



A poly (ethylene oxide)/graphene oxide electrolyte membrane for low temperature polymer fuel cells

Yuan-Cheng Cao^{*,1}, Chenxi Xu¹, Xu Wu, Xu Wang, Lei Xing, Keith Scott^{*}

School of Chemical Engineering and Advanced Materials, University of Newcastle, Merz Court, Newcastle NE1 7RU, UK

ARTICLE INFO

Article history:

Received 28 January 2011
Received in revised form 20 April 2011
Accepted 22 June 2011
Available online 29 June 2011

Keywords:

Poly (ethylene oxide)
Graphene oxide
Polymer electrolyte membrane
Proton-exchange membrane fuel cells

ABSTRACT

A novel method to prepare poly (ethylene oxide)/graphene oxide (PEO/GO) composite membrane aimed for the low temperature polymer electrolyte membrane fuel cells without any chemical modification is presented in this work. The membrane thickness is 80 μm with a GO content of 0.5 wt%. And SEM images show the PEO/GO membrane is condensed composite material without structure defects. Small angle XRD results for the membrane samples show that the d -spacing reflection (001) of GO in PEO matrix is shifted from $2\theta = 11^\circ$ to 4.5° as the PEO molecules intercalated into the GO layers during the membrane preparation process. FTIR tests show the typical $-\text{COOH}$ vibration near 1700 cm^{-1} . Tensile tests show the resultant PEO/GO membrane tensile strength of 52.22 MPa and Young's modulus 3.21 GPa, and the fractured elongation was about 5%. The ionic conductivity of this PEO/GO membrane increases from 0.086 to 0.134 S cm^{-1} when the operation temperature increases from 25 to 60°C with 100% relative humidity. And further tests show the DC electronic resistance of this membrane is higher than $20\text{ M}\Omega$ at room temperature with 100% relative humidity. Polarization curves in a single cell with this membrane give a maximum power density of 53 mW cm^{-2} at the operation temperature around 60°C , without optimizing the catalyst layer composition.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

During the last decade, polymer electrolyte membrane fuel cells (PEMFC) have attracted increasing attention, as the promising energy conversion devices with benefits of high power density and low green house gas emission [1–4]. Fuel cell technology is a leading sustainable alternative to conventional energy generation methods, which could operate with better efficiency. Among several types of fuel cells, great progress has been made with low temperature PEMFC, which has many attractive features such as quick start-up and high efficiency, which make them attractive for various applications in clean energy technology [2–6].

However, the widespread commercialization for transportation and stationary applications of the PEMFC has been hindered by several challenges, including the high cost of perfluorinated polymer electrolyte membranes (PEM), such as Nafion, which are the leading materials in the field with good chemical resistance and

high conductivity [7–9]. Therefore, new molecular designs for PEMs have focused on creating alternative membrane materials to the poly (perfluorosulfonic acid) related membranes or acid doped polymers. Much emphasis has been placed on designing new membranes with high conductivity and low cost [10–14]. Up to now, however, only a few membranes have exhibited promising conductivity.

Graphite oxide (GO), formerly called graphitic oxide or graphitic acid, is a compound of carbon, oxygen, and hydrogen in variable ratios. The structure and properties of graphite oxide depend on the particular synthesis method and degree of oxidation [15–19] and how it typically preserves the layer structure of the parent graphite, although the layers are buckled and the interlayer spacing is much larger than that of graphite [16,18]. The carboxylic acid groups on the GO sheets are so active that a wide range of reactions at the carboxylic acid groups has been developed over the course of small molecule organic chemistry. For example, amines or hydroxyls were reported to attach covalently with the $-\text{COOH}$ groups via the formation of amides or esters [16–18]. Hydrophilic graphene oxide disperses readily in most polar solvents such as water, breaking up into macroscopic flakes, which are mostly one layer thick. Furthermore, pure GO itself is an electronic insulator with differential conductivity between 1 and $5 \times 10^{-3}\text{ S cm}^{-1}$ at a bias voltage of 10V [16–18]. On other

* Corresponding authors. Tel.: +44 191 222 8771; fax: +44 191 222 5292.

E-mail addresses: yuancheng.cao@gmail.com, caosome@gmail.com (Y.-C. Cao), k.scott@ncl.ac.uk (K. Scott).

¹ These authors are contributed equally to this work.

hand, poly(ethylene oxide) (PEO) is a widely used film-forming polymer with high tensile strength and flexibility [19]. PEO can assist the development of GO based polymers composites for ion conductive membranes, and has facilitated materials design from an electrochemical viewpoint. As acid, the $-\text{COOH}$ groups on the GO are partially existing in the format of $-\text{COO}^-$ and H^+ at room temperature, which can provide abundant protons in the PEO/GO composite membrane, leading to ionic/protonic conductivity.

In this work, we prepared a PEO/GO membrane to study the membrane proton conductivity and fuel cell performance, which to our knowledge has not been reported previously. The initial results show the PEO/GO membrane has relatively high conductivity at low temperatures 20–60 °C, which is better than conventional PEMs. This feasibility study may provide an alternative approach for novel, low temperature membrane material development for PEMFC.

2. Experimental

2.1. Chemicals and reagents

Expandable graphite powder was supplied by Shandong Qingdao graphite company (China) with average size of 50 μm (Grade: EXP LMF D EGB 99.9SC and EX CX-325 HMy). Concentrated sulphuric acid, potassium permanganate, hydrochloric acid, hydrogen peroxide, iso-propanol and poly-ethylene oxide (PEO), with average molar mass (M_w) of 85,000–124,000 Da were purchased from Sigma-Aldrich. Microscope glass slides (76 mm \times 26 mm) were obtained from Fisher Scientific (UK). All other chemicals were used as received and the water used in this work was distilled water.

2.2. Preparation of graphene oxide

Graphene oxide was prepared according to the procedure in Ref. [18] using the sulphuric acid and potassium permanganate. Briefly, 60 cm^3 (ml) of concentrated sulphuric acid was cooled to 5 °C and then 10 g of graphite powder was added slowly into the cold sulphuric acid with constant stirring. Once the graphite was completely mixed, 20 g of potassium permanganate was added slowly to the solution. Then the mixture was stirred for another 5–10 min in an ice bath. The mixture was then heated to 35–40 °C. This resulted in the formation of a thick black paste. 150 ml of distilled water was then added drop-wise to the overall mixture. This mixture was then further diluted with a mixture of 500 ml distilled water and 20 ml of hydrogen peroxide (5%). The mixture was then left overnight which was followed by washing with HCl several times and then centrifuged at 4000 rpm to remove the upper solution. This was then followed by washing with the distilled water several times to obtain the graphene oxide solution.

2.3. PEO/GO membrane preparation

5 g PEO was first completely dissolved in 10 ml distilled water in a round-bottom flask and then one portion (2 ml) of the graphene oxide solution (containing 1 g of graphene oxide) was added into the flask under stirring for 2 h to obtain the resultant PEO/GO solution (0.5% by wt). And then the PEO/GO solution was poured onto the prepared glass slides mould (10 mm \times 10 mm) which was kept at room temperature for 48 h until the membrane was solid. The membrane was peeled from the mould and dried for 12 h at room temperature before undergoing characterisation and use in

fuel cell tests. PEO blank membranes were prepared under the same conditions.

2.4. Conductivity measurement

Membrane conductivity was measured using a four-point probe and Frequency Response Analyser (Voltech TF2000, UK). The membranes were cut into 10 mm \times 50 mm and placed across four platinum foils with equal spacing of 0.5 cm. AC impedance measurements were carried out at scanning frequencies from 1 to 20 kHz. The polymer membranes were held at the desired temperature and humidity for 0.5 h, to ensure steady state was achieved, and measurements were taken at 1 min intervals.

2.5. Membrane electrode assemblies

Membrane electrode assemblies (MEA) were prepared according to the reference [1] with modifications. Briefly, catalyst inks, for anode and cathode, were prepared by blending carbon-supported catalysts (50 wt% Pt/C, AlfaAesar) and polytetrafluoro-ethylene (PTFE, 60 wt% Aldrich) in a water-ethanol mixture under ultrasonic vibration for 10 min. The inks were sprayed onto a carbon-supporting layer covered with a gas diffusion layer (Freudenberg Inc.) at 100 °C, and then the electrodes were held at 150 °C for 2 h. The Pt loading was calculated to be 0.7 mg cm^{-2} on both cathode and anode. Membrane electrode assemblies were made by pressing the anode and cathode onto the membrane at room temperature 0.1 t cm^{-2} pressure for 5 min.

2.6. Fuel cell tests

The MEA was set between two high-density graphite blocks impregnated with phenolic resin, and the active electrode area (1 cm^2) was formed by the parallel gas flow channels area. Electric cartridge heaters were mounted at the rear of the graphite blocks to maintain the desired temperature, which was monitored by imbedded thermocouples and controlled with a temperature controller. Gold-plated steel bolts were screwed into the blocks to allow electrical contact. O_2 and H_2 were fed to the cell at flow rates of 20 and 40 ml min^{-1} , respectively without back pressure.

2.7. Characteristic

The GO was tested by FR-IR with PerkinElmer Universal STR Sampling PerkinElmer Spectrum 100 Series and the samples were directly loaded onto the plate. All XRD of the samples were determined by powder X-ray diffraction (XRD) analyses with Hilton brooks modified Philips X-ray diffractometer (Cu $\text{K}\alpha$, $\lambda = 1.5418 \text{ \AA}$) and generated at 30 kV, 30 mA. Scattering angles ranged from 1° to 60°.

3. Results and discussion

Graphene oxide (GO), which is generated from the oxidation of graphite, contains a range of reactive groups such as carboxyl and oxygen, and these groups make it a good candidate for use in the various applications including polymer composites materials. Hence GO has attracted intensive study for decades [16–18]. Aside from the study of the oxidative mechanisms using different oxidants, the precise chemical structure of GO has been the subject of debate for a long time. Although the detailed structure is still not completely clear, due to its amorphous character, a number of reactions involving carboxylic acids have been developed in organic chemistry, and many of these reactions can be applied to graphene oxide such as the formation of amides or esters. The typical structure model widely accepted for GO is shown in Fig. 1(a). Sulphuric

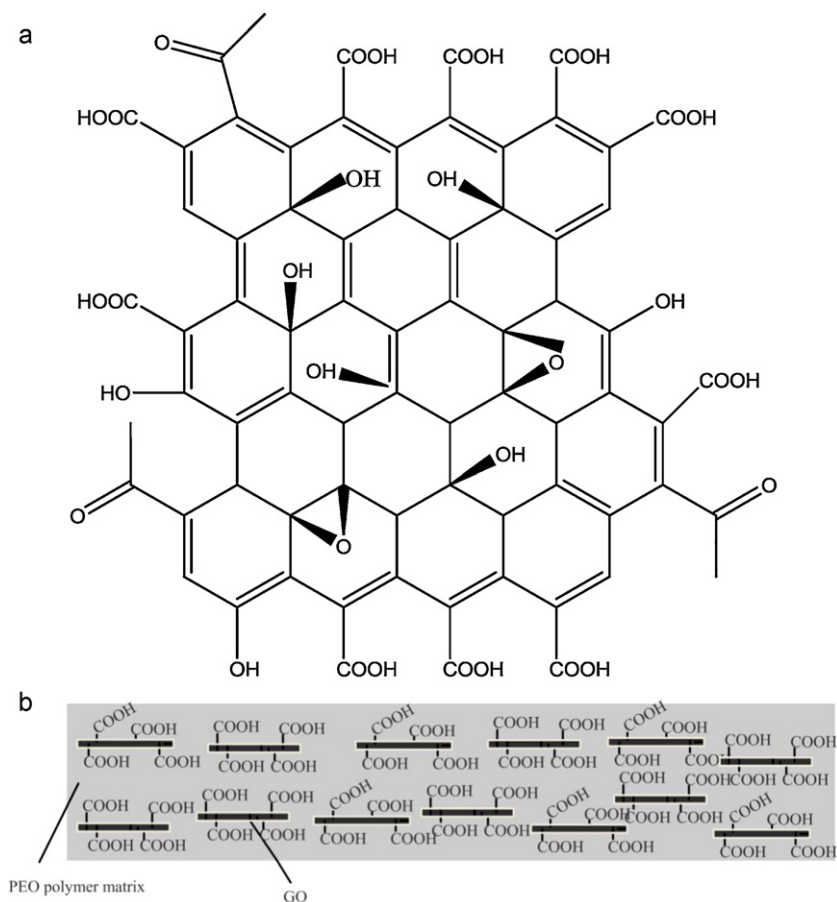


Fig. 1. Graphene oxide (GO) structure (a) and the illustration of PEO/GO membrane (b).

acid and potassium permanganate oxidised expandable Graphene was used in this study. Expandable graphite has been reported to easily introduce more functional groups into its galleries than natural graphite by treatment with sulphuric acid and these groups have been experimentally observed, including carbonyl ($=\text{CO}$), hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$), phenol groups, and oxygen epoxide groups (bridging oxygen atoms) [16–18] attached to both sides of the sheet. GO and hydrophilic polymers are highly compatible for the formation of composite membranes, in which the H^+ will be released from the $-\text{COOH}$ groups on the sheets of GO in the polymer matrix when humidified and the resultant membrane might be useful for application in PEMFC. Fig. 1(b) illustrates the proposed GO membrane for the proton-exchange fuel cells when poly (ethylene oxide) (PEO) is used as the polymer matrix.

The photo of the prepared PEO/GO membrane is shown in Fig. 2(a). Poly (ethylene oxide) (PEO) is a widely used hydrophilic polymer with high tensile strength and flexibility. Importantly, for our work, it also exhibits ion-transport behaviour when ionic salts are dissolved in it [19]. SEM images showed that the membrane is the condensed composite materials without defects such as air bubbles or pores (Fig. 2(b) and (c)). The as-prepared membrane was around $80\ \mu\text{m}$ in thickness and the GO in the PEO polymer matrix was the source of H^+ ions imparting the ion conductivity.

The membrane was tested by the XRD first to look into the GO layers in the PEO matrix. And the results are shown in Fig. 3. From the results we can see that the typical expandable graphene diffraction peak (001) at about $2\theta=27^\circ$, corresponding to the (001) plane reflection, can be observed from the spectrum of graphene (Fig. 3(a)); while in the spectra of GO, the diffraction peak

for the corresponding (001) reflection was at $2\theta=11^\circ$ (Fig. 3(b)), which means that the layer distance was much higher than that of graphite. And it can be concluded that the expandable graphene was successfully oxidized. Further more, by comparing the XRD spectra of PEO membrane (Fig. 3(c)) and PEO/GO membrane (Fig. 3(d)) which were prepared under the same conditions, we can see that the reflection peak near $2\theta=19.75^\circ$ is contributed by the PEO matrix itself. The (001) reflection of GO in the PEO membrane was shifted from $2\theta=11^\circ$ to $2\theta=4.5^\circ$ (Fig. 3(d)), which indicates that the PEO molecules intercalated into the layers of the GO, which further expand the gallery spaces of the GO. And also, this intercalation indicates that these two materials can be well mixed during the membrane preparation process and they are highly compatible.

FTIR studies were applied to confirm the functional groups in the PEO/GO membrane and the results are showed in Fig. 4. The FTIR spectrum of GO in Fig. 4(b) shows the presence of different type of oxygen functionalities in graphene oxide at $3300\ \text{cm}^{-1}$ (O–H stretching vibrations), at $1700\ \text{cm}^{-1}$ (stretching vibrations from $\text{C}=\text{O}$ or COOH) [20–22], while no significant peak was found in graphite (Fig. 4(a)). And the FTIR spectrum of PEO/GO membrane includes all the GO vibrations which indicate the presence of proton releasing groups in the membrane (Fig. 4(c)). These results depict OH and other functionalities, such as COOH groups, in the resultant PEO/GO membrane.

Tensile tests were carried out on both the PEO/GO membrane and PEO membrane that made under the same conditions to determine the mechanical properties and the results are shown in Fig. 5. The stress–strain curve for the PEO/GO membrane shows the tensile strength was 52.22 MPa and Young's modulus was 3.21 GPa,

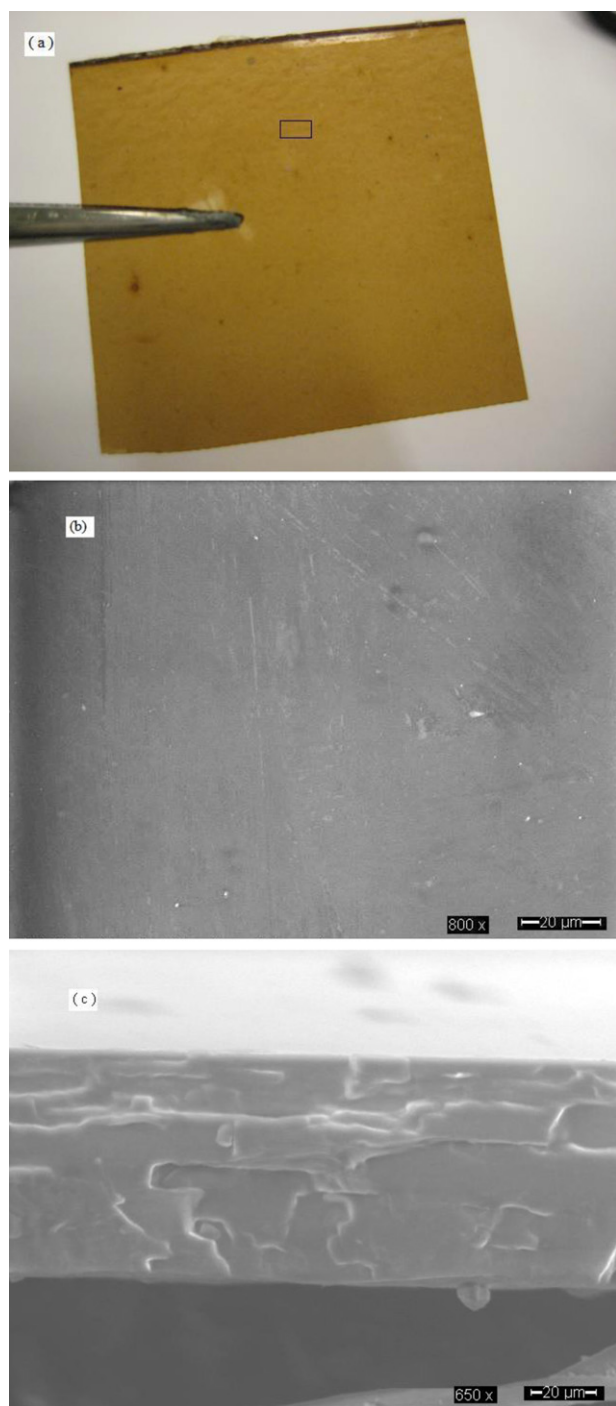


Fig. 2. Image of PEO/GO membrane with 0.5 wt% GO (a) and the SEM of the surface (b) and cross-section (c) morphology.

and the fractured elongation was about 5%. For the PEO membrane, the tensile stress was 37.78 MPa, and the Young's Modulus was 0.31 GPa, and the fractured elongation was more than 40%. The elongation of the PEO/GO membrane decreases which means the membrane becomes soft. These results indicate that the PEO/GO membrane is more stiff and brittle than the starter PEO polymer. The tensile strength and the Young's modulus both increase. This may be caused by the GO sheets which can greatly improve the modulus in the polymer nanocomposite material [23].

Fig. 6 shows the ion conductivity of the PEO/GO membrane at temperatures from 25 to 60 °C, at a relative humidity of 100%. The ion conductivity increased from 0.086 S cm⁻¹ at 25 °C to

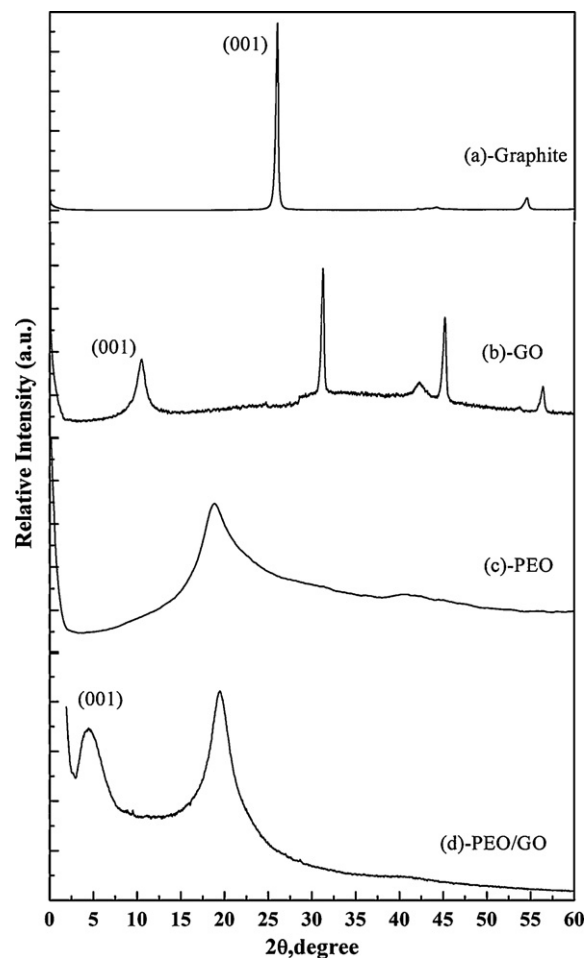


Fig. 3. Powder XRD spectra of graphene (a), graphene oxide (b), PEO (c) and PEO/GO membrane (d).

0.134 S cm⁻¹ at 60 °C. Although the ion conductivity continued to increase at temperatures above 60 °C, the membrane became soft during the test. Hence, with the current membrane, the optimum operating temperature will be around 60 °C for application in a PEMFC. Although a higher temperature resulted in higher conductivity, and reduced the membrane tensile strength and mechanical property, other composites of PEO and GO may still be functional at higher temperatures. The proton in the polymer matrix is the key for protonic conductivity, which is therefore dependant on the H⁺ released from the COOH groups. These results indicate that temperature plays an important role for the water, PEO polymer and GO interaction process.

As ionic resistance was measured with high frequency ac impedance method, DC method was also applied to measure the electronic resistance of this PEO/GO membrane. The results showed that it was greater than 20 MΩ at room temperature 100% RH. The conductivity also support the formation of GO which has a reported electrical conductivity lower than 1 × 10⁻⁹ S cm⁻¹ (10⁷ fold lower when compared to graphite) [16–18].

The PEO/GO membrane was used to make an MEA for hydrogen fuel cell applications, and also for the reference, a standard membrane Nafion-117 was tested under the same conditions. The polarization and power density data obtained at room temperatures are shown in Fig. 7. From the results we can see that the open circuit potentials for the fuel cell were relatively high, around 950 mV, at room temperature. The peak power densities were only 15 mW cm⁻² for the PEO/GO membrane, while for the Nafion-117, it could reach to 60 mW cm⁻² at 16 °C without ionomer in the MEA.

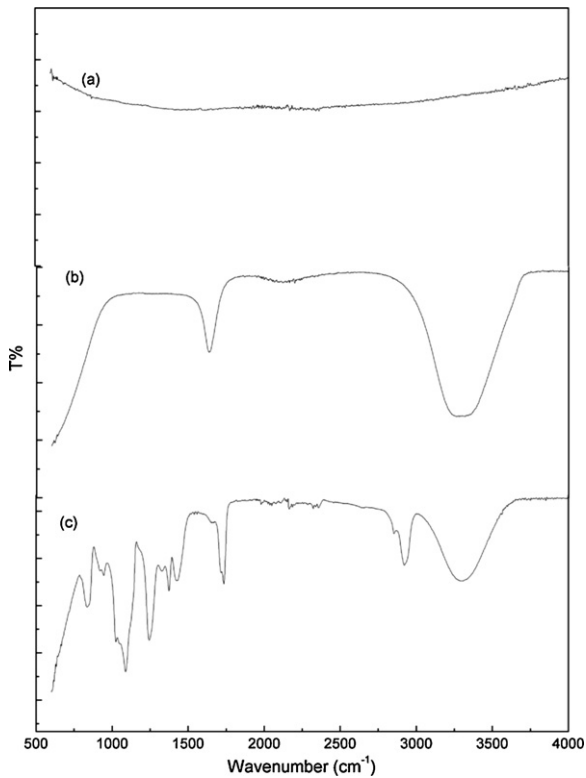


Fig. 4. FTIR spectrum of graphene (a), graphene oxide (b) and PEO/GO membrane (c).

When the operation temperature was increased to 30 and 60 °C with RH 100%, the power density increased from 21 to 53 mW cm⁻² (Fig. 8), nearly 2.5 times than achieved at 30 °C, and the limiting current increased from 90 to 180 mA. At 60 °C the open circuit voltage fell significantly to 760 mV, which is indicative of greater gas crossover, presumably associated with softening of the membrane. The loss of voltage seen in the polarization curves cannot be mainly attributed to the IR loss in the membrane, as this at 100 mA cm⁻², is estimated at 9 mV (at 30 °C), and will be due to kinetic and Ohmic voltage losses in the catalyst layers. Without optimizing the composition of catalyst layers, these power density results may be attributed to high catalyst/membrane interfacial resistance. However, such performance still confirms the feasibility of applying the PEO/GO composite membranes in fuel cells.

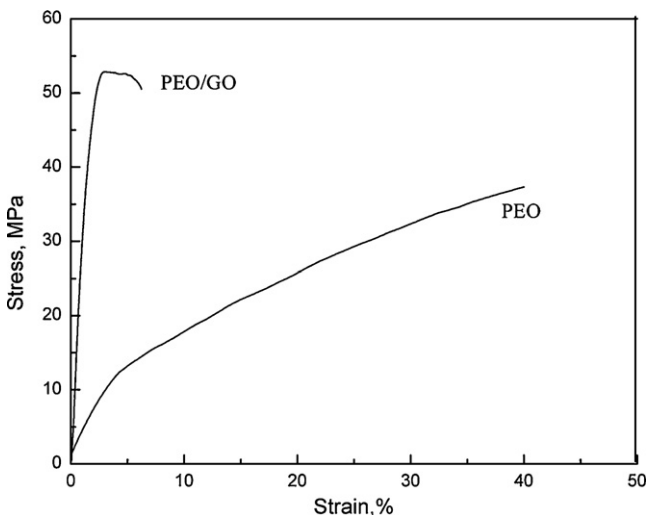


Fig. 5. Stress–strain curves of the PEO/GO and PEO.

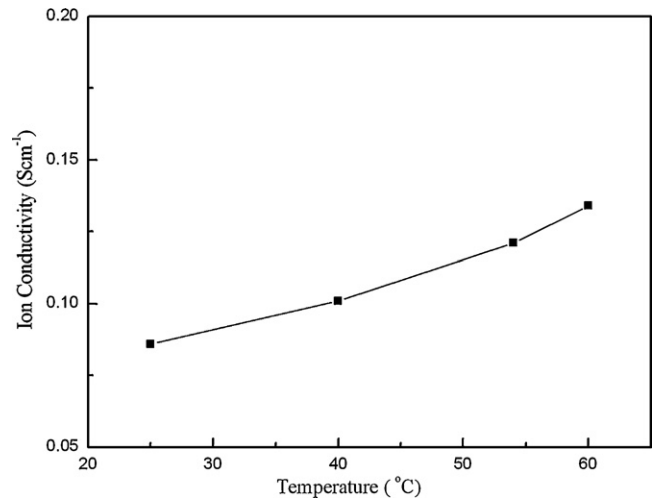


Fig. 6. Temperature effect on ion conductivity of PEO/GO membrane at relative humidity of 100%.

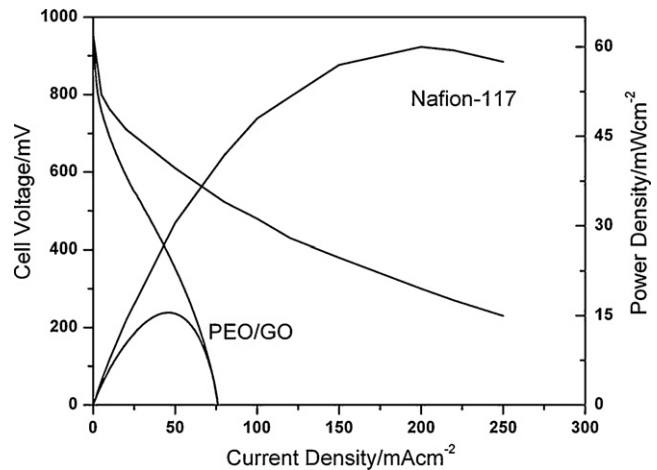


Fig. 7. Polarization and power density curves of PEO/GO and Nafion-117 membrane in fuel cell test at room temperature (16 °C) without humidity. The Pt loading was 0.7 mg cm⁻² and H₂ and O₂ was used in the test without back pressure.

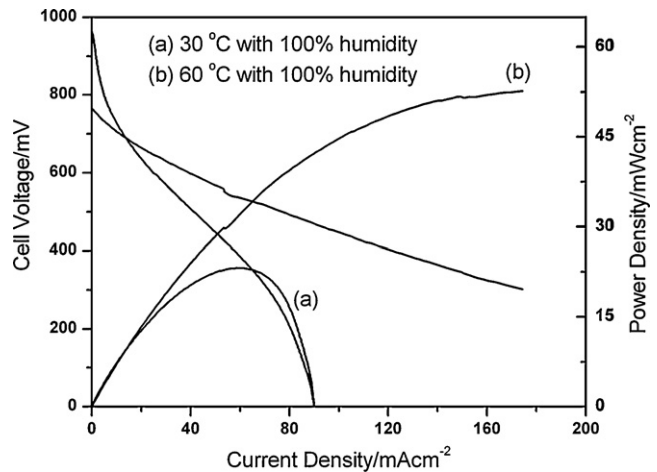


Fig. 8. Polarization and power density curves of PEO/GO membrane in fuel cell test at different operation temperature. The Pt loading was 0.7 mg cm⁻² and H₂ and O₂ was used in the test without back pressure.

4. Conclusions

PEO and GO are both hydrophilic and are highly compatible to form ionic conducting composite membranes for fuel cell applications. Proton exchange membranes can be prepared without polymer modifications. The key for this membrane's ion conductivity is the proton released from the COOH groups on the GO sheets in the PEO polymer matrix. Humidity is necessary for ionic transport in the membrane as water absorbed into the polymer acts as the medium for the releasing protons. The ionic conductivity is also dependent on the temperature which when increased may improve the release of proton from the COOH groups. But higher temperatures, above 60 °C cause deterioration in the membrane mechanical property. The PEO/GO composite membrane had a proton conductivity of 0.09 S cm⁻¹, at 60 °C, and gave a power density of 53 mW cm⁻² in hydrogen PEMFC. More improvements such as better mechanical properties and crossover should be further investigated to enable higher temperature use and catalyst layer formulation should be further studied in subsequent development for fuel cell applications.

Acknowledgement

The EPSRC in the UK partly supported this work.

References

- [1] M. Li, K. Scott, *Electrochim. Acta* 55 (2010) 2123–2128.
- [2] T.H. Bradley, B.A. Moffitt, D.N. Mavris, D.E. Parekh, *J. Power Sources* 171 (2007) 793–801.
- [3] M. Rikukawa, K. Sanui, *Prog. Polym. Sci.* 25 (2000) 1463–1502.
- [4] P. Jannasch, *Curr. Opin. Colloid Interf. Sci.* 8 (2003) 96–102.
- [5] B. Smitha, S. Sridhar, A.A. Khan, *J. Membr. Sci.* 259 (2005) 10–26.
- [6] A. Bıyıkoglu, *Int. J. Hydrogen Energy* 30 (2005) 1181–1212.
- [7] E. Antolini, *J. Appl. Electrochem.* 34 (2004) 563–576.
- [8] T. Higashihara, K. Matsumoto, M. Ueda, *Polymer* 50 (2009) 5341–5357.
- [9] U. Sen, A. Bozkurt, A. Ata, *J. Power Sources* 195 (2010) 7720–7726.
- [10] K. Sopian, W.R.W. Daud, *Renewable Energy* 31 (2006) 719–727.
- [11] J. Zhang, Z. Xie, J. Zhang, Y. Tang, C. Song, T. Navessin, Z. Shi, D. Song, H. Wang, D.P. Wilkinson, Z.-S. Liu, S. Holdcroft, *J. Power Sources* 160 (2006) 872–891.
- [12] R.K. Nagarale, W. Shin, P.K. Singh, *Polym. Chem.* 1 (2010) 388–408.
- [13] S. Slade, S.A. Campbell, T.R. Ralph, F.C. Walsh, *J. Electrochem. Soc.* 149 (2002) A1556–A1564.
- [14] E. Antolini, E.R. Gonzalez, *Appl. Catal. A: Gen.* 365 (2009) 1–19.
- [15] I. Jung, D. Dikin, S. Park, W. Cai, S.L. Mielke, R.S. Ruoff, *J. Phys. Chem. C* 112 (2008) 20264–20268.
- [16] G. Eda, M. Chhowalla, *Adv. Mater.* 22 (2010) 2392–2415.
- [17] D. Chen, L. Tang, J. Li, *Chem. Soc. Rev.* 39 (2010) 3157–3180.
- [18] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, *Chem. Soc. Rev.* 39 (2010) 228–240.
- [19] C.H. Manaratne, R.M.G. Rajapakse, M.A.K.L. Dissanayake, *Int. J. Electrochem. Sci.* 1 (2006) 32–46.
- [20] R. Bissessur, P.K.Y. Liu, S.F. Scully, *Synth. Metals* 156 (2006) 1023–1027.
- [21] R. Bissessur, S.F. Scully, *Solid State Ionics* 178 (2007) 877–882.
- [22] H.K. Jeong, M.H. Jin, K.P. So, S.C. Lim, Y.H. Lee, *J. Phys. D: Appl. Phys.* 42 (2009) 065418.
- [23] J.R. Potts, D.R. Dreyer, C.W. Bielawski, R.S. Ruoff, *Polymer* 52 (2011) 5–25.