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Nanoscale Effects in Solid Oxide Fuel Cells

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Types of Fuel Cells

	SOFC	Molten Carbonate	Phosphoric Acid	Alkaline	Polymer Membrane
Electrolyte	Y_2O_3-Stabilized ZrO_2 (YSZ)	Li_2CO_3-K_2CO_3	H_3PO_4	KOH	Perfluoro-sulfonic acid
Cathode	Sr-doped $LaMnO_3$	Li-doped NiO	Pt on C	Pt-Au	Pt on C
Anode	Ni/YSZ	Ni	Pt on C	Pt-Pd	Pt on C
Temperature	750-1000°C	650°C	200°C	100°C	90-120°C
Fuel	H_2, CO	H_2, CO	H_2	H_2	H_2

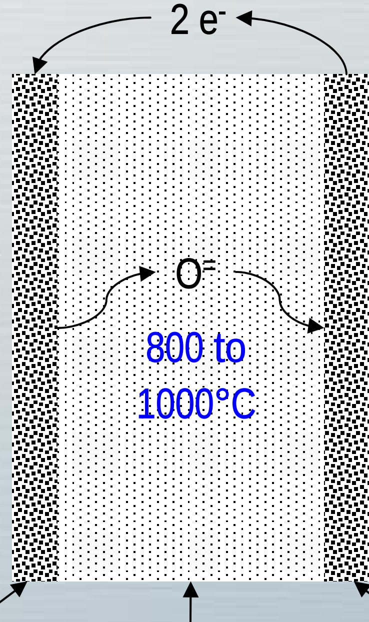
Solid Oxide Fuel Cells - Advantages

- High electric conversion efficiency
- High environmental performance
  - No SO_x or NO_x ; Lower CO_2 emissions
  - Quiet
  - Vibrationless
- Cogeneration potential
  - High quality exhaust heat for heating, cooling, additional power generation
- Fuel flexibility
  - Liquefied natural gas
  - Pipeline natural gas
  - Coal gas
  - Naphtha
  - Methanol
  - Biogases
- Size and siting flexibility
  - Modularity permits wide range of system sizes
  - Siting flexibility for distributed power

SOFC Operating Principle

external electrical load

$2\ e^-$



High Po_2 environment

air

Cathode reaction:

$\frac{1}{2} O_2 + 2e^- \rightarrow O^=$

Low Po_2 Environment

fuel

$(H_2 + CO)$

Anode reaction:

$O^= \rightarrow \frac{1}{2} O_2 + 2e^-$

Oxidation reactions:

$\frac{1}{2} O_2 + H_2 \rightarrow H_2O + \text{heat}$

$\frac{1}{2} O_2 + CO \rightarrow CO_2 + \text{heat}$

porous electronic conducting cathode

$La(Sr)MnO_3$

dense oxide ion conducting electrolyte

Yttria-stabilized zirconia (YSZ)

porous electronic conducting anode

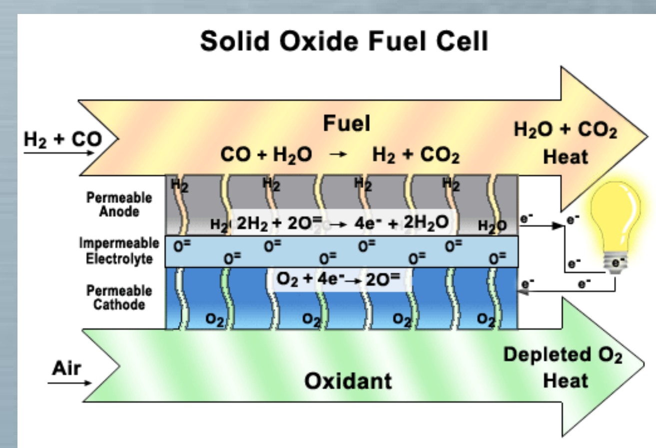
Ni - YSZ cermet

The open circuit voltage is given by the Nernst equation:

$$E^o = \frac{RT}{4F} \ln \frac{Po_{2(c)}}{Po_{2(a)}}$$

at 1000°C:

$$\frac{RT}{4F} \ln \frac{0.2}{10^{-18}} = 1.1\ V$$



Cell Component Materials

Component	**Material**
Cathode	Doped Lanthanum Manganite
Electrolyte	Yttria-stabilized ZrO_2(YSZ)
Anode	Nickel-YSZ
Interconnection	Doped $LaCrO_3$; High-temperature alloys

SOFC Designs

Tubular
(anode- and cathode-supported; microtubular)

Flattened Tubular
(anode- and cathode-supported)

Planar
(anode-, electrolyte-, and metal-supported)

Tubular vs. Planar Cell Designs

	Tubular Cells	Planar Cells
Specific Power (W/cm^2)	Low (0.2-0.35)	High (0.6-2.0)
Volumetric Power (W/cm^3)	Low	High
Manufacturing Cost ($/kW)	High	Low
High Temperature Seals	Not Necessary	Required
Performance Degradation	None	1-4%/1000 hrs

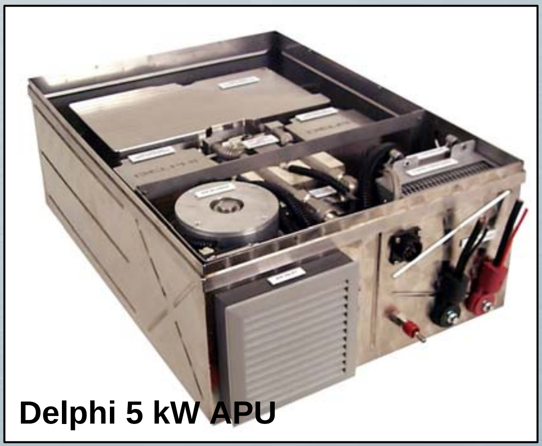
SOFC Systems

Hexis 1 kW


FCT/SWPC 5 kW


Siemens/Westinghouse 100 kW

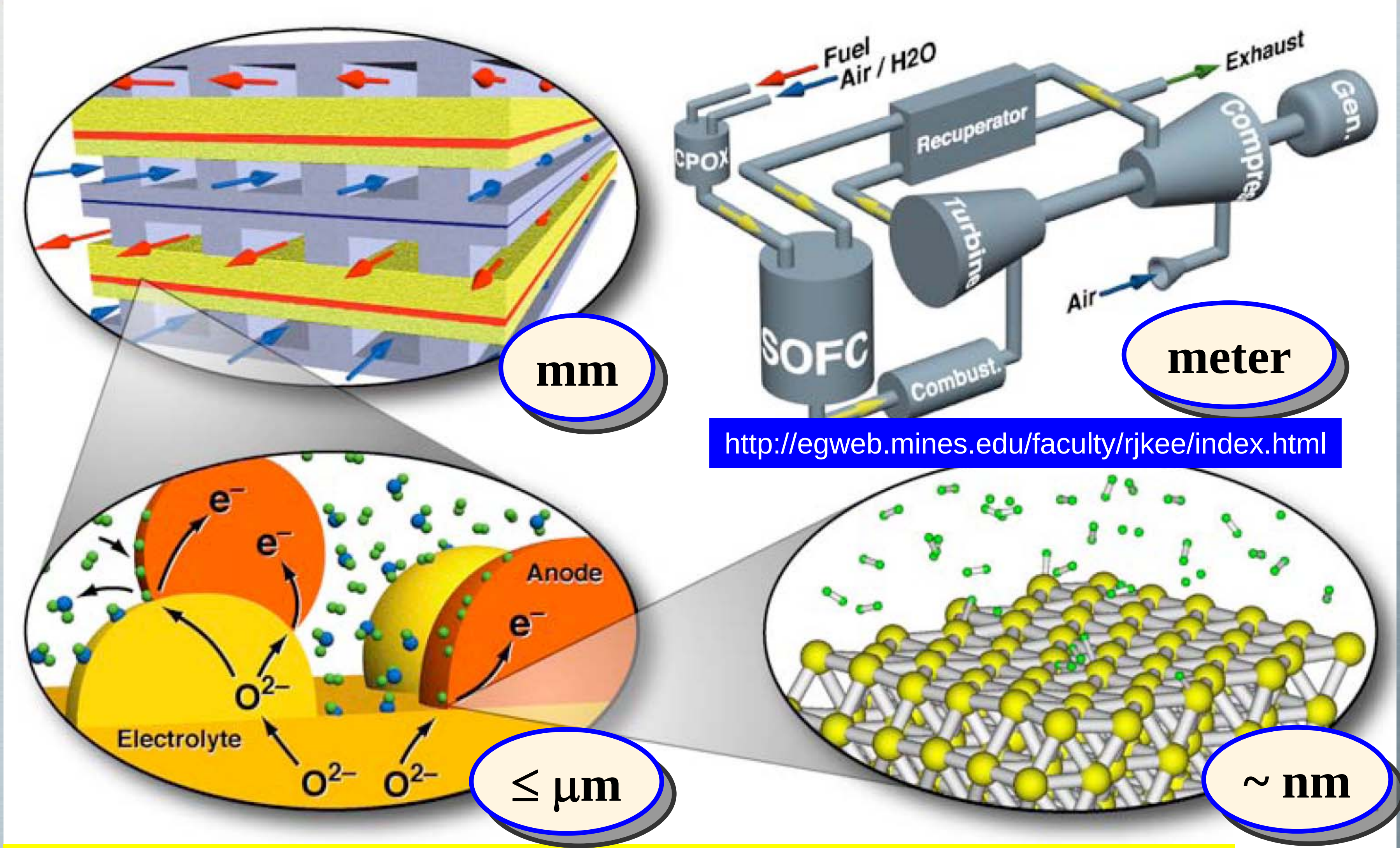
Mesoscopic Devices(20 W to 250 W)


Delphi 5 kW APU

SOFC Market Drivers

- **Positives**
  - Low emissions
  - High efficiency, even in small size systems
  - Fuel Flexibility
- **Negatives**
  - Cost
  - Cost
  - Cost
  - Lifetime
  - Performance Degradation

SOFC Research on Various Length Scales



***Uncertainty:* Elementary charge-transfer chemical reaction mechanisms, particularly related to triple phase charge exchange.**

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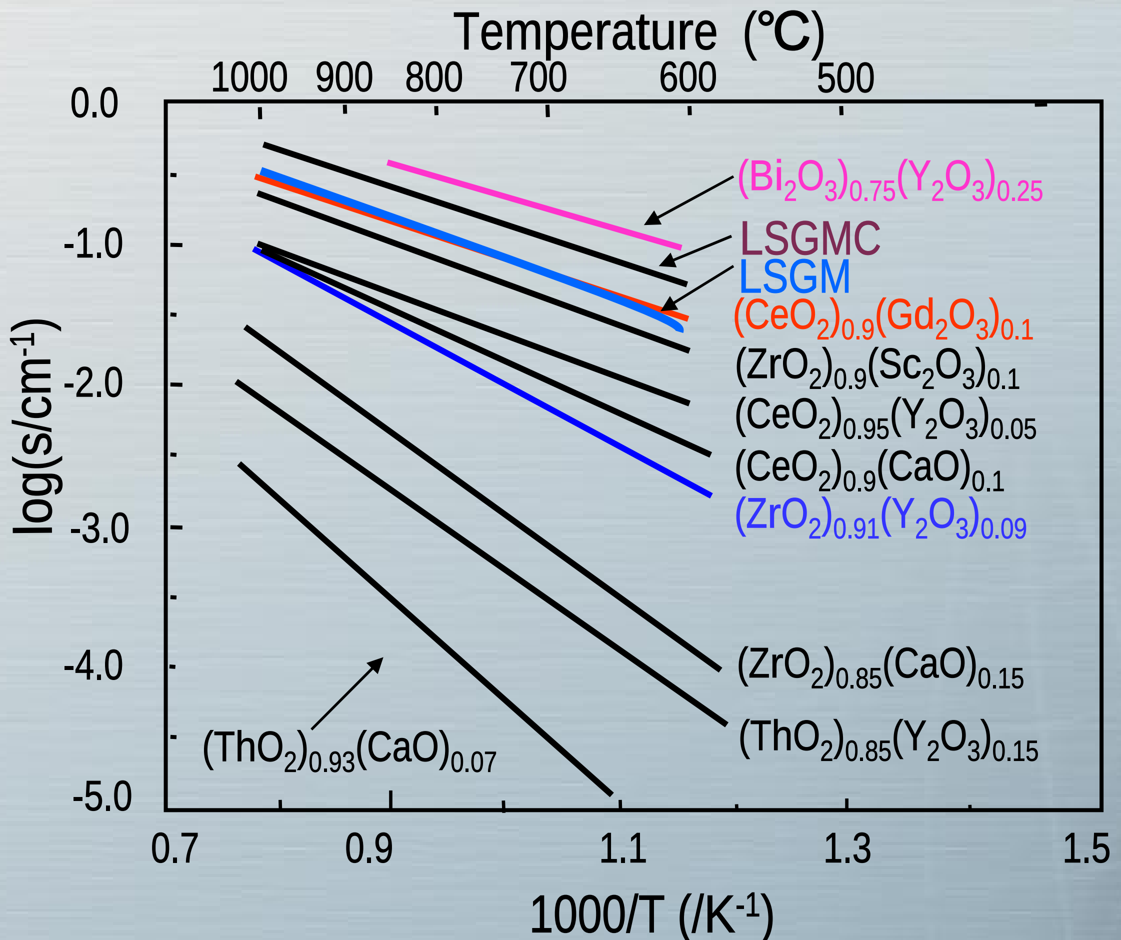
Zirconia-Based Electrolyte

- **Very low electronic conduction (energy band gap: >7 eV)**
- **Very high thermodynamic stability (decomposition P_{O_2} at 1000ºC: $<10^{-35}$ atm)**
- **Easily doped with lower valence cations (e.g., Ca^{2+}, Y^{3+}, Sc^{3+}, etc.) to create oxygen vacancies**
- **Doped material is highly oxide ion conductive (conductivity: >0.1 $\Omega^{-1}cm^{-1}$ at 1000ºC)**

Oxide Ion Conductivity

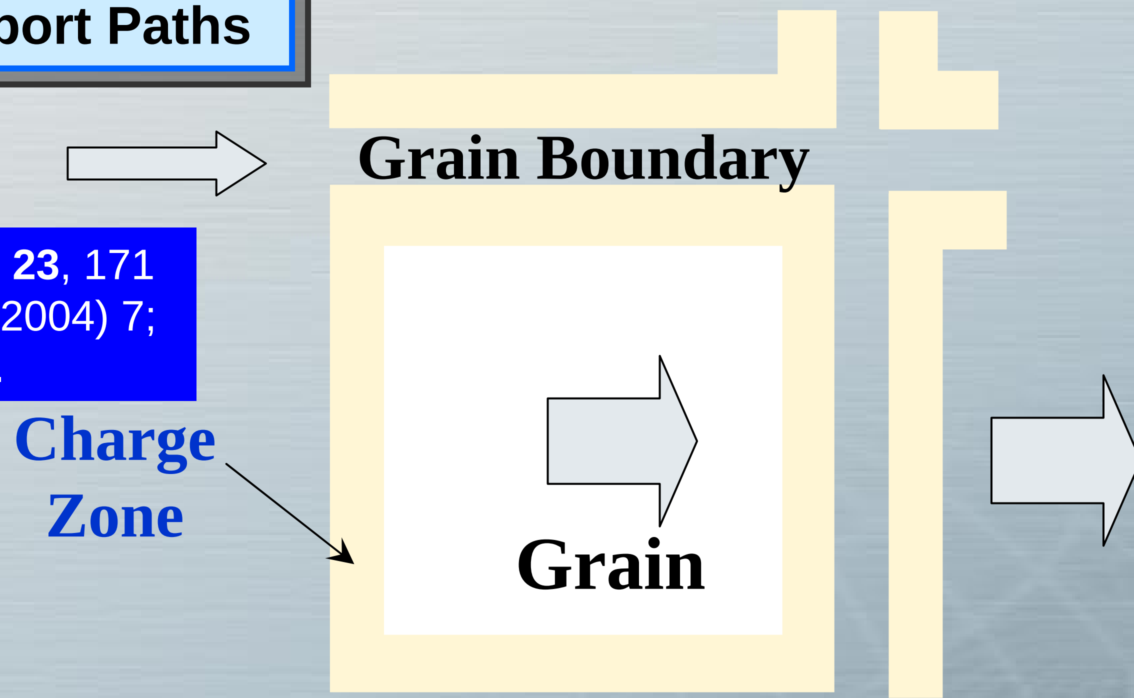


(LSGMC: $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_3$; LSGM: $La_{0.9}Sr_{0.2}Ga_{0.8}Mg_{0.1}O_3$)

Nanoionics – Space Charge Model

Different Charge Transport Paths

J. Maier, *Prog. Solid St. Chem.*, **23**, 171 (1995); *Solid State Ionics,* **175** (2004) 7; *Nature Materials*, **4**, 805 (2005).



Microcrystalline Materials

(Grain size » t_{gb} & t_{sc})

Grain boundary can act as:

- Blocking layer at low T
- Effect is negligible at high T

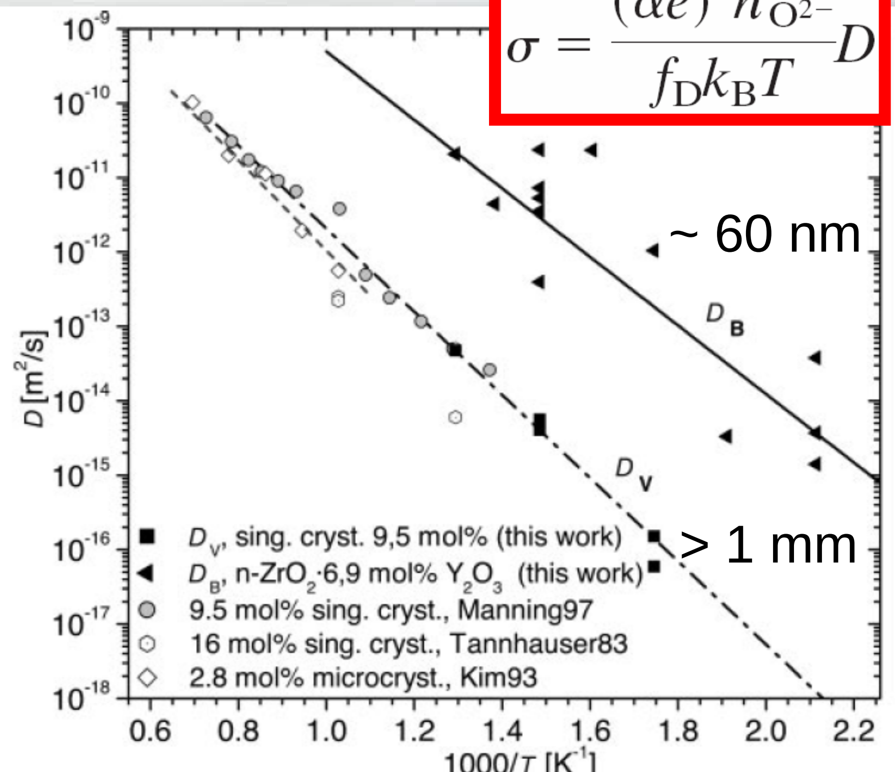
Nanocrystalline Materials

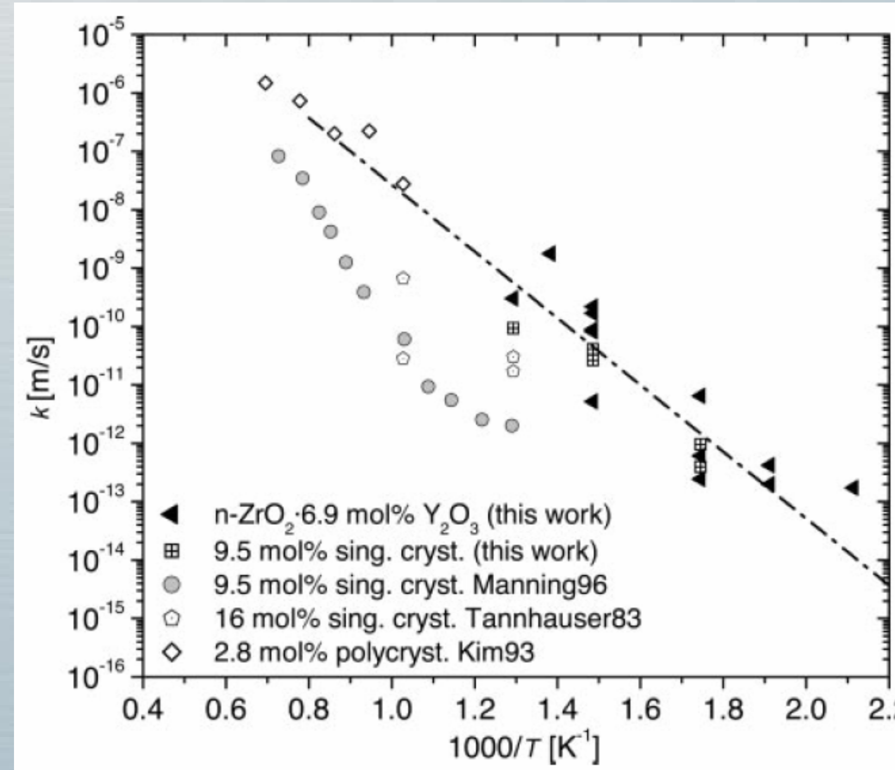
(Grain size ~/< t_{gb} & t_{sc})

- Space charge zone can cover the whole grain, changing mobility of charge carriers.

Enhanced Oxygen Diffusivity in Interfaces of Nano YSZ Disk

$$\sigma = \frac{(\alpha e)^2 n_{O^{2-}}}{f_D k_B T} D$$



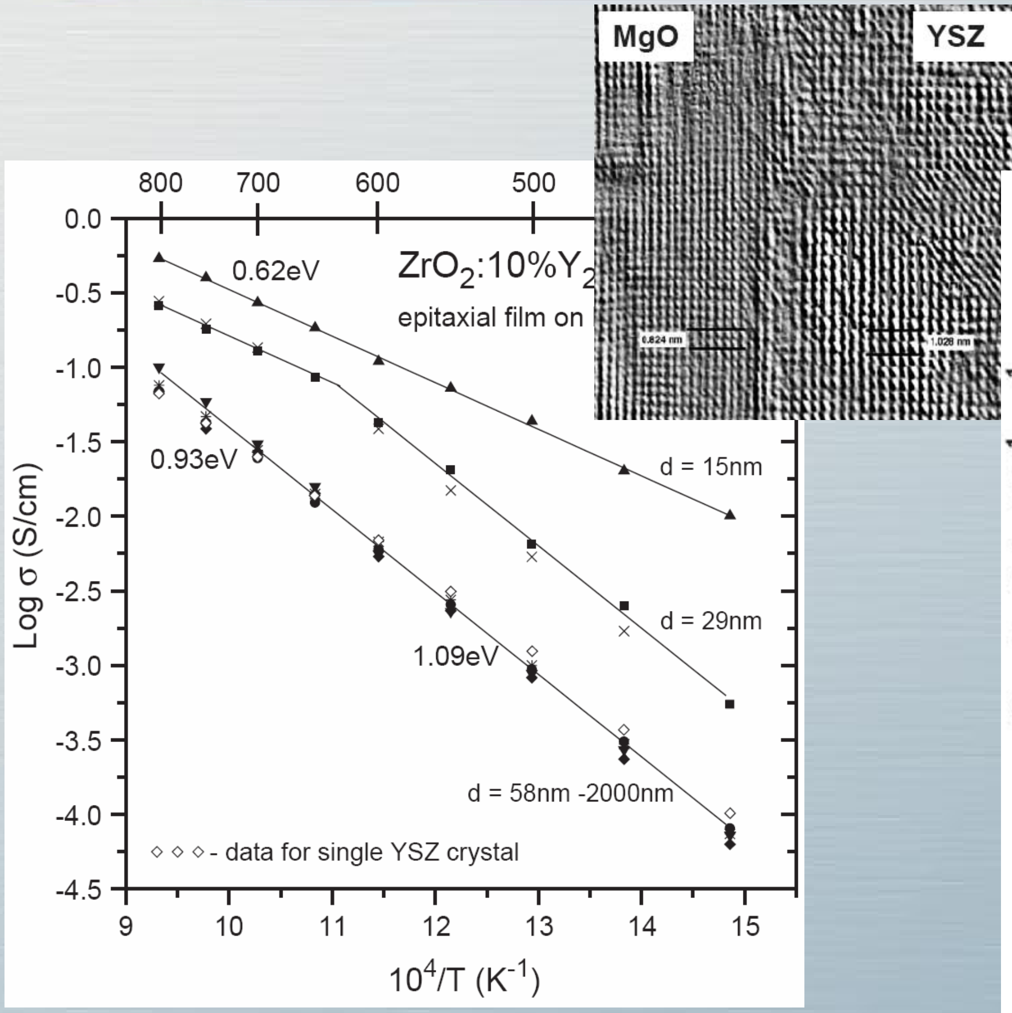


- ^{18}O Diffusion profile analysis
- Bulk and interface diffusion 3 order faster in nano than in micro YSZ

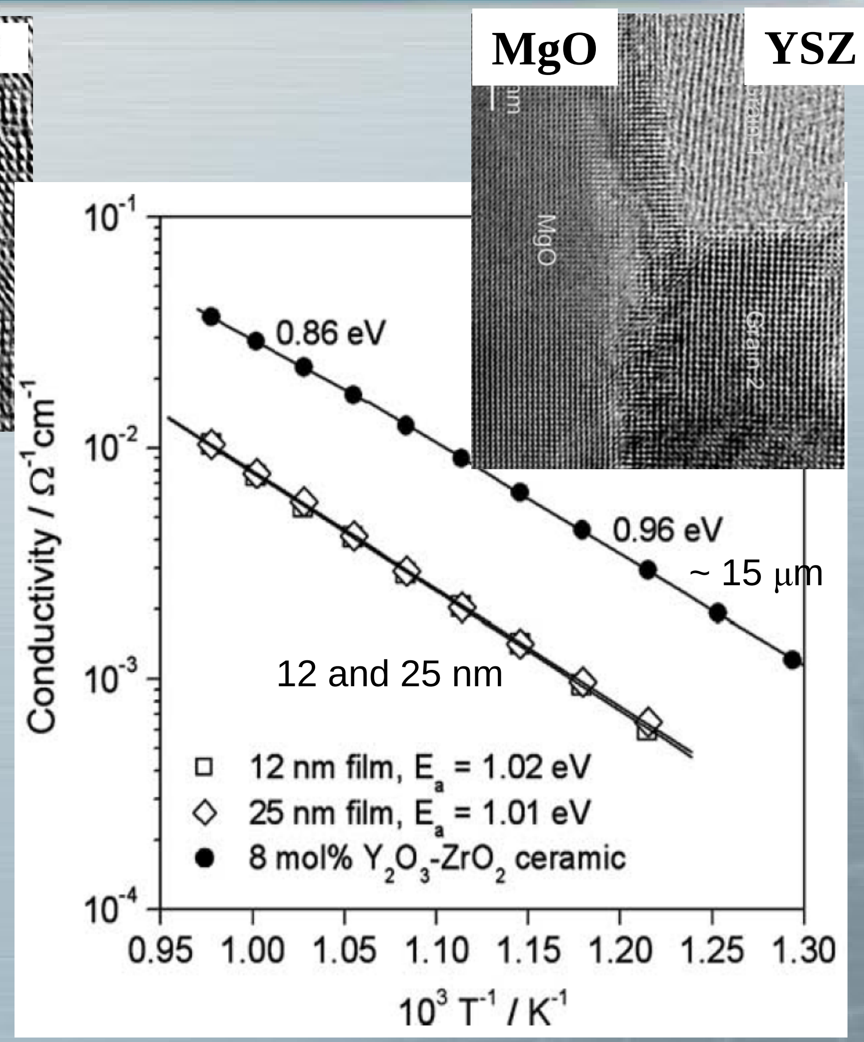
- Similar magnitude of oxygen exchange coefficient for nano and micro YSZ

G. Knoner, K. Reimann, R. Rower, U. Sodervall, and H. E Schaefer, *PNAS*, **100**, 3870 (2003).

Ionic Conduction in Nano-crystalline YSZ Films

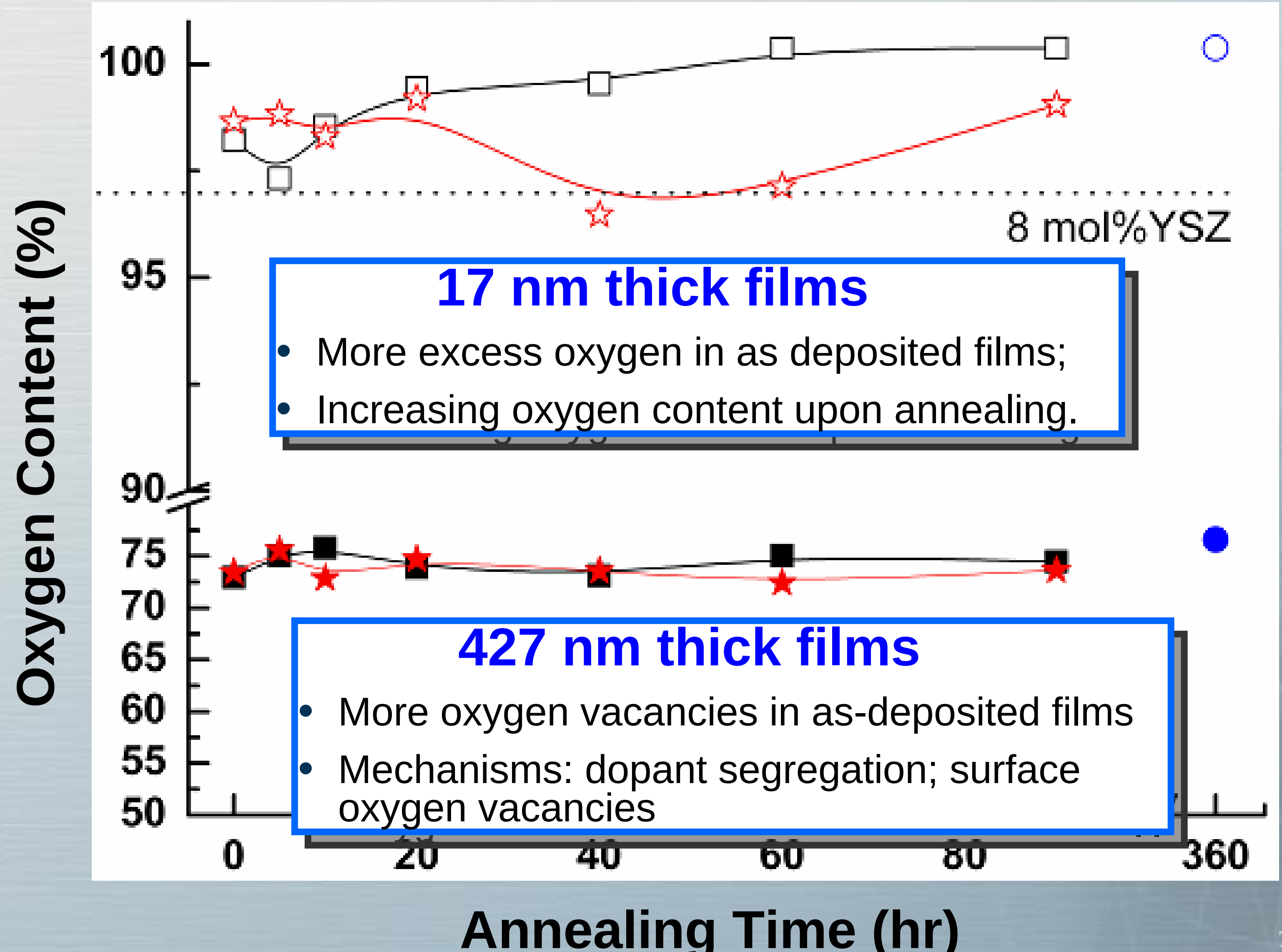


I. Kosacki et al., *Solid State Ionics*, **176**, 1319 (2005).



X. Guo, *Acta Mater.*, **53**, 5161 (2005).

Oxygen Content in YSZ Films Determined by RBS and NRA



17 nm thick films

- More excess oxygen in as deposited films;
- Increasing oxygen content upon annealing.

427 nm thick films

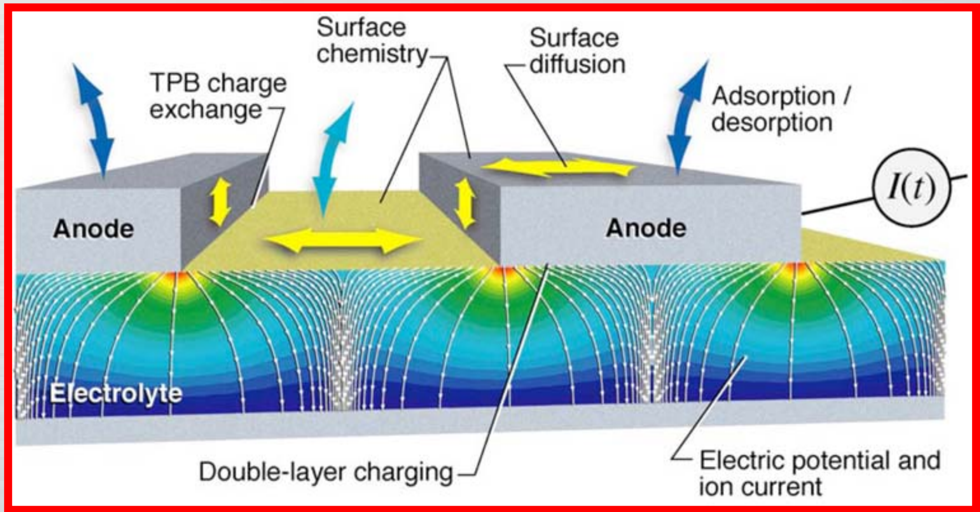
- More oxygen vacancies in as-deposited films
- Mechanisms: dopant segregation; surface oxygen vacancies

Nanosize Effects on Electrolyte Properties

- Additives which contribute to ion blocking at grain boundaries are diluted in nanocrystalline oxides giving rise to substantial reductions in specific grain boundary resistivities. ***This leads, in some cases, to an overall decrease in grain boundary resistance***.
- The case for ***enhanced ionic conduction in nominally undoped nanocrystalline oxides remains unresolved***. In thin films, enhancements of several orders of magnitude are reported. It remains to be seen if this discrepancy is related to differences in the manner in which the dopants are distributed between grain and grain boundary during processing, or, in the case of the films, are due to spurious effects such as humidity or film substrate interactions.

H. L. Tuller, *Solid State Ionics*, **131**, 143 (2000).
E. D. Wachsman, MRS Spring Meeting, (2007).

Reaction and Length Scale in SOFC Anode



H_2 on Ni: $H_2 \leftrightarrow 2H$

Desorption Rate:

$$r_d \sim n_o \upsilon_d \exp(-E_d/RT)\theta_H^2$$

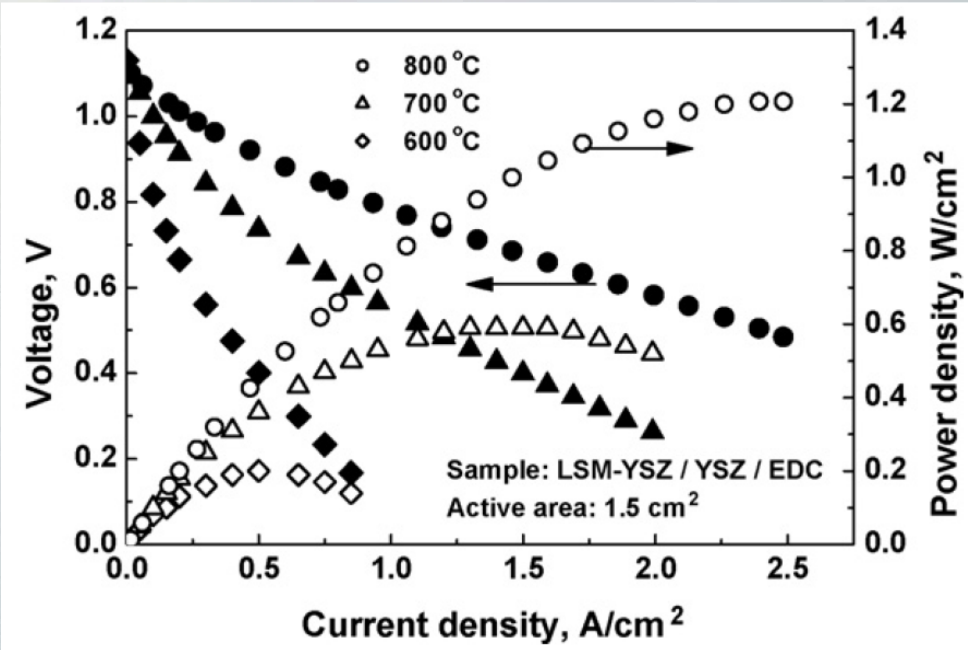
Mean lifetime of chemisorbed H ~ 700°C $\tau_H = \dfrac{\exp(E_d/RT)}{\upsilon_d \theta_H} \approx 12\,\text{ns}$

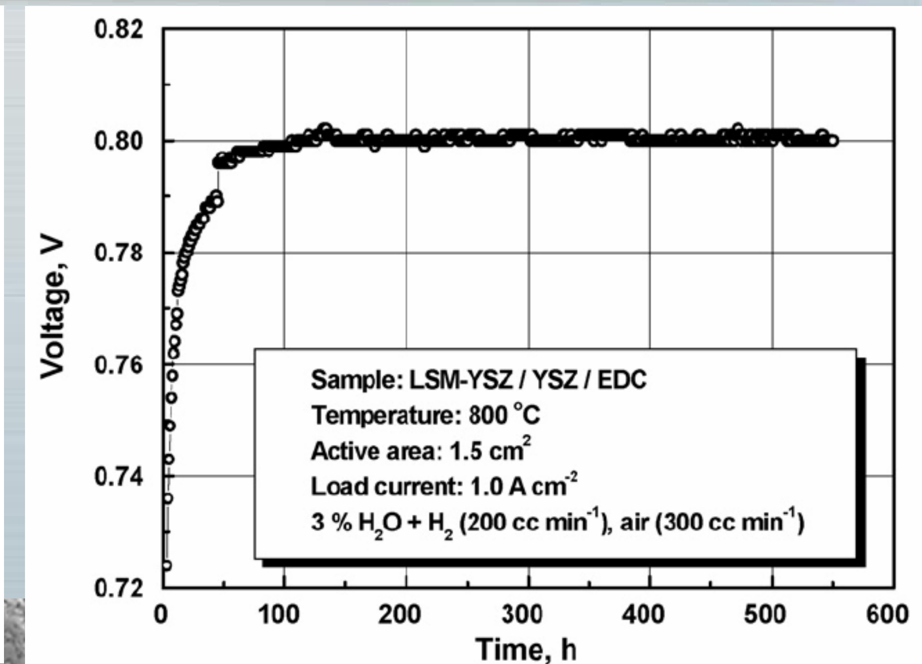
Diffusion of H on Ni: $D_H \approx 0.0025 \exp(-1762/T)\,\text{cm}^2/\text{s}$

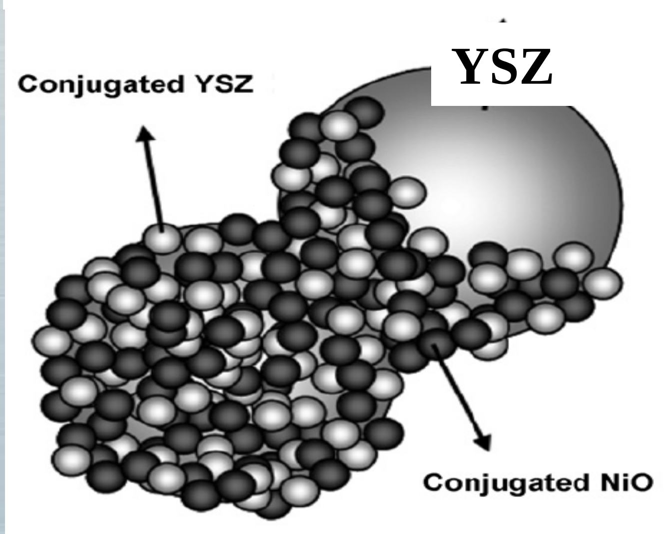
Diffusion length scale at ~ 700°C: $t_d \approx \sqrt{D_H \tau_H} \approx 20\,\text{nm}$

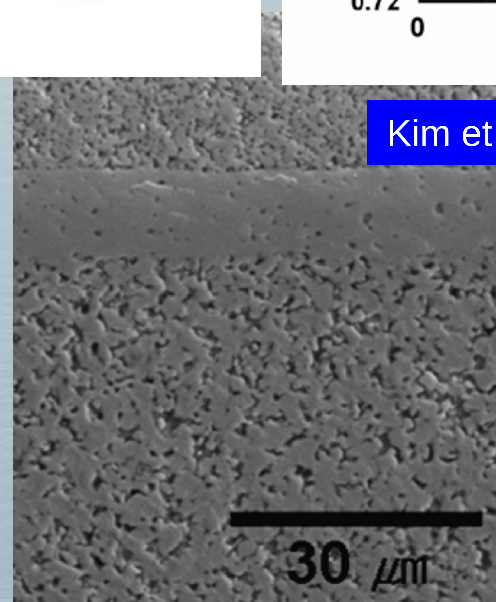
R. J. Kee, H. Zhu, D. G. Goodwin, *Proc. Comb. Institute*, 30, 2379 (2005).

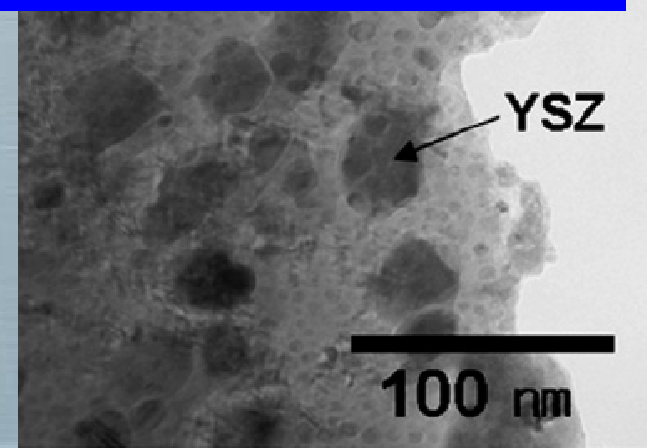
Improved Anode Performance





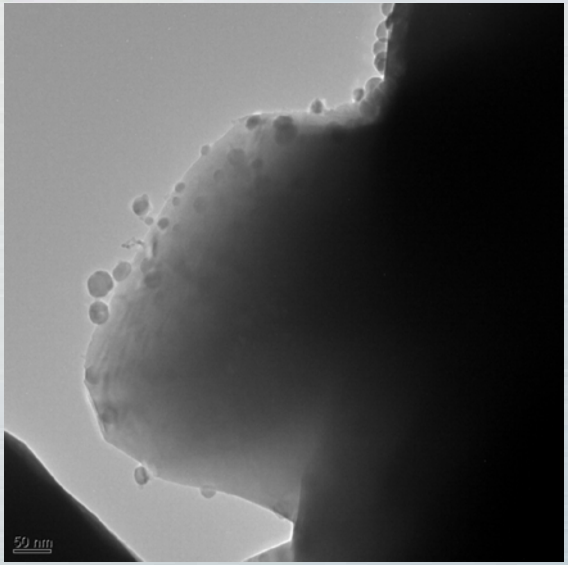


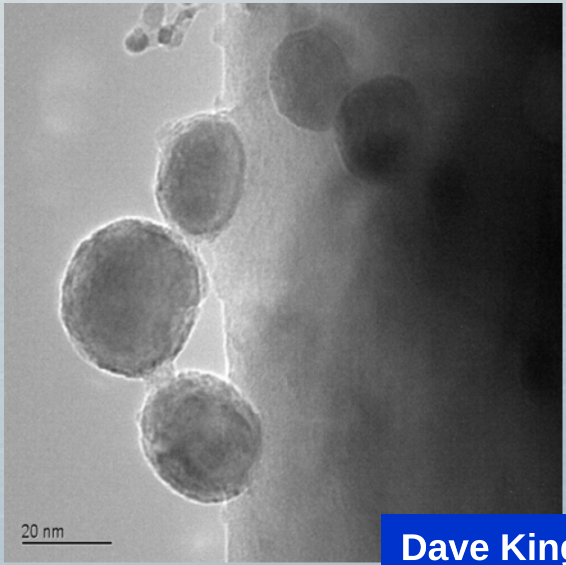


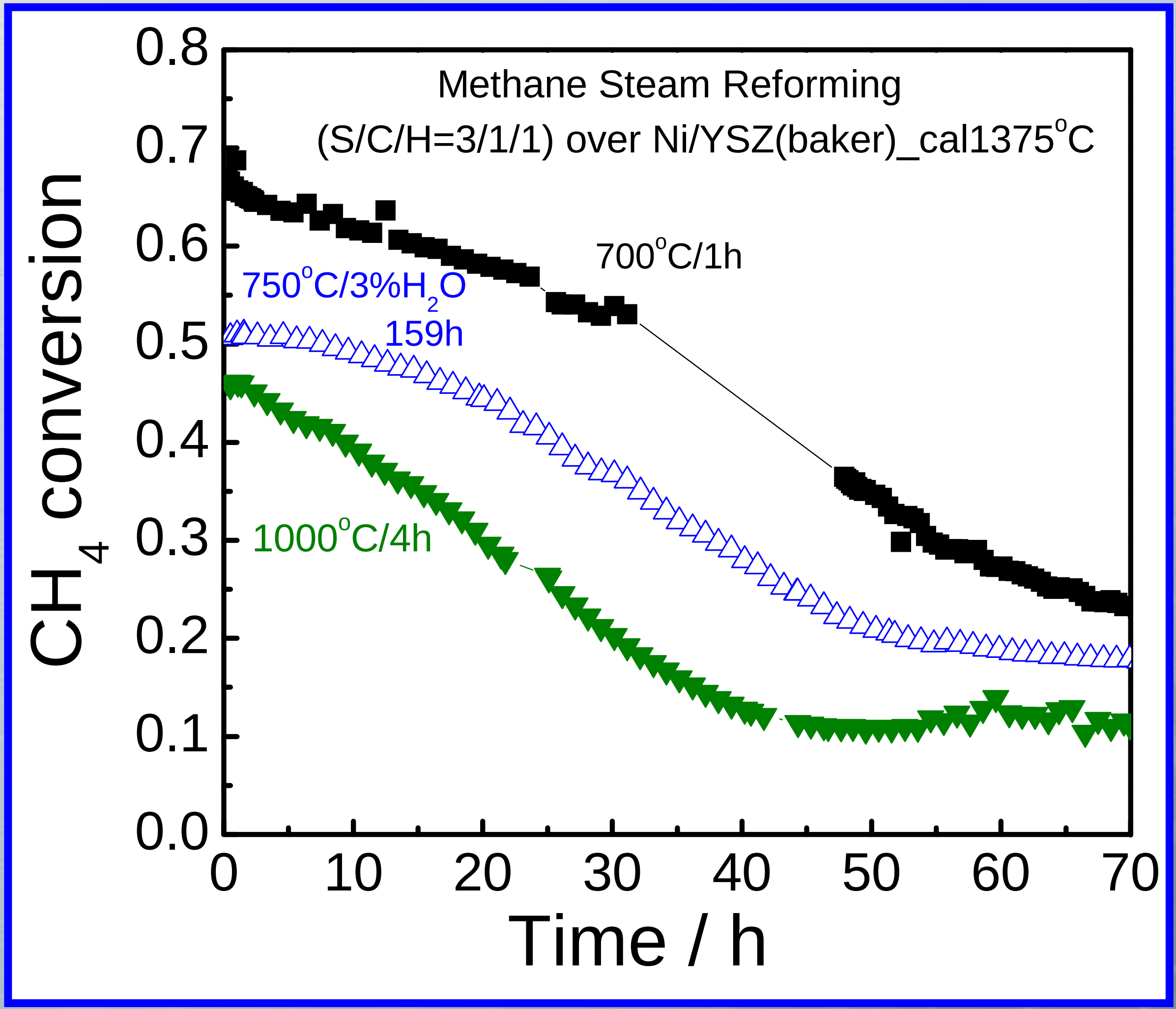


Kim et al, *J. Power Sources*, **163**, 392 (2006).

Ni Particle Size vs CH_4 Reforming

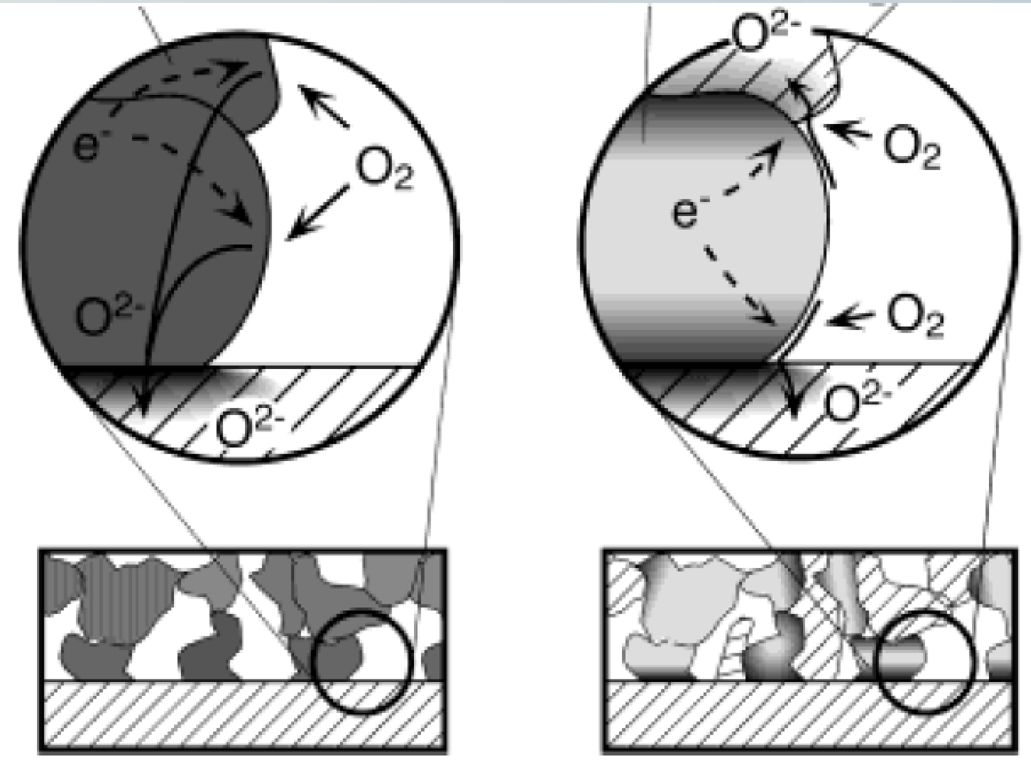






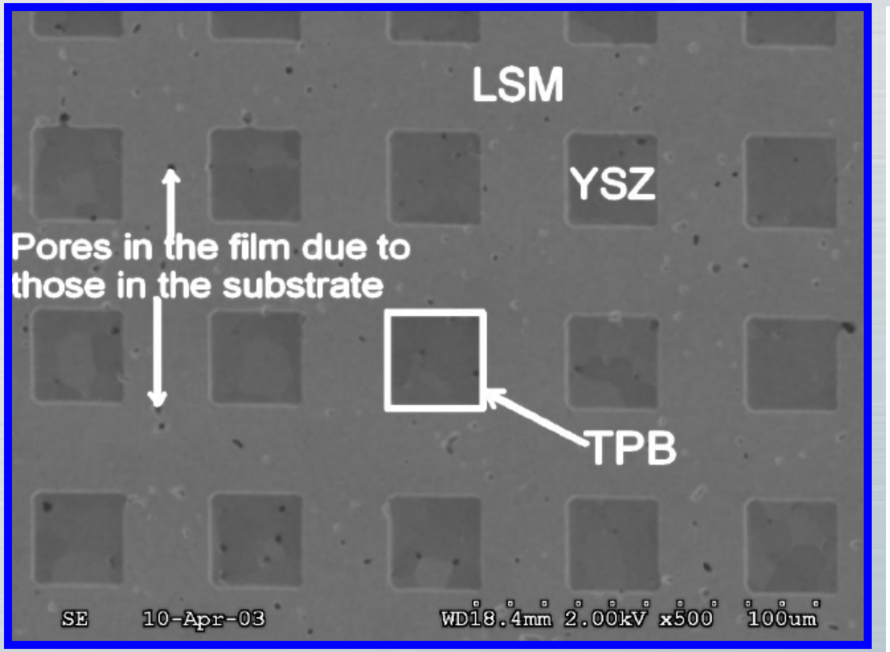
Dave King et al. 2006 Office of Fossil Energy Fuel Cell Program Annual Report.

Cathode for Oxygen Reduction



Length scale in SOFC cathode

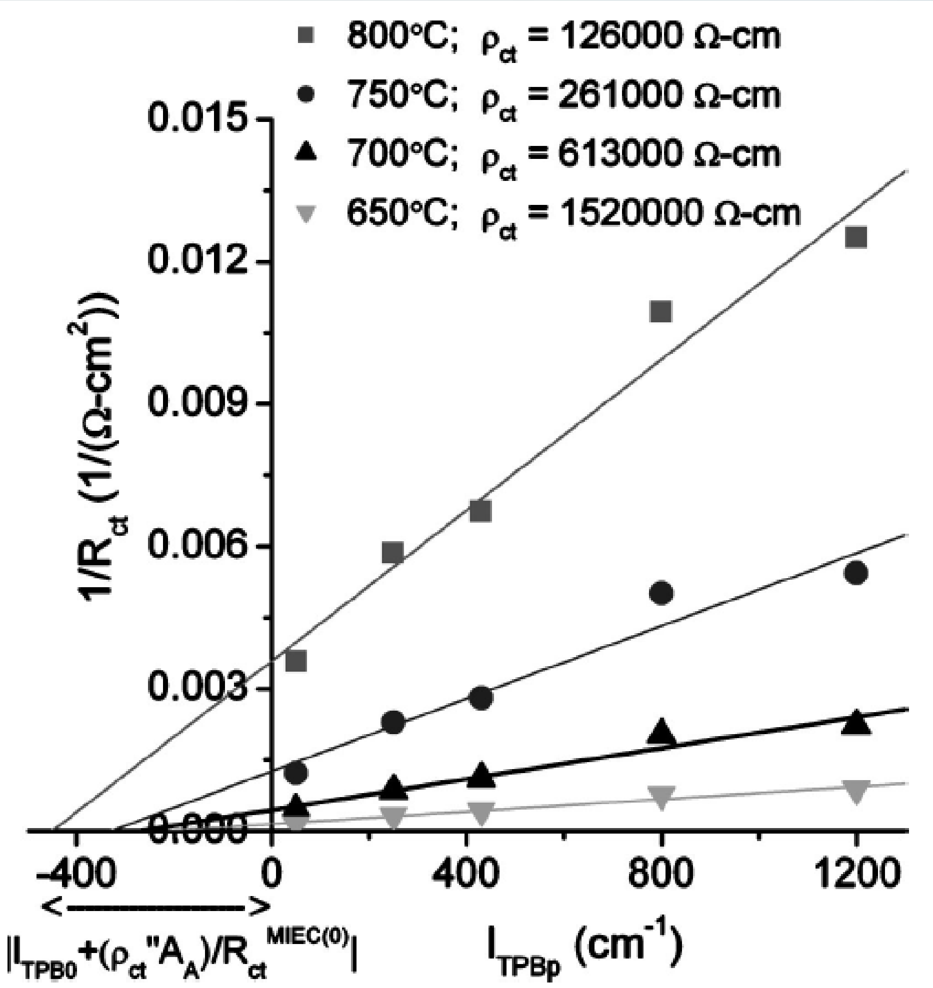
Cathodic Resistance vs. Triple Phase Boundary Length



$$R_{ct}^{TPB} = \frac{\rho''_{ct}(1 + b' p_{O_2} + b'' p_{N_2})}{l_{TPB} b' p_{O_2}}$$

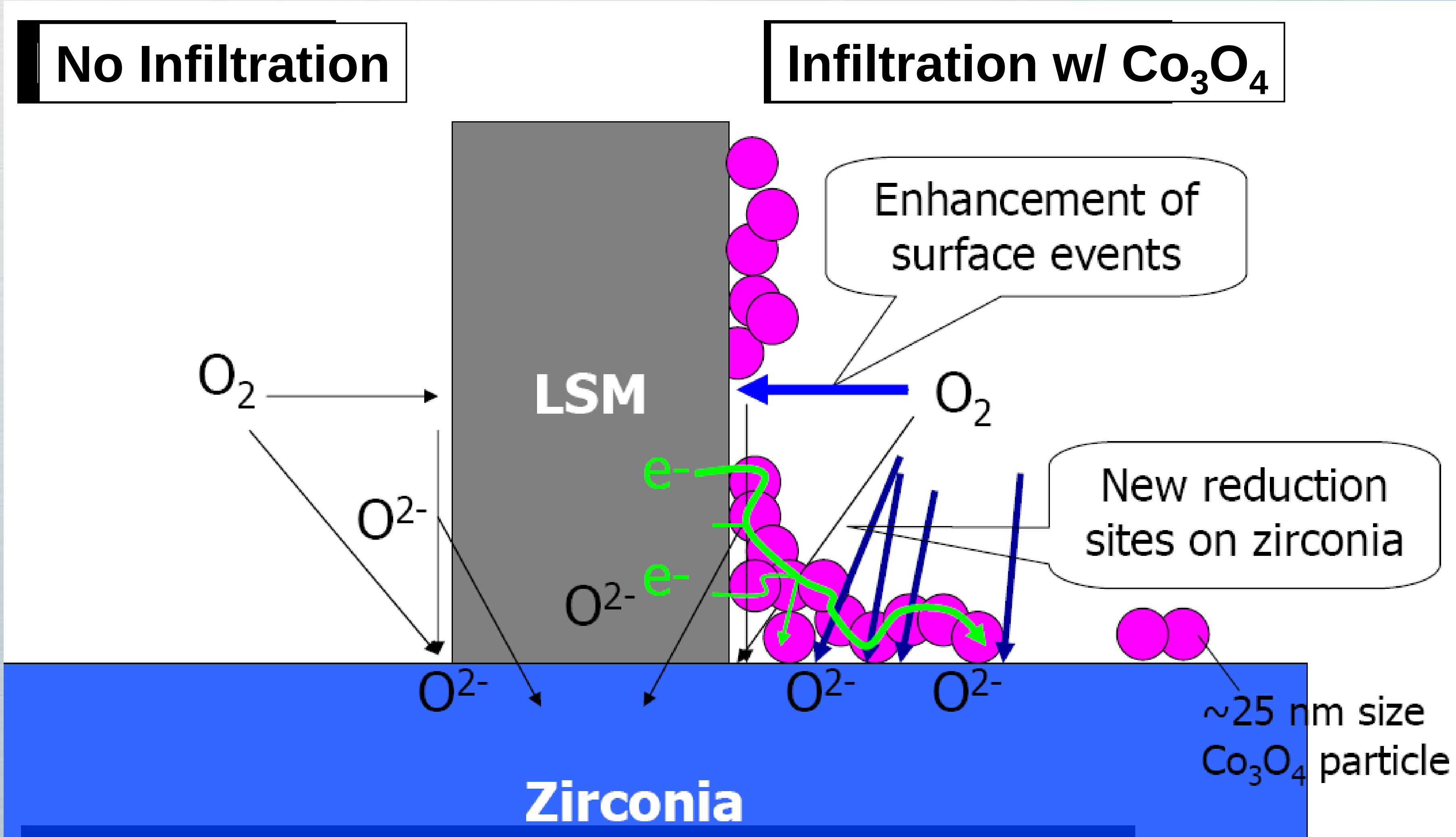
$$l_{TPB} \propto 1/d$$

(d: grain size)



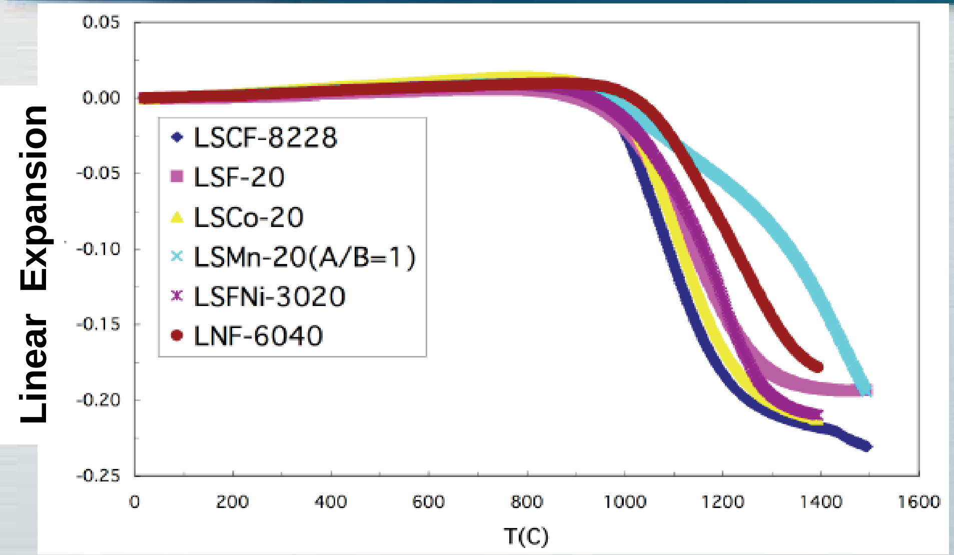
R. Radhakrishnan, A. V. Virkar, and S. C. Singhal, *J. Electrochem. Soc.*, 152, A927 (2005).
R. Radhakrishnan, A. V. Virkar, and S. C. Singhal, *J. Electrochem. Soc.*, 152, A210 (2005).

Infiltration of Nanoparticles into Cathode

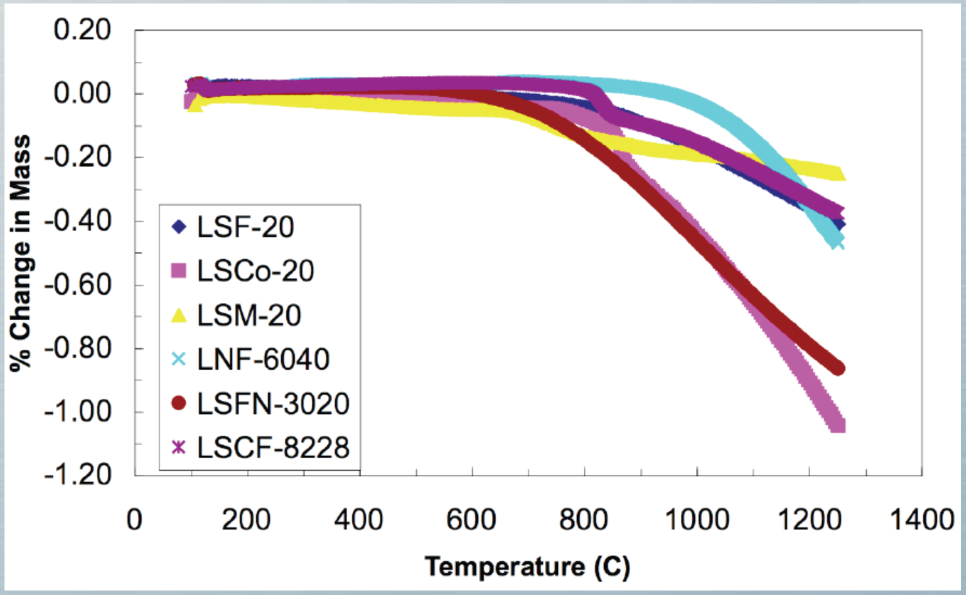


S. Visco, SECA core technology peer review workshop, (2005).

Instability of the Cathode



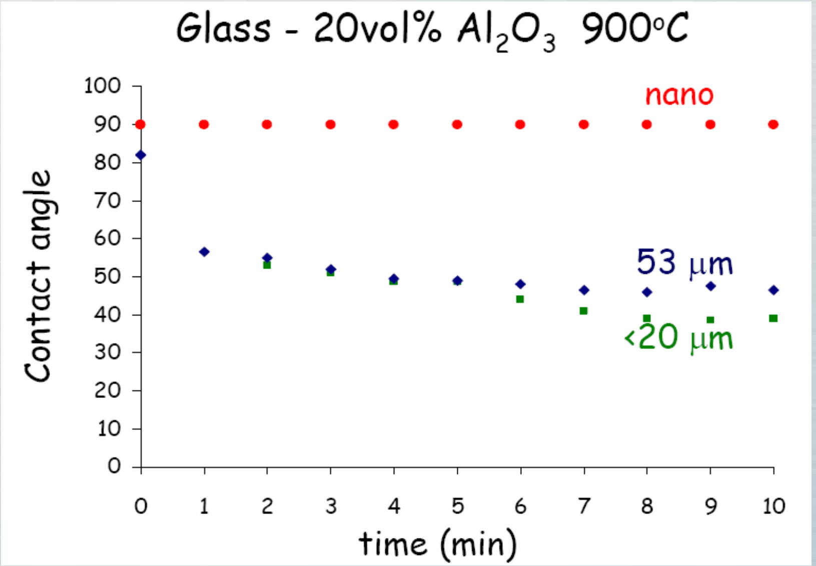
Instability of dimension and mass is because of loss of lattice oxygen, resulting in more low-valence state transition metal ions.

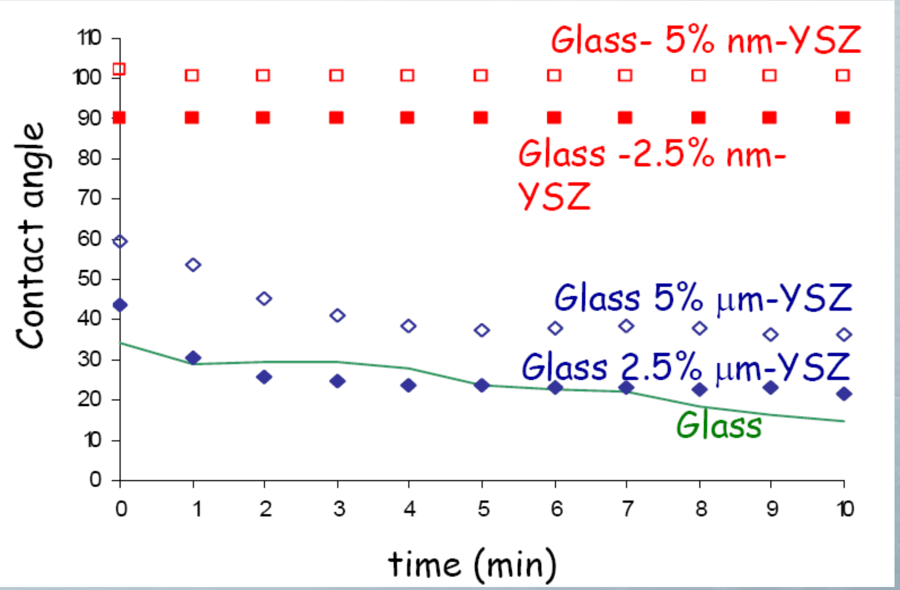


For highly active nanograin cathodes to have stable performance for ~ 40,000 hrs, temperature must be reduced to below 600°C.

J. Stevenson, PNNL, Unpublished.

Improving SOFC Seals





$$\eta = \left(1 + \frac{\kappa\phi}{1 - \left(\phi / \phi_{max}\right)}\right)^2$$

κ = 1/particle size, φ = particle packing density

Nano-scale additives have a stronger effect on glass flow than micron-size powder

Composite viscosity increases with decreasing filler particle size and with increasing filler concentration

Ron Loehman, www.osti.gov/bridge/servlets/purl/839246-r8KjrS/native/839246.pdf.

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Summary

- **Major impact of nanotechnology in SOFCs**
  - Enhancing ionic conduction in the electrolyte
  - Decreasing grain size of the electrodes (increasing surface area) to improve electrocatalysis
  - Optimizing electronic/ionic conduction paths in electrodes
  - Optimizing sinterability of the seals
- **Major Challenges**
  - Stability of the cathode at high operation temperatures
  - Stability of the anode during cell fabrication
  - Lowering operation temperature to below 600^{o}C to take advantage of beneficial effects of nanotechnology