Stable boron nitride nanocomposites based membranes for high-efficiency proton conduction

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Article info
Article history:
Received 14 December 2017
Received in revised form 6 March 2018
Accepted 2 April 2018
Available online 6 April 2018

Keywords:
Boron nitride nanocomposite
Exfoliation
Surface-charge governed proton conduction
Long-range ionic nanochannel
Freestanding membrane

Abstract
Proton conduction is a not only a universal and fundamental process in nature but also have been widely used in energy- and environment-related applications. Achieving high-efficiency proton conduction is very important in these areas. Herein, stable and selective membranes with novel ionic nanochannels based on functionalized two-dimensional boron nitride nanocomposites (NBN) are successfully fabricated. The proton conductivity of Na$_{10}$ion-sNBNM at 80 °C - 95 %RH is as high as 0.44 S cm$^{-1}$. At the same time, NBN-sNBNM shows impressing stability at high-humidity conditions and in redox environments. The high proton conductivity could be attributed to the favorable microphysical and microchemical environments of the nanochannels in the membranes. On one side, the double-layer space among the closely assembled NBN propels the local surface-charge enhanced proton conduction. On the other side, the formation of connected long-range ionic nanochannels and quasi-isotropic architecture facilitate the long-range proton conduction. Benefitting from the excellent stability of NBN, the proton conductivity of Na$_{10}$ion-sNBNM at high-temperature and low-humidity conditions could be conveniently increased by H$_3$PO$_4$ adsorption. Furthermore, Na$_{10}$ion-sNBNM also shows low methanol permeability and high membrane selectivity. These outstanding properties of Na$_{10}$ion-sNBNM demonstrate great application potential in many areas.

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1. Introduction

Proton conduction is a universal and fundamental process in nature and lives, such as proton transportation through the mitochondrial inner membrane, phosphorylation in the chloroplast, and biochemical redox reactions [1,2]. Beyond biological systems, solid electrolytes for proton conduction have been widely used in energy- and environment-related applications including fuel cells, electrodialysis, and lithium-ion batteries [3–8]. Amphipathic ionomer based membranes, Na$_{10}$ion and sulfonated poly (ether ether ketone) for instances, with bicontinuous aggregation structures, are frequently used in these areas due to the mature preparation techniques [9–11]. However, there are two inherent limitations of these ionomer based membranes. First, the ionic conduction channels in the membrane matrix are relatively short. On account of the nanophase separation of amphipathic ionomers, acidic ionic clusters would form in the membrane matrix during the membrane-fabrication process. These ionic clusters play the role as proton conduction sites, but they are in small dimension and insufficiently connected. These shortcomings lead to the lack of long-range ionic nanochannels in the membrane matrix and largely confines the proton conductivity. Second, the selectivity of the membranes is unsatisfying. Some small molecules, like methanol, have the similar conduction mechanism as protons [12,13]. This results in a trade-off effect between the membrane performance and membrane efficiency, which means the selectivity of the membranes would probably be decreased when an approach is tried to increase the proton conductivity. Thus, it is essential to develop novel membrane materials for fast and high-efficiency proton conduction.

The proton transportation in double-layer nanofluidic channels is remarkably unique, where the surface charge in the channels play a critical role in the proton conduction.

When the distance is lower than the Debye screening length, the surface-charged double layer could efficiently exclude the co-ions from the inner space of the channel and propel the proton conduction [14]. The membranes with layered microstructures could be conveniently fabricated from two-dimensional (2D) building blocks dispersion, including graphene oxide (GO), montmorillonite...
(MMT), and boron nitride nanosheets (BNNS) [15–17]. Plently of nanofluidic channels could easily form in the interfaces between the closely assembled 2D nanosheets with the large specific surface area, which provide potential physical microenvironments for proton conduction [14]. However, acidic and hydrophilic functional groups on these inorganic 2D nanosheets are limited. Thus, the surface charge on 2D nanosheets is weak, and it is also hard to form ionic nanochannels in membranes for long-range proton conduction. Considerable efforts have been put into constructing long-range ionic nanochannels in the membranes by functionalizing 2D nanosheets with abundant proton conduction sites or incorporating acidic groups into the inter-layer space of 2D nanochannels. Guangwei He et al. fabricated proton-conducting membranes via assembling of GO and MMT 2D nanosheets [4]. Highly sulfonated hydrophilic polymer (sulfonated polyvinyl alcohol) (SPVA) is incorporated into the interlayer space of 2D nanochannels via the inorganic-organic interfacial interactions. Both high proton conductivity and outstanding mechanical properties are achieved due to the connected long-range ionic nanochannels as well as the bio-inspired brick-and-mortar structures. Besides, 2D nanosheets based membranes are more selective to protons and demonstrate outstanding methanol resistance and membrane selectivity due to the intrinsic morphologies and atomic formations [18].

Compared with other 2D nanosheets, boron nitride nanosheets (BNNS) possess excellent thermal/chemical stability and low electronic conductivity while BNNS based proton exchange membranes have been rarely reported [19]. These properties bestow BNNS with significant advantages in the applications when environmental stability is required, especially under strong redox conditions. However, few functional groups on the surfaces result in two drawbacks of BNNS. One is the hydrophobicity so that it is difficult to obtain stable BNNS dispersion for membrane preparation. The other is the low surface charge, which confines the surface-charge governed proton conduction and the construction of long-range ionic nanochannels. By matching the surface energy of BNNS and the solvent, the 2D BNNS could be simultaneously functionalized by amphiphatic polymers via hydrophilic-hydrophobic and H-bonding interactions during the polymer-assisted liquid-phase exfoliation [20,21]. This method could conveniently obtain non-covalently functionalized BN nanocomposite dispersion which could be further used to prepare 2D BN nanocomposites based membranes. In our previous report, functionalized BN nanocomposites were successfully prepared via water-phase exfoliation and were blended with Nafion to prepare composite membranes [22]. The composite Nafion based membranes show obviously increased proton conductivity.

Here, stable 2D BN nanocomposites based membranes with long-range ionic nanochannels for high-efficiency proton conduction is reported. Functionalized 2D BN nanocomposites (NBN), the membrane-building blocks, were first obtained via eco-friendly ethanol-phase exfoliation method with the assistance of strongly acidic perfluorosulfonylic polymer (Nafion). Two kinds of bulk BN raw materials were used to prepare NBN with different sizes. The modification of Nafion on the surface of BNNS could not only help to stabilize the NBN dispersion but also enhance the surface charge of the nanocomposites. These properties are vital to the membrane fabrication as well as the construction of long-range ionic nanochannels in the membranes for fast proton conduction. Then, the NBN based membranes were prepared from the NBN dispersion via vacuum filtration. It is surprisingly found that the NBN based membrane fabricated from smaller NBN possesses a quasi-isotropic interior architecture where no apparent layered structure could be observed. This novel architecture largely facilitates the proton conduction within membranes and avoids the interlayer proton conduction barrier in typical 2D nanosheets based membranes with layered architectures. NBN based membranes show high proton conductivity and good selectivity at appropriate Nafion content on account of the surface-charge governed proton conduction as well as the establishment of connected long-range ionic nanochannels. Besides, NBN based membrane demonstrates good stability under high-temperature/high humidity, redox, and acidic conditions. Benefitted from the excellent stability, the proton conduction of NBN based membranes under low humidity conditions could be further increased via H3PO4 adsorption.

2. Experimental

2.1. Materials

Bulk hexagonal boron nitrides (BN) with were purchased from Aladdin Co. (China) (1–2 μm) and Alfa Aesa (10 μm). Bulk BN with smaller size from Aladdin Co. was named as bulk sBN and bulk BN with larger size from Alfa Aesa was named as bulk IBN. 5 wt% Nafion solution was obtained from Sigma-Aldrich. Poly(vinyl alcohol) (PVA, Mw – 145,000) was bought from Aladdin Co. (China). Nafion 117 membrane was purchased from Sinopharm Chemical Reagent Co. (China). All the chemical reagents were used without further purification.

2.2. Preparation of Nafion-(boron nitride) nanocomposites via exfoliation

The preparation procedure is similar to our previous report [22]. Typically, 200 mg bulk BN powder (1–2 μm) and 4 mL 50 mg/mL Nafion solution were added to 200 mL ethanol. The obtained ethanol dispersion was then ultrasonicated for 8 h. The Nafion functionalized BN nanocomposites were centrifugated at 3000 rpm for 20 min and then washed with ethanol and deionized water for several times. The obtained Nafion functionalized BN nanocomposite from small bulk BN raw material (1–2 μm) was named as sNBN. The 2D BN nanosheets were similarly prepared from small bulk BN raw material without adding Nafion and named as sBN. The nanocomposite and BN nanosheets prepared from large bulk BN raw material (10 μm) was named as INBN and IBN, respectively.

2.3. Preparation of Nafion-(boron nitride) based membranes

All the NBN based membranes were fabricated via the similar procedure. Typically, 800 μL 50 mg/mL Nafion solution and 1 mL 20 mg/mL were first added to 40 mL 1 mg/mL sBN aqueous dispersion. Then the mixed dispersion was ultrasonicated for 30 min. Second, the membrane was obtained on a microfiltration membrane (Whatman, diameter 5 cm) via vacuum filtration. Third, the acquired membrane was acidized in 1 M H2SO4 solution for 2 h and then washed with water for several times. The finally obtained membrane was named as Nafion-sNBNM. Similarly, Nafion-INBNM were prepared with INBNM dispersion. sNBNM and INBNM were fabricated via the filtration of sBN and INBN dispersion without further adding Nafion, respectively. IBNM was also prepared from IBN dispersion for comparison.

2.4. Characterizations

High-resolution transmission electron microscopy (HR-TEM) images were captured on a JEOL JEM2101 at 200 kV. The Field-emission scanning electron microscope (FE-SEM) images and energy dispersive X-ray spectrometry (EDX) data were acquired on Zeiss Ultra 55, Multimode 8 (Bruker) was used to take atomic force microscopy (AFM) images in tapping mode. The X-ray diffraction
(XRD) data were collected on Bruker D8 ADVANCE and DAVINCI-DESIGN, while X-ray photoelectron spectra (XPS) were obtained on a Perkin Elmer RBD upgraded PHI-5000C ESCA system with Mg Ka radiation. Thermofisher NEXUS 6700 was utilized to gather FTIR spectra. Zeta potential values of the nanocomposites were collected on Zetasizer Nano (Malvern). The thermos-gravity (TG) and differential thermos-gravity (DTG) data were acquired on TGA 1 Thermo Gravimetric Analyzer in the N₂ atmosphere with 20 °C min⁻¹ heating rate. LCR meter (TH2830) was adopted to measure the electron conductivity of the membranes in DCR mode. The ion exchange capacity (IEC) was determined by a titration method referring to the previous report [23]. Water uptake (WU) of the membranes were gathered similarly to our earlier report via equation (1) [24]:

\[ WU(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \] (1)

where \(W_{\text{wet}}\) and \(W_{\text{dry}}\) represent the wet membrane mass and the dry membrane mass, respectively.

The proton conductivity (σ) data were collected on a CHI660E electrochemical workstation with a four-electrode method in AC impedance mode [24]. The membranes were placed in a BPHJ-120AF temperature and humidity test chamber (Shanghai Blue-pard Instruments Co., Ltd.), which was used to adjust the testing temperature and humidity conditions. Nafion-sNBNM was immersed in 10 wt% H₂O₂ solution for stability test. The Nafion-sNBNM membrane was dipped in 40 wt% H₃PO₄ solution for 4 h before the high-temperature and low-humidity stability test. The methanol permeability (P) of the membranes were tested at 40 °C with 80 v/v% methanol/H₂O solution via the same method in our previous report on NEXUS 6700, Thermofisher [25]. The membrane selectivity (S) at 40 °C was calculated according to the equation (2):

\[ S = \frac{\sigma}{P} \] (2)

3. Results and discussion

3.1. Characterizations of Nafion-(boron nitride) nanocomposites

The size of bulk boron nitrides were observed with FE-SEM. The diameter of bulk sBN is ~500 nm while the diameter of bulk IBN is ~10 μm (Fig. S1). Two kinds of bulk BN with different dimensions were used to prepare the corresponding functionalized NBN nanocomposites (sNBN and INBN) via Nafion-assisted exfoliation. As shown in Fig. 1 (a and d), there is only a weak peak near 27°, regarding the (002) planes of the hexagonal BN, remaining in the XRD patterns of sNBN and INBN nanocomposites [26]. This proves bulk sBN and bulk IBN are successfully exfoliated to few-layer 2D nanosheets via ethanol-phase exfoliation method. With the assistance of Nafion, the exfoliation efficiency is largely elevated. The concentration of sBN dispersion (1.8 mg/mL) is 40% higher than that of sBN dispersion while the concentration of INBN dispersion (0.5 mg/mL) is increased by 67%. HR-TEM, AFM, and FE-SEM were utilized to observe the morphology of sNBN and INBN nanocomposites (Fig. 1, S2 and S3). Both sNBN and INBN possess 2D nanosheet morphology. The diameter of sNBN and INBN is ca. 100 nm and 2–4 μm, respectively. According to the AFM height images, the thickness of sNBN is near 4 nm while that of INBN is about 3.2 nm (Fig. S3).

The components of sNBN and INBN nanocomposites were studied with FTIR and XPS. As shown in Fig. 2 (a) and (b), four characteristic peaks ascribed to Nafion emerge from 1300 to 950 cm⁻¹ in the FTIR spectra of sNBN and INBN [27]. The F1s, C1s, and S2p peaks could be observed in the XPS spectra of NBN nanocomposites (Fig. 2(c)) [28]. The spectral evidence demonstrates the existence of Nafion in NBN nanocomposites. Compared with the Zeta potential values of BN nanosheets, lower values of NBN nanocomposites demonstrate that the NBN surfaces are more negatively charged, which proves the successful functionalization of Nafion on the surface of exfoliated BN nanosheets. INBN has the lowest Zeta potential value since more surface charges are needed to stabilize the larger nanosheets. In EDX mapping images, the bright spots refer to the corresponding atoms. Since F element only exists in Nafion and B element only exist in BN nanosheets, F EDX mapping images and B EDX mapping images could be used to observe the distribution of Nafion in NBN nanocomposites. Both B atoms and F atoms distribute uniformly in the EDX mapping images (Fig. S4), which indicates the uniform distribution of Nafion in NBN nanocomposites. The Nafion modification layer thickness of sNBN and INBN is 0.7 and 1 nm, respectively, as shown in the HR-TEM images (Fig. 1(c) and f)). Since BN nanosheets hardly lose weight while Nafion undergoes a complete thermal degradation from 100 to 800 °C in the N₂ atmosphere, the TGA curves could be used to estimate the Nafion content in the NBN nanocomposites (Fig. 2(e)) [29]. The Nafion content in sNBN and INBN is 18 wt% and 13 wt%, respectively.

Furthermore, the interactions between Nafion and exfoliated BN nanosheets in NBN nanocomposites are studied. According to the DTG curves of Fig. 2(f), the Nafion backbone degradation temperature of both sNBN and INBN are 467 °C, which is lower than that of recast Nafion (528 °C) [22]. Two FTIR characteristic bands ascribed to the stretching vibrations of perfluoro backbones of Nafion (1236 and 1150 cm⁻¹) appear obvious peak shifts with a comparison to those of recast Nafion (1200 and 1144 cm⁻¹) (Fig. 2(b)) [22]. These phenomenon reveal the strong hydrophobic interaction between Nafion’s hydrophobic perfluoro backbones and the exfoliated BN nanosheets in NBN nanocomposites. It could be inferred that the strong hydrophobic interaction motivates the hydrophobic backbones of Nafion to adsorb on the surface of BN nanosheets in polar environments so that the system surface energy is lowered. Consequently, the NBN nanocomposites form. The desulfonation temperature of sNBN and INBN is 340 and 369 °C, respectively, which is also lower than that of recast Nafion (377 °C) [22] (Fig. 2(f)). The decreased desulfonation temperature indicates stronger electrostatic repulsion among the sulfonic groups of Nafion due to the aggregation on the surfaces of BN nanosheets. The peripheral sulfonic groups ionize and form a negative surface charge, which could stabilize the NBN nanocomposites from reaggregation. The exfoliation is illustrated in Fig. 1(g). Also, the characteristic peaks of B-O and N-O bonds could be made out in the characteristic peaks of B-O and N-O bonds could be made out in the FTIR spectra of sNBN and lNBN [27]. The F1s, C1s, and S2p peaks could be observed in the XPS spectra of NBN nanocomposites (Fig. 2(c)) [28]. The spectral evidence demonstrates the existence of Nafion in NBN nanocomposites. Compared with the Zeta potential values of BN nanosheets, lower values of NBN nanocomposites demonstrate that the NBN surfaces are more negatively charged, which proves the successful functionalization of Nafion on the surface of exfoliated BN nanosheets. INBN has the lowest Zeta potential value since more surface charges are needed to stabilize the larger nanosheets. In EDX mapping images, the bright spots refer to the corresponding atoms. Since F element only exists in Nafion and B element only exist in BN nanosheets, F EDX mapping images and B EDX mapping images could be used to observe the distribution of Nafion in NBN nanocomposites. Both B atoms and F atoms distribute uniformly in the EDX mapping images (Fig. S4), which indicates the uniform distribution of Nafion in NBN nanocomposites. The Nafion modification layer thickness of sNBN and INBN is 0.7 and 1 nm, respectively, as shown in the HR-TEM images (Fig. 1(c) and f)). Since BN nanosheets hardly lose weight while Nafion undergoes a complete thermal degradation from 100 to 800 °C in the N₂ atmosphere, the TGA curves could be used to estimate the Nafion content in the NBN nanocomposites (Fig. 2(e)) [29]. The Nafion content in sNBN and INBN is 18 wt% and 13 wt%, respectively.

3.2. Characterizations of Nafion-(boron nitride) based membranes

The NBN based membranes were fabricated via vacuum filtration, and PVA was added to facilitate membrane formation via H-bonding interaction with Nafion. sBN membrane could not be prepared from sBN nanosheet dispersion due to the small dimension as well as the lack of Nafion modification. The composition of the membranes was determined according to the TGA curves (Fig. 3(a)). The weight loss in the temperature range from 100 to
200 °C is due to the dehydration of membranes while the weight loss in the temperature range from 200 to 300 °C is caused by the PVA degradation [30]. The residual weight loss is ascribed to the Nafion degradation [22]. The composition of the NBN based
membranes is listed in Table S1. The Nafton content of sNBNM and INBNM is in consistency with that of sNBN and INBN. The PVA content of the NBN based membranes is ~1 wt%.

The morphology of NBN based membranes was observed with FE-SEM (Fig. 4). Layered architecture could be seen within INBNM and Nafton-INBNM. Nevertheless, a quasi-isotropic architecture appears within sNBNM and Nafton-sNBNM, which might be caused by the small dimension of sNBN in a relatively fast filtration process. Nafton-sNBNM and Nafton-INBNM have more densified cross-sectional morphology than sNBNM and INBNM on account of the higher Nafton contents. The channel information of the dry and hydrated NBN based membranes was explored with XRD (Fig. 3(c and d)). The diffraction peak at 2θ originated from (002) plane could be seen in the XRD patterns of NBN based membranes, which indicates the intrinsic few-layer structure of the BN nanosheets in NBNM. Regarding the Bragg’s law, the d spacing of NBN nanocomposites in the membranes is ca. 0.23 nm, which is much lower than the Debye screening length (~30 nm with monovalent ions at a concentration of 10⁻⁴ M) [14]. This space provides an ideal physical microenvironment for surface-charge governed proton conduction. No obvious peak shift could be observed after membranes being hydrated, which demonstrates that few water molecule enters the double-layer space among closely assembled NBN nanocomposites. Besides, almost unchanged peak shape after hydration shows the well-preserved periodic spacing in the z-direction as well as the good membrane stability to water [14,31]. However, the water uptake of the NBN based membranes is 23–39 wt% (Fig. 3(b)). Hence, it could be deducted that the adsorbed water mainly enter the space among the untightly assembled NBN nanocomposites in the membranes. All the membranes show good insulating property because of the BN’s extremely low electron conductivity (Table S2).

The humidity-dependent and temperature-dependent proton conductivity of NBN based membranes are shown in Fig. 5. The proton conductivity of IBNM is consistent with the previous report...
sNBNM and lNBNM present higher proton conductivity compared to that of IBNM under various conditions, which could be attributed to the peripheral Nafoion of NBN nanocomposites (Fig. 5 (a) and (b)). The strong acidity of Nafoion bestow the double-layer nanochannels among closely assembled NBN with higher surface charge, which enhances the local surface-charge governed proton conduction (Fig. 6). The proton conductivity of sNBNM and INBNM increased rapidly at high-humidity conditions (above 80 %RH). At higher humidity, the hydration degree of the membranes is increased and more water as proton carriers enter the space among untightly assembled NBN and facilitate the proton conduction. sNBNM and INBNM shows much lower proton conductivity at 40 % RH conditions than at high-humidity conditions, which could be ascribed to the weak water retention and further proves the importance role of water in proton transportation. Compared to INBNM, the higher proton conductivity of sNBNM at low humidity conditions could be attributed to more proton conduction sites with higher content of Nafoion as well as the quasi-isotropic intra architecture. Ion exchange capacity (IEC) is used to evaluate the acidic group content of the membranes. IEC of sNBNM and INBNM is only 0.3 and 0.2 mmol/g, respectively (Table S2). Such low IEC could hardly afford to construct long-range ionic nanochannels for
long-range proton transportation so that the proton conduction is largely confined in the space among untightly assembled NBN, where surface-charge governed proton conduction is disabled (Fig. 6). As a result, the proton conductivity of sNBNM and lNBNM is lower than that of commercial Nafion 117 membrane by two orders of magnitudes.

The Nafion contents of Nafion-sNBNM and Nafion-lNBNM are elevated, and the added Nafion is immobilized in membranes via H-bonding interactions. The IEC of Nafion-sNBNM and Nafion-lNBNM is increased to 1.3 and 0.9 mmol/g, respectively, which is close to that of Nafion 117 (0.9 mmol/g) [32]. The added Nafion fills the space among untightly assembled NBN to reach a more densified architecture and provide more proton conduction sites for constructing long-range ionic nanochannels (Fig. 6). As a result, the proton conductivity of Nafion-sNBNM and Nafion-lNBNM are significantly increased. The proton conductivity of Nafion-sNBNM at 80 °C - 95 %RH is as high as 0.44 S cm⁻¹ while the proton conductivity of commercial Nafion 117 at the same condition is 0.13 S cm⁻¹ (Fig. 5 (c)). At the same time, NBN-sNBNM shows impressing stability at high-humidity conditions and in redox environments. After 720-min test at 80 °C - 95 %RH, the proton conductivity of Nafion-sNBNM keeps almost unchanged (Fig. 7(a)). After immersing in 10 wt% H₂O₂ solution for 720 min, the proton conductivity is still as high as 0.33 S cm⁻¹ (Fig. 7(b)).

The excellent proton conductivity of Nafion-sNBNM at high-humidity condition could be attributed to the well-fabricated microphysical and microchemical environments [4,33]. First, the strong acidity of Nafion’s sulfonic groups provide ideal proton conduction sites and enhance the surface charge of nanochannels. Second, the double-layer space among the closely assembled NBN with high surface charge offers ideal nanochannels for local proton transportation via surface-charge governed proton conduction. Third, the connected long-range ionic nanochannels and the quasi-isotropic architecture facilitates the long-range proton conduction. Last but not least, high water uptake ensures the high hydration degree of sulfonic groups in the membranes, which is especially advantageous for proton conduction.

However, the proton conductivity of Nafion-sNBNM and Nafion-lNBNM does not show obvious advantages over commercial Nafion 117 at low-humidity conditions. The performance stability at low-humidity condition is unsatisfying. After 720-min test at 100 °C - 40 %RH, the proton conductivity of Nafion-sNBNM is decreased from 0.032 to 0.011 S cm⁻¹ due to the poor water retention of the membranes at high-temperature and low-humidity conditions (Fig. 5 (d)). On account of the good chemical stability of NBN, this drawback could be conquered by immersing the membrane in H₃PO₄ solution. H₃PO₄ with a high boiling point could take place water as proton carriers at high-temperature and low-humidity conditions. The H₃PO₄ adsorption quantity of Nafion-sNBNM is 130 wt%. The proton conductivity of H₃PO₄ doped Nafion-sNBNM at 100 °C - 40 %RH is elevated to 0.35 S cm⁻¹ and keeps at 0.33 S cm⁻¹ after 720-min test (Fig. 7(c)). This property endows Nafion-sNBNM with great potential in high-temperature applications.

Since proton and methanol have similar transport mechanism, the traditional solid electrolytes with high proton conductivity usually have to face the severe methanol crossover problem [34]. All the NBN based membranes show lower methanol permeability than that of Nafion 117 by more than one order of magnitude (Table 1). The methanol permeability of sNBNM is as low as 3.3E-09 cm² s⁻¹. Although the proton conductivity is largely increased by three orders of magnitude, the methanol permeability of Nafion-sNBNM and Nafion-lNBNM just slightly goes up, which could be benefited from 2D morphology as well as the unique atomic formations of NBN [18]. With high proton conductivity and low methanol permeability, the selectivity of Nafion-sNBNM is twenty-two times higher than that of commercial Nafion 117. The transport properties of Nafion-sNBNM has a great competitiveness over the state-of-the-art 2D nanosheets based membranes (Table S3).

4. Conclusions

Herein, stable and selective 2D NBN based membranes with novel ionic nanochannels are successfully fabricated for high-efficiency proton conduction. 2D NBN with high surface charge was first obtained via eco-friendly ethanol-phase exfoliation method with the assistance of strongly acidic Nafion. Then, the NBN based membranes were prepared from the NBN dispersion via vacuum filtration. NBN based membranes with appropriate Nafion content show outstanding proton conductivity at high-humidity conditions as well as good selectivity. The proton conductivity of Nafion-sNBNM at 80 °C - 95 %RH is as high as 0.44 S cm⁻¹. At the same time, NBN-sNBNM shows impressing stability at high-humidity conditions and in redox environments. The high-efficiency proton conduction could be attributed to the novel ionic nanochannels with favorable microphysical and micro-chemical environments in the membranes. On one side, the double-layer space among the closely assembled NBN provides ideal nanochannels for local proton transportation via surface-charge governed proton conduction. On the other side, the connected long-range ionic nanochannels are constructed by filling the space among untightly assembled NBN with additional Nafion, which is advantageous to the long-range proton conduction. The quasi-isotropic architecture of Nafion-sNBNM further facilitates the intra-membrane proton conduction. Benefiting from the excellent stability of NBN, the proton conductivity of Nafion-sNBNM at high-temperature and low-humidity conditions could be conveniently

![Fig. 7.](image-url) (a) The long-time proton conductivity test of Nafion-sNBNM at different conditions. (b) The proton conductivity of Nafion-sNBNM after H₂O₂ processing. (c) The long-time proton conductivity test of H₃PO₄ doped Nafion-sNBNM and Nafion 117 at 100 °C - 40 %RH.

increased by H3PO4 adsorption. The proton conductivity of H3PO4 doped Nafion-sNBNM at 100 °C –40 %RH reaches 0.35 S cm–1 and demonstrates good stability. Besides, Nafion-sNBNM possesses low methanol permeability and high selectivity. These outstanding properties endow Nafion-sNBNM with intense potential in wide-range applications.

Acknowledgment

We gratefully acknowledge the financial support from the Ministry of Science & Technology of China (No. 2016YFA0203302).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2018.04.017.

Table 1

<table>
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<tr>
<th>At 40 °C</th>
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References
