

Supporting Information

Heterogeneous films of ordered CeO₂/Ni concentric nanostructures for fuel cell applications

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XRD patterns of CeO₂ nanotubes grown in AAO template were obtained on a Bruker C2 Discover (Parallel Beam) General Area Diffraction Detection (GADDs) system using a Bruker ACS Hi-Star detector. Monochromatic Cu K α radiation (40 kV and 40 mA) was used as the X-ray source. As shown in Figure S1, the X-ray diffraction patterns of CeO₂ nanotubes embedded in AAO template show amorphous and polycrystalline patterns before and after annealing, respectively.

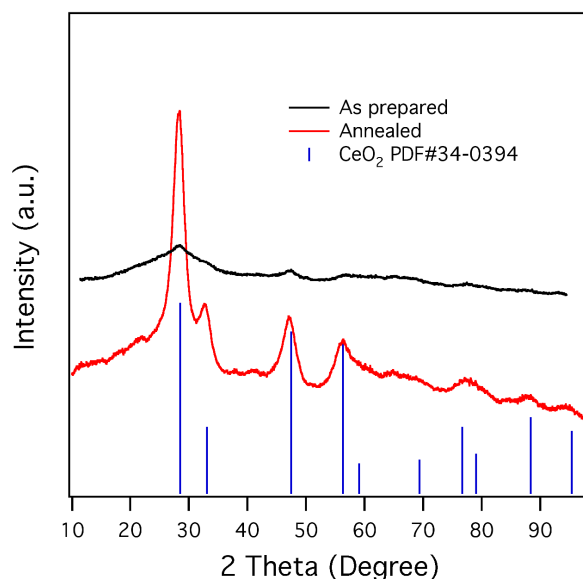


Figure S1. XRD patterns of as-prepared (black) and annealed (red) ceria nanotubes grown in an AAO template. As-prepared CeO₂ nanotubes are amorphous. After being annealed under nitrogen at 500°C for 1 hour, CeO₂ nanotubes show polycrystalline XRD pattern corresponding to PDF#34-0394 (CeO₂).

The CeO₂ nanotubes can be grown as long as 20+ μm . The TEM of a CeO₂ nanotube bundle in Figure S2a shows 23 μm tubes. In Figure S2b, the electron diffraction pattern shows the 3.1 Å lattice spacing associated with the $\langle 111 \rangle$ reflection of CeO₂.

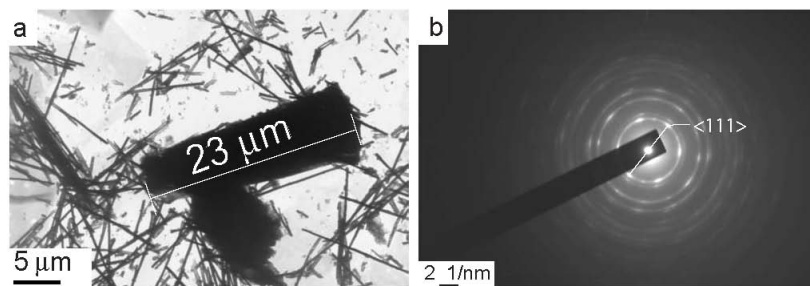


Figure S2. (a) TEM of ceria nanotubes grown inside an AAO template after both the AAO template and gold contact layer have been removed. The dark area is a bundle of CeO₂ nanotubes with total length of 23 μm. (b) Electron diffraction pattern of ceria showing polycrystalline structure of CeO₂.

Electroplated CeO₂ NTs show natural porosities illustrated by the HRTEM and SEM in Figure S3, which allows radial etching of AAO after CeO₂ was deposited.

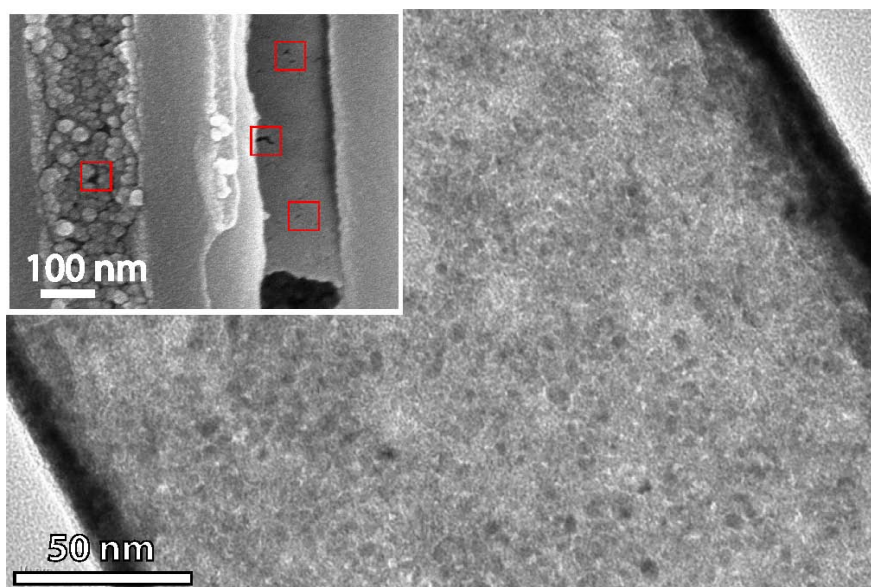


Figure S3. High resolution TEM and SEM (inset) images of CeO₂ nanotube, showing existence of porosities (marked with red squares) for electroplated CeO₂ NTs.

During electrodeposition of ceria, some of the CeO₂ nanotubes are formed with holes in the sections farthest from the Ti electrode. When these defect holes are big enough, it would allow the Ni growth inside the CeO₂ nanotubes, resulting in the formation of solid Ni wire cores. Nanotubes filled with Ni nanowires are easily differentiated through TEM and EDS line-scan and phase mapping analyses in Figure S3. While solid Ni nanowires were observed in *ca.* 30% of the CeO₂ nanotubes, they do not completely fill the tubes (Fig. S3a) and therefore do not represent a significant decrease in pore surface area. Complete removal of inner Ni wire growth is currently under investigation and will be discussed elsewhere.

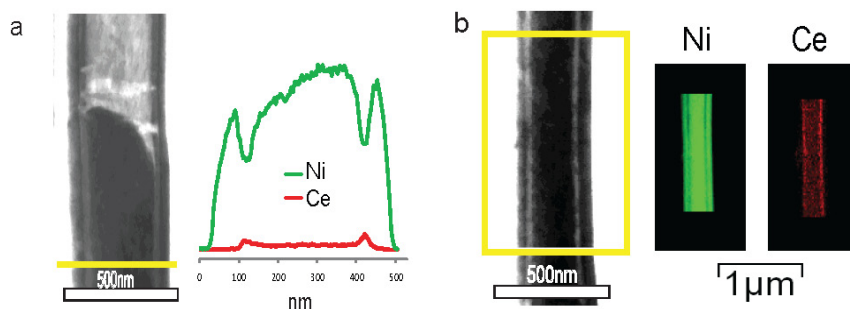


Figure S4. TEM images, EDS (a) line-scan and (b) phase map of coaxial Ni-CeO₂ nanotubes filled with nickel cores.

Preliminary electrochemical data were collected on SOFCs with a nickel-ceria nanocomposite film as the anode on a 1.0 mm thick Yttria-Stabilized Zirconia (YSZ) electrolyte.

Yttria-stabilized Zirconia electrolyte-supported cells were used in this study. Tosoh YSZ powder was die-pressed and sintered at 1450 °C for 3 hours to form electrolyte disks of 1 mm thickness and 23 mm diameter. Lanthanum Strontium Manganate – Yttria Stabilized Zirconia (LSM-YSZ) paste (*FuelCellMaterials.com*) was slurry deposited to one side of YSZ electrolyte disk. A 50 μm thick LSM-YSZ cathode layer was formed after sintering at 400 °C and 1300 °C for 1 hour respectively, where the temperature ramp rates were 0.5°/min. to 400°C, 1°/min. to 1300 °C and 2°/min to room temperature. A platinum gauze (52 mesh, from *Aldrich*) and platinum paste (from *Engelhard Corp.*) were used as the cathode current collector.

The ceria-Ni composite film anode was mounted onto the other side of YSZ disk as shown in Figure 3. Underneath the ceria-Ni film, porous YSZ paste – 60% YSZ nanopowder (*Aldrich*) and 40% glycerol (*Fisher*), and porous nickel paste (*FuelCellMaterials.com*) were applied in the center and on the edge of the YSZ surface, respectively (Figure 3). Extra nickel paste was applied on the edge of the composite film. The porous YSZ paste in the center is used to ensure the ionic connections between ceria tubes to YSZ electrolyte. The nickel paste provided strong adhesion to hold the composite film on the YSZ surface, and functioned as an interconnect with the gold wire lead. The anode structure was annealed *in situ* under 5% hydrogen diluted with argon.

The cell was tested by *GAMRY* potentiostat at 785 °C under diluted dry hydrogen flow. The membrane electrode assembly (MEA) was attached on an alumina tube (*AC Technologies*) sealed by Ceramabond 552 alumina paste (*AREMCO Products, Inc.*). The cell was fired to 785°C under 5% hydrogen diluted in argon. Under different hydrogen partial pressure (6.7%, 16.7%, 33.3% and 66.7%), Linear Sweep Voltammetry (LSV) (Fig. 4) and Electrochemical Impedance Spectroscopy (EIS) (Fig. S4) were conducted at 785°C by *GAMRY*.

Ni-CeO₂ current density contributions from the nanocomposite film in our current experiment were estimated from calculating electrochemically active areas of the film and the Ni paste. The contribution of the film was then calculated by subtracting contributions from the Ni paste from a control standard under the same conditions (Figure 4, green data). The electrolyte ohmic resistance (R_{bulk}) is $\sim 3 \Omega \cdot \text{cm}^2$ shown in the

EIS Nyquist plot in Fig. S5. While the estimated current enhancements are modest due to the usage of thick electrolyte, poor adhesion between the nanocomposite film and electrolyte, the experiment serves as a proof-of-concept experiment. Currently, attempts to make MEAs with the proposed nanocomposite membranes on ultrathin electrolytes are under investigation.

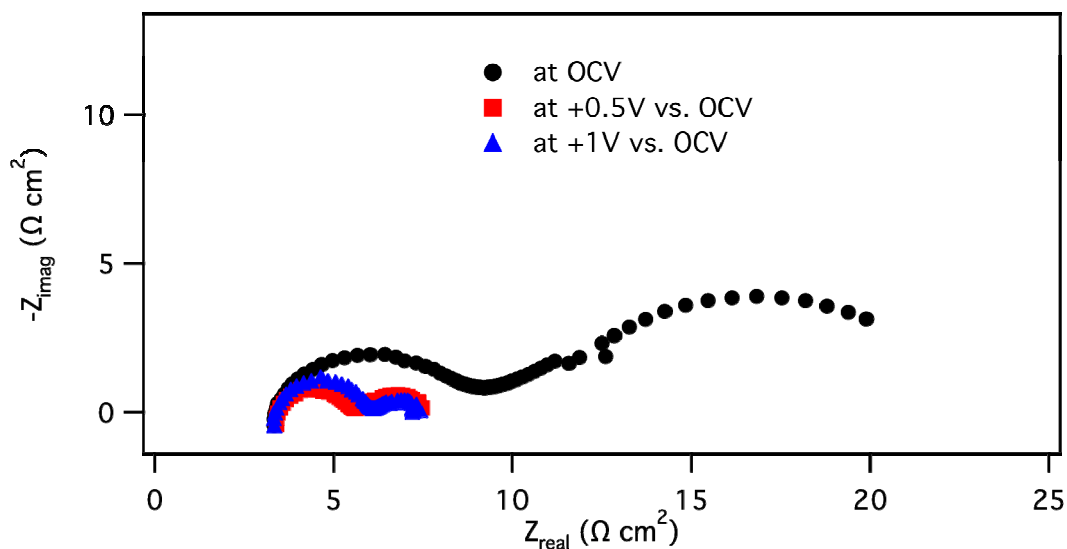


Figure S5. Impedance nyquist plots of nanocomposite Ni-CeO₂ / 1.0mm YSZ / LSM-YSZ cell operating at 785°C. Anode fuel flow is 0.67 atm. dry hydrogen diluted in Argon, and dry air flows at cathode side. The EIS spectra were taken at OCV (black dots), +0.5V (red squares) and +1.0V (blue triangles) overpotentials.