

Electronic Supplementary Information (ESI)

Elucidating the degradation mechanisms of Pt-free anode anion-exchange membrane fuel cells after durability testing

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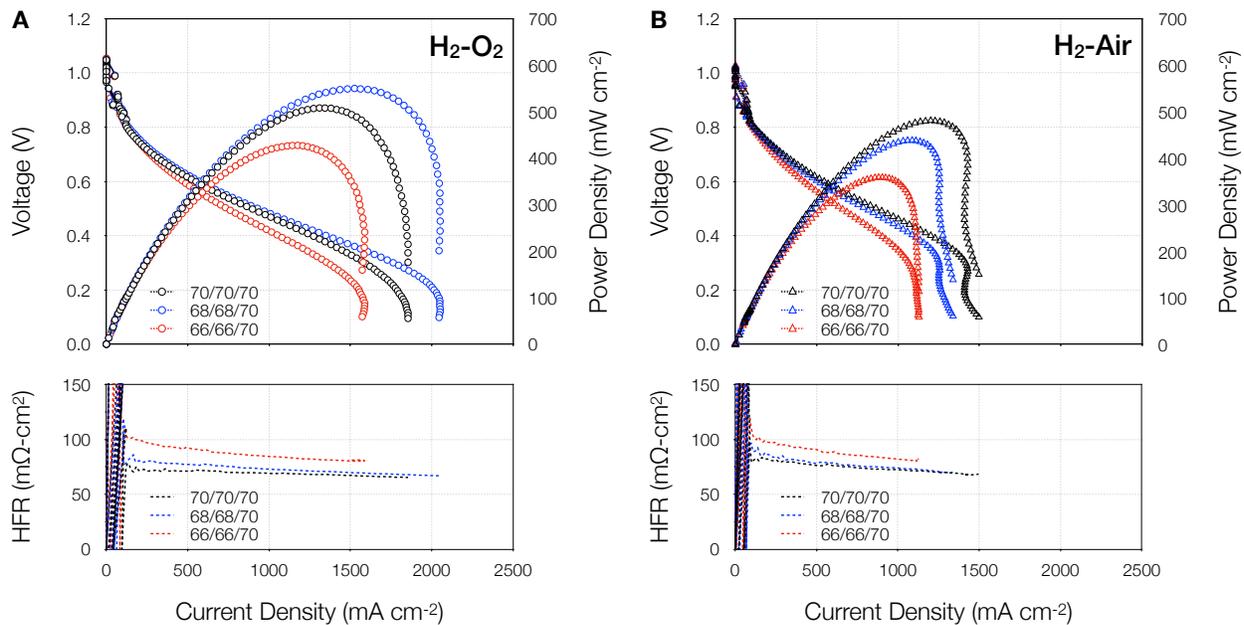
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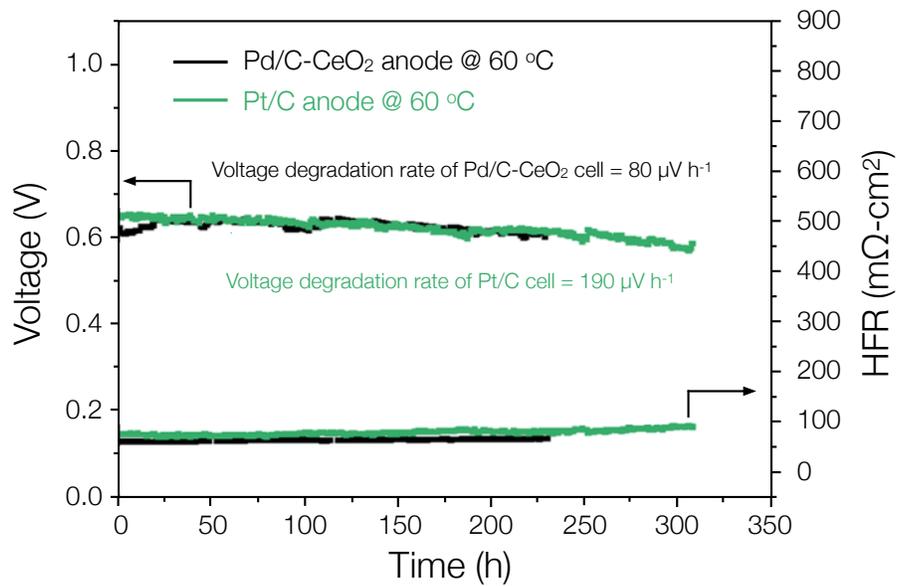
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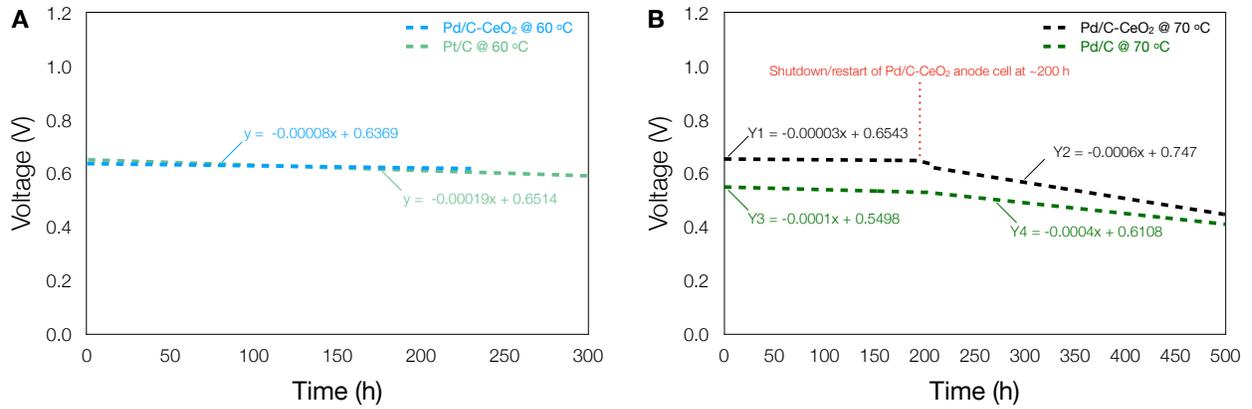
Supplementary Figures



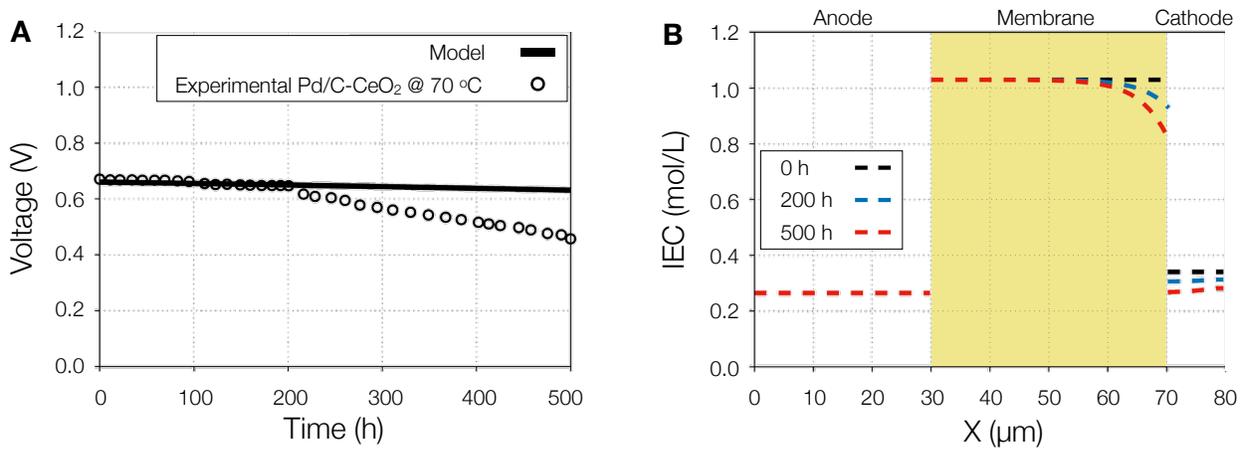
Supplementary Figure 1. Polarization curves of (a) H₂-O₂ and (b) H₂-Air AEMFCs with Pd/C anode and standard Pt/C cathode and their respective high-frequency resistance (HFR) plots are shown in the lower panels. The cell was operated at 70 °C with varying anode and cathode dew points. H₂/O₂ and H₂/Air flow rates were 1|1 slpm, with a backpressure of 131 kPa and specifics about the MEAs can be found in the Experimental section. The figure legends indicate anode dew point/cathode dew point/cell temperature. Horizontal gridlines in all Figures correspond to left y-axis.



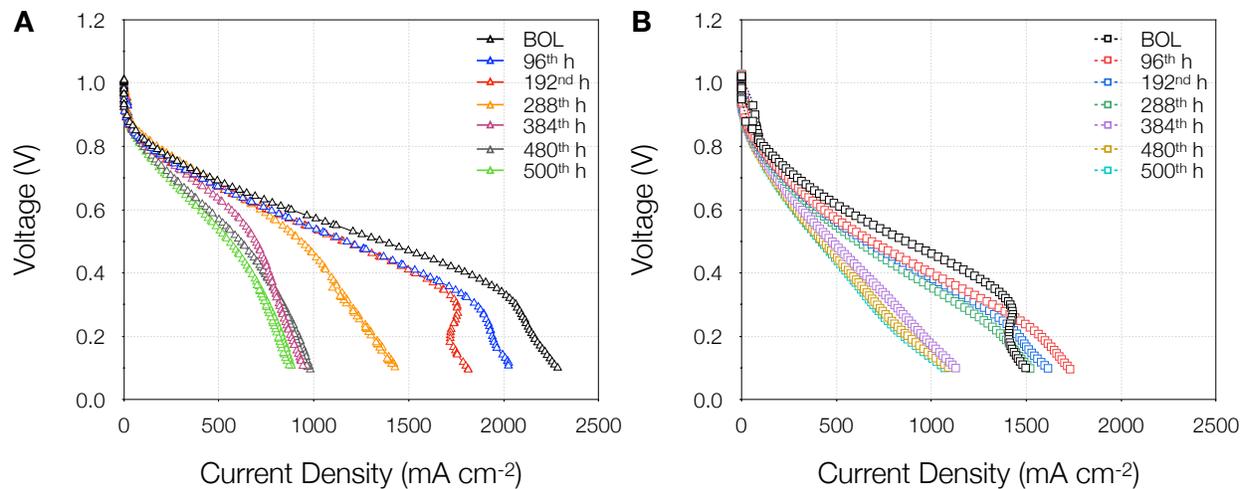
Supplementary Figure 2. H₂-Air AEMFC durability comparison at a constant current density load of 600 mA cm⁻² of Pd/C-CeO₂ and Pt anodes at 60 °C for 230 and 310 h, respectively. The H₂-Air flow rates of 1|1 slpm with a backpressure of 121 kPa on both sides and specifics about the MEAs can be found in the Experimental section. A straight-line degradation algorithm was used to calculate the voltage degradation rates listed on the plots in units of μV h⁻¹, of which further details can be found in **Experimental Section 2.4** and **Supplementary Figure 3**.



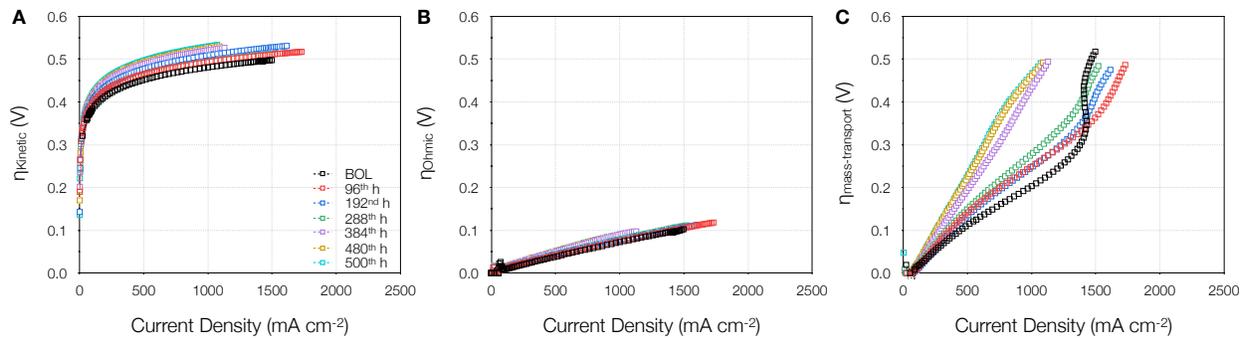
Supplementary Figure 3. Straight line degradation plots showing the equation of each straight line that was used to calculate the degradation rates in units of $\mu\text{V h}^{-1}$ for (A) **Figure 2C** and **Supplementary Figure 4** and, (B) **Figure 2D**. In (B), The Pd/C-CeO₂ anode cell (black dashed line) was processed for ~200 h before an 8 h shutdown. Afterwards, the cell was restarted and operated at the same operating conditions for an additional 300 h, while the Pd/C anode cell (green dashed-line) operated continuously for 500 h. Further details on the algorithms used to calculate the straight-line equations can be found in Experimental Section 2.4.



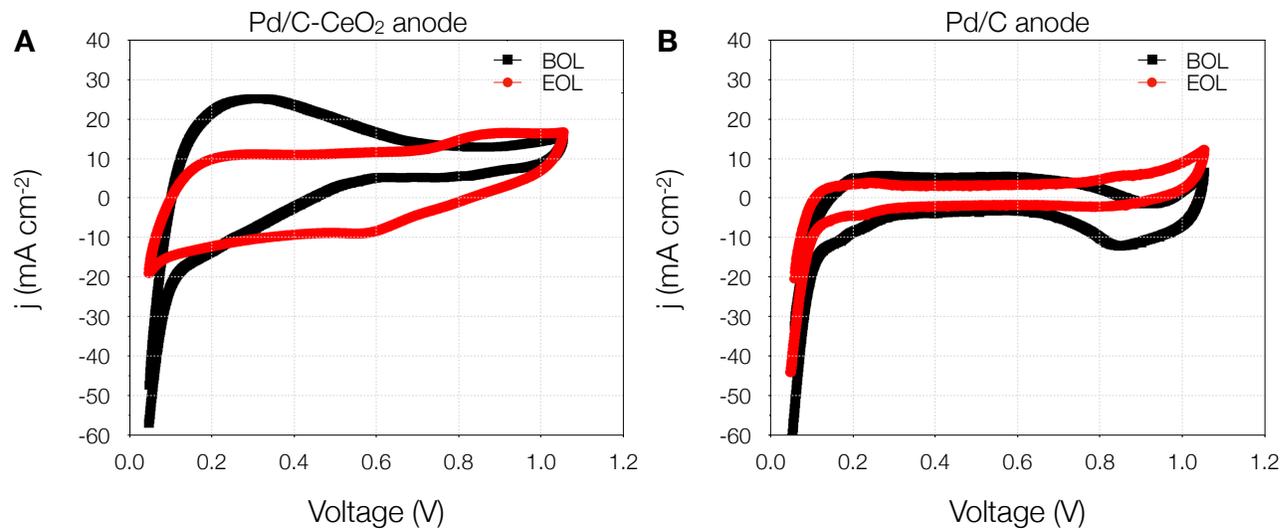
Supplementary Figure 4. 1D numerical modeling results of Pd/C-CeO₂ MEA at 70 °C: (A) cell voltage vs. time and (B) ion exchange capacity (IEC) across the cell as a function of time.



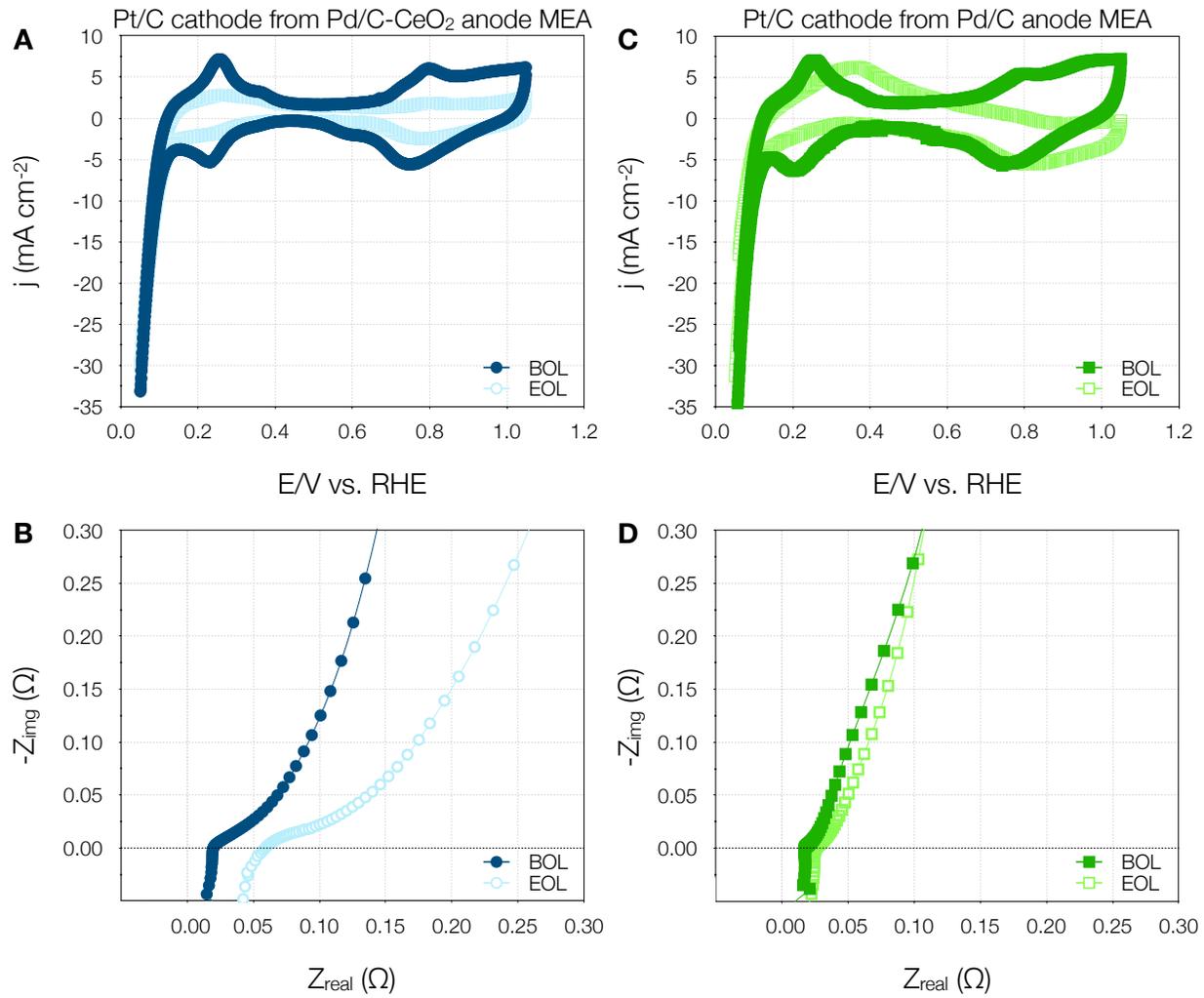
Supplementary Figure 5. H₂-Air i-V curves at 70 °C recorded during the respective durability tests shown in **Figure 2D** at the beginning of life (BOL), 96th, 192nd, 288th, 384th, 480th, and 500th h for AEMFCs made with the (A) Pd/C-CeO₂ anode and, (B) Pd/C anode.



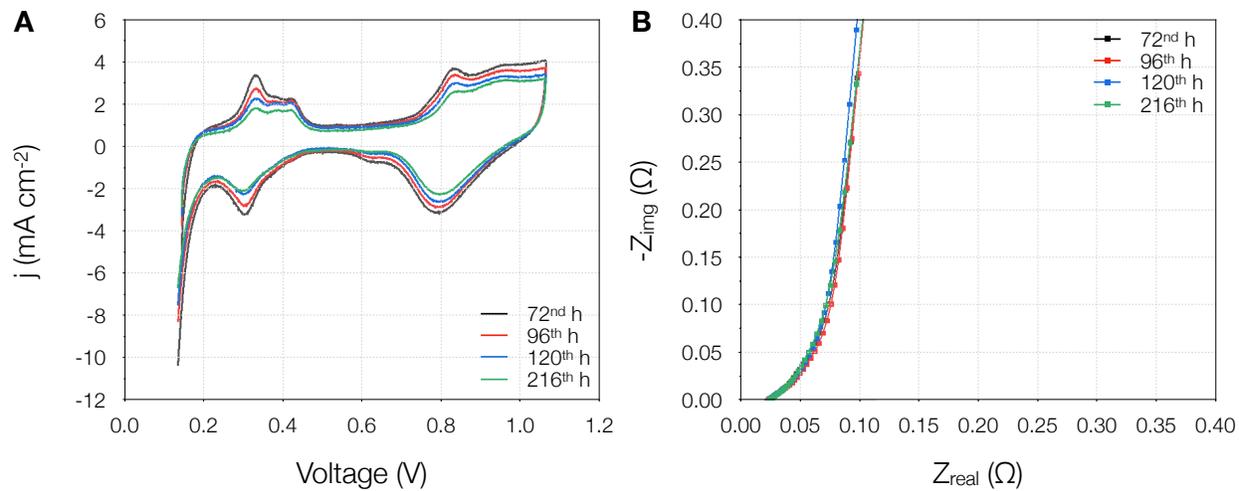
Supplementary Figure 6. The deconvoluted i-V curves of the Pd/C anode AEMFC operated in H₂-Air at 70 °C recorded during the respective durability tests shown in **Figure 2D** at the beginning of life (BOL), 96th, 192nd, 288th, 384th, 480th, and 500th h. (A) Kinetic overpotential, (B) ohmic overpotential, and (C) mass-transport overpotential.



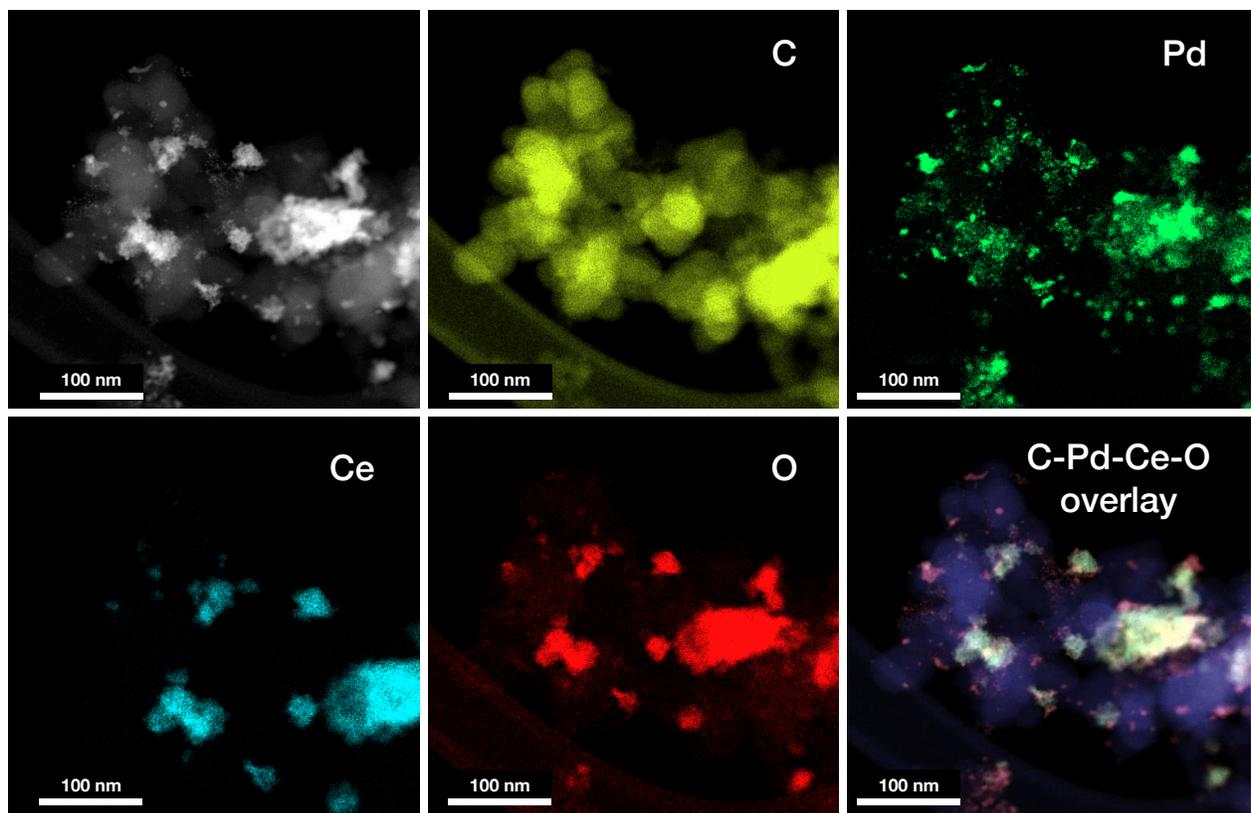
Supplementary Figure 7. H₂/N₂ *in-situ* CV diagnostics for (A) Pd/C-CeO₂ anode and (B) Pd/C anode cells tested at 70 °C before (BOL) and after (EOL) their respective 500 h durability tests. CVs were recorded at a scan rate of 20 mV s⁻¹.



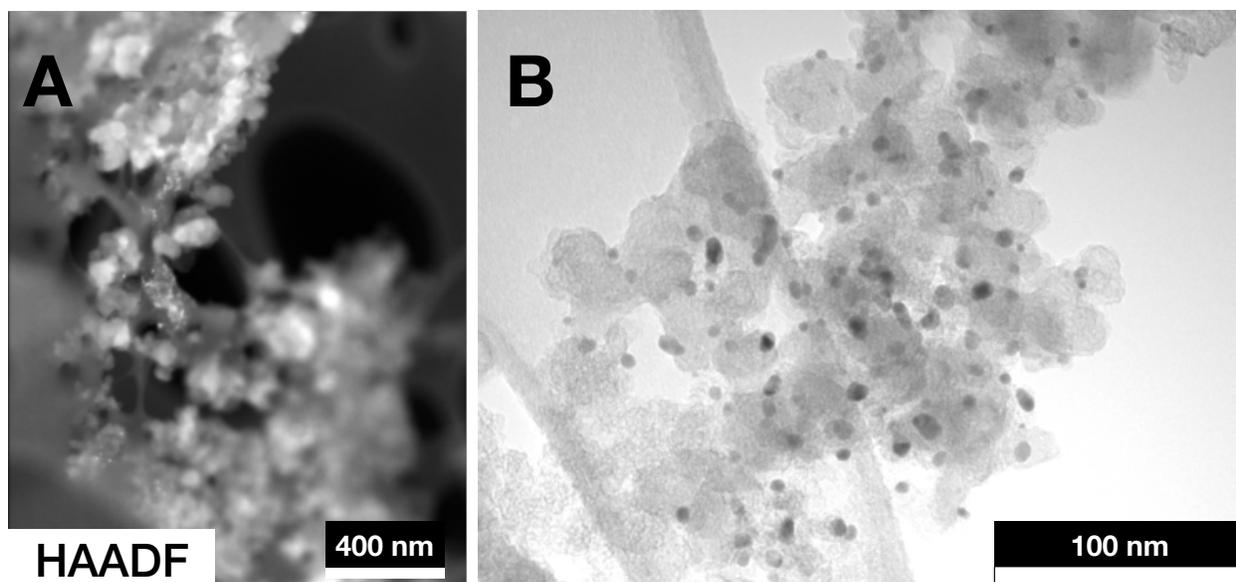
Supplementary Figure 8. H₂/N₂ *in-situ* (A,C) CV and (B,D) EIS diagnostics for common Pt/C cathodes for cells tested at 70 °C, both before and after their 500 h durability tests. (A,B) correspond to the cathode for the Pd/C-CeO₂ anode cell, while (C,D) are for the cathode of the Pd/C anode cell. CVs (A,C) were recorded at a scan rate of 20 mV s⁻¹.



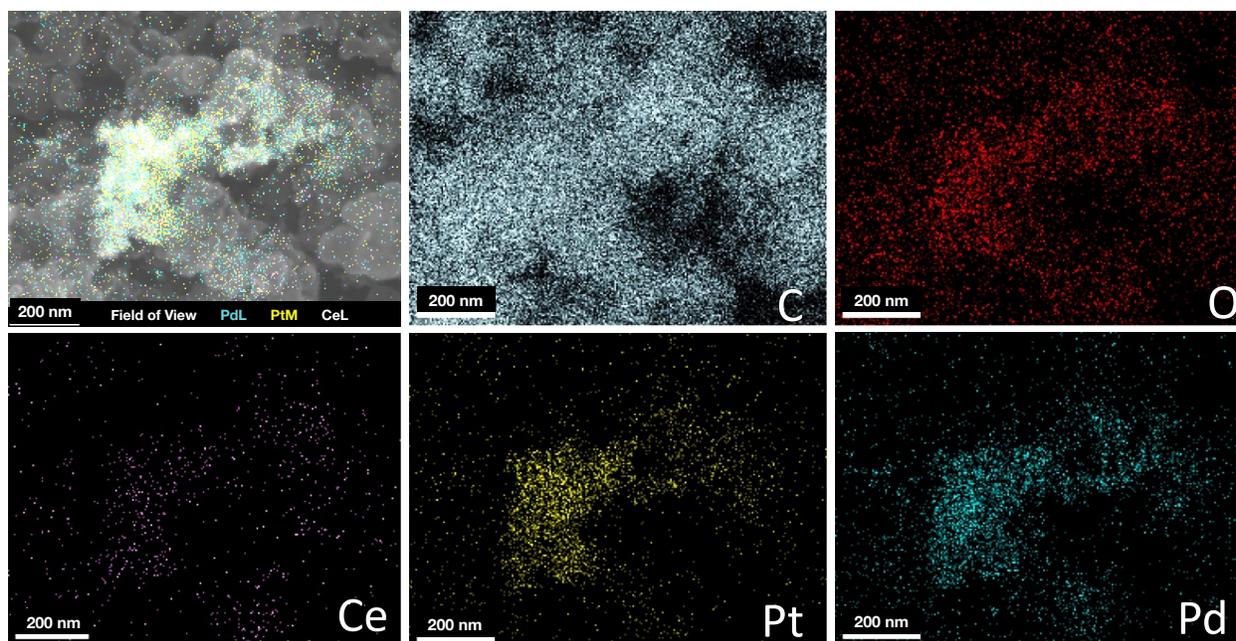
Supplementary Figure 9. H₂/N₂ in-situ (A) CV and (B) EIS diagnostics for Pt/C cathode of the Pd/C-CeO₂ anode cell tested at 60 oC for ~200 h. CVs in (A) were recorded at a scan rate of 20 mV s⁻¹.



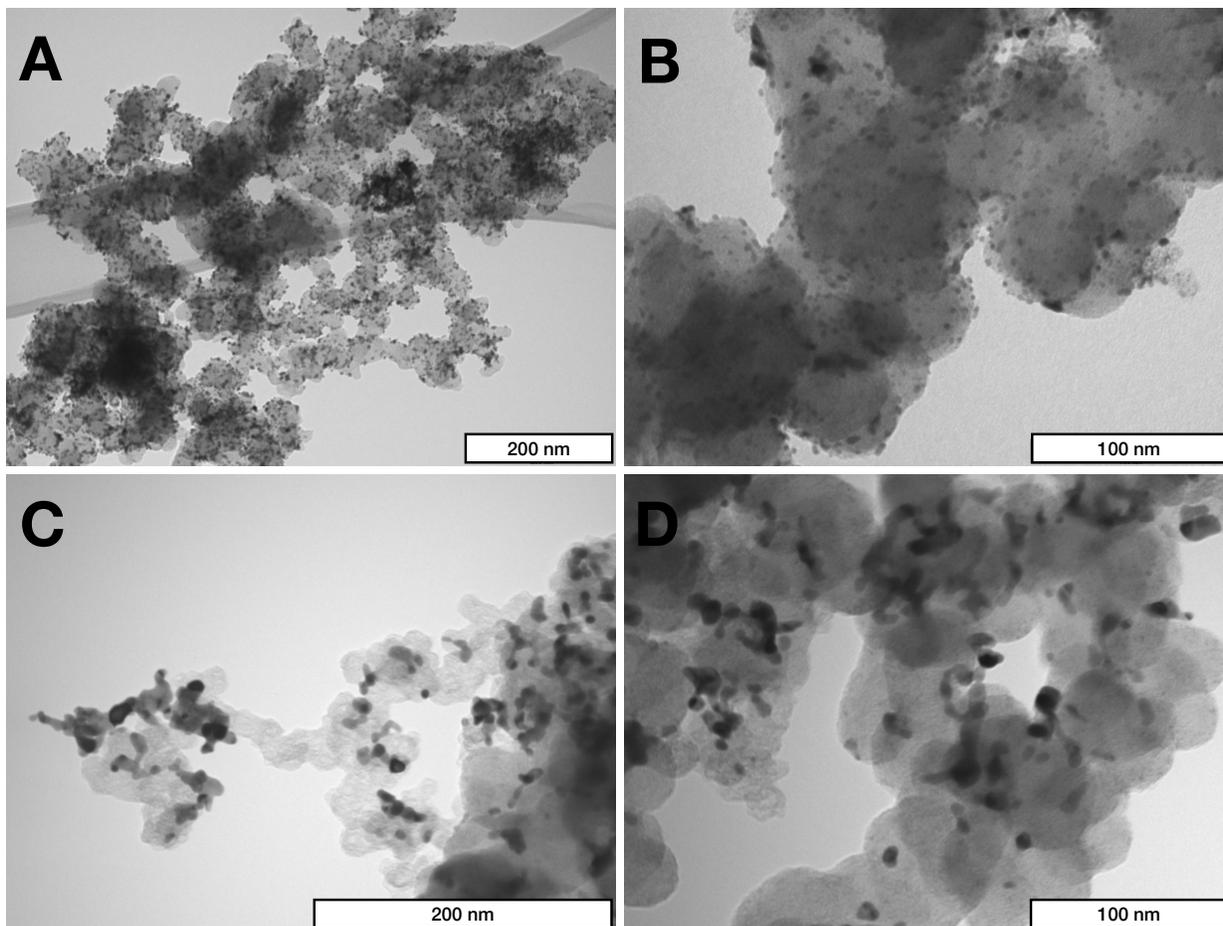
Supplementary Figure 10. Z-contrast STEM micrograph of pristine Pd/C-CeO₂ (scale bar 100 nm) and related EDAX maps for C, Pd, Ce, O, and overlay of C, Pd, Ce, and O.



Supplementary Figure 11. (A) HAADF and (B) TEM images of the pristine Pd/C catalyst.



Supplementary Figure 12. Higher magnification SEM image of a representative area of the Pd/C-CeO₂ anode catalyst layer GDE surface after 500 h AEMFC durability testing. Corresponding elemental maps for C, O, Ce, Pt, and Pd.



Supplementary Figure 13. (A, B) TEM images of pristine Pt/C and (C, D) Pt/C after 500 h AEMFC test.

Supplementary Tables

Supplementary Table 1. Cell performance parameters, namely open circuit voltage, corresponding current density values at 0.8, 0.6, and 0.4 V, limiting current density and voltage efficiency, of H₂-O₂ and H₂-Air AEMFCs operated at 70 °C using Pd/C-CeO₂ anodes.

Anode-Cathode Feed	OCV (V)	j@0.8 V (mA cm ⁻²)	j@0.6 V (mA cm ⁻²)	j@0.4 V (mA cm ⁻²)	j _{lim} (mA cm ⁻²)	η _v ^a
H ₂ -O ₂ (70/70/70)	1.042	266.9	1108.6	1913.2	2622.9	0.51
H ₂ -O ₂ (68/68/70)	1.041	228.2	1052.6	2249.4	3449.3	0.50
H ₂ -O ₂ (66/66/70)	1.040	154.3	910.1	2160.7	3581.8	0.47
H ₂ -Air (70/70/70)	1.012	152.7	867.0	1794.2	2284.5	0.46
H ₂ -Air (68/68/70)	1.010	134.2	799.4	1717.8	2303.4	0.44
H ₂ -Air (66/66/70)	1.011	113.3	662.1	1528.2	2096.6	0.42

^a Voltage efficiencies are calculated from thermodynamic cell voltage ($\eta_v = V/E_{cell}$) at 1000 mA cm⁻², V: operating cell voltage @1000 mA cm⁻² and E_{cell}: thermodynamic cell voltage of 1.23 V

Supplementary Table 2. Optimized cell performance parameters, namely open circuit voltage, corresponding current density values at 0.8, 0.6, and 0.4 V, limiting current density and voltage efficiency, of H₂-O₂ and H₂-Air AEMFC operated at 70°C using Pd/C-CeO₂ and Pd/C anodes.

Anode-Cathode Feed	Anode	OCV (V)	j@0.8 V (mA cm ⁻²)	j@0.6 V (mA cm ⁻²)	j@0.4 V (mA cm ⁻²)	j _{lim} (mA cm ⁻²)	η _v ^a
H ₂ -O ₂ (68/68/70)	Pd/C	1.051	135.9	571.0	1349.0	2047.7	0.39
H ₂ -O ₂ (68/68/70)	Pd-CeO ₂ /C	1.041	228.2	1052.6	2249.4	3449.3	0.50
H ₂ -Air (70/70/70)	Pd/C	1.022	116.7	545.8	1200.6	1496.4	0.38
H ₂ -Air (70/70/70)	Pd-CeO ₂ /C	1.012	152.7	867.0	1794.2	2284.5	0.46

^a Voltage efficiencies are calculated from thermodynamic cell voltage ($\eta_v = V/E_{cell}$) at 1000 mA cm⁻², V: operating cell voltage @1000 mA cm⁻² and E_{cell}: thermodynamic cell voltage of 1.23 V

Supplementary Table 3. EIS results of Pd/C-CeO₂ and Pd/C at the beginning of life (BoL) and end of life (EoL) of the durability test.

Anode Catalysts	High-frequency resistance (mΩ-cm ²)	Catalyst layer ionomer resistance
Pd/C-CeO ₂ (BOL)	108	149
Pd/C-CeO ₂ (EOL)	302	160
Pd/C (BOL)	93	46
Pd/C (EOL)	118	63

BOL- beginning of life, EOL: end of life