Feasibility of Composite sPEEK-PVA as Proton Exchange Membranes

Nur Hidayati, Praminta Cindy Imannurya, Alisa Mutia Sara, Elisa Putri Nastiti, Tri Harmoko
Chemical Engineering, Universitas Muhammadiyah Surakarta. Jl. A. Yani Tromol Pts 1, Pabelan, Kartasura, Surakarta, Indonesia
E-mail: nur.hidayati@ums.ac.id

Abstract. The present work deal with the fabrication and characterizations of composite membranes composed of sulfonated poly (ether ether ketone) with polyvinyl alcohol and reinforced with cesium phosphotungstic acid (Cs-HPW), graphene oxide (GO), and silica-carbon nanotube (SCNT). Compared to the blank sPEEK-PVA membrane, the uptake of composite membranes in water varies at around 30-50%, while the swelling ratio is increased. The addition of Cs-HPW, GO, and SCNT reduces the tensile strength and methanol permeability. The ionic exchange capacity slightly varies at around 0.48-0.70 meq/g. From the above studies’ viewpoint, the prepared composite membranes still need to be reviewed so that these membranes are feasible as proton exchange membranes.

1. Introduction
The development of fuel cells has continuously been motivated by green energy and the conservation of the atmosphere. High performance, high power density, compact cell size, and low emission, direct methanol fuel cell (DMFC) have recently been considered attractive power sources for portable and transport applications [1]. A critical component of the DMFC is the proton exchange membrane (PEM), which moves protons from the anode to the cathode and serves as a barrier to the permeable fuel phenomenon. High proton conductivity, low methanol permeability, high stability against the attack of radical by-products, and low cost are the criteria for a polymer electrolyte membrane used in DMFCs. Recently, fluorinated ionomers such as Nafion are the most popular commercially used PEMs due to their high proton behavior. When working under a low temperature, NafionR membranes demonstrate high proton conductivity, chemical stability, and fair longevity for up to hundreds to thousands of hours of operation [2]. However, high prices, methanol crossover, and conductivity loss above 80(C in DMFC still limit efficiency and application [3].

There have been many studies on preventing cross-over methanol with less expensive materials, including surface alteration of existing membranes, mainly NafionR, composite membrane development, and the creation of new membranes. Recent research focused on developing non-fluorinated membranes, taking into account the problems of cost and methanol permeability associated with Nafion. Some of the crucial aromatic hydrocarbon polymeric membranes based on sulfonated poly(ether sulfone) (sPES) [4], sulfonated poly(ether ether ketones) (sPEEK) [5, 6], sulfonated polyimides [7], sulfonated polysulfone [8], sulfonated
polybenzimidazoles [9], and sulfonated poly(arylene ether sulfone) [10] are important in this respect. Sulfonated polymer (ether ether ketone) (SPEEK), a proton-conducting polymer formed by electrophilic replacement of sulfonic acid groups in the PEEK backbone, is a highly desirable substance among the possible alternatives because it has excellent mechanical properties, high-temperature tolerance of up to 300°C and acid stability. The characteristics of the SPEEK membranes are determined by their sulfonation level [11]. Several attempts have been made to resolve swelling elements in sPEEK, such as (i) the introduction of hydrophobic-hydrophilic blocks in sPEEK [12], (ii) the bridging of reactive sulfonic acid groups by sufficient crosslinking and thermal activation of polymer chains with polyols [13], and (iii) the alteration of sPEEK by compatible blends of hydrophobic polymers [14–16]. The modification of sPEEK by various dispersive fillers to limit methanol cross-over in DMFCs was also suggested in several studies. For the improvement of sPEEK suitable for DMFC applications, nanofillers such as silica [17,18], graphene oxide [19], carbon nanotubes [20], and intercalated structures such as organic montmorillonite [21] have been used. For these nanocomposite sPEEK membrane electrolytes, methanol cross-over was found to have been reduced.

In this study, sPEEK was blended with polyvinyl alcohol (PVA) and then incorporated with cesium phosphotungstic acid (CsHPW), graphene oxide (GO), and silica-carbon nanotube (SCNT). PVA is a non-expensive material commonly used as a polymer matrix in combined membranes due to its strong film-forming performance, hydrophilic composition, and chemical and mechanical properties [22]. CsHPW, GO, and SCNT will be expected to improve the performance of polymer electrolyte membranes.

2. Methods
2.1. Materials
Polyether ether ketone from victrex was used as a polymer matrix for composite membranes. Polyvinyl alcohol, ammonium hydroxide, and graphite were provided from a local chemical store. CNT was from Zhengzhou Dongyao Nano Materials Co. Ltd. Nitric acid, tetraethyl orthosilicate, dimethyl formamide, cesium carbonate, phosphotungstic acid, sodium nitrate, potassium permanganate, hydrochloride acid, hydroperoxide acid were purchased from Merck. Sulfuric acid was supplied by Mallinckrodt.

2.2. Fillers Preparation
One gram of CNT was oxidized with nitric acid (HNO₃) and sulfuric acid (H₂SO₄) with a volume ratio of 3:1 for 6 hours at 70°C by reflux. The mixed solution was then vacuum filtered and washed with distilled water until the pH becomes neutral. Then, it was dried until it reaches constant weight. To coat it with silica, activated CNTs (o-CNTs) were sonicated by mixing it in a mixed solution consisting of 250 ml of ethanol, 8 ml of ammonium hydroxide (NH₄OH), and 20 ml of distilled water for 30 minutes. After that, it is stirred to obtain a stable and homogeneous suspension. The mixed solution was added with 37 ml of tetraethyl orthosilicate (TEOS), stirred for 12 hours, and precipitated. The residue was taken and washed with dimethyl formamide (DMF) and dried at 60°C to remove the solvent.

The powder cesium phosphotungstic acid (CsHPW) was prepared by reacting 3.25 grams Cs₂CO₃ with 11.20 grams of phosphotungstic acid. The phosphotungstic acid solution was poured into Cs₂CO₃ solution drop by drop. The solution was mixed at room temperature and high, stirring speed. The obtained white precipitate was heated for 24 hours at 60°C.

Graphene oxide (GO) was made by oxidating graphite. Three grams of NaNO₃ and 140 ml of concentrated sulfuric acid (>95%) were put in a beaker given an ice bath. The solution was stirred to a temperature below 20°C to prevent a spontaneous reaction. Then 3 grams of graphite and 15 grams of KMNO₄ were added slowly and stirred for 2 hours. Then the solution was kept at room temperature for 24 hours to let oxidation occur. Next, 100 ml of distilled water
is added and stirred for 1 hour. The solution is then added with 10 ml of \( \text{H}_2\text{O}_2 \), followed by washing with 1 M \( \text{HCl} \) and distilled water until it reached a neutral pH level. Dry GO was obtained by drying at 80°C.

2.3. Membrane Preparation
Concentrated sulfuric acid was used as the sulfonating agent. PEEK of 7.5 gram was reacted with 150 ml of concentrated sulfuric acid at 60°C for 4 hours. The reaction was terminated by pouring the solution into ice water. The precipitated white sPEEK was obtained. The white polymer was washed with distilled water until the pH was neutral. Then, sPEEK was dried at room temperature for 24 hours and then at 60°C and a vacuum pressure to achieve the constant weight.

The sPEEK and PVA solution was prepared by dissolving 2 grams of sPEEK in 100 ml of DMAc and 1 gram of PVA in 10 ml of distilled water, respectively. The resolution of sPEEK and PVA with the ratio of 80:20% wt was mixed. Then fillers (CsHPW, SCNT, and GOs separately) were added by 2.5% wt to the mixture and then stirred for 2 hours. Then the mixture was sonicated for 30 minutes and stirred again for 5 minutes. The membrane was made by pouring sPEEK-PVA solution with filling material on a glass plate and drying it in an oven at 60°C for 20 hours. Then, the membrane was heated to 110°C for 1 hour to facilitate cross-linking occurred between molecules. The dried membrane was then washed with distilled water and dried at room temperature.

2.4. XRD Analysis
The crystal structure of the membrane was tested using the X-ray diffraction method. The X-ray diffraction patterns were measured on a theta/theta diffractometer X’Pert PRO from PANalytical type of PW 3040/60 with CuKα radiation at \( \lambda = 0.0154 \text{ nm}, 30 \text{ mA} \) and 40 kV. Samples were scanned continuously in the \( 2\theta \) range 5 - 90°C with the scanning rate of 2° per minute.

2.5. Tensile strength and elongation
The tensile strength test was performed using the Zwck.Z05 model tensile strength test tool by clamping the two ends of the membrane, which had been cut to the size of 50 mm x 5 mm. The tensile strength tests were made at room temperature with a speed of 10 mm minute\(^{-1}\).

2.6. Water Uptake (WU) and Swelling Degree (SD)
Membranes were cut into a square shape of the same size (2 x 2 cm). The water uptake test was carried out by calculating the difference in dry membrane weight (\( W_{\text{dry}} \)), which was measured by weighing it after being heated in the oven at 100°C for 24 hours, and the weight of the membrane (\( W_{\text{wet}} \)), which is calculated after the membrane has been immersed in distilled water for 48 hours at room temperature.

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

The swelling degree test was done similarly with the water uptake measurement by calculating the difference in dry (\( L_{\text{dry}} \)) and wet (\( L_{\text{wet}} \)) membrane length.

\[
\text{Swelling Degree} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (2)
\]
2.7. Ion Exchange Capacity
The ion exchange capacity (IEC) of the membranes was determined using the titration method. The membranes were dried at 100 °C for 24 hours, then were immersed in 1M NaCl solution for 48 hours at room temperature to replace all H\(^+\) with Na\(^+\). The amount of H\(^+\) released from the membrane was measured by titration using 0.01N NaOH solution with phenolphthalein as the pH indicator. The value of IEC was obtained by equation (3).

\[
\text{IEC} = \frac{V_{\text{NaOH}} N_{\text{NaOH}}}{W_{\text{dry}}} 
\]

where \(V_{\text{NaOH}}\) is the consumed volume of NaOH (mL), \(N_{\text{NaOH}}\) is the concentration of NaOH solution (mol L\(^{-1}\)), and \(W_{\text{dry}}\) is the weight of dry membrane (g). The water content parameter, \(\lambda\), is the number of moles of water per mole acidic group. It can be calculated using the following equation [22].

\[
\lambda = \frac{10 \times \text{Water Uptake}}{18 \times \text{IEC}} 
\]

Where 18 is the molecular weight of water and IEC is the ionic exchange capacity with milliequivalents per gram of polymer.

2.8. Permeability of Methanol
The methanol permeability was performed at room temperature using 2 glasses diffusion cell connected to the membrane. Glass A contained 100 ml of 3M methanol, and glass B contained 100 ml of distilled water. The solution in each glass was stirred continuously to ensure uniformity. The change of methanol concentration was measured by using refractive index with a refractometer hourly. The value of concentration was obtained by fitting into the concentration-refractive index curve. The methanol permeability was calculated by equation (5).

\[
C_B(t) = \frac{A}{V_B} \times \frac{DK}{L} \times C_A \times (t - t_0) 
\]

where \(C_A\) and \(C_B\) are the concentration of methanol in glasses A and B, respectively, \(A\) is the cross-sectional area of the membrane, \(L\) is the thickness of the membrane, \(V_B\) is the volume of solution in the chamber glass. DK is the permeability of methanol.

3. Results and discussion
3.1. XRD Analysis
Figure 1 shows the angle X-ray diffractograms of composites sPEEK/PVA incorporated with CsHPW, GO, and SCNT, respectively. All membranes show a broad peak at around 2 = 20 indicating the crystalline of the blended polymer sPEEK/PVA. Upon the addition of filler, it is noticed that the crystalline peak at 2 = 21.3 and 23.5-23.8 in all membranes which may be due to a low degree of sulfonation. Diffraction peaks at 11.6 and 11.8 with high intensity suggest CsHPW and GO crystals, respectively) due to fillers’ accumulation in the sPEEK/PVA matrix. Amorphous nature offers a better capacity to transport protons.

3.2. Tensile Strength and Elongation at Break Analysis
Figure 2 exhibits the finding of tensile strength and elongation at break value for prepared membranes. All hybrid membranes display a reduced tensile strength than the blended sPEEK/PVA (45 MPa). The importance of tensile strength hybrid membranes is 23-41 MPa. It was reported that the tensile strength of sPEEK membranes was around 12 MPa [23] and 53 MPa [24], whereas the PVA based membranes were 10-17 MPa [25]. The elongation at break of incorporated CsHPW and SCNT membranes was increased, but that of GO membrane was reduced.
3.3. Water Uptake and Swelling Degree Properties

With the inclusion of water molecules in the microscopic polymer system’s channels, the resulting membranes’ ionic conductivity is greatly influenced by the increased number of protonic sites in the SO3H group, which provides a water-mediated ion transport pathway [26]. To preserve ion conductivity, a level of water in the membrane matrix is needed. However, excess water absorption can contribute to undesirable outcomes such as membrane fracturing, mechanical inadequacy, and lower dimensional stability, resulting in weak efficiency.

Figure 3 shows both the water uptake and swelling degree of the prepared membranes. The incorporation of CsHPW into the sPEEK/PVA membrane increases water uptake, whereas GO and SCNT fillers affect insignificantly. The incorporation of CsHPW and S(Silica)-CNT caused an increase in sPEEK/PVA membranes’ water absorption. The possible reason may be due to the hydrophilic property of CsHPW and silica for interaction with water. It does seem that GO leads to a slight blockage of water. Water absorption between 20% and 40% was ideal for high ion conductivity levels while staying mechanically stable [27]. Heo et al. reported that the GO/sPEEK membrane’s water uptake was about 26-48%, depending on the GO loading [28].
The TEOS 10% water uptake capacity is loading doped sPEEK/PVA membranes exhibited at about 33% value [22]. It is found that the swelling degree character is increased by adding all fillers. The value of a swelling degree character is comparable to the other hybrid sPEEK based membranes, which is less than 20% [29–31]. The membranes’ swelling should not be high, as it decreases longevity and mechanical stability and reduces fuel cell efficiency.

![Figure 3: The water uptake and swelling degree properties of composite sPEEK/PVA membranes with different fillers](image)

3.4. Ion Exchange Capacity

The IEC and are $\lambda$ also essential parameters related to the proton conductivity of prepared membranes. The IEC of composite membranes with different fillers is shown in Figure 4. It can be observed that the IEC values are improved by fillers of CsHPW and GO in the composite membrane, while SCNT is lowered compared to the plain composite membrane. However, the calculation of the water content parameter shows a different trend. Following IEC and $\lambda$ data indicate that incorporation of CsHPW in sPEEK/PVA exhibits the highest ion exchangeable group concentration. Sahin [22] reported that sPEEK-PVA10-TEOS10 had the water content parameter of 20 H$_2$O/mole SO$_3$ lower than that of these prepared membranes. Since IEC and $\lambda$ provide a reliable approximation about proton conductivity, it is reasonable to believe that CsHPW could raise proton conductivity. The explanation can be summarized in Table 1 with

| $\tau$   | IEC (meq g$^{-1}$) | $\xi$ |
|----------|-------------------|------|
| Blank    | 0.59              | 31.3 |
| CsHPW    | 0.70              | 42.5 |
| GO       | 0.64              | 26.7 |
| SCNT     | 0.48              | 39.4 |

Table 1: The ion exchange capacity of composite sPEEK/PVA membranes with various fillers

the notation as follows: with $\tau$ is Filler of Composite Membranes, $\xi$ is Water Content Parameter, $\lambda$ (mole H$_2$O/mole SO$_3$).
3.5. Methanol Permeability

Apart from the electrode’s catalyst activity and efficiency, low methanol permeability and high conductivity are the two important factors that control a DMFC. All membranes are subjected to a test for methanol permeability at a 3M concentration of methanol. The methanol permeability through the membrane was estimated, and the result is presented in Figure 4. Generally, methanol permeability is reduced in the presence of fillers. The values are around $2.43.8 \times 10^{-6} \text{cm}^2\text{s}^{-1}$. The composite membrane of sPEEK/PVA combining with SCNT indicates the lowest methanol blockage. The reported sPEEK/PVA had the methanol permeability values of $4 \times 10^{-6} \text{cm}^2\text{s}^{-1}$ [32], while Nafion also had value of $2.9 \times 10^{-6} \text{cm}^2\text{s}^{-1}$ [28]. The SPEEK matrix’s microstructure has narrower hydrophobic-hydrophilic variations since the backbone is less hydrophobic and the sulphonic acid group is less acidic. At the same time, Nafion has the relatively high hydrophobicity of the perfluorinated backbone and the sulphonic acid groups’ high hydrophilicity. Sulfonic acid groups form hydrophilic regions, which are proton channels and polar molecules such as methanol [28]. The composite sPEEK/PVA contained with CsHPS, GO, and SCNT has obstructed sufficiently the migration of methanol molecules, even though its rate is still comparable with Nafion.

![Figure 4: The methanol permeability of composite sPEEK/PVA membranes with various fillers](image-url)

4. Conclusion

In this study, CsHPW, GO, and SCNT was incorporated into the sPEEK/PVA membranes. Characterization by XRD showed fillers modified in the sPEEK-PVA matrix. The fillers affected the mechanical properties, ability to keep water in, number of counter ions exchangeable in membranes, and methanol permeability. According to a study on IEC and methanol permeability, further investigation should focus on these issues.

References

[1] Zhong S, Cui X, Cai H, Fu T, Zhao C and Na H 2007 Crosslinked sulfonated poly(ether ether ketone) proton exchange membranes for direct methanol fuel cell applications J. Power Sources 164 65–72
[2] Chiu K F, Chen Y R, Lin H C and Ho W H 2010 PTFE coated Nafion proton conducting membranes for direct methanol fuel cells Surf. Coatings Technol. 205 1647–50
[3] Iulianelli A and Basile A 2012 Sulfonated PEEK-based polymers in PEMFC and DMFC applications: A review Int. J. Hydrogen Energy 37 15241–55
[4] Nagar H, Sahu N, Rao V V B and Sridhar S 2020 Surface modification of sulfonated polyethersulfone membrane with polyaniline nanoparticles for application in direct methanol fuel cell Renew. Energy 146 1262–77

[5] Purnama H, Hartoko I V, Mujiburohman M and Hidayati N 2020 Effect of graphene oxide on the characteristics of SPEEK-Chitosan membranes for direct methanol fuel cells Automot. Exp. 3 1–5

[6] Wattanakul K, Sirivat A, Chuesutham T, Changkhamchom S, Krathumkhet N, Anumart S, Paradee N and Khampim J 2019 Improvement of sulfonated poly(ether ketone)/Y zeolite -SO3H via organo-functionalization method for direct methanol fuel cell Renew. Energy 138 243–9

[7] You P Y, Kamarudin S K and Masdar M S 2018 ScienceDirect Improved performance of sulfonated polyimide composite membranes with rice husk ash as a bio-filler for application in direct methanol fuel cells Int. J. Hydrogen Energy

[8] Lufrano E, Somari C, Vecchio L, Arico A S, Baglio V and Nicotera I 2020 Barrier properties of sulfonated polysulfone / layered double hydroxides nanocomposite membrane for direct methanol fuel cell operating at high methanol concentrations Int. J. H 45 20647–58

[9] Muhammad A. Imran, Li T, Wu X, Yan X, Khan A S and He G 2020 Sulfonated polybenzimidazole/amine functionalized titanium dioxide (sPBI/AFT) composite electrolyte membranes for high temperature proton exchange membrane fuel cells usage Chinese J. Chem. Eng. 28 2425–37

[10] Li X, Bu F, Zhang H and Zhao C 2020 Facile synthesis of poly (arylene ether ketone) s containing flexible sulfonated alkyl groups with enhanced oxidative stability for DMFCs Int. J. Hydrogen Energy 45 27632–43

[11] Zaidi, S. M 2003 Polymer Sulfonation A Versatile Route to Prepare Proton-Conducting Membrane Material for Advanced Technologies Arab. J. Sci. Eng. 28 183–94

[12] Properties E and Nanoparticles F O 2019 A Comparative Study on Physiochemical , of Sulfonated Poly ( Ether Ether Ketone ) Block Polymers (Basel). 11 2–15

[13] Zhang N, Zhang G, Xu D, Zhao C, Ma W, Li H, Zhang Y, Xu S, Jiang H, Sun H and Na H 2011 Cross-linked membranes based on sulfonated poly (ether ether ketone) (SPEEK)/Nafion for direct methanol fuel cells (DMFCs) Int. J. Hydrogen Energy 36 11025–33

[14] Wang J, Liao J, Yang L, Zhang S, Huang X and Ji J 2012 Highly compatible acid-base blend membranes based on sulfonated poly(ether ether ketone) and poly(ether ether ketone-alt-benzimidazole) for fuel cells application J. Memb. Sci. 415–416 644–53

[15] Gao C, Zhang S, Lin Y, Li F, Guan S and Jiang Z 2015 High-performance conductive materials based on the selective location of carbon black in poly (ether ether ketone) / polyimide matrix 79 124–31

[16] Song H, Luo M, Qiu X and Cao G 2016 Insights into the endurance promotion of PtSn / CNT catalysts by thermal annealing for ethanol electro-oxidation

[17] Gao H, Dong C, Wang Q and Zhu H 2018 Improving the proton conductivity of proton exchange membranes via incorporation of HPW-functionalized mesoporous silica nanospheres into SPEEK Int. J. Hydrogen Energy 1–9

[18] Roelofs K S, Hirth T and Schiestel T 2010 Sulfonated poly(ether ether ketone)-based silica nanocomposite membranes for direct ethanol fuel cells J. Memb. Sci. 346 215–26

[19] Jiang Z, Zhao X and Manthiram A 2013 Sulfonated poly(ether ether ketone) membranes with sulfonated graphene oxide fillers for direct methanol fuel cells Int. J. Hydrogen Energy 38 5875–84

[20] Rambabu G and Bhat S D 2014 Simultaneous tuning of methanol crossover and ionic conductivity of sPEEK membrane electrolyte by incorporation of PSSA functionalized MWCNTs: A comparative study in DMFCs Chem. Eng. J. 243 517–25

[21] Hasani-Sadrabadi M M, Dashtimoghadam E, Sarikhani K, Majedi F S and Khanbabaei G 2010 Electrochemical investigation of sulfonated poly(ether ether ketone)/clay nanocomposite membranes for moderate temperature fuel cell applications J. Power Sources 195 2450–6

[22] Sahin A 2018 The development of Speek / Pva / Teos blend membrane for proton exchange membrane fuel cells Electrochim. Acta 271 127–36

[23] Elumalai V, Ganesh T, Selvakumar C and Sangeetha D 2018 Materials Science for Energy Technologies Phosphonate ionic liquid immobilised SBA-15 / SPEEK composite membranes for high temperature proton exchange membrane fuel cells Mater. Sci. Energy Technol. 1 196–204

[24] Zhou X, Zhu B, Zhu X, Miao J and Sun X 2020 Novel nanofiber-enhanced SPEEK proton-exchange membranes with high conductivity and stability Polymer (Guildf). 210 123016

[25] Gouda M H, Gouveia W, Elessawy N A, Sljukic B, Nasr A A A and Santos D M F 2020 Simple design of PVA-based blend doped with SO 4 ( PO 4 ) -functionalised TiO 2 as an effective membrane for direct borohydride fuel cells Int. J. Hydrogen Energy 45 15226–38

[26] Okada T, Xie G, Gorseth O and Kjelstrup S 1998 Ion and water transport characteristics of Na @ on membranes as electrolytes Electrochem. commun. 43 3741–7

[27] Yee R, Zhang K and Ladewig B 2013 The Effects of Sulfonated Poly(ether ether ketone) Ion Exchange
Preparation Conditions on Membrane Properties Membranes (Basel). 3 182–95

[28] Heo Y, Im H and Kim J 2013 The effect of sulfonated graphene oxide on Sulfonated Poly (Ether Ether Ketone) membrane for direct methanol fuel cells J. Memb. Sci. 425–426 11–22

[29] Zheng L, Wang H, Niu R, Zhang Y and Shi H 2018 Electrochimica Acta Sulfonated poly(ether ether ketone)/sulfonated graphene oxide hybrid membrane for vanadium redox flow battery Electrochim. Acta 282 437–47

[30] Salarizadeh P and Pourmahdian S 2017 Enhancing the performance of SPEEEK polymer electrolyte membranes using functionalized TiO$_2$ nanoparticles with proton hopping sites RSC Adv. 7 8303–13

[31] Porchelvi S, Kannan R, Palani P B, Abidin K S and Rajashabala S 2017 High conductive proton exchange membrane (SPEEK/MMT) and its characterization Mater. Res. Innov. 1–6

[32] Yang T 2008 Preliminary study of SPEEK/PVA blend membranes for DMFC applications Int. J. Hydrogen Energy 33 6772–9