Supporting Information

I. SOFC Electrochemical Measurement

The SOFC test chamber used in these experiments consisted of an insulated, heated stainless steel cylindrical chamber, through which forming gas (5% hydrogen, 95% nitrogen) or air, both at 30 psi, were selectively flowed using manual valves. Figure S1 schematically depicts the test chamber. Once the test chamber had been heated and stabilized thermally at a desired temperature, the SOFC was placed on the chamber’s inset opening, with a gold gasket (0.80” inner diameter, 0.5mm thick; Scientific Instrument Services) between the device and chamber surface. The gold gasket established both a hermetic seal for the anode environment directly below the SOFC, and electrical contact between the anode current collector and the test chamber body. External wires attached to the chamber’s gas inlet served as the direct electrical link to the anode. On the cathode side (ie. the air-exposed, “top” side of the SOFC), a mica gasket and torroid-shaped stainless steel cap loaded with weights on ceramic stilts were then placed on top of the device to ensure adequate pressure for the anode-side hermetic seal. Platinum wire (0.009” diameter; Scientific Instrument Services) held in place with a micromanipulator probe holder served as the cathode electrical probe. Using shielded wiring

FIG. S1. Schematic of SOFC test chamber.

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to avoid stray inductance effects, each SOFC was thus electrically connected to a Princeton Instruments VSP potentiostat and impedance analyzer.

Current density data from the SOFCs were collected using voltage increments of 0.75 mV/s, and EIS was performed in the frequency range of 1 mHz – 1 MHz with an ac oscillation amplitude of 75 mV under zero bias. EIS data were analyzed using the equivalent circuit $R_{YSZ} + Q_{\text{electrodes}}/R_{\text{electrodes}}$ with the ZFit procedure of BioLogic’s EC-Lab software using Randomize + Simplex. **Figure S2** shows a schematic Nyquist plot depicting the displacement on the resistance axis from the origin, and a single arc labeled as regions I and II. EIS data were analyzed using the equivalent circuit $R_{YSZ} + Q_{\text{electrodes}}/R_{\text{electrodes}}$. In fact, “$R_{YSZ}$” combines both the YSZ electrolyte resistance and the resistances of the leads and the other various electrical contacts in the measurement circuit. The area-specific resistance (ASR) results plotted in Fig. 6 (b) of the main paper were extracted from the measured complex impedance using this circuit model. In the range of temperatures tested, the electrode resistance after $P(\text{O}_2)$ cycling pre-treatment was consistently lower than that of a corresponding no pre-treatment device, by at least one order of magnitude.

![Nyquist plot](image)

**FIG. S2.** Equivalent circuit model for sputtered Pt/YSZ/sputtered Pt SOFC complex impedance.

The FG/air cycling pre-treatment of SOFCs resulted in improved device performance, as shown in the J-V and J-P curves of **Figure S3**. Peak power values measured from Figure S3(b) are plotted in Figure 5(b) of the paper and are also listed in Table I.
FIG. S3. (a) J-V curves and (b) J-P curves at 350°C–550°C of FG/air cycling (thick lines) and no pre-treatment SOFCs (thin lines).

II. Pt Electrode Morphology after Stability Testing

FIG. S4. Low-magnification SEM images of nanoporous Pt SOFC electrodes after ~15-hour stability tests at 550°C. The underlying YSZ substrates are exposed and visible. The Pt and exposed YSZ regions are labeled accordingly.

The effect of P(O_2) cycling pretreatment on the evolution of the initially nanoporous Pt cathode and anode morphology is summarized in representative SEM images in Figure S4.
The effect is pronounced for the cathodes whereas the morphology of the anodes is apparently unaffected by FG/air cycling across the SOFC prior to stability testing at 550°C.

III. X-ray Photoelectron Spectroscopy

XPS (~ 5 nm depth resolution) was used to evaluate ex-situ the surface chemical states of the ‘no pre-treatment’ and ‘FG/air cycling’ pre-treated cathodes after stability tests.\[9\] For all samples tested, a PHI VersaProbe Scanning XPS Microprobe with an Al Kα X-ray source was used with the following settings: 58.70 eV beam energy, 45° angle of incidence, 200 μm spot size. Energy calibration for all spectra was performed using the common C 1s peak at 284.8 eV resulting from air exposure and deposition of adventitious carbon on the sample surface prior to XPS analysis. Figure S5 shows the XPS spectra for carbon, oxygen, and platinum of the as-deposited Pt, untreated device cathode, and FG/air pre-treated device cathode. The carbon peaks were nearly identical, indicating little change in the carbon chemical state for both cathodes compared to the as-deposited Pt material. The shallow peak to the left of the as-deposited C 1s peak was attributed to carboxyl (-COOH) groups. The oxygen 1s peak for the untreated SOFC showed a slight broadening relative to the as-deposited state, and the air-cycled O 1s peak showed a moderate broadening and greater intensity, both indicative of oxide contributions different from the as-deposited material. For example, Zr-O bonding from exposed YSZ may account for the additional peak contribution beyond Pt-O and C-O related oxides expected on the as-deposited Pt surface (which had effectively 100% Pt coverage). The Pt 4f\(_{7/2}\) peaks of both air-cycled and untreated cathodes exhibited a slight shift to lower binding energy of < 0.3 eV compared to the as-deposited Pt. This may be evidence of thermal decomposition during testing of possible PtO\(_x\) surface species\[s1\] present on the nano-porous Pt film prior to SOFC testing. It has been suggested\[s2\] that surface PtO\(_x\) formation during exposure of Pt electrodes to oxidizing atmospheres during SOFC operation may suppress the rate of O\(_2\) reduction at the cathode.
surface. The very similar XPS spectra obtained from the untreated and P(O_2) pre-cycled Pt cathodes suggest that there is no significant difference in PtO_x coverage of these two surfaces and, therefore, that a change in PtO_x surface coverage is not responsible for the observed pretreatment dependence of electrode ASR and SOFC performance.

![XPS spectra](image)

**FIG. S5.** Cathode comparison after ~14-hour 550 °C stability testing: XPS spectra of C 1s, O 1s, and Pt 4f peaks for as-deposited Pt, untreated SOFC cathode (“FG-only” present in anode compartment), and FG/air cycling pre-treated SOFC cathode. Vertical lines indicate peak locations.

References