

Correlating high temperature thin film ionomer electrode binder properties to hydrogen pump polarization

Gokul Venugopalan[†], Deepra Bhattacharya[†], Subarna Kole[†], Cameron Ysidron[†],
Polyxeni P. Angelopoulou[‡], Georgios Sakellariou[‡], Christopher G. Arges^{†*}

[†]Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803

[‡]Department of Chemistry, National and Kapodistrian University of Athens, 15771 Athens,
Greece

Email: carges@lsu.edu

Manufacturing of IDEs with nanoscale Pt

The method to manufacture IDEs is based upon the work by Arges *et al.*^{1,2}. The procedure for block copolymer (BCP) self-assembly on IDEs was adopted from Arges *et al.*^{3,4} Lamella-forming poly(styrene-*block*-2-vinyl pyridine) (PS_{40k}-*b*-P2VP_{44k}) was self-assembled on gold current collector IDEs. Briefly, a non-preferential layer was grafted on the IDE surface by spin coating (4500 rpm for 45 s) 1 wt% of mono-hydroxy terminated poly(styrene-*random*-2-vinyl pyridine) (OH-PS-*r*-P2VP, 80% styrene weight fraction) in toluene and subsequently heating the sample at 200 °C for 10 minutes under nitrogen. Unreacted OH-PS-*r*-P2VP was removed by immersion and sonication in toluene (3 cycles). Then, 1.5 wt% of PS_{40k}-*b*-P2VP_{44k} in toluene was spin coated on the IDE with a non-preferential layer at 4000 rpm for 45 s. The resultant BCP film was solvent annealed with acetone vapor in a flow chamber, where the microphase separation and formation of perpendicular lamellae occurred. The IDE with self-assembled BCP film was thereafter exposed to iodomethane vapors for 4 hours, alkylating the

pyridine moiety in the BCP film via a Menshutkin reaction. Next, the IDE with alkylated BCP film (poly(styrene-*block*-2-vinyl pyridine/N-methyl pyridinium iodide) (PS-*b*-P2VP/NMP⁺I⁻) was immersed in H₂PtCl₆ (10 mM aq.) for 3 hours to exchange the iodide counterions with chloroplatinate [PtCl₆]²⁻. The chloroplatinate infiltrated BCP film was then subjected to oxygen plasma treatment (Oxford Plasma Lab System 100 RIE tool) at 50 sccm gas flow rate, 70 mTorr chamber pressure, and 50W RF power for 7.5 min, removing the sacrificial polymer template and oxidizing the chloroplatinate to platinum oxide. Finally, the platinum oxide nanowires were treated with argon plasma at 50 sccm gas flow, 90 mTorr chamber pressure, and 50 W RF power for 15 s to convert the platinum oxide to metallic platinum.³ At the end of the process, periodic and dense 22 nm diameter platinum nanowires with an out-of-plane thickness of 28 nm were covered across the IDE chip. The platinum nanowires do not short the cell because interconnected domains within the platinum nanostructure terminate within a few microns and the distance between the electrode teeth in the IDE is 100 μm.⁵ The loading of nanostructured Pt was calculated using a Perkin Elmer Optima 8x00 Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) after microwave digestion of the nanostructured Pt (developed on 1cm² Si wafer) in 10 ml aqua regia (mixture of 7.5 ml of 37% HCl and 2.5 ml of 69%).

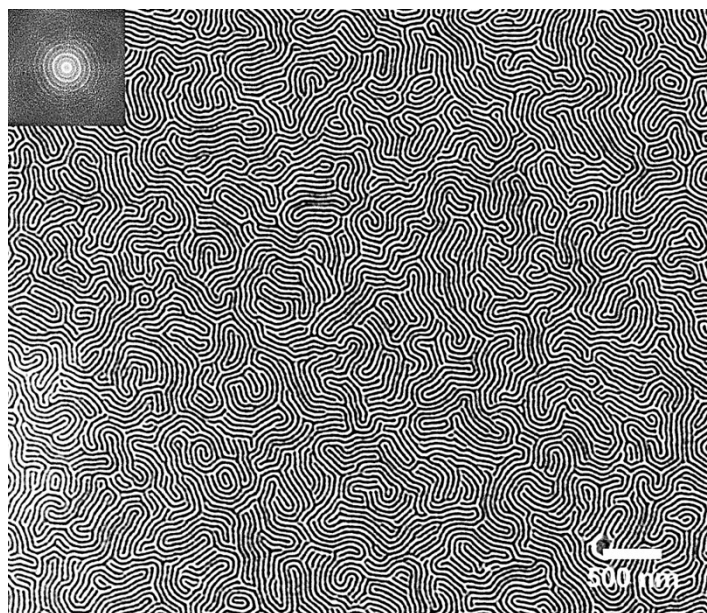


Figure S1. SEM image of platinum nanowires on IDEs from self-assembled block copolymer templates. The inset on top left shows the Fast Fourier Transform. The geometric platinum loading on the IDE is $9.6 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$.

HOR/HER on IDEs using chronoamperometry

HOR/HER studies with IDEs were carried out in a custom-built stainless-steel chamber that can be sealed and that has heating capabilities. This chamber has inlets and outlets for gas feeds and electrical connections. **Figure S2** provides a picture of the chamber. After purging the chamber with dry nitrogen gas for 15 minutes at 1 SLPM, the flow of dry nitrogen to the chamber was stopped and a continuous flow of dry hydrogen was fed to the chamber 1 SLPM. A Gamry Reference 3000 Potentiostat/Galvanostat was used for obtaining the polarization curves for HOR/HER on IDEs containing nanoscale platinum and with different thin film ionomers. Chronoamperometry experiments were performed for generating the polarization curves. These experiments used 0.05 V potential steps and held the voltage for 30 seconds at each step to attain a steady-state current value. The chronoamperometry experiments were conducted from 0 V to 0.7 V.

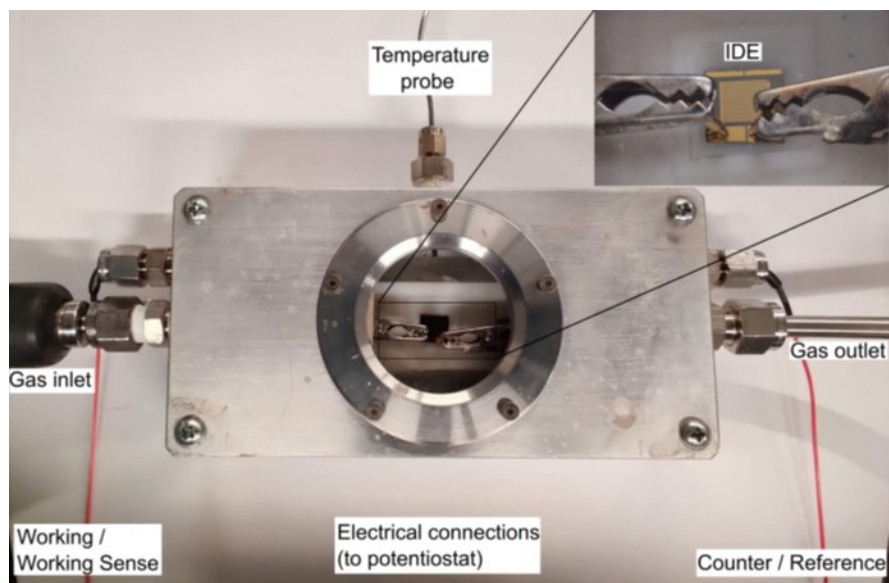


Figure S2. Custom-built flow chamber for performing HOR/HER studies on IDEs.

Synthesis of QPPSf (quaternary benzyl pyridinium poly (arylene ether sulfone))

QPPSf was synthesized by converting the chloromethylated groups in chloromethylated poly (arylene ether sulfone) (CMPSf) to quarterly benzyl pyridinium groups. CMPSf was synthesized by Friedel-Crafts reaction.⁶ **Figure S3a** depicts the synthesis scheme. 20 g of Udel[®] poly (arylene ether) sulfone (PSf) was dissolved in 1000 mL of chloroform in a round bottom flask at 40 °C. Once the PSf was completely dissolved, 13.6 g of paraformaldehyde and 60 mL of chlorotrimethylsilane was added. The reaction temperature was further increased to 55 °C, the flask was sealed with a rubber septum and filled with nitrogen. To the sealed flask, 1050 μL of SnCl_4 was added. The reaction was monitored by withdrawing a sample from the flask, to control the degree of functionalization (DF), i.e., the addition of chloromethylated groups per repeat unit. The sample was precipitated in methanol (5:1 methanol to sample ratio). The precipitate obtained was dried and analyzed via ^1H NMR to calculate the DF. Once the desire DF

was obtained, the reaction solution in the flask was precipitated in methanol (5:1 volume ratio). The precipitate was filtered and dried. To convert the CMPSf to QPPSf, CMPSf was dissolved in NMP (5 wt.%). To the CMPSf solution, pyridine was added (3:1 mole ratio) and reacted overnight, to convert the chloromethylated groups to quaternary benzyl pyridinium chloride groups. The resulting QPPSf solution (5 wt.%) were used for ionomer solution.

Synthesis of PTFSPA (poly(tetrafluorostyrene phosphonic acid-co-pentafluorostyrene))

The addition of phosphonic acid to poly(pentafluorostyrene) was carried out following the procedure by Atanasov *et al.*⁷ (**Figure 3b**). 1 g PPFS (200 kDA M_w) (5.2 mmol) was dissolved in DMAc (4 g) at room temperature in a round bottom flask equipped with magnetic stirrer, reflux condenser and an oil bath. The temperature was increased to 170 °C and tris(trimethylsilyl) phosphite (TSP; 1.07 g, 3.6 mmol) was added dropwise, and the reaction was carried out for 16 hours. The resulting polymer solution was poured into DI water and the white solid was precipitated. The white solid polymer was refluxed in DI water for 30 minutes, by changing fresh water every 10 minutes, followed by boiling in 2 wt.% phosphoric acid solution and washing with DI water till a neutral pH was obtained. The PTFSPA white solid was dried in vacuum oven overnight. The phosphonic acid tethered groups were confirmed via ³¹P NMR. A 70% degree of phosphonation was assumed theoretically, controlled via TSP to PPFS ratio.^{8,9} The resulting PTFSPA was dissolved in DMSO to make an ionomer solution (5 wt.%).

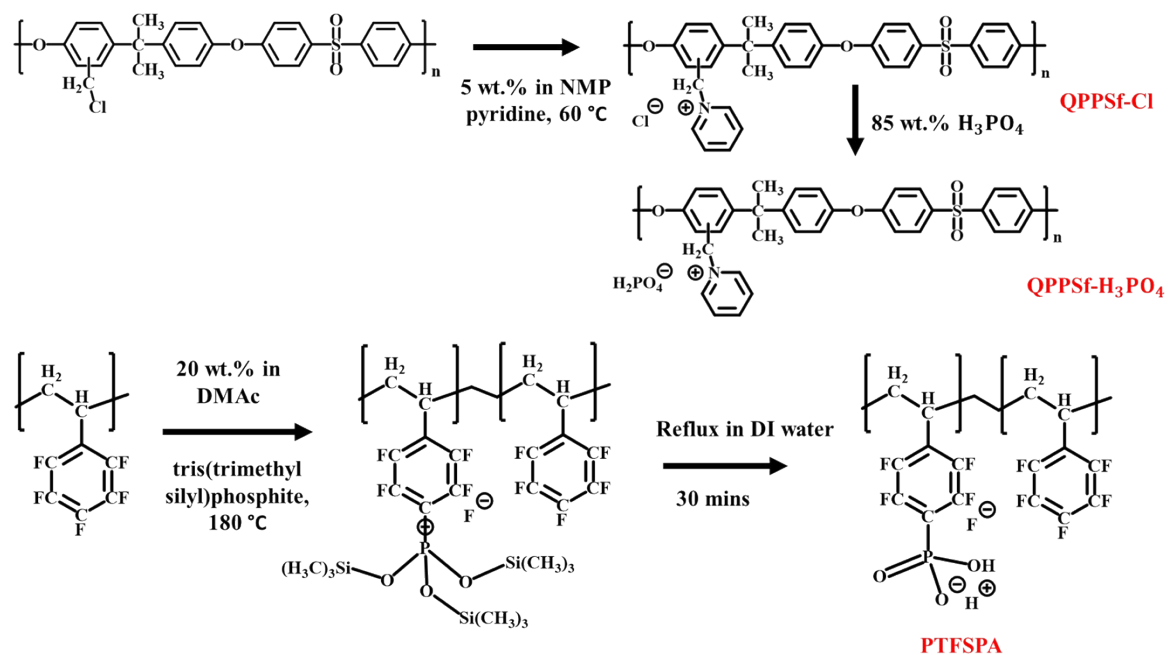


Figure S3. Synthesis schemes for a.) QPPSf-H₃PO₄ and b.) PTFSPA.

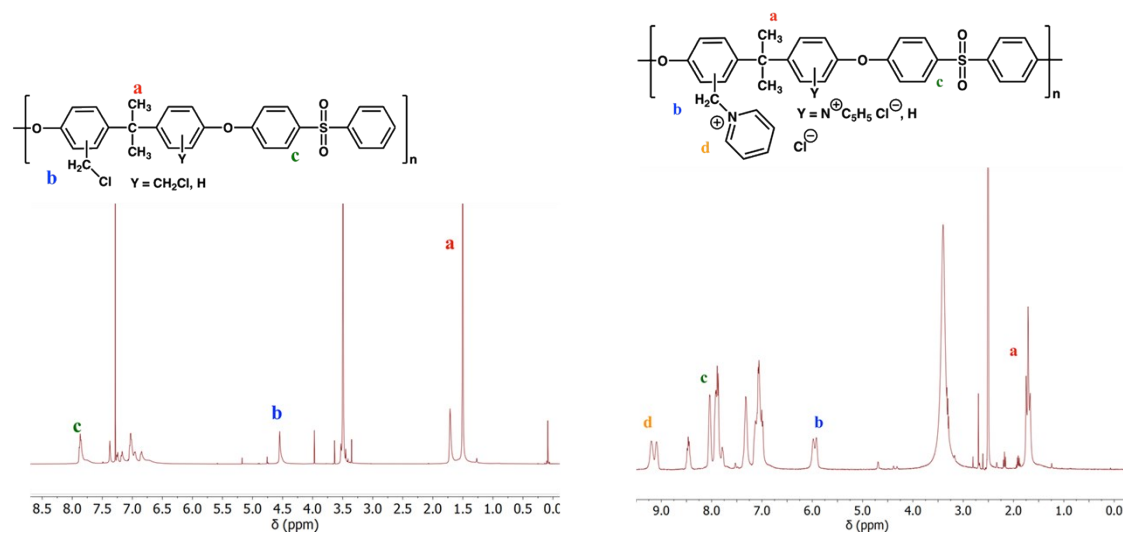


Figure S4. ¹H NMR of CMPSf (left) and QPPSf (right)

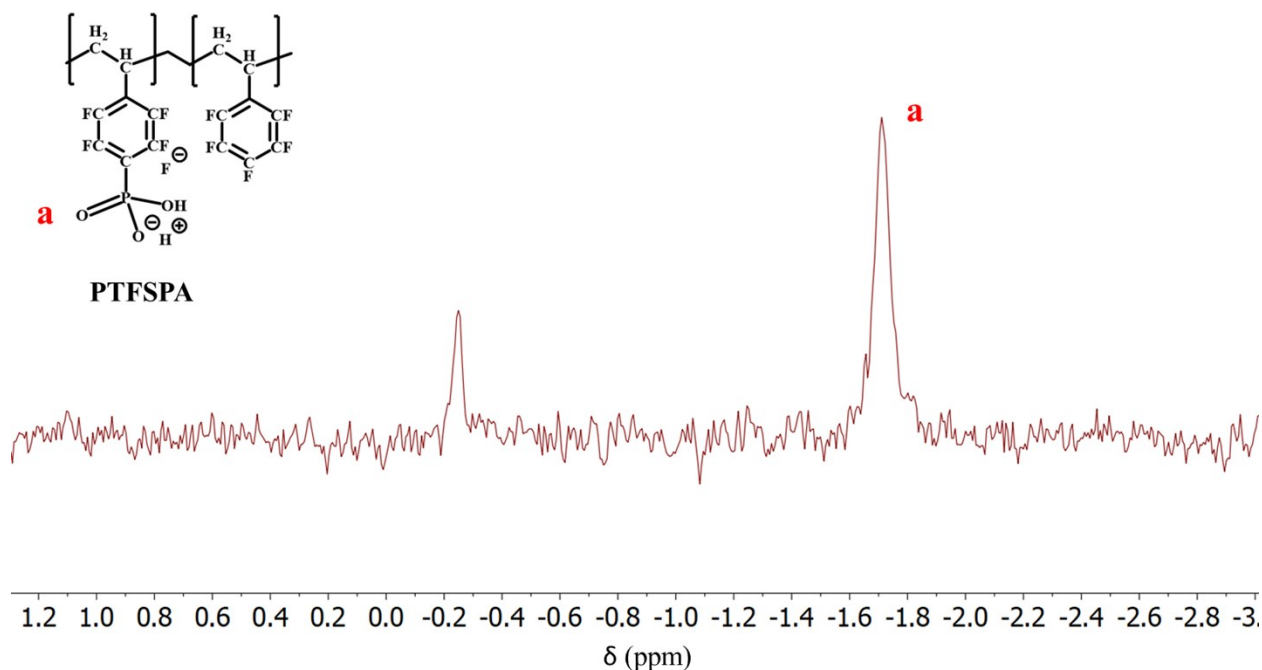


Figure S5. ^{31}P NMR of PTFSPA

IEC of samples

Ion-exchange capacity (IEC) of QPPSf was determined using ^1H NMR. Theoretical IEC of QPPSf was calculated using equations 1 and 2⁶:

$$\text{IEC} \left(\frac{\text{mmol}}{\text{g}} \right) = \frac{DF \times 1000}{(MW_{\text{PSf, monomer}} + DF \times MW_{\text{cation}})} \cdot \text{Conversion} \quad (1)$$

$$MW_{\text{cation}} = (MW_{\text{cation free base conjugate}} + MW_{\text{counteranion}} + MW_{\text{CH}_2} - 1) \quad (2)$$

The DF of CMPSf was calculated using the procedure from our previous work.¹⁰ The DF of CMPSf used in this work was 1.26. The percentage of conversion of chloromethylated groups to

quaternary benzyl pyridinium groups calculated from **Figure S4** was 91%. The IEC of QPPSf was using **equation 1** was 1.7 mmol g⁻¹ (for the sample not containing H₃PO₄). For the sample containing acid, the number of H₃PO₄ per base (n H₃PO₄ B⁻¹) was calculated using the procedure from our previous work.¹⁰ QPPSf-H₃PO₄ had n H₃PO₄ B⁻¹ of 9.4.

IEC of PTFSPA was determined using a base titration. A sample of PTFSPA was immersed in 1 M sodium chloride (NaCl) for 24 hours for exchanging the protons for sodium ions. This solution was titrated against 0.1 M sodium hydroxide (NaOH) solution until equivalence point observed using potassium permanganate indicator. The IEC of PTFSPA was calculated using equation 3.

$$\text{IEC} \left(\frac{\text{mmol}}{\text{g}} \right) = \frac{V_{\text{NaOH}} \times N_{\text{NaOH}}}{w_{\text{dry}}}$$

(3)

w_{dry} is the weight of dry PTFSPA.

The IEC of PTFSPA was using the base titration method was 2.5 mmol g⁻¹.

Thermal stability assessment

The thermal stability of PTFSPA and QPPSf-H₃PO₄ was determined using Pyris 1 TGA (TA instruments) instrument under nitrogen. The samples were initially heated to 100 °C and equilibrated at that temperature for 10 minutes. Then, the temperature was heated up to 700 °C at the rate of 10 °C min⁻¹. The change in weight of the sample was monitored during the heating from 100 °C to 700 °C. **Figure S6** provides the TGA data of PTFSPA and QPPSf-H₃PO₄.

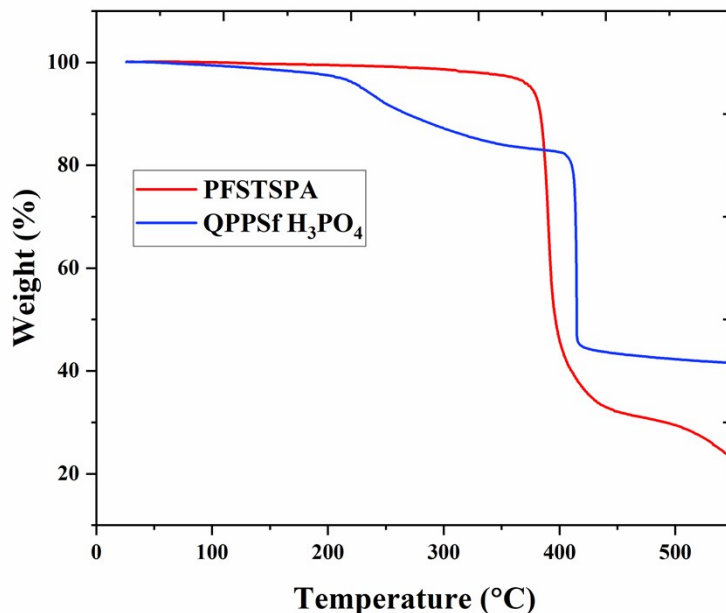


Figure S6. TGA of PTFSPA and QPPSf H₃PO₄. PTFSPA does not undergo thermal decomposition until 340 °C. The initial weight loss for QPPSf H₃PO₄ at 170 °C was due to excess H₃PO₄ loss. The QPPSf polymer did not degrade until 400 °C.

Ionic conductivity (κ_{H^+}) of thin films

Thin film in-plane ionic conductivity was measured on the IDEs using the procedure by Arges *et al.*¹¹. Thin films of QPPSf and PTFSPA were deposited on the IDEs by spin coating a 1 wt.% solution at 4000 rpm for 45 seconds. The IDE with thin films of polymer electrolytes were then heated at 120 °C in nitrogen atmosphere to remove the excess solvents from the samples. H₃PO₄ was imbibed into the QPPSf thin films by placing a drop of 85 wt.% H₃PO₄ on the thin films for 10 minutes. Complete hydrolysis and activation of PTFSPA thin films were ensured by adding a drop of 5 wt.% H₃PO₄ on the thin films for 10 minutes. The excess acid was removed by blot drying the IDEs carefully. The electrode pads of the IDE substrate were scraped away using a cotton Q-tip to make electrical connections. The thickness of the thin films (t) was

calculated using ellipsometry. The thickness of QPPSf-H₃PO₄ films ranged from 12-15 nm and PTFSPA films ranged from 10-12 nm. The thin film resistance of QPPSf H₃PO₄ and PTFSPA was determined using electrochemical impedance spectroscopy (EIS). The frequency range was set to 100,000 to 1 Hz with an oscillatory amplitude of 0.0001 mA as described in our previous work.^{1,12} Equation 4 and IDE dimensions used to calculate in-plane ionic conductivity of the thin films.

$$\kappa = \frac{1}{R} \cdot \frac{d}{l (N - 1) \cdot t}$$

(4)

κ : in-plane ionic conductivity

R : in-plane ionic resistance

d : spacing between teeth on IDE (100 μm)

l : length of teeth on IDE (4500 μm)

t : Ionomer film thickness on IDE substrate

n : number of teeth on IDE substrate (22)

Preparation of GDEs and MEA fabrication

The catalyst inks for fabrication of gas diffusion electrodes (GDEs) were prepared by mixing 0.2 g of platinum electrocatalyst supported on high surface area graphitic carbon (37% Pt/C, Tanaka Kikinzoku International) with 1.715 g of ionomer solution diluted with approximated 5.5 g of isopropyl alcohol (IPA). The prepared inks were sonicated for 30 minutes for dispersing the particles in the ink. The gas diffusion layers (GDLs) were then painted with the prepared catalyst inks using an aerosolized spray gun (nitrogen gas) to make GDEs. The

active area of the resultant GDE was 5 cm². The catalyst loading was measured gravimetrically by measuring the weight change before and after painting and drying. The catalyst loading was maintained at 0.5 mg_{Pt} cm⁻² (or 1 mg_{Pt} cm⁻²) for each GDE (one used as the anode and the other as the cathode). The weight fraction of the ionomer in the electrode layer was 30 wt.%. The QPPSf GDEs were then immersed in 85wt% H₃PO₄ for 10 minutes to imbibe acid into the electrodes. The MEAs were prepared by sandwiching the prepared GDEs with 50:50 QPPSf-PBI H₃PO₄ HT-PEM in a Fuel Cell Technologies Hardware setup (5 cm² geometric area). The assembled cell was plumbed to an 850 E Scribner Associates, Inc. Fuel Cell test station for HT-ECHP studies.

HT-ECHP studies with MEAs

ECHP tests were conducted using 850 E Scribner Associates, Inc. Fuel Cell test station. Before testing, the cell was heated to 120 °C under nitrogen on both anode and cathode. The cell was heated further to 180 °C under pure hydrogen on the anode and no sweep gas at the cathode. The polarization curves were obtained for 160 °C, 180 °C, 200 °C, and 220 °C by performing chronoamperometry with 0.05 V potential step by holding the voltage for 30 seconds at each step to reach steady-state current from 0 V-0.7 V.

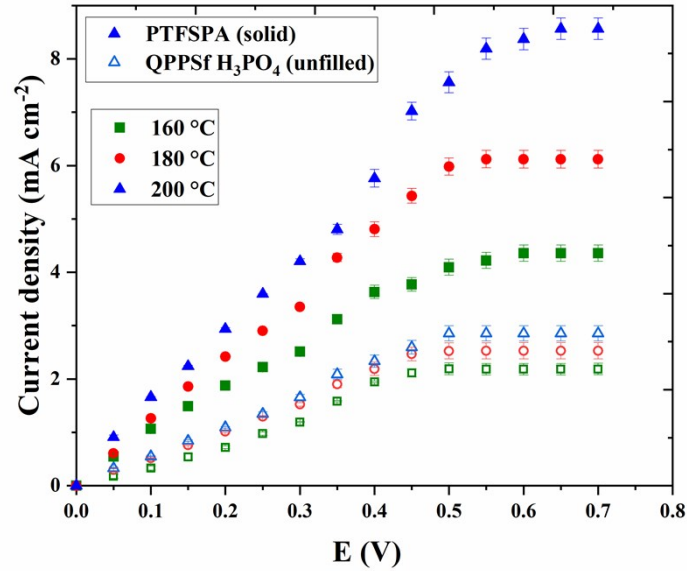


Figure S7. Non-iR corrected polarization curves for HOR/HER on IDE platform with PTFSPA and QPPSfH₃PO₄ thin films as a function of temperature (160 °C to 200 °C).

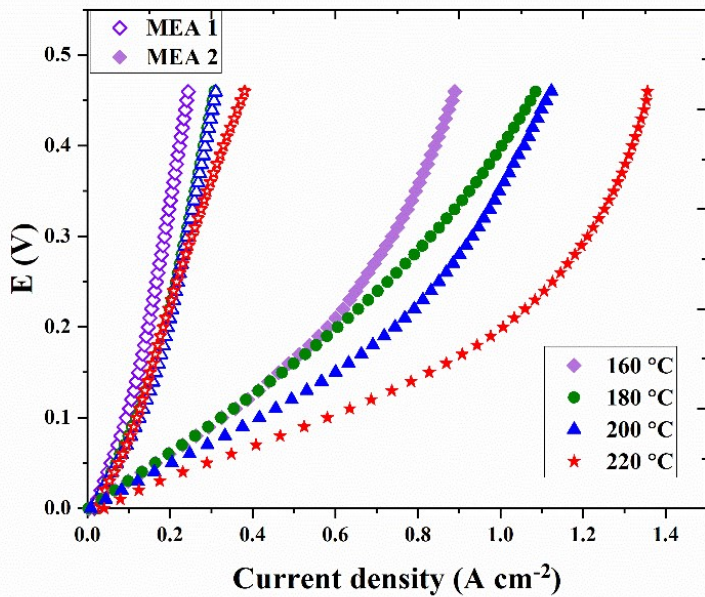


Figure S8. Non-iR corrected polarization curves for the ECHP at 160 °C to 220 °C.

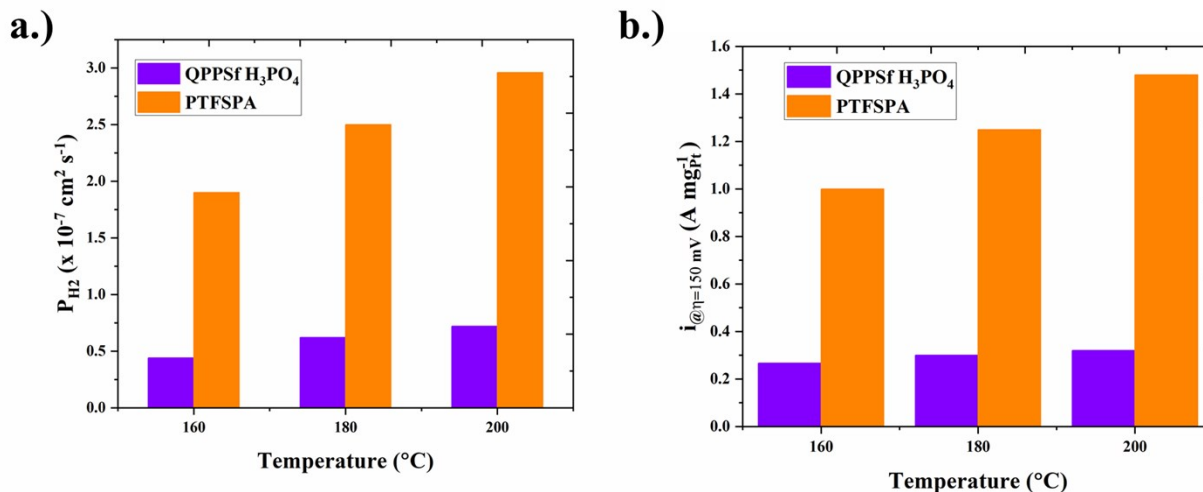


Figure S9. a.) The hydrogen permeability (P_{H_2}) values and b.) current density at 150 mV (i.e., $i_{@150 \text{ mV}}$) as a function of temperature for the two different MEAs. These values were extracted from the limiting currents and the linear regime in the polarization curves from Figure 3a in the main manuscript.

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