Electronic Supplementary Information

Preparation of Proton Exchange Membranes with High Performance by a Pulsed Plasma Enhanced Chemical Vapor Deposition Technique (PPECVD)

Zhongqing Jiang[a],*, Zhong-jie Jiang [b],*

[a] *Department of Chemical Engineering, Ningbo University of Technology, Ningbo 315016, Zhejiang, China.*

[b] *Department of Nature and Sciences, University of California, Merced 95343,USA.*

Corresponding authors.

E-mail addresses: zhongqingjiang@hotmail.com (Z. Jiang),

zhongjiejiang1978@hotmail.com (Z.-j. Jiang).

Experimental Section

Materials.

Methanol (CH$_3$OH, ≥99.7%), sulfonic acid (H$_2$SO$_4$, 98%), styrene (99.0%) and hydrogen peroxide aqueous solution (H$_2$O$_2$, 30%) were obtained from Shanghai Chemical Reagent Co. Ltd. Trifluoromethane sulfonic acid (CF$_3$SO$_3$H, 98.0%+) was purchased from Alfa Aesar®. These chemicals were used as received without further purification. Nafion® 117 (perfluorinated membrane) received from Dupont was treated in turn with hydrogen peroxide, distilled water and dilute H$_2$SO$_4$, and then stored in dilute H$_2$SO$_4$. Hydrogen (H$_2$ >99.999%) as diluting and carrier gas and argon (Ar, >99.999%) as working gas used in the plasma polymerization process were obtained from Air Liquide. Deionized (DI) water through Millipore system (Milli-Q®) was used in all experiments.

Plasma reactor.

The reactor used for the PEM preparation is a stainless steel vessel composed of two regions (i. e. the plasma discharge region and the plasma polymerization region) connected with a vacuum system consisting of a mechanical booster pump, a rotary pump, and a cold trap. The upper part of the reactor is the plasma discharge region for the radio-frequency (rf) plasma glow discharge. The plasma discharge is triggered by a power supplier (Institute of Microelectronics of Chinese Academy of Sciences) using Ar as the working gas. A power controller is used to monitor the power supply. The pulsed plasma discharge can be achieved by alternatively switching the power on and off, and an oscilloscope is used to detect the pulse profile. The generated energetic active electrons or ions of the plasma, i.e. energetic active particles, can be streamed down to the plasma polymerization region through two screen grids (G1 and G2). In the region of the plasma polymerization, the energetic plasma particles

extracted from the plasma discharge region collide with monomer molecules to initiate polymerization. The monomers were introduced into the plasma polymerization region using a double pipeline gas showering system to ensure a uniform distribution. The pipeline gas line is wrapped by heating wires to avoid the polymerization and/or condensation of monomers on their inner walls. During the preparation, all the gas lines was kept at 40 °C. The monomer flow rate was controlled by a gas-handling system with H_2 as carrier gas. At the bottom of the plasma reactor is a polymer deposition substrates. For a better deposition of the polymerized compounds, a controllable bias voltage −10 V d.c to substrate is applied.

Preparation of plasma polymerized proton exchange membranes (PEMs).

PEMs were synthesized by the plasma polymerization of a monomer mixture of styrene and trifluoromethane sulfonic acid. The total pressure of the reactor was first vacuumized down to less than 0.10 mbar. The monomer streams with a partial pressure ratio between trifluoromethane sulfonic acid (0.10 mbar) and styrene (0.05 mbar) kept constant at 2:1 were then fluxed into the plasma reactor. For the plasma polymerization, the Ar working gas was fluxed in and the total pressure of the reactor was kept between 0.32 and 0.35 mbar. The power controller was used to trigger the plasma discharge. By alternatively switching the power on and off, a pulsed plasma discharge can be achieved. In this work, a short period (1s) of the power on state which triggered the plasma discharge used to produce energetic particles necessary for the polymerization was followed by a relatively longer period (9s) of the power off state allowing for polymerization and the deposit of the obtained polymers to the substrate. The thicknesses of membranes could be well controlled by the time used for the membrane preparation. For the preparation of membranes with a thickness of 7.8 μm as shown in the main text, it took ~4 hours. After the plasma polymerization, the deposited membrane was stored in the chamber with flowing monomers for 10 minutes, which allowed for the removal of the active species by their reaction with monomers.

Characterizations of PEMs.

A Hitachi S-4500 scanning electron microscope (SEM) at operation voltage 5.0 kV was used to measure the morphology and thickness of the PEMs obtained. Fourier transform infrared spectroscopy (FTIR) analysis was conducted with a Nicolet NEXUS 870 spectrometer, in the range of 4000–500 cm^{-1}. The attenuated total reflection FTIR spectroscopy (ATR-FTIR) analysis was conducted with a Nicolet NEXUS 870 spectrometer, in the range of 4000–675 cm^{-1}. For the SEM and FTIR characterizations, a piece of the membrane deposited onto silicon wafer was first immersed in Milli-Q® water for 24 h and then dried before the measurments. X-ray photoelectron spectrum (XPS) analysis was conducted with a PHI-1600 model machine (Physical Electronics) at a passing energy of 20.0 eV, with Al Kα as target. Calibration of the spectra was performed by using the C1s peak (binding energy 285.0 eV) as internal reference.

Water Uptake(WU).

The WU was determined by measuring the change of weight between the wet and dry membranes. First, the membranes were soaked in water at 30 °C for 2 days after acidification. After the removal of the liquid water, the membrane was blotted to remove surface droplets, and the weight of this wet membrane were then recorded. The membrane was then dried at 120 °C under vacuum for at least 24 h. After the weight of the dried membrane was measured,

the water uptake could be obtained by the Eq. (1), where $mass_{dry}$ and $mass_{wet}$ referred to the mass of the dry membrane and the wet membrane, respectively.

$$WU\% = \frac{mass_{wet} - mass_{dry}}{mass_{dry}} \times 100 \qquad (1)$$

Ion Exchange Capacity(IEC).

The IEC of plasma polymerized membrane was determined by a titration method. Before testing, the dried membrane with proton exchange groups in the form of sulfonic acid was soaked in 50 mL of a saturated NaCl solution for 48 h to librate the H^+ ions to the solution by an ion exchange with the Na^+ ions. With the membrane kept in the solution, the released H^+ was then titrated with a NaOH solution using phenolphthalein as an indicator. The value of IEC was determined by Eq. (2).

$$IEC = (N_{NaOH} \times V_{NaOH}) / mass_{dry} \times 100\% \qquad (2)$$

Where N_{NaOH} and V_{NaOH} are the concentration and the consumed volume of the NaOH solution, respectively, $mass_{dry}$ referred to the mass of the dry membrane.

Proton conductivity measurement.

The proton conductivity of membrane was measured by a three-electrode AC impedance spectroscopy method as described in the literature.[1-3] The AC impedance spectra of the membranes were measured using an Autolab potentiostat/galvanostat (IM6e, Zahner, Germany) over a frequency range of 1 MHz to 100 mHz with an oscillating voltage of 10 mV. The outer two platinum wires were used as current generator electrodes (A and C), and the inner platinum wire (B) was potential-sensing electrode. The counter electrode (CE) was connected to A, reference electrode (RE) was connected to B, and the working electrode was connected to C.

The plasma polymerized PEMs were loaded between two PTFE plates to improve the electrical contacts with the interphase. Before the measurements, the membrane samples (20 mm×30 mm) were immersed in a 3 M aqueous solution of sulfuric acid for 24 h at 70 °C. The residual acid was then removed by immersing the samples in de-ionized water at 80 °C for 4 h, until the neutral pH was obtained. After the surface water was removed, the hydrated membrane was rapidly placed between two PTFE plates. The test cell was then immersed into deionized water, the water content of the membrane was assumed to remain constant during the short period of time required for the measurements. This method avoided contact resistance effectively and the results were well reproducible in the measurements. The proton conductivity σ was calculated from the impedance data, using the Eq. (3):

$$\sigma_{H^+} = \frac{L}{R_m A} \qquad (3)$$

Where L and A represent the distance between the working electrode and the reference electrode and the cross-sectional area of the membrane, respectively, while R_m is the ionic resistance of the membranes.

Methanol permeability measurement.

The methanol permeation through the membrane was measured by an open circuit potential method as described in our previous work.[1] The measurement was performed on an Autolab potentiostat/galvanostat (IM6e, Zahner, Germany) at a temperature of 20 ± 1 °C. The membrane was clamped between donor and receptor compartments by an O-ring joint with a membrane cross-sectional area of 2.0 cm^2 exposed to the solution as shown in Figure S1. Before the measurements, the samples of membranes (20 mm×20 mm) were immersed in a 3 M aqueous solution of sulfuric acid for 24 h at 70 °C. During the experiments, the solutions of the closed compartments were kept stirred using the Teflon coated magnetic paddles. A 10 % of methanol and 0.5 M H_2SO_4 in deionized H_2O was added to one compartment (A). An equal volume of a solution of 0.5 M H_2SO_4 in deionized H_2O was present in the other compartment (B). In this compartment, a Pt/C gas diffusion electrode (GDE) continuously flowing pure O_2 served as the working electrode, a Pt foil was used as counter electrode (CE), and a Ag/AgCl, KCl (saturated) was used as reference electrode (RE). The potential values were given against this reference electrode. The gas diffusion electrode (GDE) was prepared as reported in ref. (4) by using carbon paper (0.4×0.6 cm; HCP020P) as substrates, the Pt/C (40 wt%, Johnson Matthey) catalyst mixed with 5 wt % Nafion solution DE520 (Dupont$^®$) was pasted on it. The carbon paper coated with Pt/C was then placed in the opening of compartment B with a platinum ring as a current collector. The resulting GDE had an effective area of 0.283 cm^2 and a Pt loading of 1 mg cm^{-2}. Methanol flux arose across the membrane as a result of the concentration difference between the two compartments, and thus caused the GDE potential drop. The concentration could be determined by this drop from the calibration curve of potential shift against the methanol concentration.

To establish a calibration curve of potential shift against the methanol concentration, a membrane was not used in the permeation cell, and both compartments were initially filled with 0.5 M H_2SO_4 aqueous solution. The potential of the Pt/C electrode was monitored for ~ 1 h to ensure a stable value. A prescribed amount of methanol was stepwise added into compartment A to increase methanol concentration of the whole cell. The long time steady-state open circuit potential of the GDE was determined to be the potential shift at the corresponding methanol concentration. The methanol flux in a separate experiment with a 2 cm^2 membrane installed was determined by comparing the measured potential shift with the established calibration curve of potential shift versus methanol concentration.
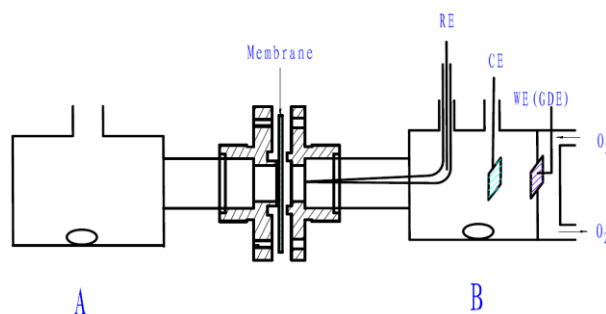

Figure S1. Schematic diagram of diffusion cell for open circuit potential measurements.

Table S1. Quantitative analysis of the XPS spectra for the plasma membranes and Nafion$^{@}$ 117 (%).

Membrane	C	S	F	O	N	-SO$_3$H
Plasma membrane	65.30	4.99	1.18	23.8	4.73	4.83
Nafion$^{@}$117	37.14	1.44	51.23	10.50	0.68	1.23

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