Unprecedented Low-Temperature Power Generation in Nanostructured Oxides

S. Kim[1], U. Anselmi-Tamburini[2], M. Martin[3], and Z. A. Munir[1]

[1]Department of Chemical Engineering and Materials Science
University of California
Davis, CA 95616

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[2]Visiting Professor, University of Pavia, Italy; [3]RWTH Aachen University, Aachen, Germany

Solid Oxide Fuel Cells (SOFCs)

Current Status:

Cells based on electrolytes of yttria-stabilized zirconia (YSZ) and samaria-doped ceria (SDC).

Advantages:

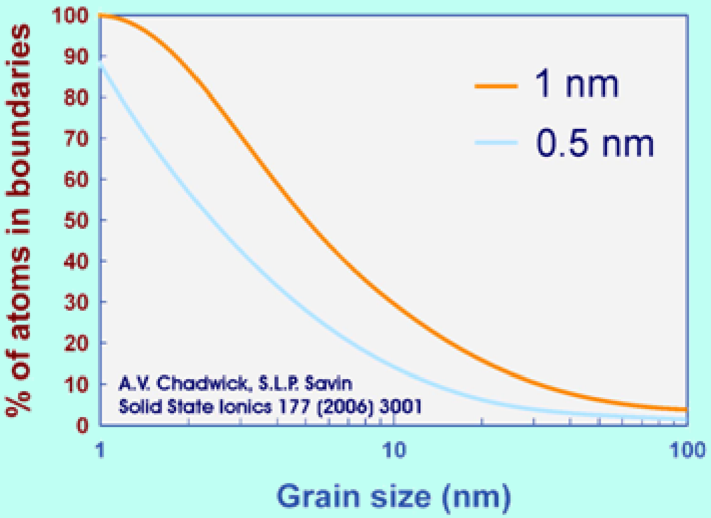
- Direct conversion of chemical energy to electrical energy.
- High efficiency: up to 55%.
- Environmentally benign.
- Flexible fuel requirement; less susceptibility to impurity
- Can be used for power generation systems adapted for small power units (including mobile applications) and for large scale power plants.

Solid Oxide Fuel Cells (SOFCs) - Continued

Disadvantages:

- Required operating temperature (YSZ): 800-1000°C.
- Major obstacles: High cost, degradation, and compatibility issues.
- Desire (and effort) to reduce temperature to intermediate range (500-700°C).

Nanostructured Electroceramics



- Grain size influences defect concentration distribution and transport mechanism.
- Marked effect expected when grain size ~ Debye length.

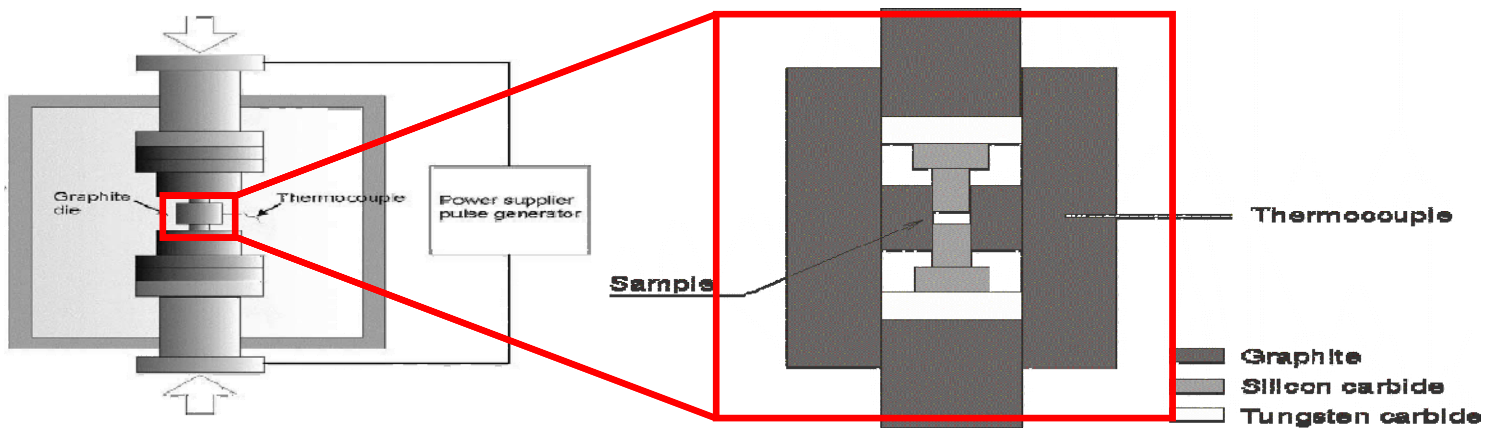
Preparation of Dense, Bulk Nanoceramics

- Previous lack of success : Difficulty in making dense *bulk nanostructured* YSZ due to grain growth (Ostwald ripening).

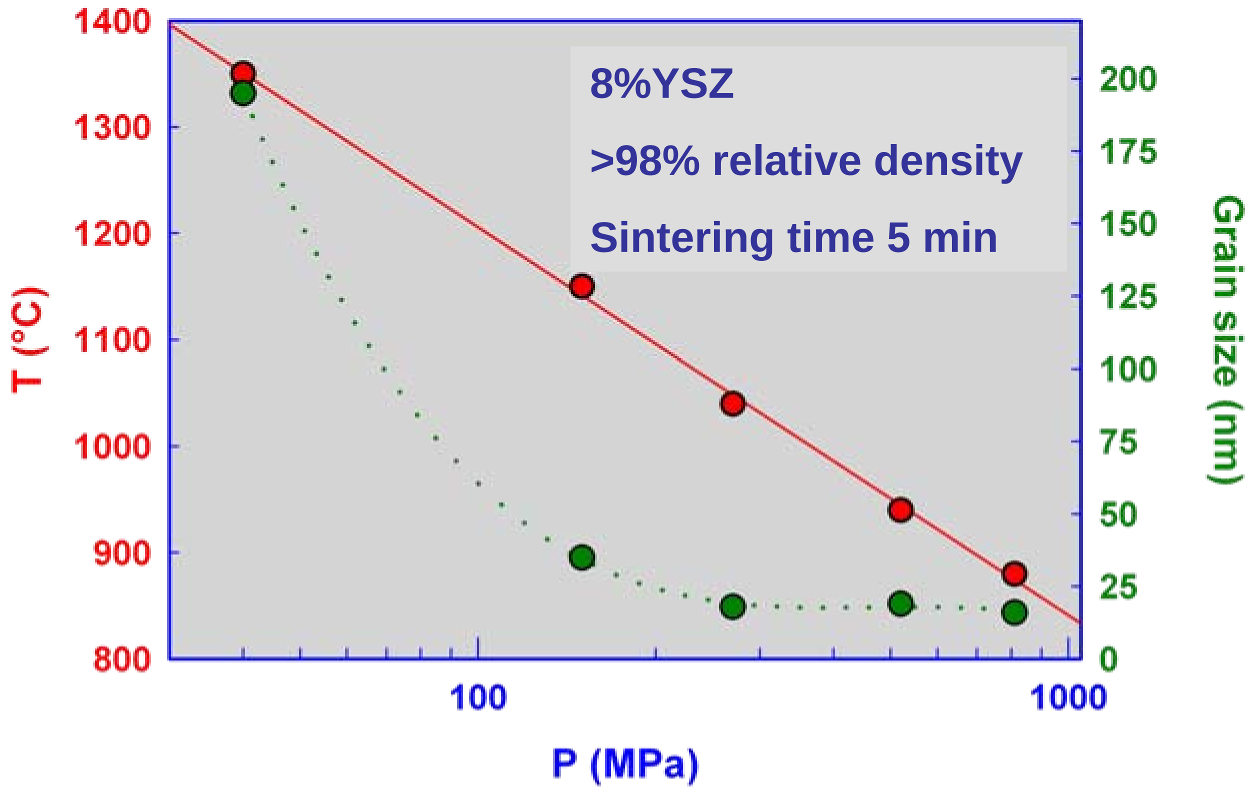
- Our approach: Use of field activation (*modified* Pulse Electric Current Sintering, PECS).

- Success in making highly dense (98%+) with crystallite size < 20 nm.

Pulse Electric Current Sintering

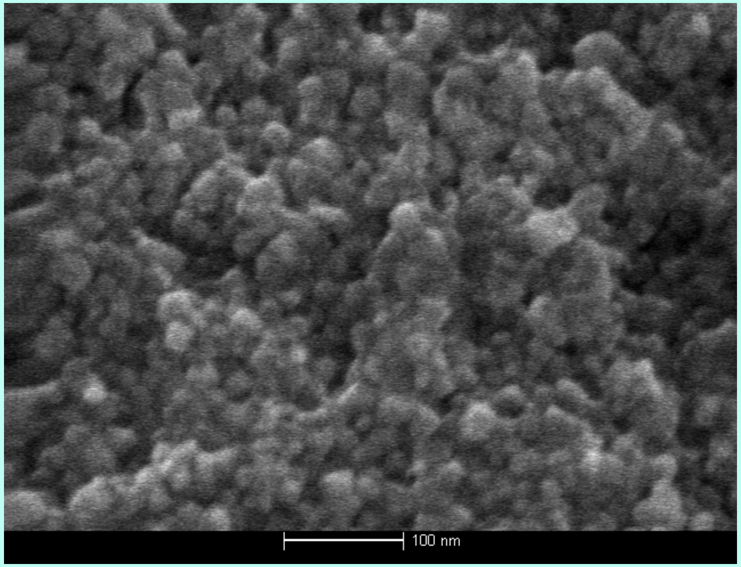


Effect of Pressure

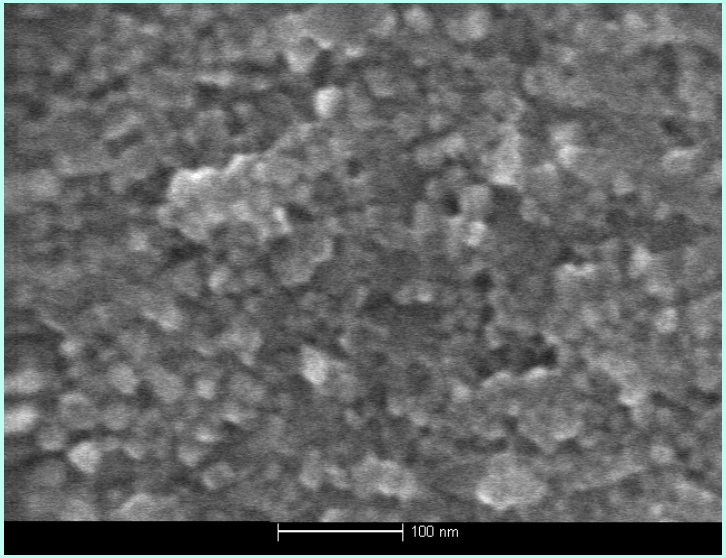


SEM Images of Fracture Surfaces of PECS Consolidated YSZ and SDC

YSZ, 8 mol% Yttria
Bar = 100 nm



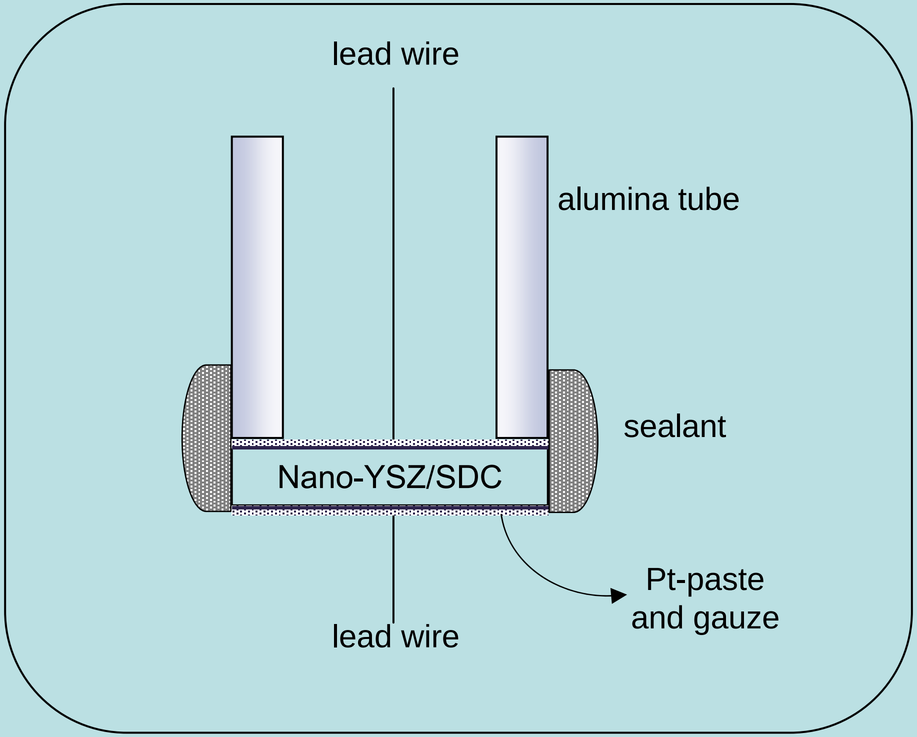
SDC, 20 mol% Samaria
Bar = 100 nm



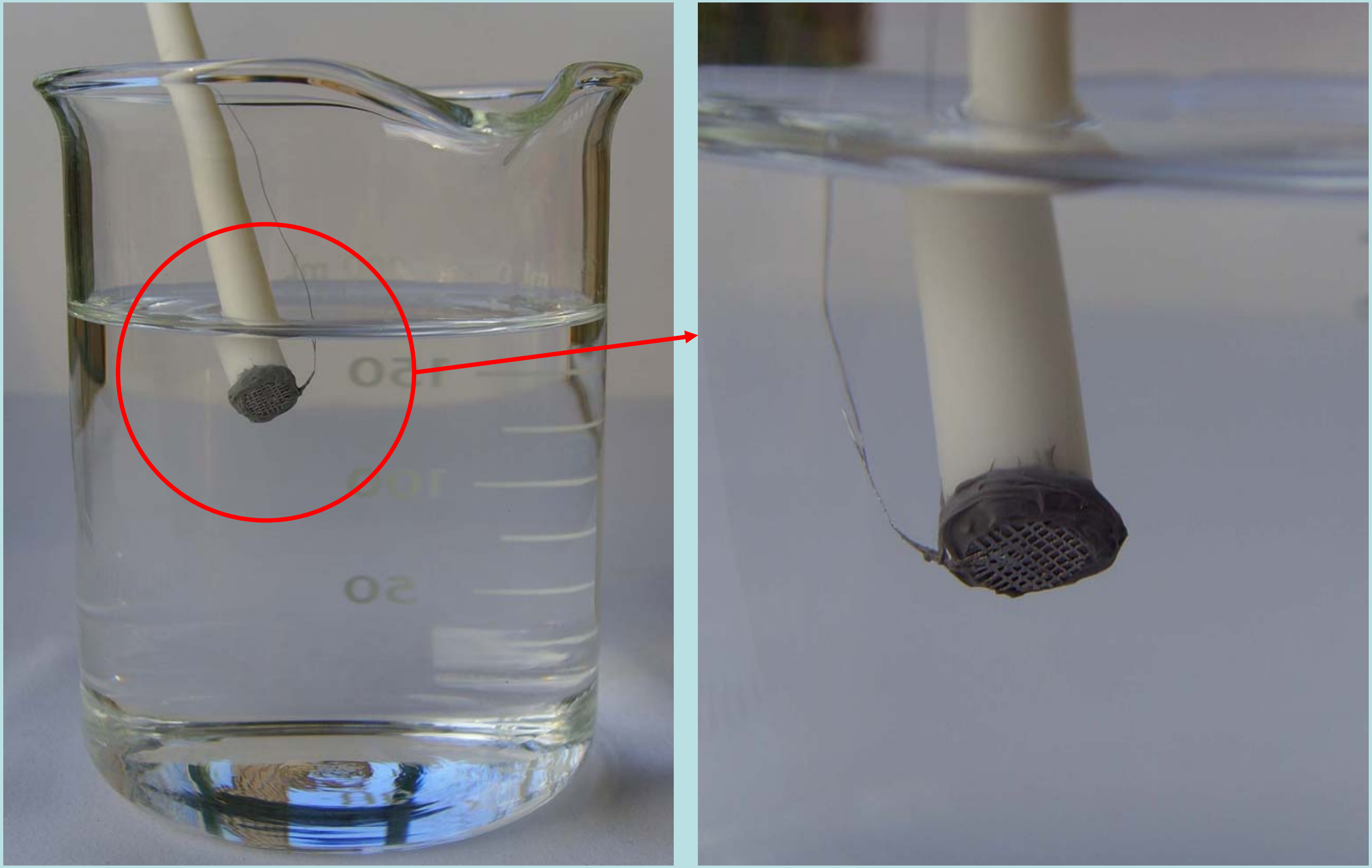
Examples of Sintered Electroceramics by Field Activation

Material	Starting powder grain size (nm)	Heating rate (C/min)	Hold temp. (C)	Hold pressure (MPa)	Hold time (min)	Relative density (%)	Grains size (nm)
CeO_2	7	200	625	600	5	> 98	11.6 ± 2.1
$Ce_{0.7}Sm_{0.3}O_2$	8	200	750	610	5	> 98	16.9 ± 3.1
YSZ (8%)	6.6	200	850	530	5	> 98	15.5 ± 3.2

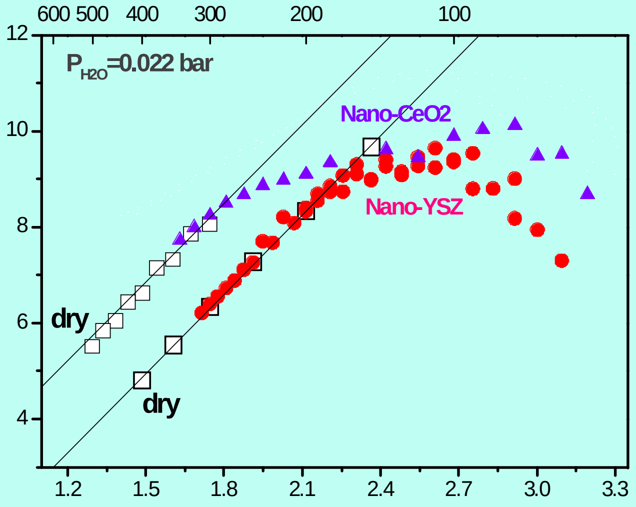
Electrochemical Cell Configuration

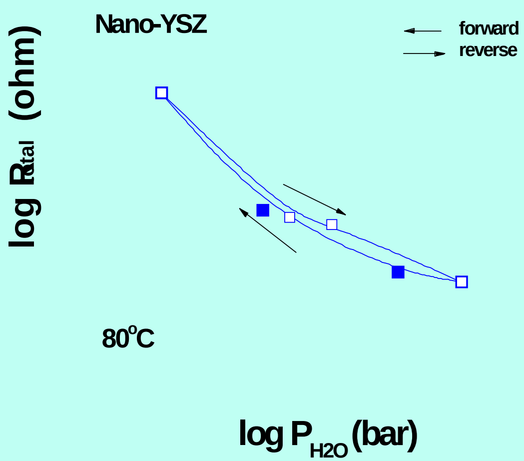


Photos of a Working Electrochemical Cell in Pure Water at RT

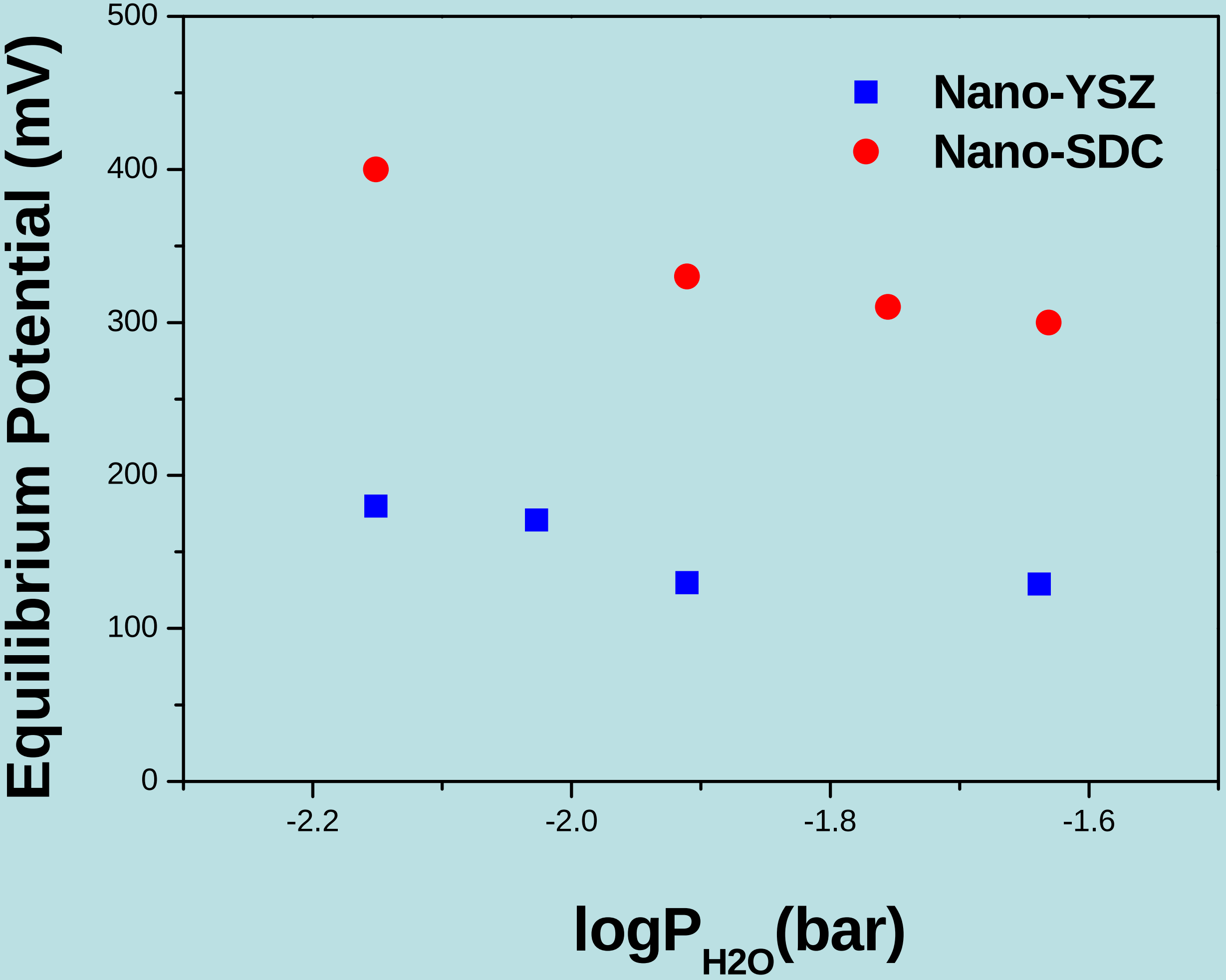


Low-Temperature Protonic Conductivity and Reversibility

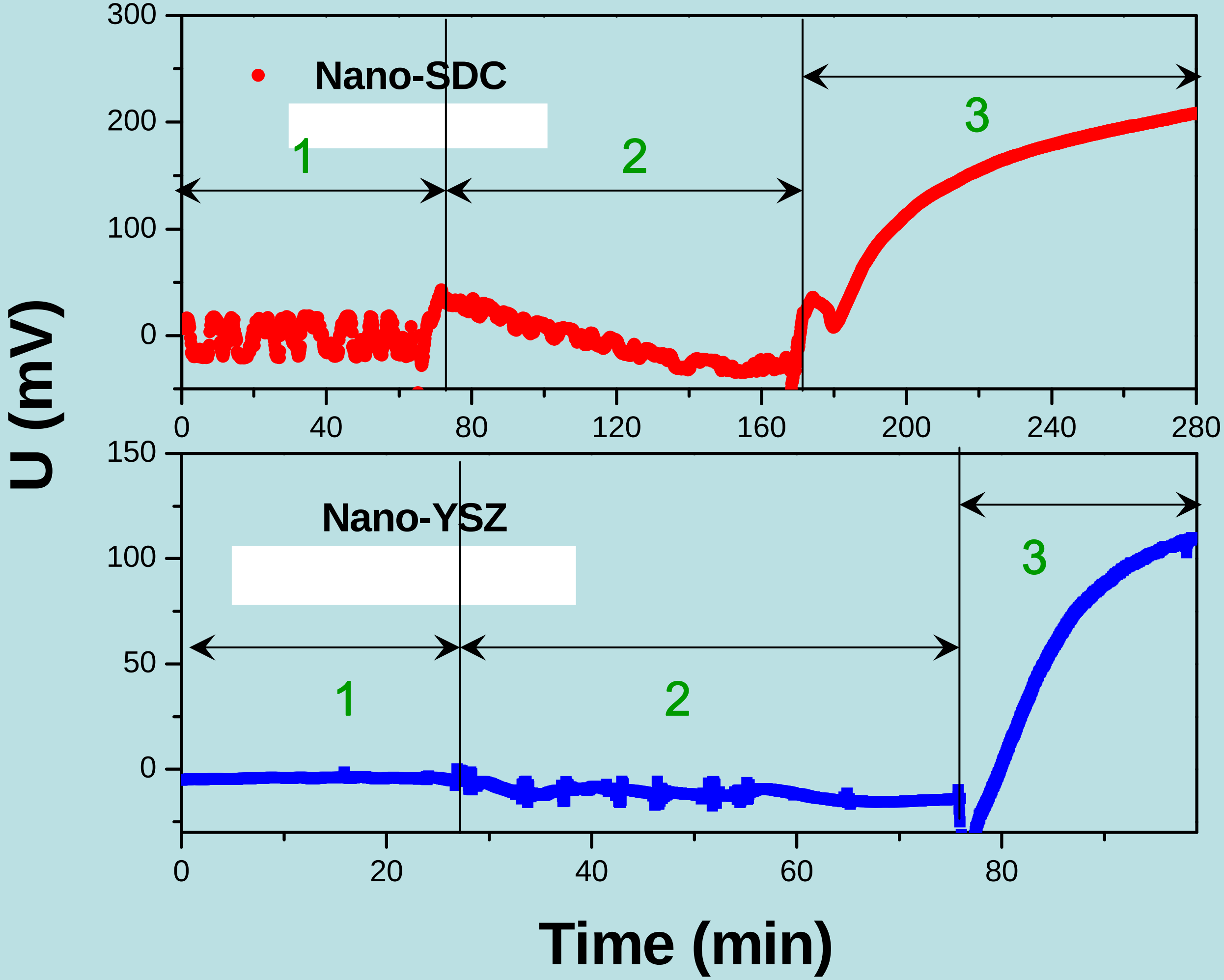




Water |nano-solid electrolyte| P_{H2O}



EMF Measurements

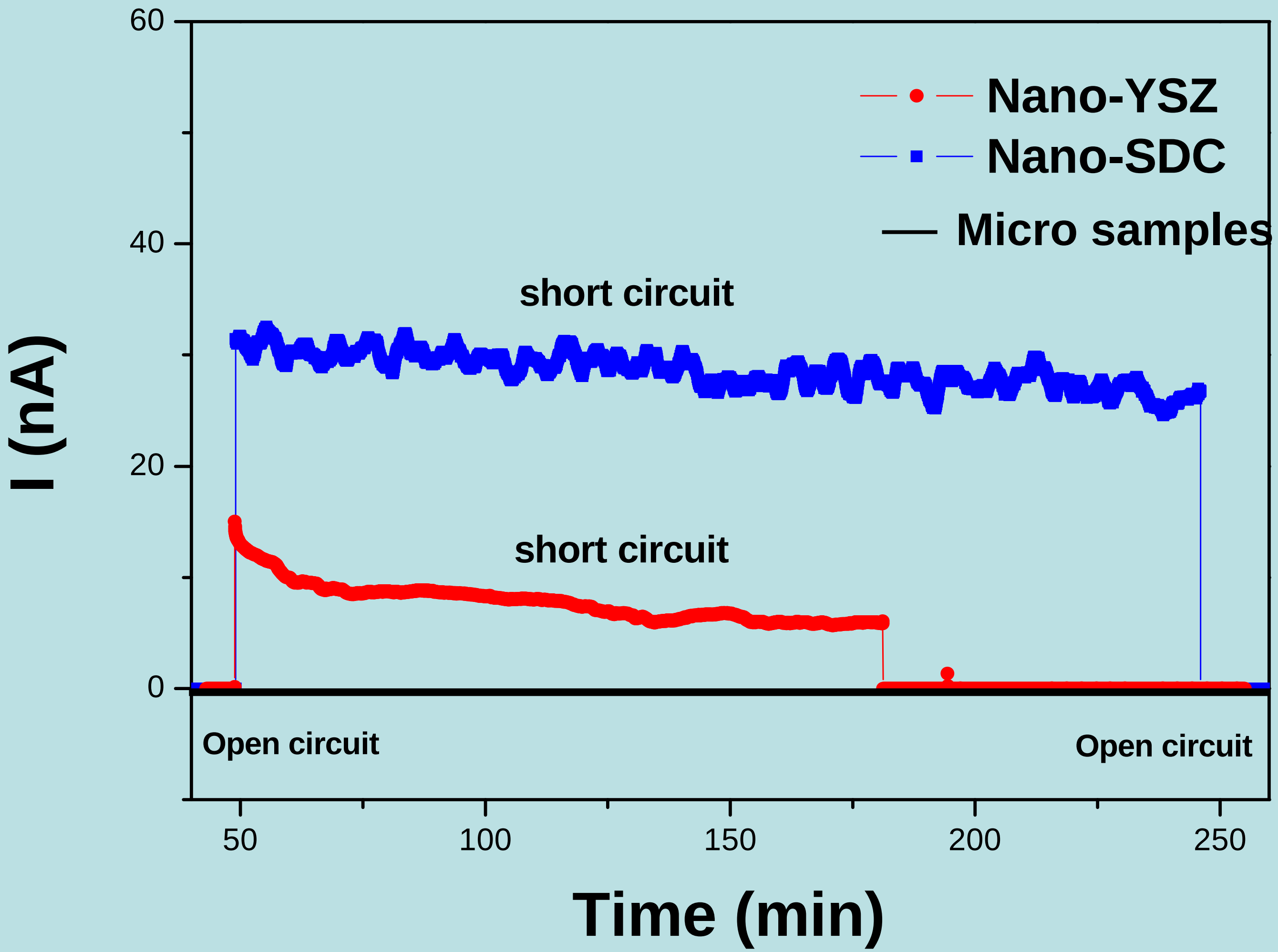


1. Dry air |nano-S.E.| Dry air

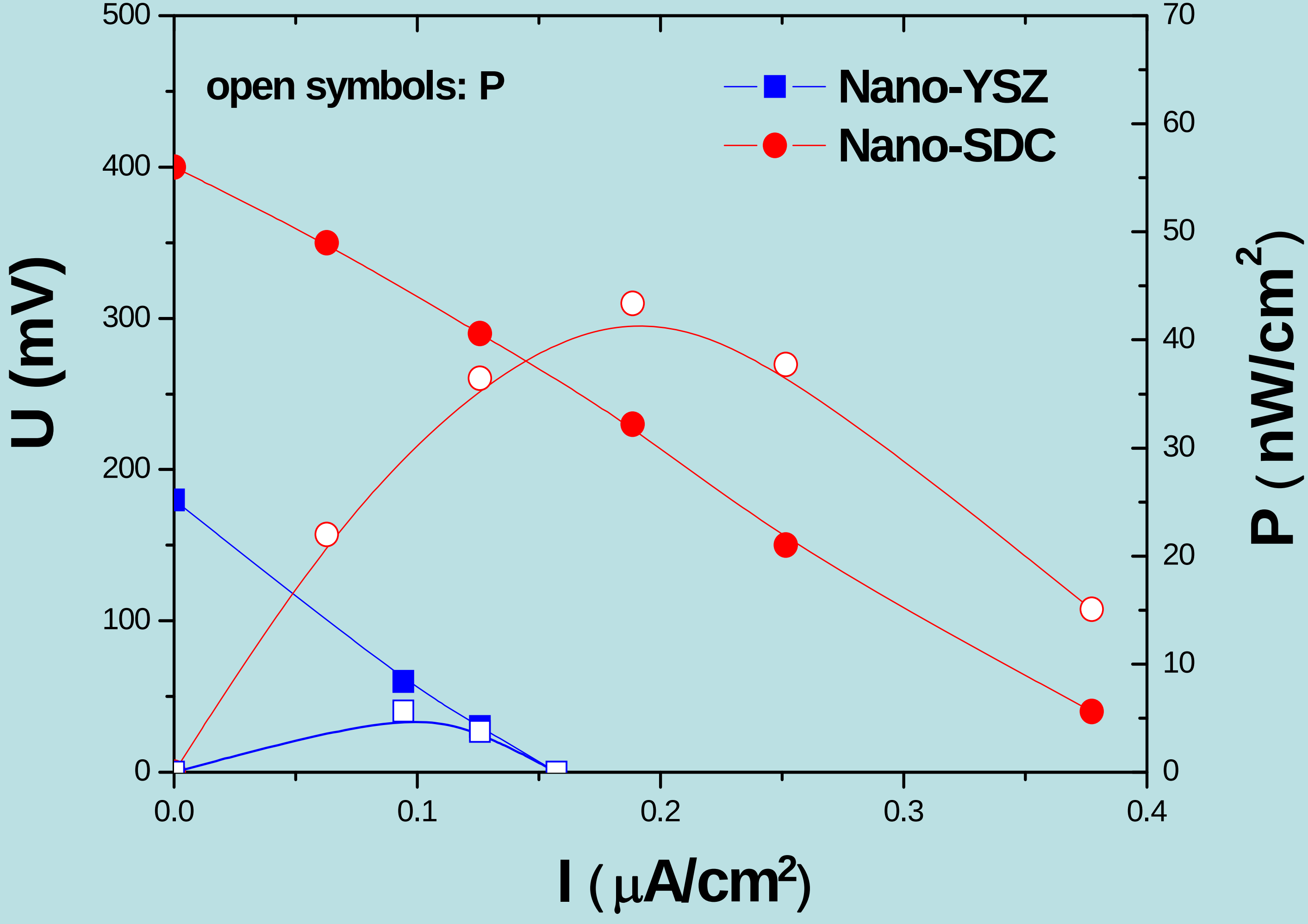
2. Dry air |nano-S.E.| wet air

3. Water |nano-S.E.| wet air

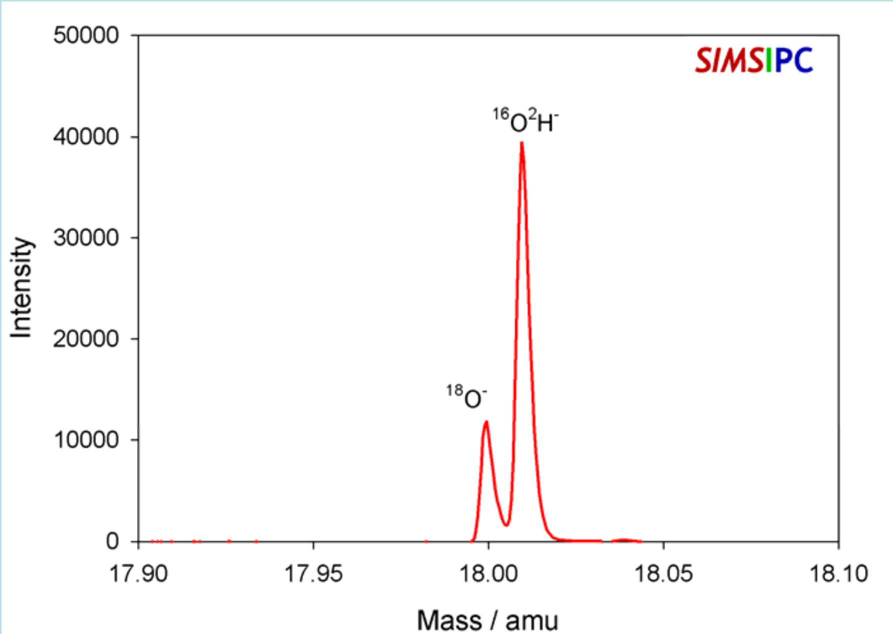
Short-Circuit Current



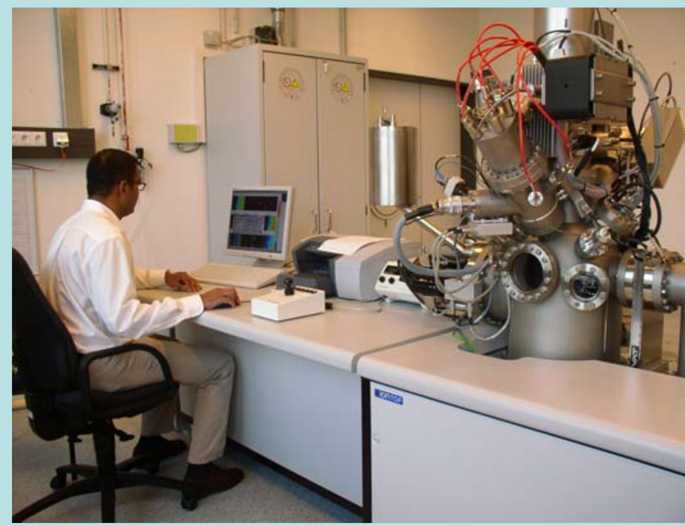
Power Density Measurements



Detection of Hydrogen by Means of Secondary Ion Mass Spectrometry (SIMS)



SIMS spectrum of nano-crystalline YSZ exposed to D_2O-saturated air. The observed negative ion $^{16}O^2H^-$ in the mass spectrum gives clear evidence for the incorporation of deuterium, ^2H.



SIMS at the Institute of Physical Chemistry at RWTH Aachen University, Germany

Comparison to other Protonic Conductors

- Other low temperature protonic conductors: polymeric electrolytes (PEs) and hydrated oxides (HOs).
- But these have limitations with respect to thermal stability, limited to temperatures < 100°C.
- PEs require a catalyst with optimal operating temperature inconsistent with thermal stability of the polymer. Another factor for these systems is the cost.
- HOs lose structural water (at low temperatures, <100°C) $\rightarrow$ irreversible changes the protonic conductivity with concomitant degradation of mechanical properties.

Summary

- Preparation of highly dense (98%+) YSZ with crystallite size < 20 nm through field-activated consolidation.
- When nanostructured (crystallite size ~ 15 nm), YSZ conducts at room temperature.
- Conductivity by protons.
- No conductivity with microstructured oxide.
- Power generation at very low levels; optimization work in progress.

Possible Applications

- To produce power (when used in fuel cells).
- As hydrogen separators (when in mixed conducting mode).
- In electrolysis for hydrogen production.
- For reactions to hydrogenate and dehydrogenate organic compounds.
- For use as tritium monitors.
- Possible biological and medical application (to introduce oxygen where needed).