Int. J. Electrochem. Sci., 12 **(2017)** 240 – 247, doi: 10.20964/2017.01.47

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Proton-Exchanged Graphite oxide-incorporated $Cs_XH_{3-X}PMo_{12}O_{40}$ with High Conductivity at Intermediate Temperatures

Min Huang, Xin Huang, Mingming Fei, Jian Sun, Yuming Deng, Chenxi Xu, Jigui Cheng**

School of Materials Science and Engineering, Hefei University of Technology, Hefei, Anhui, China
*E-mail: xuchenxi31@126.com, jgcheng63@sina.com

Received: 3 October 2016 / *Accepted:* 19 November 2016 / *Published:* 12 December 2016

Proton conductors operating at a high temperature condition have attracted great attention for intermediate temperature proton exchange membrane fuel cells (PEMFCs). Inorganic electrolyte membrane fabricated from Cs substituted Phosphomolybdic acid ($Cs_XH_{3-X}PMo_{12}O_{40}$) is considered as a suitable potential candidates for membranes without a liquid phase for PEMFCs using between 160 to 280°C. Graphite oxide is incorporated with this solid material to improve the proton conductivity, and the activation energy is also calculated by the Arrhenius equation. The $Cs_XH_{3-X}PMo_{12}O_{40}$/GO composite electrolyte exhibits the high proton conductivities of $1.7*10^{-3}$ S cm^{-1} at 280°C.

Keywords: Intermediate-temperature proton exchange membrane fuel cells; Graphite Oxide; Caesium salts of Heteropolyacid

1. INTRODUCTION

For the intermediate temperatures (200-400°C) proton exchange membrane fuel cells (PEMFCs), the proton conductors capable of operation in this temperature range is the key point [1]. PEMFCs using at high temperature would reduce the lower activation energy requirement and enhance the reaction rates resulting in a lower Pt loading or even non-noble catalyst used, and also simplified fuel cell system [2]. Since only a few proton conductors could provide sufficiently conductive at these temperatures, the suitable membrane has proven difficult for the fuel cell technology to access. The inorganic materials such as cesium dihydrogen phosphate (CsH_2PO_4) and tetravalent metal ion pyrophosphates (MP_2O_7, M=Sn, Ti, Ce, or Zr) exhibit proton conductivities at temperatures between 200 °C and 400 °C [3, 4]. The Keggin-type heteropolyacids (HPAs) with strong acidity is ease of preparation [5]. Solid HPAs possess a discrete ionic structure including mobile basic structural heteropolyanions and countercations as H^+, H_3O^+, etc. [6]. This unique structure exhibits extremely high proton mobility, so the HPAs powders are well known inorganic with high acidity and proton conductivity solid acids, but their chemical stability is unsatisfactory according to their hygroscopicity [6]. Caesium salts of Heteropolyacid (CsHPA) are insoluble in water as reported by Li. et al. [7]. CsHPA have already used as modifier in Nafion [6] and PBI [8] membranes that exhibited higher proton conductivity and fuel cell performance, but the CsHPA directly used as electrolyte was rarely reported.

The low conductivity and weak strength of CsHPA inorganic materials membrane limit its application for using in high-temperature PEMFCs. Therefore, the solid modifiers that could improve the conductivity and form strong structure have received great interest. According to our previous work [9], Graphite oxide (GO) has various acidic functional groups, such as carboxylic acid, offers more facile proton hopping to improve the conductivity, and also GO extends the amount of available ion exchange sites per cluster leading to a rapid proton mobility. The high temperature stability of GO is another reason that make GO as a potential filler to improve proton conductivities of composite membrane at intermediate temperatures. [9].

In this work, $Cs_XH_{3-X}PMo_{12}O_{40}$ (CsPOMo) was chosen as the based material, and the CsPOMo/GO composite membranes are applied as proton conductivity membrane. The conductivity of the inorganic CsPOMo solid membranes are improved with the addition of GO in the intermediate temperature range.

2. EXPERIMENTAL

$Cs_XH_{3-X}PMo_{12}O_{40}$ was prepared from $H_3PMo_{12}O_{40}$ (Aldrich) and Cs_2CO_3 (Aldrich) as pervious work [8]. Briefly, 0.407 g Cs_2CO_3 dissolved in 10 cm^3 deionised water and then was added to a solution of 1.825 g $H_3PMo_{12}O_{40}$ dissolved in 30 cm^3 de-ionised water to achieve the molecular ratio of 1.25: 1. The resulting precipitate was recovered from the solution by evaporation at 60 °C, and rinsed in deionised water. GO sheet was synthesized from the graphite sheet with concentrated H_2SO_4 and $KMnO_4$ powder. This mixture was stirred at 35 °C for 30 min, and the temperature was increased to 98 °C with 150 mL distilled water added. The reaction was terminated by the addition of a large amount of distilled water and 30 wt% H_2O_2 solution. Finally, the mixture was filtered and rinsed with a 5% aqueous HCl solution and deionised water [1]. The 5 wt% GO/$Cs_XH_{3-X}PW_{12}O_{40}$ composite membranes were pressed under a pressure of 200 MPa as a pellet with sintering at 250 °C for 8 hrs. The 13-mm diameter sintered disk was polished with sandpaper and painted with colloidal silver on both sides. A silver wire mesh was separately placed in contact with the painted pellet on both sides and was pressed between mica sheets to ensure the electrical contact.

The proton conductivity of membrane was measured by two-point method with an Autolab PGSTAT302. The measurements were carried out at the frequencies range of 1 to 10^6 Hz with 10 mV applied voltage. The morphologies of the $Cs_XH_{3-X}PMo_{12}O_{40}$/GO membranes were investigated via a SU-8020 Scanning Electron Microscope. The crystal structures were analysed from 5–45° by X-ray diffraction (XRD, X’Pert PROMPD). The thermal behaviour was analysed by thermos-gravimetric analysis (TGA, STA449F3).

3. RESULTS AND DISCUSSION

The morphology of CsPOMo membrane in comparison with the CsPOMo /GO pellet is depicted from the SEM images. It is observed in Fig. 1a that the CsPOMo particles are mostly spherical in shape and they are formed as fine micro-metric particles around 1 µm. GO is dispersed throughout the whole composite membrane surrounding with the CsPOMo particles as shown in Fig 1b. The GO fillers remain exfoliated in the composite matrix and are tightly held among the inorganic material matrix through the interfacial interactions which may also benefit to reduce the pores in the pellet. Therefore, the conduction path for proton is established in the composite pellet throughout the whole membrane that may explain the high conductivity of the membrane. Fig. 1(c-g) exhibits the homogeneous elements dispersion of Cs, Mo, P, O and C on the cross-section of the CsPOMo/GO pellet by EDX mapping. The Cs, Mo P, and O come from the CsPOMo that is through the whole image. The C and O elements are from the GO indicating the GO was successfully dispersed in the CsPOMo matrix as the composite membrane.

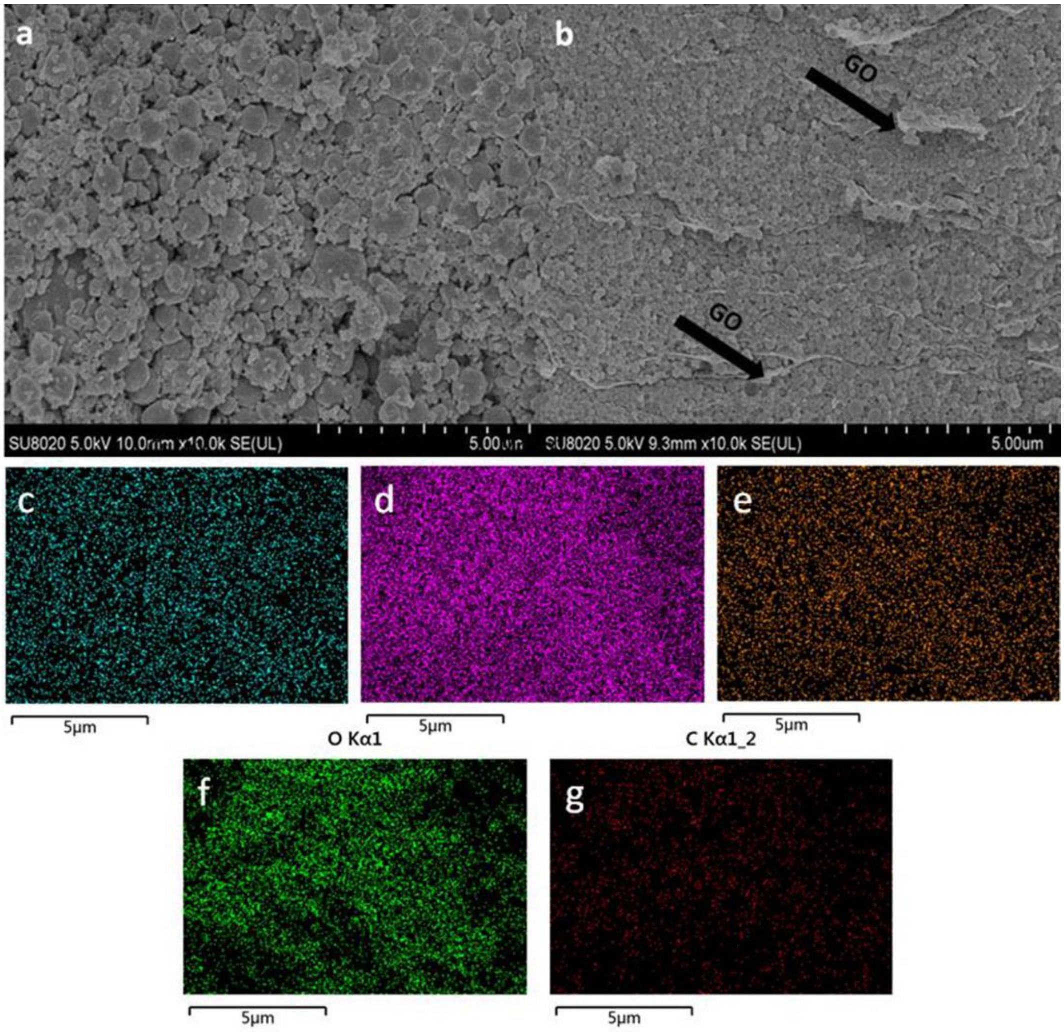

Figure 1. SEM images of membrane cross-sections: a) CsPOMo, b) CsPOMo /GO, and c-g) EDX image of Cs, Mo, P, O and C mapping for the cross-section of CsPOMo/GO

The structural characterisation by XRD in Fig. 2 confirms that the diffraction peaks of $Cs_XH_{3-X}PMo_{12}O_{40}$ (JCPDS 43-0314) are observed. The XRD angles at 10.55°, 18.35°, 23.76°, 26.04°, and 30.17° belong to the (110), (211), (310), (222), and (321) crystal planes of $Cs_XH_{3-X}PMo_{12}O_{40}$ are in good agreement with the literature reported, respectively [6]. This XRD results suggest that our CsPOMo sample possess the Keggin structure units, which are arranged in a single cubic lattice [10]. Meanwhile, in CsPOMo /GO structure, the GO diffraction peak exhibits as 9.6° corresponding to the (001) plane reflection, and this peak is left shifted from the typical peak of 10.5° reported in our previous work [1]. This is attributed to the CsPOMo particles inserted into the GO exfoliation layer.

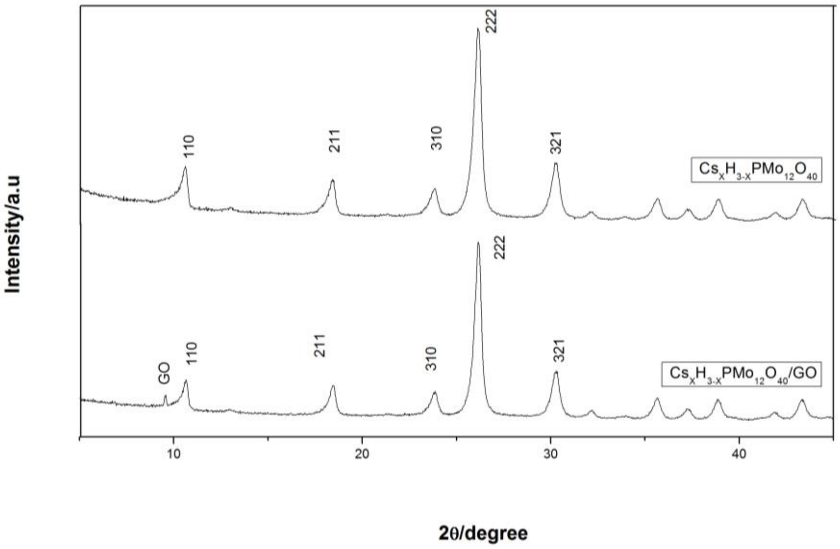

Figure 2. XRD spectra of CsPOMo and CsPOMo /GO

The thermal stability is studied from room temperature to 1000 °C by TGA, depicted in fig. 3. It is obvious that the CsPOMo and CsPOMo /GO remain stable until 800 °C. The TGA curve of CsPOMo exhibits two typical degradation steps. The first step is assigned to the loss of free water in the range of 80–120°C. It is stable for the weight loss of the CsPOMo sample from 120°C to 700 °C, indicating that the materials are stable under non-humid conditions. The second step is attributed to the dehydration and dimerization of the heteropolyacid forming meta-oxide and other ceasium phosphates above 700 °C. The degradation of CsPOMo could be attributed to the followed process reaction [11]:

$$\mathrm{Cs}_x\mathrm{H}_{3-x}\mathrm{PMo}_{12}\mathrm{O}_{40}\cdot mH_2O \rightarrow \mathrm{Cs}_x\mathrm{H}_{3-x}\mathrm{PMo}_{12}\mathrm{O}_{40} + mH_2O \quad (1)$$

$$\mathrm{Cs}_x\mathrm{H}_{3-x}\mathrm{PMo}_{12}\mathrm{O}_{40} \rightarrow \mathrm{Cs}_x\mathrm{H}_{3-x-2y}\mathrm{PMo}_{12}\mathrm{O}_{40-y} + yH_2O \quad (2)$$

$$\mathrm{Cs}_x\mathrm{H}_{3-x}\mathrm{PMo}_{12}\mathrm{O}_{40} \rightarrow \mathrm{Cs}_xPO_b + 12\mathrm{MoO}_3 + \frac{3-x}{2}H_2O \quad (3)$$

The curve of CsPOMo/GO is almost no obvious sharp degradation until 800°C. This results evidenced an appropriate water retention capability of GO, which benefits the composite membrane stability.

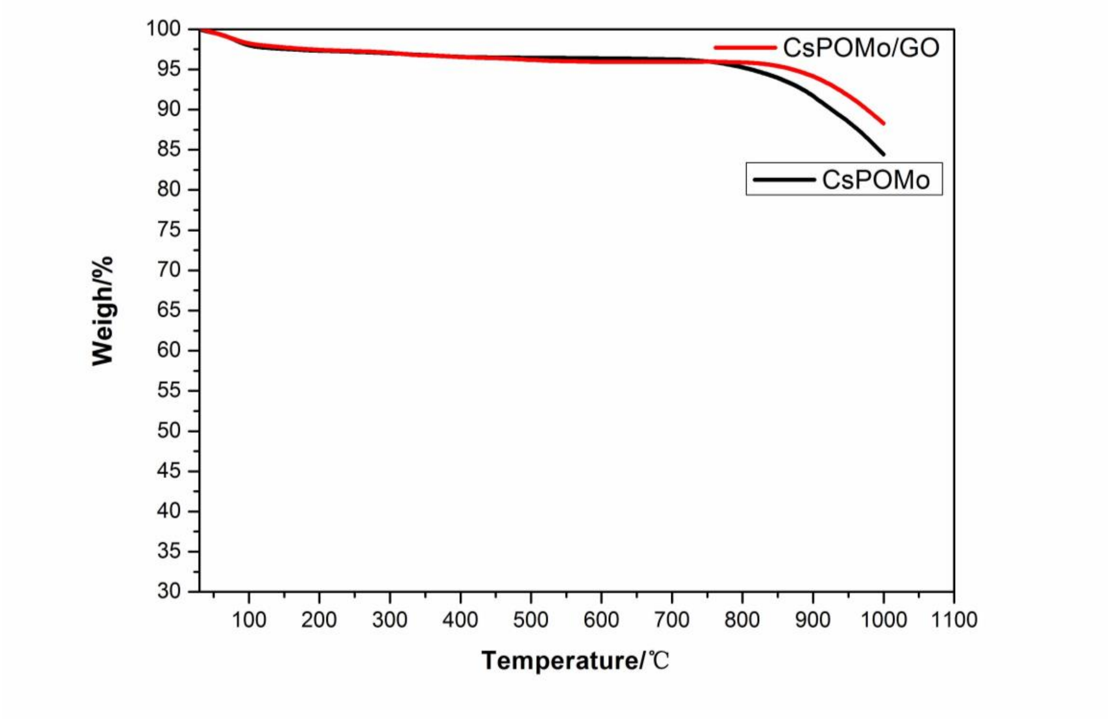

Figure 3. TGA of the CsPOMo and CsPOMo /GO from room temperature to 1000 °C

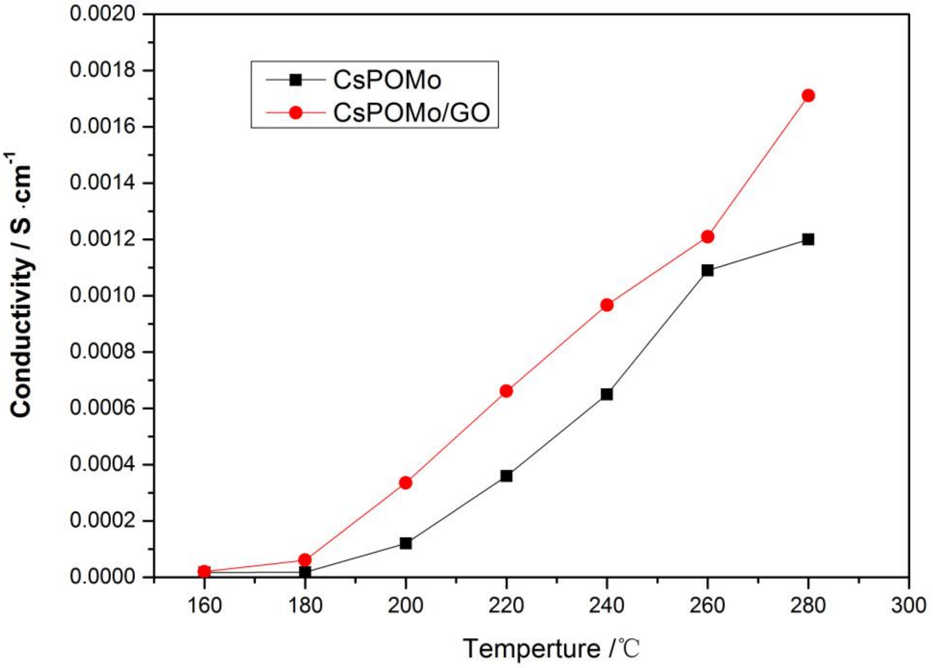

Figure 4. The conductivities of CsPOMo and CsPOMo/GO membranes under anhydrous conditions

The conductivities of the membranes are depicted in fig. 4 in the range of 160–280°C. The $Cs_XH_{3-X}PMo_{12}O_{40}$ exhibits a measurable conductivity at non-humid atmosphere when temperatures up to 280°C. The conductivity increases from $1.1*10^{-5}$ S cm^{-1} to $1*10^{-3}$ S cm^{-1} as the temperature increased from 160°C to 280°C. According to the literature [12], the protonic conduction of the CsPOMo may be caused by the mobility of the heteropolyanions and countercations (e.g. H^+, H_3O^+)

which come from the $Cs_XH_{3-X}PMo_{12}O_{40}$ phase transition. The high protonic conductivity of the crystal structure are believed to cause by the dynamically disordered hydrogen bonds and strongly disordered phosphate anions partially occupied oxygen sites [12]. The curve in Fig. 4 clearly illustrates that the CsPOMo/GO composite electrolyte has a superior conductivity compared with the CsPOMo membrane at different temperatures. At 280°C, the maximum conductivity of CsPOMo/GO reaches to $1.7*10^{-3}$ S cm^{-2} that is 50% higher than CsPOMo. This result indicates that the GO filler in the composite membrane provides efficient pathways for proton mobility resulting in a faster transmit. Therefore, the GO is an ideal material used in solid proton conductors to enhance the conductivity up to 280°C.

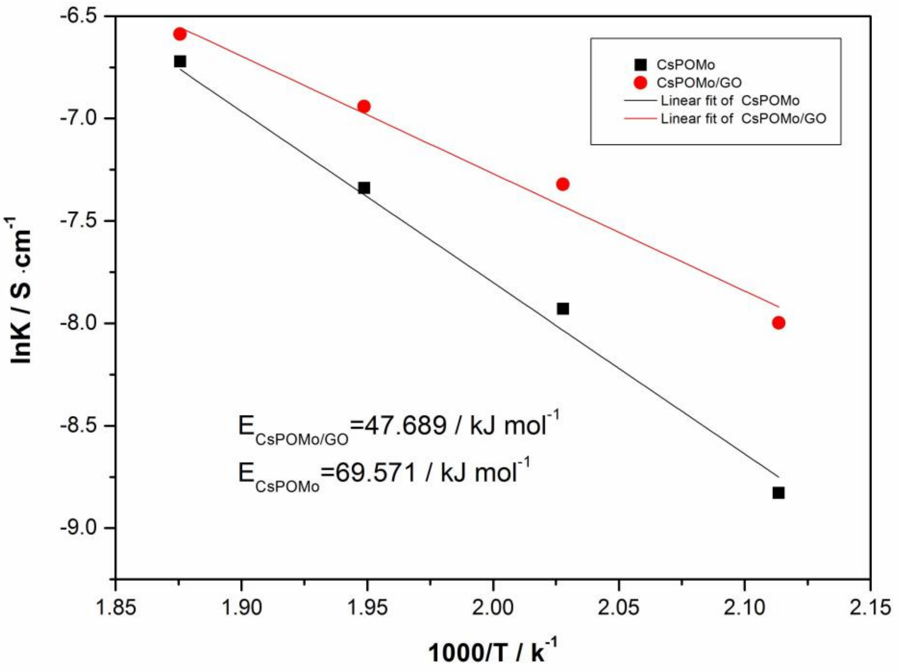

Figure 5. Arrhenius plots of CsPOMo and CsPOMo/GO membrane

Ion transport activation energies (Ea) of pellets were obtained by the Arrhenius equation which linear fitting from the conductivity value. The barrier of charge carriers are decoupled from the sites movement which presented by the activation energy [13]. As shown in fig. 5 and table 1, the activation energy of the CsPOMo membrane is 69.6 kJ mol^{-1}, which is much higher than that of CsPOMo/GO (47.7 kJ mol^{-1}), indicating a large energy barrier for proton jumps between sites in pristine CsPOMo. This is the explanation that the conductivity of CsPOMo/GO membrane is higher than that of SnP_2O_7 membrane.

Table 1. Activation energy and conductivity of the membrane at 280°C

Membrane sample	Conductivity (S cm^{-1})	Ea (kJ mol^{-1})
CsPOMo	$1*10^{-3}$	69.6
CsPOMo/GO	$1.7*10^{-3}$	47.7

The comparison cesium dihydrogen phosphate (CsH_2PO_4) and tetravalent metal ion pyrophosphates (MP_2O_7) described in literature with $Cs_XH_{3-X}PMo_{12}O_{40}$ composite membranes were exhibited in Table 2. It indicated that the $Cs_XH_{3-X}PMo_{12}O_{40}$ and $Cs_XH_{3-X}PMo_{12}O_{40}$/GO pellet as the electrolyte membranes provide a competitive conductivity over 250° C which could be considered as potential materials for intermediate temperature PEMFC.

Table 2. Comparison the proton conductivity of membranes

Membrane sample	Conductivity (S cm^{-1})	Ref
CeP_2O_7	$3.6*10^{-6}$ at 400 °C	14
SnP_2O_7	$4.7*10^{-2}$ at 250 °C	15
TiP_2O_7	$4.6*10^{-2}$ at 250 °C	15
SiP_2O_7	$1.7*10^{-3}$ at 250 °C	15
GeP_2O_7	$1.5*10^{-3}$ at 250 °C	15
CsH_2PO_4	$8.5*10^{-6}$ at 223 °C	16
$Cs_XH_{3-X}PMo_{12}O_{40}$	$1.2*10^{-3}$ at 280 °C	This paper
$Cs_XH_{3-X}PMo_{12}O_{40}$/GO	$1.8*10^{-3}$ at 280 °C	This paper

4. SUMMARY

Inorganic solid proton conductors CsPOMo and CsPOMo/GO were prepared successfully, and the morphology and structure of the membranes were characterised. GO-incorporated CsPOMo composite membranes exhibited conductivity of $1.7*10^{-3}$ S cm^{-1} at 280°C as 50% higher than CsPOMo ($1.2*10^{-3}$ S cm^{-1}). The activation energy reduced from 69.6 kJ mol^{-1} to 47.7 kJ mol^{-1} when the GO added into the CsPOMo. The GO incorporation with CsPOMo exhibited improved conductivity and fuel cell performance indicating that CsPOMo/GO is a suitable candidate solid electrolyte for intermediate-temperature PEMFCs.

ACKNOWLEDGMENTS
The authors thank the funding support provided by the Fundamental Research Funds for the Central Universities (2015HGCH0001) and the Anhui Provincial Natural Science Foundation (1508085QB45).

References

1. C. Xu, Y. Cao, R. Kumar, X. Wu, X. Wang, K. Scott, *J. Mater. Chem.*, 21 (2011) 11359.
2. A.H. Jensen, Q. Li, E. Christensen, N.J. Bjerrum, *J. Electrochem. Soc.*, 161 (2014)72.
3. A. Tomita, N. Kajiyama, T. Kamiya, M. Nagao, T. Hibino, *J. Electrochem. Soc.*, 154 (2007) 1265.
4. Y.C. Jin, M. Nishida, W. Kanematsu, T. Hibino. *J. Power Sources*, 196 (2011) 6042.
5. M. Amirinejada, S. S. Madaenia, E. Rafieeb, S. Amirinejad, *J. Membr. Sci.*, 377 (2011) 89.
6. M. Sun, J. Zhang, C. Cao, Q. Zhang, Y. Wang, H. Wan, *Appl. Catal. A: Gen.*, 34 (2008) 212.
7. M. Li, Z. Shao and K. Scott, *J. Power Sources*, 183 (2008) 69.

8. C. Xu, X. Wu, X. Wang, M. Mamlouk, K. Scott, *J. Mater. Chem.*, 17 (2011) 6014.
9. X. Huang, Y. Deng, C. Xu, L. Yang, Y. Hu, P. Luo, Y. Lu, *J.* Cheng, *Fuel*, 179 (2016)299.
10. M. Langpape, J.M.M. Millet, U.S. Ozkan, M. Boudeulle, *J. Catal.*, 181 (1999) 80.
11. Z. Wang, J. Niu, L. Xu, J. Peng, E. Wang, *Acta Chimica Sinica*, 53 (1995) 757.
12. G. Kim, F. Blanc, Y.Y. Hu, C.P. Grey, *J. Phys. Chem.* C, 117, 6504 (2013).
13. Y.L. Ma, J.S. Wainright, M.H. Litt, R.F. Savinell, *J. Electrochem. Soc.*, 151 8 (2004).
14. B. Singh, H.N. Im, J. Y. Park, and S.J. Song, *J. Electrochem. Soc.* 159 (2012) F819-F825
15. M. Nagaoa, A. Takeuchia, P. Heoa, T. Hibinoa, M. Sanoa and A. Tomitab, *Electrochem. Solid St.*, 9 (2006), A105-A109
16. S. M. Haile, C. R. I. Chisholm, K. Sasaki, D. A. Boysen, and T. Uda, *Faraday Discuss.*,134 (2007) 17