3D-Zipped Interface: In Situ Covalent-Locking for High Performance of Anion Exchange Membrane Fuel Cells

Xian Liang, Xiaolin Ge, Yubin He, Mai Xu, Muhammad A. Shehzad, Fangmeng Sheng, Rachida Bance-Soualhi, Jianjun Zhang, Weisheng Yu, Zijuan Ge, Chengpeng Wei, Wanjie Song, Jinlan Peng, John R. Varcoe,* Liang Wu,* and Tongwen Xu*

Polymerelectrolytemembranefuelcellsangenhighpowerusingapotentiallygreenfuel(H2)andzeroemissionsofgreenhousegas(CO2). However, significant mass transport resistances in the interface region of the membrane electrode assemblies (MEAs), between the membrane and the catalyst layers remains a barrier to achieving MEAs with high power densities and long-term stabilities. Here, a 3D-interfacial zipping concept is presented to overcome this challenge. Vinylbenzyl-terminated bi-cationic quaternary-ammonium-based polyelectrolyte is employed as both the anionomer in the anion-exchange membrane (AEM) and catalyst layers. A quaternary-ammonium-containing covalently locked interface is formed by thermally induced inter-crosslinking of the terminal vinyl groups. Ex situ evaluation of interfacial bonding strength and in situ durability tests demonstrate that this 3D-zipped interface strategy prevents interfacial delamination without any sacrifice of fuel cell performance. A H2/O2 AEMFC test demonstration shows promisingly high power densities (1.5 W cm−2 at 70 °C with 100% RH and 0.2 MPa backpressure gas feeds), which can retain performances for at least 120 h at a usefully high current density of 0.6 A cm−2.

1. Introduction

Polymer electrolyte membrane fuel cells, including proton exchange membrane fuel cells (PEMFCs) and anion exchange membrane fuel cells (AEMFCs), have made significant strides in the highly efficient and sustainable production of electrical power.[1–4] For PEMFCs, the use of perfluorosulfonic acid (PFSA) polymers for the preparation of membrane electrode assemblies (MEAs) has resulted in PEMFC-equipped commercial vehicles.[5–10] In the past few years, AEMFCs have made great breakthroughs in achieving high performances with peak power densities (PPDs) now common above 1 W cm−2 (Fuel cell data of recently reported anionomers (also known as anion exchange ionomers, AEIs) or anion exchange membrane (AEMs) for H2/O2 AEMFCs represented in Table S1, Supporting Information).[11–34] These studies are gradually narrowing the performance gap with PEMFCs due to the development of AEMs accompanied by high OH− conductivity as well as optimization of catalytic electrode designs and water balance. However, the lack of long-term AEMFC durabilities, particularly at high temperatures, low humidities, and/or with realistic current density operation, is a critical barrier to adoption into commercial markets (cf. PEMFCs).[35] This has spurred the recent, intense effort into the development of AEIs and AEMs both with the competitive OH− conductivities and alkaline...
stabilities that has led to a notable improvement in operational H₂/O₂ AEMFC durabilities. However, AEMFC durabilities that are high enough for commercial deployment is still far away compared to PEMFCs. In this context, this critical limitation is not exclusively due to the materials making up the MEAs, but also due to a poor understanding and control over the nature of the interface between the AEM and AEI that catalyze the reactant gases (H₂ or O₂), OH⁻ ions, and H₂O molecules ultimately dictates AEMFC performance. Among these, the interfacial contact between membrane and CLs will play an essential role. In the AEMFC, four H₂O molecules are produced at the anode for every four electrons transferred, with consumption of two H₂O molecules at the cathode. This can create a large water gradient between electrodes with undesirable flooding in the anode and drying out (chemical stability problems) in the cathode, without adequate back-diffusion of H₂O from anode to cathode (with the use of thin, high diffusivity AEMs). Our previous work showed that a significant water gradient causes excessive interface delamination between AEM and the anode CL, leading to increased OH⁻ transport resistances and a rapid decline in AEMFC durability. In a PEMFC, water flooding can be mitigated because only two water molecules are electrochemical produced at the cathode for every four electrons transferred. Therefore, the difference in water environment between AEMFCs and PEMFCs will accelerate the delamination of AEM-CLs. Hence, Kim, et al. proposed that membrane–electrode interfacial resistance, suggesting that the membrane–electrode interface had a tremendous impact on fuel cell durability. Furthermore, the use of PFSA copolymers (as PEM and ionomer in the CLs), which are basically the same class of polymer and have relatively low glass transition temperature (T_g), facilitates a flexible thermal lamination process to suppress problems with the interfacial delamination. However, the AEMCs commonly use hydrocarbon AEMs and AEIs that commonly have a high T_g, which leads to difficulty in achieving adequate interfacial bonding strength (thermal lamination of the AEM to CLs requires high temperatures that risks AEM/AEI chemical degradation).

We therefore propose that a more intelligent design of a stable AEM-electrode interface is required for AEMFCs containing hydrocarbon electrolyte components. Rather than using the conventional strategy (increasing physical friction of the interface), in this study, we propose a thermally triggered interlocking strategy to obtain a tightly bound interface via chemical bonding of the hydrocarbon AEM and hydrocarbon AEIs in the CLs of the electrodes. A quaternary ammonium-QA)-functionalized polyelectrolyte, containing pendant chains with terminal vinyl groups, was synthesized for the AEM and AEI used in the CLs (Figure 1A). A N₂/N₂ in situ operation of the resulting MEA lead to inter-crosslinking of the terminal vinyl groups, forming a covalently locked interface (this MEA is designated ZIL-MEA). This QA-containing interface provides both ionically conductive interconnections and prevents interfacial delamination during wet/dry cycling. Other two MEAs containing individually pre-crosslinked AEM and gas diffusion electrodes (GDEs) (or uncrosslinkable AEM and GDEs) were fabricated as the non-interfacial-locked benchmarks (designated as M-MEA or M-MEA-B). The importance of the covalently locked interface in stabilizing the MEA, while still allowing high power outputs is discussed below.

2. Results and Discussion

2.1. Synthesis for the Crosslinkable Polymer Precursor

The vinylbenzyl-terminated bi-cationic quaternary ammonium-poly(2,6-dimethylphenylene oxide)-PPO (VBBQPPO) AEI was synthesized in two steps (Figure 1A and Scheme S1, Supporting Information). The polymer precursor tertiary-amine-terminated quaternary ammonium-PPO (TMAQPPO) was synthesized via the Menshutkin reaction between the bromomethyl groups of bromomethylated PPO (BPOPO) (¹H NMR spectra shown in Figure S1, Supporting Information) and tertiary amine groups of N,N,N⁺,N⁻-tetramethyl-1,6-hexanediamine (TMHDA) (procedure represented in Figure 1A(I)), and ¹H NMR spectra shown in Figure S2, Supporting Information). The terminal tertiary amine groups further reacted with the –CH₂Cl of the 1-(chloromethyl)-4-ethenyl-benzene (VBC) to obtain VBBQPPO (the procedure represented in Figure 1A(II)). The presence of vinyl proton signals in ¹H NMR spectra (δ_H = 5.35, 5.85, and 6.75 ppm) demonstrate that the Menshutkin reaction proceeded successfully with the vinyl groups remaining unaffected (Figure S3, Supporting Information). As a comparison, the uncrosslinkable bi-cationic quaternary ammonium-based PPO (BQPPPO) was synthesized via the Menshutkin reaction between BPOPO and 6-(dimethylamino)-N-ethyl-N,N-dimethylethlan-1-aluminum bromide (DMAQA, synthesized by one-sided quaternization of TMHDA) (Scheme S2, Supporting Information) (¹H NMR spectra of DMAQA and BQPPPO are shown in Figures S4 and S5, Supporting Information). The ion-exchange capacity (IEC) of crosslinked vinylbenzyl-terminated bi-cationic quaternary ammonium PPO (CBBQPPO) and BQPPPO was both controlled at 2.00 ± 0.02 mmol g⁻¹.

In situ FT-IR analysis shows that the terminal vinyl groups are capable of thermally initiated inter-crosslinking (conversion of VBBQPPO into CBBQPPO shown in Figure 1A(III)). This reaction occurs gradually on increasing the temperature from 30 °C to 70 °C (Figure S6, Supporting Information). The intensity of the C=C stretching vibration at 1610 cm⁻¹ decreases with increasing temperature (Figure S6A, Supporting Information), while the intensity of the overlapping C-H vibrations at 2900–3020 cm⁻¹ increases due to the methylene and methine groups generated during the thermal crosslinking reaction (Figure S6B, Supporting Information). The thermally initiated crosslinking process was verified by studying the difference in the solubility of VBBQPPO and CBBQPPO in N-methylpyrrolidone (NMP). CBBQPPO exhibits poor solubility, accompanied by the formation of colloid, compared to the VBBQPPO AEI (Figure S6C,D). Therefore, the thermal lamination of corresponding MEA, using VBBQPPO as both AEM and AEI in the CLs, is hypothesized to form an interlocked interface for enhanced fuel cell durability (Figure 1B(VII)). Additionally, in the case of similar OH⁺ conductivity at different temperature (30–80 °C, Figure S7A), water.
Figure 1. Schematic of the 3D covalently locked interface strategy and micromorphology at different stages for fabrication of durable ZIL-MEA. A) Chemical scheme of the synthesis and inter-crosslinking of VBBQPO. B) Preparation of the 3D-zipped interface layer through the thermal inter-crosslinking between the terminal vinyl groups of the VBBQPO polymer located in the CLs and AEM. C) TEM image of the VBBQPO@Pt/C catalyst nanoparticles. D) SEM image of the CL of the GDE (the inset is the SEM surface image of the CL, and the scale of the inset is 1 μm). E) SEM cross-sectional image of the MEA after thermally triggered covalent crosslinking between the AEM and CL. F) SEM cross-sectional image of MEA, which contains VBBQPO membrane and VBBQPO@metal/C catalyst layer, after lamination at room temperature. G) Tensile stress–strain curves for shear testing of the dry ZIL-MEA, the dry M-MEA (pre-crosslinked benchmark), and the dry M-MEA-B (uncrosslinked benchmark); H) cross-section SEM coupled with EDX images of initial ZIL-MEA. I) CBBQPO Pt/C CL surface of the ZIL-MEA after the shear test, with highly deformed AEIs fibers. Commercial Pt/C and PtRu/C electrocatalysts were used in the cathode and anode, respectively. To ensure the consistency of the data, SEM images of the CL were of the VBBQPO@Pt/C catalyst layer (cathode), unless otherwise specified.
uptake (Figure S7B, Supporting Information) and swelling ratio (Figure S7C, Supporting Information) of CBBQPPO are lower than that of BQPPO, indicating that CBBQPPO has better dimensional stability to maintain the structural stability of the MEA. Evidence in support of this hypothesis is discussed in the following sections.

### 2.2. Fabrication of MEA with the 3D-Zipped Interface Layer

Each MEA was fabricated by sandwiching a VBBQPPO-based AEM between two VBBQPPO-treated CLs (containing commercial Pt/C and PtRu/C electrocatalysts at the cathode and anode, respectively, as these are the most commonly reported electrocatalysts and this is in line with the feasibility of the thermally initiated covalent-locking strategy). The VBBQPPO-catalyst dispersions were fabricated by ultrasonically dispersing the cata- lysts in a solution (mixed water and isopropyl alcohol) of VB- BQPPO. Transmission electron microscopy (TEM) images of the VBBQPPO-Pt/C dispersion shows that a thin AEI shell (amorphous feature without obvious lattice fringes) uniformly enve- lop the Pt/C nanoparticles (NP) (Figure 1C and Figure S8A, Supporting Information). The highly solvated VBBQPPO@Pt/C dispersion was sprayed onto gas diffusion layer (GDL) by inkjet- printing at room temperature to fabricate a GDE precursor (the procedure presented in Figure 1B[IV]). The atomic force micro- scope (AFM) phase image (Figure S8B, Supporting Information) and X-ray photoelectron spectroscopy (XPS) spectrum (Figure S8C, Supporting Information) further demonstrate the uniform loading of the AEI on the catalyst surface. Notably, the catalyst nanoparticles (NPs, blue-purple) were uniformly dispersed and connected within the AEI phase (yellow) to form a porous morphology (Figure S8B, Supporting Information), which provides a significant three-phase reaction interface for electrode reactions. In addition, the peak at 402.25 eV in XPS spectrum represents N 1s, which is assigned to the C–N species in the QA groups of VBBQPPO, providing initial evidence of VBBQPPO polymer-encapsulated catalysts (Pt/C NPs). Meanwhile, the VB- BQPPO AEM (15 μm thickness, 2.00 ± 0.02 mmol g⁻¹ of IEC) was prepared by the solution casting method. The VBBQPPO- based MEA was fabricated by assembling the AEM between the VBBQPPO@Pt/C cathode and VBBQPPO@PtRu/C anode GDEs at room temperature (the procedure presented in Figure 1B[V]). The low fabrication temperature did not induce the self-polymerization of the vinyl functionalities of VB- BQPPO because a loose boundary interface was clearly observed in the scanning electron microscopy (SEM) cross-sectional image of the MEA (Figure 1E and Figure S9A, Supporting Information).

An AEMFC single cell was fabricated by assembling the MEA between two graphite bipolar plates at anode and cathode. To in situ convert VBBQPPO-based MEA into crosslink-immobilized form (CBBQPPO@Pt/C, CBBQPPO@PtRu/C, and CBBQPPO AEM), the cell operating temperature was increased from 30 to 60 °C over 30 min and then maintained at 60 °C for 2 h, with N₂ gas provided to both the cathode and anode (flow rate of 0.5 L min⁻¹, 100% RH). The terminal vinyl groups in the MEA undergo a thermally initiated inter-crosslinking reaction by this pretreatment, with the reaction between the VBBQPPO-based AEM and CLs (containing VBBQPPO AEI) yielding a covalently locked zipped interface. This converts the weak physical contact interface into a dense 3D-zipped interface layer (3D-ZIL) with a thickness of 100–200 nm (Figure 1E,F and Figure S9B, Supporting Information). The SEM images also indicate that the inter-crosslinking does not sacrifice the porous geometry of the CLs, thus facilitating efficient gas and ions transport during fuel cell operation.

Cross-sectional SEM and energy-dispersive X-ray (EDX) spectrometry analysis provides further evidence of the thermally trig- gered formation of 3D-ZIL. The VBBQPPO-based MEA with 3D- ZIL (ZIL-MEA) exhibits a tight chemical contact between the AEM and CLs (Figure 1H). In contrast to the EDX mapping of the distribution of Pt and Ru atoms within distinct boundary regions, N atoms were uniformly distributed throughout the cross- section of the ZIL-MEA. This supports the formation of inte- grated MEA with the 3D-ZIL after the occurrence of the interfa- cial inter-crosslinking reaction, in line with our aim of preventing the delamination of the MEA during cell discharge. Without 3D- Zipped interface, M-MEA (precrosslinked benchmark) and M- MEA-B (uncrosslinked benchmark) were fabricated for compari- son purposes: especially in M-MEA, the VBBQPPO-containing AEM and GDEs were precrosslinked at 60 °C (CBBQPPO- based) prior to MEA assembly using the same procedure as for ZIL-MEA.

The interfacial bonding strength for a dry ZIL-MEA and a dry M-MEA/M-MEA-B were compared (Figure 1G and Table S2, Supporting Information). The average interfacial bonding strength was 0.79 N mm⁻¹ for M-MEA or 1.02 N mm⁻¹ for M-MEA-B, which was significantly higher for ZIL-MEA (1.30 N mm⁻¹). This demonstrates the robustness of the covalently locked ZIL struc- ture. When the interface layer tears on application of tension at both sides of the MEA, the AEI in the CLs is expected to deform (with stretching due to its rubber-like character). Changes in the internal morphology of the CLs were probed using SEM analysis both before and after the shear test (Figure 1I and Figure S8D–F, Supporting Information). The initial surface porous geometry of VBBQPPO@Pt/C CL is shown in Figure S8D, Supporting Information. The SEM image of the fractured CL surface for the ZIL-MEA shows AEI phase is severely deformed into filaments due to energy dissipation during delamination (Figure 1I and Figure S11, Supporting Information), with retention of bonding to the AEM. This fracture behavior contrasts with that of M-MEA (Figure S8F, Supporting Information, post-shear test), where the delaminated CBBQPPO@Pt/C CL retains a porous morphology that appears similar to the initial surface (Figure S8D, Supporting Information) and without evidence of filament formation. Therefore, the 3D-ZIL concept facilitates the dissipation of stress. The applied force is distributed throughout the 3D-ZIL, giving rise to a considerably enlarged energy dissipation zone (cf. M-MEA or M-MEA-B).

It is well known a major driving force for interfacial delamina- tion within MEAs during fuel cell operation is the tension generated at the interface between the membrane and CLs due to dissimilar extents of component volume expansions upon in situ variations in hydration.[30,31] Therefore, the uniformly enveloped AEI shells within a flexible 3D-ZIL is expected to suppress the in situ interfacial delamination of the MEA during fuel cell operation.
2.3. Fuel Cell Performance

Even though ZIL-MEA exhibits high interfacial bonding strength in ex situ shear tests, to estimate its application potential, an initial in situ H2/O2 AEMFC performance evaluation is necessary. After assembly between two graphite bipolar plates, the ZIL-MEA was activated under potentiostatic control (constant cell discharge of 0.50 V at 60 °C) until a stable power density was achieved. The benchmark single cell containing the M-MEA or M-MEA-B was fabricated and activated using the same procedure. Fuel cell performances of the three MEAs were characterized at 60, 65, and 70 °C. Figure S12 (Supporting Information) presents the PPD and corresponding high-frequency resistance (HFR) data as a function of temperature for three types of MEA. The ZIL-MEA exhibits an increasing PPD with temperature, whereas the performance of M-MEA declines sharply at a high temperature (no increase for M-MEA-B after 65 °C) due to increased mass transport resistance. As shown in Figure S13A, Supporting Information, three MEAs have comparable single cell performance at 60 °C (PPD of ZIL-MEA is 695 mW cm⁻², PPD of M-MEA-B is 700 mW cm⁻², and PPD of M-MEA is 649 mW cm⁻²). The numerical discrepancy in PPD (ΔP) between ZIL-MEA and M-MEA is 46 mW cm⁻², and which between ZIL-MEA and M-MEA-B (ΔP) is only 5 mW cm⁻². The corresponding polarization curves in Figure 2A show that the performance difference is mainly derived from an increase in HFR at current densities above 0.97 A cm⁻² with the M-MEA. An increase in temperature should lead to better oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) kinetics. Hence, raising the operating temperature to 65 °C leads to an increased PPD with the ZIL-MEA (increases to 1008 mW cm⁻²). However, the PPD of M-MEA and M-MEA-B did not increase to such a large extent (761 mW cm⁻² for M-MEA-B and 926 mW cm⁻² for M-MEA-B), leading to ΔP being an increased 247 mW cm⁻² and ΔP being an increased 82 mW cm⁻² (Figure S13B, Supporting Information). Notably, ΔP increased sharply to 642 mW cm⁻² (ΔP increased to 137 mW cm⁻²) at 70 °C due to the rapidly increased HFR of M-MEA and M-MEA-B (Figure 2C and Figure S13C, Supporting Information). ZIL-MEA maintains a low HFR over the entire AEMFC test temperature range (60–70 °C) due to the stable 3D-ZIL (see cartoon in Figure 2D), which sustains facile OH⁻ transport between the AEM and CLs. On the contrary, the degradation in AEMFC performance at higher temperatures with the M-MEA or M-MEA-B supports the ex situ data where MEA delamination is more likely (especially at high current density due to increased water production at the anode) (Figure 2E). Changes in the internal resistance (IR) of these three MEAs, estimated by the slope of the Ohmic region (slope = ΔV/ΔI, mΩ) in the polarization curves (Figure S13D–F, Supporting Information), provides further evidence that the influence of 3D-ZIL on the fuel cell performance is mainly due to mass transport resistance. The IR of ZIL-MEA gradually decreases during AEMFC test (19 mΩ, 60 °C; 16 mΩ, 65 °C; 11 mΩ, 70 °C) with slowly IR decrease of M-MEA-B (19 mΩ, 60 °C; 17 mΩ, 65 °C; 14 mΩ, 70 °C), while the IR of M-MEA increases sharply (19 mΩ, 60 °C; 19 mΩ, 65 °C; 33 mΩ, 70 °C). Especially, ZIL-MEA shows a competitive PPD with 0.2 MPabackpressure gas feeds (1.5 W cm⁻² at 70 °C with 100% RH, shown as Figure 5A), which is the highest reported for PPO-based polymer materials used in AEMFCs (Table S1, Supporting Information).

To further prove this result, SEM investigations were used to detect morphological changes in the AEM-CL interfaces of both MEAs during the AEMFC operation (Figure 2D,E). ZIL-MEA maintains its tight contact interface during AEMFC testing (the duration of tests being ≈10 h) at the higher operating temperatures. In contrast, higher temperature degrades the interface integrity in M-MEA due to strong rigidity of the cross-linked AEM, resulting in clear delamination. This result is consistent with the change in ΔP and HFR data discussed above. Considering both ZIL-MEA and M-MEA possessed the same catalysts, AEIs and AEM, the significant difference in AEMFC performances must come mainly because of the difference in the AEM-CL interfaces. The stable 3D-ZIL, with reduced mass transport and ohmic losses, facilitates high AEMFC performance, especially at higher temperatures and discharge current densities. The strategy tested (in situ 3D-ZIL formation) does protect the structural integrity of the MEA to help maintain high performances.

2.4. Durability Evaluation at a Constant and Shifted Relative Humidity

To further investigate the promise of the 3D-ZIL concept, initial durability testing of both MEAs was conducted by discharging each benchmark in an H2/O2 AEMFC at a current density of 0.6 A cm⁻² at 70 °C with 100% RH (no backpressure) gas supplies (Figure 3A). In contrast to the ZIL-MEA, a sharp drop in cell voltage from 0.73 to <0.25 V (concurrent with the rapid rise of HFR) was observed for the benchmarks M-MEA-B and M-MEA, which is consistent with the results of the interfacial shear test. Although chemical degradation has an important impact on MEA failure, considering that CBQPPO and BQPPO have simultaneous degradation in alkaline environment comparable OH⁻ conductivity (Figure S7A, Supporting Information) and hydroxide stability (Figure S7D, Supporting Information), the worse durability of M-MEA (than that of M-MEA-B) was mainly caused by the faster interfacial delamination due to high rigidity of CBQPPO mixing. Our recent study has proven that the AEMFC performance attenuation related to the increase of AEM resistance (Rₛ) and contact resistances (R = Rₛ + Rₛ) in the MEA both before and after the durability evaluation test (RMGI refers to the charge-transfer resistance (R) between the membrane-GDE interface (MGI), while “Rₛ + Rₛ” refer to the charge-transfer resistance values at the catalyst–polymer interface within the GDE; quantified data are given in Table S3, Supporting Information). The equivalent circuit model is shown in Figure 3B,26) The simulated electrochemical impedance spectroscopy (EIS) data for M-MEA demonstrates a 65% increase in Rₛ (71% for M-MEA-B), a 34% increase in Rₛ (59% for M-MEA-B), but a substantial 930% increase in Rₛ (579% for M-MEA-B). In contrast, a negligible 18.8% increase in Rₛ (6.6 mΩ) increase is observed for the ZIL-MEA, again supporting negligible in situ interfacial delamination with the ZIL-MEA. IR and HFR data during fuel cell test and the impedances proposed in EIS analysis both prove that the 3D-ZIL is essential to the stable and efficient transport of ions between the polymer electrolyte components in the cell.

Furthermore, the morphological changes at the AEM-CL interface in the MEAs can also be matched with the simulated EIS data
Figure 2. Single-cell H₂/O₂ AEMFC performance data at 60, 65, and 70 °C for ZIL-MEA, M-MEA, and M-MEA-B with the corresponding cross-sectional SEM images of the post-test interfaces. A–C) Polarization curves and HFR data (geometric electrode area 12.25 cm²) at the indicated test temperatures. D) Schematic for the OH⁻ ion conduction pathway within the ZIL-MEA and the cross-sectional SEM images of cathode side of the ZIL-MEA after AEMFC testing at the indicated temperatures. E) Schematic for the OH⁻ ion conduction pathway within the M-MEA and the cross-sectional SEM images of cathode side of the M-MEA after AEMFC testing at the indicated temperatures. The AEI content for all CLs was 20 wt%. Electrocatalysts were used with a metal loading of 0.5 mg metal cm⁻² (PtRu/C in anode and Pt/C in cathode). The flow rate of all gases was controlled at 0.5 L min⁻¹.

(Table S3, Supporting Information) and the interfacial bonding strength (Figure 1G). Compared with the initial cross-sectional morphology of M-MEA-B and M-MEA (Figures S9 and S10, Supporting Information), due to the formation of crevice (Figure S16, Supporting Information, high-magnification images of Figure 4D,F), the physical contact interface in M-MEA-B or M-MEA was observed to crack during durability test, which correlates with the decline in AEMFC performance characteristics discussed above. In contrast, the ZIL-MEA showed that 3D-ZIL again maintained a tight connection between the AEM and CL (Figure 4B). More detailed SEM imaging of the post-durability test morphology for the ZIL-MEA is presented in Figure S14, Supporting Information. Moreover, changes in the internal structure of the MEAs were investigated using computed micro-X-ray tomography. Benefitting from the 3D-ZIL, even after 120 h durability test, the AEM and CLs in ZIL-MEA remain tightly bonded with no visible cracks in any position through a 3D reconstruction of the MEA sample volume dataset (Figure 4A; Videos S1 and S2, Supporting Information). While the ZIL-MEA maintains integrity, the M-MEA clearly experienced delamination events.
Figure 5. An initial RH cycling durability evaluation. A,B) H₂/O₂ AEMFC performance data at 70 °C (electrode area 12.25 cm²) for the ZIL-MEA with different RHs (60–100%) gas supplies. C,E) The macroscopic optical appearance of the front (C) (the inset is VBBQPPO ionomer solutions in ethanol) and profile (E) of ZIL-MEA after 2 days of AEMFC RH cycling. D) RH cycling of the ZIL-MEA during H₂/O₂ AEMFC discharge at 0.6 A cm⁻². The detailed RHs, backpressures of the anode and cathode gas are same in all AEMFC performance tests.

Figure 3. Initial constant RH durability testing. A) H₂/O₂ AEMFCs durability evaluation results with ZIL-MEA, M-MEA, and M-MEA-B at 70 °C and 100% RH (cell maintained at a constant 0.6 A cm⁻² cell discharge). B) In situ EIS conducted on the ZIL-MEA, M-MEA, and M-MEA-B before and after the constant current discharge test. The full equivalent circuit diagram can be expressed as $LR_M(Q_{MGI}R_{MGI})(Q_{cat}R_{cat}(Q_PR_P))$, where the contribution of the electrically conductive fuel cell components (including electrodes) was modeled by the inductance element ($L$) and $R_M$ represents the ohmic resistance of the AEM. The first circuit, $(Q_{MGI}R_{MGI})$ attributes the charge-storage ($Q = constant phase element$) and charge-transfer resistance ($R$) between the MGI. The second circuit, $(Q_{cat}R_{cat}(Q_PR_P))$ represents the charge-storage and charge-transfer resistance values at the catalyst–polymer interface within the GDE. Details of the measured (msd) and best-fit simulated (sim, equivalent electrical circuit model) EIS–Nyquist data are given in Table S3, Supporting Information (insert, error <0.5%).
during the durability test (Figure 4E). Meanwhile, due to the better molecular chain flexibility of BQPOPO (than CBBQPOPO), the M-MEA-B partially experienced delamination (Figure 4C).

AEMFC performance and durability can be limited by the water differential across the MEA, with the potential for undesirable flooding in the anode and dry out of the cathode. Figure 5A shows \( \text{H}_2/\text{O}_2 \) AEMFC performance of the ZIL-MEA at 70 °C with different RH gas supplies. Only a minor performance loss was observed with a drop of RH to 60%, while the HFR showed very little variation (Figure 5B); this illustrating that no mechanical degradation occurs on changes of RH due to the tight contacts (by design) at the interface between the AEM and CLs.

To further probe this RH resilience, the durability of the ZIL-MEA-based \( \text{H}_2/\text{O}_2 \) AEMFC was studied during RH cycling (Figure 5D). The ZIL-MEA maintained cell voltage and HFR in the initial 10 h with 100% RH gases supplies to both the anode and cathode. Voltage fluctuations (≈0.1 V amplitude) were observed during the subsequent 10 h when the RH was lowered to 80%. However, as the RH was further decreased to 60%, the magnitude of the voltage fluctuations increased and then gradually decreased on continued operation at 60% RH. The low ion conduction at low moisture is responsible for this decreasing trend. The RH was then gradually increased again to 80% and 100%. During the final period of operation at 100% RH, the AEMFC voltage and HFR had returned to its initial level (with a slight increase in voltage noise). However, these results do show that the ZIL-MEA is resilient to RH cycling, which is essential to the stable and efficient transport of ions between the polymer electrolyte components in the cell (Figure 5C,E and Figure S15, Supporting Information). Therefore, compare with the
reported conventional strategy (increasing physical friction of the interface) for AEMFCs, our thermally triggered interlocking strategy can better prevent the interfacial delamination in the MEA at high temperature and RH cycling during fuel cell test.

3. Conclusions
We present a thermally triggered covalent-locking strategy to fabricate a durable MEA in AEMFCs. SEM images and 3D reconstruction using computed micro-X-ray tomography confirm thermal inter-crosslinking between the AEM and CLs, which creates a stable 3D-zipped interface. Ex situ evaluation of interfacial bonding strength shows that the 3D-ZIL significantly improves the mechanical properties of the MEA. In situ fuel cell durability evaluations (constant current with and without gas humidity cycling) demonstrate that the 3D-ZIL prevents interfacial delamination during AEMFC operation, thus maintaining sufficient ion and reactant mass transport in the MEA, even with high current density cell discharges. A competitive AEMFC peak power density of 1.50 W cm$^{-2}$ is demonstrated at 70 °C and 0.2 MPa gas-back pressures. Initial durability evaluations show that the ZIL-MEA-based AEMFC can maintain its performance for at least 120 h while discharging at 0.6 A cm$^{-2}$ with the integrity of ZIL-MEA.

For ionomer research, some current state-of-the-art high IEC ionomers, such as poly(arylpiperidinium), side-chain-type polyfluorene, with excellent power density are actually faced with insufficient molecular weight or over-large swelling. The present in situ crosslinked strategy can be a large swelling. The present in situ crosslinked strategy can be a potential solution for these high IEC ionomers for durable AEM-FCs or AEM water electrolyzer (AEMWEs).

4. Experimental Section

Preparation of BPPO: Bromoethane (4.2 mL) in ethanol (30 mL) was added dropwise to a stirred solution of TMHDA (12 mL) in ethanol (150 mL). After stirring for 24 h at room temperature, ethanol was evaporated in vacuum followed by the washing of the residue by ether for several times. Then, the white precipitate was added to acetone (50 mL) after filtration. As acetone was removed by filtration, the product was collected as white powder. Recrystallization from acetone/ether mixture was used to obtain pure DMAQA.

Preparation of VBBPPO: VBC (6.0 mL) was added to a solution of TMAQPPO (2.0 g) in NMP (30 mL). After being stirred for 24 h at room temperature, the crude VBBPPO powder was precipitated into ether and recovered by filtration. The slightly yellow powder was then washed with ether for at least a further three times and dried under vacuum at room temperature for 48 h.

Preparation of DMAQA: Bromoethane (4.2 mL) in ethanol (30 mL) was added dropwise to a stirred solution of TMHDA (12 mL) in ethanol (150 mL). After stirring for 24 h at room temperature, ethanol was evaporated in vacuum followed by the washing of the residue by ether for several times. Then, the white precipitate was added to acetone (50 mL) after filtration. As acetone was removed by filtration, the product was collected as white powder. Recrystallization from acetone/ether mixture was used to obtain pure DMAQA.

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Measurement of the Interfacial Bonding Strength: The interfacial bonding strength for both ZIL-MEA and M-MEA based laminates were characterized in air using a Q800 dynamic mechanical analyzer (DMA, TA Instruments) with a stretch rate of 0.5 N mm$^{-1}$. The assembly involved two GDEs (20 × 5 mm$^2$) where a quarter of each was laminated at 60 °C and

Fabrication of ZIL-MEA: ZIL-MEA was fabricated by assembling VBBPPO-AEM with VBBPPO-GDEs first and then in situ crosslinking during break-in procedure under 60 °C for 2 h. In contrast, M-MEA was fabricated by assembling precrosslinked CBBPPO-AEM with CBBPPO-GDEs. The resulting tough and transparent AEMs were peeled off with a controlled thickness of 15 ± 1 μm.

Fabrication of MEAs: The MEAs were prepared by the GDE method. 10.2 mg Pt/C catalyst (HISPEC 9100, cathode) or PtRu/C catalyst (HISPEC 10 000, anode) (both 60 wt% metal content, produced by Johnson Matthey Co.) were ultrasonically mixed with 100 mg deionized water, 400 mg 2-propanol, and 51.1 mg AEi ethanol solution (5 wt%, VBBPPO or BPPO) to obtain well-dispersed ink (catalyst:AEi = 4:1). The AEMs and AEIs (VBBPPO or BPPO) in the CLs have same IEC value (2.0 ± 0.02 mmol g$^{-1}$), water uptake, and swelling ratio. The resulting catalyst inks were inkjet-printed onto the GDEs (Toray TGP-H-060) to control loadings of 0.5 mg$\text{cm}^{-2}$ of metal loading (12.25 cm$^2$ of electrode area for both anode and cathode) to obtain the relevant GDEs. The prepared GDEs and AEM were then immersed in aqueous 1 m NaOH solution to convert them to the OH$^{-}$ form. The resulting GDEs were then placed on each side (PtRu/C at anode and Pt/C at the cathode) of the AEM to fabricate the MEA.

Electron-Microscopy Analyses:
- A Hitachi-7700 (working at 100 kV) was used to record TEM micrographs of the catalyst powders. The surface morphology of the catalyst layers (anode or cathode) and the cross-section sandwich structure (catalyst layer and membrane) were characterized by cold field environmental scanning electron microscopy (Hitachi, SU8220).
- Energy-Dispersive X-ray Spectrometry: To analyze the element distribution of nitrogen, carbon, platinum, and ruthenium in two MEAs, energy dispersive X-ray spectrometry was collected using an X-max 80 (Oxford Aztec).

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X-ray Photoelectron Spectroscopy: Powder X-ray diffraction patterns of catalyst samples were conducted on X-ray photoelectron spectroscopy (ESCALAB 250 System) using Al Kα excitation radiation (1486.6 eV).

Atomic Force Microscopy: The surface morphology of VBBPPO@Pt/C catalyst was further characterized using a Bruker high-resolution AFM powered by PeakForce Tapping (Bruker Dimension icon with ScanAsyst).

3D Characterization of the MEAs: The computed micro-X-ray tomography (micro-CT) tests were performed on a lab-based X-ray CT system (Zeiss Xradia Versa 520, Carl Zeiss XRM). Samples were mounted on the holder with aluminum tube as the adapter. This was rotated horizontally by ±180°, pausing at discrete angles to collect 2D projection images, which were then combined to produce a 3D reconstruction of the sample’s volume dataset. The ZIL-MEA and M-MEA samples (post durability test) were imaged with scanning resolutions of 0.7 μm per voxel, respectively, using a scanning energy of 50 kV per 4 W.
5 MPa for 2 h. The test was conducted by pulling the two un laminated sides in opposite directions. For each sample, the tests were repeated five times at 0% RH state, and the curves presented above average curves. The interfacial bonding strength of the interface is defined as the force required to separate the interface normalized by the specimen width (5 mm).

**Single-Cell Performance Test:** Single-cell AEMFCs were tested using an 850e fuel cell test station (Scribner Associates, USA) in a galvanostatic mode with cell temperatures of 60 to 70 °C. To fully convert VBBQPPPO in the MEA to the thermally crosslinked CBQPPPO form, the cell temperature was increased slowly from 30 to 60 °C over 1 h and held at 60 °C for 2 h with N2 gas feeds (100% RH, 0.5 L min\(^{-1}\)) being supplied to both anode and cathode. After this MEA curing stage, the gases were switched to H2 and O2 gas (100% RH, 0.5 L min\(^{-1}\), anode and cathode, respectively) followed by an electrochemical activation stage (potentiostatic discharge at 0.50 V cell voltage and 60 °C until the current density stabilized for at least 30 min). After the break-in procedure, the cell voltage at each controlled current density was recorded at different temperatures (60, 65, or 70 °C) or RH (60%, 80%, or 100% RH both in anode and cathode sides)—these RHs were calculated from the dew points and cell temperature (with no back-pressure) of the gases being used. High frequency impedances (HFR) at each current density were recorded at a frequency of 1000 Hz during AEMFC testing.

**Durability Test:** The durability test was conducted at 70 °C with a flow rate of 0.5 L min\(^{-1}\) for both H2 and O2 at RH = 100% and with no back-pressure. The operating voltages were recorded as a function of current density (at 70 °C with the cell held at 0.6 A cm\(^{-2}\) constant current density galvanostatic discharge.

The RH Cycling Evaluation: The RH cycling evaluation was conducted at 70 °C with a flow rate of 0.5 L min\(^{-1}\) for both H2 and O2 with no back-pressure with changes in the RH after every 10 h. The operating voltages were recorded as a function of time at 70 °C with the cell held at 0.6 A cm\(^{-2}\) constant current density galvanostatic discharge.

**Electrochemical AC Impedance Spectroscopy Analysis:** EIS analysis is a well-established experimental technique which can in situ elucidate polarization effects in the fuel cell using AC stimuli. Simulation of the EIS data can further quantify the deconvoluted capacitive and resistive contributions of both the membrane and interfaces in the single fuel cell (Table S3, Supporting Information), including prediction of the change in the morphology of the MEAs. Herein, the EIS analysis for the MEAs was performed for a single AEMFC containing the MEA under test, a pair of gaskets, and a pair of graphite blocks. Flow rates for both H2 and N2 gases (at the anode and cathode, respectively) were supplied at a constant 0.5 L min\(^{-1}\). Temperatures for the cell and gases were controlled at 70 °C. All the testing parameters such as gas flow rates and testing temperature were controlled using the Scribner 850e fuel cell test station. The EIS analysis was performed by an externally connected Autolab workstation (PGCST 302N, Metrohm, The Netherlands) controlled by Nova 2.1.2 software. Under potentiostatic EIS testing mode, a small sinusoidal potential perturbation (10 mV amplitude, f range 0.01–100 kHz) was applied between the cathode and anode plates, and the AC current response was measured. Impedance data was presented as Nyquist plots and were also simulated using ZSimpWin electrochemical analysis software (PAR Inc., USA). The electrical equivalent circuit (EEC) model selected was based on the possible physical replica comprising membrane and GDE. The best fitted results for each EEC parameter are presented in Table S3, Supporting Information.

**Conflict of Interest**

The authors declare no conflict of interest.

**Authors Contribution**

X.L. and X.L.G. contributed equally to this work. L.W., J.R.V., and T.W.X. conceived the project. L.W., T.W.X., and X.L. designed the experiments. X.L. and X.L.G. prepared the MEAs and conducted corresponding tests. X.L.G. and Y.B.H. helped with ionomers preparation. M.A.S. and M.X. helped with EIS testing. F.M.S. helped with sample preparation for SEM. R.B.-S. helped with XPS and fuel cell testing. J.J.Z. and W.S.Y. prepared the membranes, collected and analyzed the data. Z.J.G. helped with AFM testing. C.P.W. and W.J.S. helped with membrane preparation and conducted TEM and SEM testing. X.L. and X.L.G. wrote the original draft. L.W., J.R.V., and T.W.X. further wrote and revised the manuscript. All authors contributed to the data analysis.

**Data Availability Statement**

Research data are not shared.

**Keywords**

catalyst layers, fuel cells, membrane electrode assembly, interfaces, ionomers

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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