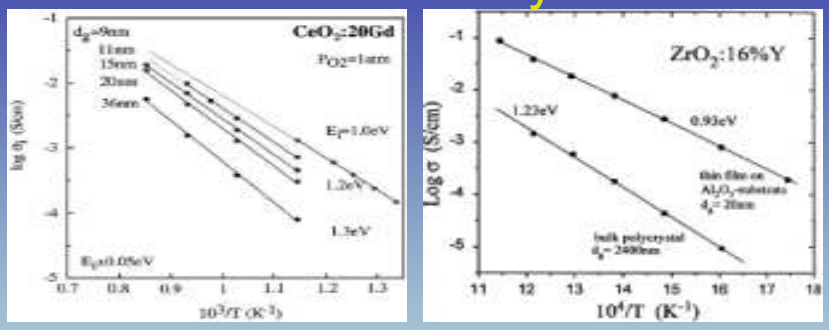
Solid Oxide Fuel Cell Nano- and Micro-Structure Effects

- Nano-phases in SOFCs
  - Motivation: low-temperature SOFCs
  - Nano-electrolyte materials
  - Nano-cathode materials
  - Nano-anode materials

Reduced Temperature SOFCs

- Nano-materials may help enable low-T devices
  - Temperatures 500°C or below possible
  - Nano-materials may be stable at low T
- Why reduced temperature?
  - Lower-cost balance of plant
    - *E.g.* heat exchangers
  - Better materials stability
  - Better, lower-cost materials
    - Seals, interconnects
  - New applications, *e.g.* portable and transportation
- How can nano-materials help?
  - Mitigating reduced reaction/transport rates as T is reduced

Enhanced Ionic Conductivity: Nano-Electrolytes

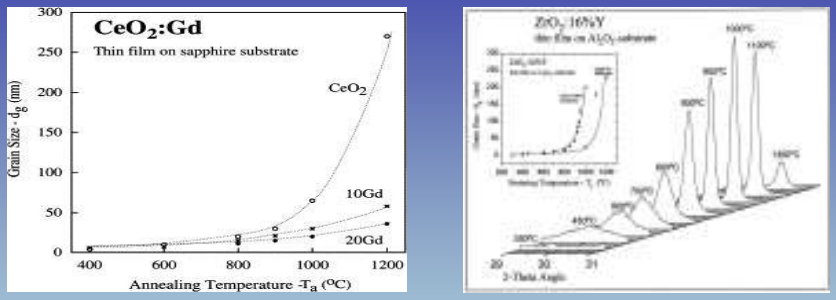


Thin films on sapphire from multiple spin coats from polymer precursor solutions containing nitrates

- Converts to nano-crystalline oxide film as low as 300C in air
- Left: Gd-doped Ceria
- Right: Y-stabilized Zirconia

Suzuki et al., Solid State Ionics, 151 (2002) 111
Kosacki et al., Solid State Ionics, 136-137 (2000) 1225

Nanocrystalline Film Stability



- Average grain size versus annealing temperature (400-nm-thick films)
  - Isothermally annealed for 4 h
  - Grain size from XRD line broadening analysis
- Possible stability at <600°C
  - Long-term (40,000h) stability needs to be established

Issues

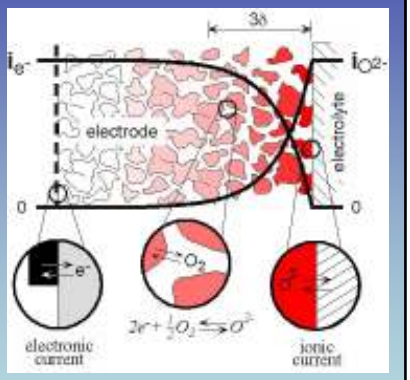
- Results not widely reproduced
- Not yet reproduced in bulk materials
- No nano-electrolyte fuel cell results to date
- Long-term stability
- Scientific issues
  - Solute segregation/concentration at grain boundaries
    - "Blocking" species, e.g., Si diluted in nano-crystalline case
  - Space-charge effects/defect gradients
  - Differential transport ⊥, ll to grain boundaries
  - Altered point defect energetics
    - Enhanced defect mobilities near GBs

Mixed Conductor Electrodes: Nano-Effects

- Model - mixed-conducting cathodes
  - Two processes in series
    - Oxygen surface exchange
    - Oxygen bulk diffusion

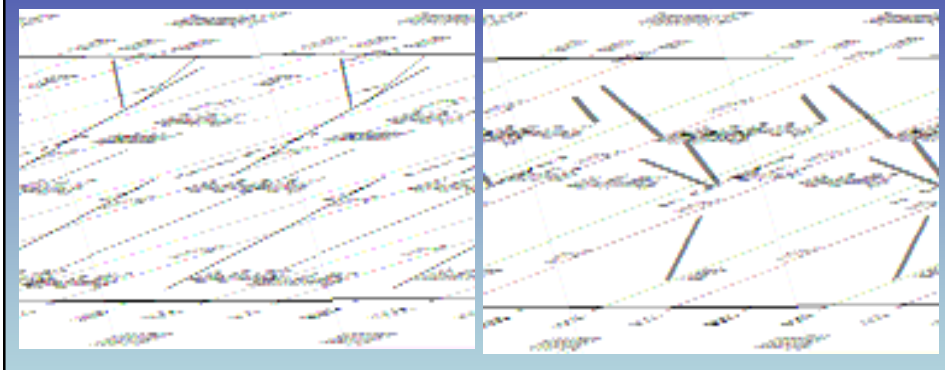
$$R_{chem} = \frac{RT}{2F^2}\sqrt{\frac{\tau}{(1-\varepsilon)aC_0^2D^*k}}$$

  - τ = solid phase tortuosity
  - ε = fractional porosity
  - a = surface area/volume
  - C_0 = oxygen concentration
  - D^* = oxygen bulk diffusion coefficient
  - k = surface exchange coefficient
- Structure: large a, reasonable τ and ε
- Cathode properties: large D^*, k, along with good electronic conductivity



Adler, Lane, Steele, J Electrochem Soc, 143 3554 (1996).

Electrode Transport Data

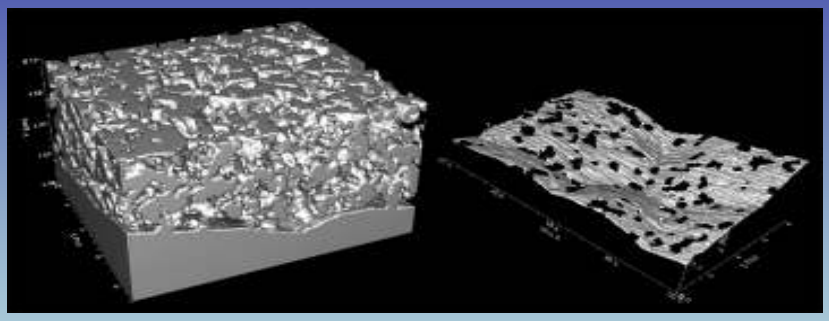


•Co-based cathodes have highest *k* values, but *D** not large enough below 700°C

•Ceria has much higher *D**

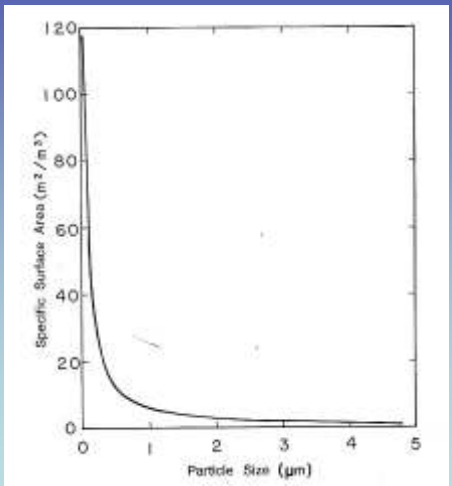
Doshi et al., J. Electrochem. Soc. 146 (1999) 1273.

Example: $(La,Sr)CoO_3$ Cathode



- Feature sizes in the sub-micron range (1100°C)
  - a = 2.6 μm^{-1}, τ = 1.4, ε = 0.46
- Calculation yields ASR ~ 1 Ω cm^2 at 750°C
  - Agrees with measured ASR's
- Could be improved by appropriate nanostructure
  - a inversely proportional to feature size
    - Needs to be well into nano range, *I.e.,* ~10 nm

Surface Area Versus Particle Size



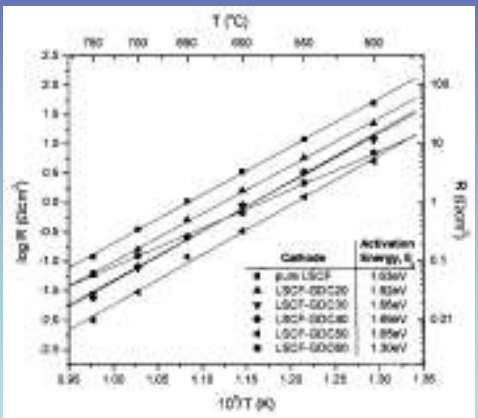
- Surface area per volume *a*
  - Inversely proportional to average particle radius $\bar{r}_{V/A}$
- $\bar{a}_L \sim 3/\rho \ \bar{r}_{V/A}$
  - ρ = oxide density
- Very large increases are possible!

Composite "Nano"-Cathodes: LSCF-GDC

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

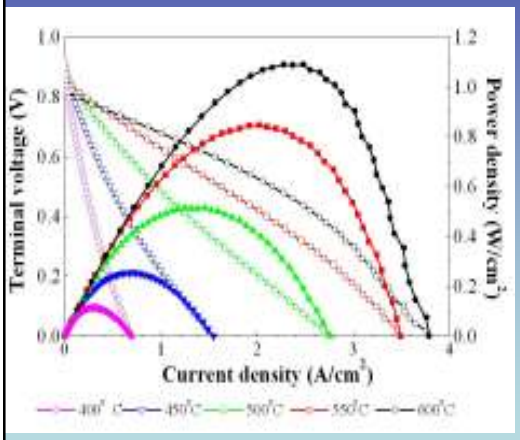
- LSCF = $(La,Sr)(Co,Fe)O_3$
- Various cross-sectional views of cathode on YSZ electrolyte
- Shows porosity and particle sizes ~200nm
  - Yields high surface-to-volume ratio (*a* in ALS model)
  - Useful to further decrease size

Polarization Resistance: LSCF versus LSCF-GDC



- Low polarization resistance for LSCF-GDC:
  - 0.3 Ωcm^2 at 600°C
  - 10 times better than LSCF
- Combines desirable properties of two phases:
  - Mixed conductivity of LSCF
  - High oxygen surface exchange coefficient of LSCF
  - High oxygen ion conductivity of GDC
- Feature sizes ~ 200 nm
- *Murray and Barnett, Solid State Ionics, **143**, 265 (2001)*

Low-Temperature SOFC

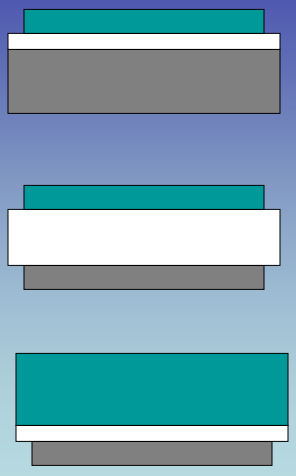


- Ni-GDC/GDC/LSCF-GDC
- Power density:
  - >1W/cm^2 at 600°C
  - 0.5W/cm^2 at 500°C
- Amongst best low T SOFCs
- **Employs low-T materials set, but not fully nano!**
- Further reduction to 400°C possible
  - Will require nano-structured materials

Nano-Structured SOFC Anodes

- Goal: improve upon Ni-YSZ anodes
  - Reduced carbon deposition with hydrocarbon fuels
  - Improved reduction-oxidation stability
  - Reduced poisoning from sulfur-containing species
- Alternative materials:
  - Electronically- or mixed-conducting oxides
    - E.g. $SrTiO_3$, $LaCrO_3$, $Sr(Mg,Mo)O_3$
  - Combined oxide-metal
    - E.g., Cu-CeO_2
- However, these materials lack catalyst activity
  - Anode performance worse than Ni-YSZ
  - Possible solution: add nano-phase catalysts

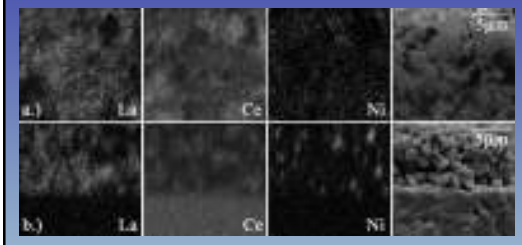
Processing Challenge For Nano-Phase Electrodes



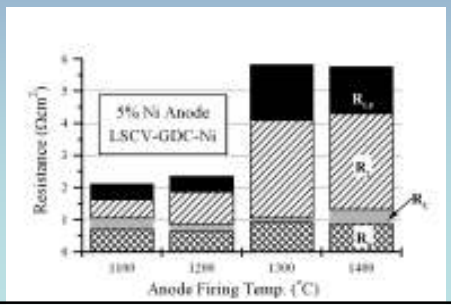
- Cell operation: 500-1000°C
  - Stability a potential issue
- High firing temperatures will coarsen nano-particles
  - Cathode- and electrolyte-supported cells
    - Anode firing temperature:
    - 1000 - 1300°C
  - Anode-supported cells
    - Anode fired with electrolyte at high temperature
    - ~1400°C
- Solution: introduce nano-phases after high-temperature firing steps
  - Wet impregnation (calcination at 600 - 1000°C)
  - Catalyst precipitation

Co-Mixed Anode Example

1100°C



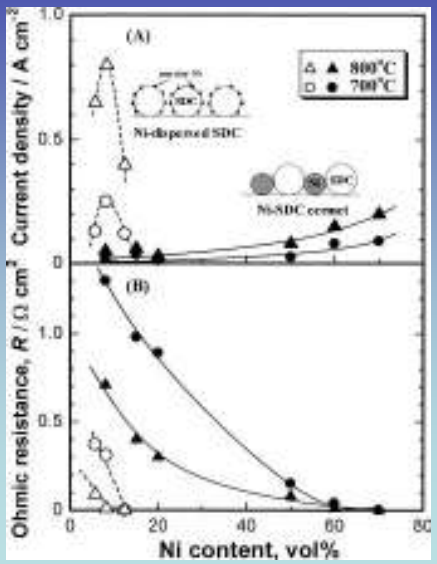
1400°C



- $(La,Sr)(Cr,V)O_3$ - GDC with nano-NiO
  - Co-fired at high T
- TOP: SEM-EDS
  - 1100°C: Ni particles too small to resolve (< 1m)
  - 1400°C: Coarse Ni particles
- BOTTOM: EIS data versus firing T
  - Increased anode polarization resistance at higher T
  - Cathode and anode components unchanged

Madsen et al., J Power Sources, in press

Ni-Impregnated SDC Anodes

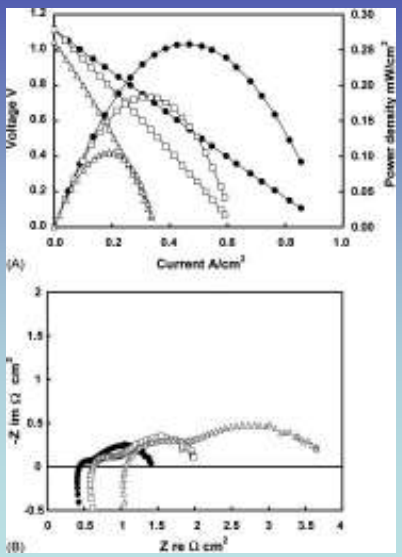


- Improved electrochemical performance (2-3 times higher current density)
- Lesser amount of metals needed than co-mixed anodes
- SEM: feature sizes sub-micron
- Ni activity decreased with time
  - Probably due to sintering

*Uchida, Suzuki, Watanabe, Electrochem Solid-State Lett **6**, A174 (2003)*

- Similar results for Pt or Ru impregnation into SDC

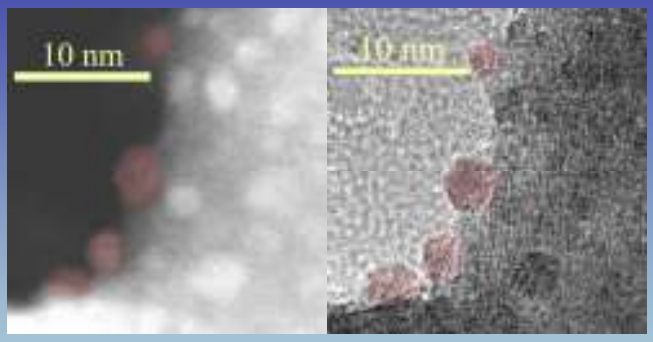
Performance Degradation During Cell Operation



- YSZ impregnated with 16 vol% Cu and 12 vol% CeO_2
- Current-voltage curves and EIS results (latter at 300 mA/cm^2)
  - Measured at 700C
  - Degraded performance with increasing anode firing temperature
    - 700°C for 2 h
    - 800°C for 3 h
    - 900°C for 2 h

- *Jung, J Power Sources **154**, 42 (2006)*

Catalyst Precipitation: Ru Nano-Clusters

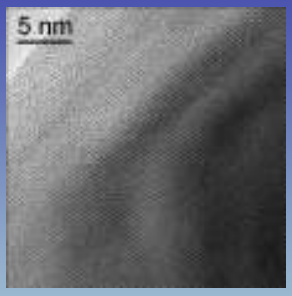


STEM HREM

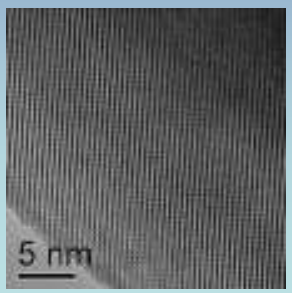
- Images of $La_{0.8}Sr_{0.2}Cr_{0.82}Ru_{0.18}O_3$ powder after reduction in H_2
  - 45 h at 800°C
- Nano-clusters are ≤ 5 nm diameter
- Cluster lattice fringe spacings matched (110) and (002) hexagonal Ru

Madsen et al., J Power Sources 166, 64 (2007)

Control Experiments

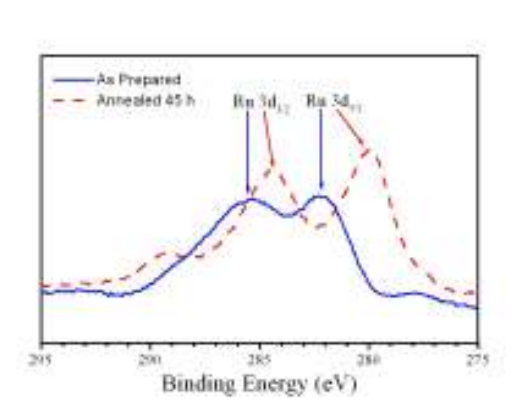


- Unreduced $La_{0.8}Sr_{0.2}Cr_{0.82}Ru_{0.18}O_{3-\delta}$
  - No nano-clusters



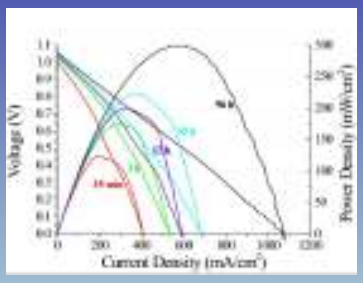
- $La_{0.8}Sr_{0.2}CrO_{3-\delta}$: 45 h at 800C in H_2
  - No nano-clusters

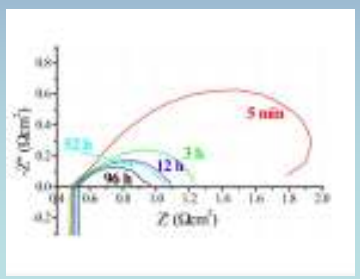
X-Ray Photoelectron Spectroscopy



- Comparison:
  - $La_{0.8}Sr_{0.2}Cr_{0.82}Ru_{0.18}O_3$ as-calcined in air
  - After 45 h in H_2 at 800°C
- Reduction shifts peaks to lower binding energy
  - Consistent with metallic Ru formation on chromite surface

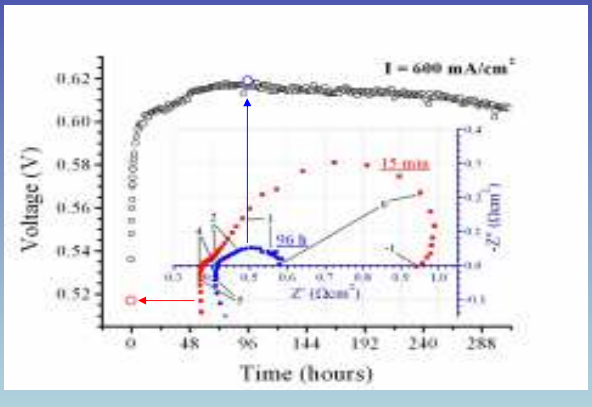
SOFC Performance: Effect of Anode Ru Doping





- Large increase in power density with Ru-doped anode (750°C)
  - From 0.1 to 0.3 W/cm²
  - From 1.4 to 0.4 Ω cm²
- Only a minor increase with non-Ru-doped anode
  - Much lower power density
- Best anode to date:
  - 0.5 W/cm² at 800°C

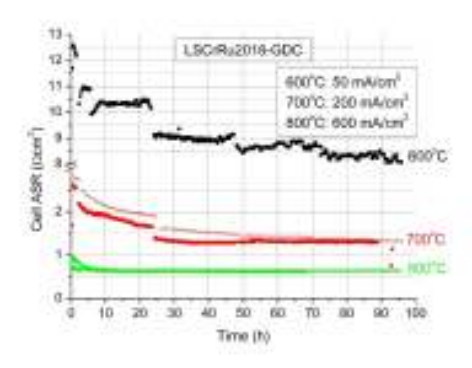
Time Dependence - 800°C



- EIS data:
- LSGM Ohmic loss
  - 0.4 Ω cm²
- Rapid decrease in electrode arcs with time
- Minimum polarization resistance
  - < 0.2 Ω cm²
- Cells limited mainly by LSGM electrolyte

- 0-12 h: Rapid improvement
- 12 to 90 h: Continued improvement
- 90+ h: Slight (2%) degradation
  - Both ohmic and polarization resistances increase

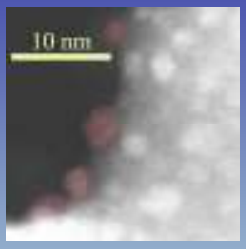
Effect of Precipitation Temperature

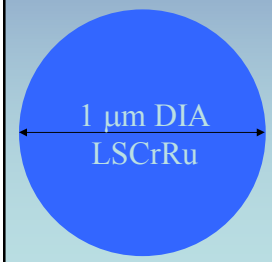


- Kinetics of Ru-induced performance increase
- Area-specific resistance decreases with time
  - Slower resistance decrease at lower temperature
  - Consistent with slower Ru out-diffusion from chromite particles
  - Breaks in curves - current stopped for I-V and EIS measurements

WK1

Nano-Cluster Kinetics





- Estimate net amount of Ru on surface (45h)
  - Hemispherical Ru ~5 nm diameter, ~4x10^{12} cm^{-2}
  - Corresponds to ~15% of Ru in ~ 1 μm diam LSCrRu (y_{Ru} = 0.18) particle
    - Ru comes from surface layer with thickness L ~ 25 nm

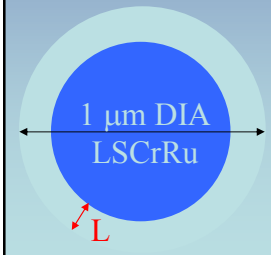
Slide 23

WK1 Data showing rate of increase of performance versus temperature

See slides 18 and 19 for more options

Worawarit Kobsiriphat, 1/18/2007

Nano-Cluster Kinetics



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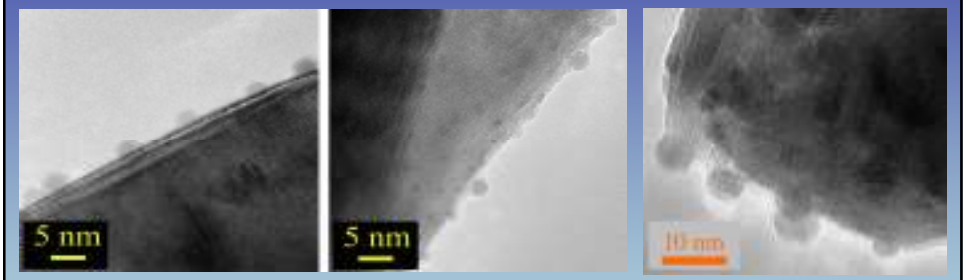
  - Hemispherical Ru ~5 nm diameter, ~4×10^{12} cm^{-2}
  - Corresponds to ~15% of Ru in ~ 1 μm diam LSCrRu (y_{Ru} = 0.18) particle
    - Ru from surface layer with thickness L ~ 25 nm
- Esimated diffusion coefficient:
  - $D \sim L^2/t \sim 10^{-21}$ m^2/s at 800ºC
  - Consistent with $LaCrO_3$ cation diffusion coefficients reported by Sakai, SOFC V, 2001
- Ru out-diffusion may also be limited by increasing B-site deficiency in $La_{0.8}Sr_{0.2}Cr_{0.82}Ru_{0.18}O_3$

Ru Cluster Size Versus Time

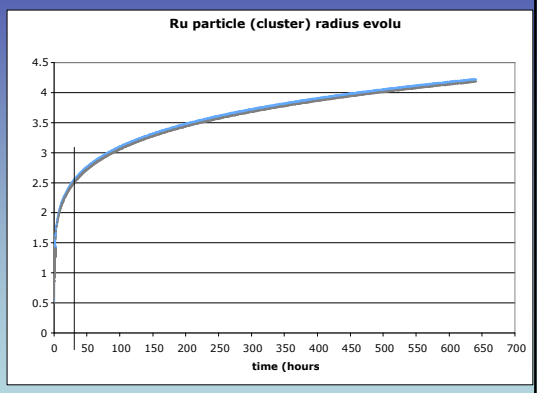
1 h | 311 h | 1000 h



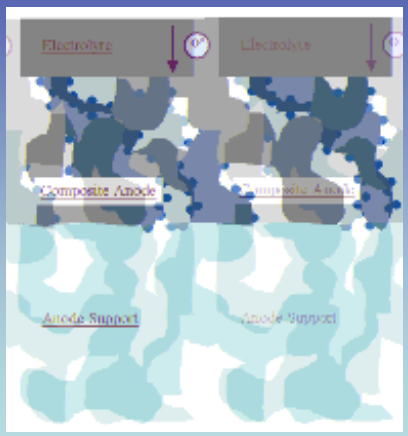
- $La_{0.8}Sr_{0.2}Cr_{0.82}Ru_{0.18}O_3$ powder reduced at 800ºC in H_2
- Measurable coarsening after 1000 h
- May be stable at lower T, *e.g.* 600 - 700C

Ru Nano-Particle Growth

- Calculated Ru cluster size versus time
  - Assuming simple out-diffusion model
  - No coarsening or cluster growth
  - Diffusion distance estimated as $\sqrt{Dt}$
- Calibrated using experimental data at 45 hours
  - Particle size of ~ 2.5 nm at 45 h
  - Cluster growth due to continued Ru accumulation
- Phase field calculation under way to consider both coarsening and growth



Comparison with Infiltration



- No additional processing steps required
- Precipitation yields uniformly small (< 5nm) nano-clusters
  - May be smaller than infiltrated materials
- Nano-catalyst selectively added to active layer
  - Infiltration adds material to active layer and current collector / support layer
    - May limit use of expensive materials

Summary and Conclusions

- Reduced temperature operation can widen range of SOFC applications
- Nano-electrolytes have potential for new lower-temperature (<500C) SOFCs
- Nano-cathodes will be critical for achieving good performance at 500C and below
  - Combine nano-structure and composites of optimal materials
- Nano-anodes may provide increased functionality for working with real fuels
  - Hydrocarbons with contaminants