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Novel anion exchange membranes based on pyridinium groups and fluoroacrylate for alkaline anion exchange membrane fuel cells



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ABSTRACT

Novel fluorinated anion exchange membranes with pyridinium salt functionalized groups for alkaline anion exchange membrane fuel cells have been prepared and characterized. These membranes have shown a combination of good thermal stabilities, high ionic conductivities, and excellent chemical stabilities. The ionic conductivity of the membranes can be as high as 2.7×10^{-2} S cm⁻¹ in deionized water at 30 °C. An alkaline H₂/O₂ fuel cell employing the resulting membrane was assembled and revealed a maximum power density of 124.8 mW cm⁻² at 60 °C. The preliminary performances have demonstrated their potential as electrolytes for alkaline anion exchange membrane fuel cells.

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Introduction

Fuel cell power generation technology is now widely regarded as a potential approach to solve the energy crisis owing to its high energy conversion efficiency and lower pollution [1-3]. The development of polymer electrolyte membrane is very important in the present energy field, not only fuel cell but also other devices [4-6]. Although the proton exchange membrane fuel cell (PEMFC) has significant performance and promising prospects, its commercialization has been hampered by several problems, such as prohibitive cost, sluggish reaction kinetics in acidic condition, fuel (e.g. methanol, ethanol, etc.) crossover and complex water management [7-9]. Unlike PEMFC, the alkaline anion exchange membrane fuel cell (AEMFC) using anion exchange membrane (AEM) as the polymer electrolyte membrane operates under alkaline condition, which has many merits in cathode kinetics, ohmic polarization and water management [10,11]. The development of AEMFC can lead to higher efficiencies and enable the use of non-noble metal catalysts, such as silver, nickel and palladium, considerably reducing the cost of the cell. In an AEMFC, water is produced at the anode and consumed at the cathode (that is, the consumption and production of water in the reaction processes are significantly different from PEMFC), thus water management can be potentially simplified [12]. Therefore, alkaline anion exchange membrane fuel cell exhibits unpredictable developing potential and has been extensively attracting researchers' interest [13–15].

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The polymer electrolyte membrane is very important in the present energy field, as one of the key components of an AEMFC system, anion exchange membrane (AEM) has been actively studied and a lot of research achievements have been made. Hong et al. obtained PEI-CPP membrane by amination reaction [16]. Zhou et al. synthesized crosslinked anion conductive polysulfone membranes via epoxy functionalities with good physical and chemical stability [17]. The research team of Tongwen Xu developed the organic-inorganic hybrid alkaline membranes based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [18]. Abuin et al. prepared a quaternary ammonium polymer by chloromethylation and amination of a commercial polysulfone which exhibits excellent mechanical properties [19]. In our laboratory, a series of anion exchange membranes based on alkyl quaternary ammonium salts and imidazolium salts have been synthesized and characterized [20-22]. Despite considerable progress has been made by the international scholars over the past five years, still many problems need to be solved before the AEMs can be successfully applied to the fuel cell. Development of novel AEMs with high performance is urgently needed.

Aiming to explore AEMs with sufficient mechanical strength, good stability, suitable ionic conductivity, as well as high cell performance, polymerizable 4-Vinyl pyridine and fluoroacrylate have been using as monomers for polymerization in our works. Different from conventional quaternary ammonium compound, the big π bond conjugated system of the pyridine makes the pyridinium salt possess better thermal and chemical stabilities. Due to the strong water affinity of pyridine group, fluoroacrylate was introduced to tune the hydrophilic-lipophilic balance of the polymers. Furthermore, introduction of fluorine into polymer backbone has been one of the most widely adopted techniques for structure modification leading to substantial property enhancement [23,24]. In order to improve the film forming properties, a small percentage of acrylate was also used as the third monomer. In this paper, we originally report the synthesis and characterization of novel anion exchange membranes based on the copolymer of hexafluorobutyl methacrylate (HFMA), 4-vinyl pyridine (4-VP) and butyl methacrylate (BMA). The copolymer with pendant pyridinium groups has been prepared by free radical copolymerization which is an effective method to control the properties of the reaction products by adjusting mole ratio of the monomers. The chemical structures and the some physicochemical properties of the membranes, such as thermal stability, water uptake, IEC, ion conductivity and chemical stability were also investigated. The single fuel cell using the synthesized membrane was tested at 60 °C and achieved a peak power density of 124.8 mW cm^{-2} .

Experimental

Materials

Hexafluorobutyl methacrylate (HFMA) (\geq 96%) was purchased from Harbin XEOGIA Fluorine-silicon Chemical Co., Ltd. (China). 4-vinyl pyridine (4-VP) (\geq 96%) was commercial supplied by Alfa Aesar Company (USA). Butyl methacrylate (BMA) and azobisisbutyronitrile (AIBN) of analytical grade were procured from Chemical Reagent Co., Ltd. (China). HFMA, 4-VP and BMA were washed with 1 mol L^{-1} NaOH and then distilled under reduced pressure before use. Azobisisbutyronitrile (AIBN) was recrystallized in boiling alcohol then dried in a vacuum oven at room temperature. The other reagents were used as received without further purification.

Synthesis of copolymer with pendant pyridinium groups

The copolymer, poly(HFMA-co-4VP-co-BMA) (PHVB) was synthesized via free radical copolymerization of 4-vinyl pyridine with hexafluorobutyl methacrylate and butyl methacrylate using AIBN as an initiator and N,N-dimethylformamide (DMF) as a solvent, and the reaction process is shown in Fig. 1. The reactant mole ratio of HFMA, 4-VP and BMA was 6:3:1. The copolymerization was carried out in a three-necked round-bottomed flask with magnetic stirrer at 65 °C for 24 h under a nitrogen atmosphere. After precipitating and washing with deionized water, the copolymer was dried in a vacuum oven at 80 °C.

Membrane preparation

The membranes were prepared by a phase-transfer method. The synthesized copolymers were dissolved in DMF to form 5 wt% solutions. The copolymer solutions were cast onto glass plates and dried in a vacuum oven at 80 °C for 12 h. Then, the membranes were peeled off from the glass plates. The fabrication of the OH⁻ form membranes were performed according to Fig. 2. To obtain membrane 1#, the membranes were soaked in 1 mol L⁻¹ HCl for 48 h, then soaked in 1 mol L⁻¹ NaOH overnight at room temperature. And to gain membrane 2#, the membranes were soaked in butyl bromide solution (1 mol L⁻¹, dissolve in cyclohexane) for 24 h at 60 °C, subsequently soaked in 1 mol L⁻¹ NaOH overnight at room temperature. Finally, the obtained OH⁻ form membranes were washed with deionized water thoroughly and preserved in deionized water for further use.



Fig. 1 – Copolymerization of HFMA, 4-VP and BMA.



Fig. 2 - Preparation processes of the OH⁻ form membranes.

Characterization of the copolymer and the membranes

The Fourier Transform Infrared spectroscopy (FT-IR) spectra of the resulting copolymer and membranes were measured using a Nicolet FT-IR740SX spectrophotometer (Thermo Electron Corporation, USA) with a resolution 4 cm⁻¹. The elementary analysis was performed on a Vario EL III Elemental analyzer (Elementar Analysen System GmbH, Germany). Thermal Gravimetric Analysis (TGA) was carried out using a TG209F1 system (NETZSCH, Germany) under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ from 30 to 600 °C.

Water uptake

The water uptake was measured to study the hydrophilicity of the membranes. The OH⁻ form membranes were preserved in deionized water at room temperature before the test. After removing the free water on the membrane surface, the membrane was weighed immediately. Then the wet membrane was dried in a vacuum oven at 60 °C to achieve constant weight. The water uptake was calculated according to equation (1):

$$Wu(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$
⁽¹⁾

where W_u is the water uptake of the membrane; W_{wet} is the mass of the moist membrane; W_{dry} is the mass of the dry membrane.

Ion exchange capacity (IEC)

Ion exchange capacity (IEC) was measured using a standard back titration method. The OH⁻ form membranes which preserved in deionized water were soaked in 0.1 mol L⁻¹ HCl (V_{HCl}: 25 ml) for 48 h at room temperature to exchange to Cl⁻ form membranes. The Cl⁻ form membranes were dried in a

vacuum oven at 60 °C until the constant weight was obtained. The solutions were then titrated with standardized 0.1 mol L⁻¹ NaOH solution (V_{NaOH}). The IEC was calculated by the following formula:

$$IEC = \frac{(V_{HCl} - V_{NaOH}) \times C}{W_{dry}}$$
(2)

where C (mmol L^{-1}) is the concentration of HCl and NaOH solutions, W_{dry} (g) is the mass of Cl⁻ form membrane.

Ion conductivity

The hydroxide conductivities of the OH⁻ form membranes were measured by a two-electrode AC impedance method [25]. All the samples were soaked in deionized water for at least 48 h before the test. The membranes and the electrodes were set in a homemade cell and the cell was placed in a thermo-controlled chamber in deionized water. The impedance spectra were recorded by a Parstat 263 electrochemical equipment (Princeton Advanced Technology, USA) in the frequency range from 0.1 Hz to 100 KHz. The impedance measurements were performed from 30 °C to 90 °C under 100% relative humidity (RH). The hydroxide conductivity was calculated by following equation:

$$\sigma = \frac{l}{RA} \tag{3}$$

where σ (S cm⁻¹) is the ion conductivity, l(cm) is the distance between two potential sensing stainless electrodes, R(Ω) is the membrane resistance and A (cm²) is the surface area of the membrane exposed to the electric field.

Chemical stability

The alkali resistance of the obtained anion exchange membrane was evaluated by measuring the changes in weight before and after the OH^- form membranes were immersed into NaOH solution (6 mol L⁻¹) at 60 °C for a certain period. The membranes were quickly weighed after removing the solution from the surface.

The oxidative stability was evaluated by measuring the changes in weight before and after the OH^- form membranes were immersed into Fenton's reagent (4 ppm FeSO₄ in 3% H_2O_2) at 60 °C for a certain period. The sample was quickly weighed after removing the surface liquid with filter paper.

Fabrication of MEA and fuel cell test

The membrane electrode assembly (MEA) consisted of an AEM (Membrane 1#), anode/cathode catalyst layers (Pt/C, 40/60 wt %, Johnson Matthey) and diffusion layers (Toray-250). Membrane 1# was dissolved in DMF to form a 5 wt% ionomer solution (solution A). The catalyst ink for the electrode was prepared by mixing ionomer solution, Pt/C catalyst powder and propanetriol. To gain well-proportioned and stable solutions, the inks were first stirred with a magnetic stirrer for an hour and then dispersed by an ultrasonicator. After that, the catalyst ink was brushed onto the surface of diffusion layers to get an active area of 4 cm² with the catalyst loading of 1 mg cm⁻². The AEM and the electrodes were sandwiched

together and then hot-pressed under 2 MPa for 5 min at 135 $^\circ \rm C$ to obtain MEA for single fuel cell test.

The MEA was secured between two graphite plates with serpentine flow channels to assemble a single fuel cell. Hydrogen and pure oxygen was used as the fuel and oxidant in the test, respectively. The flow rate of H_2/O_2 was 100 mL min⁻¹. The single fuel cell test was performed under 100% humidity, ambient pressure at 60 °C using a fuel cell test equipment GEFC-10 (Guangdong Electronic Technology Research Institute, Guangzhou, China).

Results and discussion

FT-IR spectra

Fig. 3 shows the FT-IR spectra of PHVB and the resulting OHform membranes. For PHVB sample, the peak appearing at 1744.16 cm^{-1} is the C=O stretching vibrations absorption of alkyl methacrylate groups. PHVB sample exhibits several characteristic peaks at 1598.40 $\rm cm^{-1},$ 1558.48 $\rm cm^{-1}$ and 1406.85 cm^{-1} , which can be assigned to the ring vibration of pyridine ring of the polymer [26]. The absorption at 683.73 cm⁻¹ corresponds to stretching of -CF linkage of the polymer [24]. These bonds are the characteristic structural features of PHVB and confirm that the PHVB is successfully synthesized. For OH⁻ form membrane 1# and membrane 2#, the broad and strong absorption band around 3425 cm⁻¹ is assigned to the stretch vibration of O-H groups. For membrane 2#, this band is much stronger, because the quaternary ammonium group is a stronger basicity. Comparatively, there are no distinct changes between the spectra of PHVB and membrane 1# from 3250 to 500 cm⁻¹ because they have almost the same chemical structure. For membrane 2#, the absorption at 1598.40 cm $^{-1}$ shifted to 1638.82 cm $^{-1}$, and the absorption at 1558.48 cm^{-1} shifted to 1568.53 cm^{-1} , compared to the spectrum of PHVB. This may be due to the effect of the quaternization process. The above results indicate that the anion



Fig. 3 – FT-IR spectra of the PHVB, membrane 1# and membrane 2#.



Fig. 4 – TGA curves of PHVB, membrane 1# and membrane 2#.

exchange membranes based on 4-vinyl pyridine and fluoroacrylate were successfully prepared.

Thermal stability

Fig. 4 presents the thermo-gravimetric analysis (TGA) curves of PHVB, membrane 1# and membrane 2#. Both membrane 1# and membrane 2# are in OH⁻ form. All the samples show slight weight loss (less than 2 wt%) below 100 °C which ascribed to the loss of residual water or solvent (such as DMF) in the samples. It can be observed that the PHVB is stable until 280 °C, when decomposition of the pyridine groups occurs. However, after alkalizing, thermal stabilities of the polymers decrease. For membrane 1# and membrane 2#, the second weight loss appears at 120 °C and 230 °C, respectively. Membrane 2# is more stable at elevated temperatures than membrane 1# due to quaternarization. These curves indicate that the obtained membrane 1# and 2# have appropriate thermal stability and they are suitable for being used in low temperature AEMFCs.

Water uptake and ion exchange capacity (IEC)

Table 1 listed the water uptake and ion exchange capacity of membrane 1# and membrane 2#. Water uptakes of membrane

1# and membrane 2# are 34.07 wt% and 56.38 wt%, respectively. The quaternization process modifies the polarity and hydrophobicity of the polymer, making the membrane more hydrophilic and subsequently absorbing more water, so the water uptake of membrane 2# is higher than that of membrane 1#. However, the ion exchange capacity (IEC1) of membrane 1# is higher than that of membrane 2#. This may be due to the larger steric hindrance of membrane 2#, which influences the mobility of the exchangeable ion. IEC2 is the ion exchange capacity calculated from the N content (shown in Table 2). The N content of membrane 2# is less than that of membrane 1# due to the incorporation of n-butyl inside the polymer matrix.

Ionic conductivity

Ionic conductivity is one of the important factors of ion exchange membrane for AEMFCs. Fig. 5 is the dependence of ion conductivity on temperature. The ion conductivity of membrane 1# and membrane 2# are 2.7 \times 10⁻² S cm⁻¹ and $0.47~\times~10^{-2}~S~cm^{-1}$ at 30 $^\circ C$ under 100% relative humidity, respectively. The ion conductivities of both membranes dramatically increase with increasing temperature. For example, the conductivity of the membrane 1# increases from 0.027 to 0.0545 S cm^{-1} as the temperature goes up from 30 to 90 °C. This trend is in accordance with our previous studies [20-22]. The ion conductivity of membrane 1# is higher than that of membrane 2#, which is benefited from the higher ion exchange capacity of membrane 1#. The results show that the ion conductivities of both membranes can fulfill the basic conductivity requirement of AEMFCs. Fig. 6 is the relationship between ln (σ) and 1/T. From Fig. 6, it is also found that the temperature dependence of hydroxide conductivity follows the Arrhenius equation. According to the Arrhenius law, the apparent activation energy (Ea) of the membrane was calculated. The Ea value of membrane 1# and membrane 2# are 10.401 kJ mol^{-1} and 18.998 kJ mol^{-1} , respectively. It shows that the membrane 1# has a lower Ea value. The steric hindrance of membrane 2# is larger, so that the mobility of anion exchange groups of membrane 2# lower is lower than that of membrane 1#.

Chemical stabilities

Chemical stability of anion exchange membrane is the key factor affecting the lifetime of fuel cells. It's greatly desirable

Table 1 – Water uptake and IEC of the membranes.						
Sample	Water uptake (wt%)	IEC1 (mmol/g)	IEC2 (mmol/g)	First weight loss (quaternized pyridine degradation) of TGA (%)		
				Theor.	Expt.	
Membrane 1#	34.07	1.71	1.73	16.79	12.65	
Membrane 2#	56.38	1.63	1.65	31.50	39.83	
IEC1: IEC values obta IEC2: IEC values calcu	ined by back-titration method. Jated from N content.					

Table 2 – N content of the membranes.	
Sample	N content (wt%)
PHVB	2.535
Membrane 1#	2.422
Membrane 2#	2.305

to develop the anion exchange membrane with both high ion conductivity and excellent chemical stability. To investigate the alkali resistance, the wet membranes were immersed into 6 mol L⁻¹ NaOH solutions at 60 °C for 120 h and weighed every 24 h. The results are shown in Fig. 7. In the first 24 h, both membranes had a slight mass increase which is due to the incremental water uptake at higher temperature. No obvious changes can be observed in weight and appearance after the membranes were treated with NaOH solutions. The weight fluctuation range of membrane 1# is less than 1%, while the fluctuation range of membrane 2# is less than 3%. The small decline in weight of membrane 2# which introduced butyl groups may be due to the degradation of trace amounts of pyridinium salt groups. Membrane 1# is more stable than membrane 2#, because there is no β -H in the membrane 1#, thus, the Hofmann elimination reaction can be avoided [27]. These results manifest that the obtained membranes are stable in 6 mol L^{-1} NaOH solutions at 60 °C.

To study the oxidative stability, the membranes were immersed into Fenton's reagent (4 ppm $FeSO_4$ in 3% H_2O_2) at 60 °C for 120 h and weighed every 24 h. The Fenton's reagent test results in terms of weight losses of the membranes are shown in Fig. 8. It is found that the weights of the membrane 1# and membrane 2# almost remain constant during 120 h tests. No visible changes can be discovered in weight and appearance of the membranes.

The excellent oxidative stabilities of the membranes can be attributed to the introduction of fluoroacrylate. Fluorine is the most electronegative element, so negative charges gather around fluorine atoms and electron clouds cover densely in fluorinated polymers [23,24]. Introduction of fluorine into polymer backbone has become one of research hotspots



Fig. 5 – Ion conductivity of membrane 1# and membrane 2# as a function of temperature.



Fig. 6 − Arrhenius plots of ionic conductivities for the OH[¬] form membranes.

because it often gives rise to dramatic improvements in several properties of the polymer [28–30]. The fluorine—carbon bond is short and the bond energy is very strong, leading to high chemical stabilities of fluorinated polymer. Polymers containing fluorinated groups can be endowed with higher oxidative stabilities comparing to their non-fluorinated counterparts.

The experiment results reveal that both membranes 1# and Membrane 2# possess high oxidative resistance, rendering them suitable for application in alkaline anion exchange membrane fuel cell.

Fuel cell test

Due to the higher ion conductivity and better chemical stability of membrane 1#, a single fuel cell was assembled using a 50 μ m thick membrane 1# as the electrolyte membrane, and



Fig. 7 – Weight changes of the membranes after treated with 6 mol/L NaOH solution.



Fig. 8 – Weight changes of the membranes after treated with Fenton's reagent solution.

membrane 1# in DMF solution as ionomer solution. Pt/C was used as a catalyst with a loading of 1 mg cm^{-2} . The performance of the H₂/O₂ cell was tested under 100% relative humidity (RH) at 60 °C. Fig. 9 shows the polarization and power density curves for MEA equipped with membrane 1#. As can be seen, the open circuit voltage (OCV) of the H₂/O₂ fuel cell was 1.08 V, indicating that the membrane 1# was a good barrier between H_2 and O_2 gases [31,32]. However, the cell voltage dropped sharply after an initial increase in current density due to an activation loss of the interfacial electrochemical charge-transfer reaction in the catalyst layer of the MEA [33]. After the initial activation loss, the fuel cell voltage deceased gradually with an increase in current density mainly owing to the ohmic polarization. The fuel cell could deliver a peak power density of 124.8 mW cm^{-2} at a current density of 240 mA cm^{-2} .

In this article, we focused on the synthesis and characterization of the membrane. The preliminary results of the single fuel cell test were not the optimal. Method of MEA fabrication and the operating conditions, such as flow rate and



Fig. 9 – Polarization and power density curves of AEMFC with membrane 1#.

concentration of the fuel, temperature of testing, still need further improvement and optimization.

Conclusions

Novel anion exchange membranes for alkaline anion exchange membrane fuel cells based on the copolymer of HFMA, BMA and 4-VP were prepared. The structure of the resulting copolymer and OH⁻ form membranes were verified by FT-IR. The TGA curves show good thermal stability of these membranes and the onset decomposition temperatures are above 120 °C, rendering them good candidates for low-temperature fuel cell applications. These membranes exhibit high hydroxide ion conductivities at room temperature, while retaining good stabilities after immersed in NaOH concentration at 60 $^{\circ}$ C for 120 h. A H₂/O₂ fuel cell employed membrane 1# was assembled and evaluated under 100% relative humidity (RH) at 60 °C. The maximum power density of the single fuel cell was 124.8 mW cm⁻² at a current density of 240 mA cm⁻². Future work will be committed to MEA architectures and optimization of the fuel cell operating conditions.

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REFERENCES

- Birry L, Bock C. DMFC electrode preparation, performance and proton conductivity measurements. J Appl Electrochem 2009;39:347–60.
- [2] Kirubakaran A, Jain S, Nema RK. A review on fuel cell technologies and power electronic interface. Renew Sustain Energy Rev 2009;13:2430–40.
- [3] Gubler L, Scherer GG. Trends for fuel cell membrane development. Desalination 2010;250:1034–7.
- [4] Ledwon Przemyslaw, Andrade Juliana R, Lapkowski Mieczyslaw, Pawlicka Agnieszka. Hydroxypropyl cellulose-based gel electrolyte for electrochromic devices. Electrochim Acta 2015;159:227–33.
- [5] Colòa Francesca, Bellaa Federico, Naira Jijeesh R, Destro Matteo, Gerbaldi Claudio. Cellulose-based novel hybrid polymer electrolytes for green and efficient Na-ion batteries. Electrochim Acta 2015;174:185–90.
- [6] Sacco Adriano, Bella Federico, De La Pierre Stefano. Electrodes/electrolyte interfaces in the presence of a surfacemodified photopolymer electrolyte: application in dyesensitized solar cells. ChemPhysChem 2015;16:960–9.
- [7] Borup Rod, Meyers Jeremy. Scientific aspects of polymer electrolyte fuel cell durability and degradation. Chem Rev 2007;107:3904–51.
- [8] Dai Wei, Wang Haijiang. A review on water balance in the membrane electrode assembly of proton exchange membrane fuel cells. Int J Hydrogen Energy 2009;34:9461–78.

- [9] Pivovar Bryan S. An overview of electro-osmosis in fuel cell polymer electrolytes. Polymer 2006;47:4194–202.
- [10] McLean GF, Niet T. An assessment of alkaline fuel cell technology. Int J Hydrogen Energy 2002;27:507–26.
- [11] Fang Jun, Shen Pei Kang. Quaternized poly(phthalazinon ether sulfone ketone) membrane for anion exchange membrane fuel cells. J Membr Sci 2006;285:317–22.
- [12] Danks TN, Slade RCT, Varcoe JR. Alkaline anion—exchange radiation-grafted membranes for possible electrochemical application in fuel cells. J Mater Chem 2003;13:712–21.
- [13] Clark Timothy J, Robertson Nicholas J, Kostalik IV Henry A, Lobkovsky Emil B, Mutolo Paul F, Abruna Héctor D, et al. A ring-opening metathesis polymerization route to alkaline anion exchange membranes: development of hydroxideconducting thin films from an ammonium-functionalized monomer. J Am Chem Soc 2009;131:12888–9.
- [14] Luo Y, Guo J, Liu Y, Shao Q, Wang C, Chu D. Copolymerization of methyl methacrylate and vinylbenzyl chloride towards alkaline anion exchange membrane for fuel cell applications. J Membr Sci 2012;423–424:209.
- [15] Varcoe JR, Slade RCT. Alkaline prospects for anion-exchange membranes in low temperature fuel cells. Fuel Cells 2005;5:187.
- [16] Hong Joo-Hee, Li Dan, Wang Huanting. Weak-base anion exchange membranes by amination of chlorinated polypropylene with polyethyleneimine at low temperatures. J Membr Sci 2008;318:441–4.
- [17] Zhou Junfeng, Ünlü Murat, Anestis-Richard Irene, Kohl Paul A. Crosslinked, epoxy-based anion conductive membranes for alkaline membrane fuel cells. J Membr Sci 2010;350:286–92.
- [18] Wu Yonghui, Wu Cuiming, Xu Tongwen. Novel silica/ poly(2,6-dimethyl-1,4-phenylene oxide) hybrid anionexchange membranes for alkaline fuel cells: effect of heat treatment. J Membr Sci 2009;338:51–60.
- [19] Abuin Graciela C, Nonjola Patrick. Characterization of an anionic-exchange membranes for direct methanol alkaline fuel cells. Int J Hydrogen Energy 2010;35:5849–54.
- [20] Xu Hankun, Fang Jun. Novel anion exchange membrane based on copolymer of methyl methacrylate, vinylbenzyl chloride and ethyl acrylate for alkaline fuel cells. J Membr Sci 2010;354:206–11.
- [21] Li Wei, Fang Jun, Lv Ming. Novel anion exchange membranes based on polymerizable imidazolium salt for alkaline fuel cell applications. J Mater Chem 2011;21:11340.

- [22] Fang Jun, Yang Yixu. Cross-linked, ETFE-derived and radiation grafted membranes for anion exchange membrane fuel cell applications. Int J Hydrogen Energy 2012;37:594–602.
- [23] Souzy R, Ameduri B. Functional fluoropolymers for fuel cell membranes. Prog Polym Sci 2005;30:644–87.
- [24] Zhang Yanmei, Fang Jun, Wu Yongbin, Xu Hankun, Chi Xianjun, Li Wei, et al. Novel fluoropolymer anion exchange membranes for alkaline direct methanol fuel cells. J Colloid Interface Sci 2012;381:59–66.
- [25] Guo Mingli, Fang Jun, Xu Hankun, Li Wei, Lu Xiaohuan, Lan Chunhua, et al. Synthesis and characterization of novel anion exchange membranes based on imidazolium-type ionic liquid for alkaline fuel cells. J Membr Sci 2010;362:97–104.
- [26] Wang Liyan, Wang Zhiqiang. A new approach for the fabrication of an alternating multilayer film of poly(4vinylpridine) and poly(acrylic acid) based on hydrogen bonding. Macromol Rapid Commun 1997;18:509–14.
- [27] Fujimoto Cy, Kim Dae-Sik, Hibbs Michael, Wrobleski Debra, Kim Yu Seung. Backbone stability of quaternized polyaromatics for alkaline membrane fuel cells. J Membr Sci 2012;423–424:438–49.
- [28] Hougham G, Cassidy PE, Johns K, Davidson T, editors. Fluoropolymers 1: synthesis. Fluoropolymers 2: properties. New York: Plenum Press; 1999.
- [29] Drobny GJ. Technology of fluoropolymers. New York: CRC Press; 2000.
- [30] Dhara Mahua G, Banerjee Susanta. Fluorinated highperformance polymers: poly(arylene ether)s and aromatic polyimides containing trifluoromethyl groups. Prog Polym Sci 2010;35:1022–77.
- [31] Mehta Viral, Cooper Joyce Smith. Review and analysis of PEM fuel cell design and manufacturing. J Power Sources 2003;114:32–53.
- [32] Kang JJ, Li WY, Lin Y, Li XP, Xiao XR, Fang SB. Synthesis and ionic conductivity of a polysiloxane containing quaternary ammonium groups. Polym Adv Technol 2004;25:61–4.
- [33] Luo Yanting, Guo Juchen, Wang Chunsheng, Chu Deryn. Quaternized poly(methyl methacrylate-co-butyl acrylate-covinylbenzyl chloride) membrane for alkaline fuel cells. J Power Sources 2010;195:3765–71.