Supporting Information for:

Ionomer Degradation in Catalysts Layers of Anion Exchange Membrane Fuel Cells

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Experimental Methods:

MEA fabrication and fuel cell test: Commercial Pt/C (Johnson Matthey, HISPEC 9000) together with 20wt% QAPPT ionomer (95% GR) solution (40 mg/mL in DMSO) was dispersed in iso-propanol with a concentration of 5 mg/mL to form the catalyst ink. The ink was sonicated with an ice bath for 30 min to achieve a good dispersion of both the catalyst and ionomer. The ink was then sprayed onto the QAPPT membrane (25 μm, 90% GR) placed on vacuum hot plate using a SimCoat ultrasonic spray system (SONO-TEK). The hot plate temperature was set to 70 °C and the ultrasonic nozzle power was set to 3 W. The electrode area was set to 2×2 cm^2 with a plastic cover, and the catalyst loading was 0.4 mg_{Pt}/cm^2 on both the anode and cathode. The MEA was then soaked in 1 M KOH at 60 °C for 24 hours to fully convert it to the hydroxide form. The MEA was washed with ultrapure water (18.4 MΩ) 3-5 times to remove excess KOH, and then assembled with 200 μm PTFE gaskets and AvCarb GDS3250 carbon gas diffusion layers for fuel cell test. The fuel cell performance was tested using a Scribner 850e fuel cell test system with 100% RH hydrogen and CO_2-free air (SynAir). The cell was initially activated by increasing the current until no obvious potential increase was observed. Polarization curves were then recorded at different current densities at constant current mode. The stability was tested at constant current mode, the HFR was recorded at a frequency of 5000 Hz.

^{1}H-NMR: ^{1}H NMR spectra of the QAPPT membrane, before and after the stability testing, were obtained on a Bruker spectrometer at 400 MHz using deuterated dimethyl sulfoxide as the solvent and tetramethyl silane as the internal reference. The QAPPT samples were exchanged to Cl^- form in 1 M KCl solution and dried before dissolving in DMSO due to its poor solubility in OH^- form. A drop of triflic acid was added to remove trace amount of water signal in 1H-NMR.

Catalyst Layer Cyclic Voltammetry: The catalyst layer was purged with N_2 while the other electrode was purged with H_2 until the cell voltage was below 0.2 V to ensure the complete removal of residual O_2. The CV was then performed in a 2-electrode configuration with the electrode purged with H_2 serving as both the counter and reference electrodes. The scan rate was 10 mV/s.

Electrochemical Impedance Spectroscopy: EIS spectra of the fuel cell were acquired with a Gamry Interface 1000E potentiostat from 10000 to 0.1 Hz with a 5 mV amplitude. When performing EIS for catalyst layer ionic resistance measurements, the electrode was purged with N_2 while the other electrode was purged with H_2, following the same procedures as for the CV test.

X-ray Photoelectron Spectroscopy: N1s XPS spectra were acquired with a Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectrometer. The spectrum was scanned from 392 eV to 409 eV with a resolution of 0.1 eV. 20 scans were performed to increase S/N.

Catalyst Layer X-ray Diffraction: The XRD spectra of the catalyst layers, before and after the AEMFCs stability test, were acquired by applying the MEA to a hollow sample holder using a Rigaku D/ Miniflex 600 X-ray diffractometer employing a Cu Kα radiation source operating at 40 kV and 15 mA., at a scan rate is 4 °/min. The crystallite size of Pt was calculated with all four peaks using Scherrer's equation:

$$D = \frac{K\lambda}{B\cos\theta}$$

where D is average crystallite size, K is Scherrer constant (0.94), λ is X-ray wavelength (1.54178 Å), B is full width at half maximum (FWHM) of XRD peaks, and θ is XRD peak position (one half of 2θ).

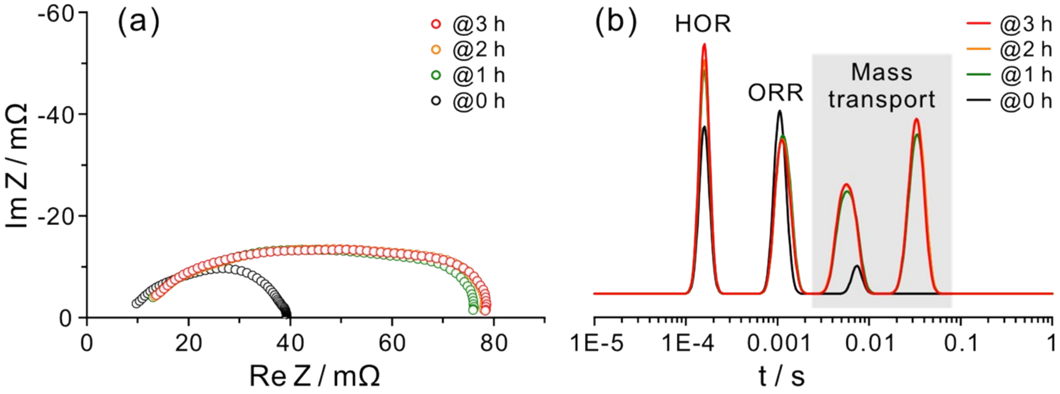

Figure S1: (a) The electrochemical impedance spectroscopy (EIS) spectra of the AEMFCs during the first 3 hours of stability testing with a 1-hour interval, and (b) the corresponding distribution of relaxation times (DRT) analysis using the method reported before.[1, 2]

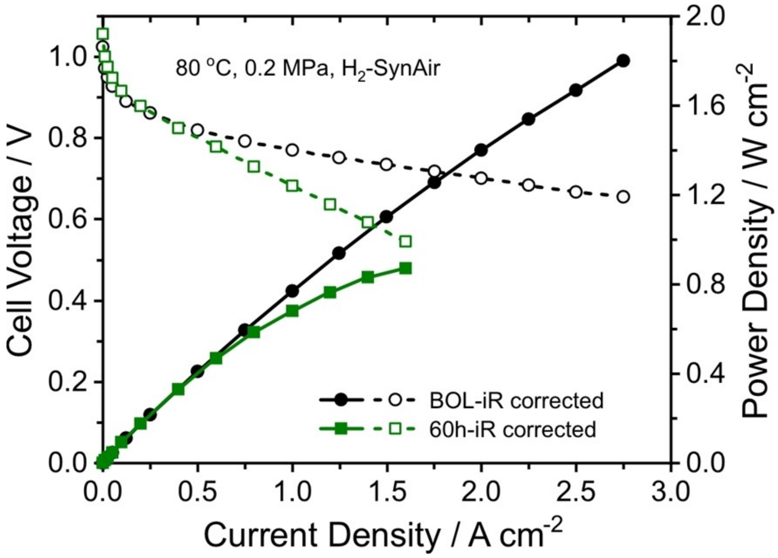

Figure S2. iR-corrected AEMFC fuel cell performance at the beginning of life (BOL) and after 60 hours of stability testing.

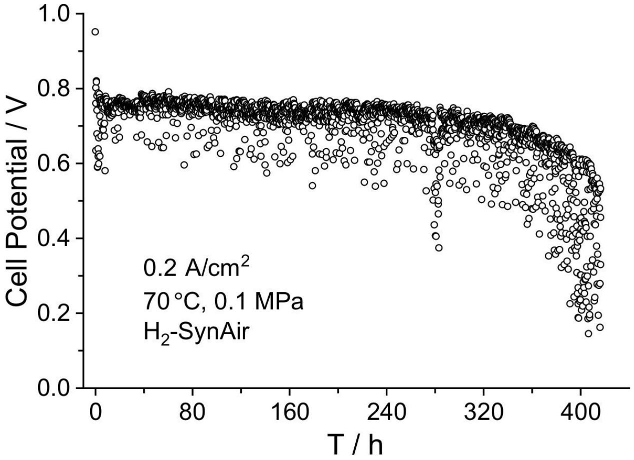

Figure S3. Fuel cell voltage during a stability test at a constant current density of 0.2 A/cm^2 using the quaternary ammonia poly (N-methyl-piperidine-co-p-terphenyl) (QAPPT) as both membrane and ionomer. The cell temperature was 70^{o}C with a back pressure of 0.1 MPa. Hydrogen and CO_2 free air (SynAir) were flown into the anode and cathode, respectively, at a flow rate of 400sccm.

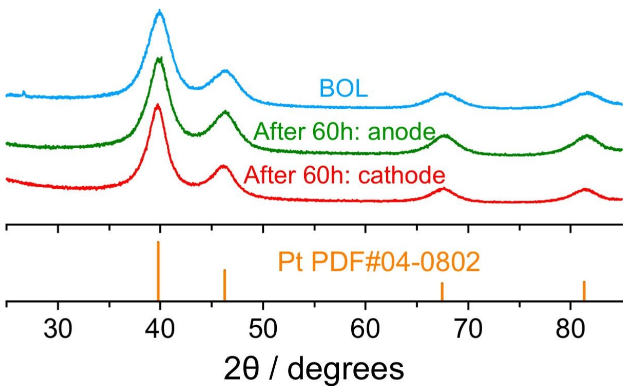

Figure S4. XRD spectra of catalysts layer at the beginning of life (BOL) and the anode and cathode after 60 hours of stability testing.

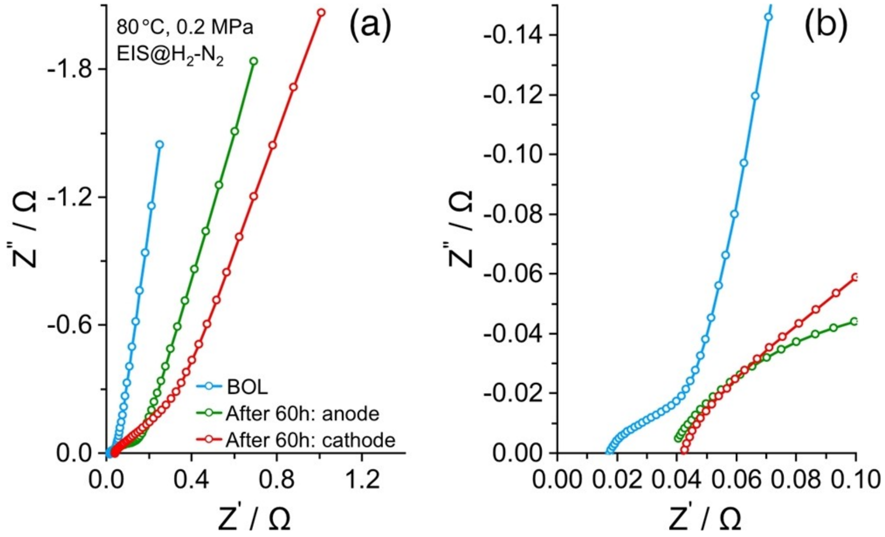

Figure S5. (a) Electrochemical impedance spectroscopy (EIS) spectra of catalysts layer under an inert N_2 atmosphere at the beginning of life (BOL) and the anode and cathode after 60 hours of stability testing. The anode was flown with hydrogen and the working electrode potential was held in the double-layer region (0.5 V vs. anode). (b) High-frequency region of the EIS spectra.

References

1. T. H. Wan, M. Saccoccio, C. Chen and F. Ciucci, Influence of the Discretization Methods on the Distribution of Relaxation Times Deconvolution: Implementing Radial Basis Functions with DRTtools, *Electrochim. Acta*, 2015, **184**, 483-499.
2. M. Hu, Q. Li, H. Peng, H. Ma, L. Xiao, G. Wang, J. Lu and L. Zhuang, Alkaline polymer electrolyte fuel cells without anode humidification and H_2 emission, *J. Power Sources*, 2020, **472**, 228471.