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Role of phosphate source in improving the proton conductivity of tin pyrophosphate and its composite electrolytes

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Indophenol measurements for ammonia quantification.

Ammonia quantification was carried out using the indophenol method of Weatherburn and is summarized here.[1] Solution A was prepared by dissolving 5 g of phenol in 250 ml of DI water and dissolving 25 mg of nitroprusside in 250 ml of DI water. These two solutions are mixed and stored in an amber bottle. Solution B was prepared by mixing 2.5 g of NaOH in 250 ml of DI water. To this 4.2 ml of sodium hypochlorite with 5% available chlorine was added and made up to 500 ml. This was stored in another amber bottle. Both the solutions are kept in a refrigerator when not in use.

For calculating the ammonia content of the as prepared TPP powders, 100 mg of TPP powders were dispersed in 10 ml of 0.01M sulfuric acid followed by centrifugation to separate the TPP powder from the solution. 40 µL of this solution was added to 5 ml of Solution A and 5 ml of Solution B and kept at 37.5°C in a water bath for 20 minutes. UV-Vis spectra for this solution was measured and a peak at ~630nm indicate the presence of ammonia in the solution.

LSV measurements

LSV measurements were taken during fuel cell operations with identical operating conditions of 285 kPa back pressure and 220°C temperature. Before LSV measurements, the cathode gas supply was changed from UHP O_2 to UHP N_2 and supplied at the same flow rate of 500 sccm. The cell was purged for about 30 minutes to avoid possible contributions from residual air. The working and sensing electrode leads were connected to the cathode while reference and counter electrode leads were connected to the anode. LSVs measured from 0.2 V to 0.5 V and the current at 0.4 V was considered as the H_2 cross-over current without considering the short-circuit.[2]

Fig. S1

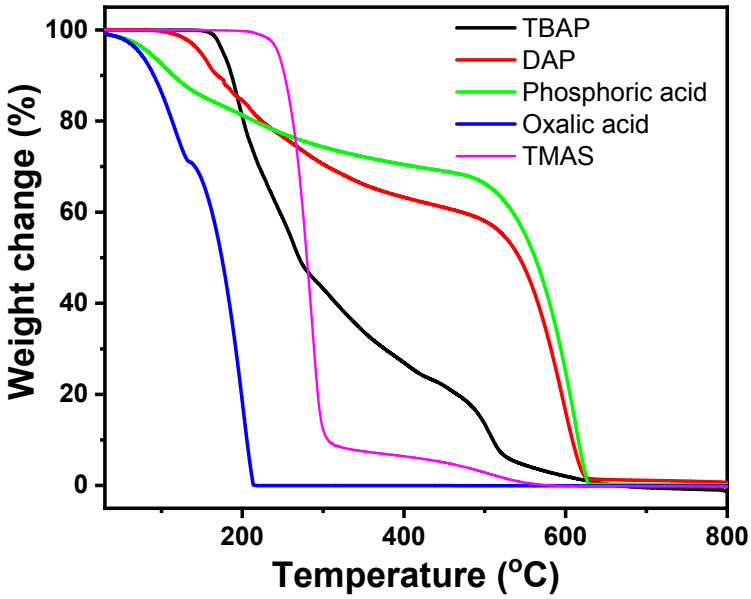

Fig. S1. TGA of various precursors used in this study for preparing TPP powders.

Fig. S2

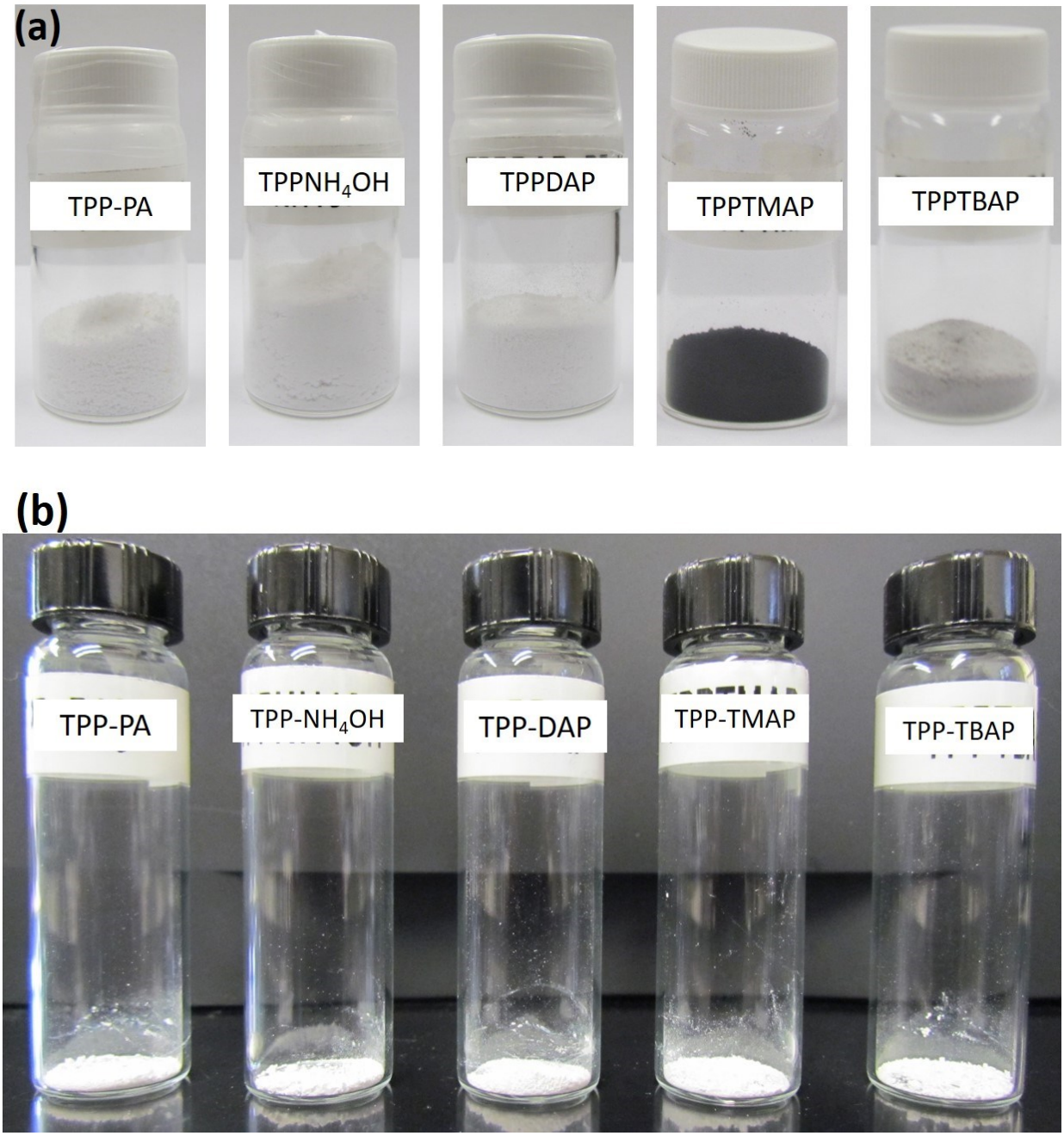

Fig. S2. (a) Photographic image of the five prepared powders showing a clear white powder for non-carbon containing precursors and black and grey colored powders for the two carbon containing precursors, TMAS and TBAP respectively. (b) after holding the above five samples at 800°C for 1 hour in TGA measurements.

Fig. S3

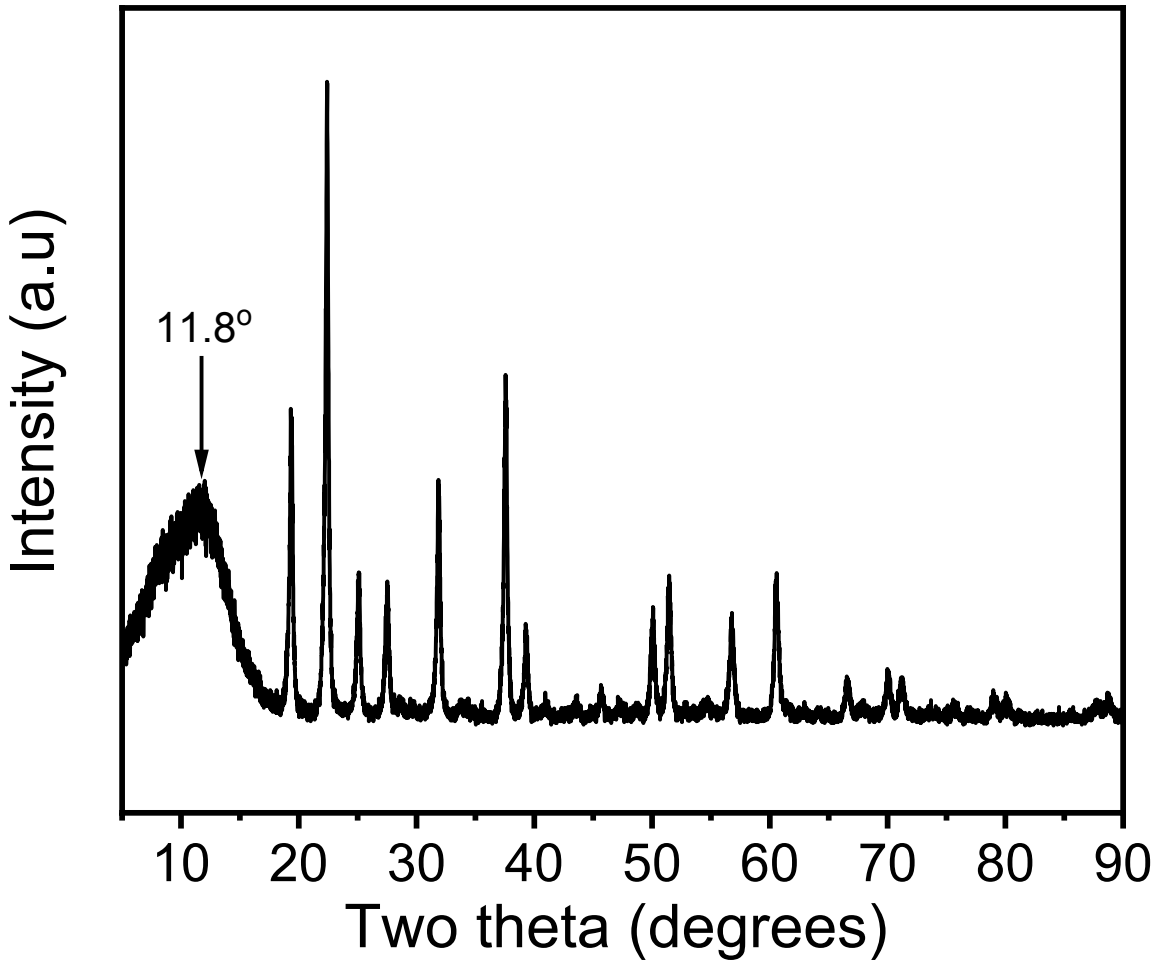

Fig. S3. pXRD of TPP-TMAP in the 2θ window of 5 - 90° clearly indicating the graphite oxide peak at 11.8°.

Fig. S4.

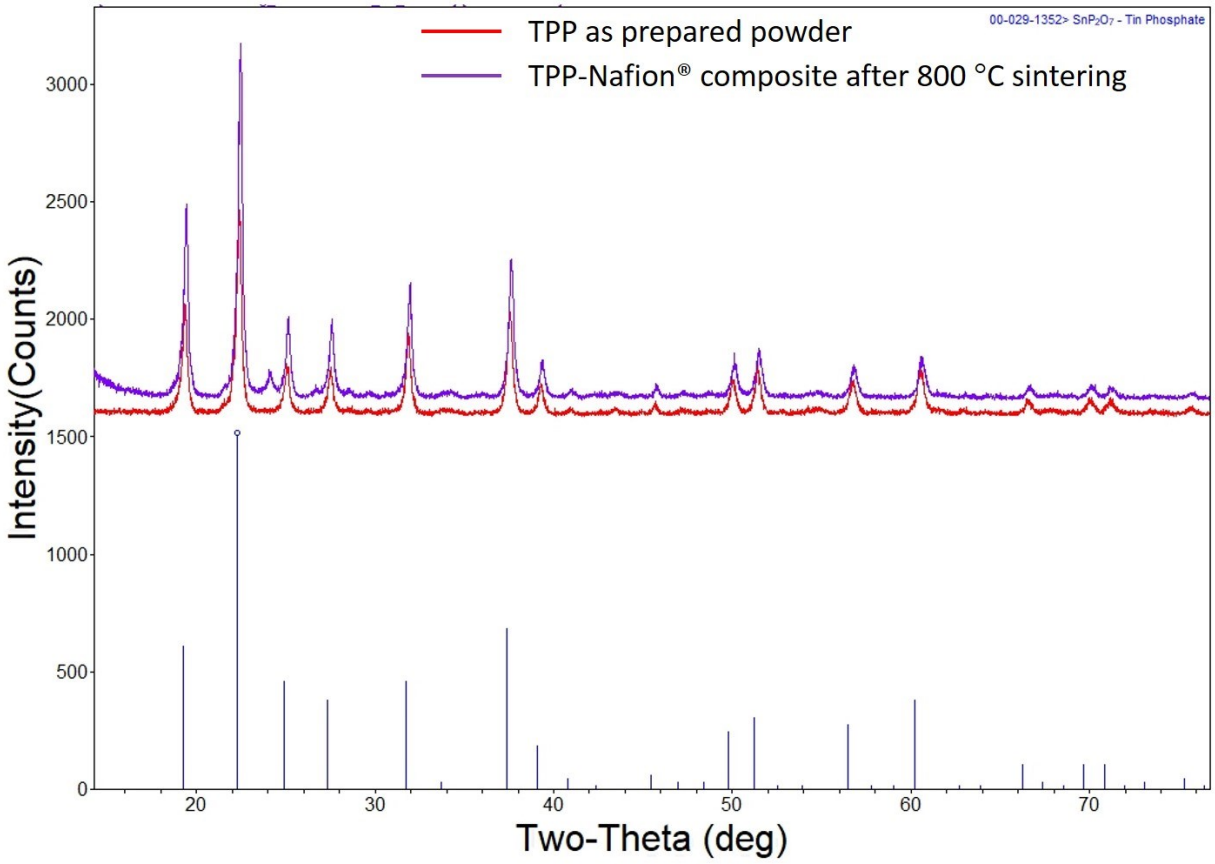

Fig. S4. pXRD obtained for as prepared TPP powders and that of TPP-Nafion composite doped in PA after holdiing at 800 °C for one hour in TGA measurements.

Fig. S5.

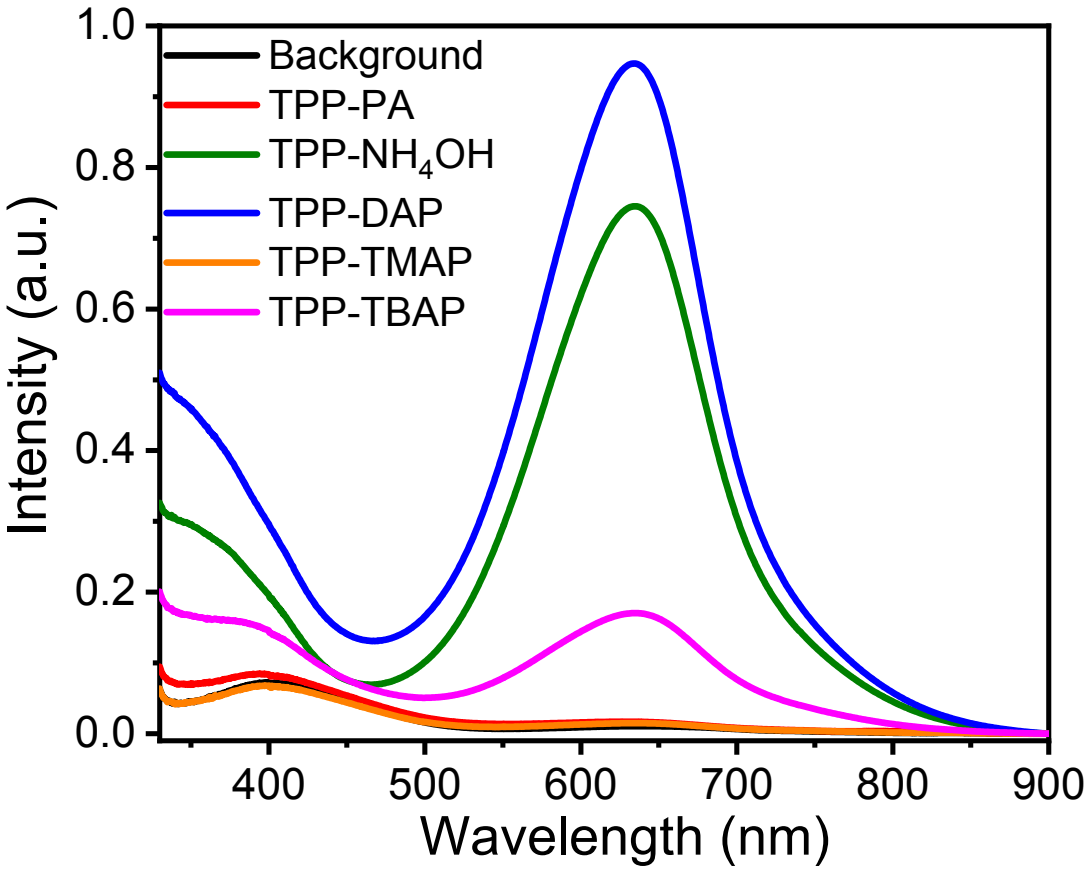

Fig. S5. UV-Vis spectra obtained on the TPP powders via the indophenol method for quantifying ammonium ions present.

Fig. S6

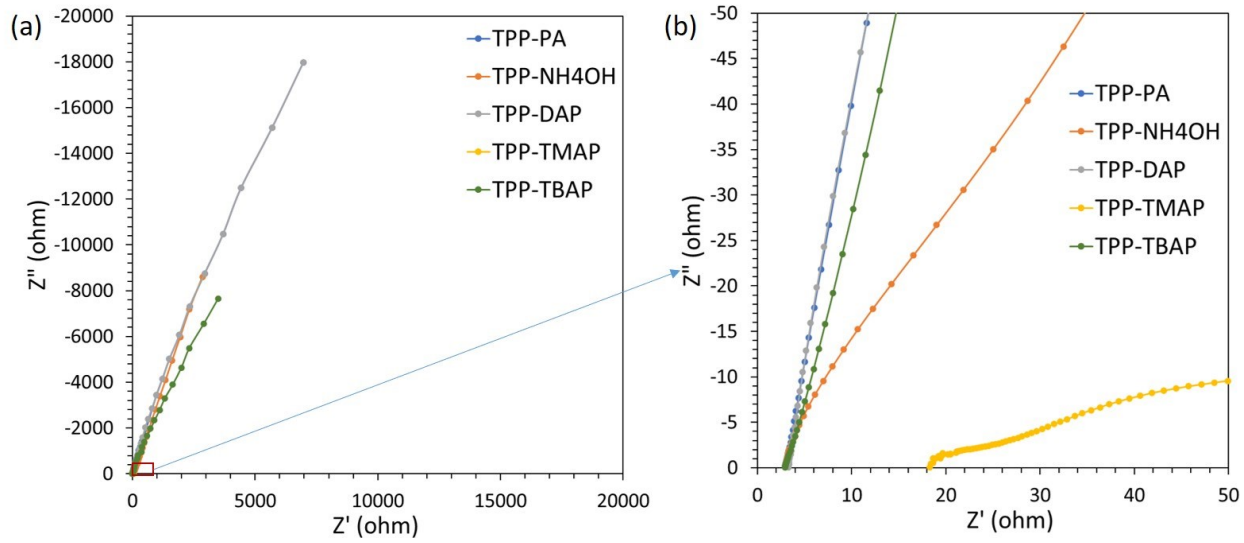

Fig. S6. (a) Impedance Nyquist plot obtained for the TPP pellets obtained from different precursor materials (b) magnified view of the high frequency intercept region.

Fig. S7

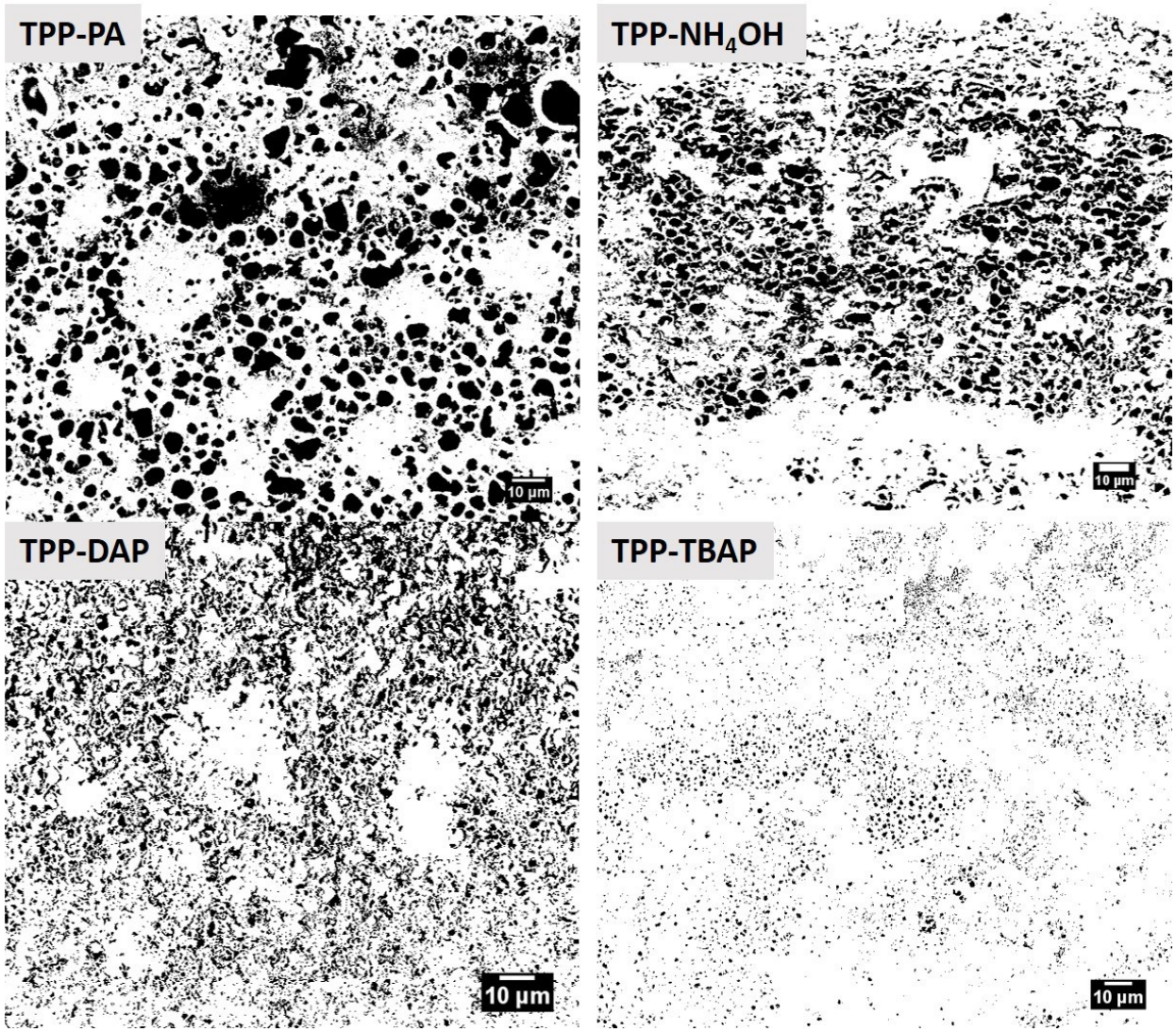

Fig. S7. Porosity calculation via ImageJ® analysis of the TPP/Nafion composite SEM images shown in Fig. 3a. The porosity of the four membranes obtained by this analysis are TPP-PA/Nafion - 35.26%, TPP-NH_4OH/Nafion - 27.14%, TPP-DAP/Nafion - 24.80% and TPP-TBAP/Nafion - 04.19%.

Fig. S8

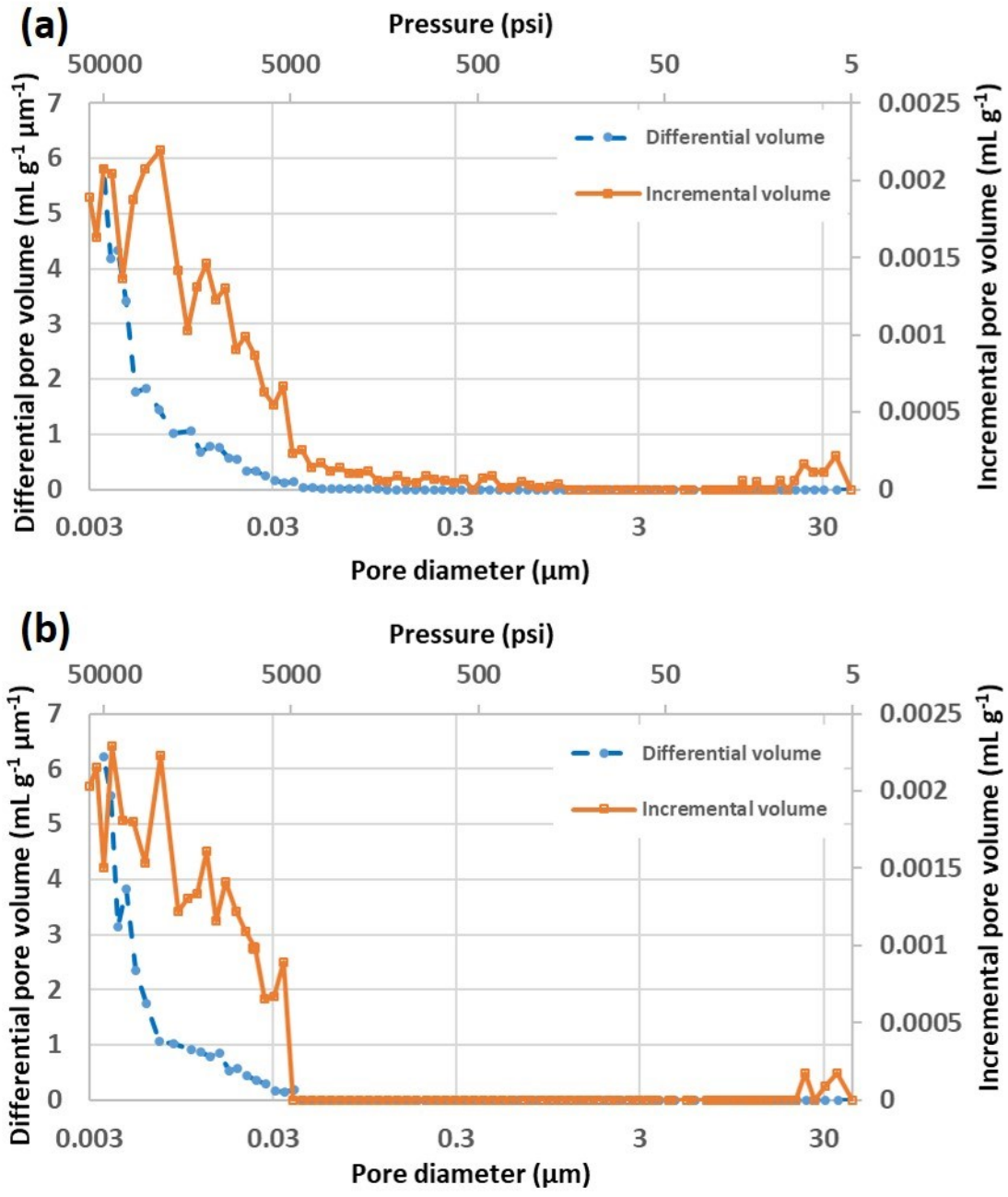

Fig. S8. Mercury porosimetry plots obtained for (a) TPP-PA/Nafion and (b) TPP-TBAP/Nafion membranes.

Fig. S9

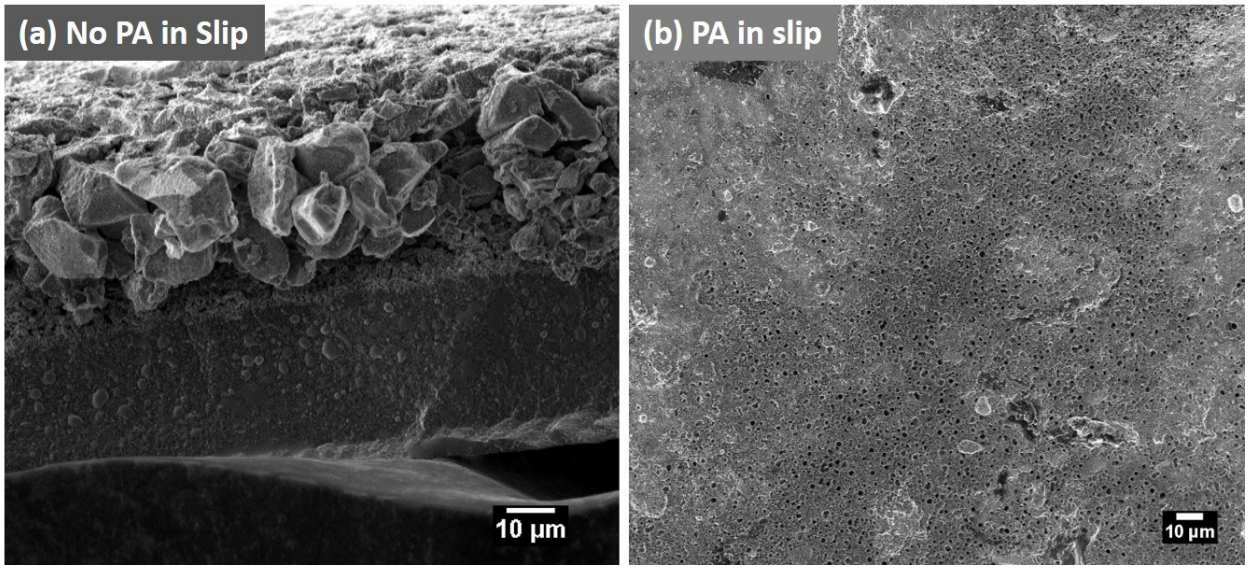

Fig. S9. Cross sectional SEM image of the TPPTBAP-Nafion® 90:10 composite membranes prepared with (a) no phosphoric acid addition in the slip formation and (b) ~30% phosphoric acid added during the slip formation.

Fig. S10

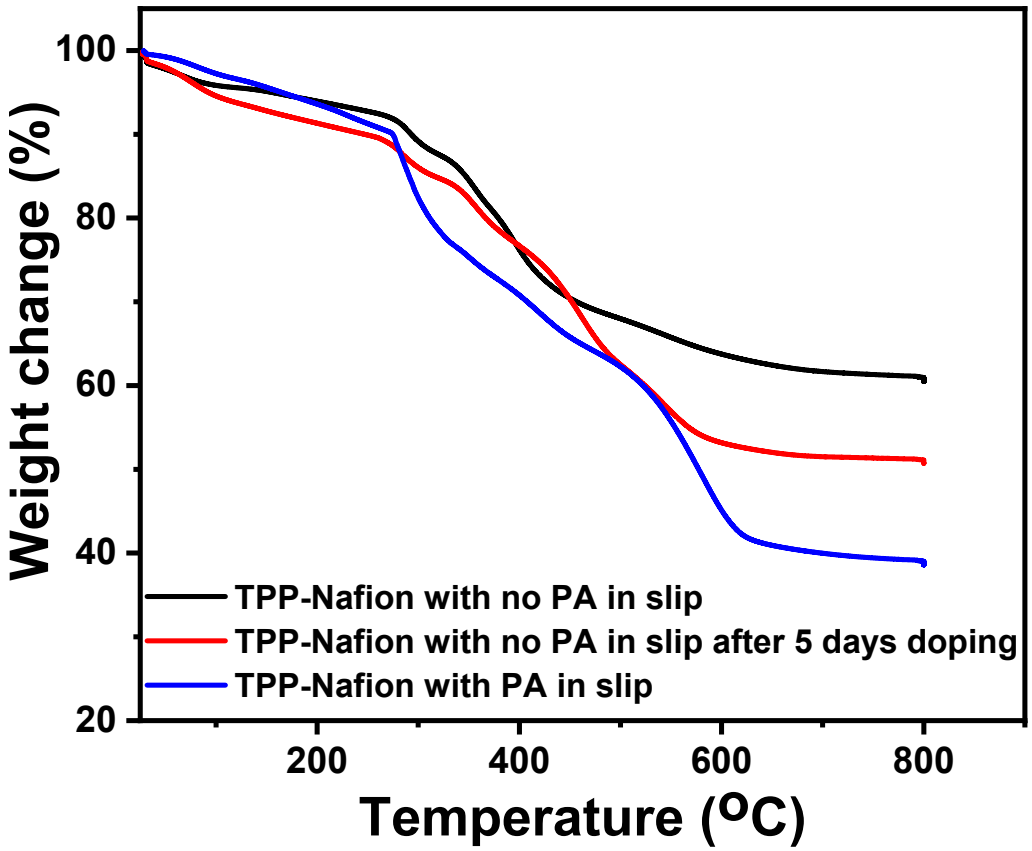

Fig. S10. TGA of TPP-Nafion composites prepared with and without PA added during the slip formation and TGA of TPP-Nafion composite prepared without PA in the slip formation that was externally doped for five days.

Fig. S11

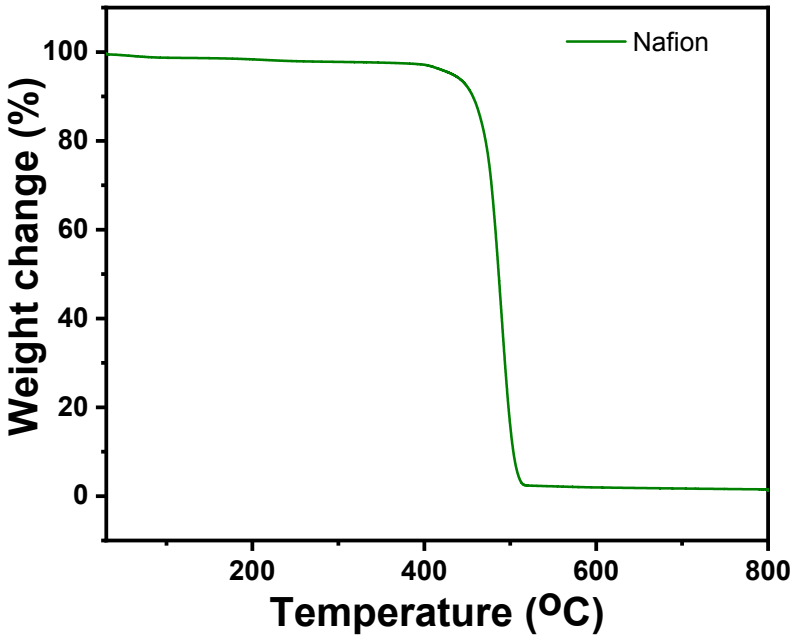

Fig. S11. TGA plot of Nafion® membrane cast from 1,2 pentane diol.

Fig. S12

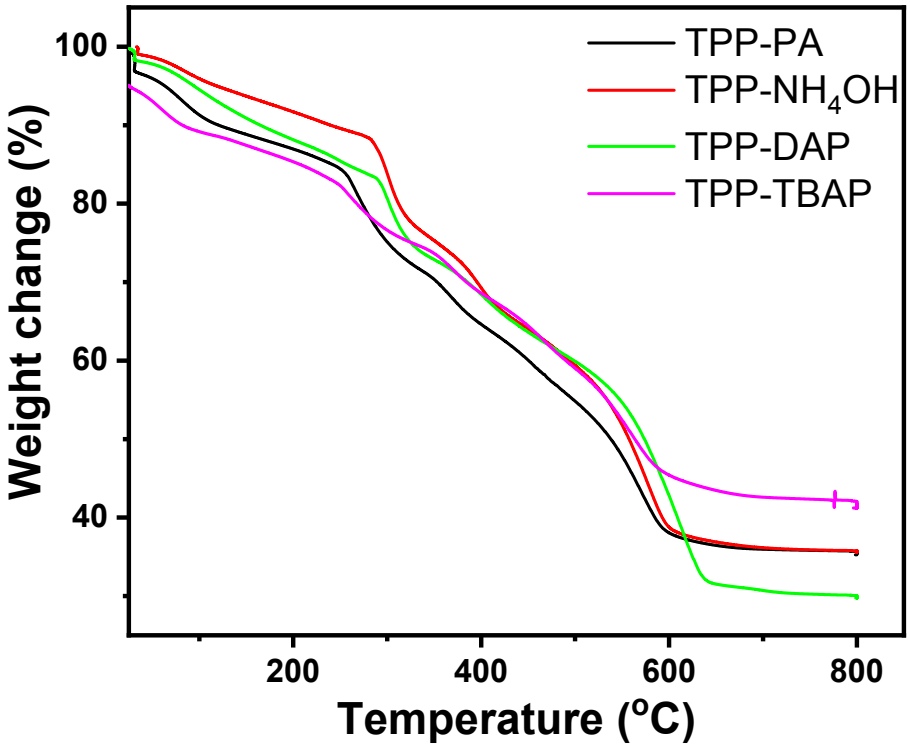

Fig. S12. TGA of TPP membranes prepared by PA in slip that was further imbibed in PA for 24 hours.

Figure S13

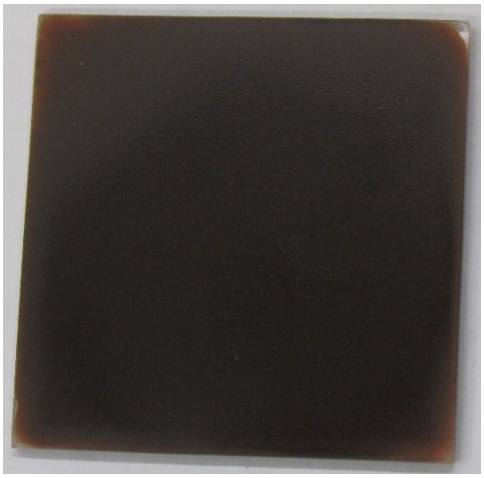

Fig. S13 The photographic image of the TPP-Nafion composite membrane cast on a 7 cm x 7 cm glass plate.

Fig. S14

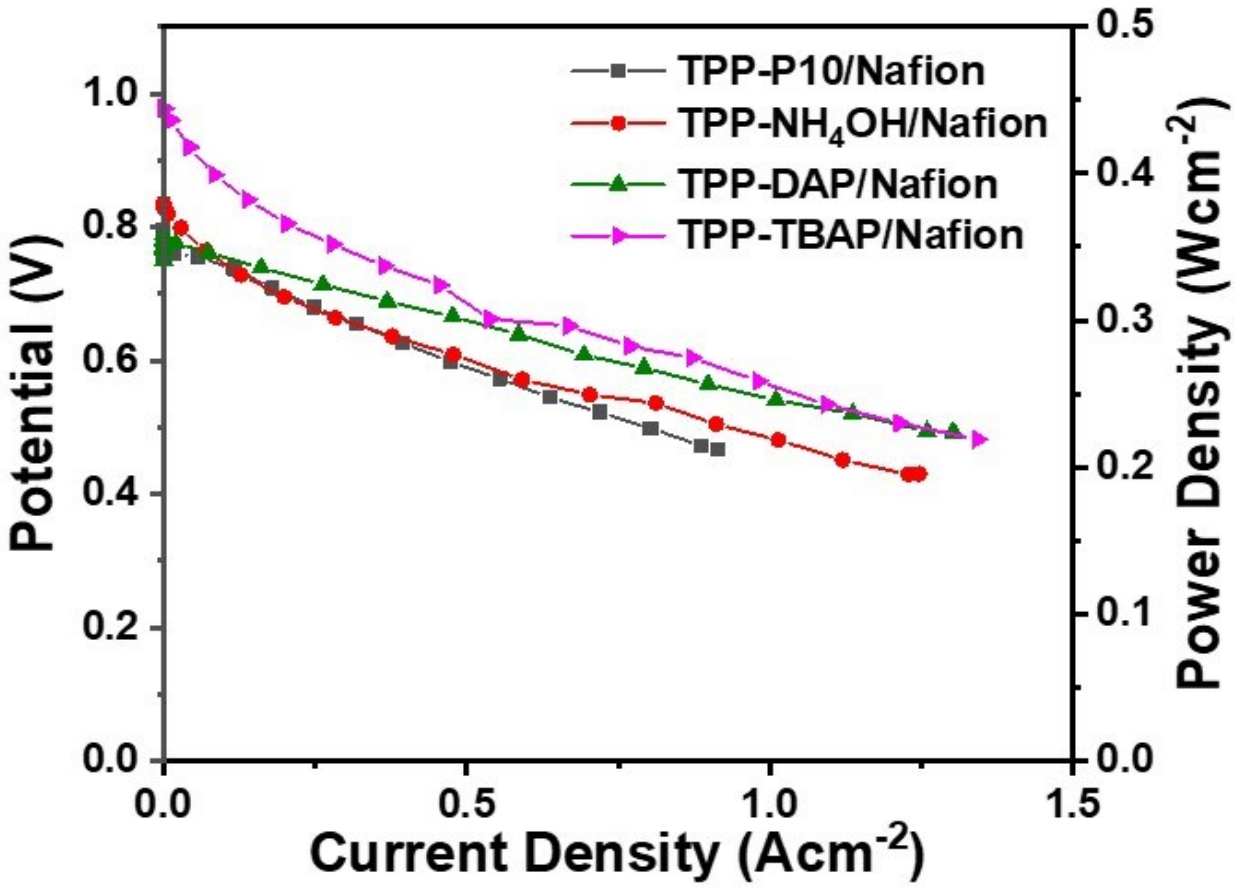

Fig. S14. IR corrected fuel cell polarization curves obtained for the four composite membranes studied.

Fig. S15

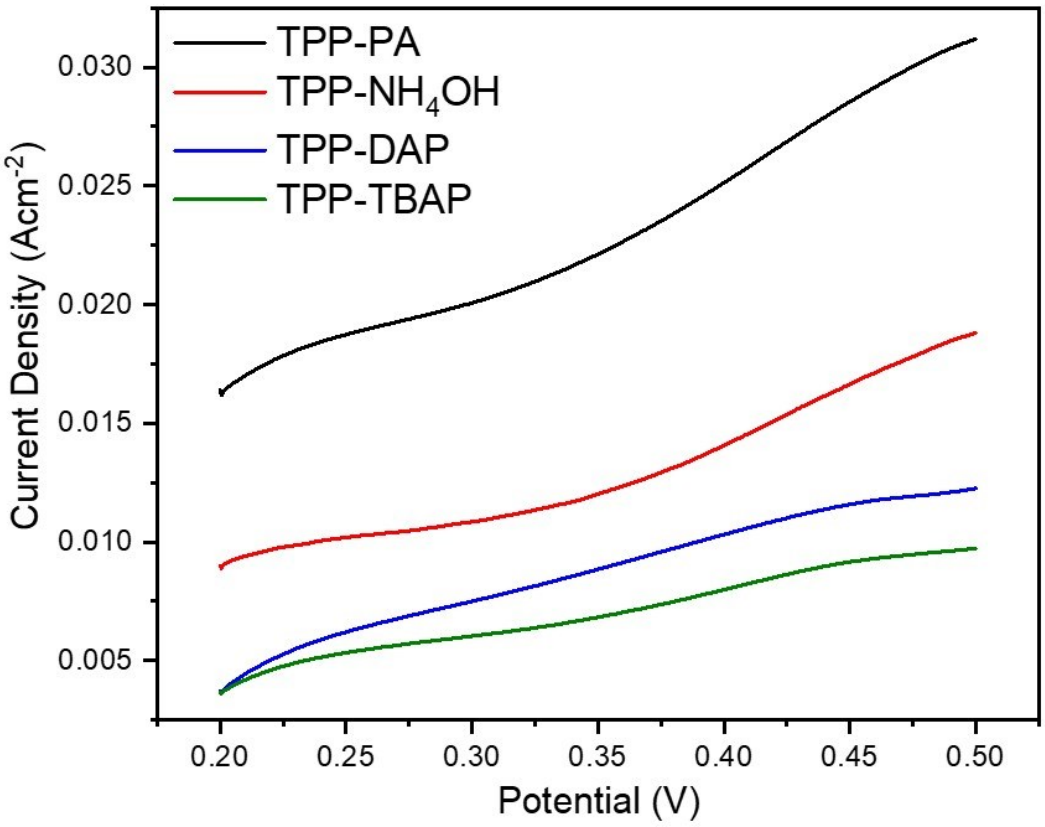

Fig. S15 Linear Sweep Voltammetry data obtained for the four tested MEAs under H_2 and N_2 flow to the anode and cathode respectively at 220°C. The working and sensing electrodes were connected to the cathode while reference and counter electrodes were connected to the anode.

Figure S16

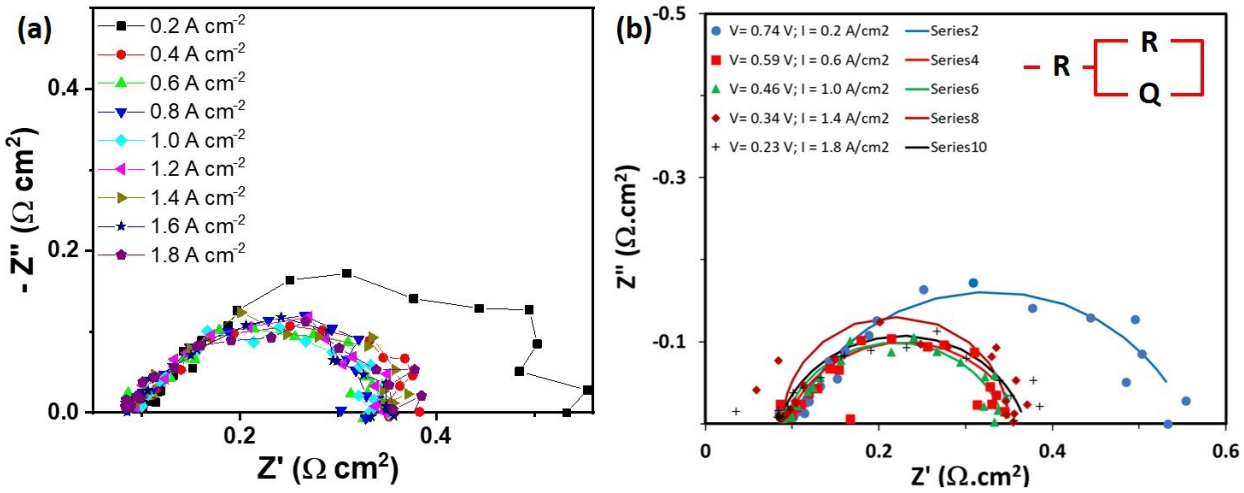

Fig. S16 (a) Impedance Nyquist plots obtained for the 50µm thick TPP-TBAP-Nafion® composite membrane based MEA during fuel cell polarization measurements (b) Equivalent circuit fit obtained using a simple RRQ circuit (shown in inset) for a select number of runs.

Table S1. Equivalent circuit fit results obtained with a simple RRQ circuit for the Nyquist plots shown in Fig. S15.

Current Density (Acm^{-2})	Voltage (V)	R(HFR) $Ohm.cm^2$	R(electrode) $Ohm.cm^2$
0.02	0.74	0.1	0.46
0.06	0.59	0.09	0.27
1	0.46	0.09	0.26
1.4	0.34	0.09	0.26
1.8	0.23	0.085	0.28

Figure S17

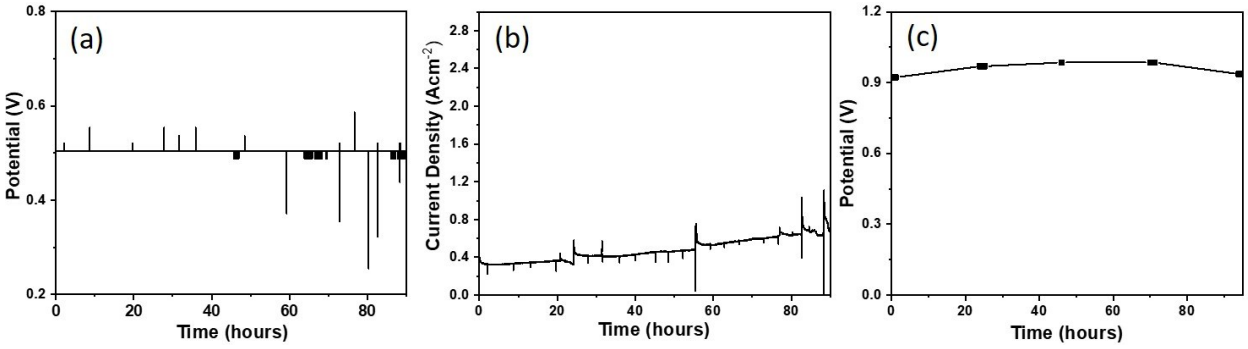

Fig. S17 Durability measurement carried out on TPP-Nafion composite membrane for 90 hours of operation (a) applied potential vs time, (b) obtained current density vs time, (c) open circuit potential vs time.

Reference

1. Weatherburn, M. W., Phenol-hypochlorite reaction for determination of ammonia. *Analytical Chemistry* **1967,** *39* (8), 971-974.

2. Pucheng, P. Ziyao, W. Yuehua, L. Xiaoning, J. Dongfang, C. Shangwei, H., Improved methods to measure hydrogen crossover current in proton exchange membrane fuel cell. *Applied Energy* 2018, 215, 338-347.