A bismuth oxide/graphene oxide nanocomposite membrane showing super proton conductivity and low methanol permeability†

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Proton exchange membrane fuel cells are still limited as state-of-art proton exchange membranes perform poorly at high and low temperature and are easily damaged by harsh electrochemical conditions such as reactive peroxide species. One effective solution to this issue is to develop new types of proton conductive materials that are capable of working in a broad temperature range. A simple vacuum-assisted filtration method is employed to obtain a well-ordered proton-conducting membrane by immobilizing nanosized bismuth oxide clusters [H6Bi12O16(NO3)10·6H2O] (H6Bi12O16) onto graphene oxide (GO) supports (named as (H6Bi12O16)/GO). (H6Bi12O16)/GO is stable in acidic media and has high proton conductivity over the temperature range from −40 to 80 °C. The proton conductivity of the (H6Bi12O16)/GO membrane is 0.564 S cm−1 at 80 °C in aqueous solution (in plane), and 0.1 S cm−1 at 80 °C and 97% RH (out of plane), respectively. Without loss of high proton conductivity, the membrane also exhibited 100-fold lower methanol permeability than a Nafton 117 membrane. Moreover, (H6Bi12O16)/GO displayed good catalytic decomposition of hydrogen peroxide and superior humidity response and recovery properties. These advantages mean that (H6Bi12O16)/GO holds great promise as a solid-state electrolyte that can potentially be applied in energy conversion devices in the future.

Introduction

Proton exchange membrane fuel cells have been regarded as promising energy conversion devices due to their high efficiency, environmentally friendly characteristics and extensive applications, including in portable electronic devices, electric vehicles, and smart grids. The proton exchange membrane is one of the key components that affect the overall performance of fuel cells.

Currently, the most widely used perfluorinated sulfonated polymer, Nafton, is deemed to be the benchmark for proton-conducting materials. Its unique oriented ionic nanochannels can facilitate fast proton transportation, with a proton conductivity of up to 0.1 S cm−1 at 80 °C under 100% RH.2

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However, it suffers from several drawbacks, such as high cost, significant decline of proton conductivity above 80 °C or below its freezing point, poor endurance of membranes caused by freeze/thaw cycles and high methanol permeability. More importantly, the oxygen reduction reaction in proton exchange membrane fuel cells produces strong oxidizing groups such as hydrogen peroxide/basicals [OH or ·OOH) that can attack the internal skeleton structure of Nafton and initiate decomposition, which may dramatically increase the risk of fuel cell breakdown and reduce their service life.3

Recently, much effort has been devoted to creating new materials conquering these disadvantages, such as metal–organic frameworks, polyoxyometalate-based hybrids, etc.4 As we know, there exists a distinct trade-off effect between proton transportation and methanol permeation. An effective method to reduce methanol permeability without lowering proton conductivity is to introduce hydrophilic groups (e.g., hydroxyl groups or sulfonic, phosphonic or carboxylic acids) which can facilitate fast proton transportation and methanol permeation. An effective method to reduce methanol permeability without lowering proton conductivity is to introduce hydrophilic groups (e.g., hydroxyl groups or sulfonic, phosphonic or carboxylic acids) which can facilitate fast proton transportation and methanol permeation. An effective method to reduce methanol permeability without lowering proton conductivity is to introduce hydrophilic groups (e.g., hydroxyl groups or sulfonic, phosphonic or carboxylic acids) which can facilitate fast proton transportation and methanol permeation. An effective method to reduce methanol permeability without lowering proton conductivity is to introduce hydrophilic groups (e.g., hydroxyl groups or sulfonic, phosphonic or carboxylic acids) which can facilitate fast proton transportation and methanol permeation.
times higher proton conductivity (0.564 S cm\(^{-1}\)) than Nafion (\(~0.1\) S cm\(^{-1}\)) at 80 °C (Scheme 1).

**Results and discussion**

**Structural characterization of \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) and the \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}\) composite**

The \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}\) nanocomposite membrane was synthesized via a co-precipitation mechanism (Fig. 1a). The \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\])\(^{0+}\) polyanion nanoclusters interacted with GO via strong electrostatic force and hydrogen bonds. \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) clusters are composed of two \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\])\(^{5+}\) groups joined across the symmetry centres through two bridging O atoms, together with nitrate anions and water molecules (Fig. S1†).

The scanning electron microscopy (SEM) images showed the cross-sectional morphology of the \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}\) membrane. It is clearly observed from Fig. 1b and c that \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) cluster nanoparticles were randomly distributed on the surface and edge of the multilayer stacked graphene oxide sheets with an average size of ca. 8.66 nm. This result was further verified by the TEM images in Fig. 1d-f. For comparison, pure \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) bulk material is comprised of regular nanoplates with an average size of 0.28 μm (Fig. S2†). The introduction of GO is helpful to improve the specific surface area of the composite materials and reduce the size of particles.\(^{12}\) At the same time, it is also confirmed that we have successfully downsized the bulk \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) crystalline material to \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) nanocrystals tethered onto GO supports. The high-resolution TEM images of \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) clusters presented lattice fringes with a d-spacing of 0.32 nm, associated with their (−5 1 3) crystallographic plane (Fig. S3†). The high-resolution TEM image of the \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}\) exhibited the presence of GO layers and clear lattice fringes of bismuth oxide \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) nanocrystals with interplanar distances of 0.32 nm (Fig. 1d-f), which is consistent with the \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) bulk material. This can further explain that the \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) nanocrystals spread on the graphene oxide sheets forming a bismuth oxide/GO composite. Fig. 1g-k show the corresponding elemental mapping images of \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}\), which confirmed the distribution of Bi, C, O and N across the entire range. The EDX results further confirm the composition of \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}\) as depicted in Fig. S4†.

The powder X-ray diffraction (XRD) patterns of GO, \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) and \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}\) are shown in Fig. 2a. The XRD pattern of the \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}\) composite contains both peaks of GO and \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\), indicating the successful combination of the two components; characteristic 2θ peaks located at 6.519°, 11.634°, 24.894°, 27.770° and 42.548° were indexed to the (1 0 0), (1 1 0), (−3 2 2), (−5 1 3) and (−8 0 6) facets of \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}\) [JCPDF 70-1226]. The peak of GO at 11.8° indicates that the interlayer spacing is 0.82 nm. The chemical and thermal stability of the composite was characterized by XRD as well. The XRD patterns remain unchanged after soaking in boiling water and 8 M nitric acid. The temperature-varied XRD patterns demonstrate that the composite is stable up to 120 °C (Fig. S5†).

The FT-IR spectra (Fig. S6†) and Raman spectra (Fig. S7†) also confirmed the combination of \(\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}\). X-ray photoelectron spectroscopy (XPS) measurements were...
performed to investigate the chemical composition and valence states of the $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$ composite. The full scan XPS of $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$ indicated the presence of Bi, C, O and N elements (Fig. 2b).

The binding energy of Bi 4f and C 1s indicates that Bi and C are present in the composite (Fig. S8†). Furthermore, the BET surface areas of the $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}$ and $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$ were measured to be 7 m$^2$ g$^{-1}$ and 49.6 m$^2$ g$^{-1}$, respectively, suggesting that GO can slightly increase the specific surface area of the composite (Fig. 2c). The N$_2$ adsorption isotherm of $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$ was not a hysteresis loop, suggesting its nonporous structure.$^{14}$

Thermogravimetric analysis (TGA) of $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}$ and $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$ showed excellent thermal stability for these materials (Fig. S9 and S10†). $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$ showed a much higher weight loss than $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}$, proving that more water molecules or hydroxyl groups exist in $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$. Water vapour adsorption of $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}$ and $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$ dried samples was carried out at 25 °C to test their water adsorption and water retention abilities. As shown in Fig. 2d, the water adsorption increased slowly with the increase of water vapour relative pressure for $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}$ and $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$. Surprisingly, when the relative pressure continued to rise to above 0.9, the amount of adsorption increased rapidly for $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$, and the maximum water uptake is 177.5 cm$^3$ g$^{-1}$, corresponding to approximately 14.4 wt% water molecules adsorbed, which might be attributed to surface adsorption.$^{15}$

The water adsorption isotherm of $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$ with large hysteresis loops appeared to be a type-IV isotherm, showing that the material had excellent hydrophilic properties and high water holding capacity.$^{16}$ The huge water adsorption at high relative pressure might be attributed to the capillary action. $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}$ nanoparticles assembled next to each other on the hydrophilic surface of GO, leading to many pinholes that caused capillary action. Due to the synergistic effect of GO and $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}$, the composite showed better water adsorption and retention compared with bulk $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}$ under high relative pressure.

![Fig. 1](image-url)  
(a) The $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$ membrane was obtained via vacuum-assisted filtration. (b and c) Scanning electron microscope (SEM) cross-sectional images of $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$. (d–f) TEM images of $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$. (g–k) Corresponding elemental mapping images of Bi, C, O and N of $\{\text{H}_6\text{Bi}_{12}\text{O}_{16}\}/\text{GO}$. 

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Proton conductivity of the \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) membrane

The proton conductivity of the \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) was evaluated by AC impedance spectroscopy using the vacuum-assisted filtration method to assemble well-ordered membranes attached to the surface between four platinum electrodes.\(^7\) The \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) membranes exhibit higher proton conductivities than the pristine \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}\) (Fig. 3a and S11, ESI†). The proton conductivity of \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) membranes is 0.14 S cm\(^{-1}\) in an aqueous solution at 30 °C. As the temperature was elevated to 80 °C, the proton conductivity of the \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) membrane exhibited large enhancement, its proton conductivity reaching 0.564 S cm\(^{-1}\) (Fig. 3a & S12†). We proposed that in aqueous solution, more loosely bonded water molecules on the surface of the composite membrane behave like free liquid water, eliminating innumerable grain boundaries of \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) in the nanocomposite, achieving consecutive in-plane proton transfer paths for rapid proton migration. The XRD patterns of the \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) composite film exhibits good ion exchange capacity (IEC) and water uptake capacity (WU), as reported in the ESL†.

To further explore the humidity sensitivity of \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) under harsh working conditions, the resistance responses to humidity based on the \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) membrane were measured at 1000 Hz.\(^8\) Fig. 3b shows four cycles of response and recovery processes between 43% and 97% RH for the \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) membrane. Apparently, the composite membrane presented an impedance change between ~6000 Ω and ~200 Ω for humidity increments from 43% to 97% RH, showing a high magnitude response to different relative humidities. Moreover, the \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) membrane presented much faster water adsorption and desorption process response times \(t_{97\%}\) of 2 s and 4.3 s, respectively. In comparison, the Nafion 117 film revealed that for hysteresis as large as 97% RH (Fig. S13†), the response times for both adsorption and desorption procedures were much longer. This can be attributed to the surface oxygen atoms of the \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) membrane, providing a larger number of active sites for humidity sensitivity. In particular, the adsorption process could not reach an equilibrium state, even after 10 hours. To further elucidate the correlation between proton conductivity in the vertical direction of \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) and different relative humidities, we measured the proton transfer performance of \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) under varying relative humidity values, ranging from 35% to 97% RH at 30 °C. The proton conductivity was evaluated by AC impedance spectroscopy using a compacted pellet of the powder sample attached to the surface of two gold electrodes. As shown in Fig. S14† proton conductivity increases with the rise of relative humidity. The proton conductivity of pure \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}\) material ranges from \(1.0 \times 10^{-8}\) S cm\(^{-1}\) to \(7.4 \times 10^{-8}\) S cm\(^{-1}\) from 35% RH to 97% RH (Fig. S12†). As for the \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) composite, its proton conductivity can only reach \(9.74 \times 10^{-7}\) S cm\(^{-1}\) under a relative humidity of 35%, due to the lack of adequate water molecules to build abundant hydrogen bonding networks under low relative humidity (Fig. S14†). But when RH increased to 97%, the value increased rapidly to \(5.5 \times 10^{-2}\) S cm\(^{-1}\), which is almost \(10^5\) times higher than that under low relative humidity at 30 °C. The value is much higher than that of most MOF/POM-based materials at ambient temperature. We proposed that the obvious improvement in proton conductivity of \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) resulted from the following factors: firstly, \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) materials can provide a higher concentration of protons as well as proton donor and receptor sites for proton transportation. Secondly, the bismuth oxide surface contained multiple water layers, including molecularly adsorbed water hydroxyls, a hydrogen bonded layer and a first physisorbed layer. This effectively reduced the energy barrier and facilitated the fast transportation of protons in the composite. Thirdly, graphene oxide nanosheets had high surface area to promote nanocrystallization of \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}\) particles and cause nanogaps. Meanwhile GO provides hydrophilic sites and constructs continuous hydrogen bonding networks for proton transfer between \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}\) particles. All these reduced grain boundary resistance between pure bismuth oxides effectively constructing long-range hydrogen-bonding networks. Under high relative humidity, the gaps of \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}\) nanoparticles were filled with water molecules due to capillary action, which facilitates quick proton transfer via continuous hydrogen bonding networks between \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}\) particles.

Proton conducting materials that suitably work below the freezing point have gradually received attention due to real application demand.\(^9\) The \([\text{H}_6\text{Bi}_{12}\text{O}_{16}\text{]}/\text{GO}\) composite showed a remarkable proton conductivity of \(2.17 \times 10^{-4}\) S cm\(^{-1}\) at \(-40\) °C (Fig. S15 and S16†). We also confirmed the...
cycle stability of the {H$_6$Bi$_{12}$O$_{16}$}/GO material via performing heating and cooling cycle measurements (Fig. 3c), and little variation in its proton conductivity was found from $40\degree C$ to $0\degree C$. We proposed that the crystalline water is retained between particle gaps under the freezing point and forms a more extensive hydrogen-bond network for improving the proton conductivity to a large extent. {H$_6$Bi$_{12}$O$_{16}$}/GO represents a new type of solid state proton-conductive material with relatively high proton conductivity at sub-zero temperatures.

Proton-conducting materials as electrolytes for fuel cells were required to be electric insulators to inhibit interelectric breakdown. We investigated the electron conductivity of {H$_6$Bi$_{12}$O$_{16}$}/GO by direct-current measurements, and the electron conductivity was negligible. Thus, {H$_6$Bi$_{12}$O$_{16}$}/GO itself was an electric insulator. Simultaneously, we conducted ionic conductivity measurements of {H$_6$Bi$_{12}$O$_{16}$}/GO in deuterated water under different RH% conditions to prove that the ionic conductivity is due to proton transfer (Fig. S17†). Under 65% RH, proton conductivities at various temperatures are shown in Fig. S20; the activation energy of {H$_6$Bi$_{12}$O$_{16}$}/GO is 0.49 eV, which suggests that a mixed Grotthuss and Vehicle mechanism may exist under lower relative humidity. To investigate the durability of the composite material, we measured the proton conductivity of the {H$_6$Bi$_{12}$O$_{16}$}/GO sample at 80$\degree C$ under 97% RH for 12 h (Fig. S21†). The proton conductivity of {H$_6$Bi$_{12}$O$_{16}$}/GO remained at approximately 0.1 S cm$^{-1}$, suggesting its long-term durability under high relative humidity, which is comparable to that of the commercial Nafion membrane (0.1 S cm$^{-1}$, 80 $\degree C$, 100% RH). This value is also higher than those of previously reported studies regarding GO and/or MOF-modified membranes (Table S1†). Meanwhile, the structural integrity was evaluated from the PXRD patterns before and after the proton conductivity measurement (Fig. S5†).
Cyclic voltammetry was performed to prove that the composite can electrocatalyse the decomposition of hydrogen peroxide. As shown in Fig. 4, two well-defined redox couples can be observed in PBS solution at pH 7.4. \{H₆Bi₁₂O₁₆\}/GO shows promising electro-catalytic activity towards reduction of H₂O₂, as revealed by the changes in peak current upon the addition of H₂O₂. As the concentration of hydrogen peroxide increases continuously, the cathodic current increases, while the related anodic current decreases. This indicates that in the fuel cell application, the hydrogen peroxide formed during the oxygen reduction reaction will be decomposed by \{H₆Bi₁₂O₁₆\}/GO and lower the effect on the efficiency of the fuel cell.

It is noteworthy that most proton exchange membrane materials cannot electrocatalyse the decomposition of hydrogen peroxide. Above all, the \{H₆Bi₁₂O₁₆\}/GO composite showed super proton conductivity even at sub-zero temperatures and catalysed the decomposition of hydrogen peroxide.

As an important indicator to evaluate the resistance for fuel permeation of membranes applied in direct methanol fuel cells, methanol permeability (P) tests were carried out with comparison between \{H₆Bi₁₂O₁₆\}/GO and Nafton. As shown in Fig. 5, the methanol permeability of \{H₆Bi₁₂O₁₆\}/GO decreased with increasing thickness of membranes as a general rule. Moreover, membranes of \{H₆Bi₁₂O₁₆\}/GO with thickness from 30 µm to 200 µm have a lower methanol permeability compared to those of Nafton with similar thicknesses (approximately 2 orders of magnitude). Combined with the above results, the introduction of graphene oxide leads to the \{H₆Bi₁₂O₁₆\}/GO composite membrane exhibiting obviously lower methanol permeability than the Nafton membrane, and the methanol permeability of the membranes remained almost unchanged with increasing the reaction time, remaining at \(10^{-10}\) cm² s⁻¹ (Fig. S22 & Table S3†).

We discussed that ultralow methanol diffusion can be achieved through the interlayer spacing of multilayer stacked GO nanosheets to prevent methanol from entering, while facilitating fast transport of protons by the construction of highly continuous ionic channels. On the other hand, we assumed that the composite material induced hydrogen-bond barrier from hydrophilic groups results in more tortuous channels, preventing methanol crossover.

The high proton conductivity combined with the excellent resistance against methanol permeation make the \{H₆Bi₁₂O₁₆\}/GO suitable for use in DMFCs. The \{H₆Bi₁₂O₁₆\}/GO composite material cannot endure super strong mechanical extrusion during membrane electrode assembly and so we mixed \{H₆Bi₁₂O₁₆\}/GO with polyvinyl alcohol (PVA). The cell performance of the \{H₆Bi₁₂O₁₆\}/GO/PVA membranes was evaluated at 80 °C under fuel cell operating conditions of 1 M methanol solution at the anode side and oxygen gas at the cathode side. The DMFCs using the \{H₆Bi₁₂O₁₆\}/GO/PVA membranes have better performance because of the enhanced proton conductivity and reduced methanol permeability of the \{H₆Bi₁₂O₁₆\}/GO/PVA membranes (Fig. 6). The open-circuit voltage (OCV) and the maximum power density of the DMFCs using the \{H₆Bi₁₂O₁₆\}/GO/PVA membranes reach 0.89 V and 3.2 mW cm⁻², respectively. It is worth mentioning that the open-circuit voltage (OCV) is higher than that of most reported ones due to the excellent methanol resistance of \{H₆Bi₁₂O₁₆\}/GO/PVA membranes.
humidity response and recovery properties. The \{H_6Bi_{12}O_{16}\}/GO catalytic decomposition of hydrogen peroxide, as well as quick loss of superior proton conductivity, and meanwhile show permeability, that is, lower methanol permeability without the \{H_6Bi_{12}O_{16}\}/GO mixed solution. The above mixed solution was adjusting the pH of the solution to 0 using 6 M NaOH. The \{H_6Bi_{12}O_{16}\}/GO nanocomposite can effectively overcome the trade-off effect between proton conductivity and methanol permeability, that is, lower methanol permeability without the loss of superior proton conductivity, and meanwhile show catalytic decomposition of hydrogen peroxide, as well as quick humidity response and recovery properties. The \{H_6Bi_{12}O_{16}\}/GO composite membrane showed better proton conductivity than Nafion in aqueous solution with a proton conductivity (in plane) of 0.564 S cm$^{-1}$ at 80 °C and also showed good performance at sub-zero temperatures with a value of $2.17 \times 10^{-4}$ S cm$^{-1}$ at $-40$ °C. \{H_6Bi_{12}O_{16}\}/GO followed the Grotthuss mechanism under 97% RH. The composite membrane showed 100-fold lower methanol permeability than a Na\{H_6Bi_{12}O_{16}\}/GO membrane was obtained by a direct self-assembly method, as illustrated in Fig. 7.

Conflicts of interest

There are no conflicts of interest.

Acknowledgements

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