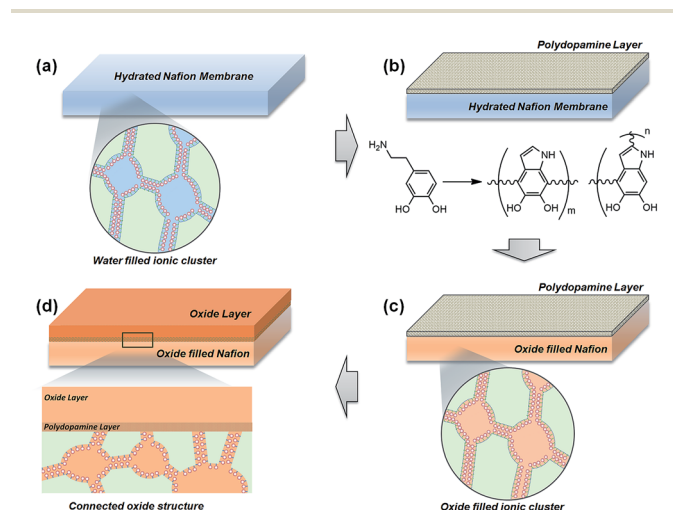


Fig. 1 Fabrication of tungsten oxide/Nafion hierarchical composite membrane (h-DNf/oxide): (a) blank hydrated Nafion membrane; (b) polydopamine coating (DNf); (c) *in situ* formation of tungsten oxide in hydrophilic ionic cluster regions of Nafion membrane (c-DNf/oxide); (d) tungsten oxide coating on the surface (h-DNf/oxide). Green: fluorocarbon backbones of Nafion; red spheres: sulfonic acid groups of Nafion.

c-DNF/oxide was manually dip-coated in the tungstic acid solution, resulting in double-sided coatings. The coated Nafion was cured in the same way as the previous method. The coating and curing steps were repeated three times to achieve h-DNF/oxide with the desired thickness of coating.

Membrane characterization

The morphology and thickness of h-DNF/oxide were characterized using scanning electron microscopy (FEI Quanta 250 SEM and Zeiss Sigma 500 SEM for obtaining an ultrahigh magnification image) with atomic composition and elemental mapping analyses performed by an integrated energy-dispersive X-ray (EDX) spectrometer. The chemical composition of the membrane was characterized by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum Two) and Raman spectroscopy (Renishaw inVia). The crystal structure of the membrane was investigated by X-ray diffraction (XRD, Bruker D2 Phaser). The thermal stability of the membrane was characterized by thermal gravimetric analysis (TGA, PerkinElmer Pyris 1 TGA) from 25 to 650 °C (heating rate: 5 °C min⁻¹).

Mechanical properties

The mechanical properties of the membranes were measured using tensile tests (Instron 5960) to generate stress-strain curves at a strain rate of 0.01 mm s⁻¹ at room temperature and sampled at 10 Hz rate. Membrane samples were cut into dog-bone-shaped specimens; overall dimensions: 25 mm × 15 mm, gauge dimensions: 15 mm × 2 mm. Dry and wet membranes were pre-treated with the mentioned methods for water uptake measurements.

Water uptake and swelling

Water uptake (WU) and in-plane swelling ratio (SW) of the membranes were calculated based on the percent changes in the wet and dry weights (WU) and areas (SW). All the measurements were carried out right after the treatment for obtaining accurate data. The dry membranes were dried at 80 °C under vacuum for 24 hours to remove residual water and then cooled to room temperature under vacuum. The wet membranes were immersed in deionized water at 60 °C for 24 hours to reach complete hydration.

Conductivity

The proton and potassium ion conductivities of the membrane were measured in a conductivity cell using AC impedance spectroscopy, and the membrane resistance was probed with a potentiostat (Bio-Logic, VSP-300) at an oscillating voltage of 20 mV over a frequency range of 7 MHz to 1 Hz. Prior to testing, the membrane sample was fully hydrated in water. The conductivity (σ) was calculated with the following equation:

$$\sigma [\text{mS cm}^{-1}] = \frac{L}{RS}$$

L is the distance (cm) between the two electrodes, R is the impedance (Ω) of the membrane, and S is the surface area (cm²) of the electrodes.

Permeability

An H-cell setup was used for the permeability measurement of Fe(II) and Cr(III) ions. The left reservoir was filled with 1 M Fe(II) ion solution (FeCl₂·4H₂O) in 2 M HCl, and the right reservoir was filled with 1 M Cr(III) ion solution (CrCl₃·6H₂O) in 2 M HCl. The geometrical area of the exposed membrane was 1.77 cm² and the volume of the solution for each reservoir was 25 mL. Crossover contamination was measured by ultraviolet-visible spectrometry (UV-vis) on the samples of solutions, which were taken from each reservoir at different time intervals. The samples were analyzed for Fe(II) concentration in right reservoir of Cr(III) solution and for Cr(III) concentration in left reservoir of Fe(II) solution. The measured absorbance of the samples from the H-cell was converted into concentration based on standard absorbance-concentration curves. The permeability was calculated with the following equation:

$$V_B \frac{dc_B(t)}{dt} = A \frac{P}{L} (c_A - c_B(t))$$

here, c_A is the ion concentration in the original reservoir, and $c_B(t)$ is the time-dependent concentration of ions in the other reservoir, which went through the membrane; V_B is the volume of one reservoir, A and L are the area and thickness of the membrane, respectively, and P is the permeability of ions. P is assumed to be independent of the concentration. The permeability of the coating layer was calculated based on the data of h-DNF/oxide and c-DNF/oxide using the following equation:

$$\frac{L_A + L_B}{P_{A+B}} = \frac{L_A}{P_A} + \frac{L_B}{P_B}$$

A represents c-DNF/oxide, B is the dense top oxide layer, and $A + B$ is h-DNF/oxide.

An empirical figure of merit (β) is defined in the form of $\beta = \sigma/P$ to demonstrate the ratio between the diffusivities of the desired and undesired ions in the membrane, *i.e.*, the ratio of proton conductivity (σ) to Fe(II) permeability.

Flow battery test

A flow battery hardware was designed and fabricated in-house. A picture of the device is shown in Fig. S8.† Activated by 3 : 1 sulfuric acid and nitrate acid for 6 hours at 50 °C, two pieces of 0.6 cm-thick graphite felt (AvCarb G200) were used as the electrodes. Viton® fluoroelastomer rubber gaskets were used to seal the hardware. The active area of the membrane was 1 × 1 cm². Densified and resin-filled impervious graphite plates (Graphtek FC-GR347B) served as the current collectors, which were sandwiched between the copper end plates. The catholyte was prepared by dissolving 1 M FeCl₂ in 2 M HCl solution, while the anolyte was prepared by mixing 1 M CrCl₃ in 2 M HCl solution with 0.01 M Bi³⁺. Furthermore, we circulated 8.5 mL catholyte and anolyte at a flow rate of 5 mL min⁻¹ by a two-channel peristaltic pump (EW-77921-75, Cole-Parmer). All the flow battery tests were performed at room temperature (25 °C). The galvanostatic charge and discharge experiments were conducted at 20 mA cm⁻² with cut-off voltages between 0.7 and 1.2 V. Bismuth, serving as a catalyst for the anodic reaction, was

plated onto the anode at 20 mA cm^{-2} before the initial charging.⁵¹

Results and discussion

Fig. 1 shows the fabrication steps for the hierarchical membrane structure. A hydrated Nafion membrane is coated with a thin polydopamine layer (DNf) to improve the hydrophilicity of the surface. DNf is then filled with tungsten oxide in its hydrophilic ionic cluster regions, resulting in a composite structure (c-DNf/oxide). A dense tungsten oxide film is then coated onto c-DNf/oxide to form the final membrane (h-DNf/oxide).

In order to realize the hierarchical structure, strong adhesion at the interface between the oxide coating and Nafion is essential. However, Nafion has a hydrophobic surface due to the perfluoroalkane backbone structure. To enable tungstic acid aqueous solution to wet the Nafion surface, surface modification is required to render it hydrophilic. Inspiration was drawn from biological systems such as mussels that adhere to rocks through the use of dopamine.^{52,53} Dopamine monomers are readily oxidized in air under basic pH conditions at room temperature to self-polymerize.^{42,54} The polydopamine layer adheres strongly to almost any material, including PTFE and other anti-fouling materials.⁵² Here, we utilized polydopamine as the adhesive layer to enhance the interaction between the Nafion membrane and tungsten oxide coating layer and its hydrophilicity to facilitate the coating process. The polydopamine layer formed on Nafion was presumably very thin ($\sim 10 \text{ nm}$ based on the literature)⁵⁰ and could not be observed in the cross-sectional SEM images (Fig. S2(a)†). A successful coating process was visually confirmed as the clear, transparent Nafion membrane became brown and semi-transparent (Fig. S1†); it was also confirmed by a change in the surface wetting properties. The contact angle of the Nafion membrane decreased from 89° to 61° after polydopamine coating (Fig. S3†).

Tungstic acid, which becomes tungsten oxide at an elevated temperature or at a low pH, is the precursor to both c- and h-DNf/oxide structures. The acid was synthesized at around 25°C through the reaction of tungsten powder with hydrogen peroxide. Nano-sized particles were formed as the aging progressed and then served as nucleation sites during the transformation from tungstic acid to tungsten oxide, thus enhancing the formation of the coating layer.

A c-DNf/oxide structure was achieved by filling the ionic channels and clusters with the oxide precursor. Due to the small sizes of the ionic clusters ($\sim 5 \text{ nm}$) in Nafion,⁵⁵ directly soaking the dry membrane was ineffective; therefore, an infiltration method was used. The membrane was first soaked in methanol, causing it to swell; then, methanol was exchanged after soaking in the precursor solution. While there was no noticeable change in the color of the membrane after the exchange with the tungstic acid solution, the membrane became opaque and dark brown after a curing process, during which the precursor tungstic acid transformed into solid tungsten oxide. This indicated the successful filling of tungsten oxide into the polymer membrane matrix (Fig. S1†). Repeated solvent exchanges and

curing further increased the oxide loading amount in Nafion with infiltrated tungsten oxide (c-DNf/oxide).

h-DNf/oxide was prepared by a simple dip-coating method followed by a curing process. As a result of the enhanced hydrophilicity due to the polydopamine coating, the surface of DNf was readily wetted when dipped in a tungstic acid solution. The solution formed a uniform thin liquid layer covering the entire surface when the membrane was pulled out of the solution. During the curing process, an elevated temperature promoted the solidification of the precursor solution layer, while humidity kept the membrane hydrated to avoid shrinkage and possible cracking or delamination of the surface oxide layer due to mismatch in the size changes between Nafion and oxide. Smooth and uniform dark-brown layers were coated on the membrane after repeated coating and curing processes (Fig. S6(b)†). The quality of the coating was confirmed by SEM; the film is uniform and crack-free (Fig. 2(a and b)). At a very high magnification, the coating layer is found to be formed by the aggregation of small particles of $5\text{--}15 \text{ nm}$ size (Fig. S2(b)†). Additionally, a membrane with a tungsten oxide layer only on the surface but not in the bulk (l-DNf/oxide) was prepared by directly coating DNf to confirm the contribution of the oxide-in-polymer structure to the stability of the oxide-on-polymer structure (Fig. S6†).

EDX mapping was conducted on the surface of h-DNf/oxide (Fig. S4†). Tungsten and oxygen are distributed homogeneously in the coating layer. Cross-sectional SEM images also clearly show the dense and uniform coating layer when EDX mapping is conducted on the surface of h-DNf/oxide (Fig. S4†). Tungsten and oxygen are distributed homogeneously in the coating layer. Cross-sectional SEM images also clearly show the dense and

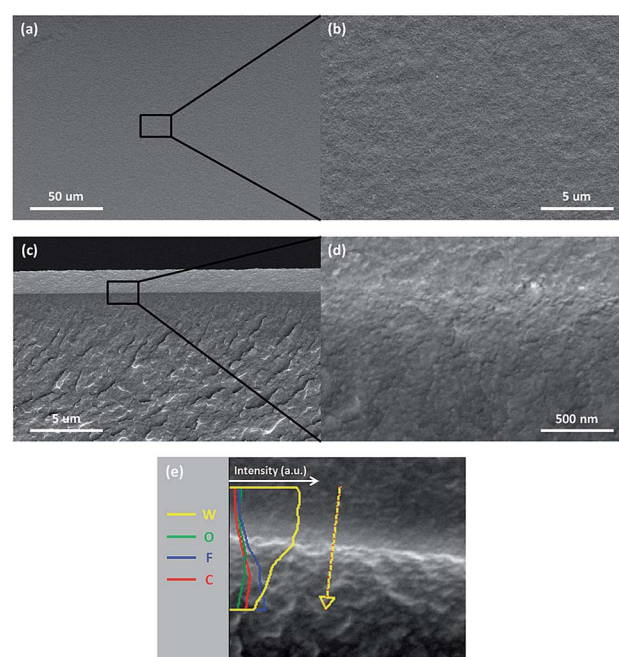


Fig. 2 SEM images of h-DNf/oxide: (a, b) surface; (c, d) cross-sectional; (e) line-scan EDX at the interface of tungsten oxide coating layer and Nafion membrane.

uniform coating layer with thickness of 1.6 μm , confirming that the structure is not porous even though it is formed from aggregation of particles (Fig. 2(c and d)). The interface between the supporting Nafion membrane and coating layer is of exceptional quality with no visible voids, and the boundary at the interface is not visible, as observed in the high-magnification SEM image (Fig. 2(d)). Line-scan EDX shows a gradual compositional gradient across the interface, most noticeably for W (Fig. 2(e)). This observation confirmed that our original design has been realized: the tungsten oxide phase is a continuous film on the surface but extends deeply into the Nafion structure. Such a structure is expected to contribute to a robust composite membrane. Such excellent connection and adhesion can mitigate possible delamination at the interface, which is a critical problem for multilayered composite materials. EDX was also conducted on the cross-section of h-DNF/oxide (Fig. S5†). Low-magnification EDX mapping shows that the bulk polymer is mainly composed of carbon, oxygen, fluorine, and sulfur. The surface coating layer contains concentrated tungsten and oxygen, while tungsten is also uniformly distributed in the bulk polymer matrix, further confirming the bilayer oxide-in-polymer and oxide-on-polymer structures.

XRD was performed to investigate the structure of the membranes (Fig. 3). The shifts in the Nafion peaks for h-DNF/oxide from 16.83° and 39.11° to 18.11° and 39.98° , respectively, indicate denser packing of the polymer chains due to the interaction with tungsten oxide. The peak at 23.83° matches with several different types of tungsten oxide crystalline structures. As a result, the specific structure of filled tungsten oxide in Nafion cannot be determined based on XRD data. Further characterizations were performed to confirm the structure.

FTIR spectra were used to examine the chemical structures of Nafion and h-DNF/oxide (Fig. 4(a)). The peaks at 1200, 1144, and 512 cm^{-1} are related to the C-F bonds on the Nafion polymer backbone. C-O-C and C-S bonds on the side chain lead to twin peaks at 980 and 968 cm^{-1} and a weak peak at 880 cm^{-1} respectively. The shoulders at 1300 and 1144 cm^{-1} are assigned to the SO_3^- group. For h-DNF/oxide, the peaks in the range of $500\text{--}900\text{ cm}^{-1}$ are assigned to the W-O bond. Due to covering by a dense tungsten oxide coating layer, all peaks from Nafion decrease significantly. Raman spectroscopy was also

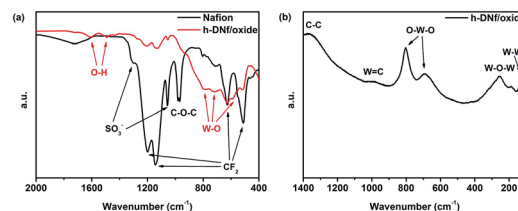


Fig. 4 Spectra of Nafion and h-DNF/oxide: (a) FT-IR; (b) Raman.

performed on h-DNF/oxide (Fig. 4(b)). The C-C bond from the Nafion polymer backbone exhibits a broad peak at 1370 cm^{-1} . The peaks observed at 1000, 690, 254, and 130 cm^{-1} correspond to W=O, O-W-O, W-O-W, and W-W bonds. The peak at 800 cm^{-1} , also corresponding to the O-W-O bond, is associated with the monoclinic structure of tungsten oxide. It is thus concluded that tungsten oxide is successfully formed in the ionic clusters and its structure is probably monoclinic.

The thermal properties and compositions of the membranes were investigated by TGA (Fig. 5). Both blank Nafion and h-DNF/oxide exhibited three-step thermal degradation: loss of water during the first step before 270°C ; desulfonation of Nafion during the step around 350°C ; and decomposition of the Nafion polymer backbone during the last step above 400°C . For both membranes, the first step can be ignored as a result of pre-drying. After incorporating tungsten oxide into Nafion, the peaks of the second and third steps in the derivative thermal gravimetric curves shift from 363.9°C and 448.9°C to 377.0°C and 469.5°C , respectively (Fig. 5(b)). The enhanced thermal stability of h-DNF/oxide provides evidence for the interaction between the oxide and polymer. The residual weight indicates that the tungsten oxide loading is 6.6%.

High mechanical stability of PEM is necessary for long-term practical operation of flow batteries. The Nafion membrane in its dry state showed a Young's modulus of 142.5 MPa, yield stress of 7.67 MPa with 8.5% strain, and failure stress of 25.9 MPa with 223.3% strain (Fig. 6, Table S1†). The Nafion membrane became much weaker when hydrated; it exhibited Young's modulus of 35.5 MPa, yield stress of 4.95 MPa, and failure stress of 20.4 MPa. The yield strain increased by 2.6 times to 22%; however, the ultimate strain remained almost the same. A decrease in the Young's modulus and change in the yield point after hydration were due to the high water uptake and swelling ratios of the Nafion membrane. High water

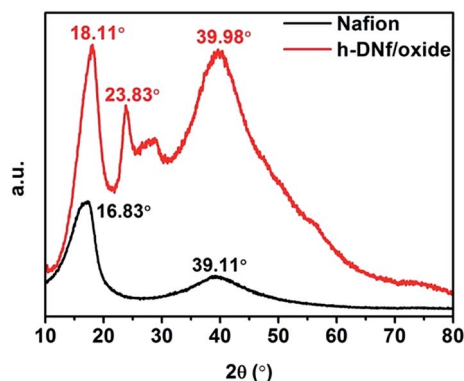


Fig. 3 XRD of Nafion and h-DNF/oxide.

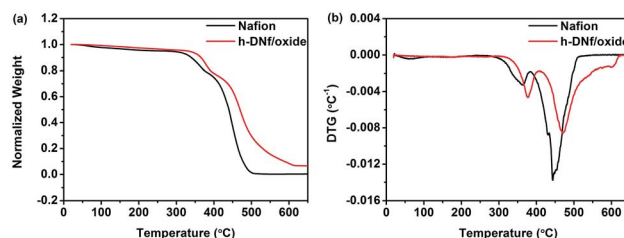


Fig. 5 Thermogravimetric analysis of Nafion and h-DNF/oxide: (a) TG; (b) DTG.

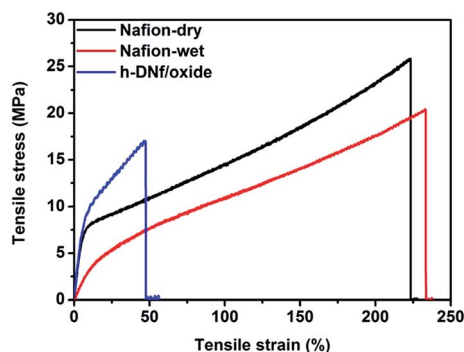


Fig. 6 Stress-strain curves of Nafion and h-DNf/oxide.

content enables faster proton transport but also increases polymer chain mobility, leading to poor mechanical stability. h-DNf/oxide was significantly reinforced, achieving Young's modulus of 148.7 MPa and yield stress of 9.29% at elongation of 9.1%; these performances were superior even when compared with those of dry Nafion membranes. The ultimate strain significantly decreased to only 47.3% without a large drop in the ultimate stress. The coated tungsten oxide layer on the polymer contributed negligibly to the mechanical properties of bulk membrane due to its limited thickness. Tungsten oxide in the polymer probably changed the mechanical properties of the membrane in three aspects: (1) interactions between tungsten oxide and polymer chains suppress chain mobility and increase chain packing density; (2) tungsten oxide filled in ionic clusters forms a continuous rigid oxide network across the polymer matrix, serving as reinforced concrete to achieve outstanding mechanical stability; (3) tungsten oxide replaces water in the hydrated polymer, which can also reduce chain mobility. The mechanical stability of h-DNf/oxide is not only beneficial toward cell operation but also helps prevent the failure of the coating layer caused by mechanical deformation or dimensional variations due to humidity changes.

Water uptake (WU) and swelling (SW) are important parameters for composite ion exchange membranes (Table 1). While high water uptake usually facilitates ion transport, correspondingly high swelling might compromise the mechanical integrity of the composite structure, particularly for the oxide-on-polymer configuration. The DNf membrane exhibited water uptake of 38.2% and swelling of 44.1%, which were similar to those for baseline Nafion. Due to its very low thickness, the polydopamine coating layer has negligible influence on the water uptake and swelling of the bulk membrane.

Consequently, the significant reduction in the swelling ratio was due to the incorporation of tungsten oxide. Most failures of composite membranes with layered structures, especially those formed by coating rigid inorganic materials on soft polymer supports, are caused by delamination or cracks due to different swelling ratios of the layers. Controlling the water uptake and swelling can effectively enhance the stability as well as mechanical properties of the composite membrane. The tungsten oxide coating layer of l-DNf/oxide exhibited dramatic delamination after soaking in DI water for 24 hours, while h-DNf/oxide maintained its original structure after one week, confirming the contribution of infiltrated tungsten oxide for membrane stability (Fig. S6†).

Ionic conductivities (σ) were measured by a through-plane two-probe method at the hydrated state (Table 1). The proton conductivity (σ_{H^+}) of DNf membranes was 4.6 mS cm^{-1} , which was only 8.5% of the conductivity of Nafion (54.1 mS cm^{-1}). The dramatic conductivity drop caused by the additional layer with negligible thickness suggested that the conductivity of polydopamine is very low. Interestingly, after introducing tungsten oxide, the conductivity of h-DNf/oxide increased to 22.8 mS cm^{-1} , which represented manageable reduction from that of Nafion. Filling polydopamine with proton-conductive tungsten oxide and rebuilding the proton transport pathway probably contributed toward the recovery of conductivity. The ratio of conductivity over water uptake (σ/WU) is a metric that measures the effectiveness of water in promoting ion conduction. The $\sigma_{\text{H}^+}/\text{WU}$ ratio of h-DNf/oxide was 1.88 when compared with 1.39 for baseline Nafion. Hence, tungsten oxide filling in the ion channels appeared to help enhance water-facilitated proton conduction.

We also measured the potassium ion conductivity (σ_{K^+}) of Nafion and the composite membranes (Table 1). For flow batteries such as Fe/Fe and Cr/Fe, KCl is often used as the supporting electrolyte and K^+ transports through the cell membrane. During ion exchange, we expected hydrated tungsten oxide to change into its potassium form. In this regard, hydrated potassium tungsten bronze is well-known. However, their K^+ conductivities have not been well studied. Our measurement indicated conductivity of 8.0 mS cm^{-1} for K^+ -exchanged Nafion or 14.8% of the proton conductivity. h-DNf/oxide showed K^+ conductivity of 4.6 mS cm^{-1} or 20.2% of the proton conductivity. The $\sigma_{\text{K}^+}/\text{WU}$ value for h-DNf/oxide reached 0.38; in comparison, the value for Nafion was 0.21. The smaller difference in σ/WU for K^+ vs. H^+ when compared with that of Nafion indicated that h-DNf/oxide does not rely much on water to transport ions.

Table 1 Water uptake, swelling ratio and ion conductivity of Nafion and composite membranes^a

	WU [%]	SW [%]	$\sigma_{\text{H}^+}^b$ [mS cm^{-1}]	$\sigma_{\text{H}^+}/\text{WU}$	$\sigma_{\text{K}^+}^b$ [mS cm^{-1}]	$\sigma_{\text{K}^+}/\text{WU}$
Nafion	38.9	46.6	54.1	1.39	8.0	0.21
DNf	38.2	44.1	4.6	0.12	—	—
h-DNf/oxide	12.1	16.9	22.8	1.88	4.6	0.38

^a All data are measured at room temperature. ^b Through plane, at 100% RH.

The permeability of active species is another key parameter of CEM for flow batteries. The permeabilities for Fe(II) and Cr(III) ions were measured simultaneously by filling two sides of an H-cell with solutions containing different ions. This represents the discharged state of an Fe/Cr flow battery. The crossover of Cr(III) ions could be visibly observed based on their dark-green color, while the crossover of Fe(II) ions could not be observed since their light-green color is similar to that of Cr(III) ions. h-DNF/oxide showed much smaller crossover for both Fe(II) and Cr(III) ions when compared with baseline Nafion. Fig. 7(a) and (b) show the test results for both ions while using three different membranes: baseline Nafion, h-DNF/oxide, and c-DNF/oxide. The Fe(II) ion crossover rate of Nafion is the highest; after 50 hours, it starts to decrease as the solution reaches concentration equilibrium. As shown in Fig. 8(a), for both Fe(II) and Cr(III) ions, h-DNF/oxide still maintains a constant low crossover rate after 210 hours, suggesting that the stability of the coating layer is not compromised over extended testing. For h-DNF/oxide, the permeabilities of Fe(II) and Cr(III) ions decrease by an order of magnitude (from $2.66 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $8.84 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ to $2.31 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and $8.34 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, respectively). Cr(III) ions exhibit lower permeability for both baseline and h-DNF/oxide due to their higher valence state. c-DNF/oxide also exhibited some capability to decrease metal ion crossover; the values were measured to be $8.14 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and $3.85 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for Fe(II) and Cr(III) ions, respectively. The permeability difference between the membranes of h-DNF/oxide and c-DNF/oxide can be attributed to the dense surface of the tungsten oxide layer. Considering the thicknesses of the Nafion membrane and coating layer, the dense tungsten oxide coating layer showed extraordinarily low permeability: $4.88 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for Fe(II) ions, which is 0.18% of that of baseline Nafion and 1.94% of that of c-DNF/oxide; $1.48 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for Cr(III) ions, which is 0.17% of that of bare Nafion and 1.77% of that of c-DNF/oxide. An empirical figure of merit (β) is defined as the ratio of conductivity to permeability to demonstrate the ratio between the diffusivities of the desired ions and undesired ions in the membrane. In Fig. 8(b), h-DNF/oxide shows increased β of H^+ and K^+ over that of Fe^{2+} and Cr^{3+} . The $\text{H}^+/\text{Cr}^{3+}$ β value of h-DNF/oxide reaches $2.74 \times 10^9 \text{ mS s cm}^{-3}$. Therefore, hierarchical composite structures considerably enhance the selectivity of membranes.

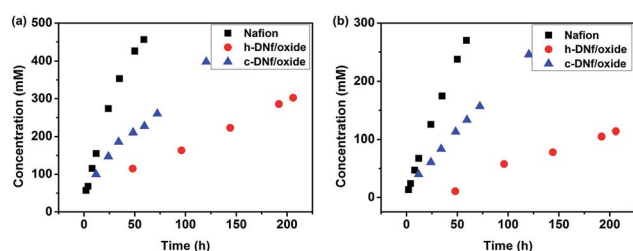


Fig. 7 Ion-crossover tests of Nafion, c-DNF/oxide, and h-DNF/oxide: (a) Fe(II); (b) Cr(III).

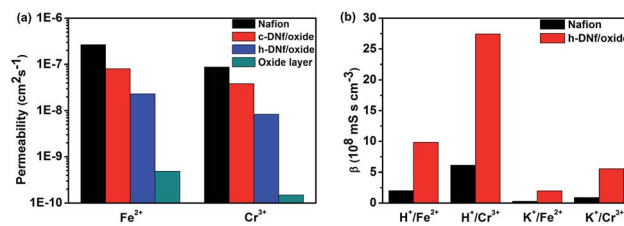


Fig. 8 Comparisons of (a) ion permeabilities and (b) β values for Nafion and composite membranes. β is defined as the ratio of conductivity to permeability.

The flow battery performances of membranes were evaluated in a lab-scale single-cell iron-chromium flow battery (Fig. S8†) as a proof of concept. For the galvanostatic charge and discharge experiments, relatively high capacity to the active membrane area was utilized to emphasize the effect of crossover by prolonging the time of each cycle (Fig. 9). Although only a limited number of cycles were performed, the total duration of tests was actually similar to those commonly reported in the literature.^{56–58} At a current density of 20 mA cm^{-2} , the flow battery assembled with Nafion as the separator exhibited quick and dramatic discharge capacity decay, retaining only 29.5 mA h after 42.2 hours from the first-cycle capacity of 106.6 mA h. The dark color of the catholyte after cycling indicated the high rate of irreversible crossover, which led to rapidly decreasing capacity (Fig. S9†). Benefiting from the much decreased crossover rate due to the hierarchical composite structure, the capacity decay was mitigated by the dense oxide layer of h-DNF/oxide (Fig. S11†). The flow battery with h-DNF/oxide delivered capacity of 87.9 mA h after 47.9 hours, which was about 3 times that of the battery with Nafion. The color change of the catholyte was also very small. Compared with Nafion, even without the dense surface oxide layer, c-DNF/oxide still showed significant improvement and maintained a discharge capacity of 55.4 mA h. As shown in Fig. 9(b), due to severe crossover, the flow battery with Nafion exhibits much larger overpotential than those with either h-DNF/oxide or c-DNF/oxide. Coulombic efficiency is a commonly used performance metric; we should note that for all the three batteries, the coulombic efficiencies were very similar (at about 85%) despite the large difference in capacity retentions. This indicated that the crossover in this case

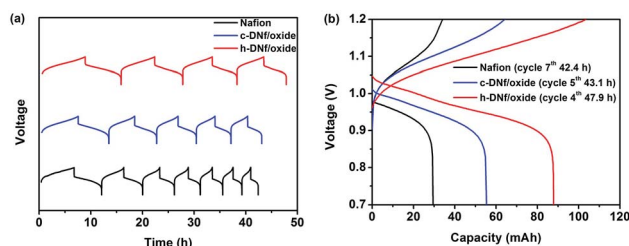


Fig. 9 Charge-discharge profiles of Nafion and composite membranes at 20 mA cm^{-2} : (a) cycling; (b) comparison after similar cycling times.

reduced the reversible capacity of batteries, while the coulombic efficiency was determined by other processes such as hydrogen evolution.⁴ In summary, the overall trend of flow battery performance is consistent with the permeability and selectivity results from static H-cell tests. With no significant influence from the slight decrease in conductivity, the hierarchical composite structure can considerably mitigate the crossover of active species, which represents an important progress in addressing the well-known trade-off between conductivity and selectivity for flow battery membranes.

Conclusions

A hierarchical composite ion exchange membrane was developed by integrating Nafion and tungsten oxide. Proton-conducting tungsten oxide infiltrated into ionic clusters of Nafion membranes to reduce water uptake and swelling ratios and enhance stability while maintaining reasonable conductivity. A dense, crack-free tungsten oxide layer was coated onto the surface to reduce the permeability of active species. A stable oxide-on-polymer structure was obtained due to the dimensionally stable oxide-in-polymer composite structure. An order-of-magnitude decrease in the permeabilities of Fe(II) and Cr(III) ions was observed for the hierarchical composite membrane while maintaining comparable conductivities. The dense oxide coating layer showed three orders of magnitude lower permeability than Nafion. Such a composite membrane with a hierarchical structure provides a strategy to solve the trade-off between conductivity and permeability of ion exchange membranes. The positive effect of the reduced crossover was confirmed in a small lab-scale iron-chromium flow battery with improved capacity retention with cycling and time. Further work is needed to scale up the flow battery and optimize its design to fully realize the benefit of the composite membrane. Nevertheless, our method of fabricating a stable bilayer inorganic-polymer structure has the potential to be applied to many different ion conductors beneficial for energy conversion and storage devices.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 D. Larcher and J. M. Tarascon, *Nat. Chem.*, 2014, **7**, 19–29.
- 2 Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon and J. Liu, *Chem. Rev.*, 2011, **111**, 3577–3613.

- 3 G. L. Soloveichik, *Chem. Rev.*, 2015, **115**, 11533–11558.
- 4 W. Wang, Q. Luo, B. Li, X. Wei, L. Li and Z. Yang, *Adv. Funct. Mater.*, 2012, **23**, 970–986.
- 5 P. Leung, X. Li, C. Ponce de Leon, L. Berlouis, C. T. J. Low and F. C. Walsh, *RSC Adv.*, 2012, **2**, 10125–10156.
- 6 C. Ding, H. Zhang, X. Li, T. Liu and F. Xing, *J. Phys. Chem. Lett.*, 2013, **4**, 1281–1294.
- 7 A. Parasuraman, T. M. Lim, C. Menictas and M. Skyllas-Kazacos, *Electrochim. Acta*, 2013, **101**, 27–40.
- 8 G. Kear, A. Shah Akeel and C. Walsh Frank, *Int. J. Energy Res.*, 2011, **36**, 1105–1120.
- 9 A. Z. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick and Q. Liu, *J. Appl. Electrochem.*, 2011, **41**, 1137–1164.
- 10 X. Li, H. Zhang, Z. Mai, H. Zhang and I. Vankelecom, *Energy Environ. Sci.*, 2011, **4**, 1147–1160.
- 11 M. Skyllas-Kazacos, M. H. Chakrabarti, S. A. Hajimolana, F. S. Mjalli and M. Saleem, *J. Electrochem. Soc.*, 2011, **158**, R55–R79.
- 12 B. Dunn, H. Kamath and J.-M. Tarascon, *Science*, 2011, **334**, 928–935.
- 13 C. Ponce de León, A. Frías-Ferrer, J. González-García, D. A. Szánto and F. C. Walsh, *J. Power Sources*, 2006, **160**, 716–732.
- 14 B. Schwenzer, J. Zhang, S. Kim, L. Li, J. Liu and Z. Yang, *ChemSusChem*, 2011, **4**, 1388–1406.
- 15 H. Prifti, A. Parasuraman, S. Winardi, T. M. Lim and M. Skyllas-Kazacos, *Membranes*, 2012, **2**, 275–306.
- 16 H. Strathmann, A. Grabowski and G. Eigenberger, *Ind. Eng. Chem. Res.*, 2013, **52**, 10364–10379.
- 17 X. L. Zhou, T. S. Zhao, L. An, Y. K. Zeng and L. Wei, *J. Power Sources*, 2017, **339**, 1–12.
- 18 F. Cheng, J. Liang, Z. Tao and J. Chen, *Adv. Mater.*, 2011, **23**, 1695–1715.
- 19 J. Liu, J. G. Zhang, Z. Yang, J. P. Lemmon, C. Imhoff, G. L. Graff, L. Li, J. Hu, C. Wang, J. Xiao, G. Xia, V. V. Viswanathan, S. Baskaran, V. Sprenkle, X. Li, Y. Shao and B. Schwenzer, *Adv. Funct. Mater.*, 2013, **23**, 929–946.
- 20 Y. Li, G. He, S. Wang, S. Yu, F. Pan, H. Wu and Z. Jiang, *J. Mater. Chem. A*, 2013, **1**, 10058–10077.
- 21 C.-H. Lin, M.-C. Yang and H.-J. Wei, *J. Power Sources*, 2015, **282**, 562–571.
- 22 J. Zhang, G. Wang, F. Wang, J. Zhang, J. Chen and R. Wang, *J. Electroanal. Chem.*, 2016, **783**, 76–81.
- 23 B. Yin, L. Yu, B. Jiang, L. Wang and J. Xi, *J. Solid State Electrochem.*, 2016, **20**, 1271–1283.
- 24 N. Wang, S. Peng, H. Wang, Y. Li, S. Liu and Y. Liu, *Electrochem. Commun.*, 2012, **17**, 30–33.
- 25 C. Jia, Y. Cheng, X. Ling, G. Wei, J. Liu and C. Yan, *Electrochim. Acta*, 2015, **153**, 44–48.
- 26 M. A. Aziz and S. Shanmugam, *J. Power Sources*, 2017, **337**, 36–44.
- 27 Y. Liu, J. Wang, H. Zhang, C. Ma, J. Liu, S. Cao and X. Zhang, *J. Power Sources*, 2014, **269**, 898–911.
- 28 L. Yu, F. Lin, L. Xu and J. Xi, *RSC Adv.*, 2016, **6**, 3756–3763.
- 29 L. Su, D. Zhang, S. Peng, X. Wu, Y. Luo and G. He, *Int. J. Hydrogen Energy*, 2017, **42**, 21806–21816.

- 30 P. S. Goh, A. F. Ismail, S. M. Sanip, B. C. Ng and M. Aziz, *Sep. Purif. Technol.*, 2011, **81**, 243–264.
- 31 S. Liu, X. Sang, L. Wang, J. Zhang, J. Song and B. Han, *Electrochim. Acta*, 2017, **257**, 243–249.
- 32 J. Wang, X. Yue, Z. Zhang, Z. Yang, Y. Li, H. Zhang, X. Yang, H. Wu and Z. Jiang, *Adv. Funct. Mater.*, 2012, **22**, 4539–4546.
- 33 J. Wang, Z. Zhang, X. Yue, L. Nie, G. He, H. Wu and Z. Jiang, *J. Mater. Chem. A*, 2013, **1**, 2267–2277.
- 34 M. L. Di Vona, Z. Ahmed, S. Bellitto, A. Lenci, E. Traversa and S. Licoccia, *J. Membr. Sci.*, 2007, **296**, 156–161.
- 35 Y. Yin, T. Xu, G. He, Z. Jiang and H. Wu, *J. Power Sources*, 2015, **276**, 271–278.
- 36 J. Xi, Z. Wu, X. Qiu and L. Chen, *J. Power Sources*, 2007, **166**, 531–536.
- 37 X. Teng, Y. Zhao, J. Xi, Z. Wu, X. Qiu and L. Chen, *J. Membr. Sci.*, 2009, **341**, 149–154.
- 38 B. P. Tripathi and V. K. Shahi, *Prog. Polym. Sci.*, 2011, **36**, 945–979.
- 39 L. C. Klein, Y. Daiko, M. Aparicio and F. Damay, *Polymer*, 2005, **46**, 4504–4509.
- 40 Z. Chen, B. Holmberg, W. Li, X. Wang, W. Deng, R. Munoz and Y. Yan, *Chem. Mater.*, 2006, **18**, 5669–5675.
- 41 Q. Luo, H. Zhang, J. Chen, P. Qian and Y. Zhai, *J. Membr. Sci.*, 2008, **311**, 98–103.
- 42 F. Pan, H. Jia, S. Qiao, Z. Jiang, J. Wang, B. Wang and Y. Zhong, *J. Membr. Sci.*, 2009, **341**, 279–285.
- 43 S. Zhong, X. Cui, T. Fu and H. Na, *J. Power Sources*, 2008, **180**, 23–28.
- 44 Y. Zhao, K. Tang, H. Liu, B. Van der Bruggen, A. Sotto Díaz, J. Shen and C. Gao, *J. Membr. Sci.*, 2016, **520**, 262–271.
- 45 M. Hibino, H. Nakajima, T. Kudo and N. Mizuno, *Solid State Ionics*, 1997, **100**, 211–216.
- 46 Y. M. Li, M. Hibino, M. Miyayania and T. Kudo, *Solid State Ionics*, 2000, **134**, 271–279.
- 47 Y. Tanaka, M. Miyayama, M. Hibino and T. Kudo, *Solid State Ionics*, 2004, **171**, 33–39.
- 48 Y. Li, M. Hibino, M. Miyayania and T. Kudo, *Solid State Ionics*, 2000, **134**, 271–279.
- 49 P. Kumar and S. Yashonath, *J. Chem. Sci.*, 2006, **118**, 135–154.
- 50 J. Wang, L. Xiao, Y. Zhao, H. Wu, Z. Jiang and W. Hou, *J. Power Sources*, 2009, **192**, 336–343.
- 51 C. D. Wu, D. A. Scherson, E. J. Calvo, E. B. Yeager and M. A. Reid, *J. Electrochem. Soc.*, 1986, **133**, 2109–2112.
- 52 H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426–430.
- 53 H. Lee, Y. Lee, A. R. Statz, J. Rho, T. G. Park and P. B. Messersmith, *Adv. Mater.*, 2008, **20**, 1619–1623.
- 54 M. Xiao, Y. Li, M. C. Allen, D. D. Deheyn, X. Yue, J. Zhao, N. C. Gianneschi, M. D. Shawkey and A. Dhinojwala, *ACS Nano*, 2015, **9**, 5454–5460.
- 55 J. Y. Li and S. Nemat-Nasser, *Mech. Mater.*, 2000, **32**, 303–314.
- 56 Y. Zeng, X. Zhou, L. An, L. Wei and T. Zhao, *J. Power Sources*, 2016, **324**, 738–744.
- 57 Y. Zeng, T. Zhao and L. An, *J. Power Sources*, 2015, **300**, 438–443.
- 58 H. Zhang, Y. Tian, J. Li and B. Xue, *Electrochim. Acta*, 2017, **248**, 603–613.