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An Novel Anion Exchange Membrane with Accelerated Hydroxide Ions Conduction through Quaternized Covalent Organic Framework Doped Electrospinning Binary Polymer

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Experimental

Characterization

Dynamic light scattering The diameter analysis data of COF and QACOF were obtained with a Zetasizer Nano ZS90 (Malvern Instruments Ltd.).

Fourier transform infrared spectra The fourier transform infrared spectra of COF, QACOF, PVDF-SEBS and PVDF-SEBS/1%QACOF were recorded by a Vertex 70 Spectrometer (Bruker optics) in the range of 4000–500 cm^{-1}.

X-ray diffraction The X-ray diffraction scattering patterns of COF, QACOF, PVDF, SEBS, PVDF-SEBS and PVDF-SEBS/1%QACOF were recorded from 5^o to 70^o with a scan speed of 5 ^{o}/min by the Part Pro-MPD X-ray diffractometer (Panalytical B.V.) using Cu Kα radiation source (λ=1.5418 Å).

$$2\, d \sin\theta = n\, \lambda \tag{1}$$

In the Bragg's equation (Eq. S1), n is an integer, λ is the wavelength of incident wave, d is the space between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes. Notably, the increase of θ value is indicative of the decrease of d owing to the fixed value of n λ.

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Thermal stability For elevating the thermal stability of the composite membranes and the components, the thermogravimetric analysis curves were recorded on a TGA 290C system (Netzsch Company) under an air flow rate of 30 mL/min. Approximately 5 mg of samples, such as COF, QACOF, SEBS, PVDF-SEBS and PVDF-SEBS/1%QACOF were heated from the ambient temperature to 700 °C with a heating rate of 10 °C/min. Notably, all the samples were preheated at 100 °C for 4 h. Additionally, the differential scanning calorimetry was conducted using Perkin Elmer DSC 4000 from 50-700 °C.

Leakage The prepared composite membranes of PVDF-SEBS/0.5%QACOF, PVDF-SEBS/1%QACOF and PVDF-SEBS/3%QACOF were respectively soaked in deionized (DI) water and 2 M KOH solution at room temperature (RT) for 24 h. The mass variations of these membranes were recorded periodically.

Oxidative stability The prepared composite membranes of PVDF-SEBS/0.5%QACOF, PVDF-SEBS/1%QACOF and PVDF-SEBS/3%QACOF were immersed in Fenton's reagent (H_2O_2, 3wt%; Fe^{2+}, 4 ppm) at 68 °C for 9 h. After wiping with a filter paper, the membrane samples were quickly weighed and the resudial mass percents at different period were determined on the basis of the initial values. Furthermore, the membrane samples were pictured to record to the morphology variation. The Fenton reagent was renewed with every interval.

Mechanical strength The mechanical properties of the prepared composite membranes, such as PVDF-SEBS, PVDF-SEBS/0.5%QACOF, PVDF-SEBS/1%QACOF and PVDF-SEBS/3%QACOF were obtained using a CMT2000 tensile strength instrument (JNshijin Company, China). The separating speed was 5 mm/min. All samples were cut into uniform rectangle dimension of 4×25 (mm×mm) with a mold. The initial cross-sectional area A_0 was 4 L (L: the thickness of samples). The tensile stress (E) and the strain (ε) values were obtained by dividing the maximum force (F) by

A_0 as in Eq. S2 and dividing the stretch distance (ΔL) by initial length (L) as in Eq. S3 [1].

$$E = \frac{F}{A_0} \tag{2}$$

$$\varepsilon = \frac{\Delta \mathrm{L}}{L} \times 100\% \tag{3}$$

Fine microstructure Transmission electron microscopy (TEM) images of COF and QACOF were collected by a JEOL 3011 high-resolution transmission electron microscope. A sample was prepared by placing one drop of diluted solution on a copper grid coating with carbon. The microstructure morphologies of the prepared composite membranes, such as COF, QACOF, PVDF-SEBS and PVDF-SEBS/1%QACOF were observed with a Zeiss scanning electron microscope (SEM). All of the membrane samples were puttered with gold nanoparticles before observation. Atomic force microscopy (AFM) was performed on a Dimension Icon atomic force microscope (Bruker). The AFM images of PVDF-SEBS, PVDF-SEBS/0.5%QACOF and PVDF-SEBS/1%QACOF were recorded in tapping mode.

Ion exchange capacity The prepared composite membranes of PVDF-SEBS/0.5%QACOF, PVDF-SEBS/1%QACOF and PVDF-SEBS/3%QACOF in hydroxide form were firstly washed with DI water and dried in an oven at 60 °C for 4 h. Subsequently, they were immersed in 0.1 M HCl standard solution with magnetic stirring for 48 h to neutralize the hydroxide ions in membrane samples. Then the mole number (equivalent) of the neutralized hydroxide ions (n) could be determined by titrating the acid solution with 0.1 M KOH standard solution. Finally, the ion exchange capacity (IEC), termed as mili-equivalents (meq) of hydroxide ions per gram of the dry hydroxide form membranes, could be obtained by calculation with Eq. S4 [2].

$$IEC\,(\mathrm{meq/g}) = \frac{1000n}{W_{OH}} \tag{4}$$

Water uptake and dimension swelling of membranes The prepared composite membranes of

PVDF-SEBS, PVDF-SEBS/0.5%QACOF, PVDF-SEBS/1%QACOF and PVDF-SEBS/3%QACOF were immersed in DI water for 24 h at 25 °C. Water uptake (WU), dimension swelling (DS) including thickness swelling and volume swelling of the water-saturated membranes were calculated by the following Eq. S5 and Eq. S6 after wiping the excessive surface water with a filter paper. The density increase was thus calculated with the WU and DS values.

$$WU\,(\%) = \frac{W_w - W_d}{W_w} \times 100\% \tag{5}$$

$$DS\,(\%) = \frac{D_w - D_d}{D_w} \times 100\% \tag{6}$$

Where W_w, D_w and W_d, D_d were respectively indicatie of the weights, dimensions of the wet membranes and dried membranes.

Water contact angle For the prepared composite membranes of PVDF-SEBS, PVDF-SEBS/0.5%QACOF, PVDF-SEBS/1%QACOF and PVDF-SEBS/3%QACOF, the surface property was evaluated with the water contact angle (WCA) values. A contact angle goniometer (DSA 25, KRUSS, Germany) was used and the result was the average value on both sides.

Hydroxide conductivity For the prepared composite membranes of PVDF-SEBS/0.5%QACOF, PVDF-SEBS/1%QACOF and PVDF-SEBS/3%QACOF, the hydroxide conductivity (σ) values were measured in purified water (Wahaha Pure Water with a conductivity of about 2 μS cm^{-1}) with the four-probe technique [3]. Specifically, each pair of platinum electrodes supplying the 2 kHz frequency alternative current was respectively placed on both sides of a membrane sample to supply and monitor the electronic signals. The test cell was fixed in a water bath to control the test temperature from 30 °C to 80 °C. The hydroxide ions conductivity at subzero temperature was measured with methanol solution (37% volume percent). The σ values and the activation energy (Ea) values were calculated by Eq. S7 and Eq. S8. Where L (in cm) is the distance of ion conduction; R_m (in Ω) is the resistance of ion conduction, W and D (in cm) respectively represent the width and thickness of membrane samples.

$$\sigma\ (\mathrm{S/cm}) = \frac{L}{R_m WD} \tag{7}$$

$$\sigma = \sigma^0 \exp\left(\frac{-Ea}{RT}\right) = \frac{A}{T}\exp\left(\frac{-Ea}{RT}\right) \qquad \ln\sigma = -\frac{Ea}{R}\cdot\frac{1}{T} + \ln\frac{A}{T} \qquad Ea = -k\cdot \mathrm{R} \tag{8}$$

Methanol permeability The measurement on methanol permeability (*p*) was performed using a home-made diffusion setup. A membrane sample was placed in the middle of two identical flasks (120 mL). In details, flask A and flask B were respectively filled with 100 mL of 2 M methanol aqueous solution and 100 mL of DI water. The continuous magnetic stirring at 500 rpm in both flasks could guarantee the uniformity of the solution during the measurement. The methanol concentration variation in the receiving flask B could be determined at regular intervals using a gas chromatograph. Each sample of 10 μL solution from the receiving flask was taken out for the measurement. The methanol permeability (*p*) could be calculated with Eq. S9 as followed.

$$p = \frac{L}{A}\frac{C_B V_B}{C_A t} \tag{9}$$

Where *A* (cm^2) and *L* (cm) represent the effective area (1.3 cm^2) and thickness of membrane samples; C_A: 2 M; C_B is the methanol concentration in flask B at different time (*t*); V_B means the volume of the receiving flask.

$$\beta = \frac{\sigma}{p} \tag{10}$$

According to Eq. S10, The selectivity (*β*) values were obtained by dividing hydroxide ions conductivity (*σ*) by methanol permeability (*p*).

Alkaline stability The alkaline stabilities of the prepared composite membranes, such as PVDF-SEBS/0.5%QACOF, PVDF-SEBS/1%QACOF and PVDF-SEBS/3%QACOF were tested by monitoring the hydroxide conductivity variation in the ten-cycle test of -25 °C–30 °C. The membrane samples were measured in a closed low-temperature stirring reaction bath (DHJF-4005, Zhengzhou Greatwall Scientific Industrial And Trade Co., Ltd) from 30 °C to -25 °C and then heated to 30 °C for one cycle. The process was repeated for 10 times to complete the ten-cycle test. Notably, the volume ration of 37% methanol solution rather than the aqueous solution was used to guarantee the liquid state at subzero temperature. Furthermore, the hydroxide conductivity variation in 2 M of KOH solution from 30 °C to 80 °C for 480 h was monitored to determine the alkaline stability. Notably, the KOH solution was replaced every 48 h to eliminate the influence of carbon dioxide on the constant concentration.

Fuel cell performance The membrane electrode assembly (MEA) with 5 cm^2 was prepared by a catalyst coated membrane (CCM) method. Catalyst inks containing PtRu/C (60 wt%, JM, for anode) or Pt/C (47.7 wt%, TKK, for cathode), 5 wt% home-made Poly (aryl piperidinium) ionomer in ethanol, isopropanol (IPA) and DI water were sprayed on both sides of the AEM using an air spray gun. PtRu loading for anode and Pt loading for cathode were 0.4 mg_{PGM}/cm^2. MEA was then immersed in 3M KOH solution at 80 °C for 3 h and the KOH solution was changed three times to completely exchange ions, followed by washing with DI water. Afterward, the clean MEA was sandwiched between gas diffusion layers (GDL, Toray) to assemble the single fuel cell. 850E fuel cell test system (Scribner Associates, USA) was used for the test and operating temperature was controlled at 30 °C and 60 °C. H_2 (1.0 SLM) and O_2 (0.8 SLM) were respectively supplied to the anode and cathode with 0.1 MPa_g. The single cell was broken in at various constant currents and polarization curve data were finally recorded once the voltage became stable.

Results and discussions

Fine microstructures

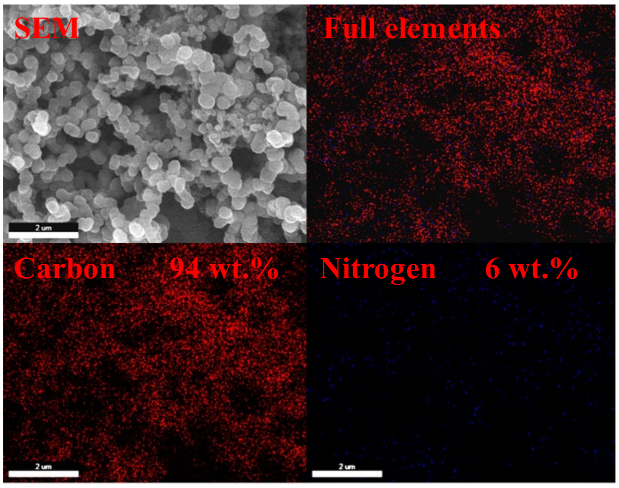

Figure S1. The SEM image and the energy dispersive spectroscopy images of element components in COF.

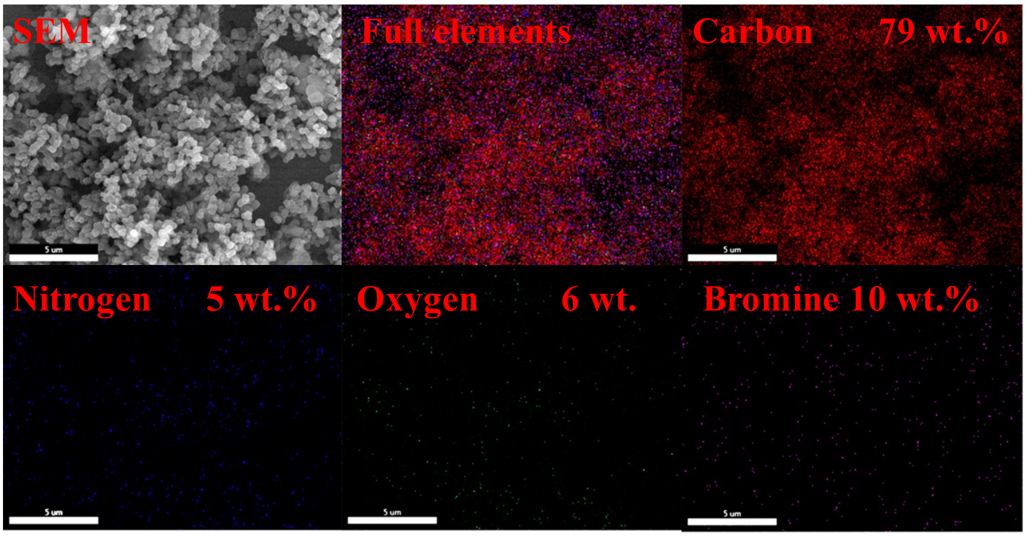

Figure S2. The SEM image and the energy dispersive spectroscopy images of element components in QACOF.

Alkaline stability

Table S1. The retention ratios of the original hydroxide conductivity of PVDF-SEBS/QACOF membranes immersing in 2 M of KOH solution in the range of 30 °C–80 °C for 480 h for 480 h.

	The retention ratios of the original hydroxide conductivity at different periods / mS/cm								
	PVDF-SEBS/0.5%QACOF			PVDF-SEBS/1%QACOF			PVDF-SEBS/3%QACOF		
	48 h	240 h	480 h	48 h	240 h	480 h	48 h	240 h	480 h
30°C	14.6	12.0	6.40	19.5	15.7	10.7	12.7	12.9	5.80
40°C	20.6	16.4	10.1	25.2	19.5	12.1	18.0	16.2	11.9
50°C	24.0	18.7	12.8	33.1	24.5	13.7	20.9	20.1	14.6
60°C	31.0	23.4	15.7	37.2	31.6	16.8	27.0	22.7	17.0

70°C	31.8	26.8	18.2	42.4	33.7	24.5	27.7	25.7	19.7
80°C	36.5	28.9	21.7	45.1	38.0	32.4	31.8	28.8	24.2

Table S2. The conductivities of the PVDF-SEBS/0.5%QACOF membrane during the cooling/heating processes in a ten-cycle of -25 °C–30 °C.

	Conductivities in the heating process / mS/cm			Conductivities in the cooling process / mS/cm		
	-25°C	0°C	30°C	30°C	0°C	-25°C
1 cycle	3.04	5.29	15.5	15.5	7.55	3.04
2 cycles	2.96	5.29	15.3	15.3	7.48	2.96
3 cycles	2.94	5.20	14.4	14.4	7.81	2.94
4 cycles	2.97	4.95	13.6	13.6	5.16	2.97
5 cycles	2.98	4.66	12.5	12.5	6.65	2.98
6 cycles	2.92	4.69	12.3	12.3	7.85	2.92
7 cycles	3.16	4.65	12.4	12.4	7.57	3.16
8 cycles	3.18	4.52	12.3	12.3	7.27	3.18
9 cycles	3.14	4.65	12.0	12.0	7.17	3.14
10 cycles	2.89	4.53	12.2	12.2	7.35	2.89

Table S3. The conductivities of the PVDF-SEBS/1%QACOF membrane during the cooling/heating processes in a ten-cycle of -25 °C–30 °C .

	Conductivities in the heating process / mS/cm			Conductivities in the cooling process / mS/cm		
	-25°C	0°C	30°C	30°C	0°C	-25°C
1 cycle	3.28	9.92	18.0	18.0	10.6	3.28
2 cycles	3.25	6.59	17.9	17.9	10.8	3.25
3 cycles	3.88	5.97	17.5	17.5	10.8	3.88
4 cycles	3.83	5.81	16.9	16.9	8.00	3.83
5 cycles	3.70	5.59	16.7	16.7	9.36	3.70
6 cycles	3.70	5.51	16.6	16.6	9.63	3.70
7 cycles	3.52	7.58	16.3	16.3	9.28	3.52

8 cycles	3.22	7.56	16.0	16.0	9.18	3.22
9 cycles	3.26	7.58	15.6	15.6	7.42	3.26
10 cycles	3.16	7.47	15.6	15.6	7.15	3.16

Table S4. The conductivities of the PVDF-SEBS/3%QACOF membrane during the cooling/heating processes in a ten-cycle of -25 °C–30 °C .

	Conductivities in the heating process / mS/cm			Conductivities in the cooling process / mS/cm		
	-25°C	0°C	30°C	30°C	0°C	-25°C
1 cycle	1.71	3.89	10.5	10.5	3.97	1.71
2 cycles	1.49	3.93	10.4	10.4	3.91	1.49
3 cycles	1.38	3.69	10.2	10.2	3.95	1.38
4 cycles	1.36	3.66	10.0	10.0	3.63	1.36
5 cycles	1.28	3.13	9.71	9.71	3.46	1.28
6 cycles	1.25	3.22	9.46	9.46	4.79	1.25
7 cycles	1.48	3.27	9.01	9.01	4.70	1.48
8 cycles	1.28	3.14	8.97	8.97	3.08	1.28
9 cycles	1.20	2.56	8.36	8.36	3.11	1.20
10 cycles	1.15	2.59	8.26	8.26	3.10	1.15

References

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