

# Air Oxidation of Carbon Supports Boosts Low-Humidity Fuel Cell

## Performance

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## Experimental Section

**Preparation of the carbon supports.** C1 was synthesized by annealing 2 g of Ketjenblack EC-300J in a tube furnace at 1000 °C for 2 hours under an argon flow. C2 and C3 involved initially heating 2 g of Ketjenblack EC-300J in a fixed bed to 500 °C for 3 and 5 hours under flowing dry air respectively. Subsequently, these samples underwent a second annealing step in a tube furnace at 1000 °C for 2 hours under an argon flow, yielding the final C2 and C3. The heating rate from room temperature to the target temperature and the gas flow rate were consistently maintained at 5 °C/min and 200 mL/min, respectively, across all experiments.

**Synthesis of the Pt/C catalysts.** In a typical synthesis, 50 mg of carbon support and 26.26 mg of H<sub>2</sub>PtCl<sub>6</sub> were firstly mixed in 17.5 ml of water and subjected to 30 minutes of ultrasonication. Next, 35 ml of ethylene glycol were added, and ultrasonication was continued for an additional hour. Subsequently, the mixed solution was heated to 120 °C and maintained at this temperature for 2 hours. Following this, the mixture was filtered and washed with deionized water. After drying at 60 °C, the powder was annealed in 5 vol% H<sub>2</sub>/Ar at 300 °C for 2 hours to obtain the final Pt/C catalyst.

## Physical Characterization

Nitrogen sorption isotherms were measured at 77 K using a Quantachrome Autosorb-iQ analyzer. Specific surface areas were determined using the Micropore BET assistant program in Quantachrome ASiQWin software package; total pore volumes were determined at P/P<sub>0</sub> = 0.99; the pore size distributions were calculated using the quenched solid density functional theory method. XPS measurements were conducted using a Thermo Scientific ESCALAB 250Xi instrument. TEM observations were performed using a JEOL-2010F transmission electron microscope with an acceleration voltage of 200 kV. HAADF-STEM images were obtained on FEI Talos F200X operated at 200 kV.

Water vapor sorption isotherms were obtained using a dynamic vapor sorption analyzer (SMS-DVS Intrinsic). Cross-sectional SEM images of the membrane electrode Assembly (MEA) were acquired using a HITACHI SU8240 Cold Field Emission Scanning Electron Microscope. Before imaging, the MEA underwent polishing with the Leica EM TIC3X ion-beam milling system.

## MEA Preparation and Fuel Cell Testing

The cathode catalyst inks were made by mixing the resulting Pt/C catalysts with the ionomer solution (Aquion D79-25BS) in a solvent mixture of deionized water and n-propanol (at a weight ratio of ~5:5), followed by sonicating the dispersion in ice water for 2 hours. The ionomer-to-carbon ratio was set at 0.8. The preparation method of the anode catalyst ink was identical to the cathode catalyst ink except for using the commercial Pt/C (TEC10E30E) as the anode catalyst. Then, the inks were spray-coated onto the Nafion membrane (GORE, ~12  $\mu\text{m}$ ) using a Sono-Tek ultrasonic spray system. The Pt loading for the cathode and anode was carefully controlled at 0.1  $\text{mg cm}^{-2}$  and 0.05  $\text{mg cm}^{-2}$ , respectively. Two gas diffusion layers (22BB, SGL Carbon, 215  $\mu\text{m}$ ), two gaskets (140  $\mu\text{m}$ ), and the prepared catalyst-coated membranes were pressed together with a torque of 10 N·m to assemble the MEA.

For all single-cell tests, a seven-channel serpentine flow field was utilized. The pressure drop between the inlet and outlet of the flow field was found to be negligible. A fuel cell test station (Scribner 850e) was used for single-cell tests. All MEAs were activated before testing, which involves a break-in procedure and a voltage recovery step. The break-in procedure was first conducted by a series of voltage cycles in  $\text{H}_2$  /air, ranging from open circuit voltages to 0.30 V, under the conditions of 80 °C, 100% RH, and 150  $\text{kPa}_{\text{abs}}$ . Subsequently, the voltage recovery step was conducted by maintaining a constant voltage of 0.1 V in  $\text{H}_2$ /air for 2 hours at 40 °C, 150% RH, and 150  $\text{kPa}_{\text{abs}}$ . Following the activation process, the  $\text{H}_2$ -air polarization curve measurement was performed in the anodic direction using the constant current mode under the conditions of 80 °C, either 40% or 100% RH, and 150  $\text{kPa}_{\text{abs}}$ . Each data point was collected over a 3-minute interval and subsequently averaged for the final 1-minute period. Throughout the activation process and the  $\text{H}_2$ -air polarization curve measurement, the flow rates of both  $\text{H}_2$  and air were maintained at 0.5 and 2 L/min, respectively.

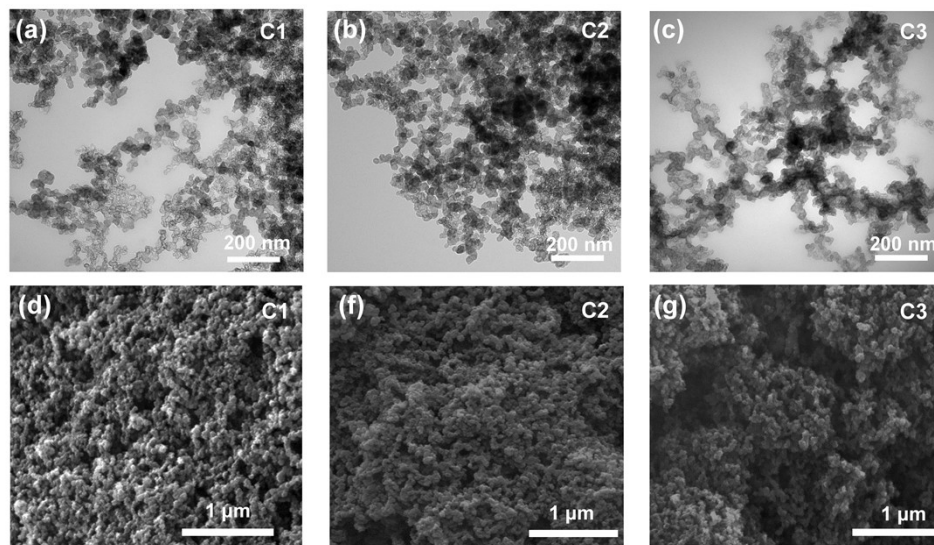
The testing procedure for mass activity included recording  $\text{H}_2$ - $\text{O}_2$  polarization curves from 0.8 V to 0.9 V at 80 °C and back pressures of 150  $\text{kPa}_{\text{abs}}$  under 100% RH, wherein the gas flow rates of anode and cathode were both 0.2 L/min. Each measurement point was maintained for 4 minutes, with the average of the final minute being used, and the measurements were taken in the anodic direction. Tafel plots were corrected for high-frequency resistance (HFR), hydrogen crossover density ( $i_{\text{H}_2}$ ), and the ohmic short of the membrane ( $R_{\text{short}}$ ), which was then used to

determine the mass activity at 0.9 V. The testing procedure for hydrogen crossover and the ohmic short of the membrane included recording H<sub>2</sub>-N<sub>2</sub> current at 0.4 V, 0.5 V, and 0.6 V at 80 °C and back pressures of 150 kPa<sub>abs</sub> under 100% RH, wherein the gas flow rates of anode and cathode were fixed at 0.5 L/min and 0.05 L/min, respectively. Each measurement point was maintained for 2 min, with the average of the final 30 s being used. The y-axis intercept, representing current, derived from the linear regression of the measured points, corresponds to  $i_{x, H_2}$ , while the inverse of the slope represents  $R_{short}$ .

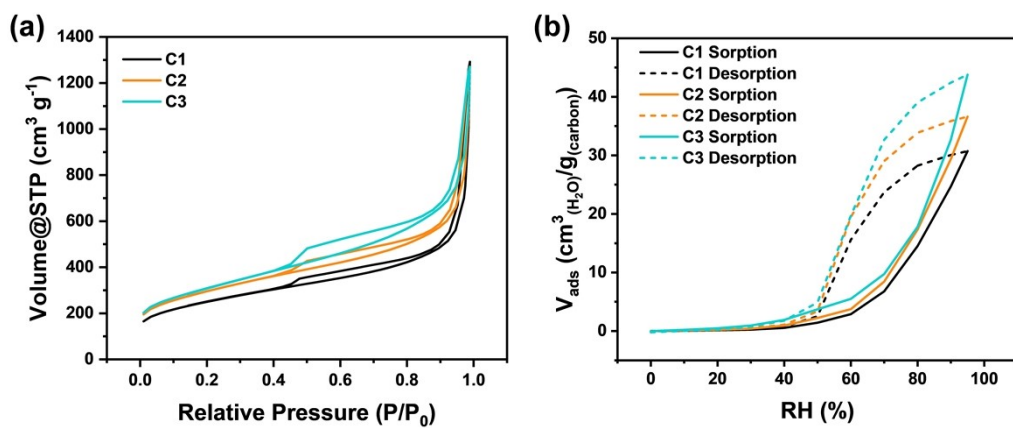
The total mass transport resistance ( $R_{total}$ ) was determined by the limiting current method at 80 °C and 70% RH under differential flow conditions (2 L/min H<sub>2</sub> and 5 L/min of O<sub>2</sub>/N<sub>2</sub> mixtures). Limiting currents ( $i_{lim}$ ) at different dry mole fractions of oxygen ( $X_{O_2}$ %) were measured to obtain the  $R_{total}$ , including 1.0, 1.5, 2.0, and 2.5% O<sub>2</sub> in N<sub>2</sub>. Besides, limiting currents were also measured at 100, 150, 200, and 250 kPa<sub>abs</sub> to determine the pressure-independent ( $R_{pi}$ ) oxygen transport resistance and the pressure-dependent ( $R_{pd}$ ) oxygen transport resistance.

The dry proton accessibility was evaluated by the ratio of electrochemical active surface area (ECSA) at 20% RH to 100% RH. The ECSA values were determined by CO stripping tests under 80 °C and 150 kPa<sub>abs</sub>. For CO stripping tests, 1% CO in N<sub>2</sub> was first introduced at a flow rate of 0.2 L/min for 30 minutes, keeping the cathode potential at 0.1 V. Following this, the cathode was purged with N<sub>2</sub> at a flow rate of 0.5 L/min for 20 minutes. Finally, under H<sub>2</sub>/N<sub>2</sub> atmosphere, the cyclic voltammetry was conducted by scanning from open circuit voltage to 1.2 V at a rate of 100 mV s<sup>-1</sup>.

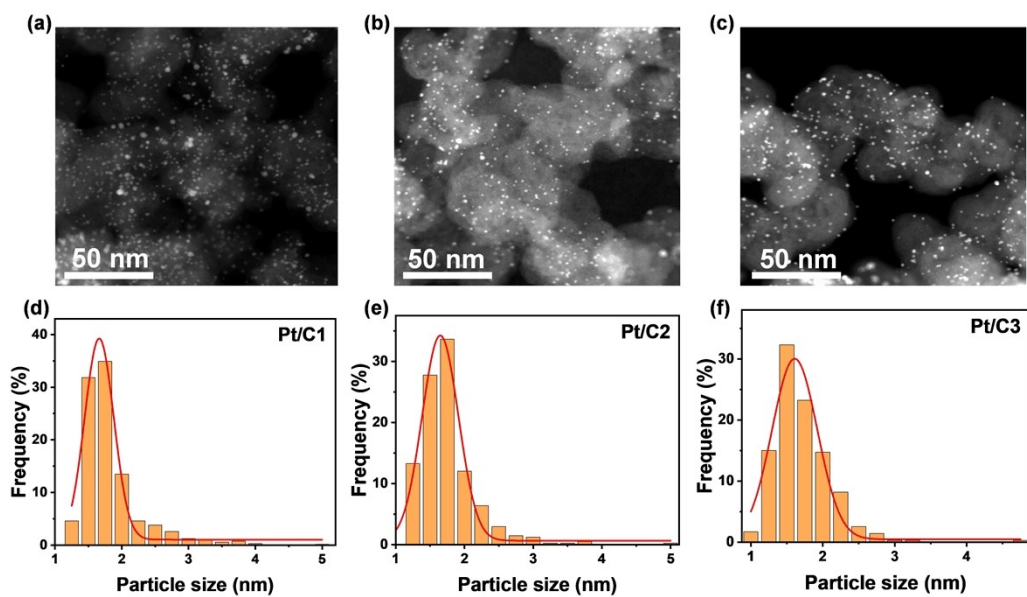
The proton conduction resistance of the cathode was determined from the electrochemical impedance spectroscopy (EIS) recorded in H<sub>2</sub>/N<sub>2</sub> at 0.2 V with a peak-to-peak perturbation of 3.5 mV between 500 kHz and 0.2 Hz. The transmission line model was used to fit the EIS data. The cathode proton resistivity ( $\rho_{H^+, cath}$ ) was obtained by dividing the proton transport resistance by the cathode catalyst layer thickness, wherein the cathode catalyst layer thickness was determined by SEM cross-section imaging.



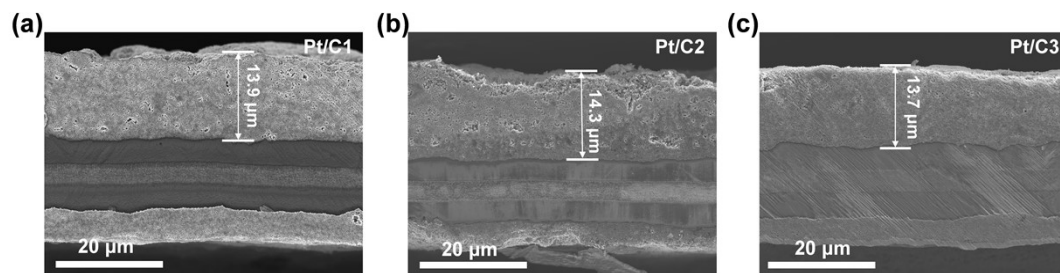
**Fig. S1** (a-c) TEM images of C1 (a), C2 (b), and C3 (c). (d-g) SEM images of C1 (d), C2 (f), and C3 (g).



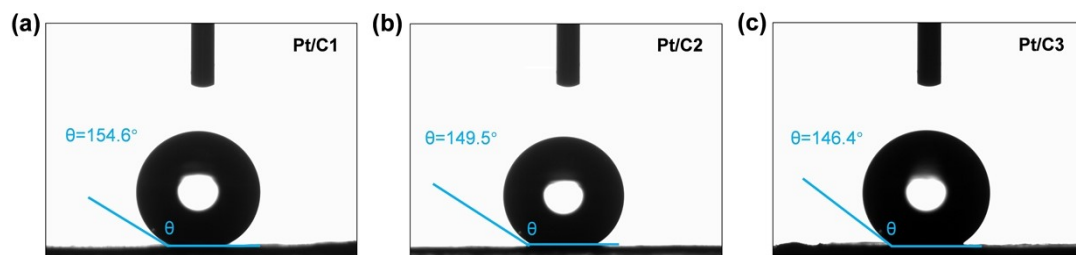
**Fig. S2** (a) Nitrogen sorption isotherms of C1, C2, and C3. (b) Water vapor sorption isotherms of C1, C2, and C3.



**Fig. S3** (a-c) HAADF-STEM images of Pt/C1 (a), Pt/C2 (b), and Pt/C3 (c). (d-f) Particle size distributions of Pt/C1 (d), Pt/C2 (e), and Pt/C3 (f).



**Fig. S4** SEM cross-section images of the MEAs made from the Pt/C1 catalyst (a), the Pt/C2 catalyst (b), and the Pt/C3 catalyst (c), respectively.



**Fig. S5** Contact angle images of the cathode catalyst layers made from Pt/C1 catalyst (a), the Pt/C2 catalyst (b), and the Pt/C3 catalyst (c), respectively.



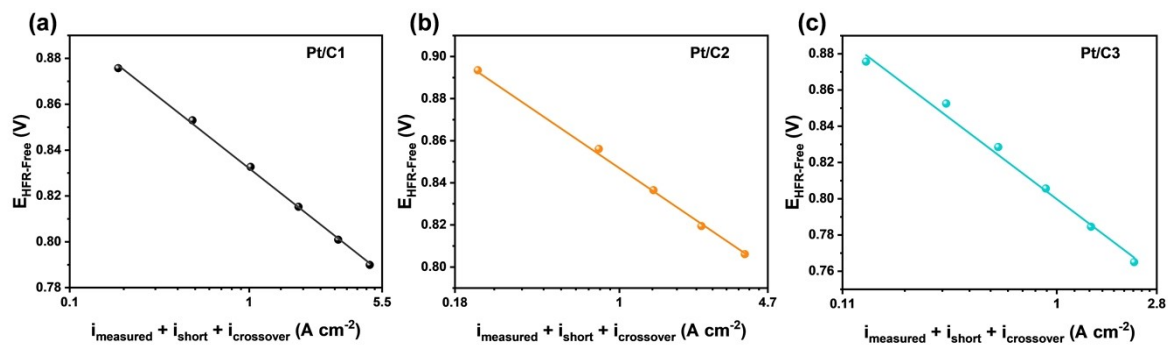


Fig. S6  $H_2$ - $O_2$  Tafel curves of the resulting Pt/C catalysts.

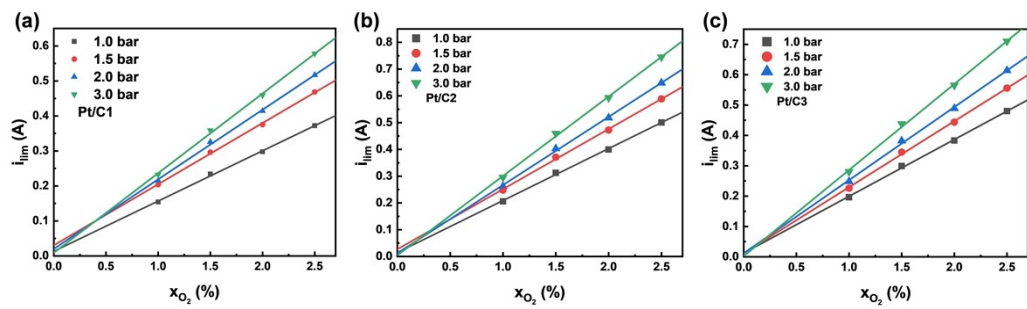
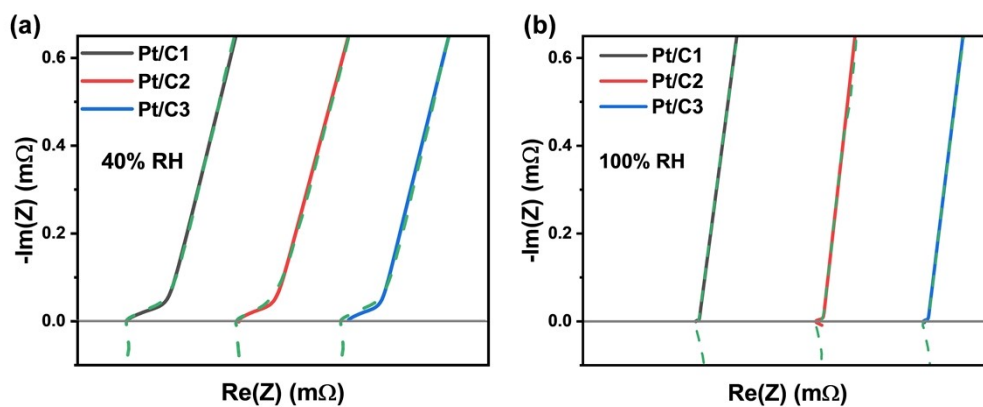
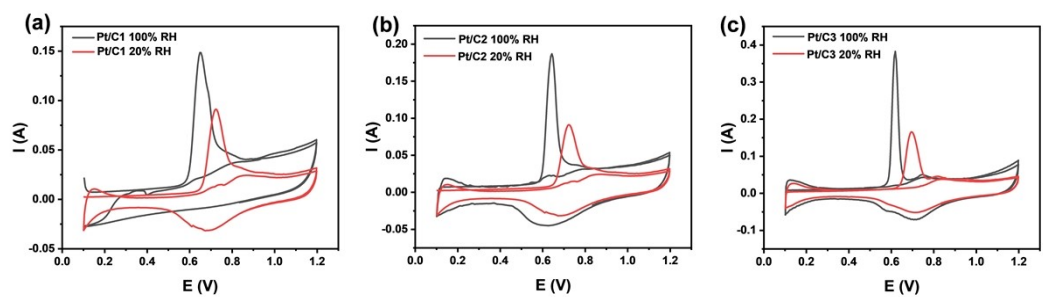


Fig. S7 Limiting currents measured at different oxygen concentrations and back pressures.



**Fig. S8** The measured  $H_2-N_2$  EIS data (solid lines) and the corresponding fitting results (dashed lines) under 40% RH (a) and 100% RH (b).



**Fig. S9** The measured CO stripping results of Pt/C1 (a), Pt/C2 (b), and Pt/C3 (c) under 20% RH and 100% RH, respectively.