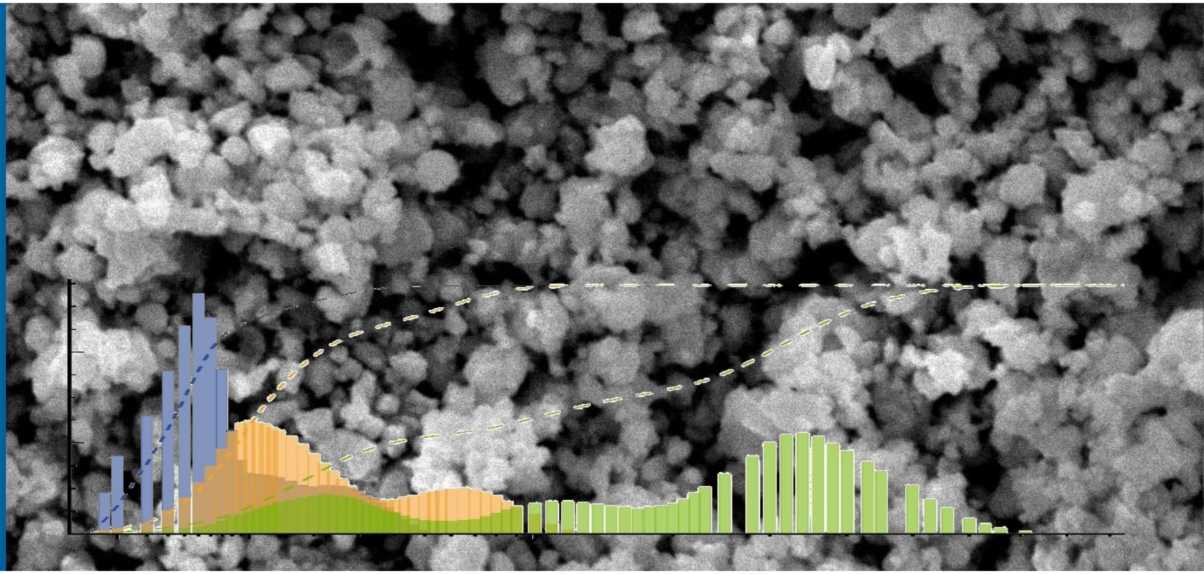
22ND ANNUAL SOLID OXIDE FUEL CELL PROJECT REVIEW MEETING
November 16-18, 2021

Reliable Evaluation of SOFC Cathodes: The Effect of Thickness and Contact Spacing



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Scope and Research Objectives

High cell fabrication yields and performance reliability

Establish materials for reliable SOFC performance

Identify key factors and tolerances of feedstock powders by mapping to cell electrochemical reliability

Validate feedstock materials

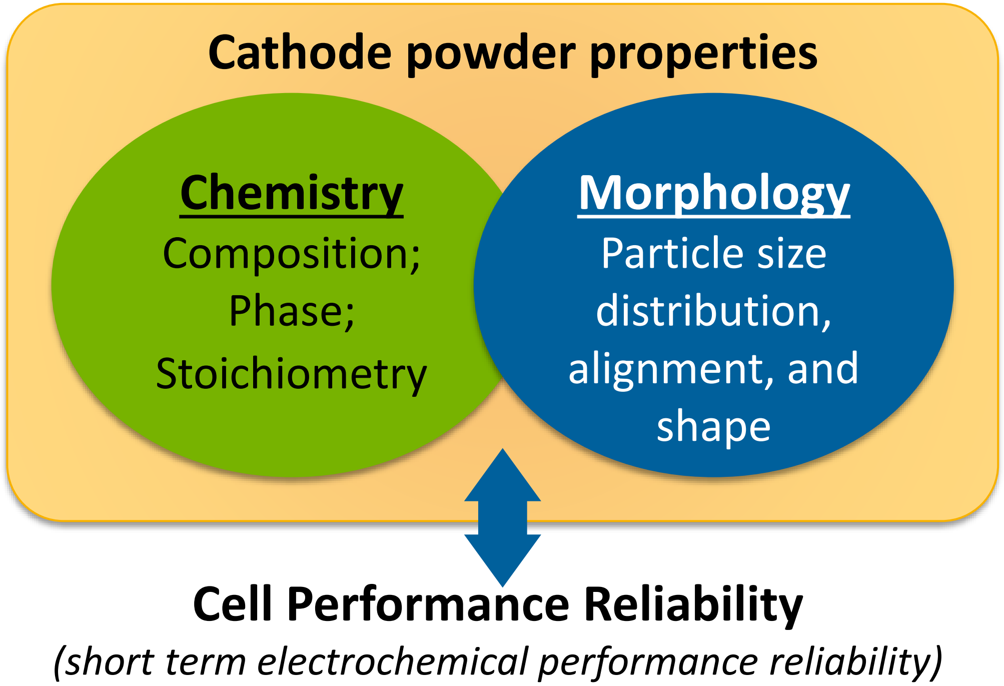
Expand rapid and simple diagnostic approaches to predict the performance of feed stock powders as they are received

Targeted cathode synthesis

Synthesize cathode powders with tailored morphology and chemistry with tenable commercial process

Make Button Cells Valuable

Refine lab-scale symmetric half-cell testing protocol with baseline performance for statistical comparison of cathode materials

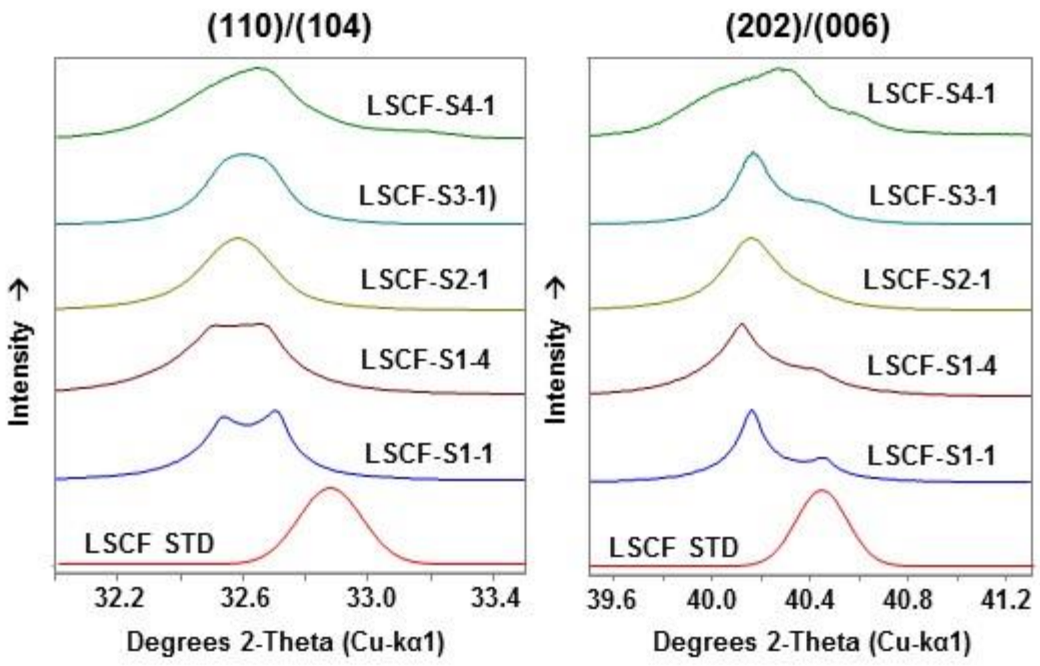


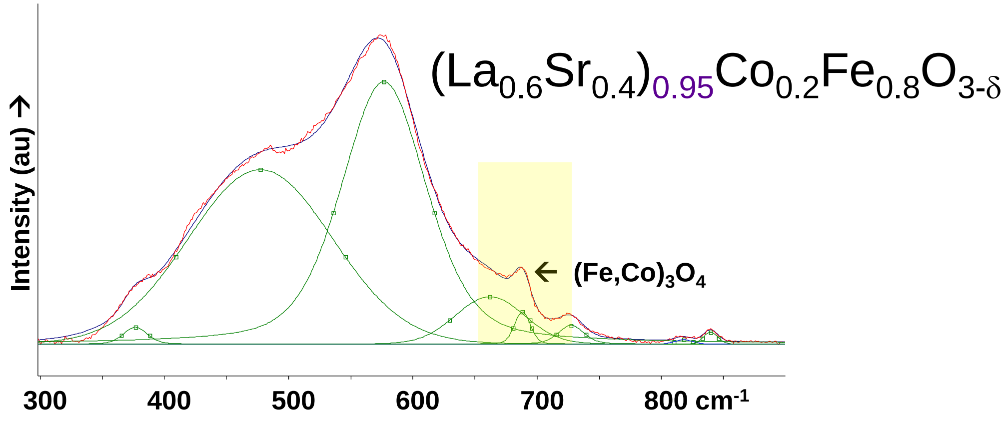
REVIEW:

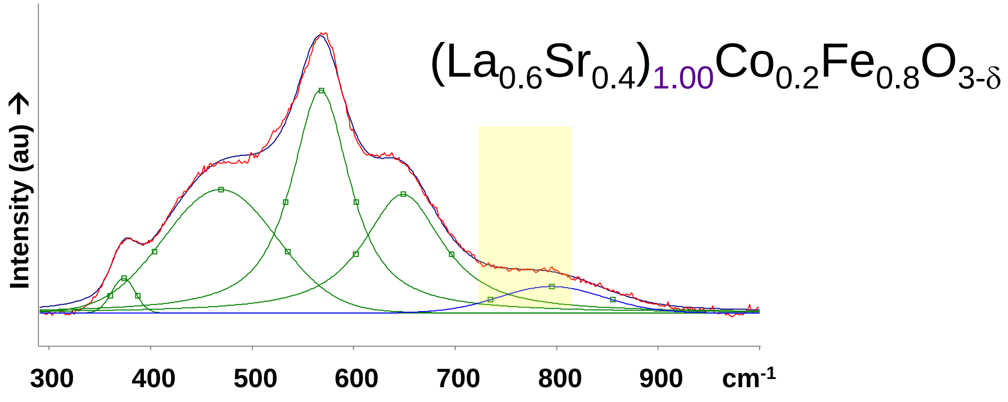
- Validated feedstock materials
- Established materials for reliable SOFC performance

Comparison of as received LSCF commercial powders

Perovskite symmetry and B-site second phase precipitation is variable in commercial LSCF powders





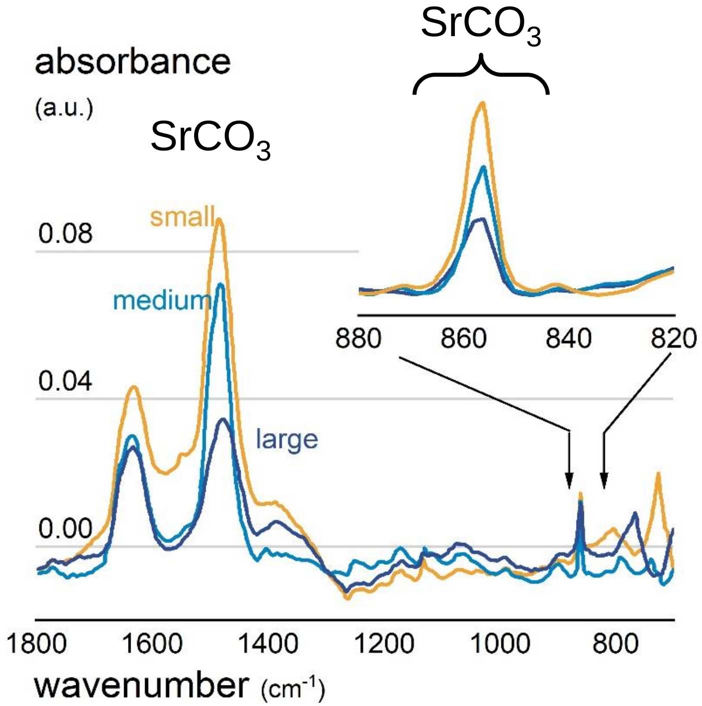


- Symmetry variation found in all commercially available LSCF powders
- A-site deficiency stabilizes single phase perovskite

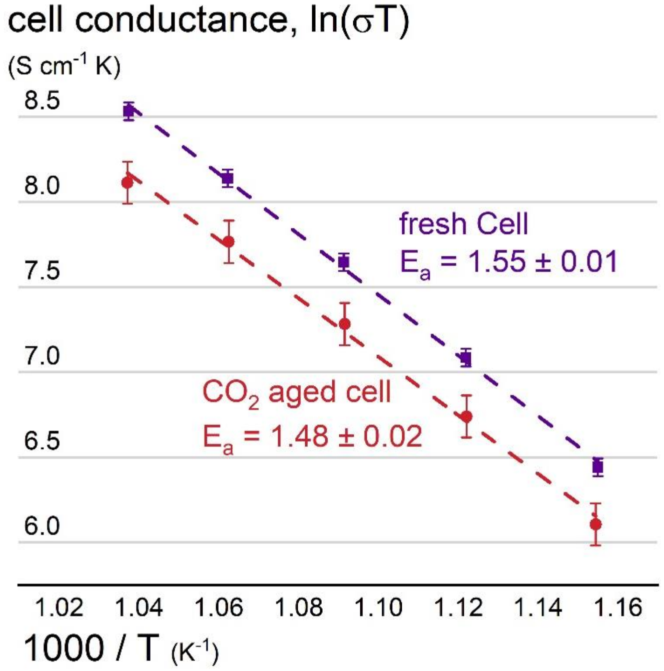
- Raman spectroscopy is powerful tool for screening B-site segregation

Quantitative analysis of $SrCO_3$ using FTIR

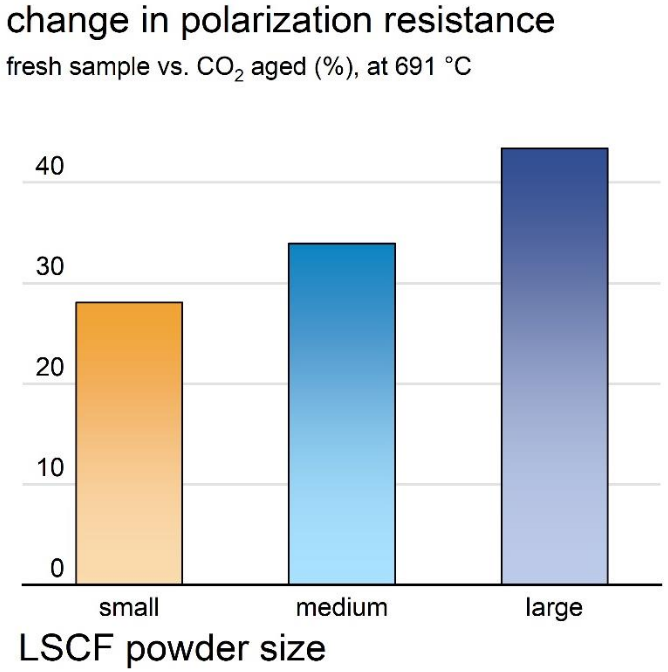
Detection and quantitative determination in high throughput measurement



Routine FTIR evaluation provides effective, quantitative and low-cost assessment of $SrCO_3$



CO_2 room temp aging affects polarization resistance 20~40%. No change in thermal activation.

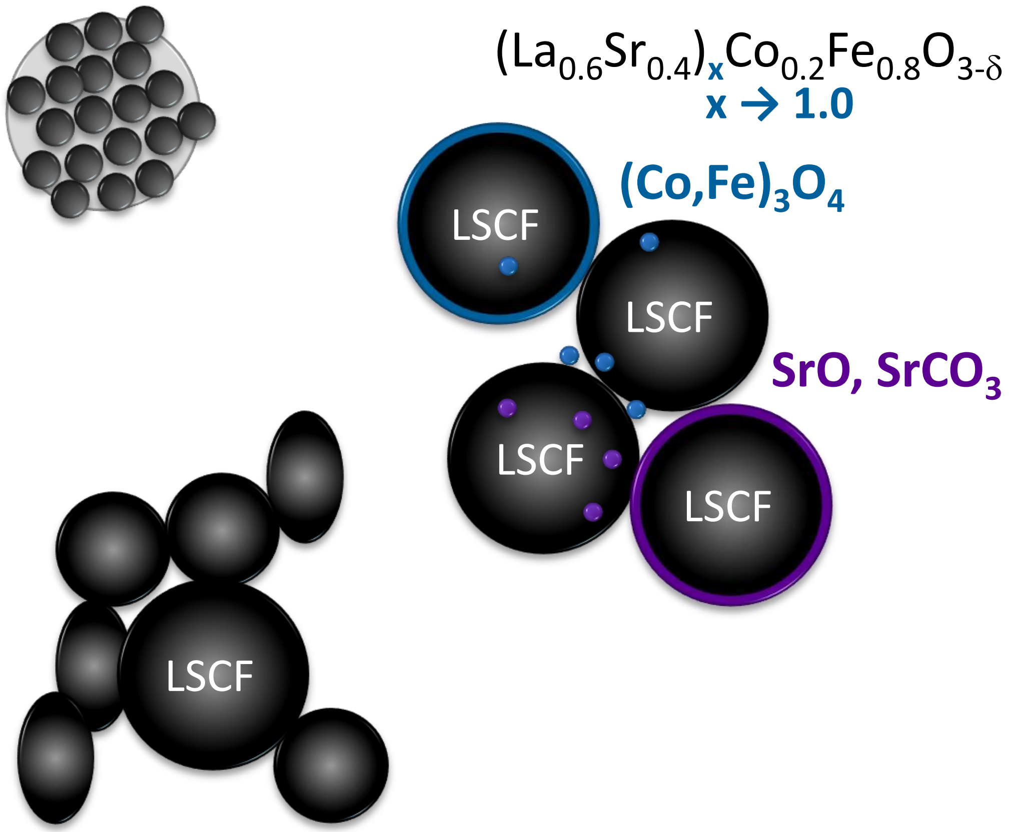


The relative effect of aging is unexpectedly inversely proportional to surface area.

Review of as-received powder characterization

Complex chemical and morphological variations quantified

- Routine screening technique for quantitative assessments of…
  - $SrCO_3$ surface content, by FTIR
  - B-site 2nd phase, by RAMAN
- Perovskite symmetry / strain:
  - Limited effect on Sr segregation rate
  - Limited effect on short-term performance
  - Long term performance uncertain
- Morphological variations, based on synthetic approaches, result in observed variations in second phase formation and evolution
- Storage of powder & fabricated cells may result in promoting $SrCO_3$ formation
  - Decreases electrochemical performance

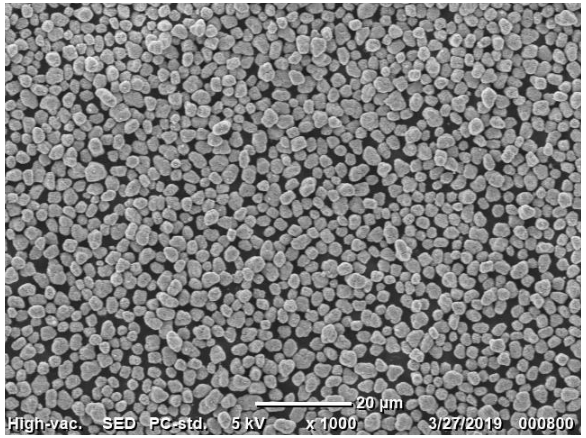


REVIEW

- **Established targeted cathode synthesis by coprecipitation in a Continuous Stirred Tank Reactor (CSTR)**

Phase and morphology control

LSCF cathode from $(Co_{0.2}Fe_{0.8})O_x$ precursor



$(Fe_{0.8}Co_{0.2})_3O_4$ precursor combine with La, Sr source

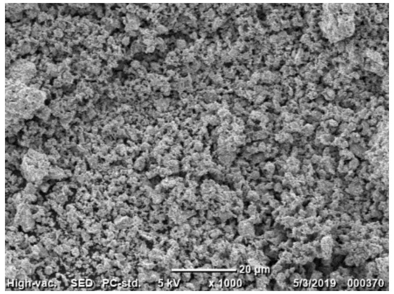
La, Sr nitrates
800-1100°C

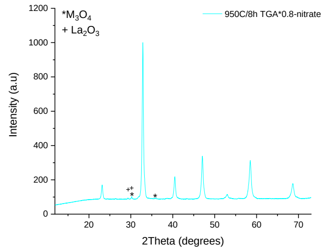
$La_2O_3/La(OH)_3$
$Sr(NO_3)_2$

$La_2(CO_3)_3$
$SrCO_3$

1) La, Sr nitrates
450°C

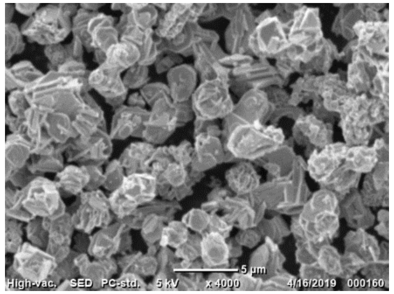
2) 950°C

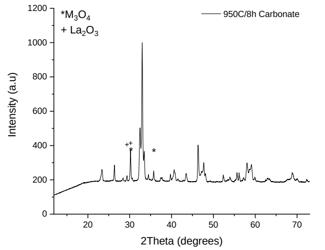




Nitrates + high temp

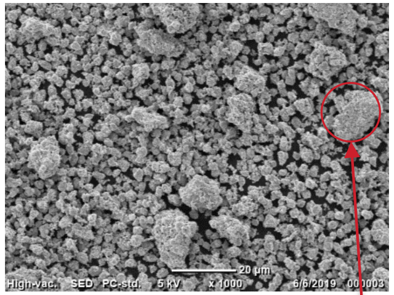
Phase purity ✓ morphology ✗

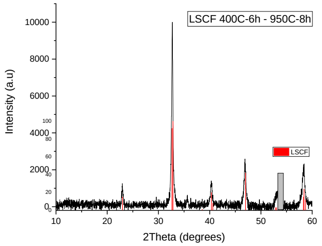




Non-nitrates + high temp

Phase purity ✗ morphology ✓





(some agglomeration is observed)

Nitrates + low then high temp

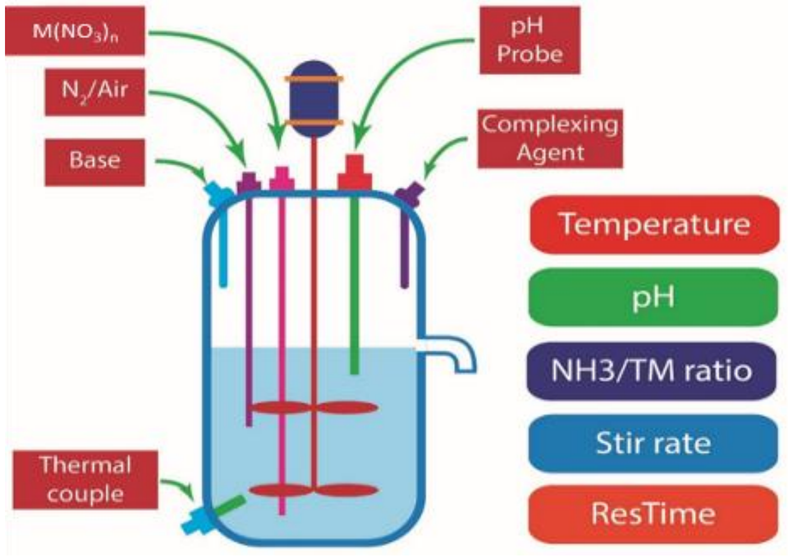
Phase purity ✓ morphology ✓

Coprecipitation synthesis of fuel cell cathode precursors

Scalable, synthetic control over morphologies

Continuous Stirred Tank Reactor (CSTR)

Adapted from Li-ion to SOFC cathode materials

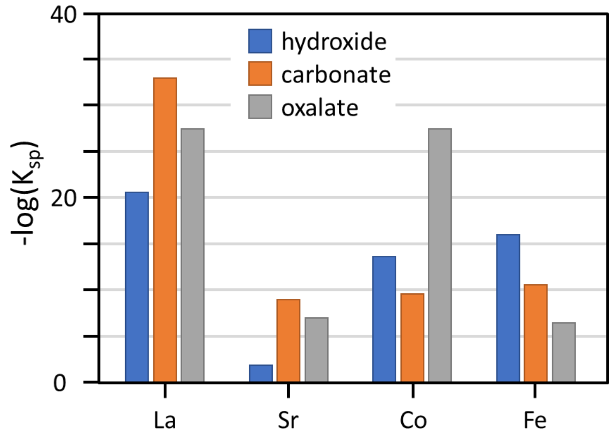


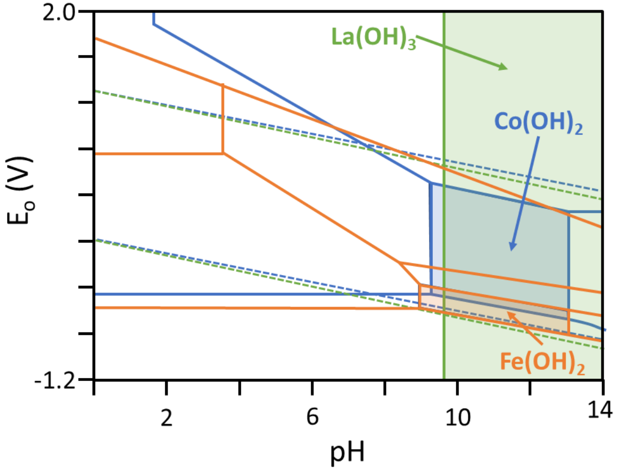
$$M(NO_3)_n + mNH_3 \leftrightarrow M(NH_3)_m^{n+} + nNO_3^-$$

$$M(NH_3)_m^{n+} + n(NH_4)_2CO_3 \leftrightarrow M_2(CO_3)_n + mNH_3 + NH_4^+$$

Coprecipitation of LCF precursor

At pH > 10, La, Fe, and Co as hydroxides





Precursors without Sr with controlled morphologies

Add Sr during the calcination

Review of LSCF synthesis

Managing Sr solubility, by including separately, maintain morphology by two temperature process

- Phase pure LSCF is obtained and verified from (Fe,Co)O precursors
  - Perovskite symmetry and phase purity to be determined by post reaction
- Morphological control is demonstrated
  - Careful size and distribution control is now possible
- Alternative complexing agents may enable 4-cation coprecipitation

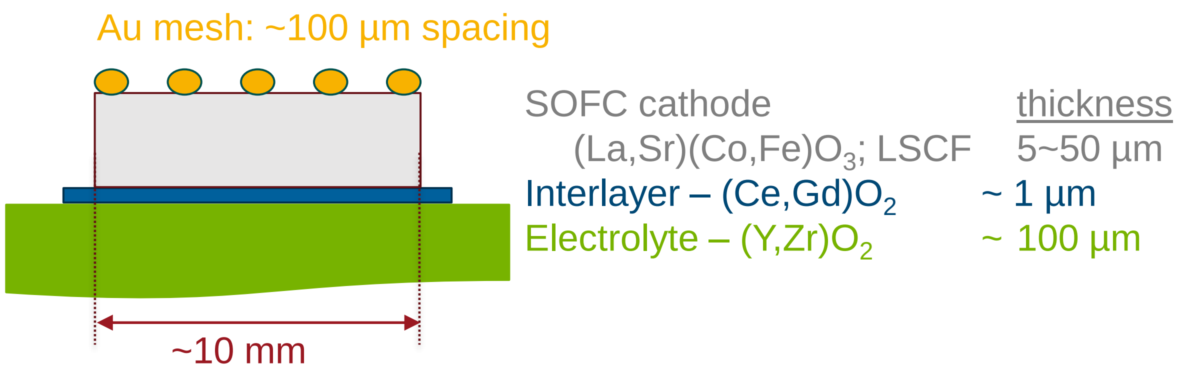
Make button cells valuable:

- **Design experimental setup based on fundamental principles of transport**

Laboratory scale testing for SOFC electrode materials

Button cells are valuable but introduce several experimental challenges for lab-to-lab comparison

Symmetric half-cell

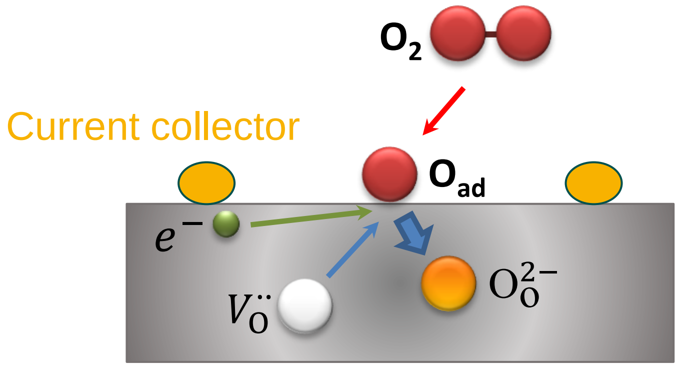


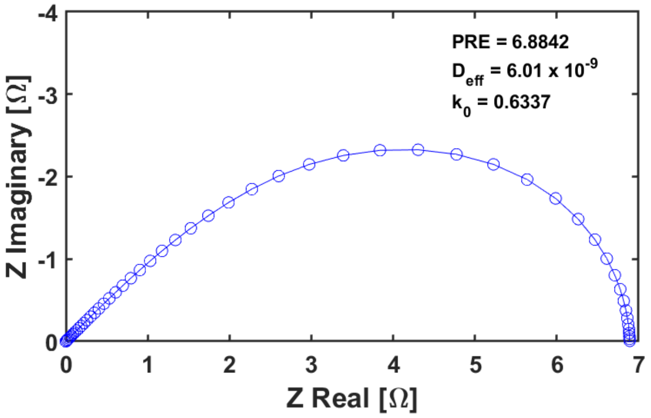
- Fast and cost-effective
  - Simple design focusing on one electrode
  - Less use of materials
- Widely used at university labs and early development stage.
- Challenge in fully activating cathode volume
  - Isolate experimental setup from materials/morphology factors
  - Current collector design coupled with electrode thickness

Reliable evaluation parameter: resistance polarization

Determined by electrochemical impedance spectroscopy and comprised of oxygen exchange resistance (R_{exch}) and bulk transport parameters

$$\frac{1}{2}O_{2(gas)} + 2e^- + V_{O(in\ solid)}^{\cdot\cdot} \rightarrow O_{O\ (in\ solid)}^{2-}$$

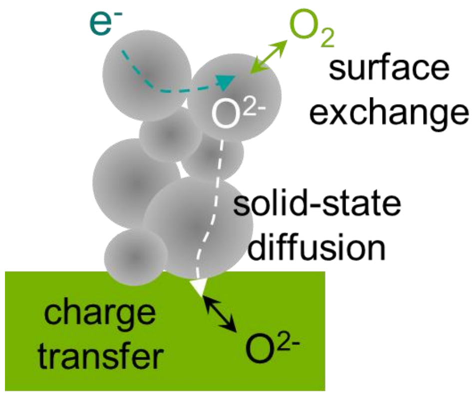


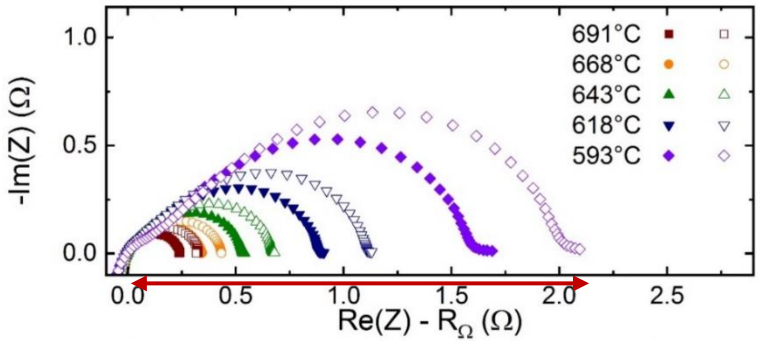


R_{exch} described by Finite-Length-Gerischer

- Solid-state bulk diffusion (D_v)
- Surface exchange kinetics (k_0)
- Tortuosity (τ), Electrode thickness (L)
- Oxygen nonstoichiometry (c_v)
- Thermodynamic factor (A)

J. Nielsen et al. *Electrochimica Acta* 56 (2011) 7963.





R_p - polarization resistance difference in high and low impedance

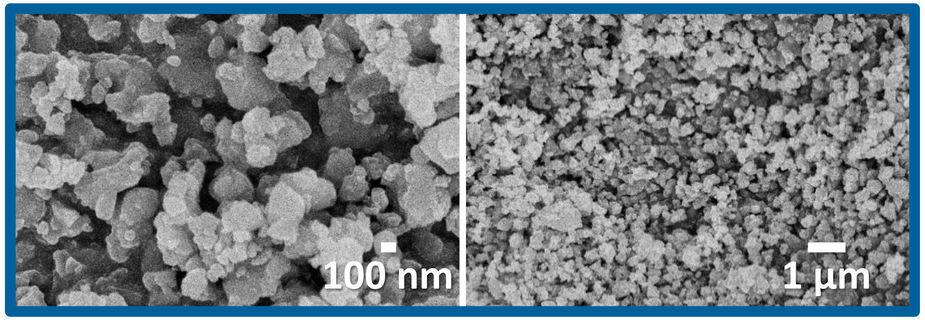
- All above parameters
- Oxygen transport and exchange at electrolyte

Two morphologies to compare connectivity and porosity

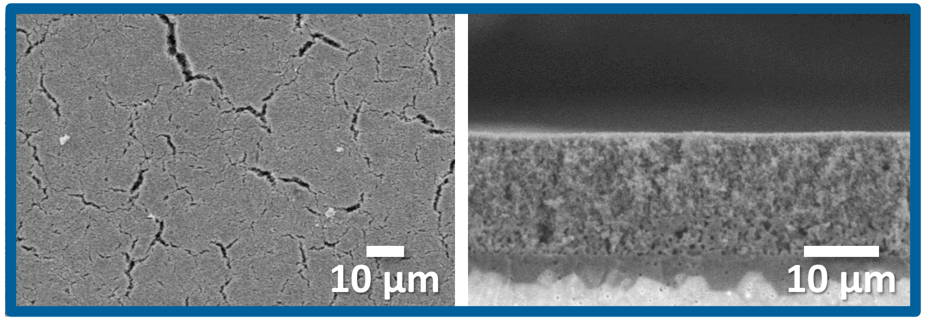
Nominally the same composition and structure

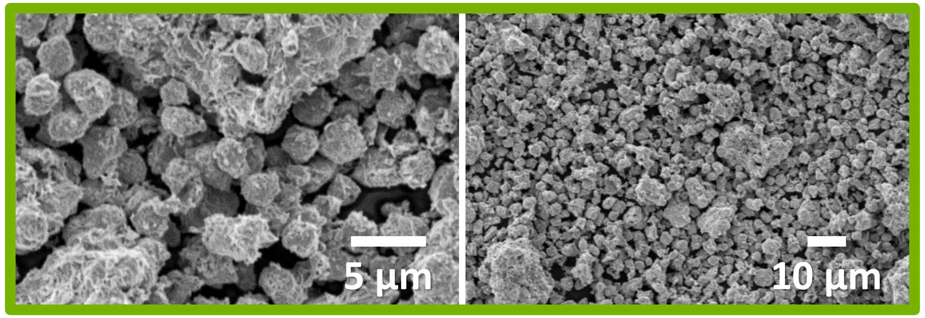
powders

screen printed electrodes

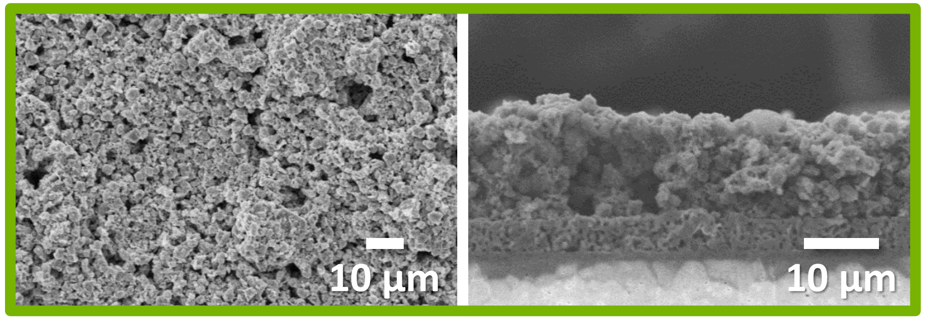


Sub-microscale LSFC
(commercial procured)



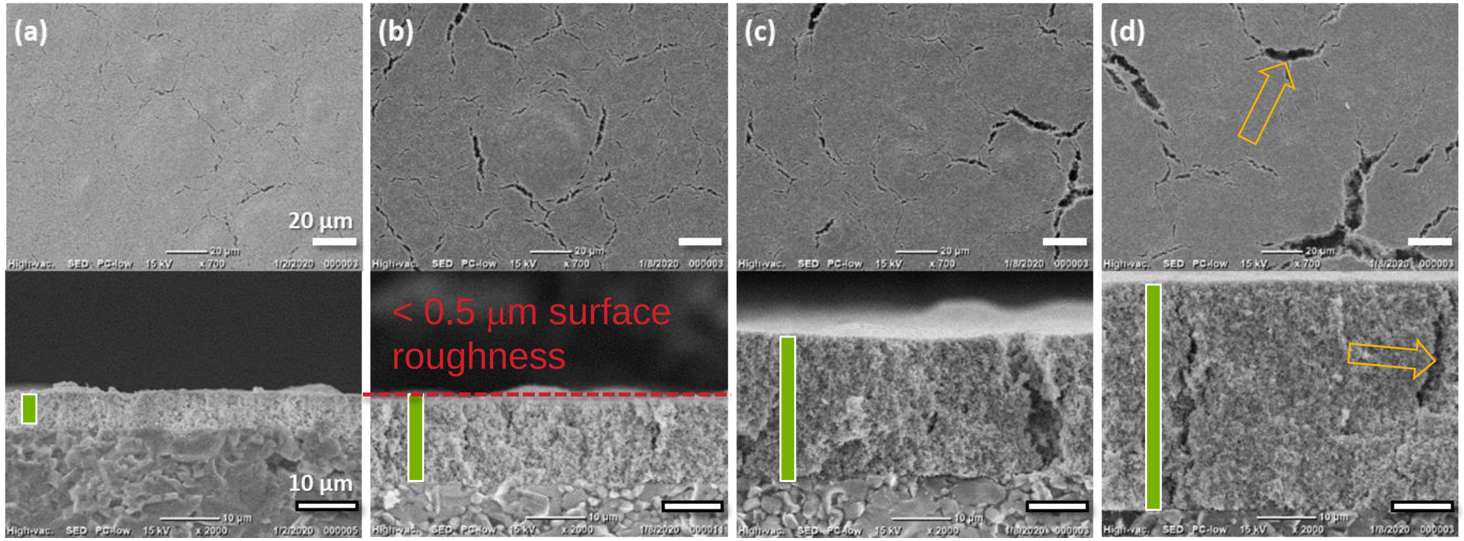


Microscale LSFC
(CSTR synthesis)



A quick note: uniform screen-printed LSCF electrodes

Minimize physical variability in laboratory setting is critical



6.2 ± 0.2 µm   14.1 ± 0.4 µm   22.7 ± 1.2 µm   39.8 ± 1.5 µm

Ceramic ink preparation

- Planetary centrifugal mixer
- Screen print vehicle + additional surfactant (PAA, Hexylene glycol)
- 15-30 min of mixing, 2000 rpm, without deforming step, 6-8 zirconia balls
- Drying at 75 °C in oven.

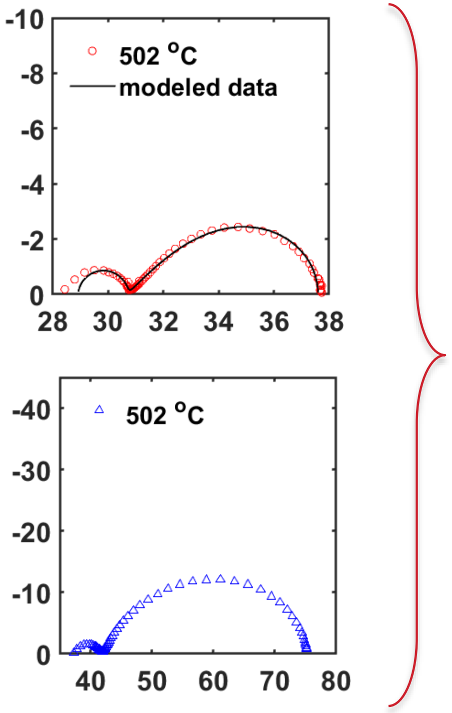
Surface cracks

- Large volume change upon decomposition of organic materials; unbounded surface.
- Micro-agglomeration can be minimized:
  - Slower heating rate.
  - More time for settlement.
  - Multilayer deposition

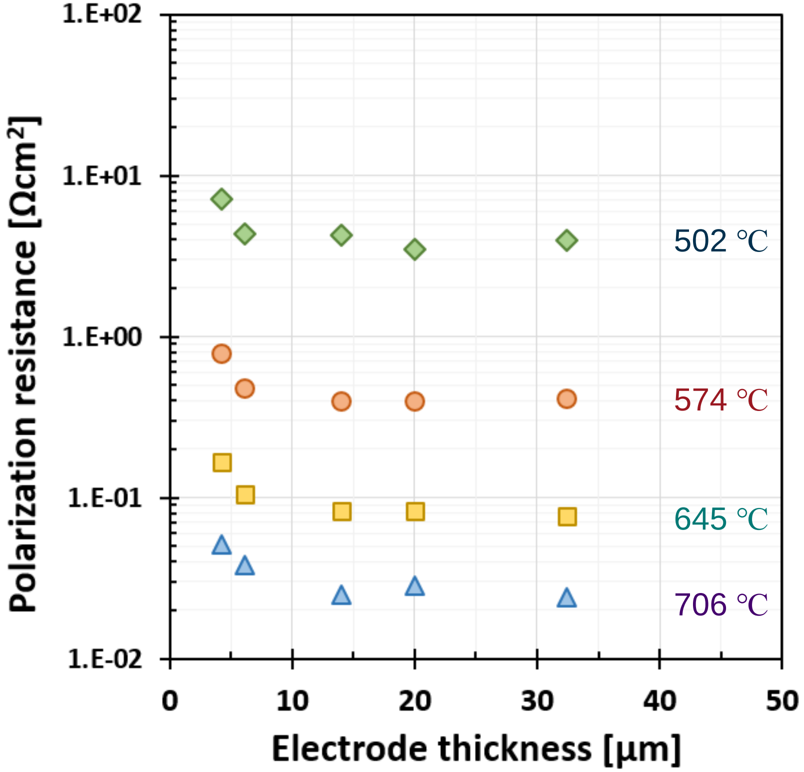
(Observed by others, private correspondence)

Thickness and temperature dependence of R_p

Goal to operate in thickness invariant regime

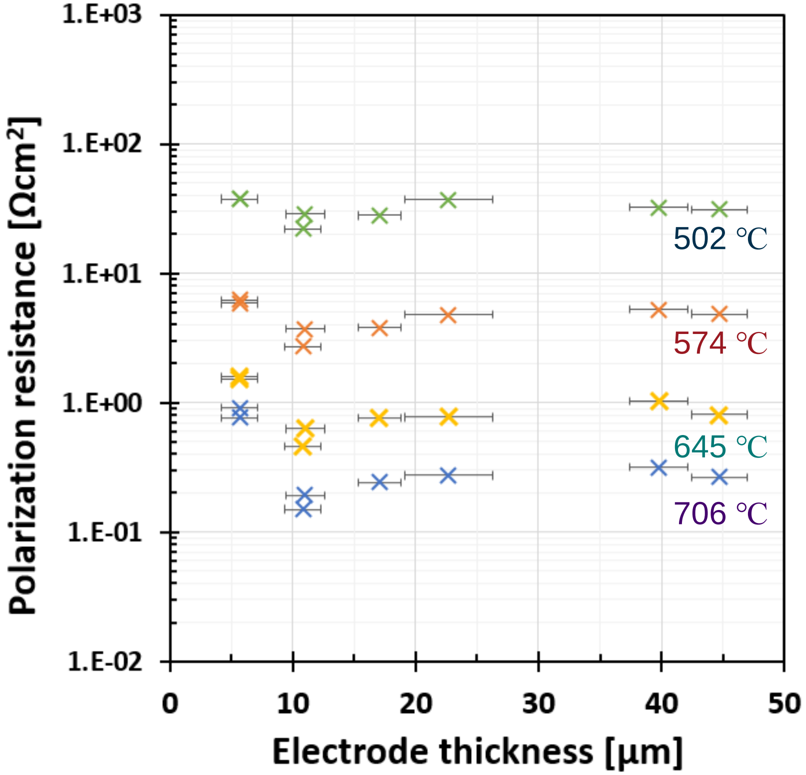


Sub-microscale LSCF6428



At all temperatures, decrease with thickness followed by saturation

Microscale LSCF6428

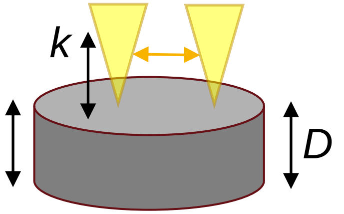


Thickness dependence pronounced at higher temperatures

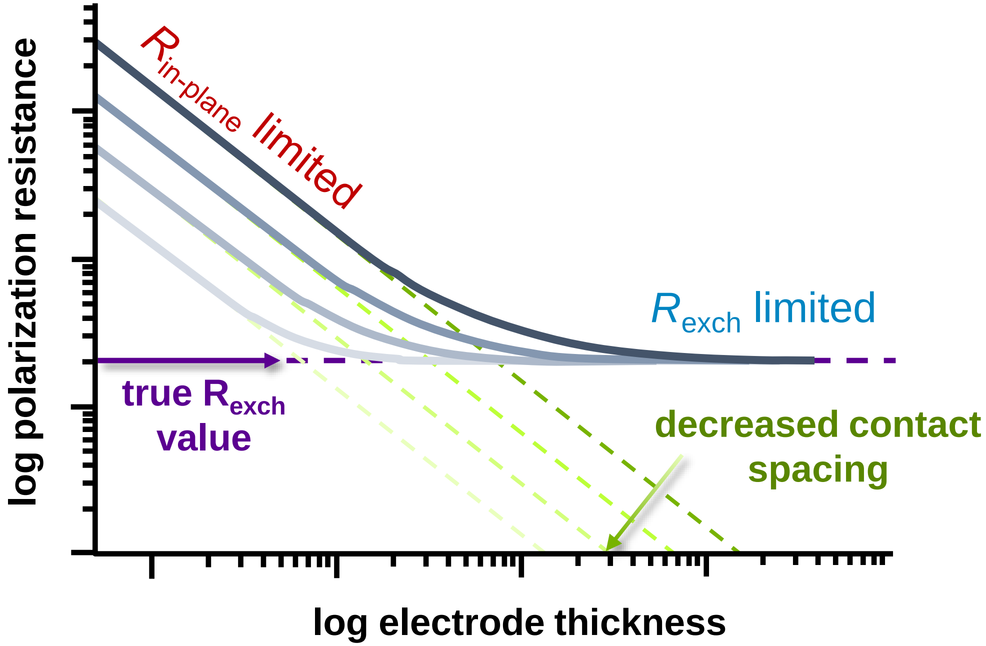
Understand role of in-plane electrical resistance

Combination of electrode thickness and current collector spacing

R_{exch} and $R_{in\text{-}plane} \propto \rho$ (electrical resistivity)



[1] $$R_{appt} = \frac{\rho}{2\pi \cdot d} \cdot \frac{\cosh(z)}{\cosh(z) - 1} \qquad z = L\sqrt{\frac{\rho}{d \cdot R_{exch}}}$$



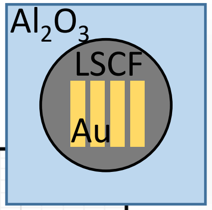
Determined for a given ρ and R_{exch}

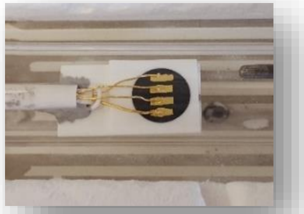
[1] B.A. Boukamp et al. *Solid State Ionics* 192 (2011) 404 / 283 (2015) 81.

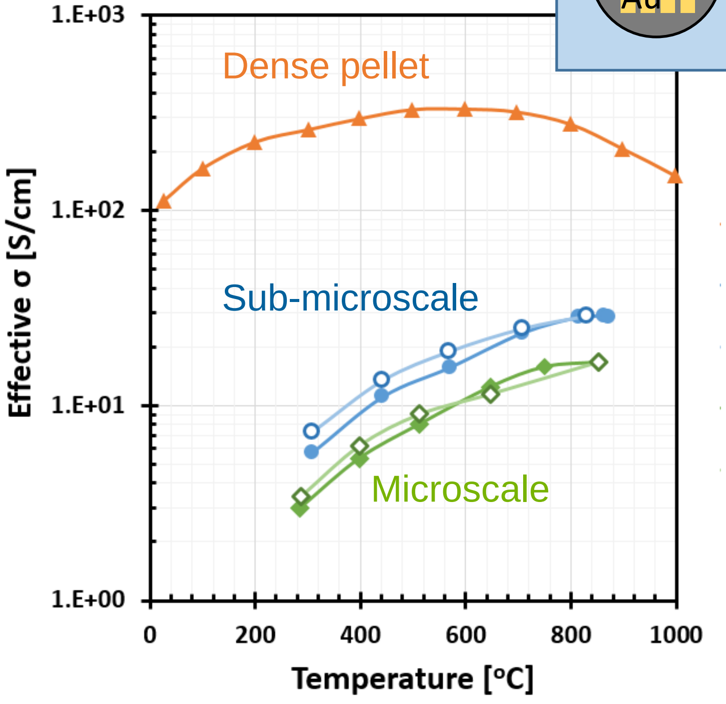
Understand role of in-plane electrical resistance

Poor charge transport in plane of electrode limits activated volume

In-plane electrical conductivity
of LSCF porous layer

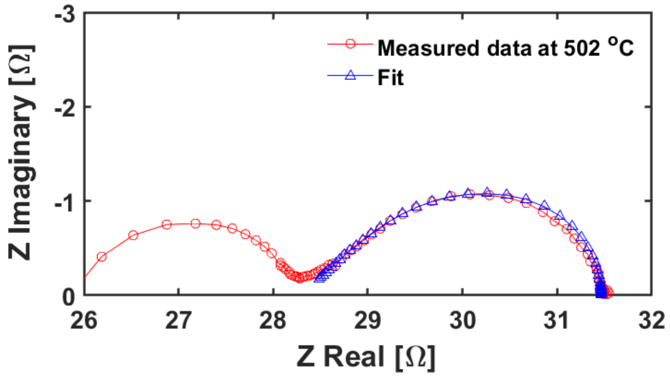






Oxygen surface exchange (R_{exch})
Sub-microscale

Fit with the FLG impedance



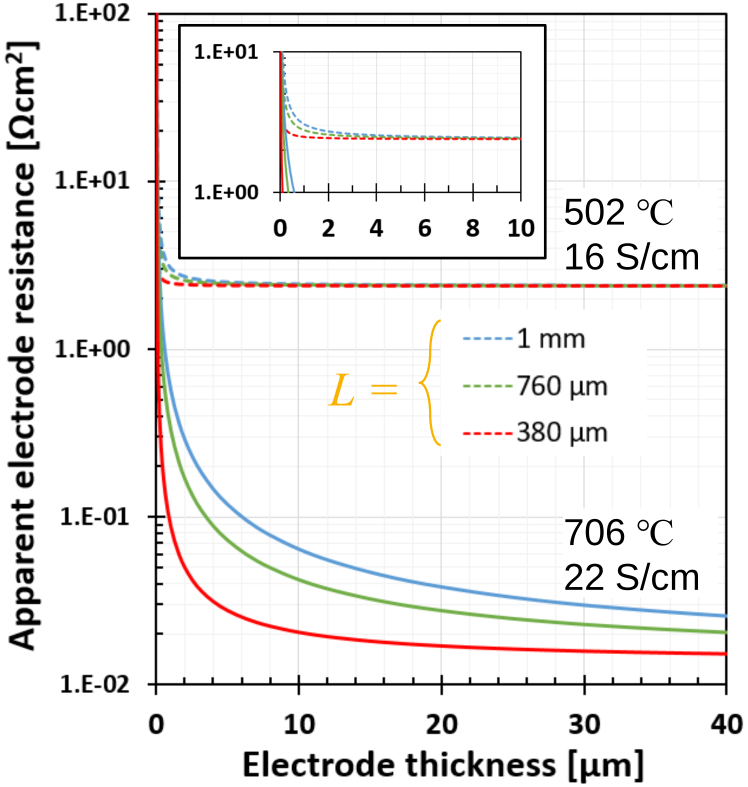
$$R_{exch} = \frac{RT}{4F^2}\frac{\tau\lambda}{D_v c_v^0}\frac{\coth\left(\left(L/\lambda\right)\sqrt{1+j\omega/k_0}\right)}{\sqrt{1+j\omega/k_0}}$$

$$\lambda = \sqrt{\frac{AD_v}{\tau k_0}}$$

J. Nielsen et al. *Electrochimica Acta* 56 (2011) 7963.

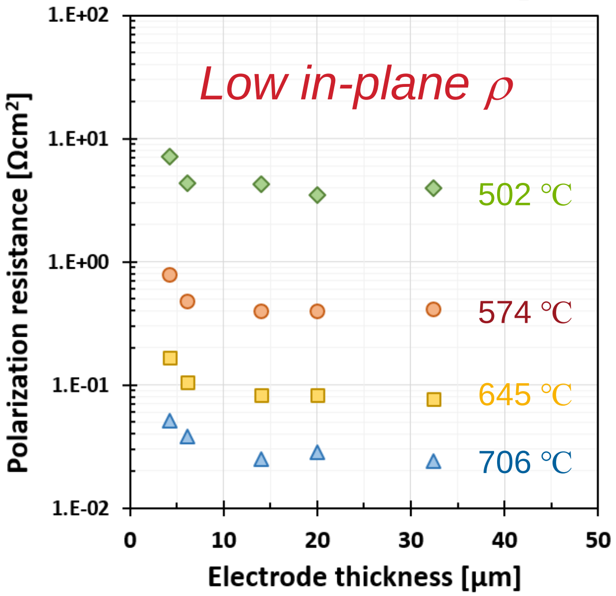
Understanding role of in-plane electrical resistance

Calculated apparent R_p with experimental in-plane ρ and R_{exch}

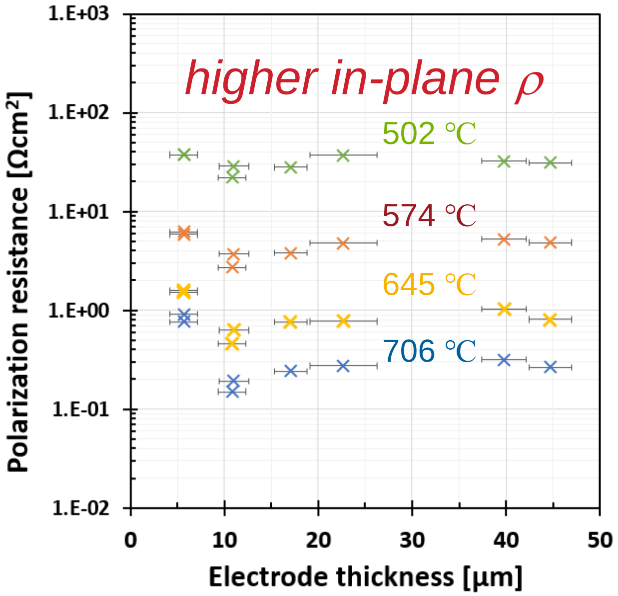


explains

Sub-microscale LSCF6428



Microscale LSCF6428



High in-plane ρ contribution more pronounced

- thinner electrodes
- higher temperature ($\propto {}^{1}/_{R_{exch}}$)
- wider current collector spacing

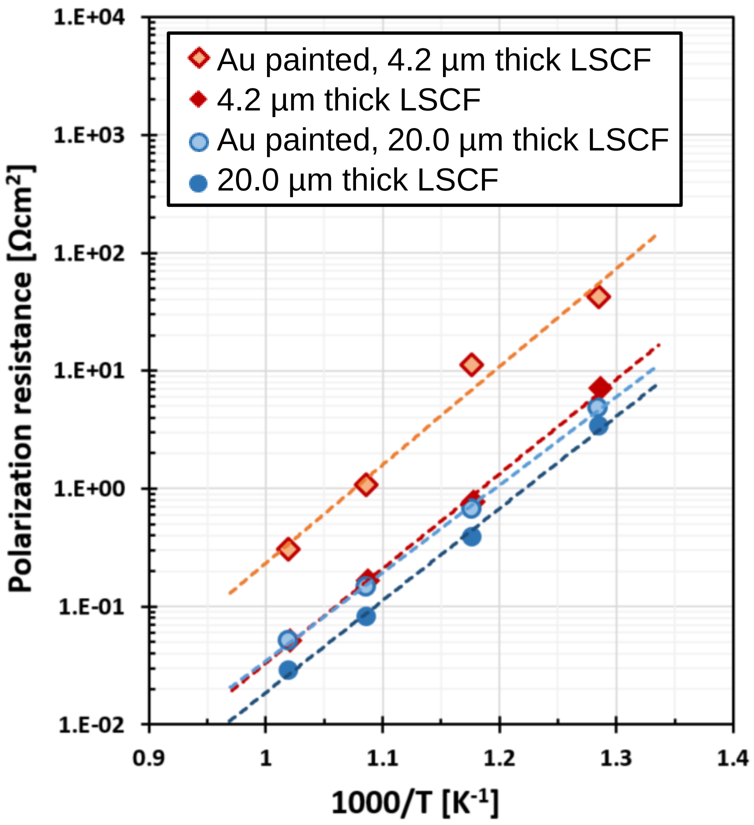
- Electron supply is available
- Electrode volume is completely activated
- Thickness dependency expected from FLG impedance of R_{exch}

- Higher in-plane ρ
- Overwhelms characteristic thickness dependance

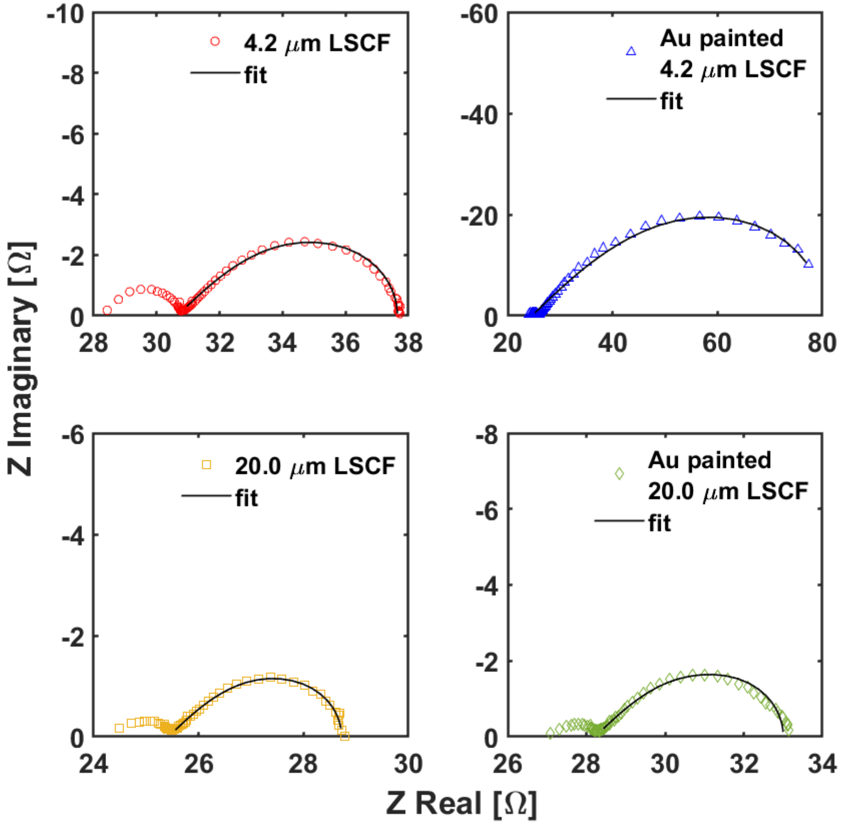
Can porous metal current collector be beneficial?

Potential impact on surface exchange and solid-state diffusion kinetics

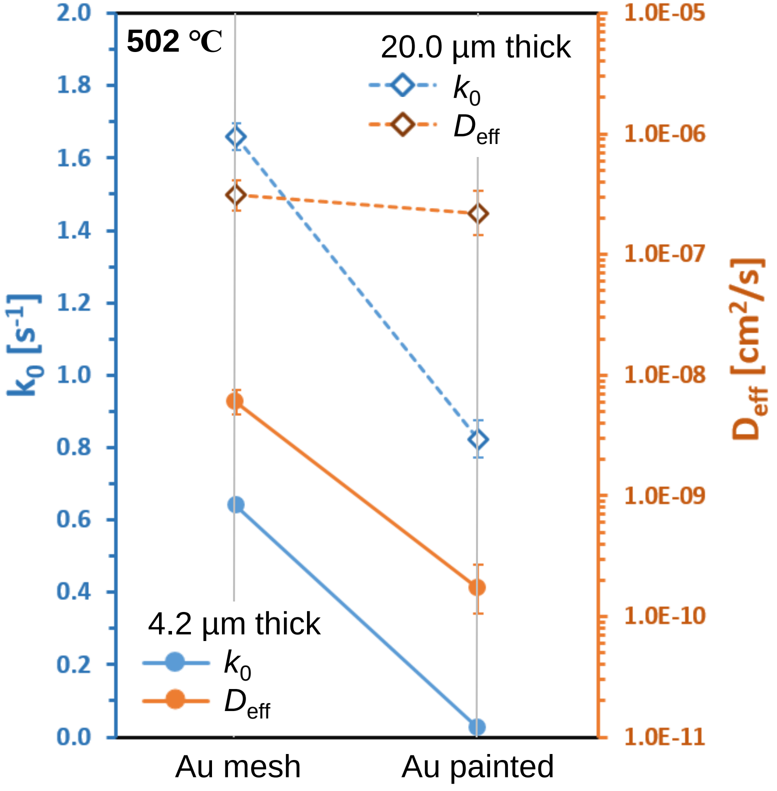
R_p change due to porous Au layer



Fit with the FLG impedance



k_0 and D_{eff} from the impedance fits



Make button cells valuable

Fundamental materials properties for smart testing design

- Established in-plane effective conductivity must be understood
- Mapped design space of electrode thickness and current collector spacing
  - Ensure activating known electrode volume
  - Electrode thickness can lead to high variability if too thin
- Decoupled k_o and D with respect to current collector
  - Particularly critical when isolating these parameters
  - Current collector, delivers electrons but can block sites for ORR
- Established route to use R_p as routine evaluative tool for electrodes

Thank you

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Debalina Dasgupta, SOFC project manager

Shailesh Vora, Technology Manager, Fuel Cells

Use of the advanced photon source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DEAC02-06CH11357

Use of the center for nanoscale materials, an office of science user facility, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC02-06CH11357