Film thickness estimation by XPS sputter depth profile analysis:

Due to the significant roughness (in the micron range) and irregular surface of the YSZ substrates combined with the conformal nature of the CeO_2 SFD films, it is not possible to use profilometry nor optical techniques such as interferometry or ellipsometry to measure the thickness of films deposited on these substrates. Film thickness was estimated from XPS sputtering results: the thickness of a CeO_2 film deposited on Si wafer was measured by ellipsometry. XPS sputter depth profile analysis was then carried out on the same sample to correlate XPS sputtering time to film thickness. This method allows estimating film thickness of a sample based on the sputtering time necessary to reach the substrate.

Film thickness uniformity was assessed with ellipsometry measurements (Gaertner L116C Ellipsometer) and SEM cross-section micrographs (Figure S1). The films are dense and do not show any sign of porosity.
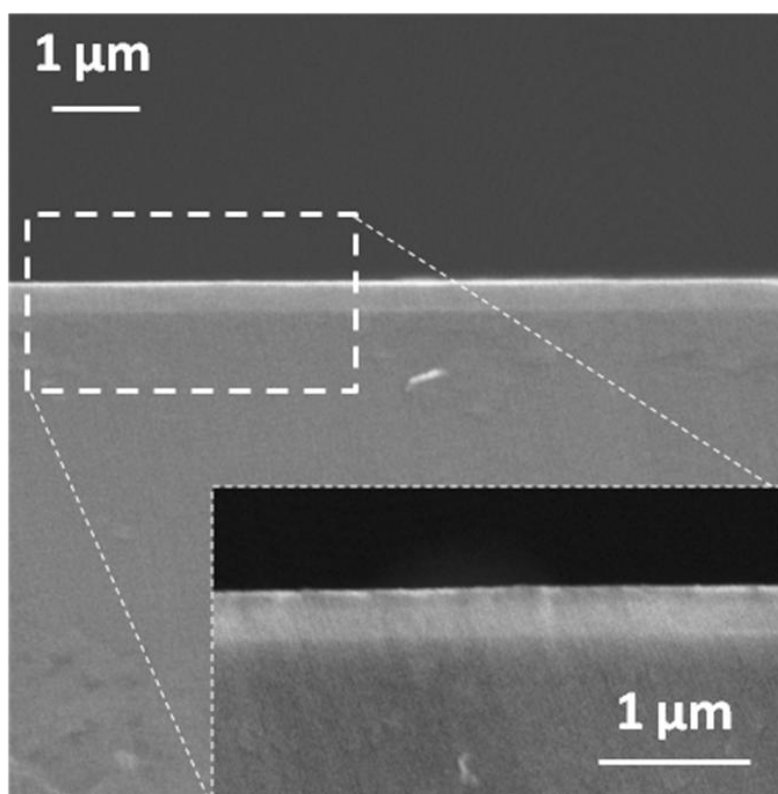

Figure S1. SEM cross-section micrographs of a CeO_2 film deposited on Si wafer (300 °C, 22 MPa, H_2O/Ce=30, 30 min).

SFD CeO$_2$ films deposited on Si wafers are very uniform in thickness and do not exhibit any edge effect. On a typical sample, ellipsometry measurements carried over 12 points on a 3x3 cm film give a film thickness of 169±9 nm. Film thickness measurements from XPS sputtering carried on various spots on CeO$_2$ films deposited on YSZ give very similar standard deviation in film thickness.

Figure S2 shows as obtained films are crystalline, heat treatments at 400 °C merely improving the crystallization. In any case, the films are pure CeO$_2$ phase.
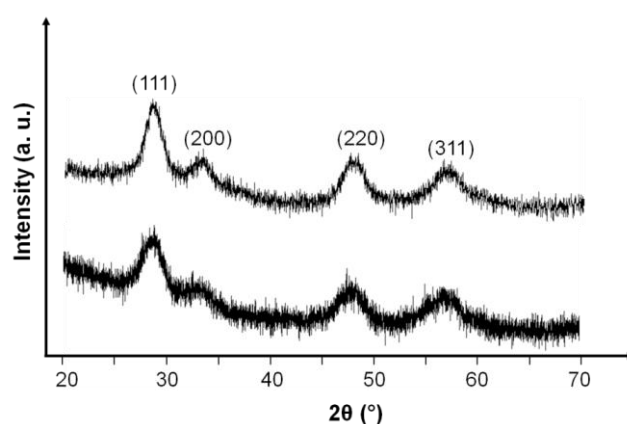

Figure S2. XRD pattern for CeO$_2$ film deposited on Si wafer (300 °C, 22 MPa, H$_2$O/Ce=12, 30 min): as-obtained film (bottom) and annealed film (top). CeO$_2$ peaks are indexed (JCPDS 34-0394).

Figure S3 shows the morphology of CeO$_2$ films deposited on Si wafers. Film morphology depends on the water content: without added water the film appears nanostructured whereas with water the film surface is uniformly smooth and does not present any distinguishable features.
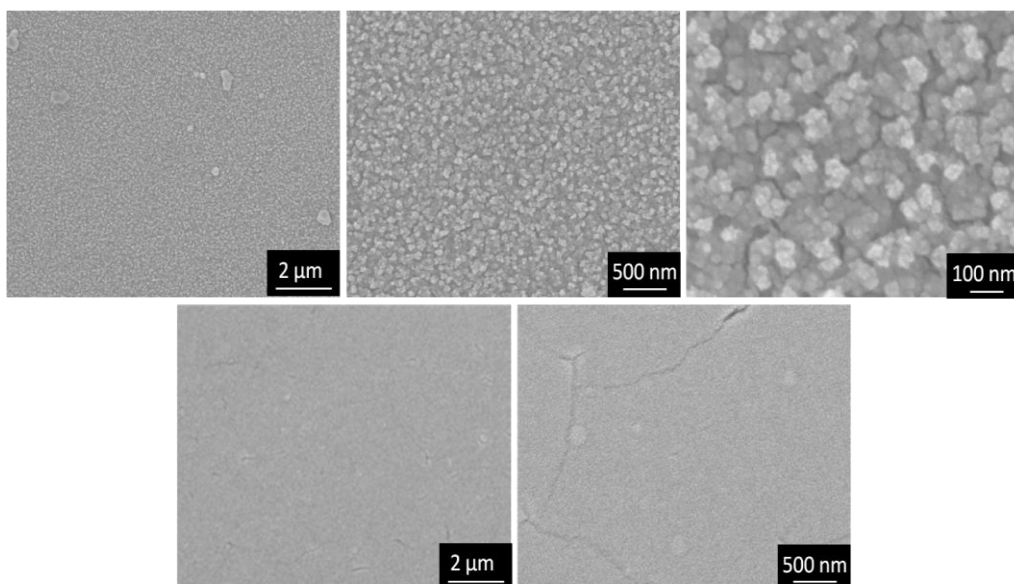
Figure S3. HR-SEM micrographs of CeO_2 films deposited on Si wafers: top pictures, without water, bottom pictures, with added water ($H_2O/Ce=12$).

Figure S4 presents XPS data for ceria films deposited on Si wafers. Heat treatment is required to eliminate the carbon pollution.
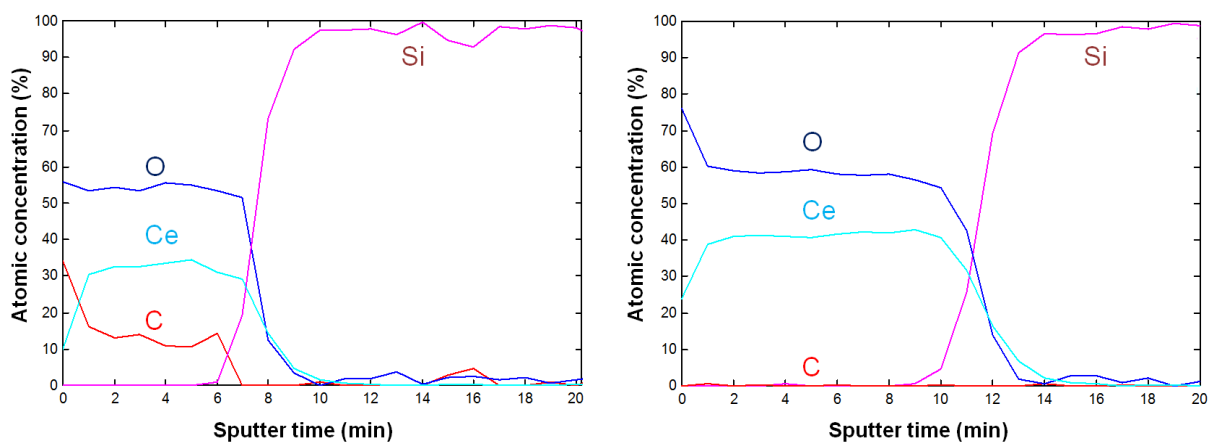

Figure S4. XPS data for CeO_2 films deposited on Si wafer at 300 °C: as-obtained film (left) and film annealed at 400 °C (right).

Figure S5 shows XPS Ce3d profile for a commercial ceria nanopowder (99,9% supplied by Sigma-Aldrich) used as a CeO_2 reference.
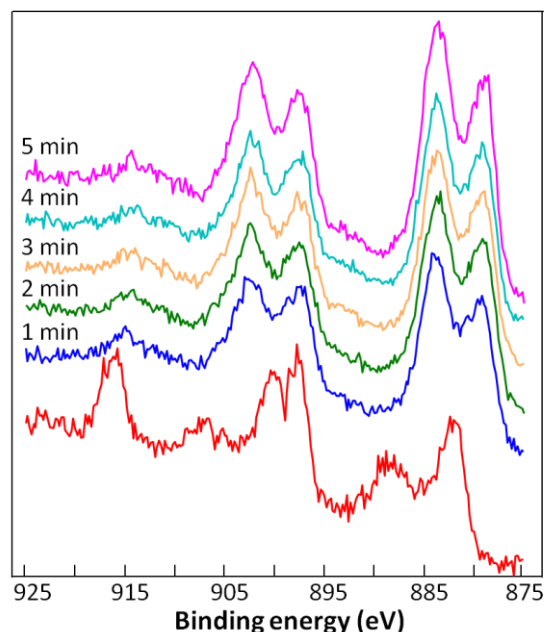
Figure S5. XPS Ce3d profile of a commercial nanocrystalline CeO_2 powder after various times of Ar^+ sputtering.

CeO_2 is known to be easily reduced under reducing atmosphere, leading to non-stoichiometric CeO_{2-x} ($0 \leq x \leq 0.3$); oxygen vacancy formation is also favored in thin films and nanoparticles. XPS data collected for ceria films (before and after annealing) have been compared with CeO_2 references: a commercial ceria nanopowder and a film after annealing under air at 800 °C for 6 h (such heat treatment would be sufficient to oxidize into Ce^{4+} any proportion of cerium at the Ce^{3+} oxidation state). XPS data for ceria films annealed at 400 °C are strictly identical to the one of references as shown in Figure S5, which confirms that the Ce^{3+} oxidation state is due to sputtering during XPS analysis and not representative of Ce oxidation state in the ceria films.

Impedance spectroscopy data:

A representative Nyquist plot is shown in Figure S6. The experimental data were fitted by means of a nonlinear least-square fit using an equivalent circuit composed of a series of one resistance and two *R*//CPE elements (where *R* is a pure resistance and CPE is a constant phase element). In the Nyquist plot, the first resistance is attributed to the electrolyte resistance, whereas the intersections of the semi-circles with the real axis define the polarization resistance (R_p) of the electrode, representative of the sum of the ionic

transfer at the electrode interface as well as electrode reaction contributions. Electrode area specific resistance (ASR) values, corresponding to the polarization resistance normalized by the electrode area, are calculated by the formula: $ASR = R_p \times S/2$ (factor 2 comes from the cell being symmetrical).
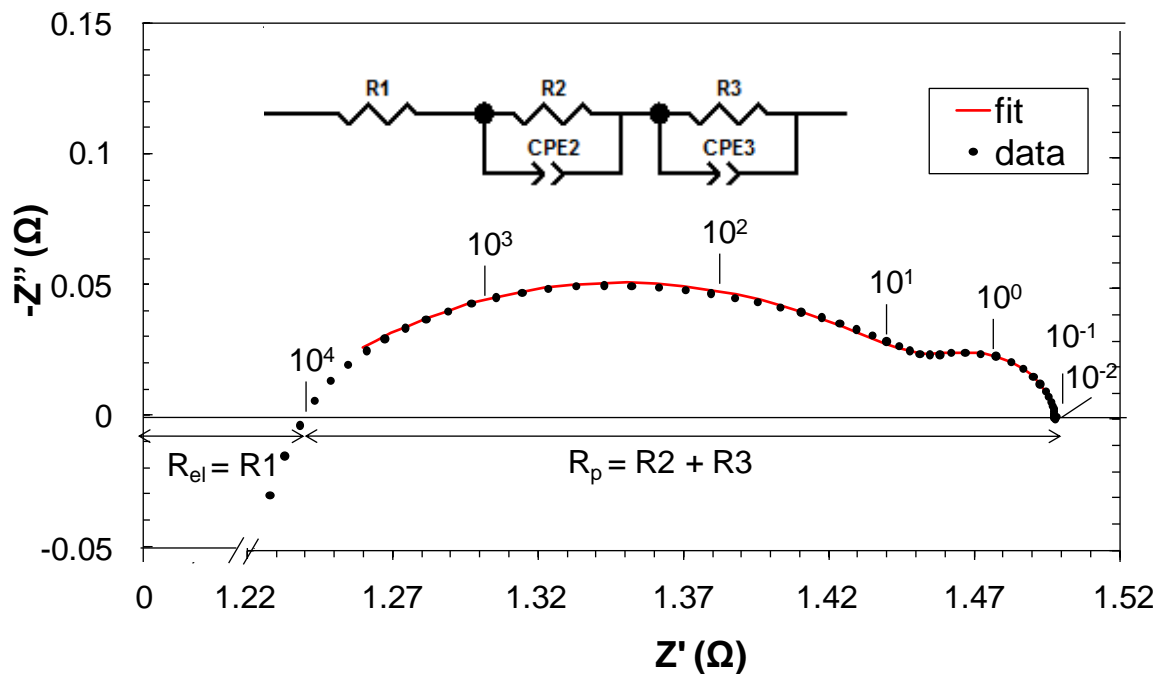

Figure S6. Typical experimental impedance diagram (S3_35b, 700 °C), modeling curve corresponding to the equivalent circuit drawn is overlaid on the data points and signal frequency (Hz) is indicated.