Supplementary Information

S1 Microstructure and porosity

Electron microscopy micrographs (SEM as well as TEM) acquired from both nanocrystalline and microscrystalline undoped CeO_2 are shown in Fig. S1. The SEM images (a) and (b) illustrate the striking difference between the microstructure of the n-CeO₂ and m-CeO₂ samples. The TEM micrograph (c) allows for a better evaluation of the grain size as well as the observation of residual pores in the n-CeO₂ sample. The average grain size of the microcrystalline sample is approximately 10 times larger than the average grain size of the nanocrystalline sample.

20 nm





Fig. S1 SEM micrographs acquired from (a) undoped n-CeO2 and (b) undoped m-CeO2. (c) TEM micrograph of the undoped n-CeO2 showing the presence of residual porosity. The average grain size of the microcrystalline sample is approximately 10 times larger than the average grain size of the nanocrystalline sample.

In addition, the pore size distribution was determined using the Barrett, Joyner, Halenda (BJH) analysis of the nitrogen desorption branch of the isotherm measured with the pore size analyzer Autosorb 1 (Quantachrome Instruments, USA).

In Fig. S2, the corresponding pore size distributions of undoped $n-CeO_2$ as well as $m-CeO_2$ are shown.



Fig. S2 Pore size distribution for the microcrystalline and the nanocrystalline undoped CeO_2 samples.

S2 Impedance spectra

The impedance spectra obtained from the microcrystalline samples (the Nyquist plots in Fig. S3a and b) exhibit two semicircles. The solid symbols refer to the wet conditions whilst the open ones refer to the dry conditions. The smaller semicircle at high frequencies (see the corresponding insets) is assigned to the bulk (capacitance $C_b = 11 \text{ pF}$ at 250°C) while the lower frequencies semicircle is ascribed to blocking grain boundaries (GB) perpendicular to the current (capacitance $C_{GB} = 800 \text{ pF}$ at 250°C).

The undoped n-CeO₂ sample exhibits only one semicircle (Fig. S3c) in both dry and wet conditions. In dry conditions, this is known to arise from the electronic GB contribution parallel to the current short-circuiting the bulk in dry condition.^{8,9} As the relative dielectric constant value changes significantly between dry and wet atmosphere below 200°C (see also Fig. 5 in the main text) and the conductivity value is higher than the bulk value of the microcrystalline sample in wet oxygen, the single semicircle (in wet conditions) likely corresponds to a different conduction mechanism, which short-circuits the bulk.

In the Nyquist plot of the doped n-CeO₂, one can recognize the presence of two semicircles (Fig. S3d), which correspond to the bulk and the GB contributions (at high and low frequencies, respectively $C_b = 20$ pF, $C_{GB} = 40$ pF at 250°C).

The assignment of the different conductivity contributions in the impedance spectra of

the nanocrystalline samples remains unaffected by the temperature change from 550° C to 200° C in dry as well as in wet conditions. However, in wet conditions and below 150° C, the bulk contribution of the nano doped sample disappears and the spectra consist of only one semicircle (Fig. S3e and f). This indicates that at low temperature the conduction mechanism short-circuits the bulk as in the case of undoped n-CeO₂.



Fig. S3 Nyquist plots of samples under dry (open symbols) and wet (solid symbols) oxygen at the different given temperatures for microcrystalline (a) undoped ceria and (b) Gd-doped CeO₂, nanocrystalline (c) undoped ceria, (d) Gd-doped ceria, (e) undoped ceria, (f) Gd-doped ceria. The red lines refer to the fitting curves.

S3 Conductivity partial pressure dependence

Conductivity measurements were also performed at different wet oxygen partial pressures (pO_2) while keeping pH₂O constant at 20 mbar. The results, shown in Fig. S4, suggest the ionic behavior of both nanocrystalline undoped and doped ceria as no pO_2 dependence can be recognized (the samples were allowed to equilibrate with the respective pO_2 for at least 72 h).



Fig. S4 Conductivity of nanocrystalline pure and Gd-doped ceria under wet conditions at different pO_2 at 200°C. No pO_2 dependence can be observed. The samples were allowed to equilibrate with the respective pO_2 for at least 72 h.