Preparation of a novel composite membrane and PtRu/Hollow carbon sphere (HCS) anode catalyst for alkaline direct methanol fuel cell (ADMFC)

Chun-Chen Yang* a,b, Yan-Ting Lin a,b
aDepartment of Chemical Engineering, Ming Chi University of Technology, New Taipei, City 243, Taiwan, R.O.C.
bBattery Research Center of Green Energy, Ming Chi University of Technology, New Taipei City 243, Taiwan, R.O.C.

Abstract

This work demonstrated the synthesis process of the anion-exchange nanocomposite membrane based on Poly(vinyl alcohol (PVA) and Quaternary ammonium silica precursor (QASP), which was synthesized by using Glycidytrimethyl ammonium chloride (GTMAC) and 3-Aminopropyl trimethoxysilane (AMPTS). The suitable amount of functional SiO₂ fillers was added into the PVA composite polymer membrane to reduce the methanol permeability and also improve the thermal and mechanical properties. A novel and high activity PtRu/Hollow carbon sphere (HCS) was synthesized to use as a catalyst in the anode for methanol oxidation. It was found that this as-prepared PtRu/HCS shows excellent electrochemical activity, as compared with PtRu black. The characteristic properties were examined by thermal gravimetric analysis (TGA), X-ray diffraction (XRD), micro-Raman and FTIR spectroscopies, scanning electron microscopy (SEM), and AC impedance method. It was observed that the maximum ionic conductivity of anion-exchange composite polymer membrane is around $5.12 \times 10^{-2}$ S cm$^{-1}$ at room temperature. It was observed that the highest peak power density of alkaline direct methanol fuel cell (ADMFC) with a 4M KOH + 2M CH₃OH fuel was around 70 mW cm$^{-2}$ at 70°C. The methanol permeability is around $10^{-6} \sim 10^{-7}$ cm$^2$ s$^{-1}$. The results demonstrate that the PVA/QASP/SiO₂ composite membranes exhibit a good candidate for application to ADMFC.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).
Peer-review under responsibility of the Organizing Committee of ICAE2014

Keywords: Poly(vinyl alcohol) (PVA), alkaline direct methanol fuel cell (ADMFC), PtRu, Hollow Carbon sphere (HCS), Anode

1. Introduction

The DMFCs have recently attracted significant attention for their potential applications on electric vehicles (EVs), stationary applications, and portable power sources, such as cellular phones and notebook computers. The direct methanol fuel cell (DMFC) is being actively studied and significant progress has been made over the past few years [1-18]. However, the development of the DMFC has been hampered due to several problems, such as slow methanol oxidation kinetics and incomplete electrooxidation of methanol, the poisoning of adsorbed intermediate species on the Pt surface, the high methanol crossover through the solid-state polymer Nafion membrane, and the high costs of the Nafion (Du Pont) polymer membrane and Pt catalyst.

Yang [1,2] synthesized the crosslinked PVA-based composite polymer membranes and applied them in an alkaline DMFC. The carbonation problem of alkaline DMFC can be significantly reduced by using an alkaline solid polymer membrane instead of an alkaline solution [3-6]. In addition, the anodic electrooxidation of methanol in an alkaline medium shows significantly faster kinetics than that in an acidic medium [7]. The works on the preparation of the anion exchange polymer membrane for alkaline DMFC have been studied intensively [8-15]. Several types of anion exchange polymer membranes based on quaternized polymers and applied for alkaline
alcohol fuel cells have recently been investigated [9,15].

In this study, we attempt to add Quaternary ammonium silica precursor (denoted as QASP), which is formed by using (3-aminopropyl) trimethoxy silane (APTMS) and Glycidyl methyl ammonium chloride (GTMAC), into 3-(trimethyl ammonium) propyl-functionalized SiO2 (that is, TAMPFS) into the PVA matrix, to act as the ionic source and solid plasticizer which is capable of enhancing the ionic conductivity, the chemical and thermal properties, and the dimensional stability for the PVA/QASP/TAMPFS solid polymer membrane. Also, the PVA/QASP/TAMPFS solid polymer was coated on PET non-woven to form a PVA/QASP/TAMPFS-PET composite membrane. Alkaline DMFC, comprised of the air cathode loaded with MnO2/BP2000 carbon ink on a Ni-foam, the as-prepared 50wt.%PtRu/Hollow carbon sphere/MWCNT anode on a Ti-screen, and PVA/Q-SiO2 composite polymer membrane, was assembled and investigated. The electrochemical characteristics of alkaline DMFC comprised of QPVA/Q-SiO2 composite polymer membrane were investigated by the linear polarization and galvanostatic methods; especially for the peak power density of alkaline DMFC at ambient conditions.

2. Experimental

2.1 Preparation of the QPVA/Q-SiO2 composite polymer membrane

The PVA (Aldrich), 3-(trimethyl ammonium) propyl-functionalized silica (TMAPFS) (Aldrich), (3-aminopropyl) trimethoxy silane (APTMS), glycidytrimethyl ammonium chloride (GTMAC) (Aldrich), and KOH (Merck) were used without further purification. The degree of polymerization and saponification of PVA were 1,700 and 98~99 %, respectively. The anion-exchange composite polymer membrane was prepared by a solution casting method. The appropriate quantities of the PVA polymer were dissolved in distilled water under stirring. The resulting solution was stirred until the solution mixture became homogeneous with a viscous appearance at 85°C for 3 h. The temperature of the viscous mixture was cooled to 65°C, after which an appropriate amount of QASP, which was prepared by GTMAC, APTMS with a molar ratio of 1:2, the resulting mixture solution was under a continuous stirring condition for 4 h. The quaternized poly(vinyl alcohol) anion-exchange composite were then dried at 65°C in a vacuum oven.

The PVA/QASP mixture solution was prepared by using a suitable amount of as-prepared PVA/QASP precipitates, 10wt. % TMAPFS or Q-SiO2 fillers, and 5 wt. % GA (a cross linking agent), 1 vol. % HCl at 85 °C for 3 h. under a continuous stirring condition. The resulting viscous blend polymer solution was poured onto a PET nonwoven matrix (prepared by Electrospinning device). The thickness of the wet composite membrane was between 0.020 and 0.040 cm. The thickness of the dried composite membrane was controlled in the range of between 0.010 and 0.020 cm. Fig. 1 shows a schematic diagram for the structure of a cross-linked PVA/QASP/TAMPFS-PET composite polymer membrane.

![Fig. 1 A schematic diagram of the structure of PVA/QASP/TAMPFS-QPET nonwoven SPE.](image)

2.2 Crystal structure and ionic conductivity

TGA thermal analysis was conducted by using a Mettler Toledo TGA/SDT 851 system. The measurements were conducted by heating from 25 to 600 °C, under N2 atmosphere at a heating rate of 10 °C min⁻¹ with approximately 10 mg samples. The surface morphology and microstructure of the PVA/QASP/TAMPFS-PET composite polymer membrane were investigated by a scanning electron microscope (SEM) (Hitachi S-2600H). The conductivity measurements of QPVA/Q-SiO2 composite polymer electrolytes were conducted via an AC impedance method. The composite samples were first immersed in a 1 M KOH solution for 24 h. for ionic exchange, washed several times with D.I. water, and finally dipped in D.I. water for 12 h. for further testing. The PVA/QASP/TAMPFS-PET anion-exchange membranes were clamped between stainless steel (SS304) and ion-blocking electrodes, each with a surface area of 1.32 cm², in a spring-loaded glass holder. A thermocouple was maintained in close proximity to the composite polymer membrane for temperature measurement. Each sample was equilibrated at the experimental temperature for a
minimum of 30 min. prior to measurement. The AC impedance measurements were conducted by using Autolab PGSTAT-30 equipment (Eco Chemie B.V., Netherlands). The AC spectra in the range of 300 kHz to 100 Hz at an excitation signal of 10 mV were recorded. AC impedance spectra of the composite anion-exchange membrane were recorded at a temperature range between 30 and 70°C. The experimental temperatures were maintained within ±0.5°C in a convection oven.

2.3 Preparation of the anode and cathode electrodes

The hollow carbon sphere (HCS) was synthesized by a hydrothermal process using 8wt.% glucose with 1%SDS at 170°C for 10 h. A suitable amount of HCS was dispersed in ethylene glycol with RuCl₃ and H₂PtCl₆·6H₂O salts (a molar ratio of Pt:Ru=1:1) by a microwave method (150W, 130°C, about 1h). The catalyst, slurry ink, for the anode was prepared by mixing 70wt. % PtRu black inks (Alfa, Hispec 6000, PtRu black with Pt:Ru=1:1 at. ratio), 30wt. % PTFE binder solution (Du Pont, 60 wt. % base solution), and a suitable amount of distilled water and alcohol. The resulting PtRu black mixtures were ultrasonicated for 2 h. The PtRu black inks for the anode were loaded onto a Ti-screen [1,10] by an impregnation method, which was loaded with 4 mg cm⁻². The as-prepared PtRu anode was dried in a vacuum oven at 110 °C for 2 h.

The carbon slurry for the gas diffusion layer of the air cathode was prepared with a mixture of 70wt.% Shawinigan acetylene black (AB50) with a specific surface area of 80 m² g⁻¹ and 30 wt.% PTFE solution (Teflon-30 suspension) as a wet-proofing agent and binder. The carbon slurry was coated on the Ni-foam that was used as a current collector, and then pressed at 100 kg cm⁻². The gas diffusion layer was then sintered at a temperature of 360°C for 30 min. The catalyst layer of the air cathode was then prepared by spraying a mixture of 15wt.% of PTFE binder and 85 wt.% of mixed powders consisting of MnO₂ catalyst mixed with BP2000 carbon black (MnO₂:BP2000=1:1). The MnO₂/C catalyst loading on the cathode was controlled at 4 mg cm⁻². The Ni-foam current collector was 1x1 cm².

2.4 Electrochemical measurements

The PVA/QASP/TMAPFS-PET anion-exchange membranes was “sandwiched” between the sheets of the anode and the cathode, and then pressed at 25 °C under 100 kg cm⁻² for 5 min. to obtain a membrane electrode assembly (MEA). The electrode area of the MEA was approximately 1 cm². The electrochemical measurements of alkaline DMFC were carried out in a two-electrode system. The polarization (I-V) and the power density curves of alkaline DMFC consisting of PVA/QASP/TMAPFS-PET anion-exchange membranes with 1~8 M KOH + 2 M CH₃OH solution or pure 2M CH₃OH fuel were recorded at 25 and 50 °C. All electrochemical measurements were performed on an Autolab PGSTAT-30 electrochemical system with GPES 4.8 package software (Eco Chemie, The Netherlands). The electrochemical performances of alkaline DMFC comprised of a PVA/QASP/TMAPFS-PET composite anion-exchange membrane and the cathode open to atmospheric air were systematically studied at room temperature and in ambient air [1,2].

3. Results and discussion

The SEM photographs of the top and cross-section views of the PVA, PVA/QASP/MMT, PVA/QASP/TAMPFS, PVA/QASP/TAMPFS-PET membranes are shown in Figs. 2(a) - (d), respectively, at a magnification of 500x. It was found that the surface morphology of PVA membrane is flat and smooth. However, it is revealed that the surface morphology of the PVA/QASP/MMT and PVA/QASP/TAMPFS composite polymer samples shows a rough surface. It is due to MMT and quaternized-SiO₂ aggregates (i.e., TAMPFS) or chunks being blend into the polymer matrix. They are randomly distributed on the top surface. It also is found that the PVA/QASP/TAMPFS-PET composite membrane is very rough with a thickness of approximately 100 μm. The SEM results indicate that the SiO₂ fillers tend to cause the formation of a number of aggregates, and thus cause a dispersion problem in the PVA polymer host. Accordingly, the hydrophilic PVA polymer and quaternized-SiO₂ fillers are homogeneous and compatible without the occurrence of any phase separation when a suitable amount of quaternized-SiO₂ fillers are added. The appropriate amount of QASP (100% vs. PVA polymer) and quaternized-SiO₂ fillers (10wt.% vs. PVA) (used as the ionic source and the methanol permeation barrier) in the polymer network matrix may assist in increasing the ionic conductivity and reducing methanol crossover through the composite anion-exchange membrane.
The typical AC impedance spectra of the PVA/QASP/TAMPFS-PET composite membrane at various temperatures are shown in Fig. 3(a). The AC spectra were typically non-vertical spikes for stainless steel (SS) blocking electrodes, (that is, the SS | PVA/QASP/TAMPFS-PET composite membrane | SS cell). An analysis of the spectra yielded information about the properties of the PVA/QASP/TAMPFS-PET composite polymer electrolyte, such as bulk resistance, $R_b$. Taking into account the thickness of the nanocomposite electrolyte films, the $R_b$ value was converted into the ionic conductivity value, $\sigma$, according to the equation:

$$\sigma = \frac{L}{R_b \cdot A},$$

where $L$ is the thickness (cm) of PVA/QASP/TAMPFS-PET composite membrane, $A$ is the area (cm$^2$) of the blocking electrode, and $R_b$ is the bulk resistance (ohm) of the alkaline composite polymer membrane.

Typically, the $R_b$ values of PVA/QASP/TAMPFS-PET composite electrolyte membrane are in the order of 0.14-0.18 ohm (as seen in the inset of Fig. 3(a) and are highly dependent on the contents of QASP and quanterized-SiO$_2$ fillers and the concentration of KOH. The composite anion-exchange membrane was immersed in a 1M KOH solution for 24 h. for ionic exchange, and then washed several times with D.I. water. Table 1 lists the ionic conductivity values of the PVA/QASP/TAMPFS-PET composite electrolyte membrane with D.I. water at various temperatures. As a result, the ionic conductivity of the PVA/QASP/TAMPFS-PET composite polymer electrolytes increases when the content of QASP and quanterized-SiO$_2$ fillers increase. When the QASP and quanterized-SiO$_2$ fillers, they all contain with the quaternized functional groups (-($\text{CH}_3$)$_3\text{N}^+$), used as the ionic source and solid plastizers materials, were added to the PVA matrix; therefore, the ionic conductivity and swelling ratio of PVA membranes were effectively reduced.

### Table 1 The ionic conductivities of PVA/100wt.%QASP/10wt.%TAMPFS-PET SPE

<table>
<thead>
<tr>
<th>Temp</th>
<th>L/cm</th>
<th>$R_b$/ohm</th>
<th>$\sigma$/S cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>0.0125</td>
<td>0.1811</td>
<td>5.35x10$^{-2}$</td>
</tr>
<tr>
<td>40°C</td>
<td>0.0125</td>
<td>0.1735</td>
<td>5.59x10$^{-2}$</td>
</tr>
<tr>
<td>50°C</td>
<td>0.0125</td>
<td>0.1669</td>
<td>5.81x10$^{-2}$</td>
</tr>
<tr>
<td>60°C</td>
<td>0.0125</td>
<td>0.1610</td>
<td>6.02x10$^{-2}$</td>
</tr>
<tr>
<td>70°C</td>
<td>0.0125</td>
<td>0.1471</td>
<td>6.59x10$^{-2}$</td>
</tr>
</tbody>
</table>

Fig. 3 The Nyquist plot (a) and Arrhenius plot (b) of PVA+QASP+TAMFS on PET.

The XRD patterns of the as-prepared hollow carbon sphere (HCS) and 50wt.%PtRu/HCS, 50wt.%PtRu/MWCNTs, and 50wt.%PtRu/Graphene samples are shown in Fig. 4. In each XRD pattern, besides the diffraction peak of C(200) at 24.6o for HCS, the XRD peaks for other three PtRu samples correspond to the (111), (200), (220), and (311) crystal
As seen from Fig. 4, the three PtRu/C catalysts are obviously very similar; the only difference is carbon matrix. In contrast, we find that the peak intensity of 50wt.%PtRu/HCS catalyst sample is stronger than those of the other two samples. Fig. 5(a) shows the FE-SEM image of 50wt.%PtRu/HCS catalyst sample with HCS particle size around 100-200 nm. All PtRu catalyst is uniformly deposited on the surface of HCS. Fig. 5(b) shows TEM images of 50wt.%PtRu/HCS catalyst sample. The HCS appears to form hollow sphere, but some is hemisphere. The PtRu catalyst is well dispersed on the surface of HCS. Also, as seen from Fig. 6, the uniformity of PtRu catalyst on HCS is excellent, without aggregation observed. Fig. 6 shows the typical cyclic voltammograms (CV) of methanol oxidation under acidic conditions, i.e., 1M H2SO4 + 2M CH3OH at 25°C, catalyzed by PtRu black (Aldrich), 50wt.%PtRu, 50wt.%PtRu/HCS+1wt.%MWCNTs, and 50wt.%PtRu/1wt.%Graphene catalyst samples, respectively. The CV was carried out in the potential window from 0V to 1.1 V at the scan rate 10 mV s⁻¹. The peak current densities due to methanol oxidation (at 0.57-0.82V) for PtRu black (Aldrich), 50wt.%PtRu/HCS, 50wt.%PtRu/HCS+1wt.%MWCNTs, and 50wt.%PtRu/1wt.%Graphene samples with the same PtRu catalyst load of 4 mg cm⁻² are 314 mA cm⁻², 254 mA cm⁻², 266 mA cm⁻², 198 mA cm⁻², respectively. Therefore, the catalyst activities can be ranked in the following order PtRu black > 50wt.%PtRu/HCS+1wt.%MWCNTs > 50wt.%PtRu/HCS > 50wt.%PtRu/1wt.%Graphene, as listed in Table 2. Furthermore, The ratio of i_f/i_b is used to evaluate the CO tolerance. The ratio the four PtRu catalysts are listed in Table 2. It can be seen clearly that the 50%PtRu/HCS has the highest value, indicating the best CO tolerance.

**Table 2**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Forward sweep</th>
<th>Reverse sweep</th>
<th>i_f/i_b ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtRu black</td>
<td>314.09</td>
<td>0.8278</td>
<td>6.908</td>
</tr>
<tr>
<td>50wt.%PtRu/HCS</td>
<td>254.82</td>
<td>0.6960</td>
<td>3.710</td>
</tr>
<tr>
<td>50wt.%PtRu/HCS +1%MWCNTs</td>
<td>266.88</td>
<td>0.6201</td>
<td>2.893</td>
</tr>
<tr>
<td>50wt.%PtRu/HCS +1%Graphene</td>
<td>198.88</td>
<td>0.5786</td>
<td>1.754</td>
</tr>
</tbody>
</table>

Fig. 6 The CV curve of varied types PtRu/C catalysts in 1M H2SO4+2M MeOH at 25°C.
3.2 Electrochemical measurements

Fig. 7(a) shows the potential-current density and the power density-current density curves of alkaline DMFCs with 4M KOH + 2M methanol fuel at 30, 50, and 70°C. As a result, the highest peak power density of 49 mW cm$^{-2}$ for the ADMFC with PVA/QASP/TAMPFS composite electrolyte without PET non-woven at 70°C is achieved at $E_{p,max} = 0.270$ V, with a peak current density ($i_{p,max}$) of 184 mA cm$^{-2}$, as listed in Table 3. Conversely Fig. 7(b), the peak power density of alkaline DMFC comprising of the PVA/QASP/TAMPFS-PET composite electrolyte with a 4M KOH + 2M CH$_3$OH fuel is 72 mW cm$^{-2}$ at $E_{p,max} = 0.29$ V, with a peak current density of 245 mA cm$^{-2}$ at 70°C, as listed in Table 4. It was clearly indicated that the electrochemical performance of anion-exchange electrolyte membrane with PET non-woven is greatly improved. It is due to the high thermal and mechanical stability of PET non-woven.

Our P.D. data are comparable to the data of Santasala-Aarnio et al. It was revealed that the peak power density value (P.D.=0.27 mW cm$^{-2}$) of the DMFC with pure 2M methanol fuel was significantly lower than those of the DMFCs with 4M KOH + 2M methanol fuel (P.D.$_{max}$= 26.09 mW cm$^{-2}$), at the same amount of catalyst loadings on the electrodes (that is, the anode with 4 mg cm$^{-2}$ PtRu black ink and the cathode with 4 mg cm$^{-2}$ MnO$_2$/C ink). It was demonstrated that the alkaline DMFC consists of the air electrode using a non-precious metal catalyst (that is, a cheap MnO$_2$ catalyst instead of an expensive Pt can be effectively used). It was found that a metal oxide catalyst of MnO$_2$ is not only inexpensive but also more tolerant towards crossover, and is active for the reduction of O$_2$ to OH$^-$ in an alkaline media. The as-prepared PVA/QASP/TAMPFS-PET composite electrolyte membrane is a low-cost non-perfluorosulfonated polymer membrane, compared with an expensive Nafion membrane.

![Figure 7(a)](image)

![Figure 7(b)](image)

**Table 3**

<table>
<thead>
<tr>
<th>Param</th>
<th>Temp./°C</th>
<th>$E_{max}$/V</th>
<th>$i_{max}$/mA cm$^{-2}$</th>
<th>P.D.$_{max}$/mW cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td></td>
<td>0.24</td>
<td>118</td>
<td>28</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>0.23</td>
<td>180</td>
<td>42</td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>0.27</td>
<td>184</td>
<td>49</td>
</tr>
</tbody>
</table>

**Table 4**

<table>
<thead>
<tr>
<th>Param.</th>
<th>Temp./°C</th>
<th>$E_{max}$/V</th>
<th>$i_{max}$/mA cm$^{-2}$</th>
<th>P.D.$_{max}$/mW cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td></td>
<td>0.24</td>
<td>70</td>
<td>17</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>0.25</td>
<td>180</td>
<td>45</td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>0.29</td>
<td>245</td>
<td>72</td>
</tr>
</tbody>
</table>

4. Conclusions

The alkaline composite anionic-exchange membrane, based on PVA/QASP/TAMPFS-PET composite electrolyte was prepared by a solution casting method. It demonstrates that the ionic conductivity of PVA/QASP/TAMPFS-PET composite electrolyte significantly increases using QASP and TAMPFS (quanterized-SiO$_2$ fillers). An alkaline direct methanol fuel cell, comprising of the PVA/QASP/TAMPFS-PET composite polymer membrane, was assembled and systematically examined. The highest peak power density of alkaline DMFC comprising of the PVA/QASP/TAMPFS-PET composite polymer membrane with 4 mg cm$^{-2}$ PtRu
black with a 4M KOH + 2M CH₃OH fuel is approximately 72 mW cm⁻² at 70°C. The PVA/QASP/TAMPFS-PET composite anionic-exchange membranes are viable candidates for applications in alkaline DMFCs.

5. Acknowledgements

Financial support from the National Science Council, Taiwan (Project No: NSC 101-2221-E-131-037) is gratefully acknowledged.

6. References