<center>**Supplementary Information**</center>

<center>**Preparation of high-performance hydroxide exchange membrane by a novel**</center>

<center>**ablation restriction plasma polymerization approach**</center>

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Experimental details

Preparation of the plasma-polymerized vinylbenzyl chloride membranes

The membranes were synthesized in an after-glow discharge plasma polymerization apparatus, consisting of two regions: the plasma discharge region (upper part) and the plasma polymerization region (lower part). Between them are a stainless steel screen grid (SG) applied a bias voltage of -30 V to hindered the electrons (generated in the plasma discharge region) from the polymerization region. VBC (95 wt%, Alfa Aesar®),

carried by hydrogen, was inlet into the polymerization region through an air distribution ring. The flow rates of argon (as working gas), VBC and hydrogen were controlled by gas mass flow controllers. The plasma polymerization parameters were fixed: 60 Pa for the reactor total pressure; 20 W for the discharge power; -10 V for the bias voltage to the substrate. There are different substrates used to support plasma-polymerized membrane: silicon wafers [P-doped Si (100)] and a conventional electrode made with commercially available 40 wt% Pt/C catalyst (HISPEC^{TM} 4000，Johnson Matthey company, JM) for SEM observations, stainless steel plates for chemical structural characterizations and polytetrafluoroethylene (PTFE) porous substrates for ionic conductivity.

QPVBC membrane

The plasma-polymerized vinylbenzyl chloride (PVBC) membranes were orderly submerged in 33 wt % trimethylamine (TMA) and 2 mol L^{-1} KOH aqueous solution for 48 h at room temperature. Then, the quaternized poly(vinylbenzyl chloride) membranes (QPVBC) were washed by deionized water and finally immersed in deionized water >48 h until required with frequent water changes.

Preparation of electrode

The electrode was made with commercially available 40 wt% Pt/C catalyst (HISPEC^{TM} 4000，Johnson Matthey company, JM). The catalyst ink was prepared by the dispersion of JM 40 wt% Pt/C catalyst (1.0 mg), 0.5 ml distilled water and 0.5 ml 2-propanol solution and 20 µL Nafion solution (0.05 wt%，Dupont®) was shaken in an ultrasonic generator for 30 min, and then the catalyst suspension was spread onto a

piece of CP (1 cm × 1 cm) leading to Pt loading of 0.4 mg cm^{-2}. To evaluate the poisoning of the catalyst, the electrochemical characterization of JM electrodes submerged in 33 wt % trimethylamine (TMA) for 48 h was analyzed by cyclic voltammetry (CV) of ethanol oxidation. For cyclic voltammetry (CV) of ethanol oxidation, the potential was cycled between –0.8 V and 0.6 V vs. SCE at 0.05 V s^{-1} and all experiments were carried out at room temperature. Several activation scans (at least ten) were performed until reproducible voltammogram were obtained, and all the voltammograms shown here were the last circle.

Characterization of membranes

The morphology and microstructure of the plasma polymerized membrane was studied by scanning electron microscope (SEM) (Sirion 200, FEI) at operation voltage of 5.0 kV. Before observation, the QPVBC membrane with silicon substrate was frozen in liquid nitrogen and broken to expose the cross-section.

The ATR-FTIR spectra of dried PVBC and QPVBC membranes were recorded using Nicolet NEXUS 870 spectrometer (Thermo Electron Corporation) in the range of 4000-670 cm^{-1}. The spectra were obtained after 256 scans at 2 cm^{-1} resolution with subtracting the contributions from CO_2 and H_2O (gas).

The XPS analysis was carried out using a Thermo ESCALAB 250 spectroscopy (Thermo Electron Corporation) at a power of 150 W with a monochromatic Al Kα radiation at 1486.6 eV. An additional electron gun was used to allow for surface neutralization during the measurements since the plasma polymerized membranes were nonconductive. XPS of PVBC and QPVBC membranes were recorded at pass

energies of 70 eV for survey spectra and 20 eV for core level spectra. The energy resolution was about 0.6 eV. The spectrometer energy scale calibration was checked by setting Ag $3d_{5/2} = 368.26$ eV and the spectra were calibrated with respect to the C 1s peak at 284.6 eV. The Cl(2p) and N(1s) signals were collected and analyzed using the software XPSPeak.

Hydroxide conductivity measurement

The hydroxide conductivity of the obtained membranes was measured by three-electrode AC impedance spectroscopy using an Autolab potentiostat/galvanostat (IM6e, Zahner) over a frequency ranging from 0.1 Hz to 1MHz in deionized water. The hydrated membrane was placed between two polytetrafluoroethylene (PTFE) plates, with one side contacted with three parallel platinum wires. The reference electrode (RE) was connected to the inner platinum wire, and the counter electrode (CE) and working electrode (WE) were connected to the outer two platinum wires, respectively. The hydroxide ion conductivity σ_{OH^-} could be calculated by

$$\sigma_{OH^-} \ (S \ cm^{-1}) = \frac{l}{R_m A}$$

where R_m was the membrane resistance (Ω) obtained from the AC impedance data, A was the cross-sectional area (cm^2) of the membrane, l was the distance (cm) between the working electrode and reference electrode.
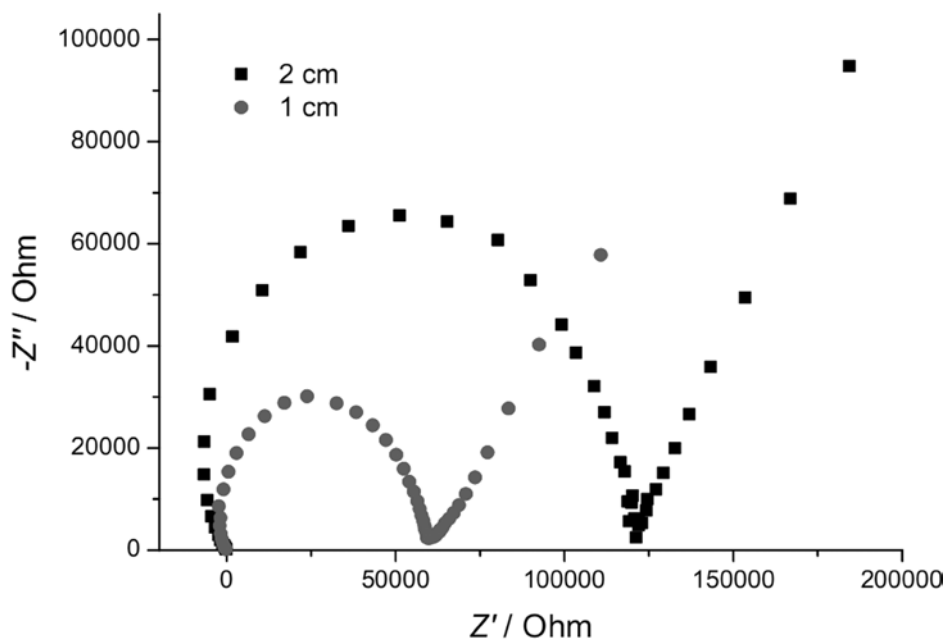
ATR-FTIR spectra

Fig. S1. ATR-FTIR spectra of (a) PVBC and (b) QPVBC membranes.
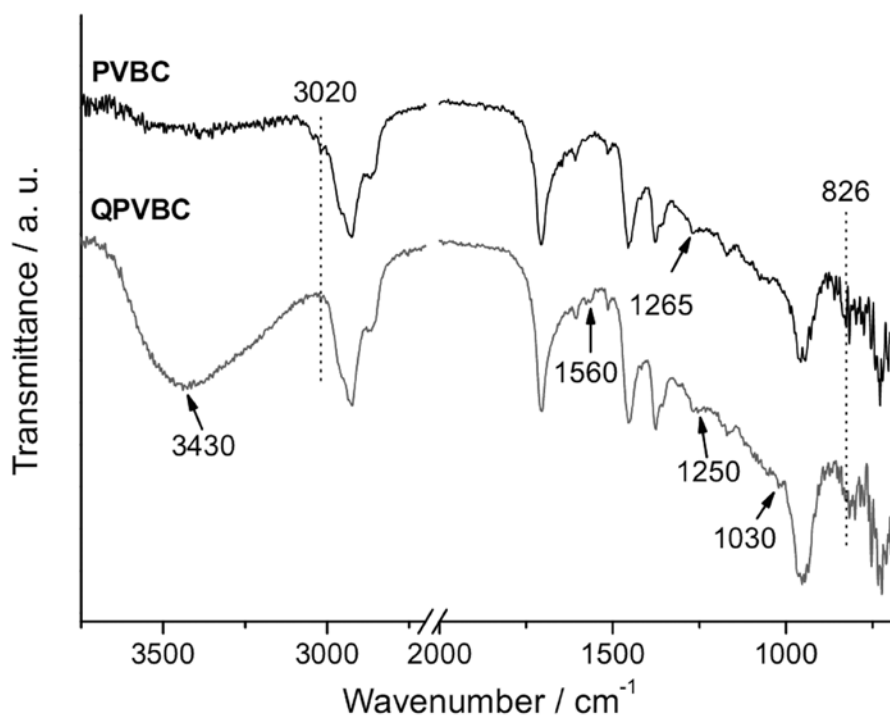
Nyquist plots

Fig. S2. Nyquist plots in different separation between reference electrode and the

working electrode

The influence on the position of the reference electrode wire was investigated by

changing the distance between the reference electrode and the working electrode (see

Fig. S2). The hydroxide conductivities of the QPVBC membrane were 0.039 S cm^{-1} and 0.040 S cm^{-1} in the RE and WE separation of 1 cm and 2 cm, respectively, indicating a good repeatablility in measurement.

Cyclic voltammetry

Fig. S3. Cyclic voltammograms of JM electrode immersion in 33 wt% TMA for different time in N$_2$-saturated 1M NaOH + 1 M EtOH at a scan rate of 0.05 V s^{-1}.
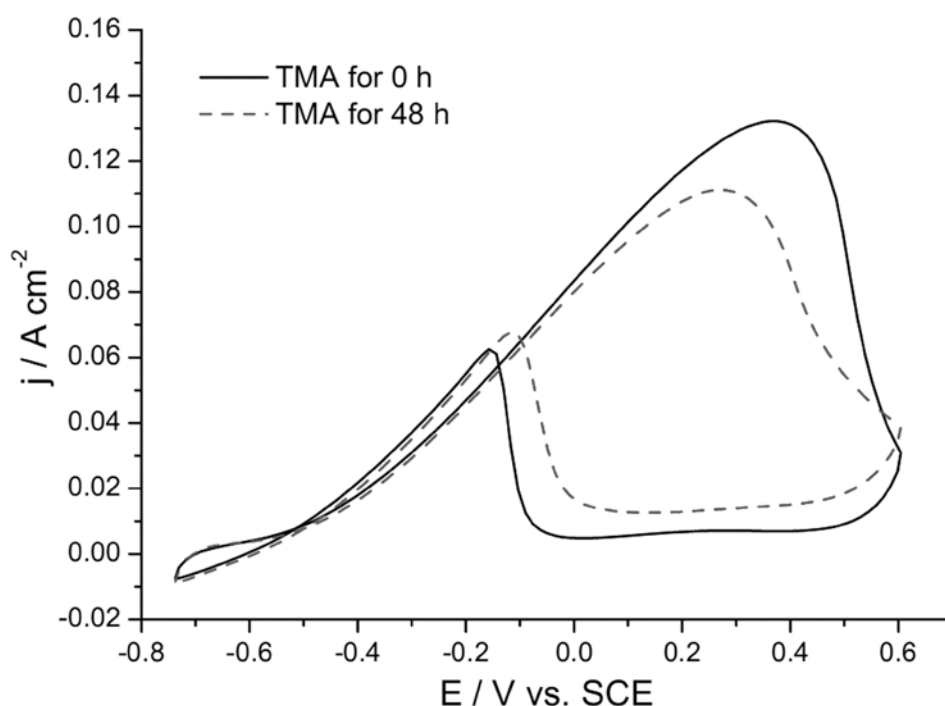
Since the plasma polymerized membrane was directly deposited on the electrode, the post-quaternization of electrode-membrane-composite may cause the poisoning of the catalysts. The ethanol oxidation of JM electrode submerged in 33 wt % trimethylamine (TMA) for 48 h, and for comparison, the JM electrode which did not immerse in TMA were evaluated by CV. As shown in Fig. S3, there are indeed some poisoning problems in the quaternization process. Two typical oxidation peaks appear for the CV curves of the TMA 0h (full curve) and TMA 48h (dash line), which arise from the oxidations of the ethanol and their intermediates.[1] The ethanol oxidation

peak current density (0.13 A cm^{-2} vs. 0.11 A cm^{-2}), peak potential (0.38 V vs. SCE to 0.27 V vs. SCE) and CO tolerance (the ratio of current density for the forward and backward peak, I_f/I_b, 2.13 vs.1.63) values were changed after the quaternization. Obviously, the ethanol electrooxidation feature of the platinum catalysts was influenced by the TMA, but it didn't show a severe poisoning towards the catalysts. Resolving the problem of catalyst poisoning needs future work and is underway.

[1] X. Zhang, W. Lu, J. Da, H. Wang, D. Zhao, P.A. Webley, *Chem. Commun.*, 2009, **45**, 195-197.