Stability of Ni-Infiltrated Solid Oxide Fuel Cell Anodes for Intermediate Temperature Operation

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SSGF Program Review

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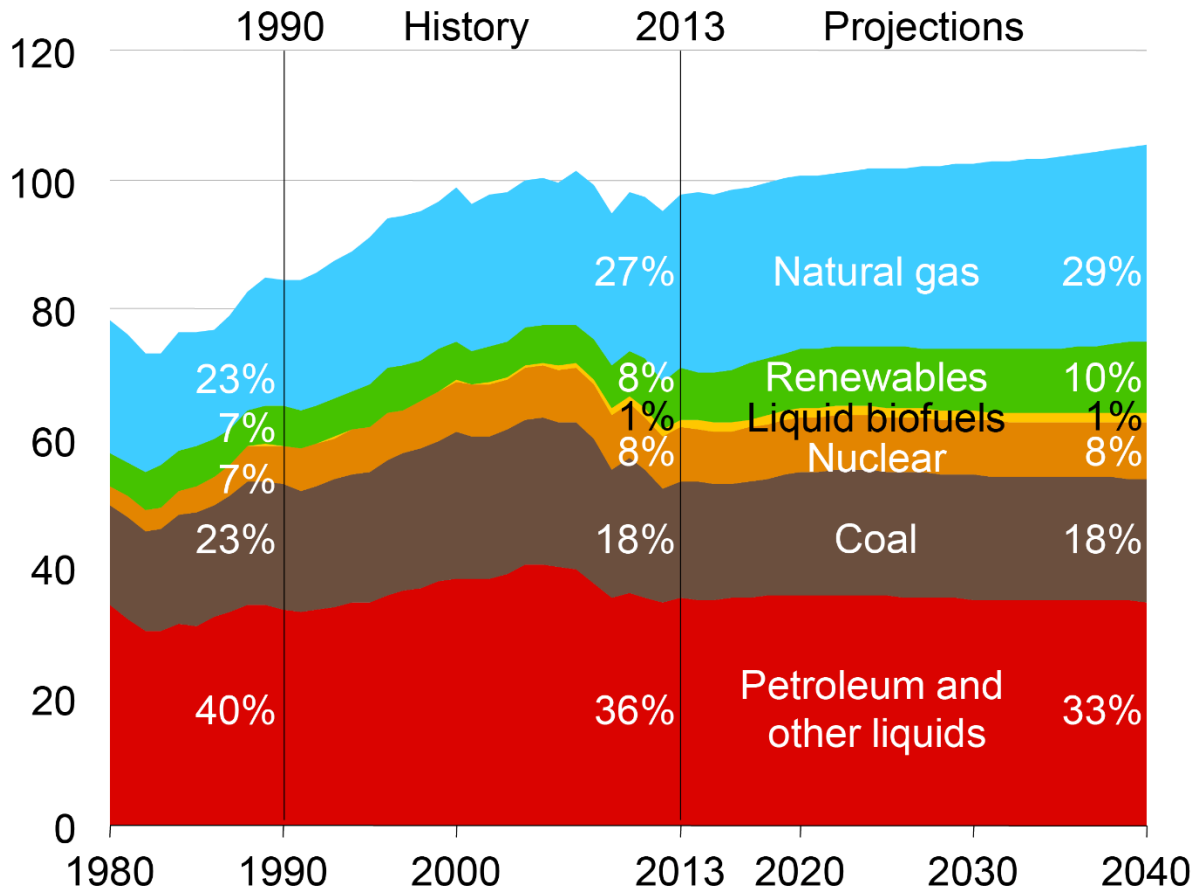
Energy Challenges

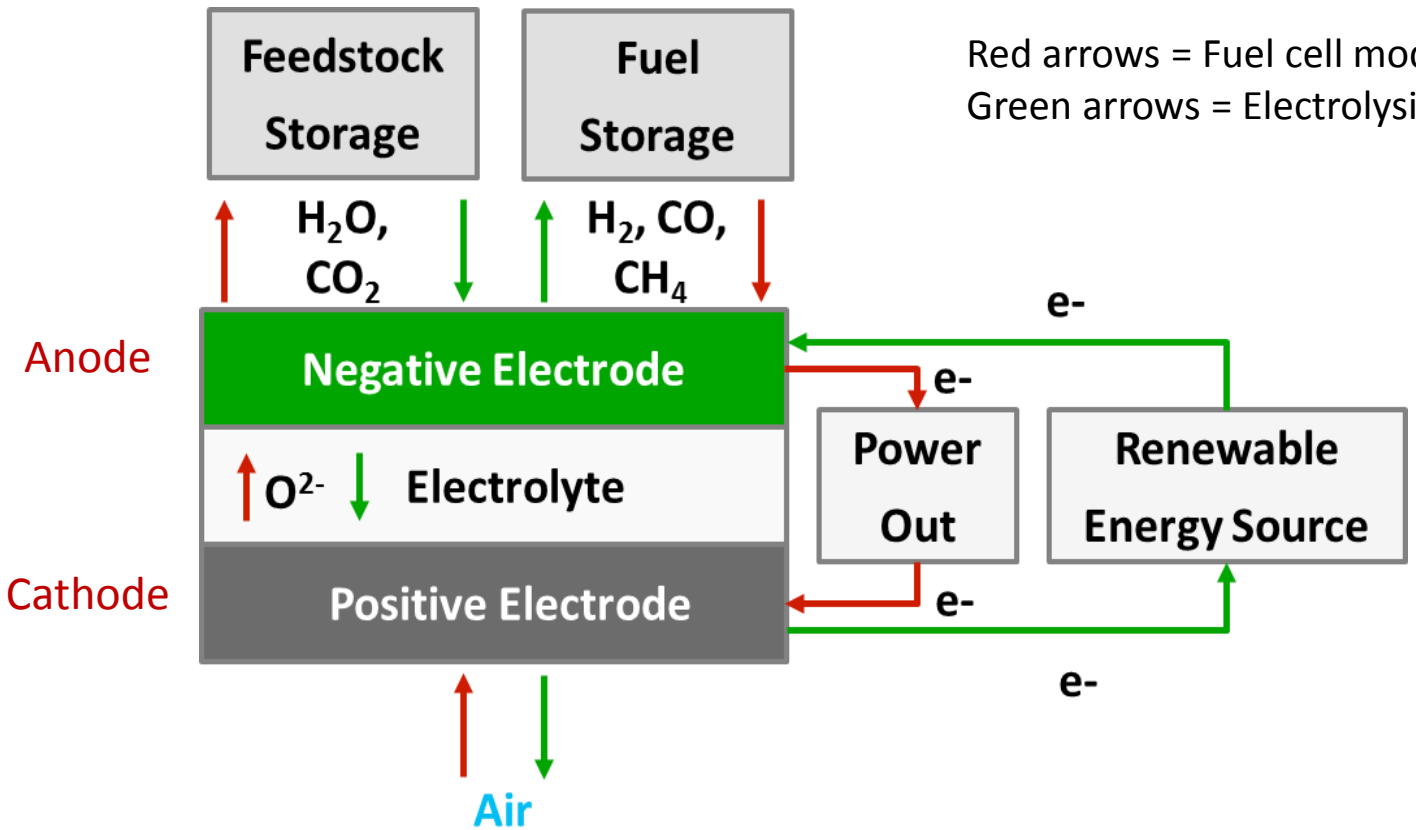
U.S. primary energy consumption by fuel, 1980-2040 (quadrillion Btu)



Modified from Annual Energy Outlook 2015, U.S. Energy Information Administration

- U.S. uses ~20% of the all energy consumed worldwide.
- In addition to energy generation, we need ways to store energy to meet demand.
- Storage is important for load leveling of intermittent renewable sources like wind and solar.

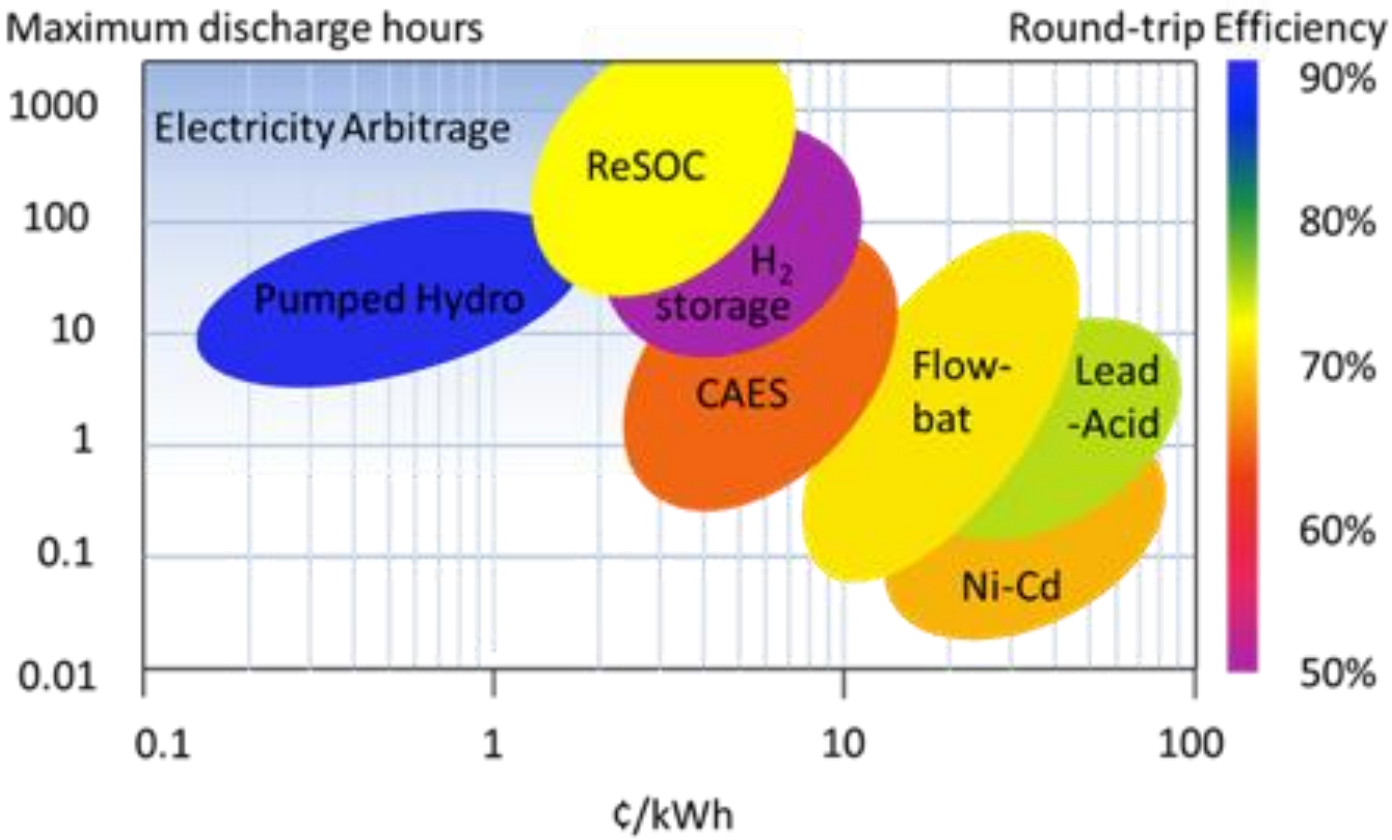
Solid Oxide Fuel Cells (SOFCs)



Red arrows = Fuel cell mode
Green arrows = Electrolysis mode

Bierschenk, et al. Energy & Environ. Sci. 4 (2011) 944

Comparison of Energy Storage Methods



Courtesy of S.A. Barnett

Intermediate Temperature SOFCs

- Current SOFCs operate at temperatures ≥ 800°C!

- Lowering SOFC operating temperature can…
  - Shorten start-up times
  - Improve long-term stability
  - Prevent sealing/interconnect issues
  - Reduce material degradation
  - Decrease thermoneutral voltage

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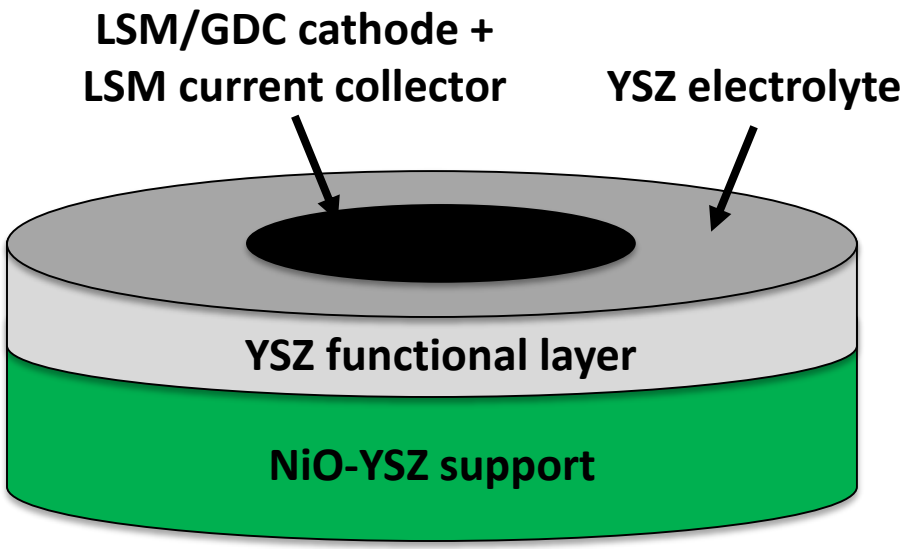
Overview

- SOFC Processing
  - Current standard
  - $La_{1-x}Sr_xGa_{0.8}Mg_{0.2}O_3$ (LSGM)
  - $Sr_{0.8}La_{0.2}TiO_3$ (SLT)
  - Nickel infiltration
- Performance & Microstructural Evaluation
  - Cell microstructure
  - Electrochemical impedance spectroscopy (EIS) characterization
  - Accelerated testing
- Coarsening Model
  - Relevant equations
  - Fitting results
- Conclusions

Standard Anode-Supported Cell Processing

- Nickel oxide and yttria stabilized zirconia (YSZ) are mixed together and co-fired into a "cermet"
  - 50:50 wt% NiO+YSZ
- YSZ porous functional layer and dense electrolyte are formed by colloidal deposition
- Lanthanum strontium manganite/gadolinium doped ceria (LSM/GDC) cathode and LSM current collector are screenprinted
- YSZ is optimized for 800°C – too resistive for use at lower temperatures

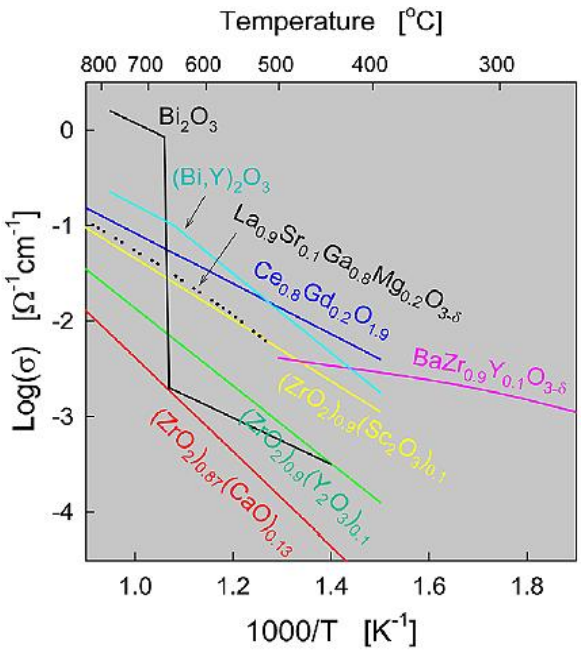


Typical power density
= 1.2-1.4 W cm^{-2}

$La_{1-x}Sr_xGa_{0.8}Mg_{0.2}O_3$ (LSGM) & $Sr_{0.8}La_{0.2}TiO_3$ (SLT)

Benefits of LSGM

- High ionic conductivity electrolyte
  - LSGM at 600°C comparable to YSZ at 800°C[1]
- Low electronic conductivity
- Chemically stable over range of T & P_{O_2}



Modified from S.M. Haile. Acta Materialia 51 (2003) 5981

Prior Work on LSGM

- *LSGM reacts with Ni-based anode during high-T co-firing*[2]
- Add Ni catalyst by infiltration after high-T firing
  - Co-fired tri-layer structure made of LSGM[3]
  - Ga is expensive – need other support material

$Sr_{0.8}La_{0.2}TiO_3$ (SLT)

- Less expensive than LSGM
- Good mechanical strength
- Thermal expansion match with LSGM
- Electronically conductive

[1]Ivers-Tiffee, et al. J. Eur. Ceram. Soc., 21 (2001) 1805
[2]Hong et al. Int. J. Hydrogen Energy, 36 (2011) 14632
[3]Zhan et al. Energy Environ. Sci., 4 (2011), 3951

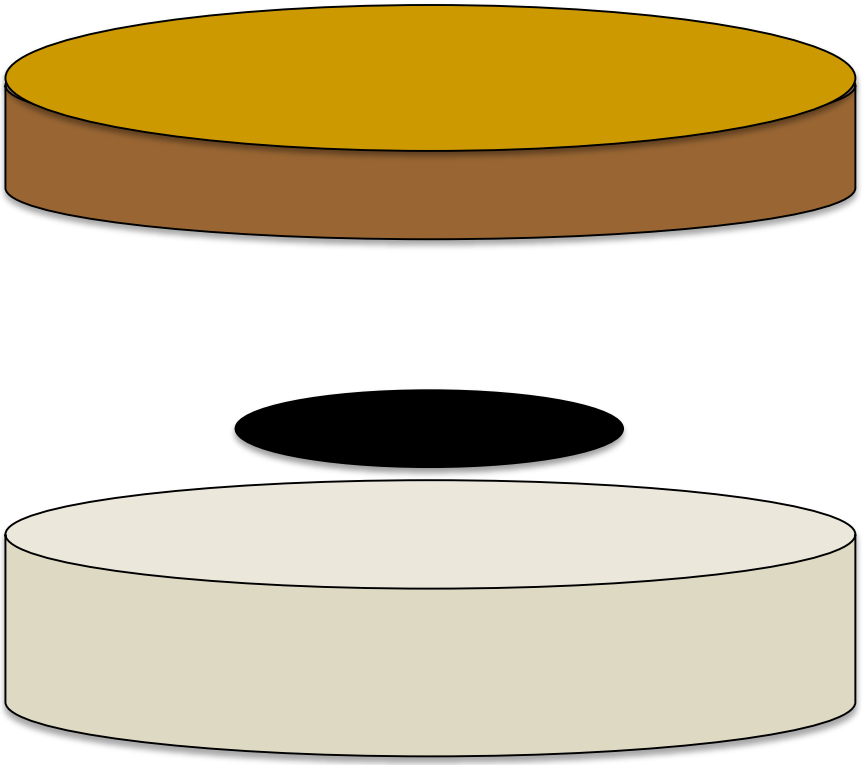
Cell Fabrication & Testing

LSCF/GDC cathode + LSCF current collector

LSGM electrolyte

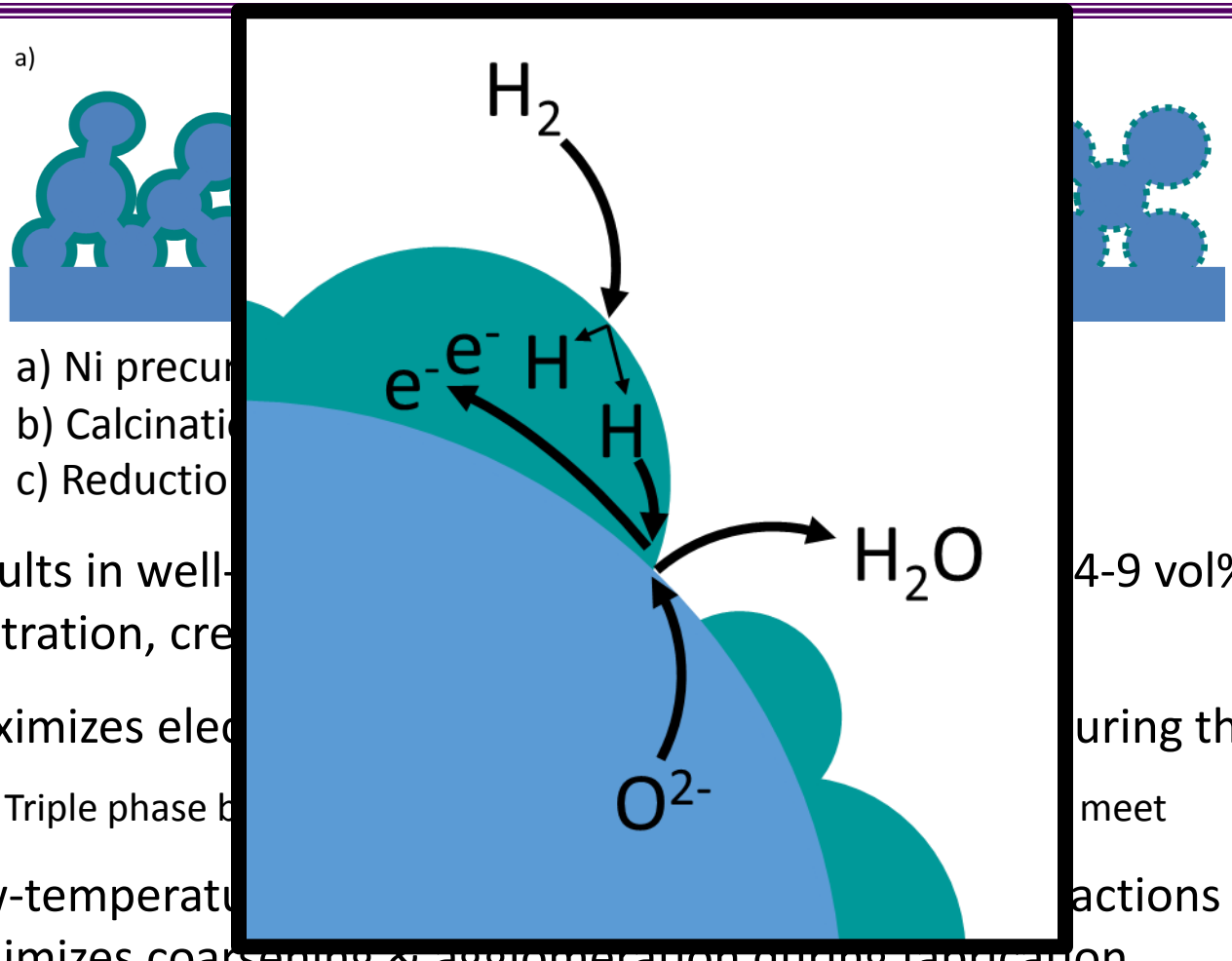
LSGM anode functional layer

SLT support



Nickel infiltration

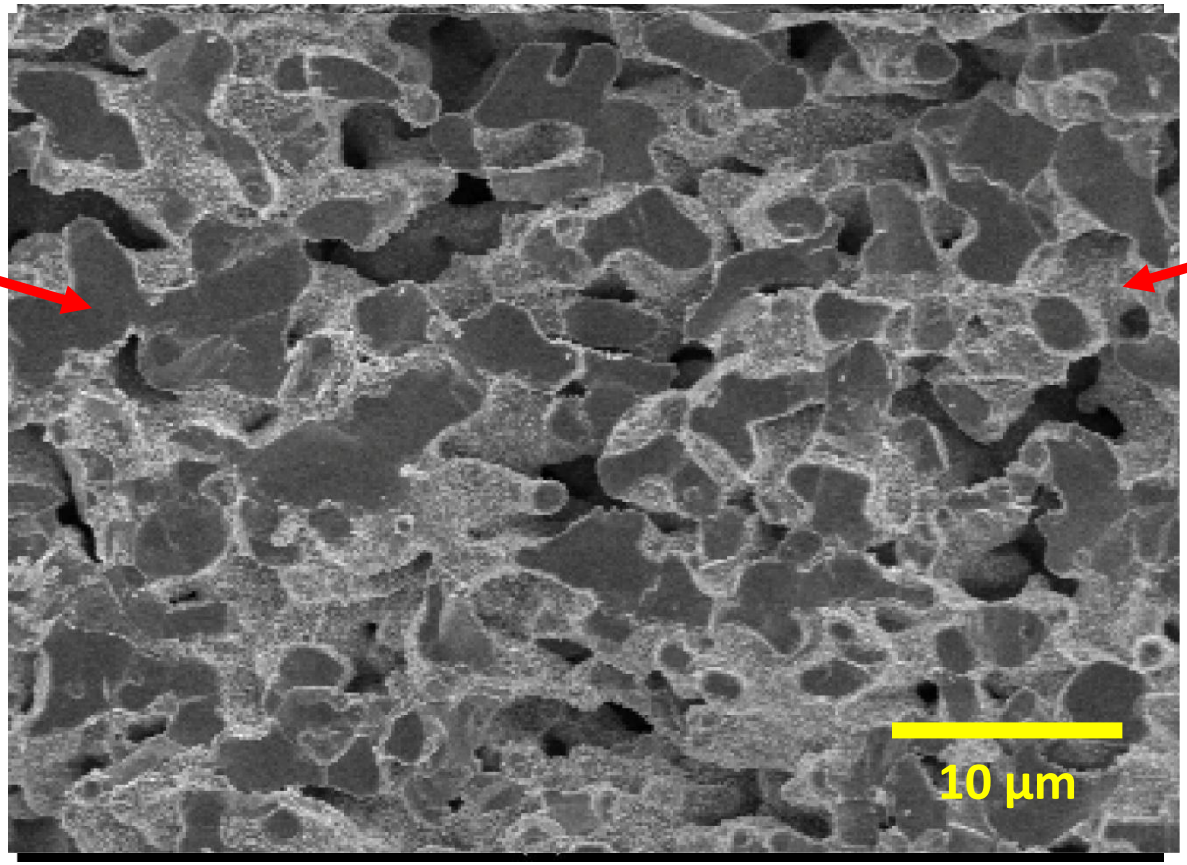
Nickel Infiltration



a) Ni precur
b) Calcinati
c) Reductio

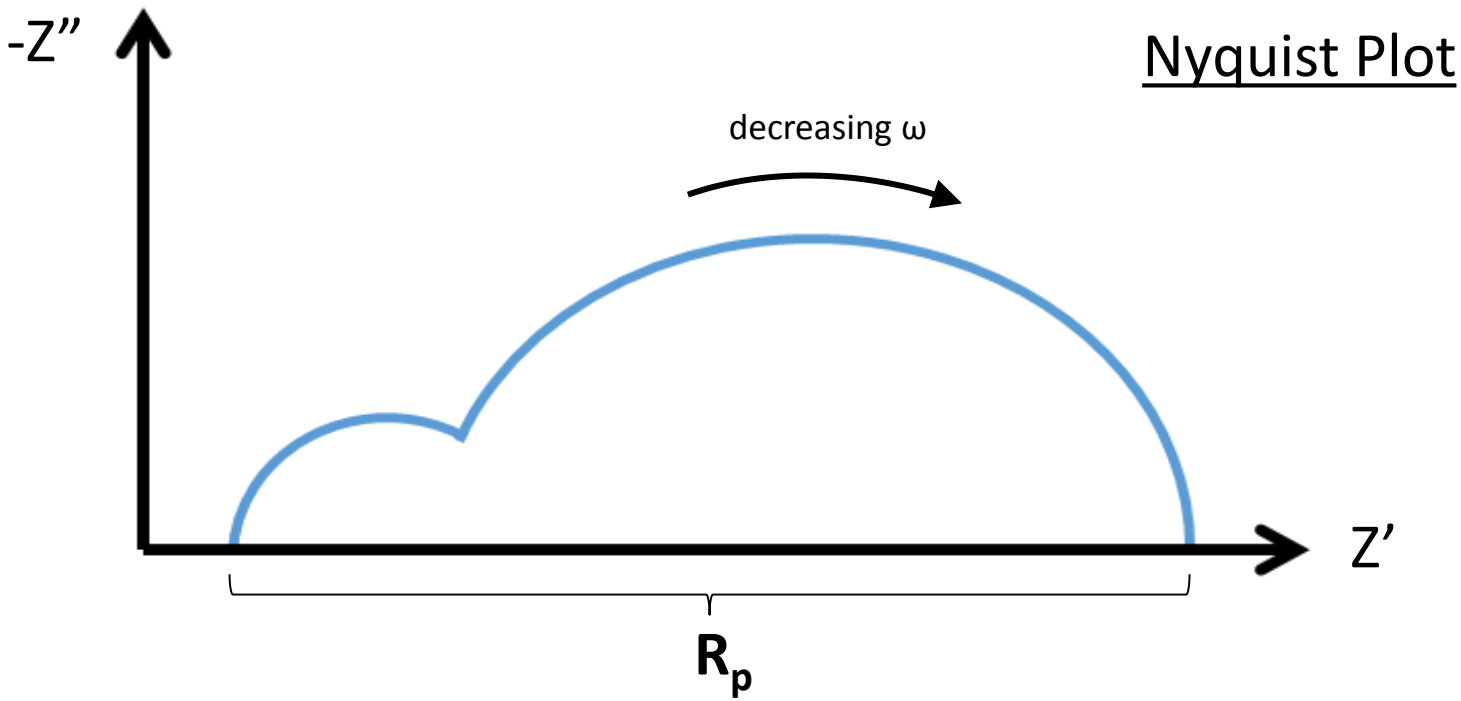
- Results in well- 4-9 vol% infiltration, cre
- Maximizes elec uring the anode
  - Triple phase b meet
- Low-temperatu actions and minimizes coarsening & agglomeration during fabrication

Cell Microstructure



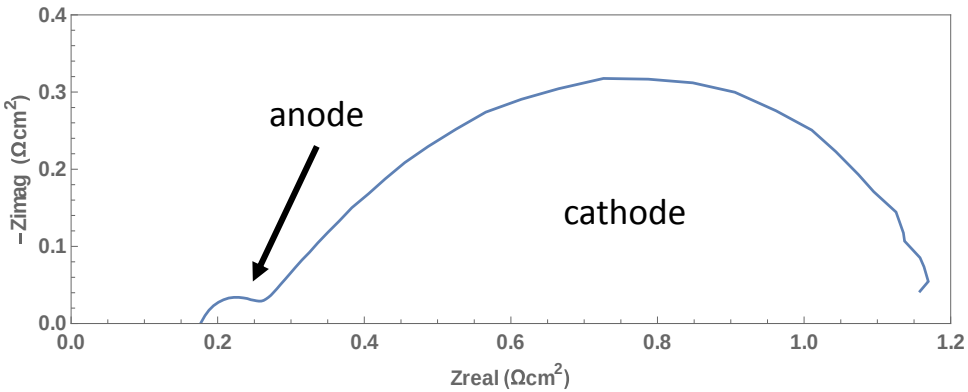
Cross sectional SEM of cell after testing

Electrochemical Impedance Spectroscopy (EIS)

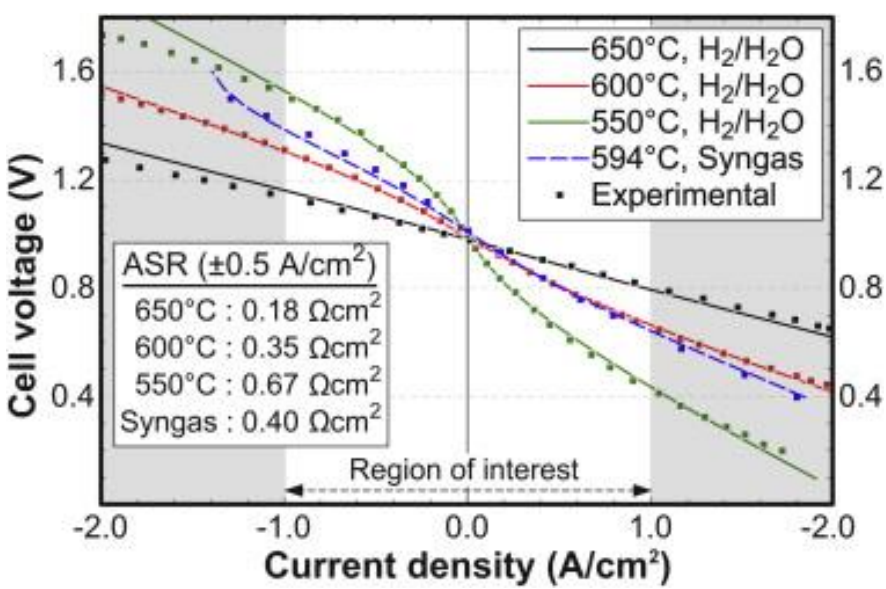


- Commonly used method for distinguishing electrochemical loss
- A small sinusoidal voltage perturbation is applied, and the resultant current response is measured
- Intercepts of Nyquist plot show R_p, polarization resistance
- Can also measure current-voltage curves to determine power density

Cell Performance



- Operated with 97% H_2/3% H_2O at anode, lab air at cathode
- Small anode arc indicates low resistance and high performance
- Large cathode arc indicates sizable cathode resistance



- Good, reversible performance
- Highest performing cells achieved power density of 1.6 W cm^{-2}
- Amongst the best cells ever reported!

Graph from Wendel et al. J. Power Sources 283 (2015) 329

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Accelerated Testing

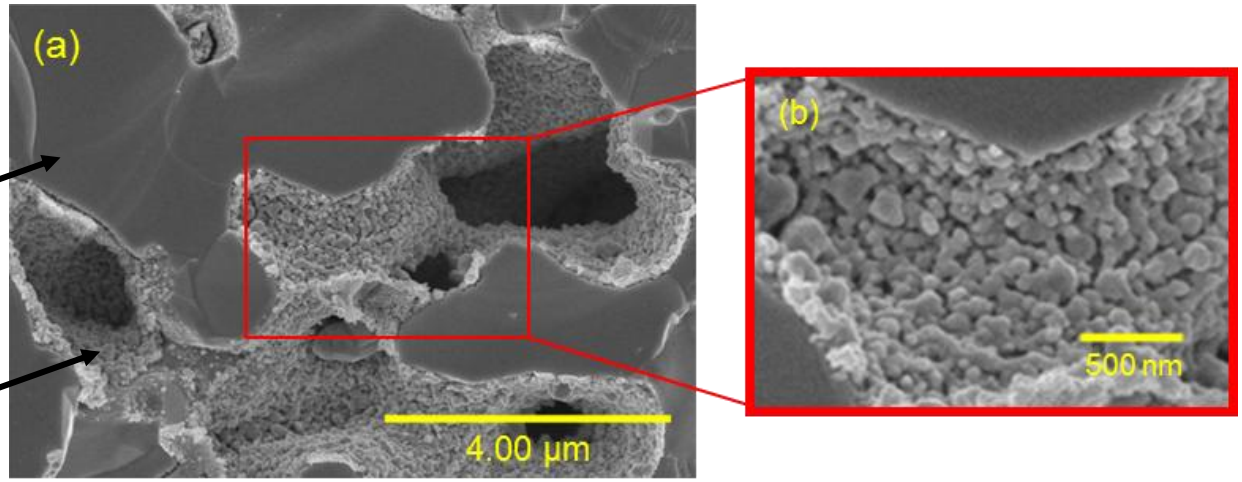
- Initial results promising and want to test long-term stability
- Department of Energy performance goal
  - Cell degradation of 0.5% or less per 1000 h over 50,000 h lifetime
- Unreasonable to run every test for 50,000 h
  - 50,000 h = 5.7 years!
- Operate cell at elevated temperature and characterize at nominal operating temperature
  - Run cell at 650°C
  - Ramp down to run impedance at 550°C (proposed operating temperature)
  - Ramp up to 650°C

Microstructural Evolution

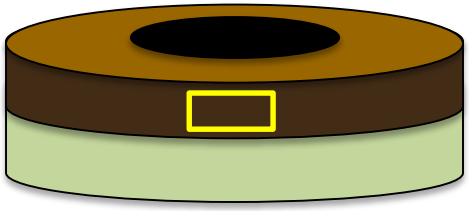
Cell operated at 650°C for 60 h

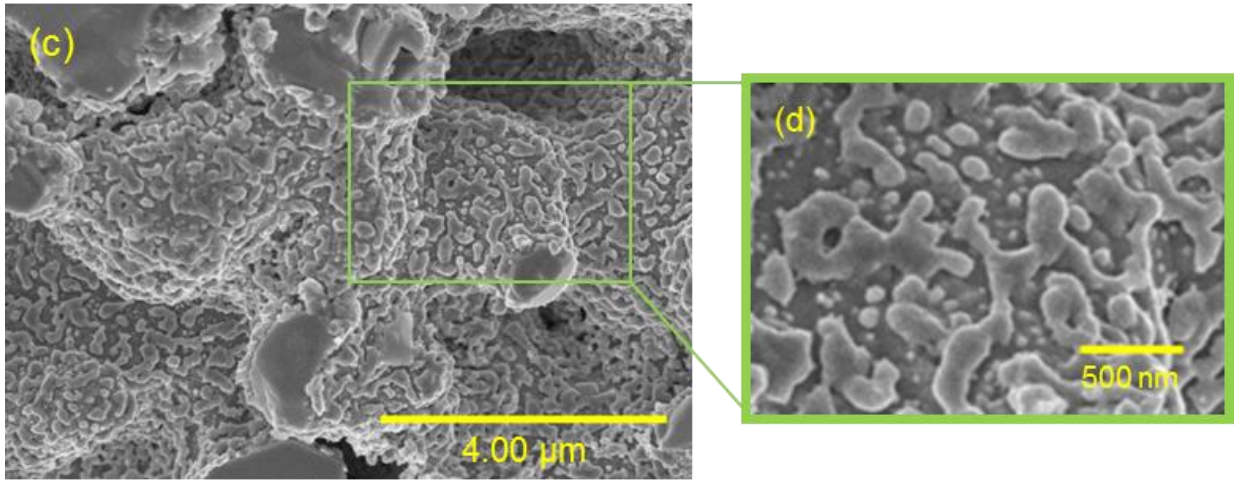
LSGM

Ni nanoparticles



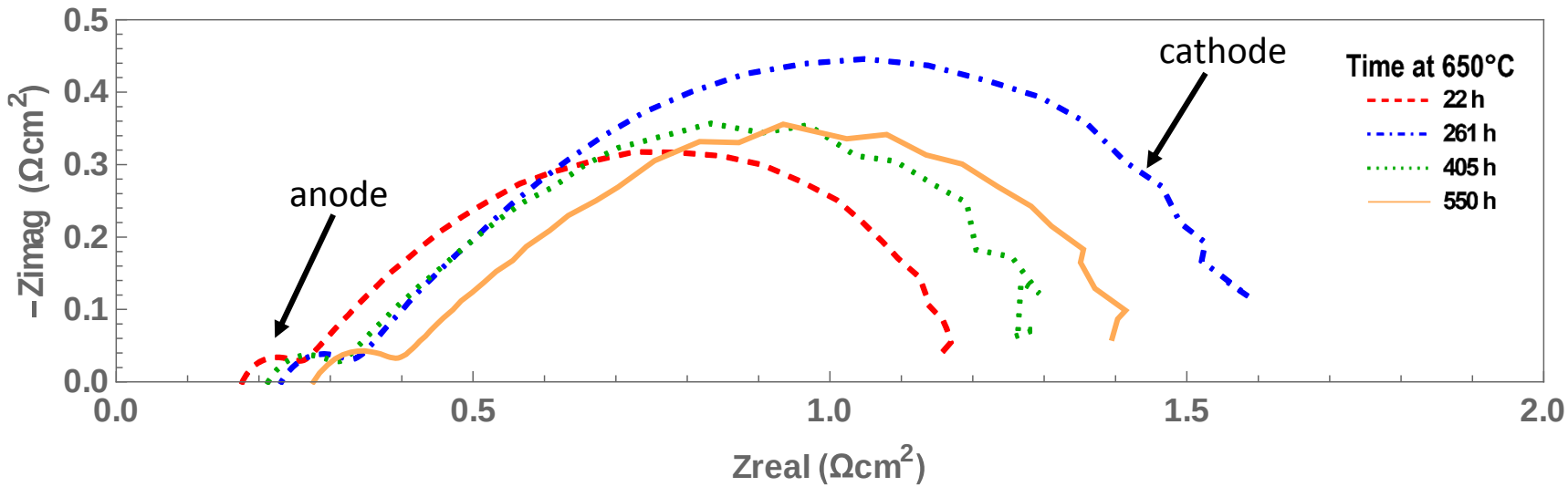
Cell operated at 650°C for 550 h





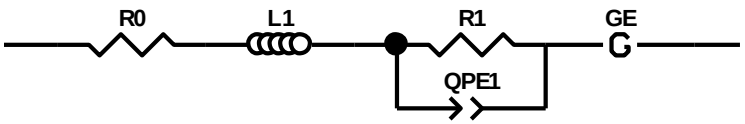
Impedance at 550°C

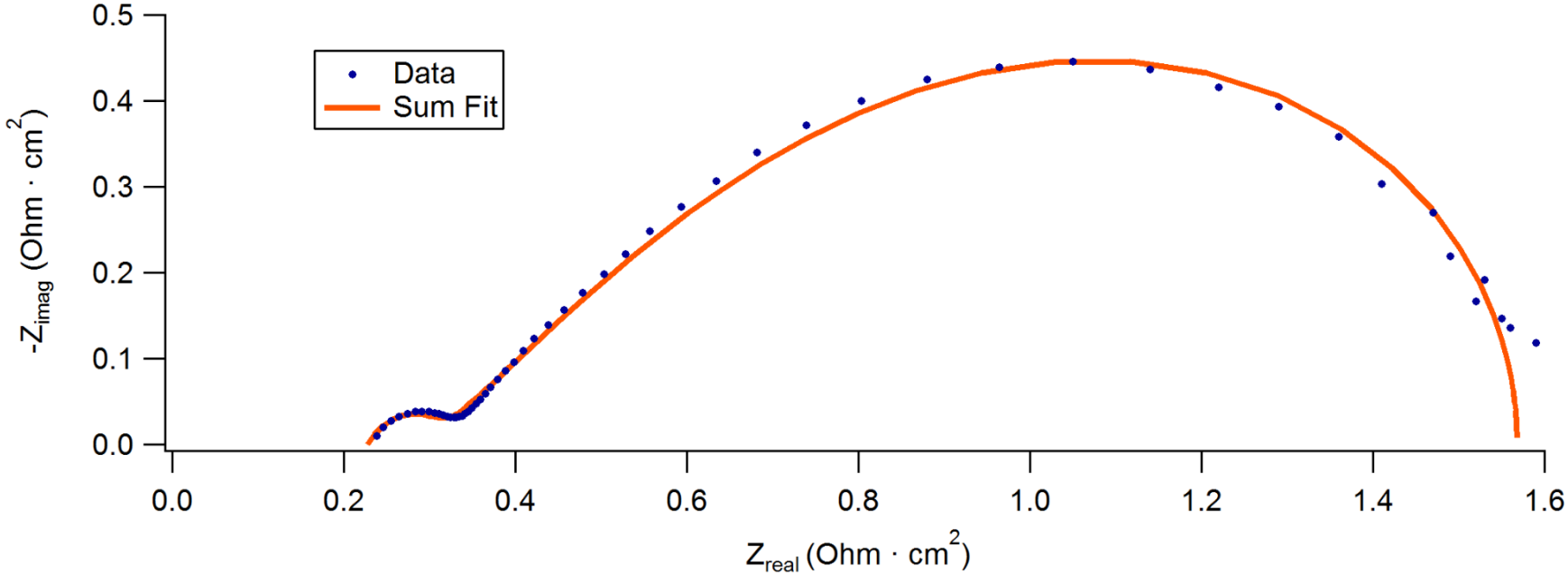
- Anode arc is very small
  - Low resistance
  - Good performance!
  - Increases with time
- Cathode arc is large
  - Higher resistance
  - Typical for LSCF
  - Increases in size, shrinks then stabilizes



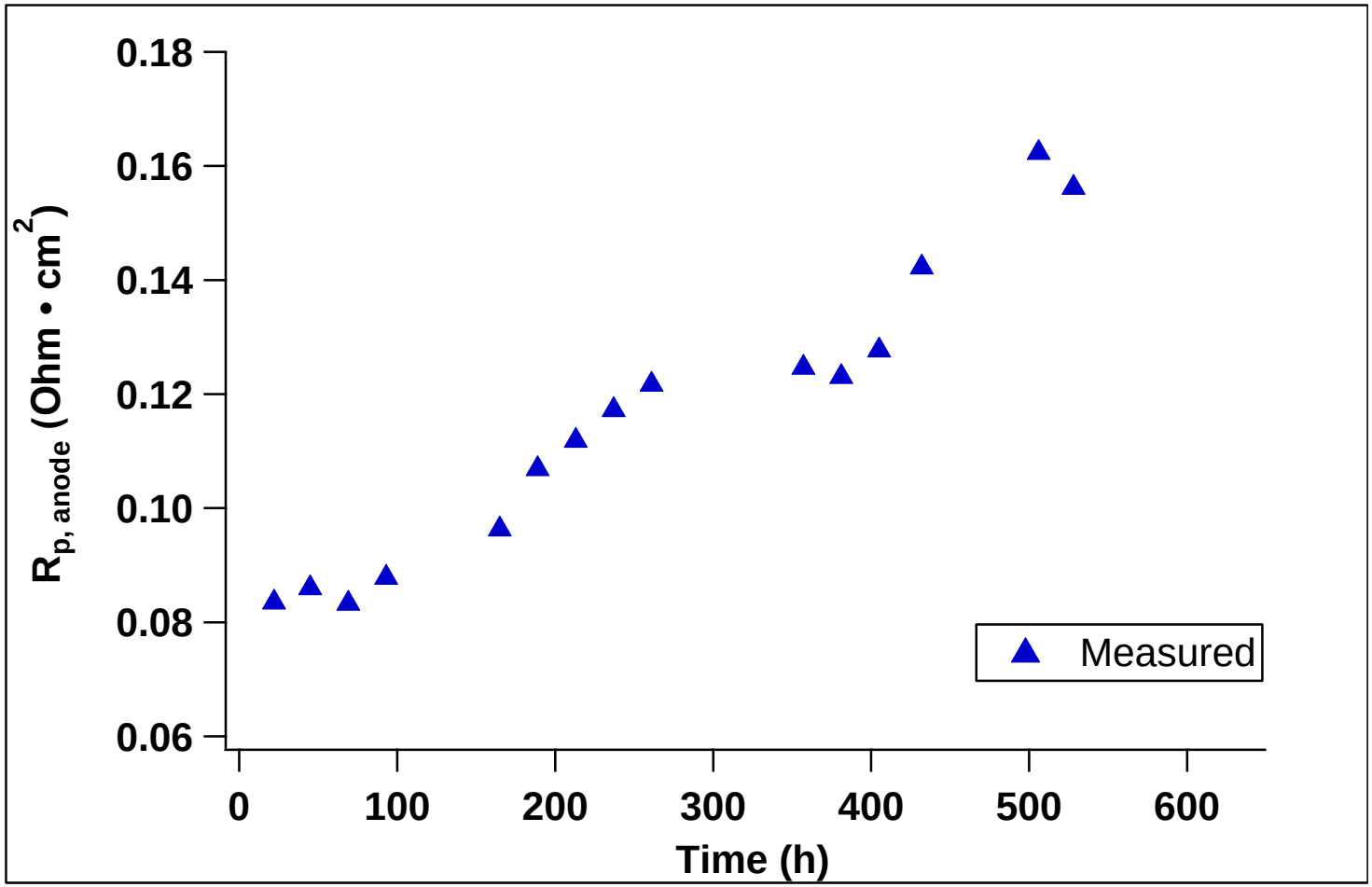
Electrode Impedance Fitting

- Zview fitting software
- Equivalent circuit modeling used to fit responses of anode and cathode





Anode Resistance Over Time



Coarsening Model

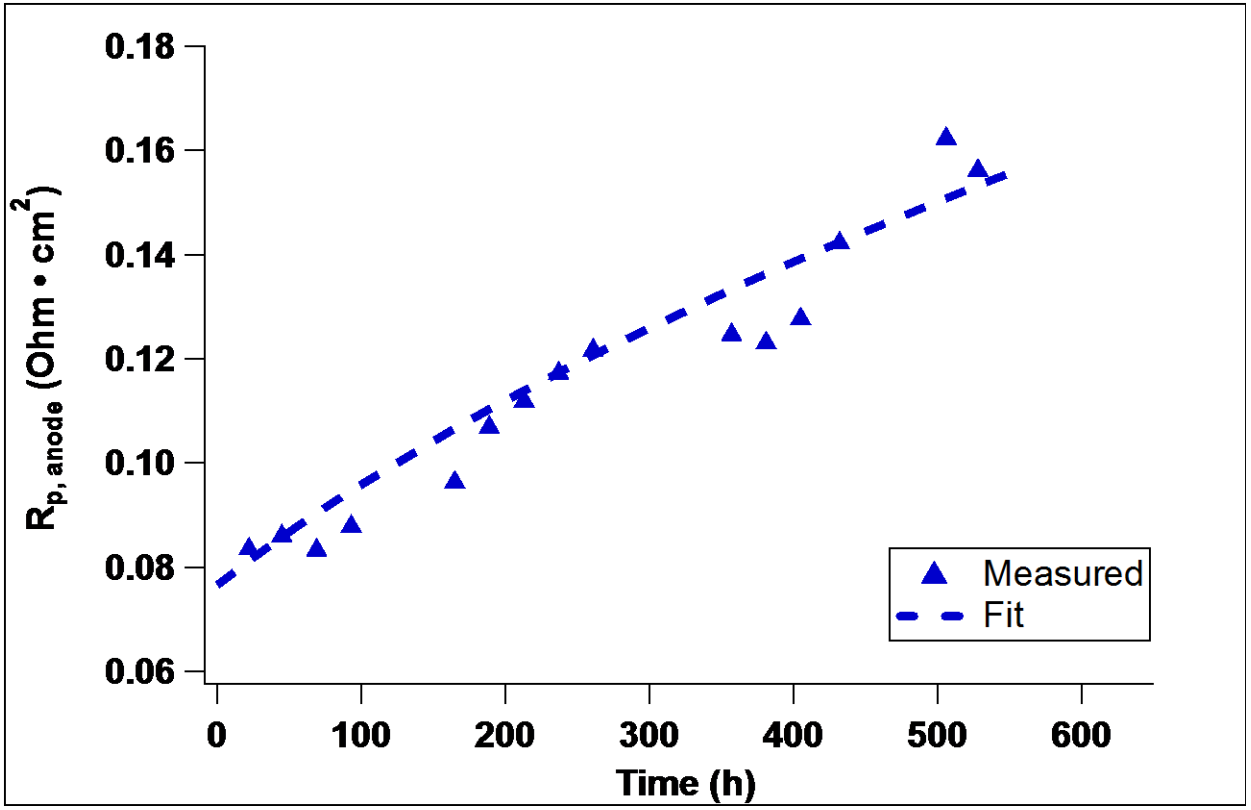
- Particle radius varies with time (seen in SEM), so we can use coarsening theory to model anode behavior.
- Results in equation for polarization resistance, R_p:

$$R_p = \left[Bte^{-E_D/kT} + R_{p,0}{}^{n/2} \right]^{2/n}$$

B = constant (geometric factors, materials properties, diffusion coefficient)
t = time
kT = Boltzmann's constant * coarsening temperature
$R_{p,0}$= initial polarization resistance
E_D= diffusion activation energy
n = coarsening process (*e.g.* n = 4 represents surface diffusion)

*Modeled after M. Shah, P. W. Voorhees and S. A. Barnett, Solid State Ionics, **187**, 64 (2011)*

Fitting Results



- Calculated values agree with experimental values
- Accelerated tests at different coarsening temperatures allow us to predict long-term stability and further refine model.

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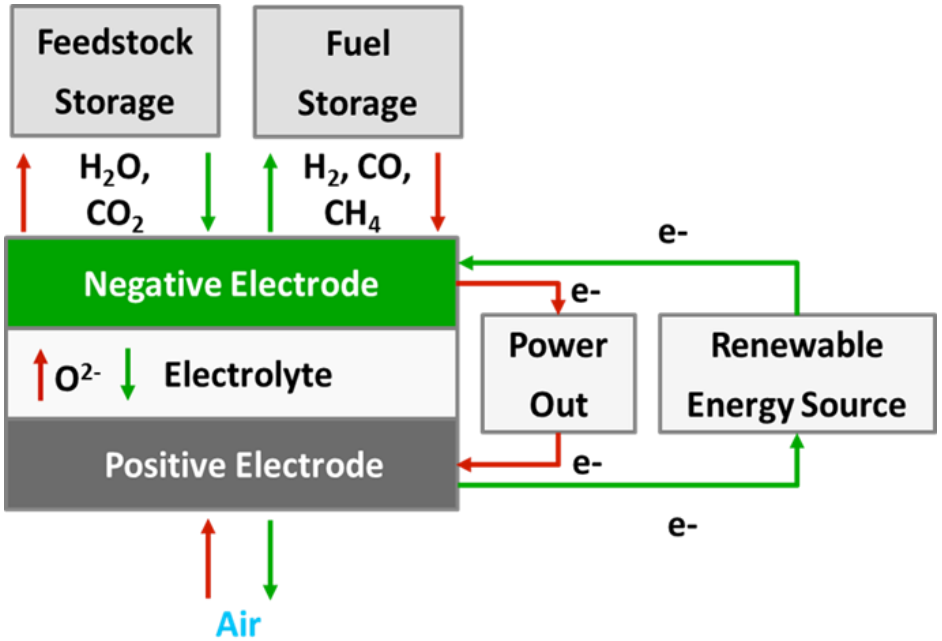
Conclusions

- SOFCs are an efficient, cost-effective option for energy storage and conversion.
- LSGM-based cells lower operating temperature, encouraging use with intermittent renewables and flexible fuels.
- Cells using a SLT support, LSGM functional layer/electrolyte, and infiltrated nanoscale Ni produce very high power density and low anode resistance.
- Using accelerated degradation testing schemes, coarsening models can predict long-term stability of SOFCs.

Future Outlook

- Develop methods to suppress coarsening
  - Co-infiltration
  - Atomic layer deposition
- New cathode materials can further decrease R_p
- Integrate reversible SOFCs with existing power infrastructure for seamless energy conversion and storage
  - Intermittent renewables (wind, solar)
  - Natural gas network



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Acknowledgements

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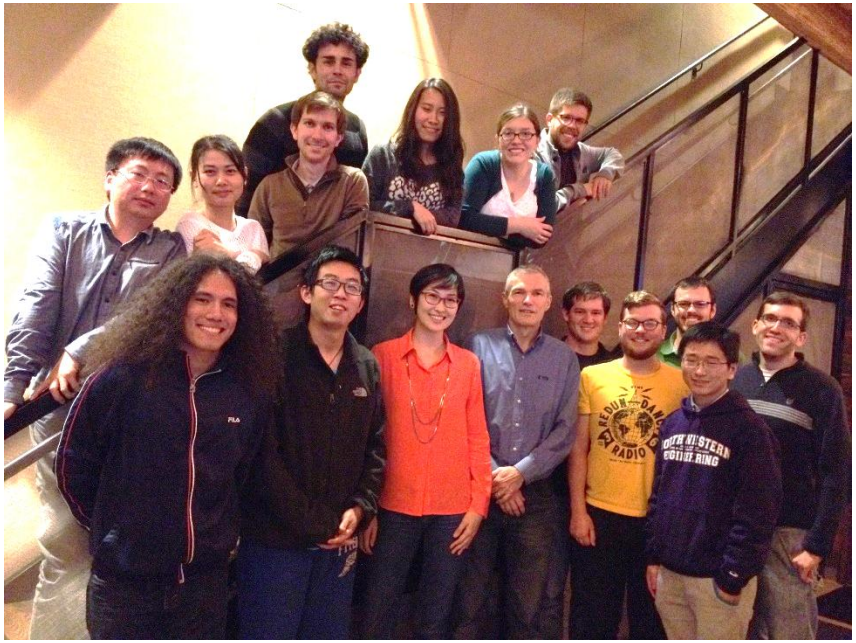
  - Department of Energy – Basic Energy Sciences
  - GCEP via Stanford University
  - DOE NNSA Stewardship Science Graduate Fellowship



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