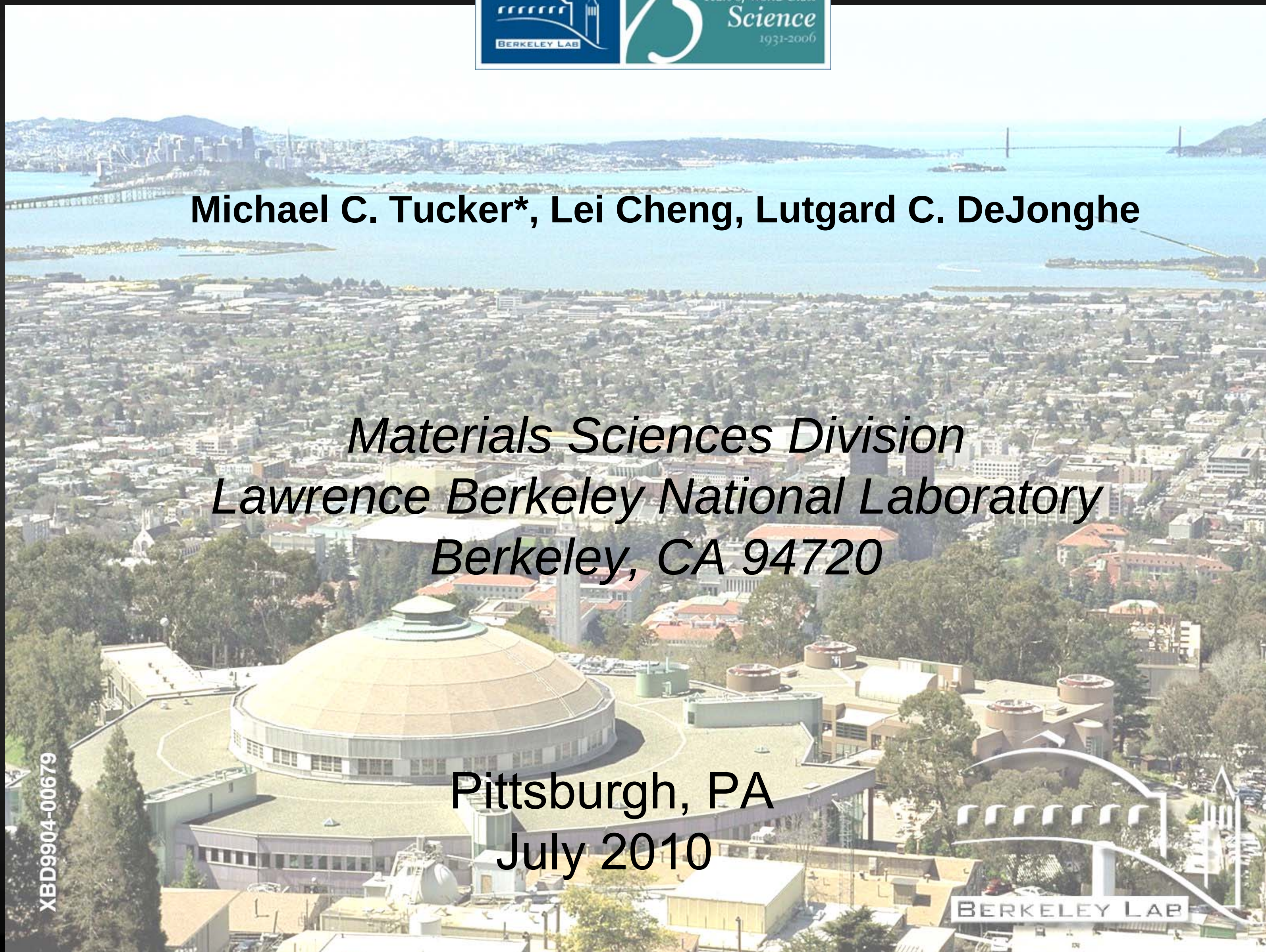
Cathode Contact Material Development



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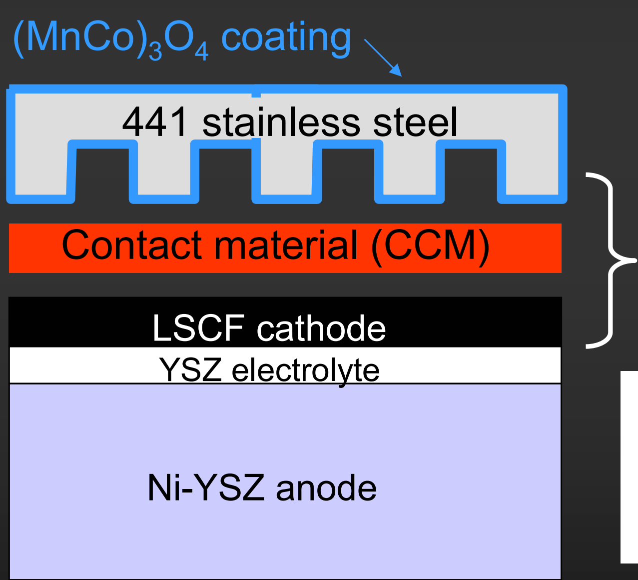
Problem Statement

Well-bonded CCM is desirable, but challenging

- Loose powder CCM is acceptable if stack experiences uniform compression

BUT: cross-cell thermal gradients, warping of components, etc causes local variation
- delamination and loss of electrical contact



Bonding at 1000°C or less
to avoid oxidation of steel

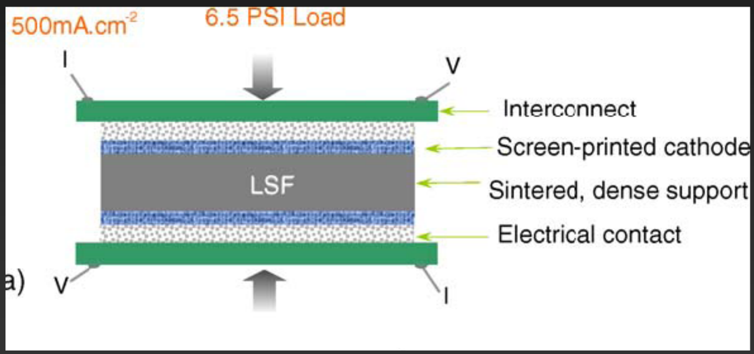
This is a low sintering/bonding temperature!!
- poor bonding
- incomplete sintering = reduced conductivity

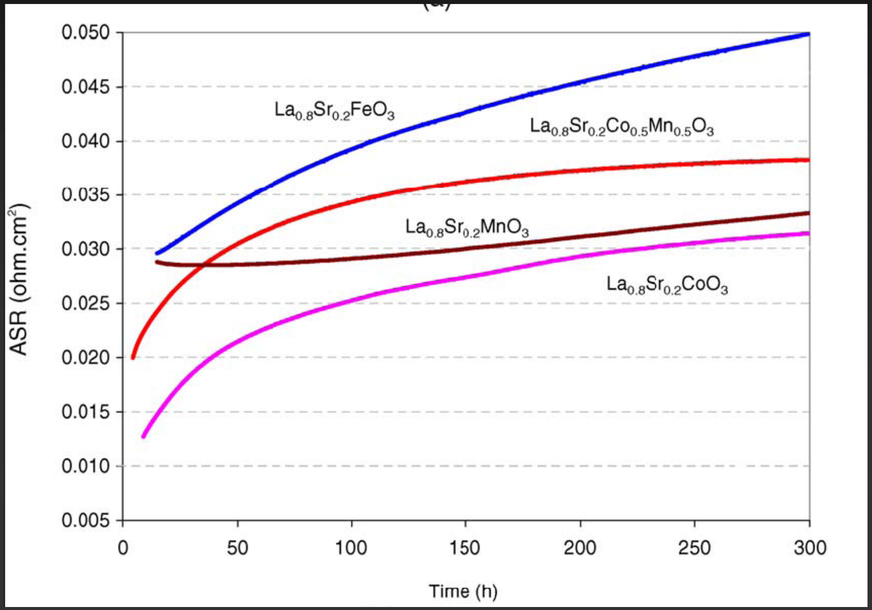
- Can we find a material that is reactive enough to bond at <1000°C but stable at 800°C operation?

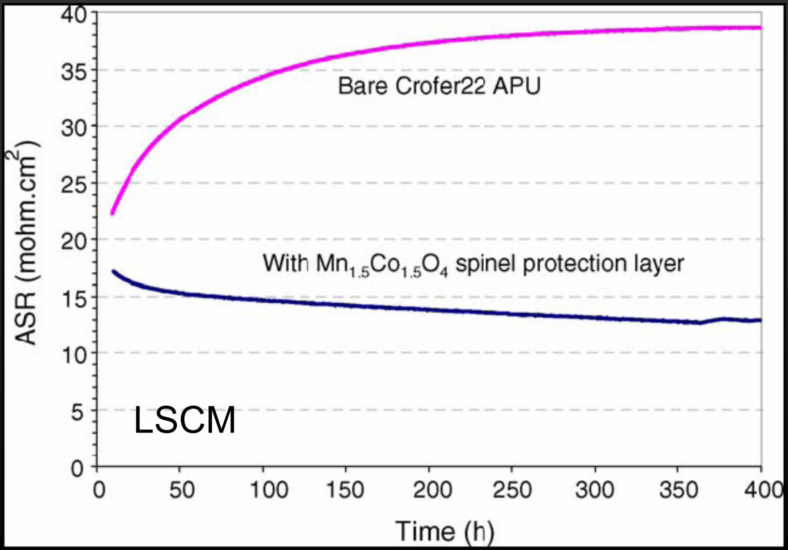
Contact Material Literature

Contact between Crofer22APu and LSF

PNNL Yang et al., Journal of Power Sources 155 (2006) 246–252

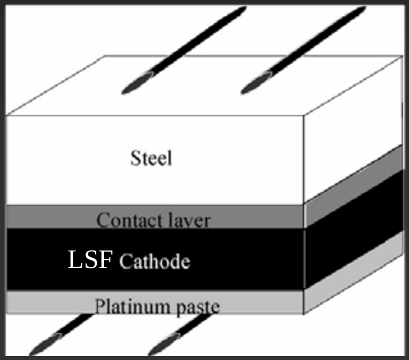




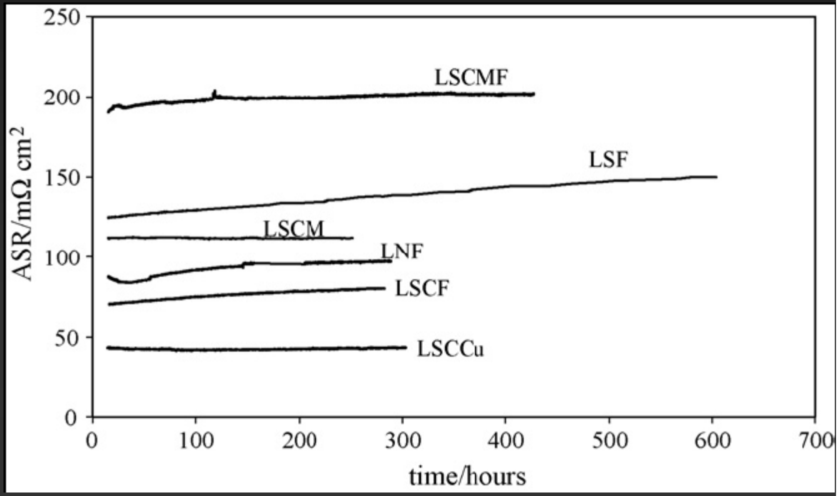


Contact between Crofer22APU and LSF

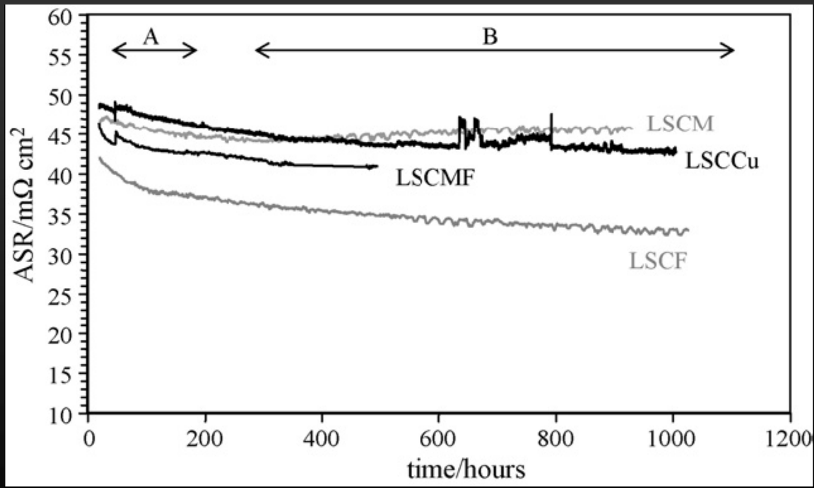
Ikerlan, Juelich   Montero et al., Journal of Power Sources 188 (2009) 148–155



Crofer22APU/CCM/LSF



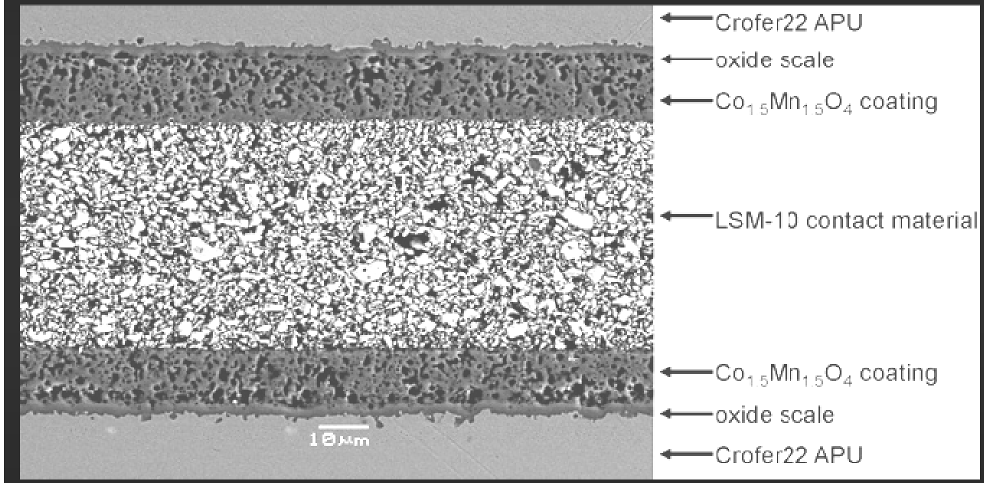
Crofer22APU/MCF/CCM/LSF

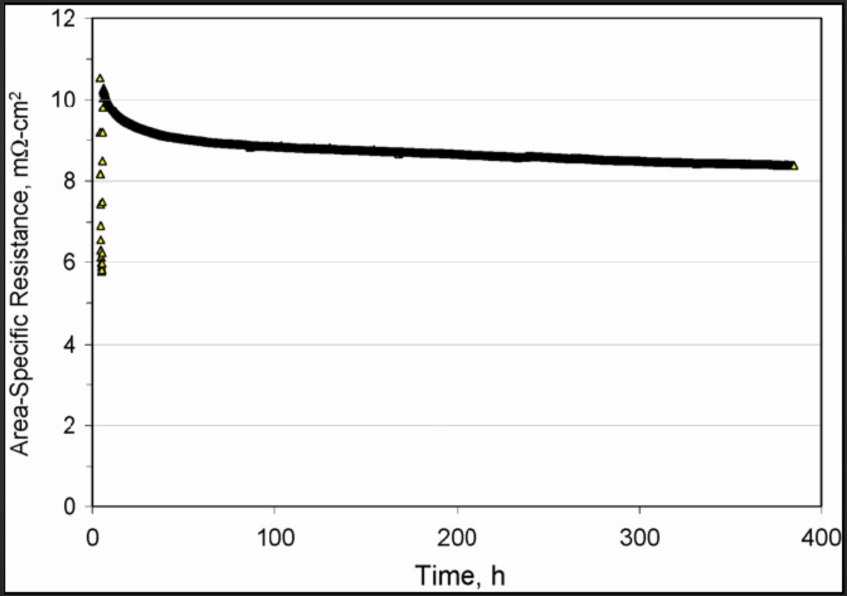


Enhancement of LSM Sintering

McCarthy et al., Journal of Power Sources 180 (2008) 294–300

Sinter at 900°C, switch between air and nitrogen
→ enhance sintering by creation of transient defects





Electrical resistivity of spinel-coated Crofer 22 APU/LSM-10 contact paste/spinel-coated Crofer 22 APU sandwich specimen versus time, measured in air at 800 ◦C.

Observations from Literature

- 200h is enough to capture initial transient

- No standard test geometry

- No standard CCM paste application method

- Compressive load applied (bonding not typically tested)

- No consensus on “best” CCM

Approach and Results

Candidate Materials

CCM requirements:
- good bonding
- high electronic conductivity
- good CTE match
- chemical compatibility with LSCF and $(MnCo)_3O_4$

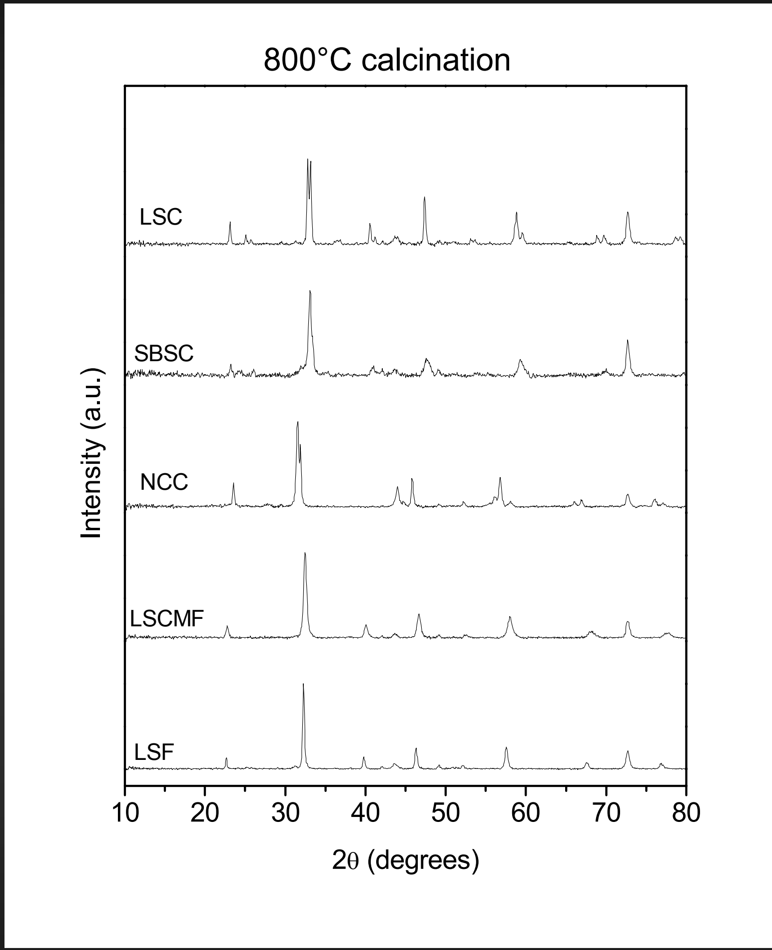
Approach:
Select candidates from cathode literature
- high conductivity
- low sintering temperature

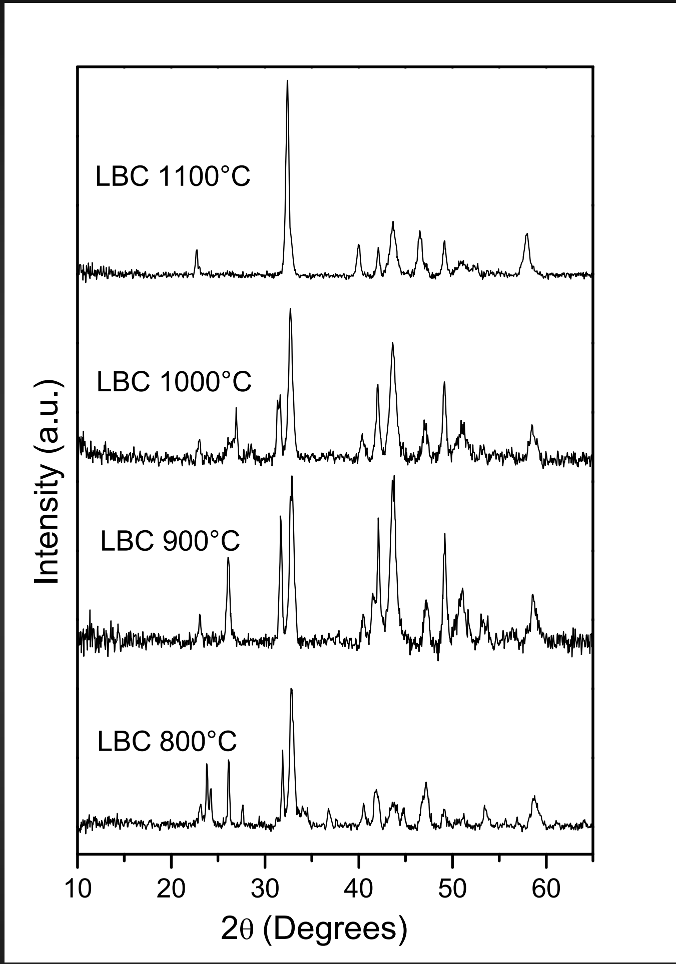
La0.6Sr0.4Co0.8Fe0.2	LSCF
La0.8Sr0.2Cu0.9Fe0.1O2.5	LSCuF
La0.7Sr0.3CoO3	LSC
Sm0.5Sr0.5CoO3	SSC
SmBa0.5Sr0.5Co2O5	SBSC
GdSrCo2O5	GSC
La0.65Sr0.30MnO3	LSM
LaBaCo2O5	LBC
YBaCo2O5	YBC
Nd1.8Ce0.2CuO4	NCC
La0.8Sr0.2Co0.3Mn0.1Fe0.6O3	LSCMF
La0.98Ni0.6Fe0.4O3	LNF
La1.2Sr0.8NiO4	LSN
La0.7Sr0.3FeO3	LSF
La2Ni0.6Cu0.4O4	LNC

LSM, LNF, SSC, LSCF purchased from Praxair

All others synthesized by GNP

GNP Synthesis, Coarsening, XRD Phase Confirmation





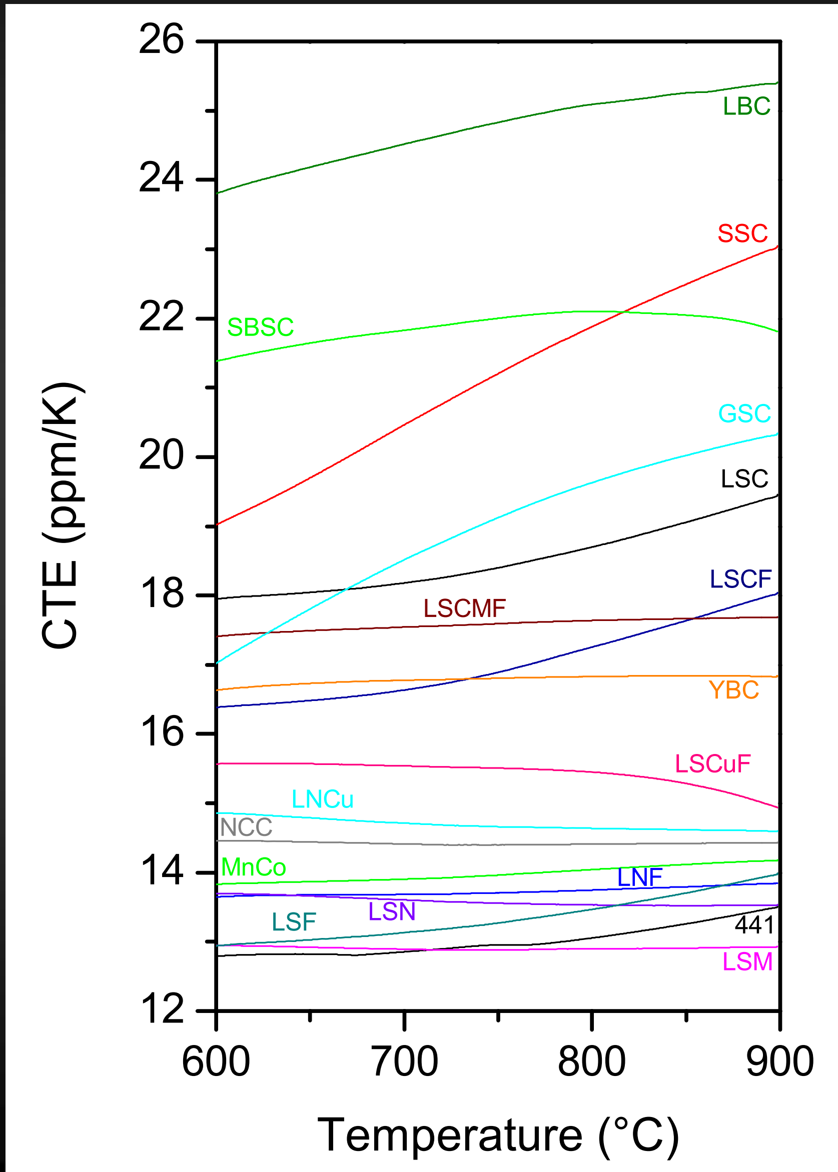
800°C: LSC, SBSC, NCC, LSCMF, LSF
900°C: GSC, LSN, LSCuF
1100°C: LBC, YBC

CTE

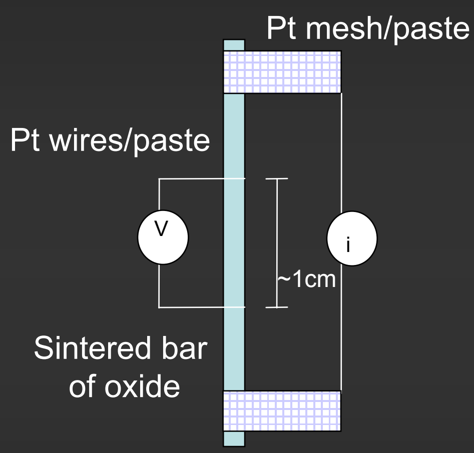
Note CTE for interconnect and cell <14ppm/K

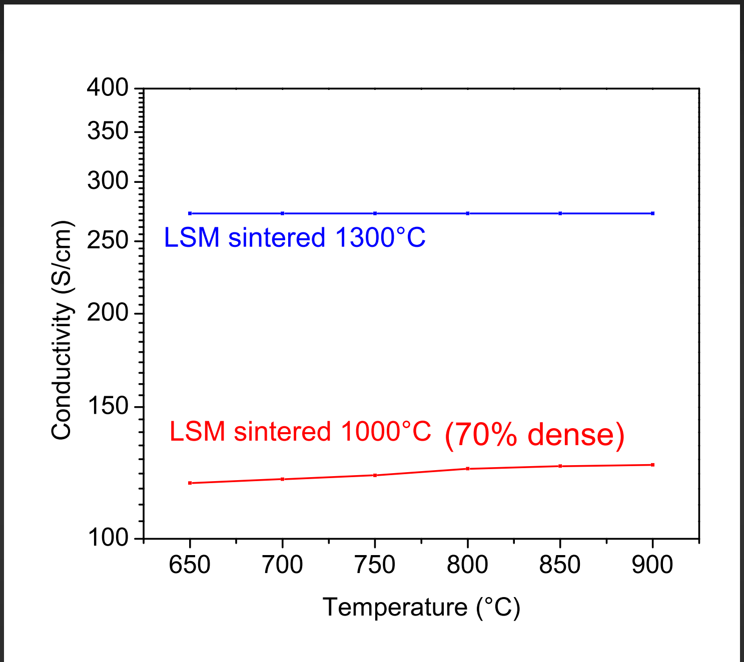
- Matched CTE is desirable

- High CTE does not disqualify candidate material
    - Thin, porous layer



Conductivity of Porous CCM



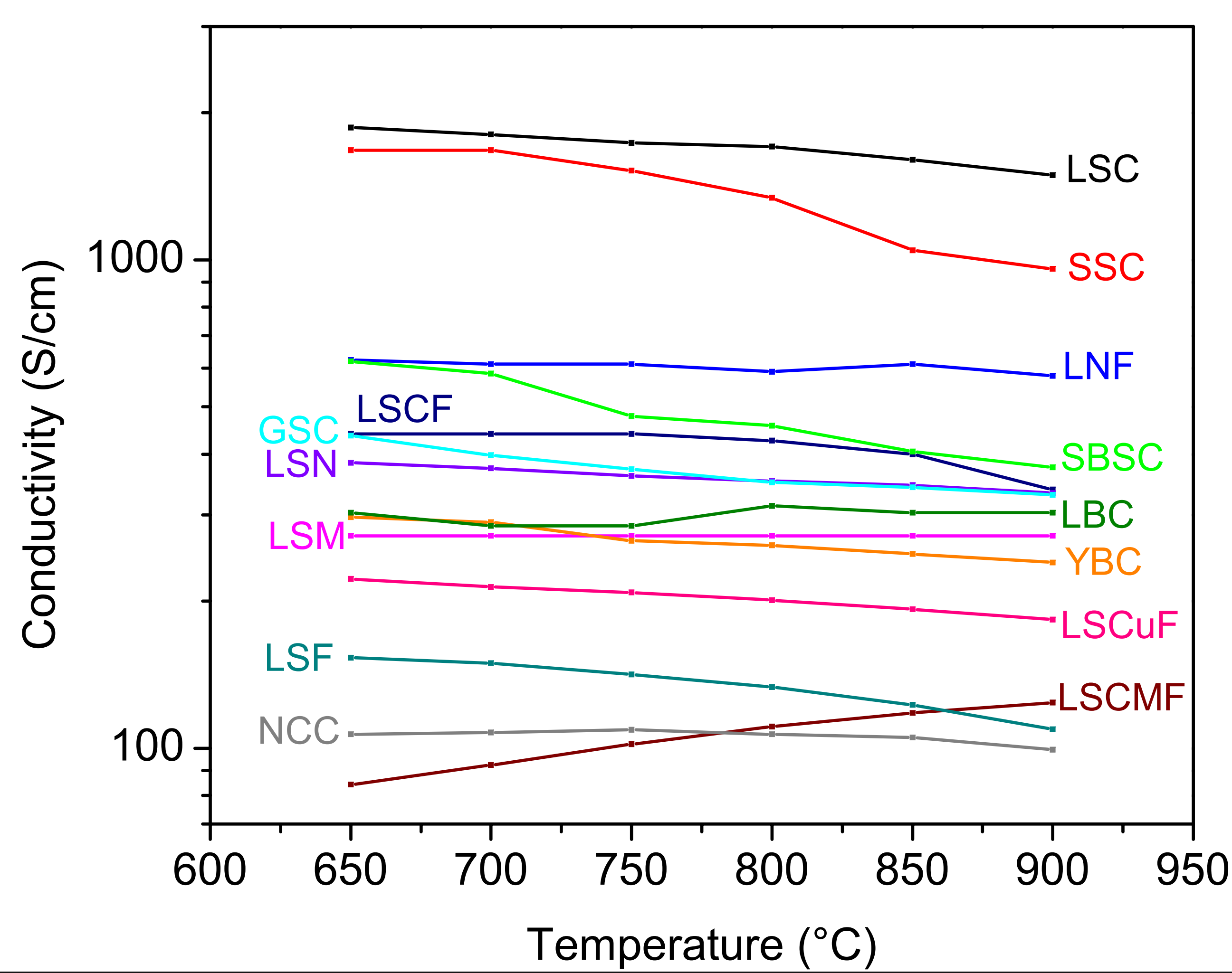


Conductivity less than predicted by density
- minimal sintering/particle necking or GB issue

Conductivity of Dense CCM

- Measured for dense bars

- Conductivity of porous CCM after bonding at 900-1000°C will be lower

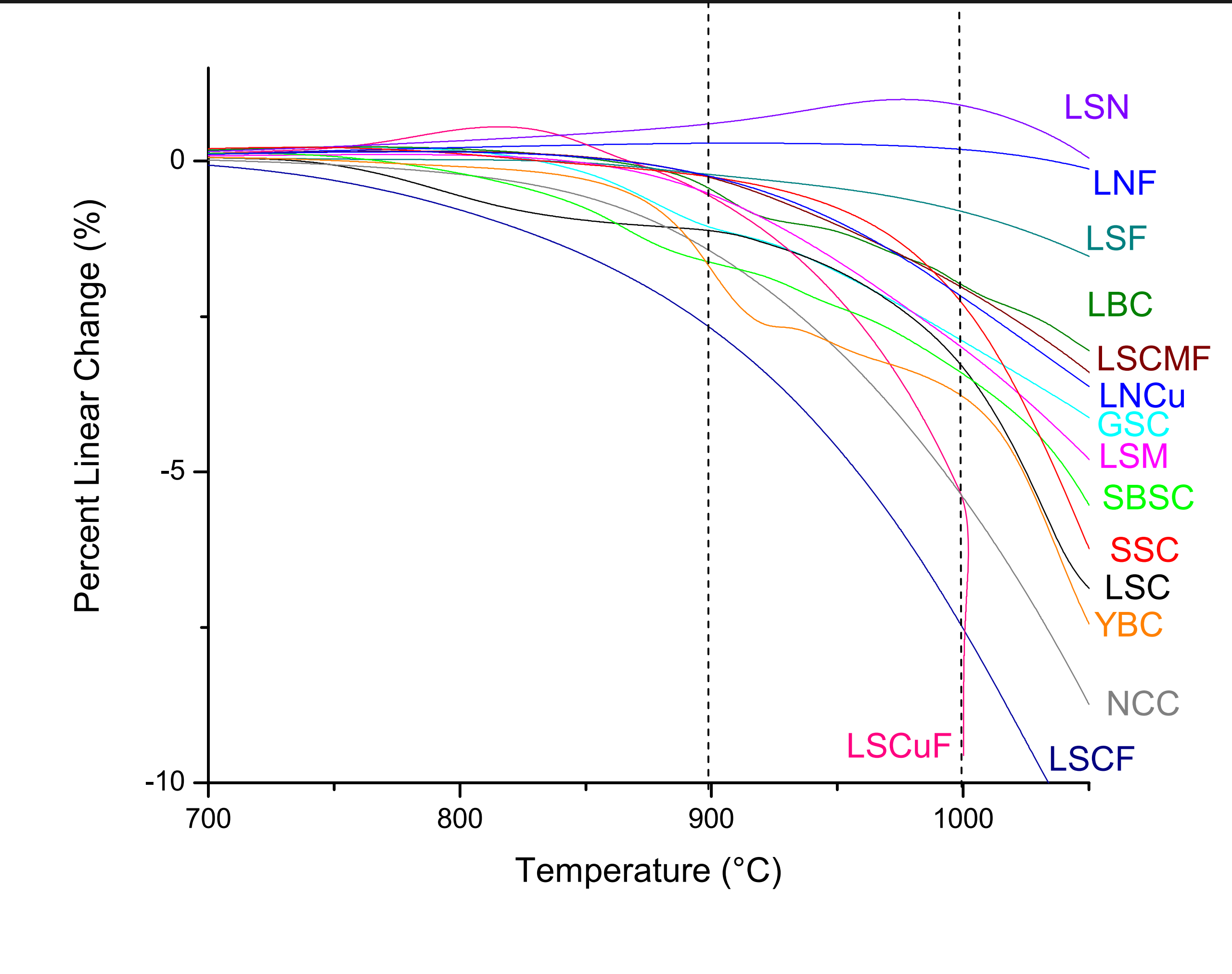


Sintering Behavior

- Extent-of-sintering related to strength in the CCM layer

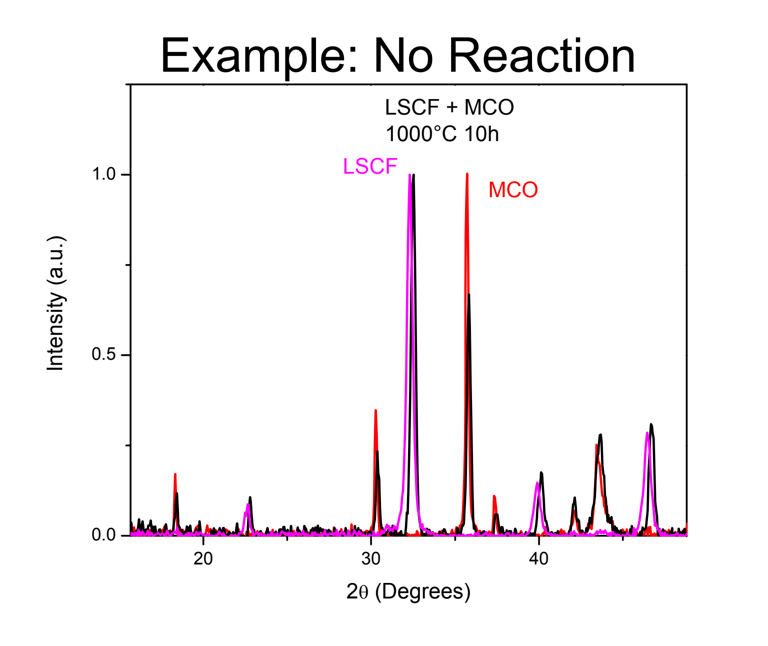
(not necessarily related to bonding at the interface with neighbor layers)

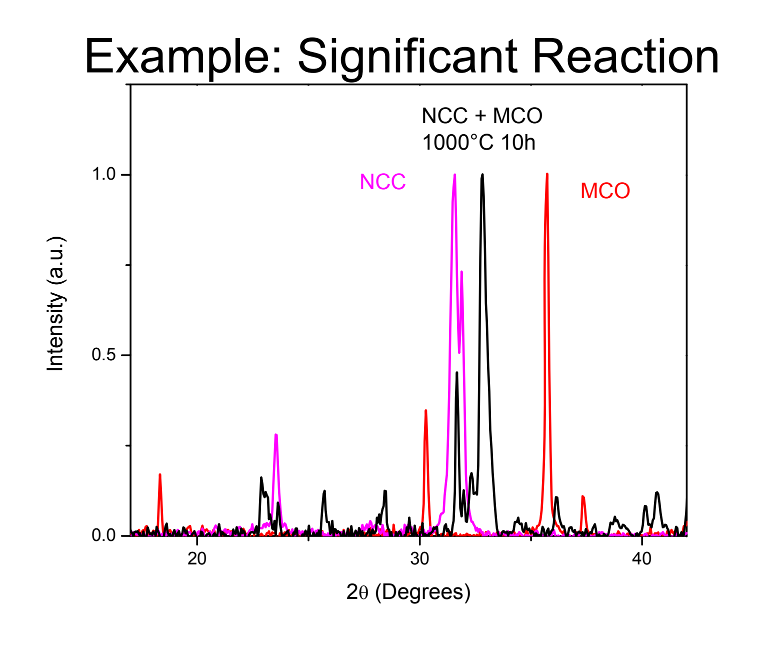
- Only a few candidates display significant sintering in the 900-1000°C range



Reactivity with Neighbor Materials

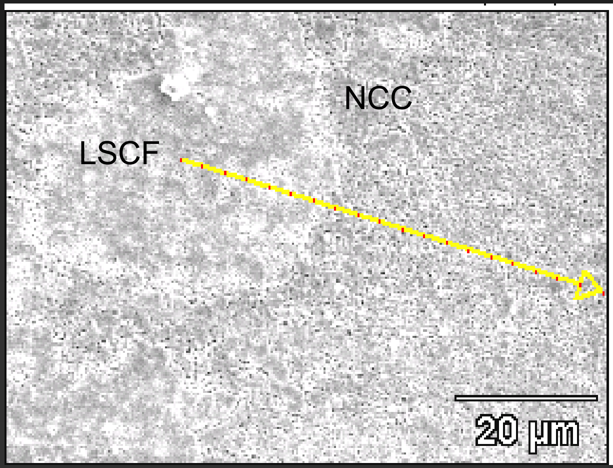
Pellets of mixed MCO/CCM and LSCF/CCM
Reacted in air at: Operating conditions (800°C 120h) and Sintering conditions (1000°C 10h)

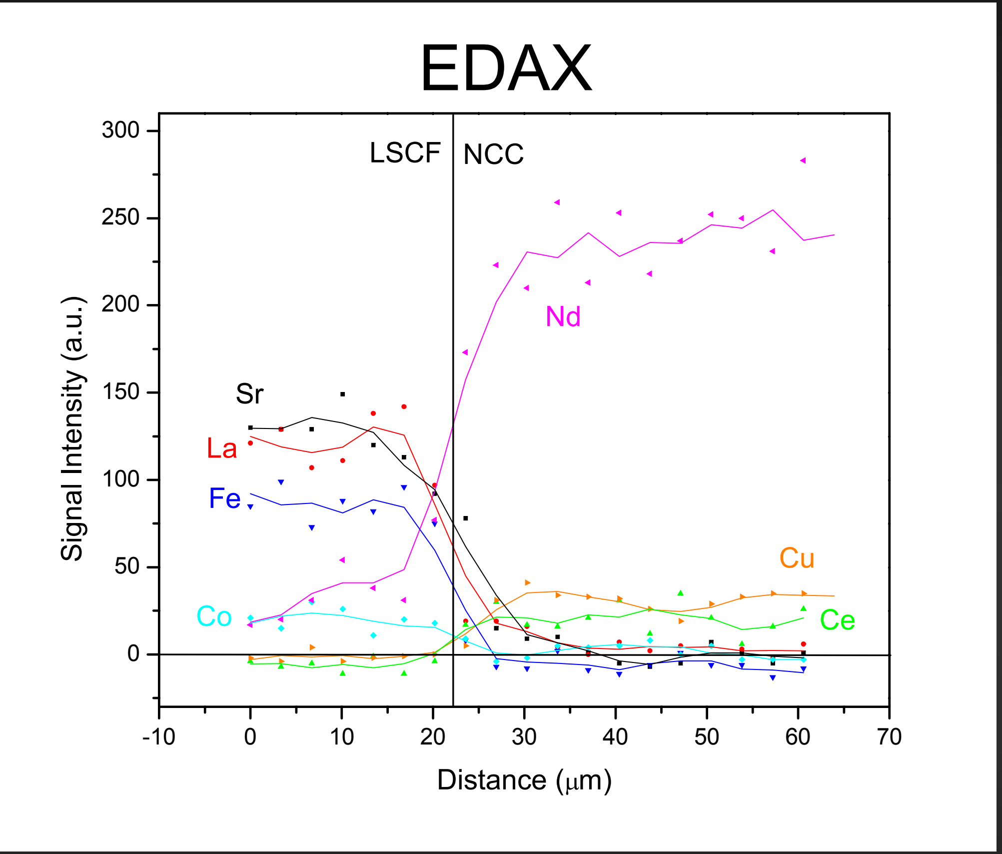




Most candidates were non-reactive with MCO, but reacted with LSCF

Reaction/Diffusion Distance





In all cases, reaction zone restricted to <40μm

→ reaction may be acceptable for

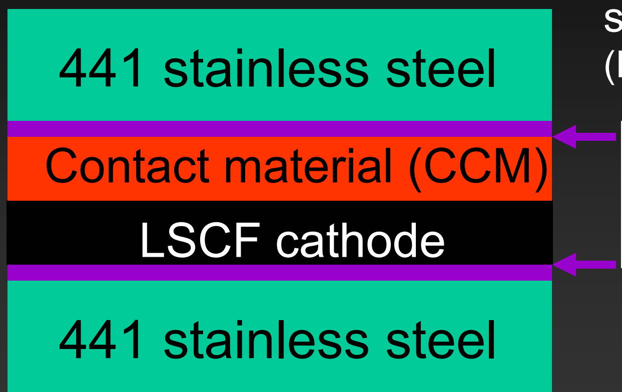
- thick LSCF layer
- electrically conductive reaction products

Screening Summary

	Incipient Sintering Point (°C)	Shrinkage at 900°C	Shrinkage at 1000°C	CTE at 800°C	Reacts with MCO? 800°C 150h	Reacts with MCO? 1000°C 10h	Reacts with LSCF? 800°C 150h	Reacts with LSCF? 1000°C 10h	Conductivity of bulk dense pellet 800°C (S/cm)
LSCF	637	2.7	7.6	17.3	NO	NO	N/A	N/A	426
LSCuF	820	1.1	10.1	15.5	NO	NO	NO	NO	201
LSC	677	1.1	3.3	18.7	NO	NO	Minor	Minor	1702
SSC	740	0.5	2.3	22	NO	Trace	NO	NO	1338
SBSC	708	1.6	3.4	22	NO	Trace	YES	YES	458
GSC	760	1.3	3.2	19.5	NO	Trace	YES	YES	350
LSM	784	0.7	3.3	12.8	NO	NO	YES	YES	272
LBC	770	0.7	2.3	25	NO	NO	Minor	Minor	314
YBC	689	1.7	3.8	16.8	NO	YES	YES	YES	260
NCC	657	1.5	5.5	14.5	YES	YES	YES	YES	107
LSCMF	786	0.4	2.1	17.6	NO	NO	N/A	N/A	110
LNF	932	0	1.1	13.8	NO	NO	YES	YES	589
LSN	975	0	0.1	13.5	Minor	YES	NO	NO	352
LSF	690	0.3	0.9	13.3	NO	NO	NO	NO	133
LNC	782	0.4	2.4	14.6	NO	NO	NO	NO	11

The most promising candidates are:
- LSCF: good sintering and moderate conductivity
- LSCuF: very good sintering at 1000°C
- LSC and SSC: extremely high conductivity, moderate sintering

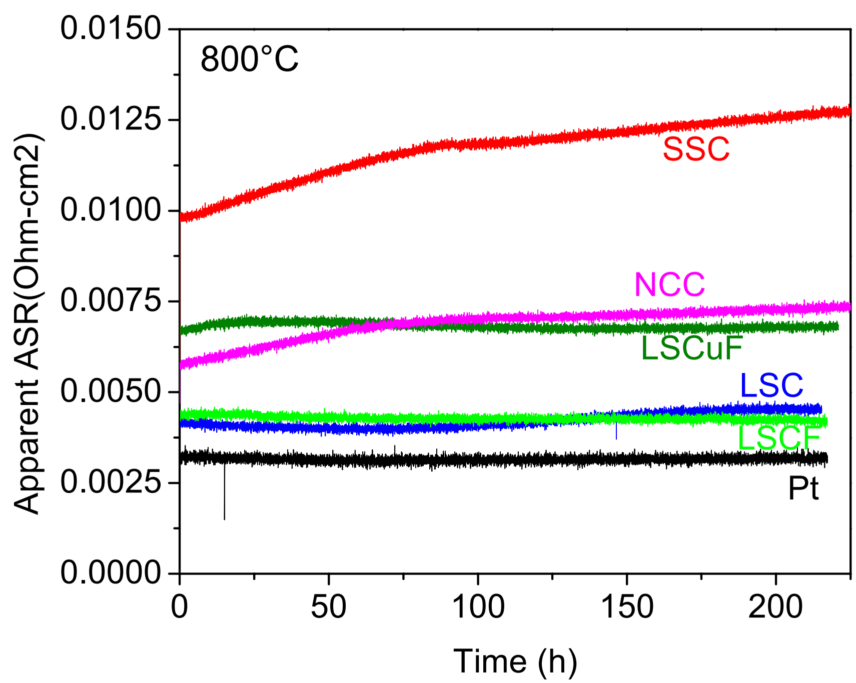
ASR Measurement



screen printed CCM and LSCF
(PNNL ink recipe)

$(MnCo)_3O_4$ coating
Prepared at PNNL

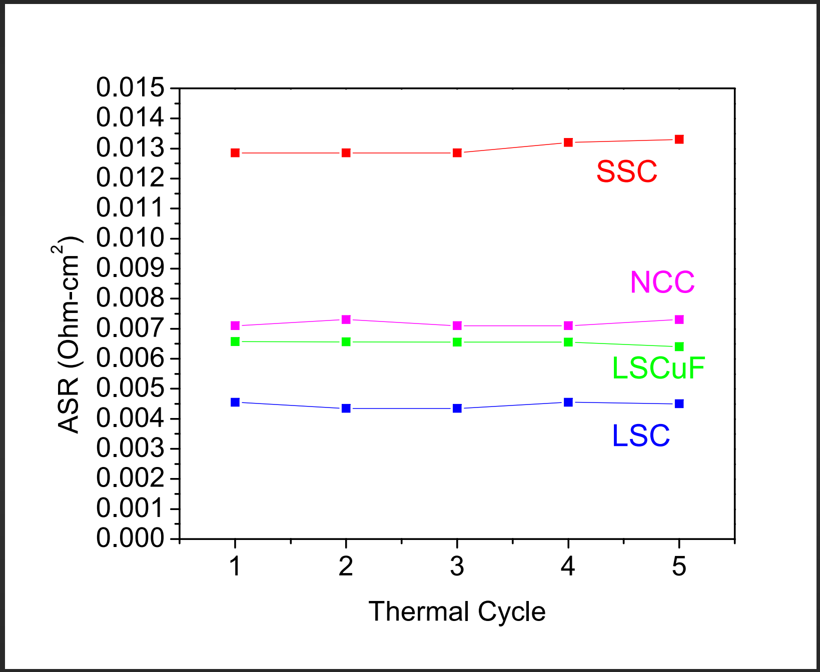
No compressive load



NCC, LSC, LSCF and LSCuF show low and stable ASR

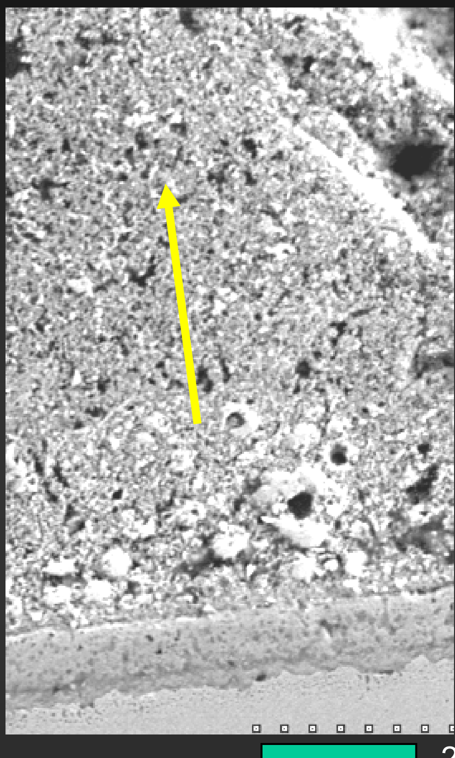
Thermal Cycling

21-800°C 10°C/min

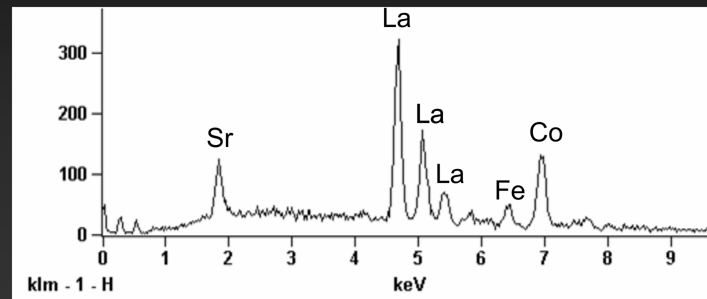


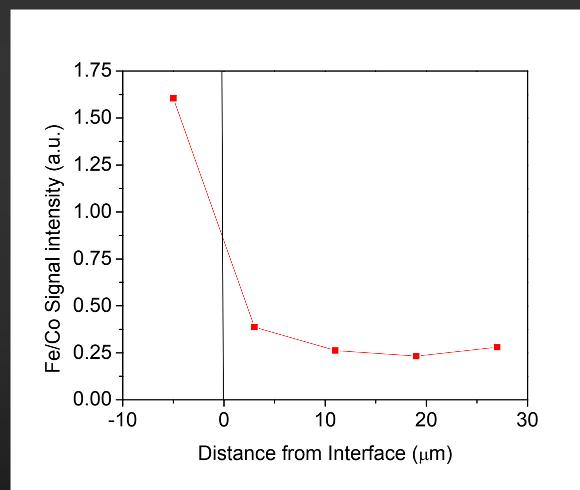
No obvious delamination despite wide range of CTE

LSC Post-Mortem



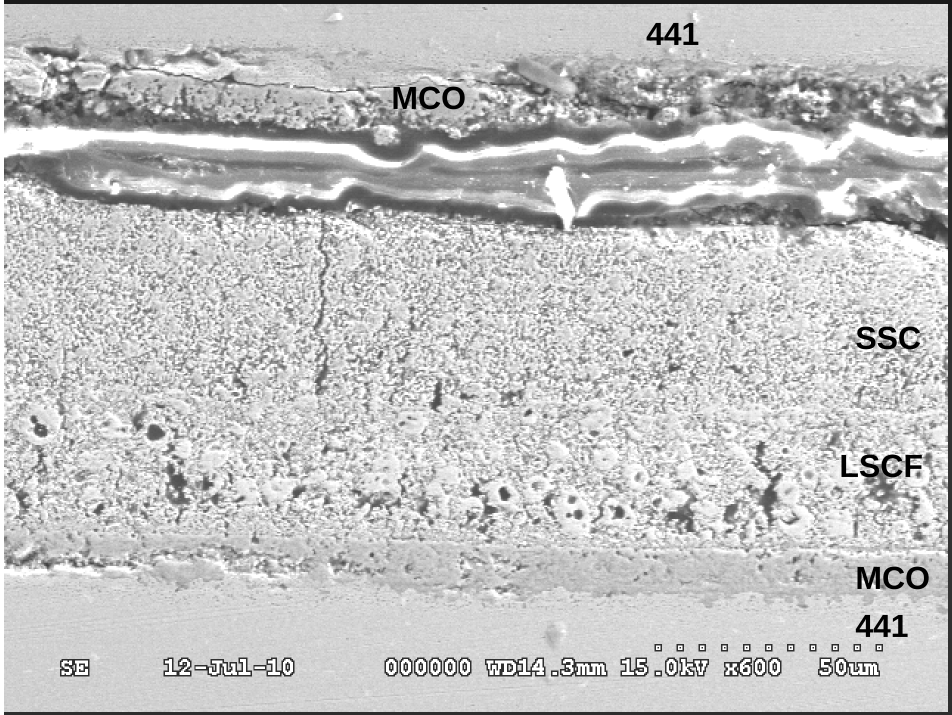
Good bonding at LSC/LSCF interface





Minor diffusion of Fe into LSC

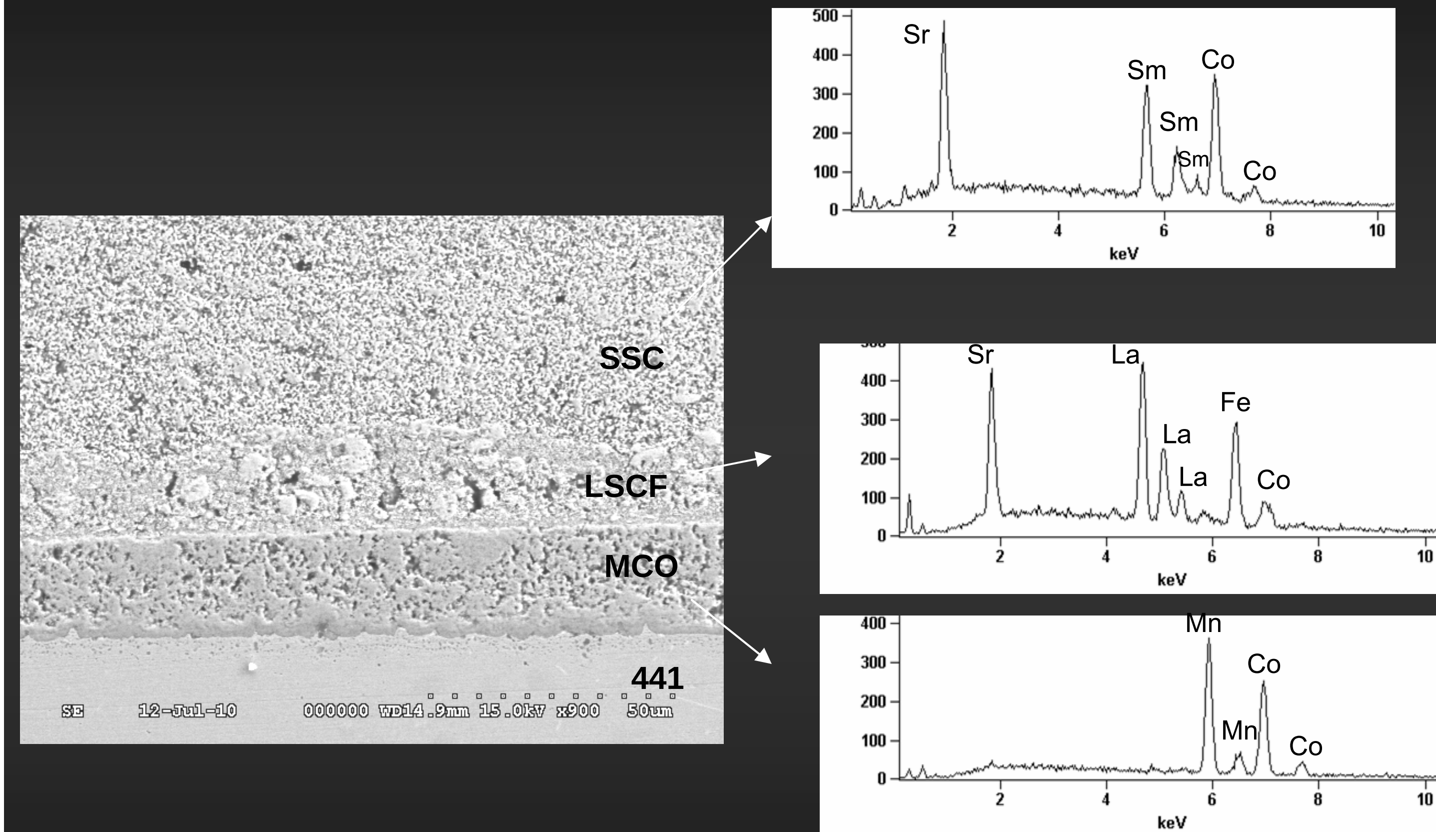
SSC Post-Mortem



Delamination at SSC/MCO interface (during sample prep?)

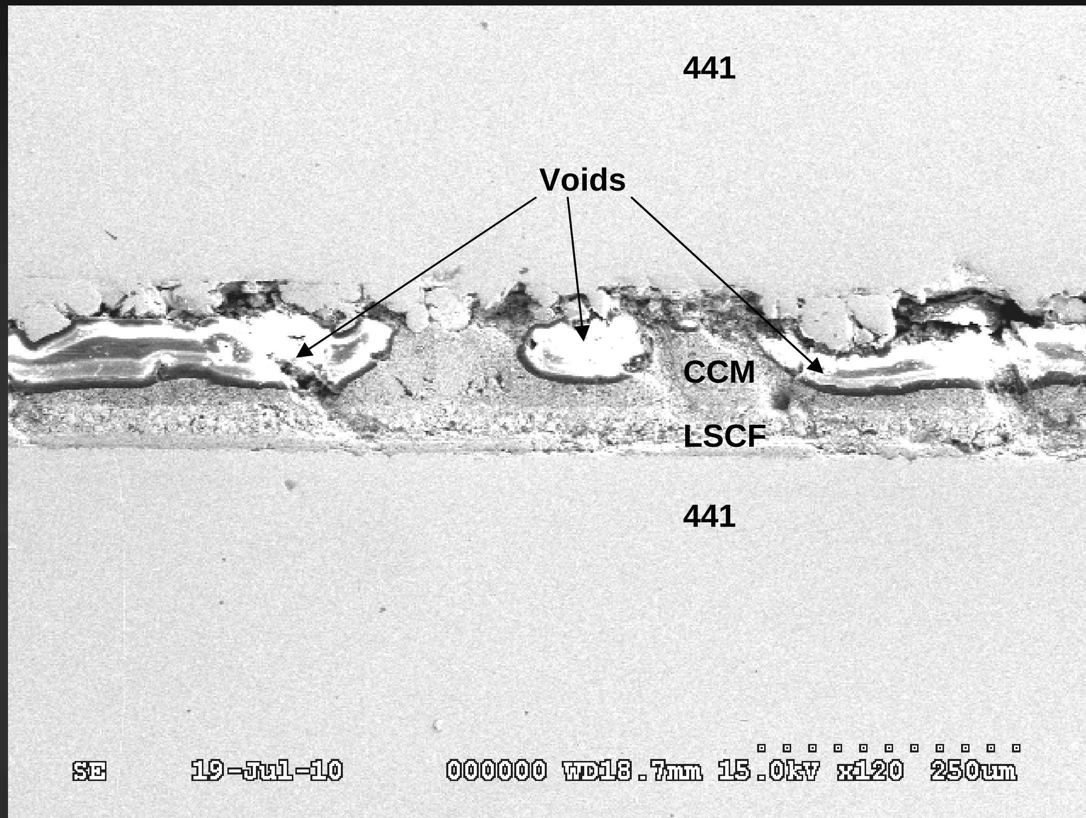
Good bonding at SSC/LSCF interface

SSC Post-Mortem



No interdiffusion detected in bulk layers

CCM Layer Uniformity



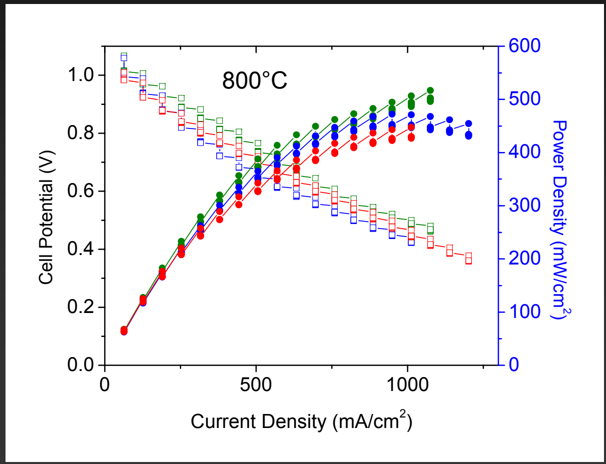
- Wet-print on both substrates and assemble
- Voids created during solvent burnout?

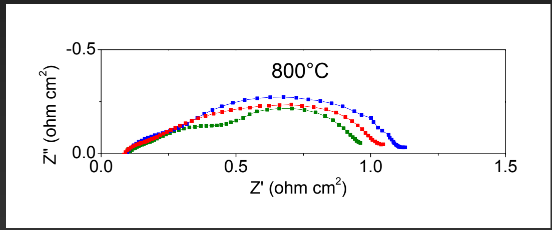
→ Develop alternative processing to ensure uniform contact

- Print / dry / assemble
- Print / dry print / assemble

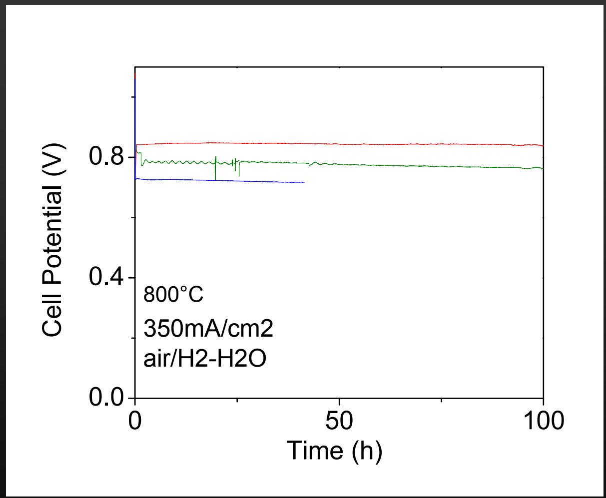
Commercial Cell Selection

Tape-cast cells from NIMTE
www.sofc.com.cn





- $24 each for 25 cell batch
- 350-425mW/cm^2 at 0.7V
- 25-38%/1000h degradation



Future Directions

- Mix LSC (high conductivity) with LSCuF (good sintering)

- Sintering aids to improve bonding and mechanical properties after firing at 1000°C

- Identify new candidates from outside the SOFC world

- Reactive sintering

- Improve uniformity of CCM printing procedure

- In-depth post-mortem analysis

Thanks to Joe Stoffa and Briggs White

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