Supplementary Material (ESI) for *PCCP*

On The Conduction Pathway For Protons In Nanocrystalline Yttria-Stabilized Zirconia
S. Kim et al.

Supplimentary Data

The following experimental details have been reported in Reference 2 cited in the manuscript.

Nano-powders of YSZ (8 mol%) were synthesized by a precipitation method, employing nitrates ($Y(NO_3)_3 \cdot 6H_2O$, $Zr(NO_3)_2 \cdot 6H_2O$, Aldrich, 99%) and aq. NH_4OH as precursors and a precipitating agent, respectively. The precipitates were collected by centrifugation and washed with water and pure ethanol. The resulting powder was dried at 120 °C for 12 h, ground, and subsequently annealed under air at 450 °C for 5 h. The desired cubic crystal structure of the synthesized YSZ nano-powder was verified with x-ray diffraction (XRD) (Scintag XDS-2000). The crystallite size of the YSZ powder was estimated from the XRD patterns using Scherrer's equation, and the average value measured from the three main peaks ((111),(220) and (331)) was (6.9 ± 0.8) nm. The YSZ nano-powders were consolidated by means of a spark plasma sintering (SPS) method.[SR1,SR2] In order to obtain high-density samples with different grain sizes, the process parameters were modified with respect to temperature, pressure, and hold-time as indicated in Table S1. Also listed in Table S1 are the desity and the grain size of the sintered pellets (OD ~ 6 mm, thickness ~ 1 mm).

SPS Conditions			Relative	Grain
Temperature (°C)	Pressure (MPa)	Time (min)	Density (%)	Size (nm)
950	723	4	96	13
950	733	5	96	22
1000	566	6	97	31
1050	566	8	99	50
1150	566	5	~100	100

Table S1. Sintering parameters and resulting density and grain size of YSZ samples (See Ref. 2 cited in the manuscript).

The density was determined by an Archimedes method and the grain size was determined from scanning electron microscope (SEM) images using a software AnalySIS (Soft Imaging System Corp. Lakewood, CO), with at least 100 grains. Figure S1 is an SEM image of a 96% and fully dense YSZ pellets showing the nano-scale size of the grains. Since the conditions in the SPS are reducing, sintered pellets were annealed in air at 700 °C for 24 h before electrical measurements were made. From XRD analysis, no indication of grain growth was observed on the samples annealed at 700 °C.

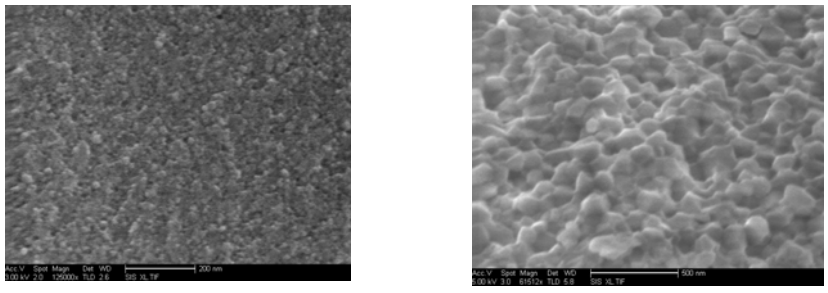

Figure S1. Representative SEM images of fractured surface of dense YSZ with the grain size of ~13 nm (on the left) and 100 nm (on the right). The scale bar indicates 200 and 500 nm, repectively.

The sintered pellets were characterized electrically by a. c. impedance spectroscopy, using a Novocontrol Alpha – AN modulus analyzer in the frequency range of 10^{-1} to 10^{7} Hz.
The electrodes were fabricated by applying platinum paint (5349, Heraeous, USA) on both faces of the pellets followed by annealing the pellets at 700 ºC for 2 h in air. To determine the conductivities of the samples, the a. c. impedance measurements were performed under both nominally dry and wet air ($P_{H2O} = 2.3\times10^{-2}$ atm) at elevated temperatures. In order to ensure the reprodiciblity of the measurents, at least two samples were measured at each grain size.

References

SR1 S. Kim, U. Anselmi-Tamburini, H. J. Park, M. Martin and Z. A. Munir, *Adv. Mater*., 2008, **20**, 556.
SR2 U. Anselmi-Tamburini, J. E. Garay, and Z. A. Munir, *Scripta Mater*., 2006, **54** (5), 823.