

## Supporting Information

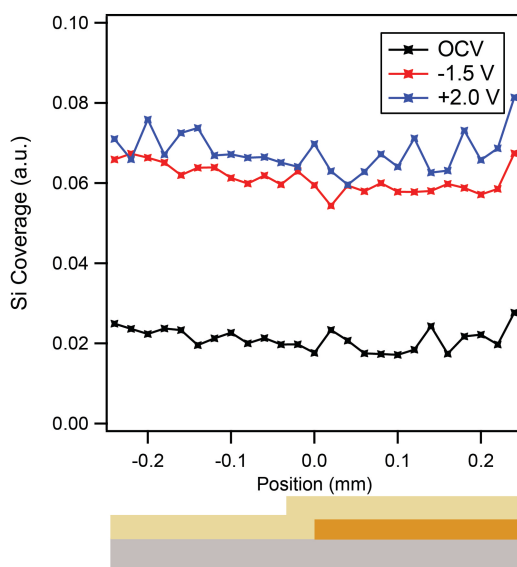


Figure S1. Coverage of silicon oxide on the ceria electrode surface under OCV, -1.5 V and +2.0 V. XPS data are collected in the order of OCV, -1.5 V and +2.0 V. The coverages are determined from the integrated intensities of the Si 2p peak. The values are normalized to the integrated signals of the Ce 4d peaks collected from the same spectrum. Corresponding schematic cell drawings are given at the bottom. Color scheme is given in Figure 1A.

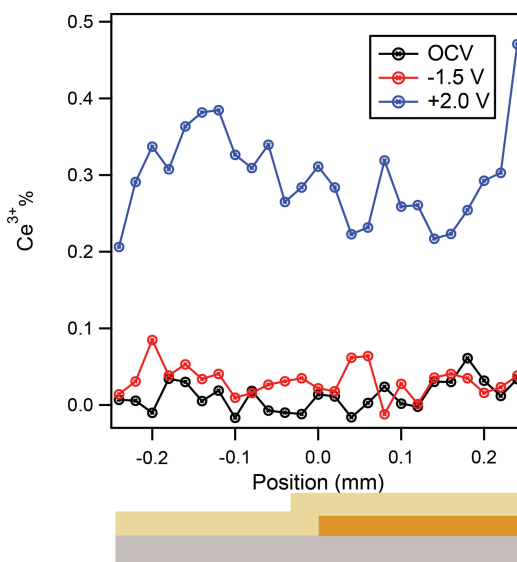


Figure S2. The relative concentrations of Ce<sup>3+</sup> measured in operando at OCV, -1.5 V and +2.0 V. The concentrations were determined from the ratio of the high binding energy Ce<sup>4+</sup> to the total fitted Ce area.

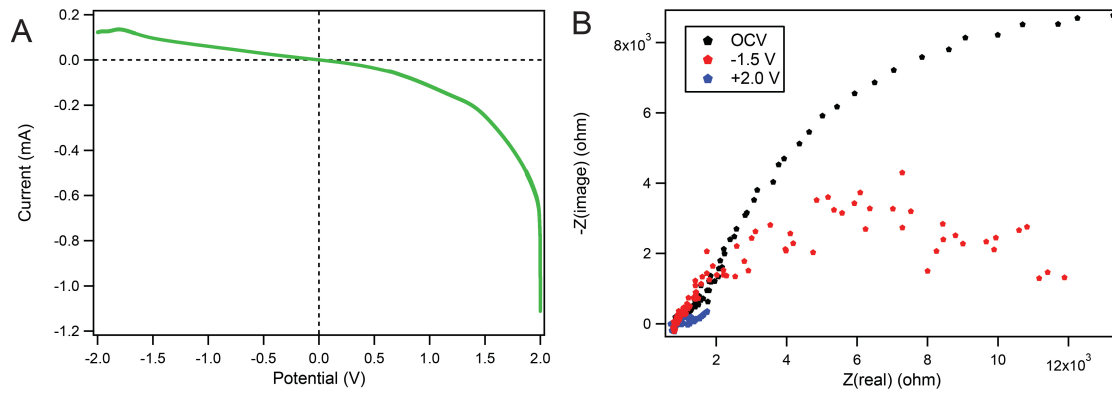


Figure S3. (A) Linear sweep voltammetry (LSV) polarization curves of solid oxide electrochemical cell with 1000-nm-thick ceria film recorded at  $\sim 600$  °C with 0.5 Torr 1:20 CO/CO<sub>2</sub> mixture. (B) Electrochemical impedance spectroscopy (EIS) of a 1000-nm-thick ceria cell under different applied biases (OCV, -1.5 and +2.0 V) and the same conditions listed in (A).

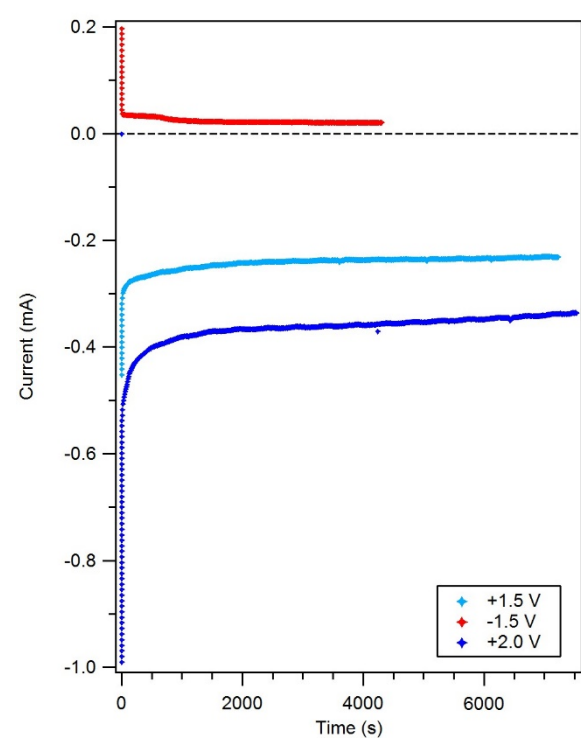


Figure S4. Plot of cell current as a function of time under different applied biases (+1.5 V, -1.5 V, and +2.0 V). Measurement were collected on a solid oxide electrochemical cell with 1000-nm-thick ceria film at  $\sim 600$  °C with 0.5 Torr 1:20 CO/CO<sub>2</sub> mixture.