Migration and precipitation of Platinum in Anion Exchange Membrane Fuel Cells

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Experimental Section

Chemicals and Materials. All chemicals were analytically pure and used without further purification. Sustainion X37-50 grade RT AEM and ionomer were bought from Dioxide Materials, which have a thickness of 50 microns. mTPN1-TMA AEM and ionomer were bought from Orion polymers, which have a thickness of 50 microns. Iron, cobalt- and nitrogen co-doped carbide-derived carbon/carbon nanotube composite (FeCo-N-C) was provided by the Technion Israel Institute of Technology and University of Tartu [1]. KOH pellets, Boron Nitride (BN) were purchased from Sigma Aldrich, Toray papers and Pt/C (40 wt%) purchased from Fuel Cell Store, respectively. H_2 (99.999%), O_2 (99.9%), and N_2 (99.9%) were purchased from Airgas.

Catalyst layer preparation. The homogenous catalyst ink was prepared by stirring a mixture of Pt/C, Sustainion ionomer or mTPM1-TMA ionomer, and 2-propanol with a mass ratio of 5:1:157. The catalyst ink was then sprayed by Airbrush onto the Toray paper which was cut to 5 cm^2 areas. The gas diffusion electrodes were moved onto a hot plate to be dried at 85 °C, resulting in a platinum loading of 0.76 mg/cm^2 for the anode and cathode after the removal of all solvents. Catalyst ink with FeCo-N-C was prepared and deposited onto Toray paper to be used as cathodes, using similar methods described in [1].

Membrane electrode assembly fabrication. The as-prepared anodes and cathodes along with the AEMs were immersed in separate petri-dishes containing 1 M KOH for 1 h and replaced with fresh 1 M KOH every 20 min to ensure complete counter-ion exchange. After 1 h, the spent 1 M KOH was drained from the electrodes and the AEMs rinsed with MilliQ-water and patted dry with the help of a paper towel. The MEAs were then assembled using commercial cell housing (Fuel Cell Technologies Inc., USA) by sandwiching the AEMs between the electrodes with equal force of 10-pound inch across the MEA. The cell was then mounted on the in-house test station.

Anion-exchange membrane fuel cell testing. The testing was performed using 99.999% pure hydrogen at the anode and oxygen at the cathode. The gases were heated to five degrees above the operating temperature to prevent condensation and humidified at 93% relative humidity (RH). Testing was performed using MEAs with active areas of 5 cm^2 at a cell temperature of 60 °C and H_2 with a flow rate of 500 sccm at the anode and 1000 sccm of oxygen at the cathode. Performance was measured after cell break-in at a constant voltage of 0.5 V for 1 h each time before running the polarization scans to purge the carbonate and bicarbonate ions.

The durability tests were performed by operating the test station at a constant current density of 0.15 A/cm^2 (corresponding to an initial voltage of approximately 0.7 V). After the durability tests, electrochemical measurements were performed to characterize the electrochemical active surface area (ECSA) of platinum on the cathode.

Electrode Characterization. Electrochemical measurements were carried out using a Potentiostat (BioLogic P200). After the durability test, a gas change was initiated for 2 h, changing the gas flow on the working electrode from oxygen to nitrogen to create an inert gas atmosphere. Cyclic voltammetry measurements were performed in an inert nitrogen gas atmosphere on the working electrode at 60 °C, 93% RH, and atmospheric pressure, and the H_2 flow was fixed at 200 sccm while the N_2 flow was 75 sccm. After 2 h, a 10-min potentiostatic hold at 0.5 V was performed to reduce residual oxygen lingering in the working electrode. After the gas change was finished, ten cyclic voltammetry sweeps were performed at a 50 mV/s scan rate, in the voltage range from 0.1 to 0.9 V, and then repeated at 100 mV/s in the same voltage range for ten more sweeps.

X-ray computed tomography. Full-field X-ray computed tomography data sets were collected for a series of specimens, employing a Zeiss Xradia 520 Versa X-ray microscope. The X-ray source was operated at 40.20 kV and 74.7 μA (3W). The isotropic voxel size was set to 2.1 μm and a series of 1601 projections were collected over 360° with a 2.5 s image collection time per step. Data reconstruction was performed using a filtered-back projection algorithm. Data was visualized in ImageJ software.

SEM and EDS analysis. Morphology and composition of the electrode layers were analyzed after in-situ measurements using high-resolution scanning electron microscopy (SEM) (Hitachi S-4800) in combination with energy-dispersive X-ray spectroscopy (EDS). Pictures were taken from the cross-section of the MEA. For both SEM and EDS, primary electron energy of 10 kV was used.

X-Ray Diffraction. Phase analysis and lattice parameters were determined for the MEAs with 5 hours and 70 hours operation with X-ray Diffraction. XRD patterns were collected in reflection geometry (Bragg-Brentano mode) using a Bruker D8 Advance (Bruker, GMBH) with a Cu source (Kα1 = 1.5406Å, Kα2=1.54439) operating at a voltage of 40 kV and current of 40 mA. A scan range of 36–90° with step size of 0.01°, and scan time of 1.5 s per step were measured for each sample. Rietveld refinements were performed using TOPAS (Bruker). XRD peak profiles were modeled using a modified pseudo-Voigt function. The instrument contribution to the broadening of the measured profiles was quantified by fitting an Alumina standard. The lattice parameters, coherent grain size and microstrain values for the face centered cubic Platinum phase (Fm3m) were allowed to vary during the refinements.

XAS. The local structure and oxidation state of Pt were analyzed by XAS. XAS spectra were collected at Beamline 4-1 at Stanford Synchrotron Radiation Lightsource (SSRL). The two MEA samples of Sustainion before and after durability test were diluted by BN and prepared as a pellet using a hydraulic press. The sample was diluted by mixing with BN followed by grounding with mortar for more than 20 min. Pt L3-edge (11564 eV) was measured in transmission mode with an edge step of 0.25-0.65 .

Results and Discussion

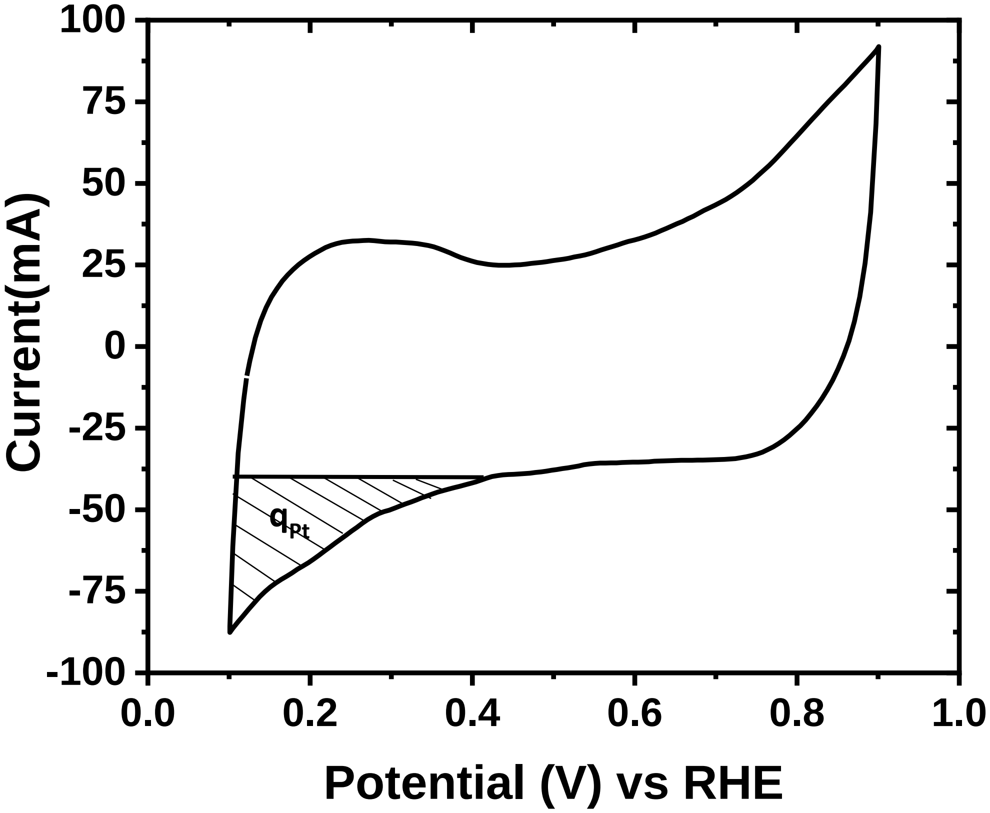

Figure S1. Cyclic voltammogram of a AEMFC catalyst layer highlighting the region of interest. The shaded area is the charge density due to H adsorption during the reverse scan and is used in the ECSA calculation. Conditions as in Figure 4.

The electrochemical surface area (ECSA) of the Pt catalyst is calculated from the charge density q_{Pt} ($C/cm^2_{electrode}$) obtained from the CV experiment; the charge required to reduce a monolayer of protons on Pt, Gamma (γ) = 210 $\mu C/cm^2_{Pt}$; Pt content or loading in the electrode, L in $g_{Pt}/cm^2_{electrode}$; and the active surface area of the electrode, A = 5 $cm^2_{electrode}$

$$ECSA\left(\frac{cm^2_{Pt}}{g_{Pt}}\right) = \frac{q_{Pt}}{\gamma . L . A} \qquad (S1)$$

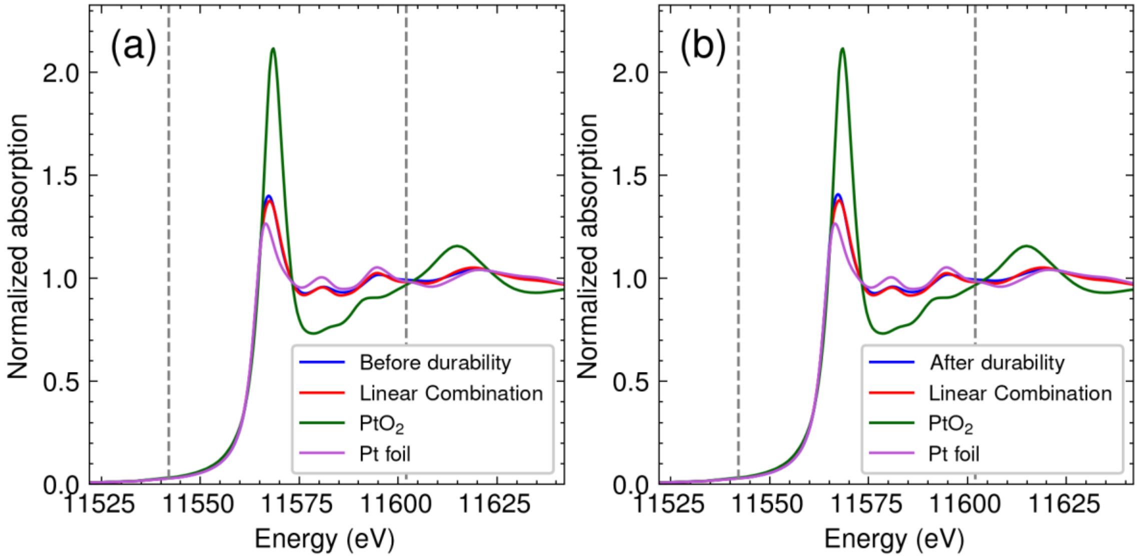

Figure S2. Linear combination fitting of the XANES spectra of (a) MEA samples of Sustainion AEM with Pt/C cathode electrode before and (b) after durability test. Pt foil and α-PtO_2 was used as references and fitted in the range of 11,542 to 11,602 eV.

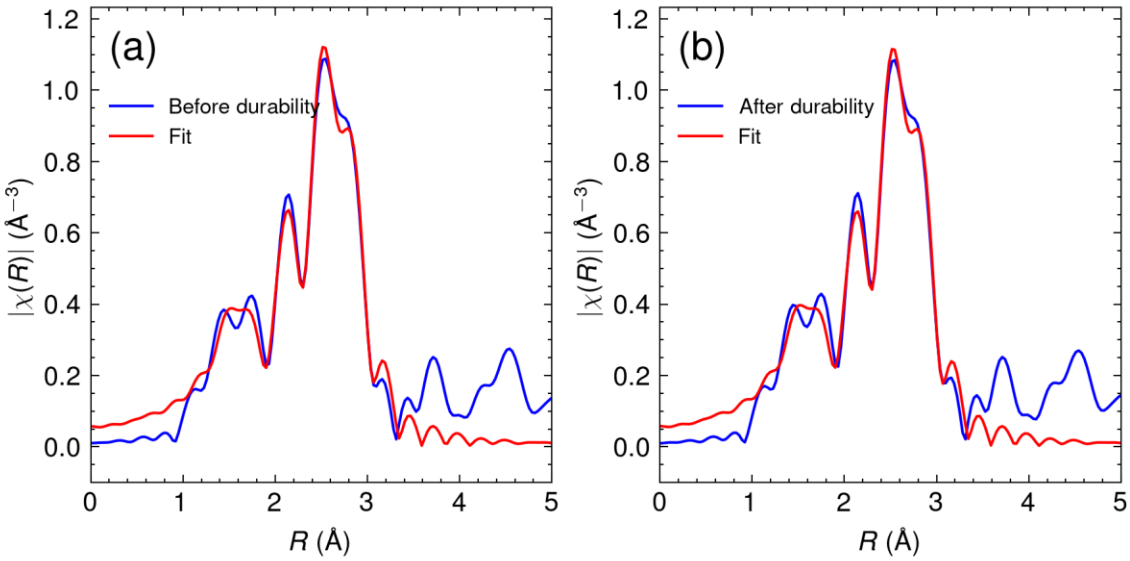

Figure S3. EXAFS fitting of (a) MEA samples of Sustainion AEM with Pt/C cathode electrode before and (b) after durability test. The k-range of 2 to 14.5 Å^{-1} and k^2 weighting were used in the Fourier transform. The r-ranges used for fitting the data were 1.35-3.00 Å.

Table S1: Summary of EXAFS Fitting of (a) MEA samples of Sustainion AEM with Pt/C cathode electrode before and (b) after durability test. EXAFS were fitted using Pt-Pt and

Pt-O single scattering paths. The amplitude reduction factor was fixed to 0.788 by fitting a Pt foil.

Sample	$N_{Pt\text{-}Pt}$	$\sigma^2_{Pt\text{-}Pt}$	$R_{Pt\text{-}Pt}$	$N_{Pt\text{-}O}$	$\sigma^2_{Pt\text{-}O}$	$R_{Pt\text{-}O}$	ΔE_0	χ_ν^2	*R*-factor
Before durability test	8.2 ± 0.5	0.0060 ± 0.0003	2.7554 ± 0.0027	0.95 ± 0.21	0.0040 ± 0.0026	1.985 ± 0.012	9.11	100.29	0.0070
After durability test	8.1 ± 0.5	0.0060 ± 0.0003	2.7556 ± 0.0030	0.98 ± 0.24	0.0041 ± 0.0028	1.984 ± 0.013	9.08	227.96	0.0082

Section S1: Scaling factor for sample average coordination and coordination number corresponding to Pt nanoparticles.

The relationship of the sample average coordination number (CN_{Pt-Pt}) can be expressed as

$$CN_{Pt-Pt} = \frac{2n_{Pt-Pt}}{N_{Pt}} \qquad (S2)$$

$n_{Pt-Pt}$is the number of first nearest neighbor Pt-Pt bonds, $N_{Pt}$is the total Pt atoms in the sample. MEA samples are analyzed as a linear combination of Pt foil and α-PtO_2, therefore n_{Pt-Pt} corresponds to the number of first nearest neighbor Pt-Pt bonds in Pt nanoparticle. By using the number of Pt atoms in the Pt nanoparticles ($N_{Pt\,NPs}$), the coefficient (scaling factor) between the sample average coordination number and the coordination number of the first nearest neighbor in Pt nanoparticles ($CN_{Pt\,NPs}$) can be expressed as a molar ratio of Pt atoms in Pt nanoparticles and total Pt atoms, which can be calculated from the molar fraction of α-PtO_2.

$$CN_{Pt-Pt} = \frac{N_{Pt\,NPs}}{N_{Pt}} \times \frac{2n_{Pt-Pt}}{N_{Pt(NPs)}} = \frac{N_{Pt\,NPs}}{N_{Pt}} CN_{Pt\,NPs} \qquad (S3)$$

1. J. Lilloja, E. Kibena-Põldsepp, A. Sarapuu, J.C. Douglin, M. Käärik, J. Kozlova, P.a.r. Paiste, A. Kikas, J. Aruväli, and J. Leis, *ACS catalysis.* **2021**, *11*, 1920-1931.