SYSTEMATIC STUDIES OF THE CATHODE-ELECTROLYTE INTERFACE IN SOFC CATHODES PREPARED BY INFILTRATION

Rainer Küngas, Eyas Mahmoud, John M. Vohs, and Raymond J. Gorte

Department of Chemical and Biomolecular Engineering, University of Pennsylvania

kungas@seas.upenn.edu

Introduction

• Solid oxide fuel cells (SOFCs) are high-efficiency energy conversion devices that operate at 600-1000°C. Fuel cell electrodes are composites of ionically conductive yttria-stabilized zirconia (YSZ) and catalyst, typically a perovskite ceramic.

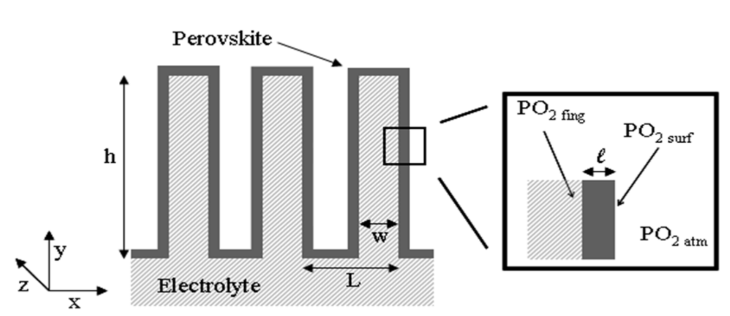
• Our understanding of the factors that lead to lower overpotentials in SOFC electrodes is still limited, mainly because the performance is highly dependent on the electrode microstructure. Until recently, it has been very difficult to elucidate the importance of a single parameter (electrode active surface area, ionic conductivity, porosity, composition of the perovskite, etc) on electrode performance.

• Infiltration method, pioneered at Penn, is becoming an increasingly popular method for the preparation of SOFC electrodes.

• Among other advantages, electrodes prepared by infiltration are good platforms for carrying out systematic studies on the effect of microstructure on electrode performance.

Theoretical approach

• A mathematical model has been developed to understand the performance of electrodes prepared by infiltration of a perovskite (e.g. $La_{0.8}Sr_{0.2}FeO_3$, LSF) into yttria-stabilized zirconia (YSZ).



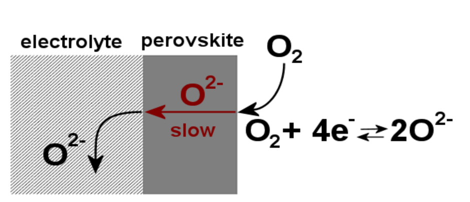
F. Bidrawn, R. Küngas, J. M. Vohs, R. J. Gorte, *J. Electrochem. Soc.*, 155, (2008) B660.

•Potential inside the YSZ fin:

$$V = iR \qquad V = \frac{R_g T}{4F} \ln\left(\frac{PO_{2\,atm}}{PO_{2\,fing}}\right)$$

•Flux through the perovskite film depends on the rate-limiting step.

1. Slow diffusion of O^{2-} through the perovskite film:



$$(\text{oxygen flux}) = J_{O_2} = \frac{R_g T \sigma_{ionic}}{16F^2 l} \ln\left(\frac{PO_{2\,surf}}{PO_{2\,fing}}\right)$$

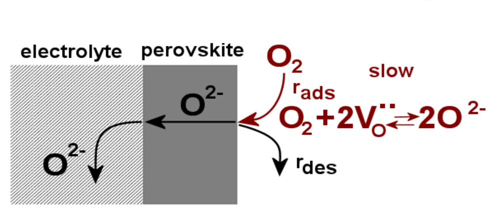
$$(\text{current flux}) = i_S'' = 4FJ_{O_2}$$

• Summing up the fluxes through all film elements gives the total current. Resistance is given as:

$$(\text{electrode resistance}) = R = \frac{1}{(1-p)}\sqrt{\frac{\frac{1}{2}wl}{\sigma_{ionic}\sigma'_{YSZ}}}$$

p - porosity
w – width of fin
l – thickness of perovskite film
σ_{ionic} – ionic conductivity of perovskite
σ'_{YSZ} – ionic conductivity of electrolyte (divided by tortuosity)

2. Slow adsorption of O_2 onto perovskite lattice sites:



$$r_{ads} = \frac{PO_{2\,atm}}{\sqrt{2\pi M R_g T}} \cdot S_0 \cdot (1-\theta) \qquad r_{des} = \text{constant}$$

$$(\text{current flux}) = i_S'' = 4FJ_{O2} = 4F(r_{ads} - r_{des})$$

• Resistance is given as:

$$(\text{electrode resistance}) = R = \frac{1}{(1-p)}\sqrt{\frac{\frac{3}{2}w}{const \cdot mS_0\sigma'_{YSZ}}}$$

p - porosity
w – width of fin
m – reducibility (slope of log pO_2 vs 3-δ)
S_0 – sticking probability
σ'_{YSZ} – ionic conductivity of electrolyte (divided by tortuosity)

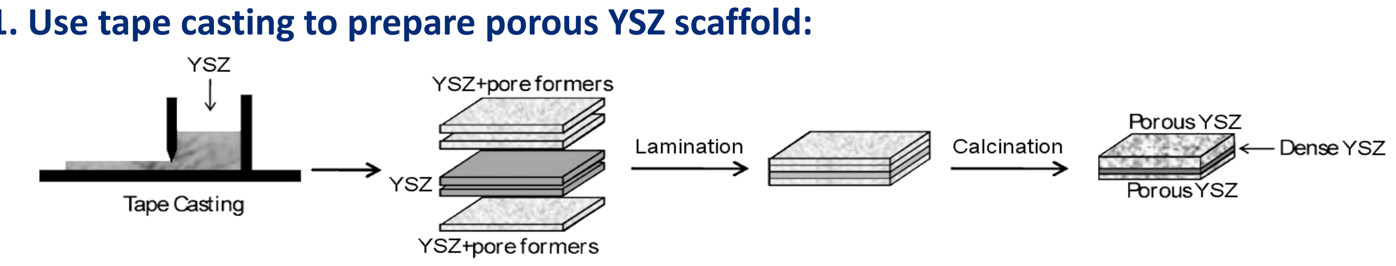
• Example calculations based on diffusion limitation at 973 K:

Composite	σ_{ionic} (S/cm)	σ'_{YSZ} (S/cm)	R_{model} (Ω cm^2)	R_{exp} (Ω cm^2)
$La_{0.8}Sr_{0.2}FeO_3$ - YSZ	$8.3 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	0.067	2.8
$La_{0.8}Sr_{0.2}BaO_3$ - YSZ	$3.1 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	0.11	2.9
$La_{0.8}Sr_{0.2}CaO_3$ - YSZ	$3.8 \cdot 10^{-5}$	$2.9 \cdot 10^{-3}$	0.31	3.0
$La_{0.8}Sr_{0.2}MnO_3$ - YSZ	$4.0 \cdot 10^{-8}$	$2.9 \cdot 10^{-3}$	9.7	8.8

→ Electrode performance is not limited by bulk diffusion as long as $\sigma_{ionic} > 10^{-6}$ S/cm.

Experimental

1. Use tape casting to prepare porous YSZ scaffold:

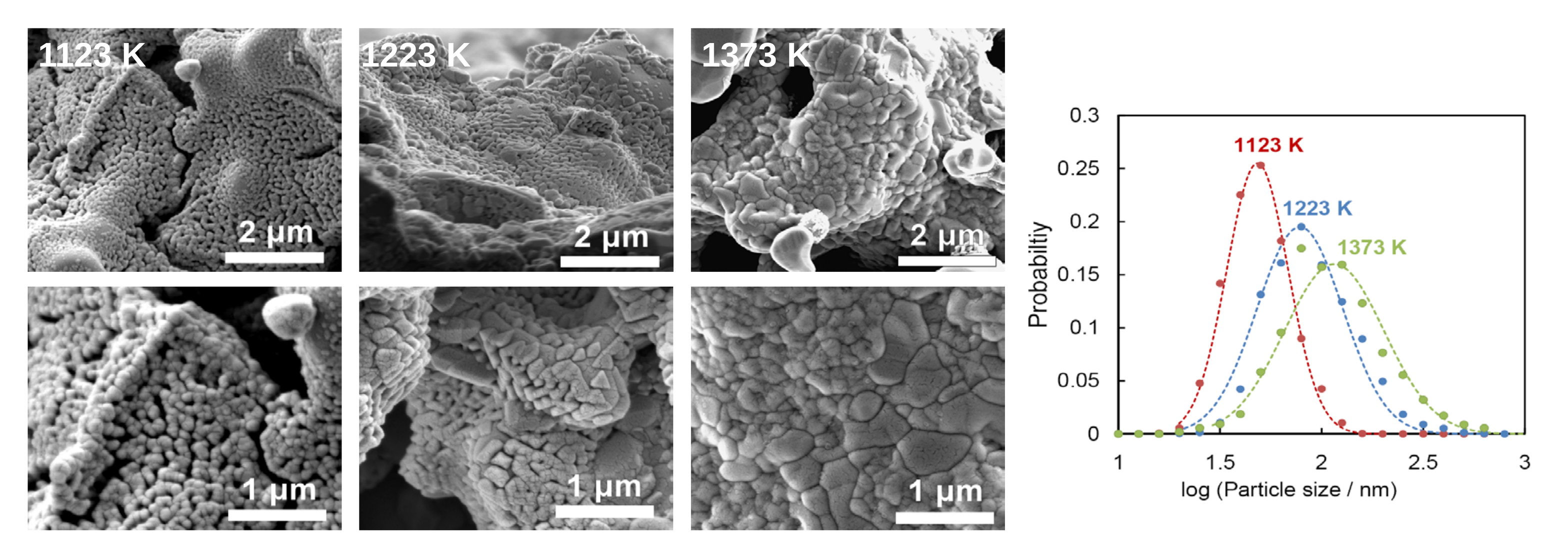


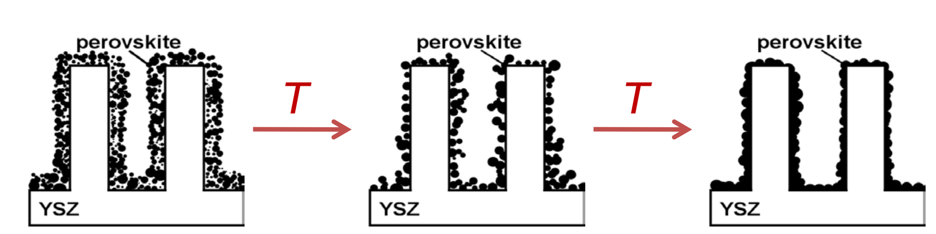
2. Infiltrate catalyst into scaffold using nitrate solutions (e.g. of LSF). Calcine to form the perovskite phase.

•Advantages of infiltration:
+ Higher electronic conductivity
+ Good thermal expansion match
+ Separate firing steps for electrolyte and perovskite
+ Catalyst not subject to high temperature during fabrication

Effect of perovskite surface area

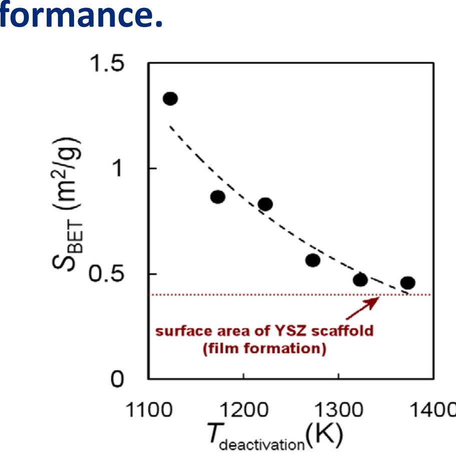
• Initially, infiltrated electrodes consist of very fine perovskite particles coating the YSZ scaffold. However, long operation at 973 K (or treatment at higher temperatures) causes coarsening:

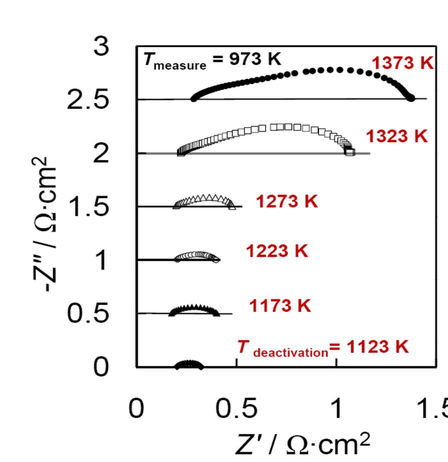




Film formation after 1373 K

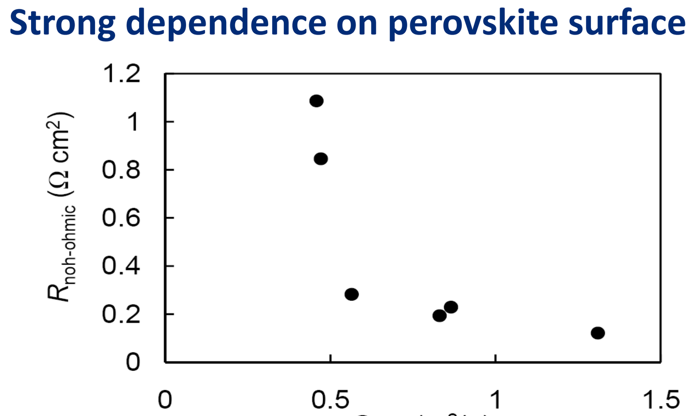
• As the structure coarsens, surface area decreases, which causes degradation in electrode performance.

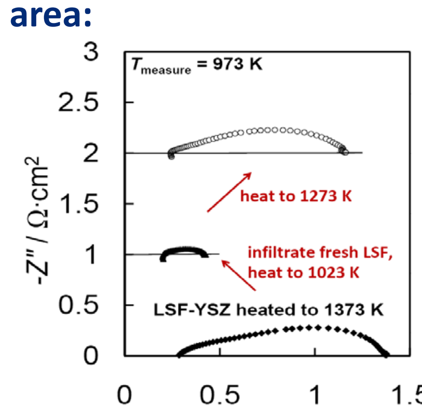




Increasing impedance

• Strong dependence on perovskite surface area:

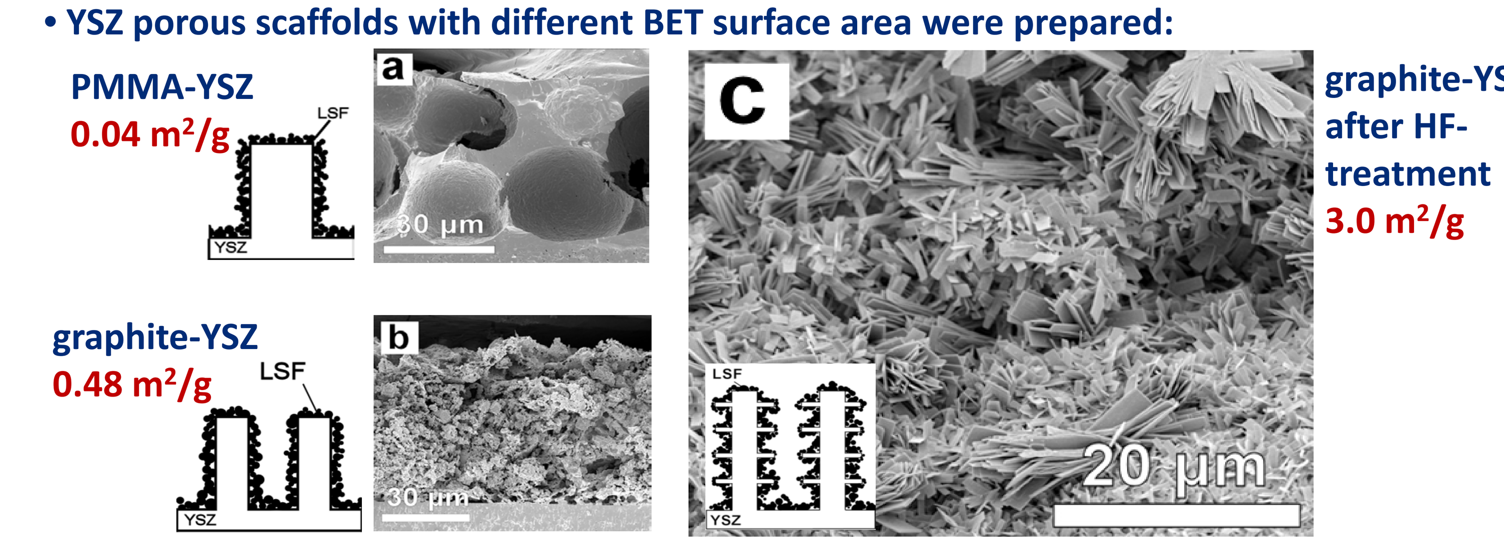




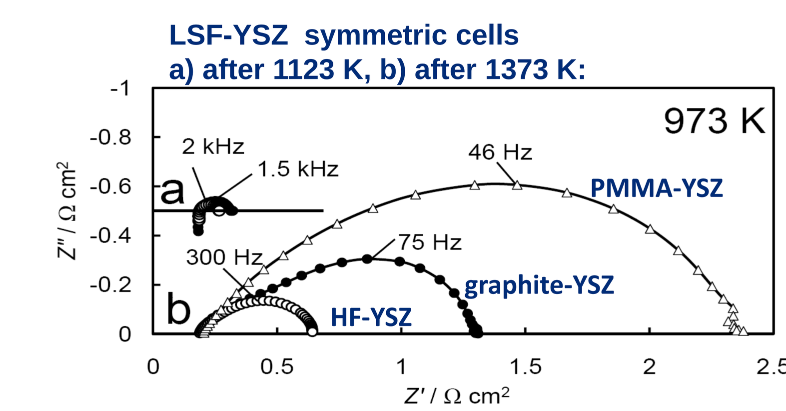
Experimental evidence of adsorption limitation!

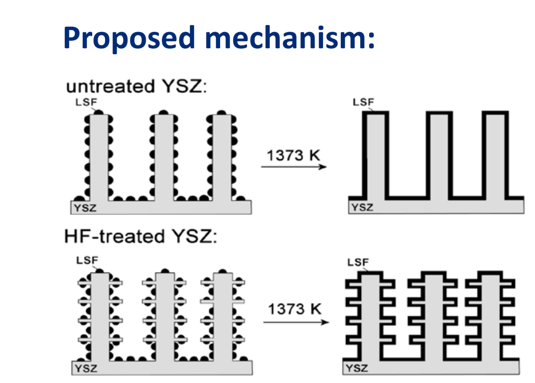
Effect of porous YSZ surface area

• YSZ porous scaffolds with different BET surface area were prepared:



• Electrode performance is highly dependent on the porous YSZ surface area:

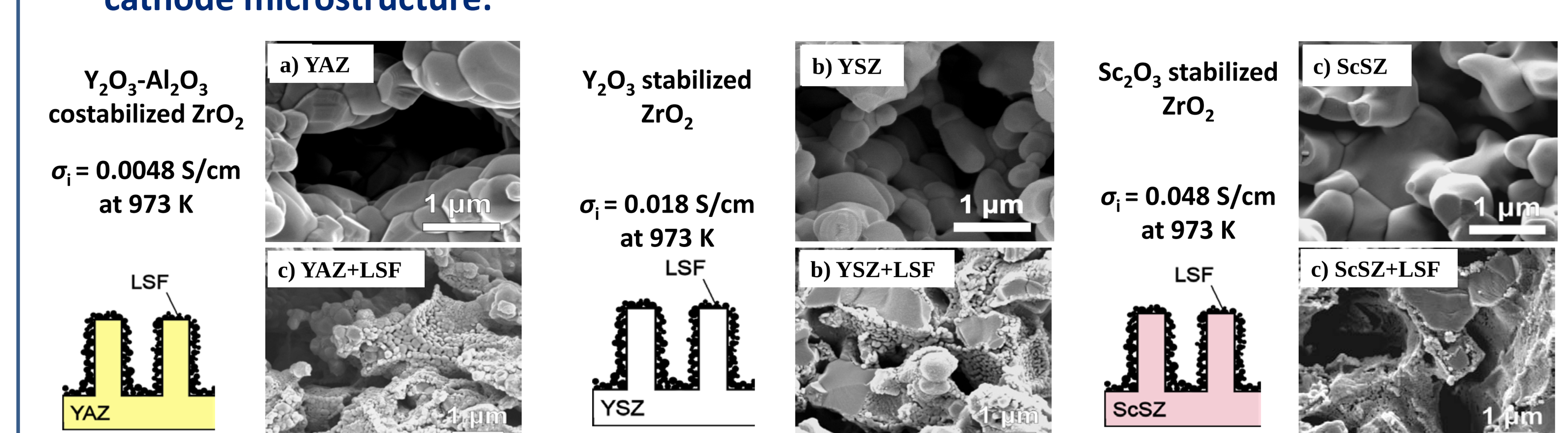




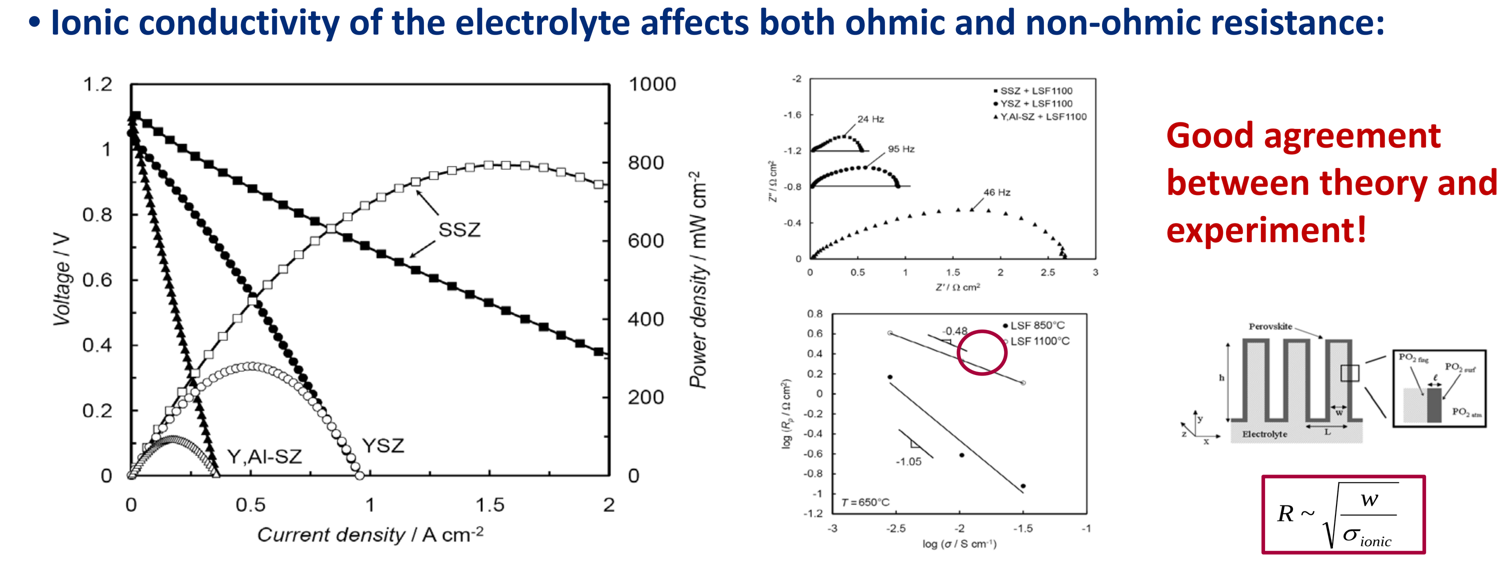
R. Küngas, J.-S. Kim, J. M. Vohs, R. J. Gorte, *J. Am. Ceram. Soc.*, (2011) in press, available online.

Effect of electrolyte ionic conductivity

• Infiltration method allows one to vary the porous electrolyte material without affecting cathode microstructure:



• Ionic conductivity of the electrolyte affects both ohmic and non-ohmic resistance:



Good agreement between theory and experiment!

R. Küngas, J. M. Vohs, R. J. Gorte, *J. Electrochem. Soc.*, **158(6)** (2011) B743.

Acknowledgements

• This work was funded by US Department of Energy H_2 Initiative.

• R.K.'s studies at the University of Pennsylvania were sponsored by the U.S. Department of State under the auspices of the International Fulbright Science & Technology Award.