



Performance of organic–inorganic hybrid anion-exchange membranes for alkaline direct methanol fuel cells

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ABSTRACT

A series of organic–inorganic membranes were prepared through sol–gel reaction of quaternized poly(vinyl alcohol) (QAPVA) with different contents of tetraethoxysilanes (TEOS) for alkaline direct methanol fuel cells. These hybrid membranes are characterized by FTIR, X-ray diffraction (XRD), scanning electron microscopy/energy-dispersive X-ray analysis (SEM/EDXA) and thermo gravimetric analysis (TGA). The ion exchange content (IEC), water content, methanol permeability and conductivity of the hybrid membranes were measured to evaluate their applicability in fuel cells. It was found that the addition of silica enhanced the thermal stability and reduced the methanol permeability of the hybrid membranes. The hybrid membrane M-5, for which the silica content was 5 wt%, showed the lowest methanol permeability and the highest ion conductivity among the three hybrid membranes. The ratio of conductivity to methanol permeability of the membrane M-5 indicated that it had a high potential for alkaline direct methanol fuel cell applications.

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1. Introduction

The application of alkaline anion-exchange membranes in direct methanol fuel cells (DMFC) has attracted considerable attention owing to their advantages, which include: (1) methanol oxidation is more facile in alkaline media, which will allow to use of Ni or Ag as the catalyst; (2) ion transport within the membrane is from the cathode to the anode, opposing the direction of methanol crossover from anode to cathode, which will reduce the methanol permeability; (3) water is produced at the anode and consumed at the cathode, which will simplify the water management [1–5].

According to the merits above, research on alkaline anion-exchange membranes in DMFC has progressed [6–10]. In our research group, research on the synthesis and characterization of alkaline anion-exchange membrane for DMFCs has continued. In our previous work, quaternized poly(vinyl alcohol) (QAPVA) membranes were synthesized [11]. The quaternary ammonium groups were introduced onto the matrix of the PVA, which made the QAPVA have exchangeable OH[−] anions and thus could be used for alkaline DMFCs. In order to enhance the performance of the QAPVA, we prepared crosslinked QAPVA membranes with glutaraldehyde (GA) as the crosslinking reagent and composite membranes of

QAPVA and quaternized chitosan [12]. Both the methanol permeability and the conductivity of the membranes were reinforced. However, in comparison with many proton membranes, the QAPVA membranes still need to be improved before they can be applied in DMFCs.

Organic–inorganic hybrid materials have been regarded as promising materials for many applications due to their unique performance to combine the remarkable functionality of organic materials with the stability of inorganic materials [13–14]. In fuel cells, organic–inorganic membranes have also been used [15–20]. Many organic–inorganic hybrid membranes such as SPEK/SiO₂ [16], PBI/SiO₂/SiWA [18], Nafion/MMT [20] have been prepared. The introduction of an inorganic component into the polymer matrix enhanced the performance of the membranes. The aims for addition of inorganic materials into organic polymers are: (1) to reduce the transport channel for methanol resulting in a decrease in the methanol permeability; (2) to enhance the thermal stability and intensity of the membranes; (3) to increase the ion conductivity [21].

In this paper, we have prepared novel organic–inorganic hybrid membranes with organic QAPVA and inorganic silica via sol–gel reaction using TEOS as a precursor. By adding a desired amount of TEOS, a series of hybrid anion-exchange membranes with different silica contents have been synthesized. The characteristics of the membranes were evaluated for potential application in alkaline DMFCs.

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2. Experimental

2.1. Materials and hybrid membrane preparation

Poly(vinyl alcohol) (polymerization degree of 2400, hydrolysis degree of 98–99%) was supplied by Sinopharm Chemical Reagent Co., Ltd (2,3-epoxypropyl)trimethylammonium chloride (EPTMAC, purity $\geq 95\%$) was purchased from the Shandong Guofeng Fine Chemistry Factory. Tetraethoxysilanes (TEOS, $\text{SiO}_2 \geq 28\%$) was purchased from the Guangdong Shantou Xilong Chemical Factory. All materials were commercial products and used as received. Quaternized poly(vinyl alcohol) (QAPVA) was synthesized according as previously described [11].

QAPVA was dissolved in deionized water to obtain a 5 wt% solution. Then a required amount of TEOS was added into the solution and the mixture was stirred for 1 h at 30 °C to obtain a clear homogeneous solution. Then the mixture was cast onto a glass plate and dried at 30 °C for 48 h. The dried membranes were peeled off from the glass plate, and then heated at 40, 100, and 130 °C for 5, 3 and 3 h, respectively. By varying the ratio of SiO_2 to QAPVA, different organic–inorganic hybrid membranes with 5, 10 and 20 wt% SiO_2 were prepared. The hybrid membranes were designated as M-X, where X is the SiO_2 content (%) in the membrane phase.

2.2. Structural characterization

The FTIR absorption spectra of QAPVA and the hybrid membranes were recorded using an FTIR740SX spectrophotometer (Thermo Electron Corporation, USA).

The crystal structures of the hybrid membranes were examined at 25 °C by an X-ray diffractometer (X'Pert Pro, Panalytical, Holland) using Cu K α radiation with a step size of 0.0167° and a scan speed of 0.167° s⁻¹. The membrane samples were scanned in the reflection mode with a 2 θ angle between 5° and 35°.

TGA thermal analyses were carried out using a TG209F1 (NET-ZSCH, Germany) system. The measurements were conducted by heating from 30 to 900 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

The membrane morphologies were investigated with a Philips LEO1530 scanning electronic microscope equipped with energy-dispersive X-ray spectroscopy (EDAX) of ISIS300 (Oxford). Element mapping was conducted with EDAX.

2.3. Water content and ion exchange capacity (IEC)

Water content studies of the hybrid membranes were carried out by measuring the change in the weight of the membranes before and after hydration using an electronic scale (AR3130, Ohaus Corporation, USA). The hybrid membranes were immersed in deionized water and equilibrated for more than 48 h. The weight of the wet composite membrane was determined after removing excess surface water. Then the wet membrane was dried under vacuum at a fixed temperature of 60 °C until a constant dry weight was obtained. The percentage water content W_c is calculated using the following relation:

$$W_c = \frac{m_h - m_d}{m_d} \times 100\% \quad (1)$$

where m_h is the mass (g) of a wet membrane and m_d is the mass (g) of a dry membrane.

The ion exchange capacity of the hybrid membranes was measured using the classical titration method. The hybrid membranes were immersed in a large volume of 0.1 M NaOH solution to convert them into the OH⁻ form. They were then rinsed with deionized water to remove excess NaOH and then equilibrated with 100 mL

Table 1

The results of element mapping of the hybrid membrane M-10 by EDAX.

Element	Wt%	At%
C	80.25	85.06
O	17.46	13.90
Si	2.28	1.04

of 0.1 M HCl solution for 48 h. The IEC values were determined from the reduction in acid measured using back titration. The IEC values (meq g⁻¹) are obtained from the following equation:

$$IEC \text{ (meq g}^{-1}\text{)} = \frac{M_{o,HCl} - M_{e,HCl}}{m_d} \quad (2)$$

where $M_{o,HCl}$ is the milliequivalents (meq) of HCl required before equilibrium, $M_{e,HCl}$ is the meq of HCl required after equilibrium, and m_d is the mass (g) of the dried membrane.

2.4. Methanol permeability

The methanol permeability was measured using a diffusion cell comprising two compartments. Magnetic stirrers were used in each compartment to ensure uniformity during the experiments. The membrane was clamped between the two compartments. One compartment was loaded with deionized water and the other with a solution containing 1 M methanol and 0.5 M KOH. The concentration of the permeating methanol was measured by gas chromatography (GC-950, Shanghai Haixin Chromatographic Instruments Co., Ltd).

2.5. Ionic conductivity

The ionic conductivity of the membranes was measured by two-probe AC impedance spectroscopy with Parstat 2273 electrochemical equipment (Princeton Advanced Technology, USA) over the frequency range from 0.1 to 1 MHz. Before testing, the OH⁻ form membranes were hydrated in deionized water for at least 48 h. The testing device with the membrane was placed in a chamber with deionized water to keep the relative humidity of 100% during the measurements.

The ionic conductivity σ (S cm⁻¹) of a given membrane can be calculated from

$$\sigma = \frac{l}{R \times A} \quad (3)$$

where l is the distance (cm) between two stainless steel electrodes, A is the cross-sectional area (cm²) of the membrane and R is the membrane resistance (Ω) from the AC impedance data.

3. Results and discussion

3.1. Structure characteristic of the hybrid membranes

Table 1 lists the results of element mapping of the hybrid membrane M-10 by EDAX. It shows that the hybrid membrane contains elements C, O, and Si, indicating that silica has embedded into the membrane matrix.

The FTIR spectra of the QAPVA and the hybrid membranes are shown in Fig. 1. The absorption peak around 3400 cm⁻¹ in the QAPVA membrane belongs to –OH groups. Also in the M-10 membrane, the peak at 3400 cm⁻¹ becomes broader due to the existence of un-reacted –Si–OH. The peak at 1080–1200 cm⁻¹ in the QAPVA membrane is due to the existence of C–O–C bonds. In the hybrid membrane M-10, the peak at 1080–1200 cm⁻¹ is attributed to C–O–C and Si–O–Si bonds due to the sol–gel process.

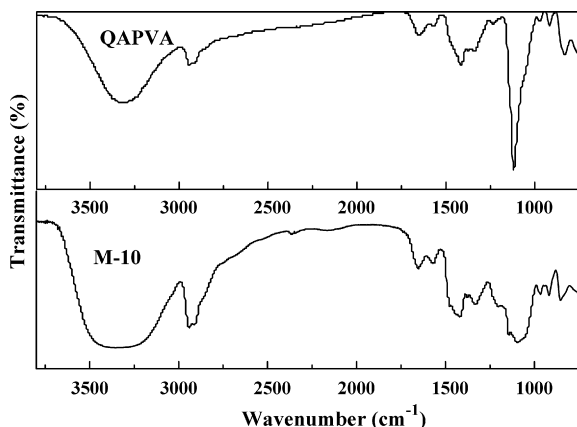


Fig. 1. FTIR spectra of the QAPVA and the hybrid membrane M-10.

The X-ray diffraction was measured to examine the crystallinity of the membranes. Fig. 2 shows the XRD patterns of the QAPVA and the hybrid membranes. Note that each peak for the three hybrid membranes is broadened compared to the QAPVA membrane, indicating a decrease of crystallinity in the hybrid membranes. The QAPVA membrane is a semi-crystalline membrane, and the hydroxyl groups in the side-chain of QAPVA determine the crystallinity of the membrane. The reaction between silica and the hydroxyl groups in the QAPVA reduces the number of the hydroxyl groups in the membranes, which results in a decrease of the crystallinity of the hybrid membranes. On the other hand, with increasing the content of SiO₂, the peak intensity of the hybrid membranes changes slightly. The peak of membrane M-10 is narrower than that of membrane M-5, while the peak of membrane M-20 becomes boarder. This is because silica will undergo self-polymerization during copolymerizing with QAPVA when the inorganic material TEOS is added into the QAPVA solution. The self-polymerization of silica causes a deficiency of copolymerization of QAPVA and silica, which affects the decrease of crystallinity. But too much self-polymerization of silica also destroys the structure of crystalline region in QAPVA and reduces the crystallinity of the hybrid membranes [22]. By the combined action of self-polymerization and copolymerization, the crystallinity of the hybrid membrane M-20 decreases.

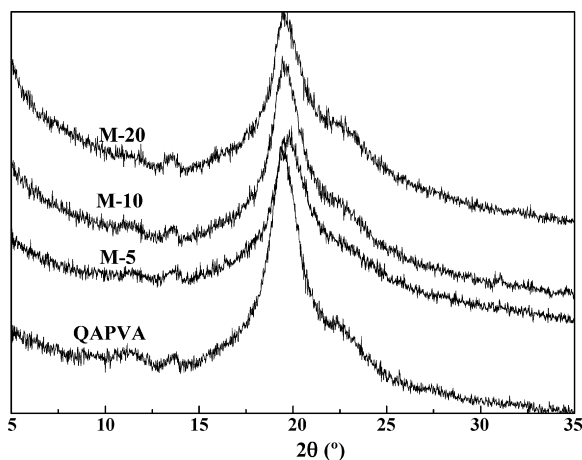


Fig. 2. XRD patterns for the QAPVA and hybrid membranes.

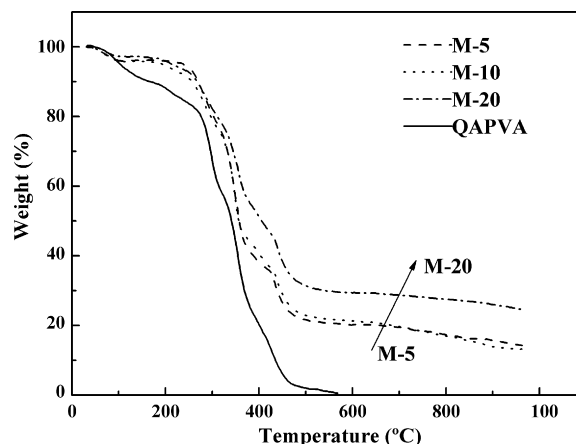


Fig. 3. TGA curves of the QAPVA and hybrid membranes.

3.2. Thermal stability

The thermal stability of the membranes is illustrated by their TGA studies. The TGA curves of the QAPVA and hybrid membranes are presented in Fig. 3 and can be divided into three regions. The first region is from 30 to 300 °C, attributing to the loss of adsorbed water or ethanol generated from the sol-gel reaction of TEOS. The second weight loss region is at 352 °C. This is ascribed to a decomposition of side chains of the matrix. The third stage is 440 °C, indicating the decomposition of main chain of the membranes.

It is found from Fig. 3 that the weight loss of the QAPVA membrane is more than that of the hybrid membranes at each stage. This suggests the successful incorporation of the silica moiety into the hybrid membranes. The improved thermal stability of membranes arises from the addition of inorganic silica, and is enhanced with increasing content of SiO₂. The high thermal stability of silica and the strong linkage between the polymer matrix and the silica phase increase the thermal stability of the hybrid membranes. The residual mass of the QAPVA is 0.58% at 566 °C. And the residual mass of the three hybrid membranes is 13.3%, 14.3% and 24.5% at 964 °C, respectively. When the temperature is above 600 °C, the QAPVA is decomposed completely. But the hybrid membranes still have residual and no further weight loss, indicating that the residual weight is the Si inorganic component and some organic component linked with it in the hybrid membranes.

3.3. IEC and water content

Table 2 lists the ion exchange capacity and water content of the hybrid membranes. Ion exchange capacity of the membranes reflects the exchangeable groups in the membranes. The IEC values of the hybrid membranes range from 0.46 to 0.57 meq g⁻¹, and are close to each other. The silica content has little effect on the IEC, because silica just reacts with the hydroxyl groups in QAPVA and does not affect the number of the exchange groups in the hybrid membranes.

When the silica content is below 10%, the water content of the hybrid membranes increases with increasing silica

Table 2
IEC and water content of the hybrid membranes.

Membrane	SiO ₂ content (%)	IEC (meq g ⁻¹)	Water content (%)
M-5	5	0.46	131
M-10	10	0.49	166
M-20	20	0.57	167

content, but is still lower than that for QAPVA membranes. QAPVA membranes can dissolve in water. The network formed by silica and QAPVA makes the hybrid membranes much more compact and reduces the absorption of water in the membranes. Meanwhile, the un-reacted $-\text{Si}-\text{OH}$ group increases the sites for bound water, so increasing the silica content in the hybrid membranes results in a higher water content. These two actions determine the water content of the hybrid membranes. For the three hybrid membranes, the latter effect is prominent, which is the reverse to results found in the literature [23] where crosslinking is thought to be a dominant factor affecting the water content of the semi-interpenetrating hybrid membranes of polyvinyl chloride (PVC)/styrene (St)/p-vinylbenzyl chloride (VBC)/3-(methylamine)propyl-trimethoxysilane (MAPTMS).

There is a slight difference in the water content between the membranes M-10 and M-20 (Table 2). This may be due to the self-polymerization of silica, which consumes the further added silica and keeps the water content almost constant.

3.4. Methanol permeability

The methanol permeability of the hybrid membranes is shown in Fig. 4. The permeability of the hybrid membranes is 8.45×10^{-7} , 9.82×10^{-7} , and $11.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 30°C , respectively, which is lower than that for the crosslinked QAPVA membranes [11], QAPVA-based composite membranes [12], and Nafion membranes [23]. This indicates that silica is a good barrier to the methanol. The reaction of silica and polymer matrix forms a crosslinked network, reducing the channel allowing the passage of methanol molecules, so that the resistance to the diffusion of methanol is increased. However, the methanol permeability of the hybrid membranes increases with increasing silica content, since with the addition of silica, the self-polymerization of silica is dominant over the copolymerization of silica and QAPVA. The silica particles formed by the self-polymerization of silica destroy the continuous structure of the hybrid membranes and ease the passage of methanol through the membrane [22]. In addition, the methanol permeability of the three membranes increased with increasing temperature. Since the relaxation of polymer chain increases with increasing temperature, this may cause the channels for methanol permeation in the membranes broaden; as a result, the crossover of the methanol molecules in the membranes may increase with increasing temperature.

The methanol permeability in this study was measured using a diffusion cell in a static state without electro current. If the membranes are applied in the DMFCs, the practical methanol per-

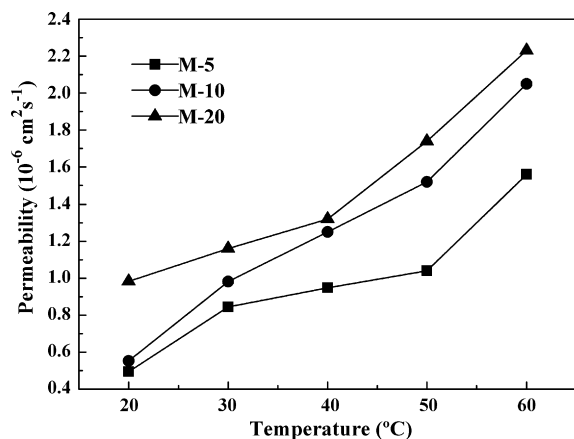


Fig. 4. Methanol permeability of the hybrid membranes.

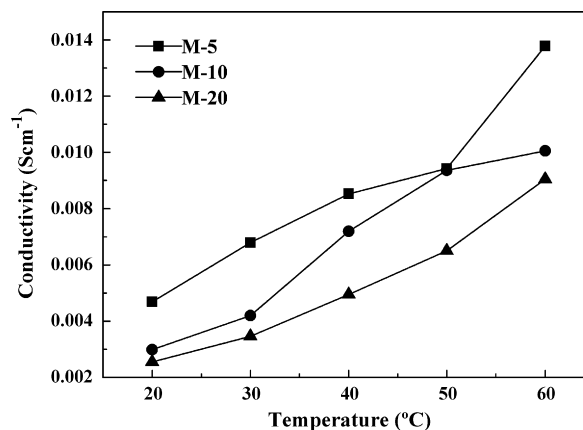


Fig. 5. Conductivity of the hybrid membranes.

meability will be less. The reason is that in the alkaline DMFC, ion transport within the membrane is from the cathode to the anode, which opposes the direction of methanol crossover from anode to cathode, and hence reduces the methanol permeability.

3.5. Ion conductivity

Fig. 5 shows the conductivity of the hybrid membranes. The conductivity of the hybrid membranes is 6.8×10^{-3} , 4.19×10^{-3} , and $3.46 \times 10^{-3} \text{ S cm}^{-1}$ at 30°C , respectively. The highest conductivity is $1.4 \times 10^{-2} \text{ S cm}^{-1}$ at 60°C for the membrane M-5, which is higher than other QAPVA-based membranes at the same temperature. This indicates that the addition of silica also increases the conductivity of the hybrid membranes. The strong reaction of silica with the polymer matrix forms networks and can hold more water molecules at high temperatures than other QAPVA-based membranes.

The ion conductivity of the hybrid membrane decreases with increasing silica content. According to the Grotthus mechanism, the proton transport depends on a chain of water molecules. It hypothesizes that the transport of OH^- anion also follows the Grotthus mechanism. The water in the membranes can be classified as free water and bound water. Only free water can affect the anion transport. As the silica content increases, the un-reacted $-\text{Si}-\text{OH}$ increases and can bind more water that cannot take part in anion transport. On the other hand, the linkage of silica and QAPVA makes the membrane structure much more compact and also weakens anion transport in the hybrid membranes. These two reactions make the membrane M-5 have a higher conductivity than the other two hybrid membranes with more silica content.

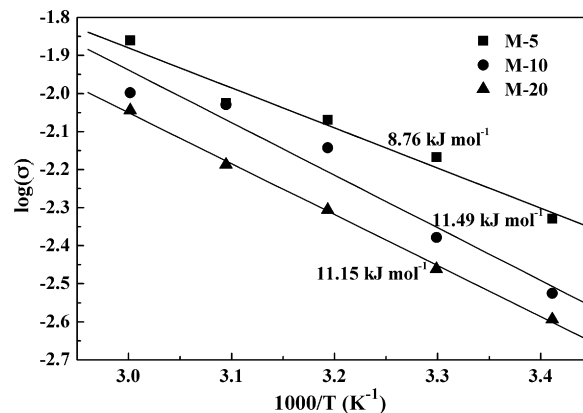


Fig. 6. Arrhenius plots for the hybrid membranes.

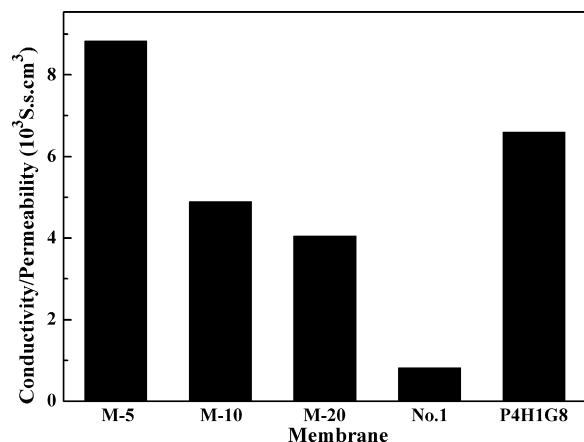


Fig. 7. Ratio of conductivity to methanol permeability of different membranes.

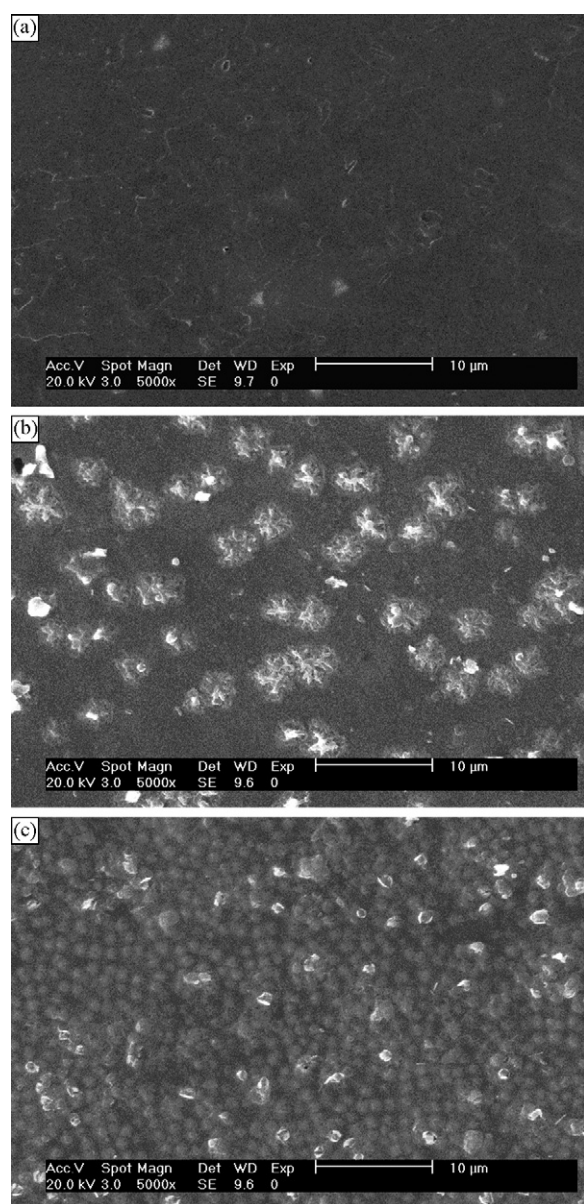


Fig. 8. The surface morphology of the hybrid membranes: (a) M-5, (b) M-10, and (c) M-20.

Fig. 6 shows the relation between $\log \sigma$ and $1000/T$, which, using the Arrhenius equation, allows the determination of the ion transport activation energy (E_a) of the hybrid membranes. The membrane M-5 has the lowest E_a (8.76 kJ mol^{-1}) of the three hybrid membranes, which is consistent with the ion conductivity results. With increasing silica content, the activation energy increases due to the more compact structure formed by silica and polymer matrix. Compared to other QAPVA membranes [11,12], the hybrid membranes have lower activation energies, indicating that the structures of the hybrid membranes are less compact than those of the composite membranes.

For fuel cell applications, the membrane should have a high conductivity and a low methanol permeability. The ratio of the conductivity to the methanol permeability suggests that the hybrid membrane M-5 can meet this requirement. Fig. 7 shows the ratio for different QAPVA-based membranes. The data for membrane No. 1 (conductivity: $8.37 \times 10^{-3} \text{ S cm}^{-1}$, methanol permeability: $10.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 60°C) are from reference [11] and those for the membrane P4H1G8 (conductivity: $12.5 \times 10^{-3} \text{ S cm}^{-1}$, methanol permeability: $1.895 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 60°C) are from the literature [12]. Comparing the ratio of conductivity to methanol permeability for these membranes at 60°C , the M-5 membrane exhibits the highest ratio, indicating that the membrane M-5 can be applied in fuel cells. The performance of the QAPVA membranes is improved by crosslinking with GA, blending with quaternized chitosan, and incorporating with silica for application in fuel cells. Among these methods, the hybridization of polymer with silica outperforms the other modifications.

3.6. Morphology

The surface morphology of the hybrid membranes is shown in Fig. 8. The surface of the membrane M-5 is smooth and homogeneous, indicating that the compatibility between the organic and inorganic parts is excellent. With increasing silica content, particles can be observed on the surfaces of the membranes M-10 and M-20 and the number of the particles tends to be more. The particles are formed by self-polymerization of silica and distribute on the surface of the hybrid membranes uniformly. The appearance of the particle destroys the structure of the membranes M-10 and M-20 and results an increase in the methanol permeability.

4. Conclusions

New organic–inorganic hybrid membranes were prepared with QAPVA and silica derived from the sol–gel reaction of TEOS. The chemical and physical performances of the hybrid membranes were studied. With the formation of networks by reaction of polymer matrix and silica, the thermal stability of the membrane is enhanced and the methanol permeability decreases. According to the performance of holding water at high temperature, the conductivity of the hybrid membranes is improved. The membrane M-5 outperforms the others for the application in fuel cells.

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