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# Ionomer Cross-linking Immobilization of Catalyst Nanoparticles for High Performance Alkaline Membrane Fuel Cell

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**ABSTRACT:** Polymer electrolyte membrane fuel cells can generate high power densities with low local emissions of pollutants. Optimal ionomer-Pt/C catalyst interactions in the electrodes enables the efficient generation and transport of ions and electrons required for high fuel cell performances. Critical durability issues involve agglomeration of the Pt/C nanoparticles (Pt/C NPs) and ionomer during discharging. Our novel approach involves ionomer cross-linking immobilization for the fabrication of durable catalyst layers for application in alkaline anion exchange membrane fuel cells (AEMFCs). Pt/C NP catalysts are employed alongside a poly (2,6-dimethyl-p-phenylene oxide)-(PPO)-based quaternary ammonium ionomer (containing terminal styrenic side-chain groups) to form porous catalyst layers. Following thermally initiated crosslinking of the terminal vinyl groups, an inter-connected ionomer network forms conductive shells around the Pt/C aggregates. Ex situ catalytic activity and in situ durability tests demonstrate that this immobilization strategy inhibits Pt/C NP coalescence without sacrificing catalyst layer porosity. An initial demonstration of an H<sub>2</sub>/O<sub>2</sub> AEMFC containing the new CBQPPO@Pt/C cathode shows that high peak power densities can be achieved (1.02 W cm<sup>-2</sup> at 70 °C, raising to 1.37 W cm<sup>-2</sup> with additional 0.1 MPa back-pressurization).

### INTRODUCTION

The development of efficient and clean energy conversion devices is urgently needed due to the growing sustainability and environmental concerns associated with the use of fossil fuels.<sup>1,2</sup> Low temperature hydrogen fuel cells, i.e. (alkaline) anion exchange membrane fuel cells (AEMFCs) and proton exchange membrane fuel cells (PEMFCs), produce electrical energy directly from electrochemical reactions (oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR)) without the local generation of pollutants.<sup>3</sup> Carbon black supported platinum nanoparticles (Pt/C NPs) are the most widely used electrocatalysts for such fuel cells.<sup>4</sup> However, Pt/C NP coalescence represents a critical durability limitation with extended fuel cell operation.<sup>5</sup> To improve in situ Pt utilization and durability, ionomers are commonly employed, in porous catalyst layers, to act as both binder and ion conductor.<sup>6,7</sup> Typically, the catalyst layer exhibits a heterogeneous morphology with inter-connections between the Pt/C NPs and ionomer. The Pt/C aggregates enable electrical current to flow to/from the catalytic sites, whilst providing the micro-/meso-porosity (interstitial voids) required for gas/water permeation. The ionomer aggregates are expected to uniformly coat and interconnect the catalyst aggregates to provide an ion conductive pathway to the polymer electrolyte membrane without inhibiting gas diffusivity.

For acidic PEMFCs, perfluorosulfonic acid (PFSA) ionomers are the state-of-the-art, which are supplied as colloidal dispersions to enable fabrication of porous catalyst layers.<sup>8</sup> The combination of these porous catalyst layers with highly proton conductive perfluorosulfonic acid membranes (namely Nafion®) have resulted in PEMFCs making great progress in recent decades. Over the past 5 years, the alkaline counterparts (AEMFCs) have made remarkable strides in improving the performances of  $H_2/O_2$  AEMFC with power densities achieving > 1 W cm<sup>-2</sup> (summarized in Table S1 in the Supporting Information).<sup>9,10</sup> These studies clearly indicate that the combination of highly conductive and stable anionomer with optimized electrode design<sup>11,12</sup> is essential for high power densities. Zhuang et al. enhanced the fuel cell performance through improving the OH<sup>-</sup> conductivity of electrolyte (AEMs) and the ORR performance of catalyst.<sup>13-</sup> <sup>15</sup> Varcoe *et al.* substantially improved the performance of the AEMFCs by development of highly conducting AEMs and anionomer powders.<sup>16-21</sup> Mustain et al. improved the fuel cell peak power density and operation durability of the AEMFC through perfect water management and optimization of electrodes - even without Pt in the cathode.<sup>22-25</sup> Most recently, Kohl et al. reported a H<sub>2</sub>/O<sub>2</sub> AEMFC with an exceptionally high peak power density of 3.4 W cm<sup>2</sup> at 80 °C, which is the highest reported, to date.<sup>26</sup> These competitive fuel cell performances are closely approaching to that of PEMFCs owing to the high



**Scheme 1**. Schematic of the ionomer cross-linking immobilization strategy for fabricating durable CBQPPO@Pt/C catalyst layers: (a) Menshutkin reaction between the bromomethyl groups of BPPO and the tertiary amine groups of VBN to obtain quaternary ammonium-functionalized ionomer with terminal vinyl pendants (VBQPPO); (b) Thermally triggered crosslinking of the vinyl groups to form CBQPPO; (c) Preparation of ionomer/catalyst ink by mixing Pt/C NPs with VBQPPO in alcohol aqueous solution; (d) Conversion of the VBQPPO@Pt/C into the thermally crosslinked CBQPPO@Pt/C catalyst layer; (e) An illustration highlighting the ionomer cross-linking immobilization effect on porosity of the catalyst layer (to maximise catalytic efficiency).

performance of the membrane electrode assembly (MEA) by the use of highly OH<sup>-</sup> conductive AEMs and well control over the subsequently heterogeneous microstructure of the catalyst layer. Particularly, the importance of the optimization of catalytic electrode design in securing high AEMFC performance requires an anionomer morphology that can generate optimized porous catalyst layers, essential for the promotion of efficient simultaneous ion and fuel transport.

In addition, the durability of catalyst layers, particularly at elevated temperatures and under high current density operation, is another area concern.<sup>10,27</sup> During fuel cell operation, the hydrophilic ionomer phases in the catalyst layers adsorb and desorb large quantities of water, which can lead to electrode flooding and impeded gas transport.28,29 Moreover, hydrated ionomers can excessively swell under such conditions, resulting in large isolated agglomerates of ionomer and/or Pt/C NPs. Isolated ionomer agglomerates would not form the desired OH<sup>-</sup> conductive networks. Unsuppressed electrochemical Ostwald ripening and Brownian-like Pt mobility will lead to Pt NP growth and coalescence.<sup>30-32</sup> The development of high performance AEMFCs mandates the advancement of a general synthetic strategy for stabilizing Pt/C NPs within high performance porous catalyst layers.

To address this challenge, this study reports an ionomer cross-linking immobilization strategy aimed at stabilizing Pt/C NPs for AEMFCs, while retaining high catalytic efficiencies. We acknowledge that AEMFCs development is focused on the aim of eliminating the use Pt-based electrocatalysts, but for development of new anionomer concepts, it is useful for initial studies to involve widely available, commercial Pt/C electrocatalysts. Scheme 1 summarizes our anionomer strategy. Pt/C NPs are mixed in alcohol aqueous solution with a poly(2,6-dimethyl-pphenylene oxide)-(PPO)-based quaternary ammonium ionomer, containing pendant groups with terminal styrenic functionality, to form a highly solvated particle dispersion. This particle dispersion can be exploited to control the porosity of a catalyst layer (Scheme 1c). Thermally triggered crosslinking of the terminal, pendant vinyl groups, converts the physically aggregated ionomer phases into covalent network shells that envelope the Pt/C aggregates, hence providing ionically conductive interconnections and preventing Pt coalescence (Scheme 1d). A vinyl-pendant-free quaternary ammonium PPO ionomer (QPPO) was prepared as a non-crosslinked benchmark. The importance of the crosslink-immobilized effect in stabilizing Pt/C NPs catalyst and securing high AAEMFC performance is discussed.

#### EXPERIMENTAL SECTION

Chemicals and Materials. Poly (2,6-dimethyl-1,4phenylene oxide) (PPO) was manufactured by Asahi Kasei Chemicals Corporation (Japan) and kindly supplied by Tianwei Membrane Company (Shandong, P.R. China). Nbromosuccinimide (NBS), 2,2'-azobis-isobutyronitrile (AIBN), and 4-vinylbenzyl chloride (VBC) were purchased

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from Energy Chemical Co. Ltd. (Shanghai, P.R. China) and used as received. N-methyl-2-pyrrolidolone (NMP, AR), dimethylamine solution, trimethylamine solution, ether, chlorobenzene, ethanol, methanol and sodium hydroxide (AR) were purchased from Sinopham Chemical Reagent Co. Ltd. The Nafion DE-521 PFSA polymer dispersions was manufactured by DuPont. The commercial Pt/C catalyst and PtRu/C catalyst were manufactured by Johnson Matthey. The commercial Pt/C catalyst is 60% wt. Pt nanoparticles (ca. 3 nm diameter) on Vulcan XC-72 carbon support. The commercial PtRu/C catalyst is 40% wt. Pt nanoparticles and 20% wt. nanoparticles (both ca. 3 nm diameter) on Vulcan XC-72 carbon support. Deionized water was used throughout.

#### Experimental.

Synthesis of BPPO: BPPO was produced as our previous work and described as follows: PPO (10 g, 83 mmol) was dissolved in chlorobenzene (200 ml) and then NBS (10.5g, 58.3 mmol) and AIBN (0.1 g, 0.61 mmol) were added. The reaction solution was heated to 130 °C for 4 h with stirring. After reaction, the mixture was poured into excess ethanol (2 L) to form a light-brown fibrous precipitate of BPPO. The precipitate was then washed with ethanol (6 ×) with a final drying in a vacuum oven at 40 °C for 48 h. The <sup>1</sup>H NMR spectrum of BPPO (in CDCl<sub>3</sub>) is shown in Figure S1.<sup>33</sup>

Synthesis of VBN: 4-vinylbenzyl chloride (3.1 g, 20 mmol) was added dropwise into 10 ml aqueous dimethylamine solution (33 % wt.) with vigorously stirring at room temperature. After 24 h reaction, the product was extracted into chloroform (3 × 50 ml). The organic fraction was collected and washed with deionized water (3 × 50 ml). The solvent was removed by evaporation and the product (VBN) was obtained as bright yellow liquid. The <sup>1</sup>H NMR spectrum of VBN (DMSO-d<sub>6</sub>) is shown in Figure S2.

Synthesis of VBQPPO: BPPO (1.0 g, 4.77 mmol, 56 % degree of bromination) was dissolved in 20 ml NMP at 25 °C, after which VBN (1.0 g, 6.21 mmol) was added dropwise followed by stirring for 24 h at room temperature. The mixture was then dropped into diethyl ether, which formed a white precipitate that was recovered by filtration. The precipitates were washed with ether (6 ×). The VBQPPO ionomer powder obtained was further dried in a vacuum oven at 30 °C for 12 h. The <sup>1</sup>H NMR spectrum of VBQPPO (CD<sub>3</sub>OD) is shown in Figure S3.

Synthesis of QPPO: BPPO (1.0 g, 4.77 mmol, 56 % degree of bromination) was dissolved in 20 ml NMP at 25 °C. A methanol solution of trimethylamine (1.0 ml, 33 % wt.) was then added and the resulting mixture was stirred for 24 h.<sup>33</sup> After reaction, the solution was dropped into diethyl ether, which formed a white precipitate that was recovered by filtration. The precipitates were washed with ether (6 ×). The synthesized QPPO ionomer powders were further dried in vacuum oven at 40 °C for 12 h. The <sup>1</sup>H NMR spectrum of QPPO (CD<sub>3</sub>OD) is shown in Figure S4.

*Formation of CBQPPO*: CBQPPO was formed via the thermally-initiated inter-crosslinking of VBQPPO during the catalyst ink preparation step (when preparing the catalyst inks for the ORR catalytic activity test and when preparing the CBQPPO@Pt/C catalyst layer for the fuel cell test). The conditions of formation of CBQPPO are reported

in the corresponding experimental sections below.

#### Instruments and characterizations.

Nuclear Magnetic Resonance (NMR) spectroscopy: <sup>1</sup>H NMR spectra were recorded on a Bruker 510 instrument (<sup>1</sup>H resonance at 400 MHz) at 298 K. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated protons in the NMR solvents (CDCl<sub>3</sub>  $\delta$  = 7.26 ppm, DMSO-d6  $\delta$  = 2.53 ppm, CD<sub>3</sub>OD  $\delta$  = 3.31 ppm).

Fourier Transform Infrared spectroscopy (FT-IR): Variable temperature FT-IR spectra were collected using a NICOLET iS10 (Thermo Fisher Scientific). All polymers were measured in the membrane form. A sample of AEM, which was naturally dried in the atmosphere in the OH anion form, was fixed between two CaF<sub>2</sub> optical plates. The samples were heated from 30 °C to 70 °C in four stages: 40 °C, 50 °C, 60 °C, and 70 °C (10 °C temperature rise over 10 minutes followed by a thermal hold at each temperature of 60 min). FT-IR absorbances were recorded with a measurement every 1 min.

X-ray and electron microscopy analyses: Powder X-ray diffraction patterns of catalyst samples were conducted on a Rigaku D/MAX2500VL/PC X-ray diffractometer with Cu K $\alpha$  radiation and X-ray photoelectron spectroscopy (XPS, ESCALAB 250 System) using Al K\_ excitation radiation (1486.6 eV). TEM and EDS micrographs of the catalyst powders were recorded by a Hitachi-7700 working at 100 kV. The cross-section structure of the catalyst layers in the MEAs were characterized using an environmental scanning electron microscopy (ESEM, XL-30 ESEM).

*Brunauer–Emmett–Teller (BET) test*: BET gas sorptometry measurements were performed on an Autosorb iQ (Quantachrome, Autosorb iQ, USA) at 77K. Before each isotherm, approximately 200-220 mg of ionomer-based MEAs samples were activated by heating for 5 hours under high vacuum at 140 °C. The samples were then transferred to a pre-weighed sample tube and de-gassed at 140 °C for approximately 7 h.

*Water contact angle (WCA) test*: The water contact angle (WCA) of the GDE surface was measured by a contact angle meter (SL200B, Solon Tech Co., Ltd., CHN) using the sessile drop technique at room temperature. Six parallel tests were conducted to gauge the precision of the experimental data.

Electrochemical testing of the catalyst inks. Electrochemical measurements were performed using a CHI 760E electrochemical workstation with a threeelectrode system and aqueous KOH (0.1 M) electrolyte. A glassy carbon (GC) rotating disk electrode (RDE, 5mm diameter) was coated with a catalyst ink and served as the working electrode; a Ag/AgCl and Pt wire were used as the reference and counter electrodes, respectively. The homogeneous Pt/C catalyst ink samples (20% wt. CBQPPO content) were prepared by ultrasonically mixing 4 mg of the catalyst powder with a mixture consisting of 480  $\mu$ L ethanol, 480  $\mu$ L H<sub>2</sub>O and 20  $\mu$ L VBQPPO/ alcohol solution (5% wt.) for 20 min, then heated at 70 °C for 2 h to ensure VBQPPO was converted to CBPPO. Other inks with 11% wt., 33 % wt., and 50 % wt. CBQPPO content were prepared by using formulations involving addition of 10  $\mu$ L, 40  $\mu$ L and 80  $\mu$ L of VBQPPO/ alcohol solution (5 % wt.). 10  $\mu$ L of the catalyst resulting inks were pipetted separately onto a polished GC-RDE (0.196 cm<sup>2</sup>) and dried under an infrared (IR) lamp for each ink tested to obtained Pt/C catalyst loadings of 0.204 mg cm<sup>-2</sup>.

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Before voltammetry was conducted, the aqueuos KOH (0.1 M) electrolyte was purged with  $O_2$  for 30 min. The linear sweep voltammetry (LSV) measurements at room temperature were measured at the rotating speed of 1600 rpm with a sweep rate of 10 mV s<sup>-1</sup>. The stability of the catalyst was evaluated by chronoamperometry (i-t) at a constant potential of -0.5 V vs. Ag/AgCl (0.498 V vs. RHE) at a rotation rate of 1600 rpm (with  $O_2$ -purged aqueous KOH (0.1 M) electrolyte).

Membrane Electrode Assembly (MEA) fabrication and fuel cell testing. The gas diffusion electrodes (GDEs) method was adopted to prepare the membrane electrode assemblies for fuel cell testing. 10 mg Pt/C (for cathode) catalyst or PtRu/C (for anode) catalyst (both 60% wt. metal content) were ultrasonically mixed with 100 mg deionized water, 400 mg 1-propanol, and 50 mg ionomer solution (5% wt. VBQPPO in alcohol aqueous) to prepare the inks that will yield catalyst layers containing 20% wt. ionomer and 80% wt. catalyst. To obtain GDEs, the catalyst inks were inkjet printed onto the gas diffusion layer (GDL, Toray TGP-H-060). The metal loading in both anode and cathode was controlled to be 0.5 mg<sub>metal</sub> cm<sup>-2</sup>, and the final electrode areas were 12.25 cm<sup>2</sup>. The prepared GDEs and anion-exchange membrane (AEM, TMImPPO type with an IEC =  $1.65 \text{ mmol g}^{-1}$  were then converted to OH<sup>-</sup> form by immersing in aqueous NaOH (1 M) solution for 12 h followed by thorough washing with deionized water. The resulting GDEs were correctly placed (PtRu/C at anode and Pt/C at cathode) on each side of the AEM to make the membrane electrode assembly (MEA). The MEA was hotpressed in situ (no hot press procedure was used prior to fuel cell assembly).

37 The single cell Anion-Exchange Membrane Fuel Cells 38 (AEMFC) were tested using an 890e multi range fuel cell 39 test station (Scribner Associates, USA) in a galvanostatic 40 mode between 30 and 70 °C. To convert the 41 VBQPPO@Pt/C cathode and VBQPPO@PtRu/C anode 42 catalysts layers into crosslinked immobilized forms 43 (CBOPPO@Pt/C and CBQPPO@PtRu/C), the cell 44 temperature was increased from 30 °C to 70 °C over 1 h 45 and held at 70 °C for 2 h with  $H_2$  and  $O_2$  gas feeds (100%) 46 being supplied to anode and cathode electrodes, respectively (flow rates of 1 L min<sup>-1</sup>). Then, the MEAs were 47 broken in under potentiostatic mode at 0.5 V cell voltage at 48 70 °C and the corresponding relative humidity (100%) of 49 both the cathode and anode were adjusted until a steady 50 current density was achieved for at least 30 min. After 51 break-in procedure, the current density at each cell voltage 52 was recorded with either no backpressure or 0.1 MPa 53 backpressure (symmetrically applied to both sides) after 54 the power output had stabilized. A short-term durability 55 test of H<sub>2</sub>/O<sub>2</sub> AEMFCs containing the different ionomers 56 (CBQPPO vs. QPPO benchmark) was conducted at 70 °C 57 with a flow rate of 1 L min<sup>-1</sup> (both  $H_2$  and  $O_2$  gas supplied) 58

under full humidification and with no backpressure applied to either gas feed. Power density of the ionomerbased MEAs held at 0.5 V cell voltage were recorded one point in each hour. A longer-term durability test was conducted with gradually decreasing gases relative humidity (RH) from 100% to 80% within 50 h. Constant current density stability tests were performed at 0.6  $A/cm^2$ , and the voltage was recorded as a function of time. The operating voltages were recorded as a function of time at 70 °C with the cell held at 0.6 A cm<sup>-2</sup> current density.

Electrochemical AC impedance spectroscopy (EIS) analysis. Electrochemical impedance spectroscopy (EIS) analysis, involving alternating current (AC) stimuli, is considered a well-established experimental technique which can elucidate individual fuel cell polarization effects. With complementary simulation of the EIS data, further quantification of the capacitive-resistive contributions at membrane-electrode interfaces in the single cell fuel cells can be achieved (Table S1), that can include the determination of changes in materials morphology.34 Herein, EIS analyses of the MEAs were performed with single cells assembled using a pair of gaskets and a pair of graphite blocks. The anode and cathode gases (H<sub>2</sub> and N<sub>2</sub> respectively) were supplied at 1 L min<sup>-1</sup>. For EIS testing, the temperatures for the cells and gases was all controlled at 70 °C. All testing parameters were by the 890e fuel cell tester.

The EIS analysis was performed by externally connected Autolab workstation (PGSTAT 302N, Metrohm, Netherlands) controlled by Nova 2.1.2 software. A small sinusoidal potential perturbation (10 mV amplitude, f range 0.01Hz - 100 kHz) was applied to the cathode and anode plates and the AC current response was measured. Impedance data is presented as Nyquist plots and simulated using ZSimpWin® electrochemical analysis software (PAR Inc. USA). The electrical equivalent circuit (EEC) model was selected based on the possible physical replica comprising membrane and GDE. The best fits for each EEC parameter are presented in Table S1.

#### RESULTS AND DISCUSSION

Synthesis. The vinyl-group containing quaternary ammonium ionomer (VBQPPO) and the ensuing ionomer/catalyst ink were prepared as summarized in Scheme 1. VBQPPO ionomer was synthesized using the Menshutkin reaction between the bromomethyl groups of bromomethylated PPO (BPPO) and the tertiary amine groups of N,N-dimethylvinylbenzylamine (VBN) (Scheme 1a, <sup>1</sup>H NMR spectra presented in Figures S1-S3 in the Supporting Information). The presence of vinyl proton signals ( $\delta_{\rm H}$  = 5.25, 5.75 and 6.75 ppm) provides evidence of successful Menshutkin reaction with vinyl groups remaining unreacted.

In situ FTIR analyses shows that the inter-crosslinking reaction between vinyl groups (VBQPPO ionomer conversion into crosslinked CBQPPO networks, Scheme 1b) occurs gradually as the temperature is increased from 30 °C to 70 °C (Figure S5): the intensity of the vinyl C-H vibrations (1320 cm<sup>-1</sup> and 3090 cm<sup>-1</sup>) and the C=C vibration (1610 cm<sup>-1</sup>) decrease on increasing temperature.

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**Figure 1**. (a) Linear scan voltammograms in O<sub>2</sub>-saturated aqueous KOH (0.1 M) solution (room temperature with a sweep rate of 10 mV S<sup>-1</sup> and a rotation rate of 1600 rpm) of the non-crosslinked benchmark cathode catalyst (QPPO@Pt/C) before (red) and after (black) chronoamperometry (i-t) test (potential hold at -0.5 V vs. Ag/AgCl reference electrode (0.498 V vs. RHE) for 250 min). TEM images of QPPO@Pt/C catalyst particles both before (b) and after (c) the i-t test. Parts (d), (e), and (f) present the analogous data for the thermally crosslinked CBQPPO@Pt/C catalyst.

Further evidence of thermally initiated crosslinking is seen on inspection of the overlapped C–H stretches (2900–3020 cm<sup>-1</sup>), attributed to the methyne and methylene groups generated on crosslinking reaction, which increase in intensity with increasing temperatures. This post-thermal treatment of the Pt/C-VBQPPO dispersions in alcohol aqueous or VBQPPO@Pt/C catalyst layer is hypothesized to lead to encapsulation of the Pt/C aggregates by the inter-crosslinked CBQPPO ionomer networks, leading to an increase in the durability of the resulting catalyst layer (designated CBQPPO@Pt/C from hereon) with retention of porosity (Scheme 1c, 1d, 1e). Evidence in support of this hypothesis is presented in the following sections.

Catalytic activity and durability of CBQPPO@Pt/C catalyst layer (ex situ evaluation). ORR catalytic activity of the electrode catalyst layer was investigated by the linear sweep voltammetry (LSV) on a rotating disk electrode (RDE) in O<sub>2</sub>-saturated aqueous KOH (0.1 M) solution. A dispersion of VBQPPO@Pt/C was deposited onto rotating disk electrodes for LSV testing. Preliminary studies (data presented in Figure S6) suggested an optimized dispersion composition of 20 wt % of ionomer and 80 wt % of Pt/C NPs. *X*-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) data for VBQPPO@Pt/C are consistent with a uniform distribution of Pt/C aggregates in the ionomer phase (Figure S7 and Figure S8). Typically, the N1s peak at 402.25 eV in XPS data is assigned to the C-N<sup>+</sup> species in the quaternary ammounium (QA) groups of CBQPPO, providing initial evidence of CBQPPO loading on Pt/C NPs surface. TEM and relative mapping images further certify the well distribution of VBQPPO ionomer on Pt/C aggregates (Figure S9).

To investigate the ionomer crosslink-immobilized effect, the optimized VBQPPO@Pt/C particle dispersing ink was heated at 70 °C for 2h, followed by being deposited onto a rotating disk electrode to form an inter-crosslinked CBQPPO@Pt/C catalyst layer. Additionally, two benchmark catalyst layer prepared from a non-crosslinked (vinyl-free) PPO-based ionomer of the same quaternary ammonium chemistry (QPPO) and Nafion ionomer were prepared as for comparison (synthesis and characterizations in Scheme S1 and Figure S4). The ORR performances of three catalysts, before and after 250 min of potential hold at -0.5 V vs. Ag/AgCl reference electrode (0.498 V vs. RHE) are shown in Figure 1 and Figure S10 (typical *i-t* curves presented in Figure S11). The activity of the benchmark QPPO@Pt/C and Nafion@Pt/C catalysts decreased in



**Figure 2**. (a)  $H_2/O_2$  AEMFC performance data at 70 °C for MEAs containing the same AEM (TMImPPO, IEC = 1.65 mmol g<sup>-1</sup>)<sup>33</sup> but different ionomers in catalyst layers (non-crosslinked QPPO benchmark vs. thermally crosslinked CBQPPO). All catalyst layers contained 20 wt % ionomer. PtRu/C anode and Pt/C cathode electrocatalysts were used where all electrodes contained a metal loading of 0.5 mg<sub>metal</sub> cm<sup>-2</sup>. All gases were supplied at 1 L min<sup>-1</sup> and RH = 80% or 100%. The inserts present illustrations highlighting the differences in morphology between the two types of catalyst layer. (b) HFR data (stack area = 12.25 cm<sup>2</sup>) at 70 °C for MEAs containing the same AEM (TMImPPO, IEC = 1.65 mmol g<sup>-1</sup>) but different ionomers in catalyst layers.

activity as seen when comparing the pre- and post-*i*-*t* test half-wave potential ( $E_{1/2}$ ): 17 mV and 14 mV negative shift in  $E_{1/2}$  were observed (Figure 1a and Figure S10). Such activity loss is recognized to be due to the formation of large agglomerates of Pt/C NPs *via* coalescence.<sup>30, 31</sup> In contrast, the ionomer crosslink-immobilized CBQPPO@Pt/C catalysts maintained its ORR activity after the *i*-*t* test (Figure 1d), supporting our hypothesis that encapsulation of the Pt/C aggregates by the intercrosslinked ionomer networks leads to an increase in the durability.

To further prove this point, transmission electron microscopy (TEM) was employed to detect changes in morphology of the Pt/C NPs distribution in both catalyst layers during the *i*-*t* tests. As shown in Figure 1b and 1e, both the pre-*i*-*t* test catalysts (QPPO@Pt/C and CBQPPO@Pt/C) show a similar morphology with the Pt/C NPs being uniformly covered by ionomer thin films (mean size of Pt: 2.3nm(QPPO@Pt/C) vs 2.5nm(CBQPPO@Pt/C)). However, the Pt/C NPs in QPPO@Pt/C agglomerate into much bigger particles after the *i*-*t* test with accompanying isolation from the ionomer aggregates (Figure 1c, mean size of Pt: 4.8nm).

During the ORR, the weak physical contact between the ionomer and Pt/C aggregates is not sufficient to prevent such agglomeration and isolation (Ostwald ripening and coalescence phenomenon can still occur).<sup>32</sup> This leads to an increased fraction of large NPs and thus a decreased ORR activity (reflected in the data discussed in Figure 1a). In contrast. no visible morphological changes to CBQPPO@Pt/C catalyst layer were detected by TEM (Figure 1f, mean size of Pt: 2.7nm), which manifests itself in the unchanged ORR LSV data (Figure 1d). This data again supports our strategy where the ionomer crosslinking immobilization stabilizes the Pt/C catalyst during cell discharge.

Fuel cell performance (in-situ evaluation). Although CBOPPO@Pt/C exhibits high catalytic activity and durability in ex situ electrochemical tests, an initial in situ evaluation of its performance in a simple benchmark  $H_2/O_2$ single cell AEMFCs is useful in order to gauge its future potential for the desired application. To achieve this aim, the ionomer/catalyst dispersions (VBOPPO@Pt/C for cathode and VBOPPO@PtRu/C for anode) were sprayed on gas diffusion layers (GDL, Toray TDP-H-060) to fabricate gas diffusion electrodes (GDEs). A benchmark AEM (TMImPPO with an IEC value of 1.65 mmol g<sup>-1</sup>)<sup>33</sup> was sandwiched between the anode and cathode GDEs to fabricate a membrane electrode assembly (MEA). The MEA was assembled between two graphite bipolar flow field plates. To convert the VBQPPO@Pt/C cathode and VBQPPO@PtRu/C anode catalysts layers into crosslinkimmobilized forms (CBQPPO@Pt/C and CBQPPO@PtRu/C), the cell temperature was increased from 30 °C to 70 °C in 1 hour and held at 70 °C for 2 h with  $H_2$  and  $O_2$  gas feeds being supplied to anode and cathode electrodes, respectively (flow rates of 1 L min<sup>-1</sup>). Then, the MEAs were activated under a potentiostatic mode by discharging the cell at a constant voltage of 0.5 V at 70 °C until a steady current density was achieved for at least 30 min. Another benchmark single cell containing a QPPO@Pt/C cathode and a QPPO@PtRu/C anode was fabricated using the same procedure for comparison. Figure 2a presents the polarization curves for the two cells. The CBQPPO-based cell (crosslinked ionomer immobilized catalysts) achieved 1.02 W cm<sup>-2</sup> peak power density (at a current density of 1.91 A cm<sup>-2</sup>), which increased to 1.37 W cm<sup>-2</sup> (at 3.0 A cm<sup>-2</sup>) on addition of 0.1 MPa backpressures to the gas supplies, attributed to the uniform distribution of CBQPPO in the MEA as shown in Figure 4b. These AEMFC performance characteristics were significantly higher to those achieved with the use of QPPO-based ionomers (0.6 W cm<sup>-2</sup> at 1.05 A cm<sup>-2</sup>). These

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tests highlight that our strategy does translate into higher *in situ* performances.

correlates with changes in membrane ( $R_M$ ) and interfacial resistances ( $R_{ct} = R_{MGI} + R_{cat} + R_P$ ) in the MEA (quantified by



**Figure 3**. (a) Power density of the ionomer-based MEAs at 70 °C with the AEMFCs held at 0.5 V cell voltage recording one point of every hour (CBQPPO vs. QPPO benchmark). The insert SEM images show the CBQPPO@Pt/C and QPPO@Pt/C cathode catalysts both before and after this in situ short-term durability test. (b) In situ electrochemical impedance spectroscopy (EIS) analysis of the same MEAs with  $H_2/N_2$  anode/cathode feeds, before and after the short-term durability test.<sup>35</sup> The measured (msd) EIS-Nyquist data was simulated (sim) with a best-fit equivalent electrical circuit model (insert, error < 0.5 %), see details in Table S2.

Considering both cells contained the same AEM, the large differences AEMFC performances must primarily result from the differences between catalyst layers, e.g. reduced ohmic and mass transport losses, which proved by the high frequency resistance (HFR) data (Figure 2b). As discussed above, the CBQPPO@Pt/C catalyst layers were formed *in-situ* during initial fuel cell start-up and operation with both  $H_2/O_2$  being continuously supplied. The thermal crosslinking under high gas flow facilitates formations of a stable porous geometry (schematically illustrated in the top insert of Figure 2a), where the inter-crosslinked ionomer covers the interconnecting Pt/C aggregates for efficient fuel permeation and ion transport. However, the physically aggregated ionomer in QPPO@Pt/C catalyst layer has the tendency to form isolated ionomer phases reducing its effectiveness as a binder and anion conductor (bottom insert of Figure 2a). Meanwhile, the MEA with CBQPPO@Pt/C exhibits higher total pore volume and BET surface area than that with QPPO@Pt/C. This result provides further evidence of the ionomer-crosslinking induced formation of the porous geometry, thus facilitating efficient gas and ions transport (Table S3). Additionally, contact angle data (Figure S12) shows that the QPPObased electrode is much more hydrophilic than the CBQPPO-based electrode. This could lead to a propensity for the OPPO@PtRu/C anode to flood, which will impede gas transport and lower the AEMFC performance.

To highlight the ionomer crosslink-immobilized effect on *in situ* Pt/C stabilization, initial short-term durability tests with each MEA were conducted by discharging each AEMFC at a cell voltage of 0.5 V at 70 °C with no gas backpressures (Figure 3a). In contrast to the AEMFC containing the new *in situ* crosslinked CBPPO ionomer, a sharp decline in peak power density from 0.6 W cm<sup>-2</sup> to < 0.2 W cm<sup>-2</sup> was observed for the AEMFC containing the benchmark QPPO ionomer. The fuel cell power loss fitting the experimental EIS data (Table S2 in SI) both before and after the durability test using the equivalent circuit shown in Figure 3b). The simulated EIS for the QPPO based MEA indicates a small change in  $R_M$  (increased by 32.7 m $\Omega$ ) and a large change in  $R_{ct}$  (640 ± 2.6 m $\Omega$ ) leading to the observed decline in power density. In contrast, negligible increases in  $R_M$  (4.2 m $\Omega$ ) and charge transfer (52.9 m $\Omega$ ) resistances were elucidated for the *in situ* crosslinked CBQPPO-MEA.

Changes in the morphology of the GDEs observed during the SEM analysis (inserts in Figure 3a) can also be mapped to the EIS simulation capacitive data (Table S2). Notably, the index value  $(0 < Q_n < 1)$  of the constant phase element (Q) is believed to be inversely related with the porosity (of the GDE).<sup>36-39</sup> Thus, the large increases, after the durability test, in  $Q_n$  values (approaching to 1) for the QPPO-based GDE confirms the shutting off of the pores and agglomeration of components observed by SEM (bottom insert in Figure 3a) and the loss in AEMFC power. However, less significant increases in  $Q_n$  values were observed for the CBOPPO-based GDE, again explaining the retention in power with the use of this ionomer crosslinking immobilization concept. This high stability stems from the inter-crosslinking of the CBQPPO, which immobilized the Pt-based NPs and keeps the pores structure intact (for fast and easy transfer of fuel and high AEMFC performance). Furthermore, BET test was conducted to analyse the change of porosity in catalyst layer before and after fuel cell durability test. N2 adsorption isotherms of QPPO@Pt/C-based MEA (Figure S13 and Table S3) show a significant decline in total pore volume and BET surface area after the durability test. However, CBQPPO@Pt/C-based MEA maintains its porosity, suggesting that the inter-crosslinking of the CBOPPO enable to produce durable electrode catalyst layers with high porosity. The BET experiment result is consistent to the SEM analysis and the EIS simulation capacitive data in Figure 3.

delamination between the anode catalyst layer and the AEM is responsible for the performance decline (Figure



**Figure 4**. (a) The durability evaluation of  $H_2/O_2$  AEMFCs containing the different ionomers (CBQPPO vs. QPPO benchmark) with gradually decreasing relative humidity (RH). The AEMFCs used the same MEAs as described in Figure 2. The operating voltages were recorded as a function of time at 70 °C with the cell held at 0.6 A cm<sup>-2</sup> current density. (b), (d) Cross-sectional SEM and EDX analysis of CBQPPO-based MEA before and after the durability test. (c) *In situ* recorded HFR data of the  $H_2/O_2$  AEMFCs during the durability test.

It is well recognized that anode flooding and cathode drying out present critical durability limitations with the AEMFCs operation. To further investigate the benefits of ionomer cross-linking immobilization concept, we conducted evaluation of the durability of H<sub>2</sub>/O<sub>2</sub> AEMFCs containing the different ionomers (CBQPPO vs. QPPO benchmark) with gradually decreasing relative humidity (RH). Cell voltages were recorded as a function of time at 70 °C with the cell held at 0.6 A cm<sup>-2</sup> current density. As shown in Figure 4a, the CBQPPO@Pt/C-based MEA maintains its stability in the initial 25h with both anode and cathode gases 100% hydrated. The voltage tends to decrease slightly within the next 25h at 90 % RH, then, to decline speedily at a lower humidity (80%). In contrast to the CBQPPO@Pt/C-based MEA, a sharp decline in voltage from 0.7 V to < 0.2 V has been observed within 20h for the AEMFC containing the benchmark QPPO ionomer. Crosssectional SEM images of the CBOPPO@Pt/C-based MEA before and after durability test suggest that interfacial

R4b, d). The corresponding HFR data of each MEA in Figure 4c provide further evidence of the increased MEA resistance, possibly resulted from the interfacial delamination. However, we would like to emphasize that this is an initial catalyst layer development study where we focused on evaluating our hypothesis that the use of ionomer cross-linking immobilization concept to prevent Pt/C NP coalescence inside the electrode catalyst layers. We will of course take this concept forward in future studies by enhancing the membrane-electrode interfacial adhesion via chemical bound or electrostatic interactions.

#### CONCLUSIONS

In conclusion, this study describes an ionomer-assisted immobilization strategy for the production of durable electrode catalyst layers for use in alkaline anion-exchange membrane fuel cells (AEMFC). TEM microscopy show that on thermally triggered crosslinking, the developed ionomer forms a conductive, interconnected network that

covers the Pt/C nanoparticles (NP), thus significantly 1 preventing NP coalescence when catalyzing the oxygen 2 reduction reaction. In situ fuel cell durability tests determine that this thermal initiated cross-linking 3 4 ionomer-assisted immobilization strategy prevents significant Pt/C NPs coalescence without sacrificing the 5 porosity of the catalyst layer. The resulting AEMFC can 6 produce competitive peak power densities of 1.02 W cm<sup>-2</sup> 7 and 1.37 W cm<sup>-2</sup> at 70 °C with unpressured gases and with 8 0.1 MPa backpressures, respectively. 9

# 10 ASSOCIATED CONTENT

12 Supporting Information.

The Supporting Information is available free of charge onthe ACS Publications website at DOI: .

15 Additional data of the performance of recently reported 16 AEIs or AEMs for  $H_2/O_2$  alkaline membrane fuel cell, 17 additional experimental procedures and <sup>1</sup>H NMR spectra of 18 BPPO, VBN, VBOPPO, OPPO and CBOPPO, additional 19 variable temperature in situ FTIR spectroscopy of VBQPPO, additional electrochemical test for binder 20 loading, additional XRD, XPS and TEM data for the 21 characterization of Pt/C catalyst encapsulated by VBQPPO, 22 additional i-t chronoamperometric analysis, static water 23 contact angle test, BET test of ionomer-based MEA, and 24 additional simulation electrical equivalent circuit (EEC) fits 25 for the impedance spectra. 26

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#### Author Contributions

The manuscript was written through contributions of all the authors. All the authors have given approval to the final version of the manuscript.

#### Notes

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The authors declare no competing financial interest.

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