Understanding Fuel Oxidation Processes in SOFC Anodes

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Objectives of Overall MURI Program

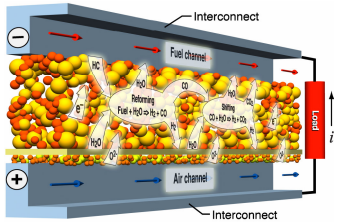


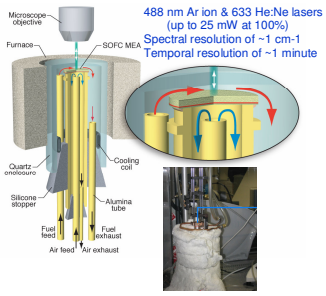
Figure provided by Bob Kee (CSM)

- *Develop a fundamental understanding of rate-controlling processes in oxidation of hydrocarbons in SOFC anodes*
- *Establish benchmark experiments for evaluating fuel oxidation processes*
- *Build multi-scale modeling tools to evaluate SOFC anode performance*

Methods for Experimental Program at Maryland

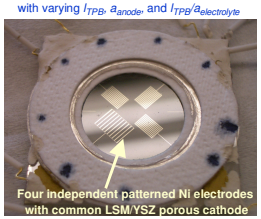
- *Use of microfabricated patterned and thin-film anodes with well-characterized geometries to assess fundamental kinetic rates of oxidation processes*
- *Ex-situ surface and bulk phase characterization to evaluate impact of oxidation and carbon deposition processes on anode structure*
- *In situ surface (Raman) spectroscopy for observing surface intermediates and carbon deposition process on anodes*

Experimental Rig with in situ Raman Spectroscopy for Operating SOFC Anodes (for Tcell up to 720 °C)

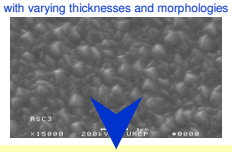


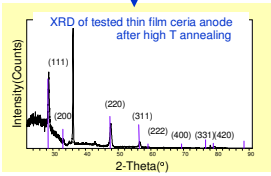
488 nm Ar ion & 633 He:Ne lasers (up to 25 mW at 100%)
Spectral resolution of ~1 cm-1
Temporal resolution of ~1 minute

Microfabricated Nickel Patterned Anodes with Varying Geometries
< 1 um thick patterns
with varying l_{TPB}, a_{anode}, and $l_{TPB}/a_{electrolyte}$



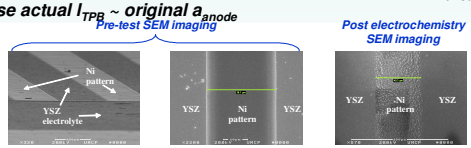
Sputtered Thin Film Ceria Anodes on YSZ Electrolytes
with varying thicknesses and morphologies





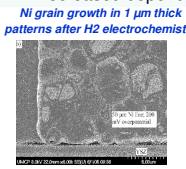
Oxidation of Reformate Species H_2, CO, and CH_4 on Ni

- *Initial studies on ~100 nm thin Ni pattern anodes indicate that dense films that under electrochemical activity with H_2 or CO rapidly restructure into interconnected networks of 1-10 µm agglomerates with good electronic conductivity and significant internal TPB due to exposed YSZ electrolyte.*
- *Agglomerated Ni shows that Tafel plots scale with original a_{anode} because actual l_{TPB} ~ original a_{anode}*

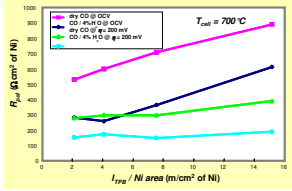


- *Thicker 1 µm Ni patterns show good stability with well-defined TPB despite grain coarsening occurring during anodic electrochemistry.*
  - grain sizes between 2-8 µm
  - l_{TPB} maintained and provides stable H_2 electrochemical oxidation.
  - Carbon deposition as indicated by EDAX impacts l_{TPB} with CH_4 oxidation
- *Measurements on stable Ni patterns provide fundamental rates with respect to pattern geometry*
  - CO oxidation shows importance of H_2O and water gas shift
  - Decreased dependence of rates on TPB geometry with increased η

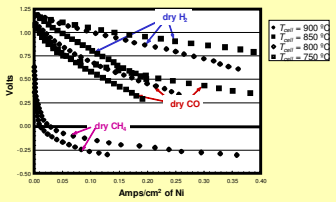
Ni grain growth in 1 µm thick patterns after H2 electrochemistry



Comparison of anode resistances for wet and dry CO electrochemical oxidation on stable Ni patterns

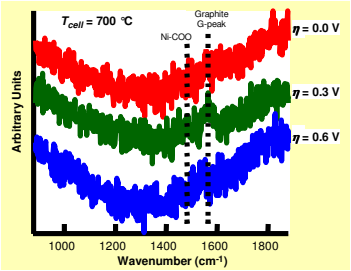


V-i curves for non-porous Ni anodes



- *V-i curves show very high R_{act} for dry CH_4 on non-porous Ni anodes*
- *At high η above 800 °C, R_{pol} for "dry" CH_4 oxidation drops to values similar for H_2 due to surface reforming reactions*

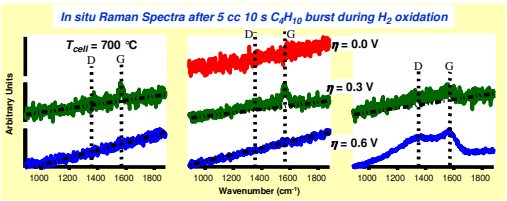
- *In situ Raman spectroscopy during CO oxidation on porous Ni/YSZ anodes reveals strong dependence of surface chemistry on η*
- *Both graphite 1570 G-peak and 1481 –COO peak strongest at intermediate η*
  - No distinguishable peaks at highest η.
  - Competitive reactions (oxidation vs. Boudouard) with different η dependence



Oxidation of Larger Hydrocarbon (n-C_4H_{10}) on Ni

- *Raman spectra of porous Ni/YSZ anodes show rapid growth of graphitic carbon after 30 s n-C_4H_{10} pulse during H_2 oxidation at 700 °C*
  - At intermediate η disordered (D-peak) and ordered (G-peak) graphite appears whereas at higher η only ordered graphite appears
- *Disappearance rate of graphitic peaks post-C_4H_{10} exposure increase with η during H_2 oxidation*

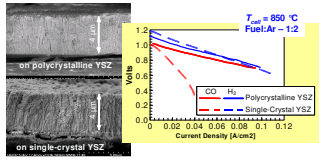
In situ Raman Spectra after 5 cc 10 s C_4H_{10} burst during H_2 oxidation



- *Transient studies of n-C_4H_{10} electrochemical oxidation with excess H_2 over Ni/YSZ porous anodes indicate initial increase in anode overpotentials vs. current density followed by a subsequent decrease*
  - Competing effects of Ni/YSZ site blocking vs. improve current collection

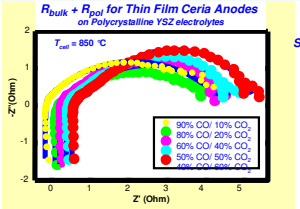
Oxidation of H_2, CO, and n-C_4H_{10} on Undoped Ceria

- *Undoped thin-film ceria anodes (sputter-deposited on YSZ electrolytes) show strong morphology dependence with YSZ structure (polycrystalline vs. single crystal)*
- *Differences in morphology (nanoporosity) impact CO electrochemical oxidation but not H_2 oxidation*

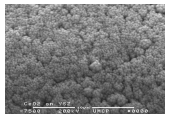


- *Coupling of bulk electronic or ionic transport in Ceria with CO/CO_2 surface chemistry observed by changes in R_{bulk} with gas feeds.*

R_{bulk} + R_{pol} for Thin Film Ceria Anodes on Polycrystalline YSZ electrolytes



Surface Morphology of Thin Film Ceria Anodes



- *Porous CeO_2/YSZ anodes show graphitic carbon formation like Ni/YSZ anodes at low η operation with C_4H_{10} feeds*
- *However, graphitic deposits in porous CeO_2 anodes are not as significant and much smaller in size (4 nm vs. 11 nm) and without similar degradation in anode performance*

Ex situ Raman Spectrum
a) 325-mesh graphite,
b) Ni/YSZ anode (5 hrs. C_4H_{10})
c) CeO2/YSZ (5 hrs. C_4H_{10})
d) CeO2/YSZ (100 hrs. C_4H_{10})
e) Cu/CeO2/YSZ (100 hrs. C_4H_{10})