Imperial College
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SOFC Cathodes, Supports and Contact Layers

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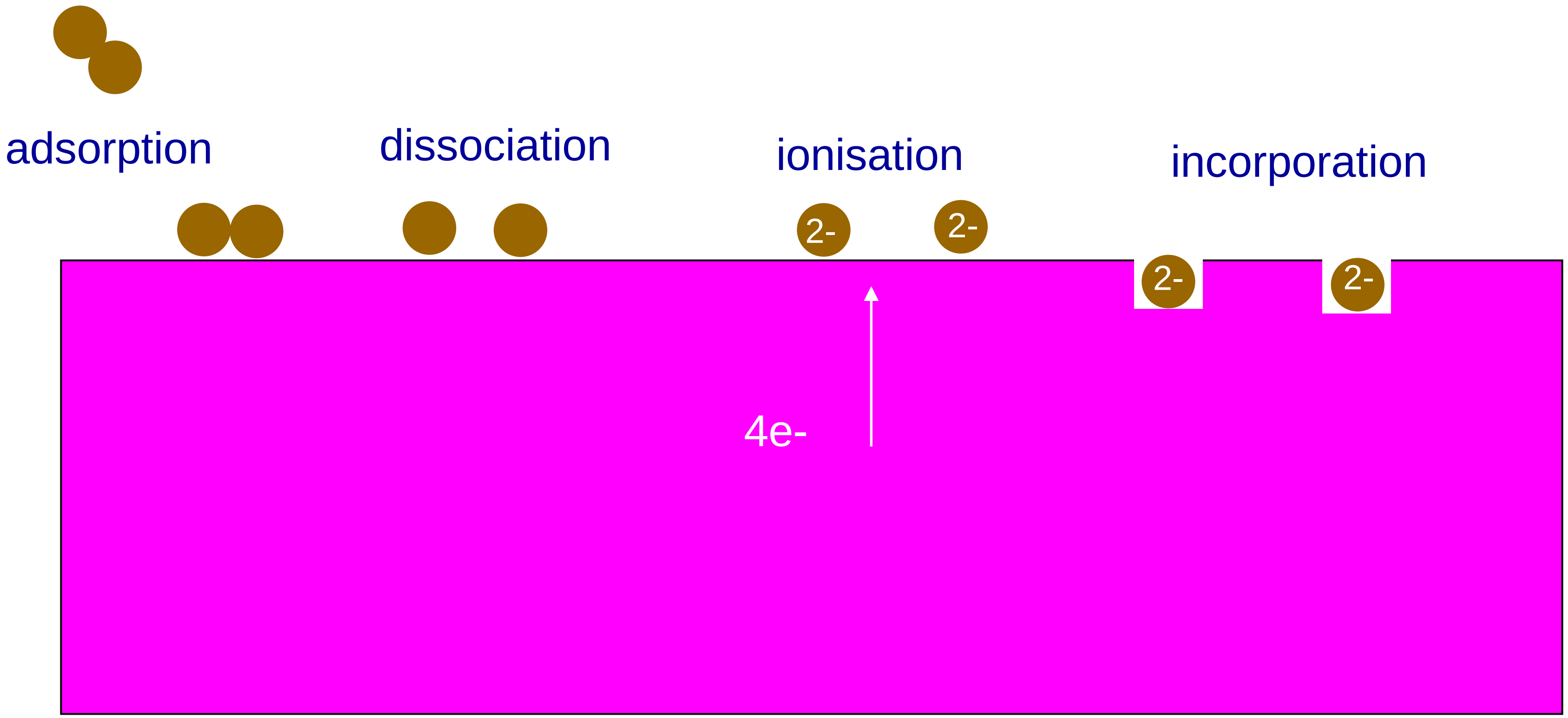
Contents for cathodes

- Requirements for application in SOFCs
- LSM based cathodes
  - defects in TM perovskites
  - temperature limitations
- Mixed conducting cathodes
- Oxygen diffusion and exchange
- Drive for lower operating temperatures
- Contamination and durability issues
  - Cr poisoning
  - water vapour sensitivity
  - surface segregation

Review: S. B. Adler, "Factors governing oxygen reduction in solid oxide fuel cell cathodes", Chemical Reviews, **104**, 4791-4844 (2004)

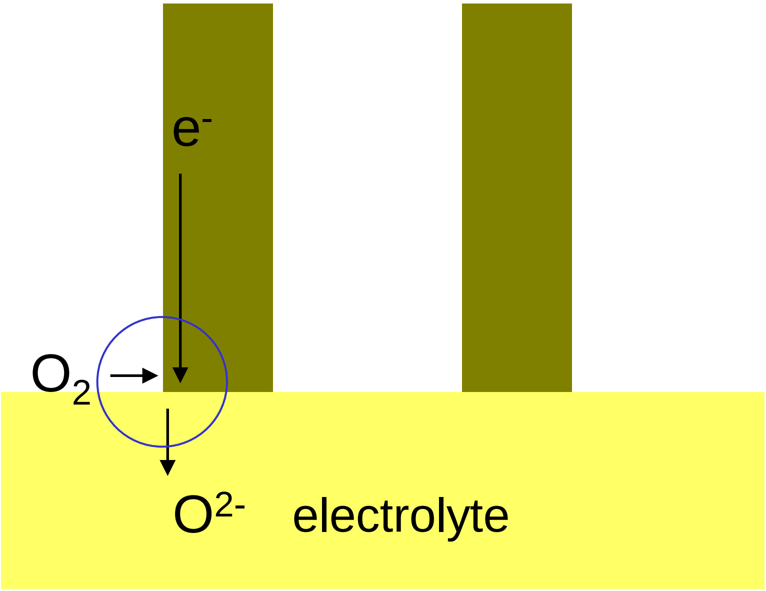
Oxygen reduction reaction



Oxygen vacancies are required for surface reaction as well as for bulk diffusion

Electrons are required for ionisation

Triple phase boundary electrodes



•Electrocatalyst has high electronic conductivity, but low ionic conductivity

•Reaction site is “at” triple phase boundary

•LSM cathodes typical example

•Composites with good ionic conductor used to improve performance (e.g. LSM/YSZ cathodes)

•Capacitance is low (e.g. 10^{-5} F cm^{-2})

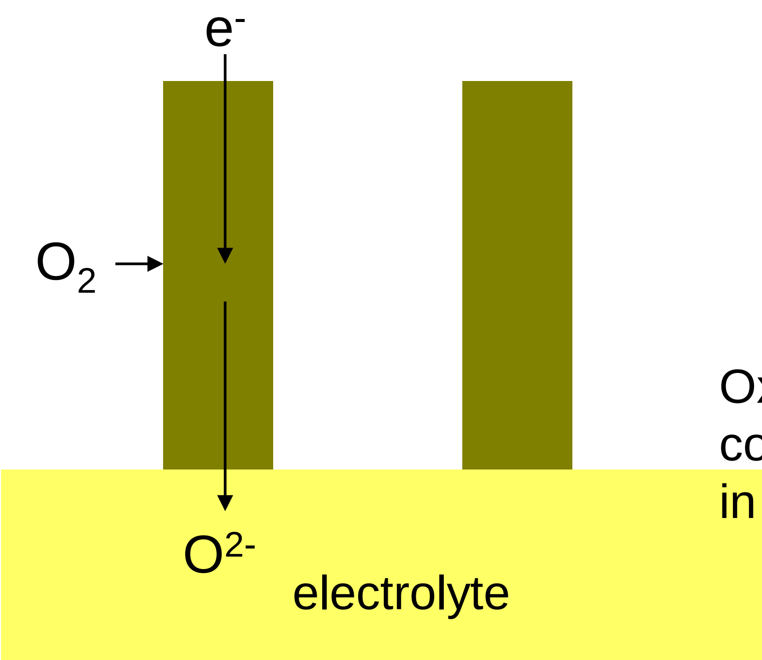
•Cathode reaction requires both electronic and (oxygen) ionic defects

•In oxides this means transition metal constituents and oxygen non-stoichiometry (vacancies or interstitials)

Working overpotentials can change oxide stability or properties

Theory for porous single phase cathode

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



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

- tortuosity (τ)
- porosity (ε)
- volume specific surface area (a)
- Oxygen ion concentration in solid (c_O)
- Oxygen tracer diffusion coefficient (D^*)
- Oxygen surface exchange rate constant (k^*)

•Microstructure is very important (a, ε, τ)

Only gives ASR close to open circuit conditions (when gas and solid are close to being in equilibrium).

Targets

$$R_{Chem} = \left(\frac{RT}{4F^2}\right)\sqrt{\frac{\tau}{(1-\varepsilon)ac_0^2 D^* k^*}}$$

Cathode

ASR = 0.15 ohm cm^2

For τ = 2, ε = 0.3, a = 10^7 m^{-1}, T = 1000K

Then $D^*k^* > 10^{-14}$ cm^3 s^{-1}

(Note: an ionic conductivity of 0.01 S/cm corresponds to $D^* = 2 \times 10^{-8}$ cm^2 s^{-1})

e.g. **$D^* > 10^{-8}$ cm^2 s^{-1} and $k^* > 10^{-6}$ cm s^{-1}**

For current collection need high electronic conductivity (e.g. 100s S/cm)

5 mm channels

σ>1,000 S cm^{-1}

All require chemical and thermo-mechanical stability (CTE match)

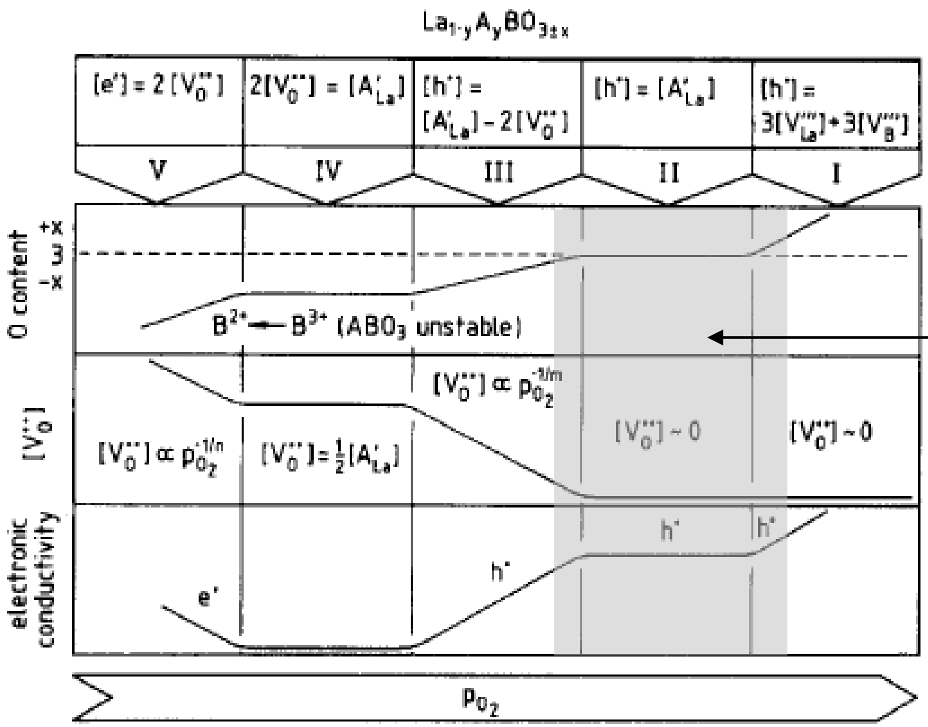
Defects in TM perovskites e.g. $La_{1-x}Sr_xMnO_3$ (LSM)

Acceptor doping $$2SrO \rightarrow 2Sr'_{La} + 2O_O^{\times} + V_O^{\bullet\bullet}$$

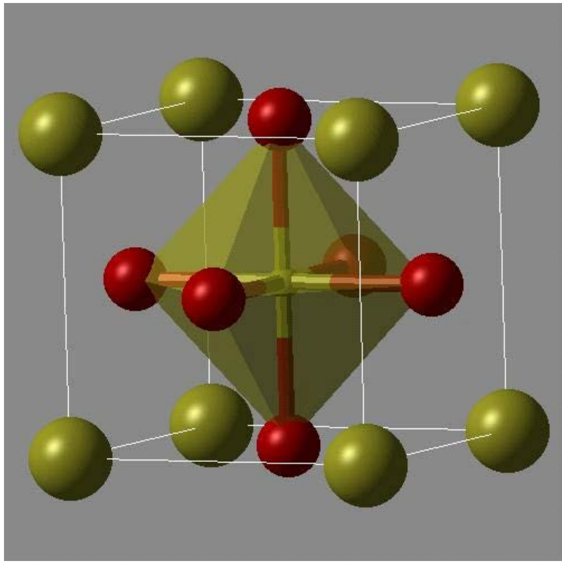
Reduction $$O_O^{\times} \rightarrow V_O^{\bullet\bullet} + 2e^- + \tfrac{1}{2}O_2(g)$$

Electronic $$null \rightarrow e' + h^{\bullet}$$ Mn valency change

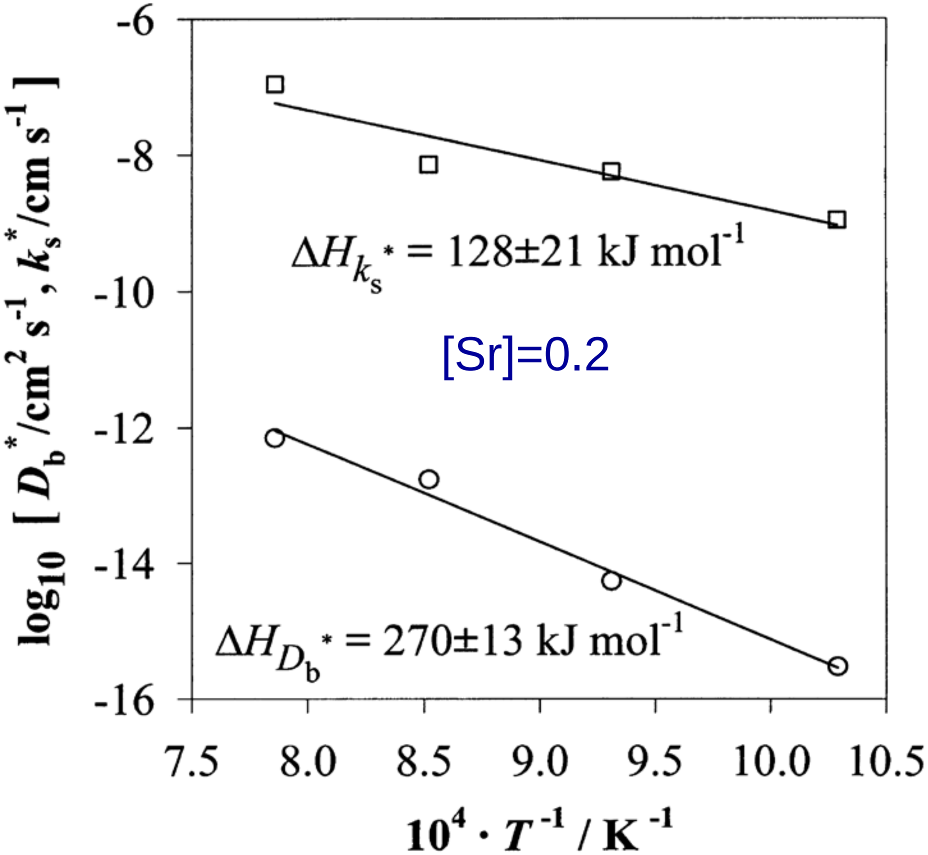
Schottky $$null \rightarrow V'''_{La} + V'''_{Mn} + 3V_O^{\bullet\bullet}$$

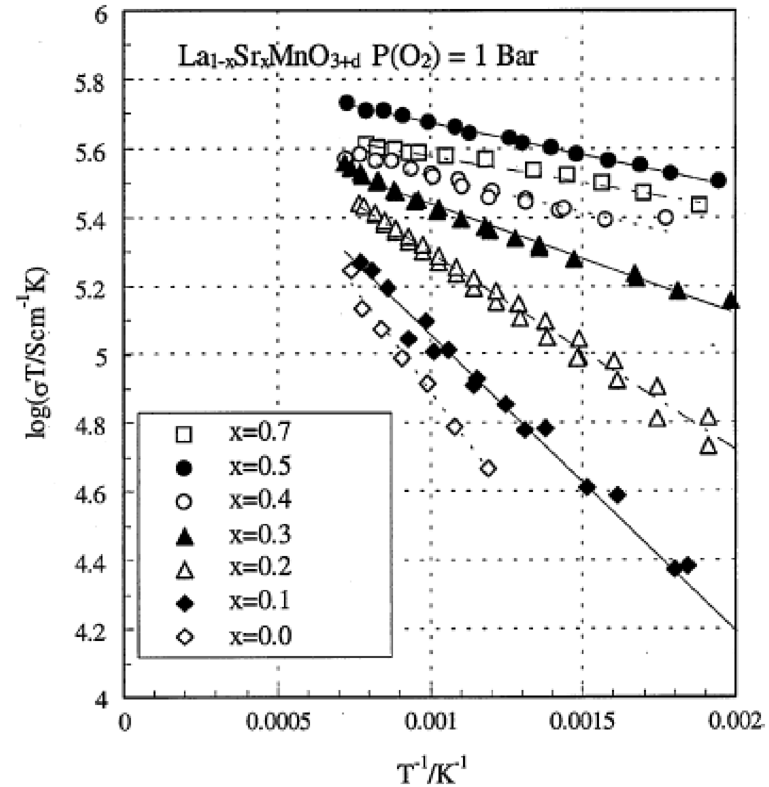


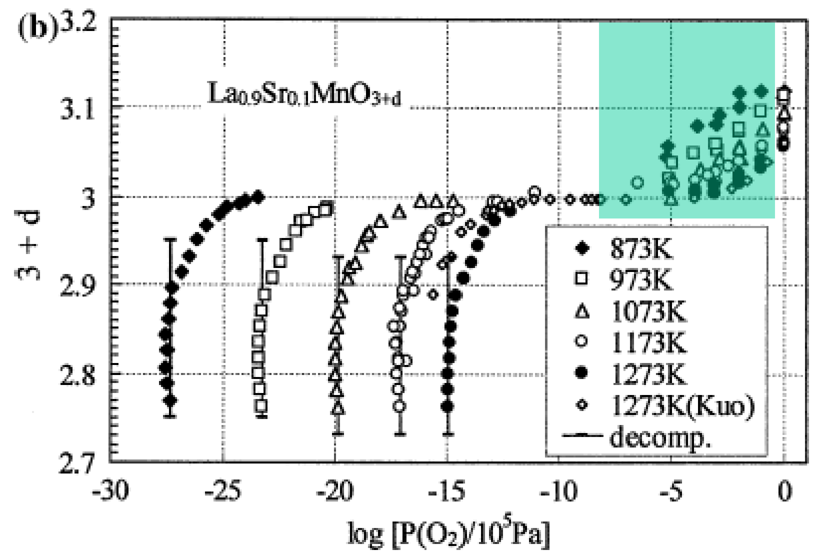
LSM in this range



Properties of LSM





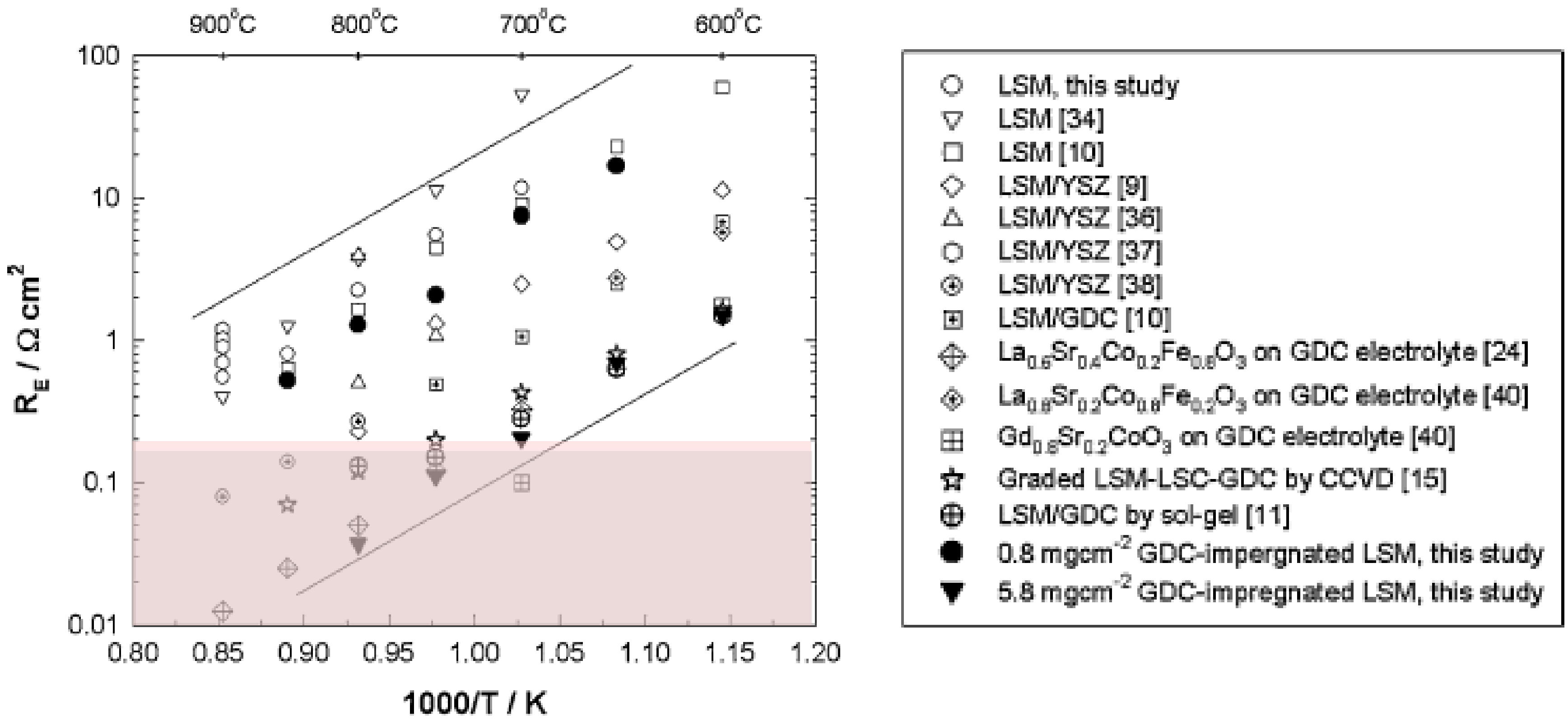


D too low for single phase cathode

Need electrolyte (YSZ) to provide ionic conductivity and vacancies for oxygen reaction

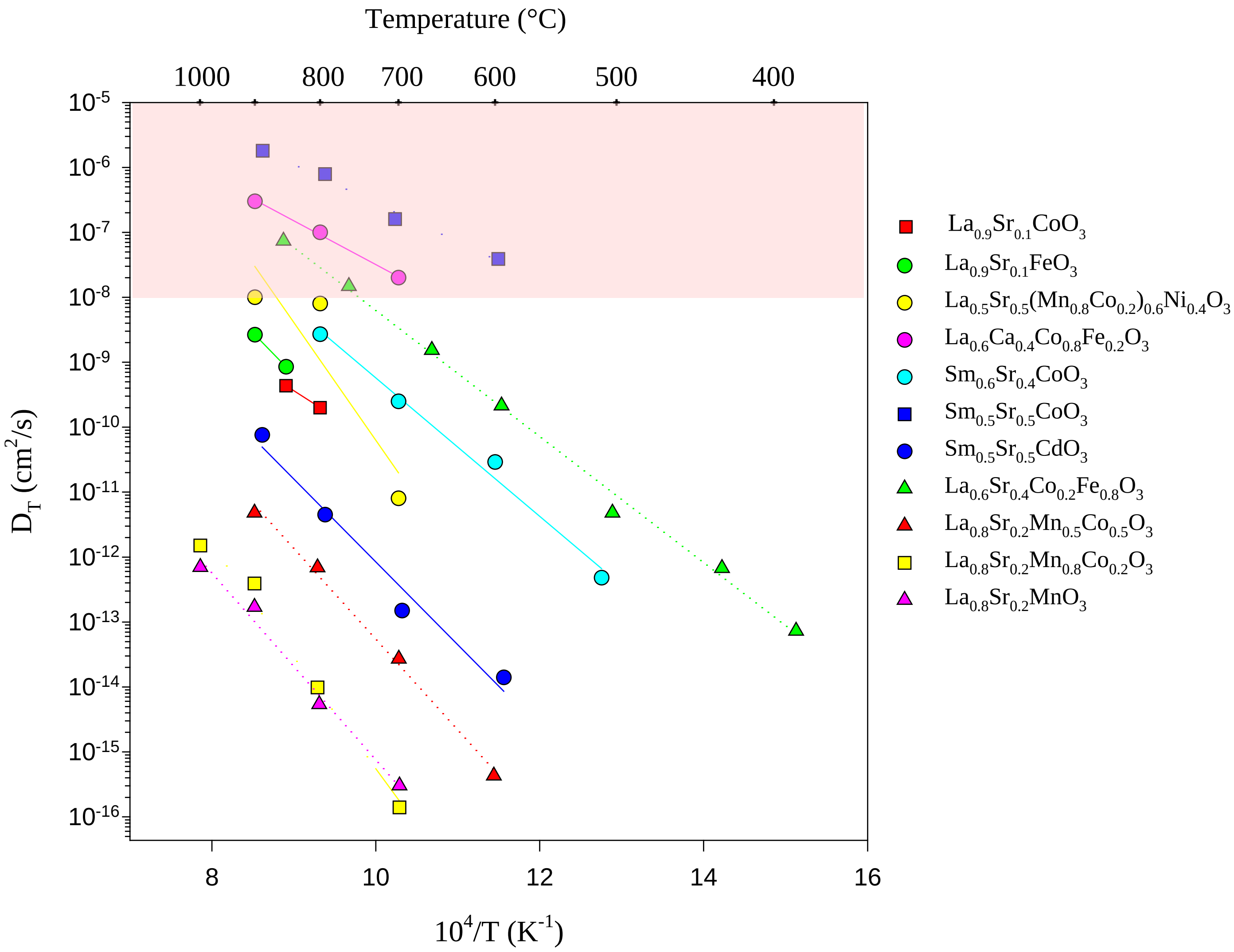
LSM-based cathodes

Review: S.P. Jiang, J. Mat. Sci. 43 (2008) 6799



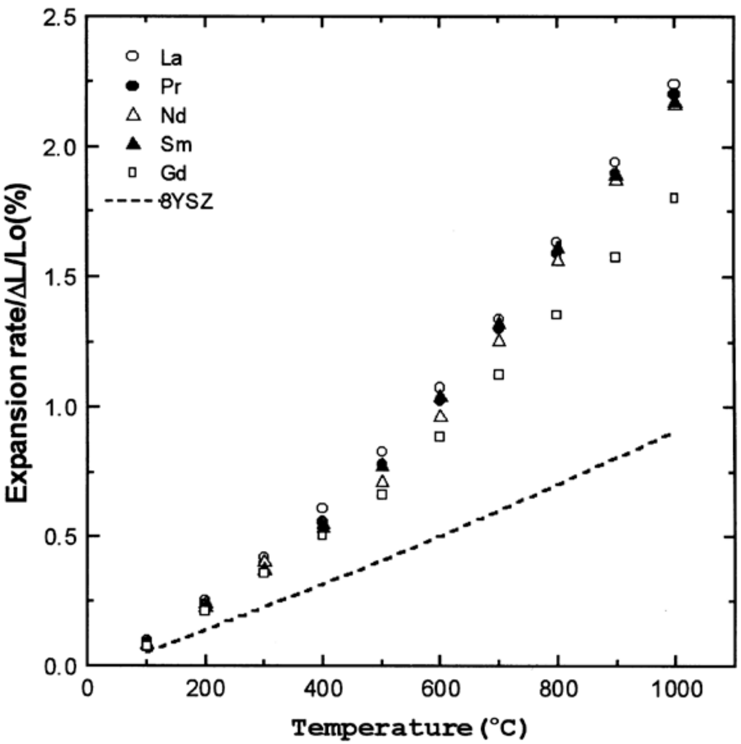
- Microstructure is very important (particle size, mixing, sintering temperature)
- Compatible with YSZ (if A-site deficient)
- Good CTE match to YSZ
- Lowest operating T about 800C
- "Conditioning" on initial polarization (initial improvement in performance) probably due to changes in surface composition

Oxygen diffusion in TM perovskites



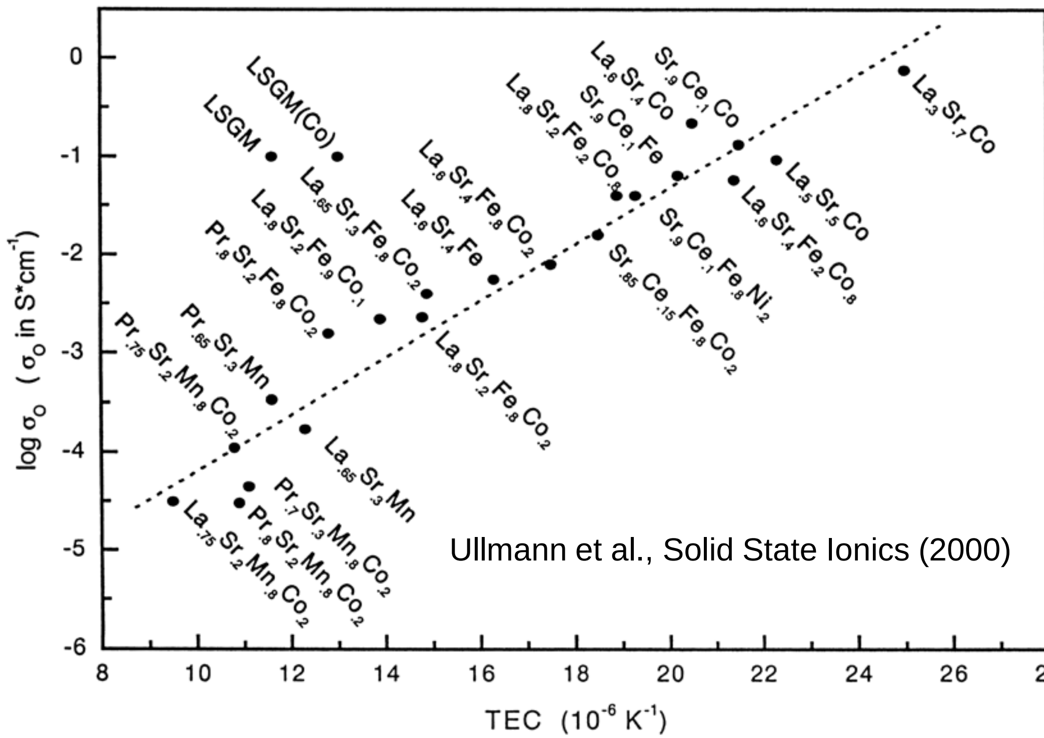
Co-containing cathodes

O vacancies that give high diffusivity also give high CTE



$Ln_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3-\delta}$

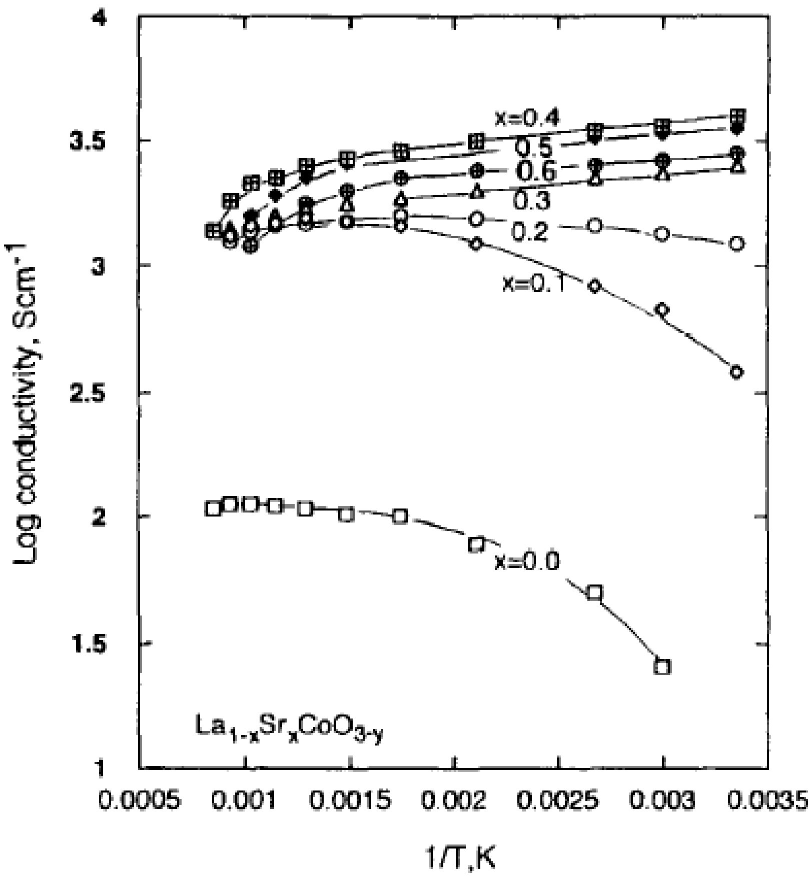
Tu et al., Solid State Ionics 117 (1999) 277–281



Ullmann et al., Solid State Ionics (2000)

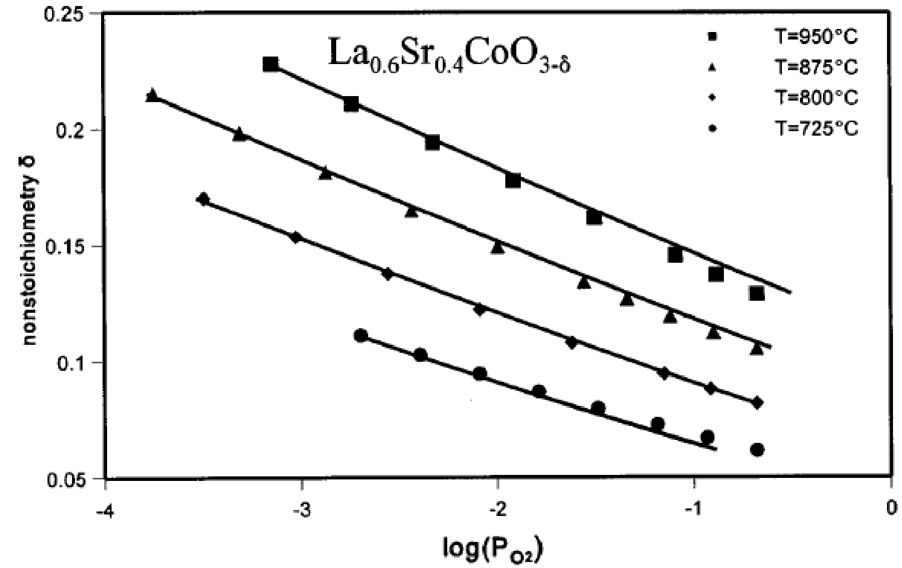
- React with zirconia electrolytes
- Need an intermediate barrier layer (e.g. CGO)

Defects in $La_{1-x}Sr_xCoO_{3-\delta}$

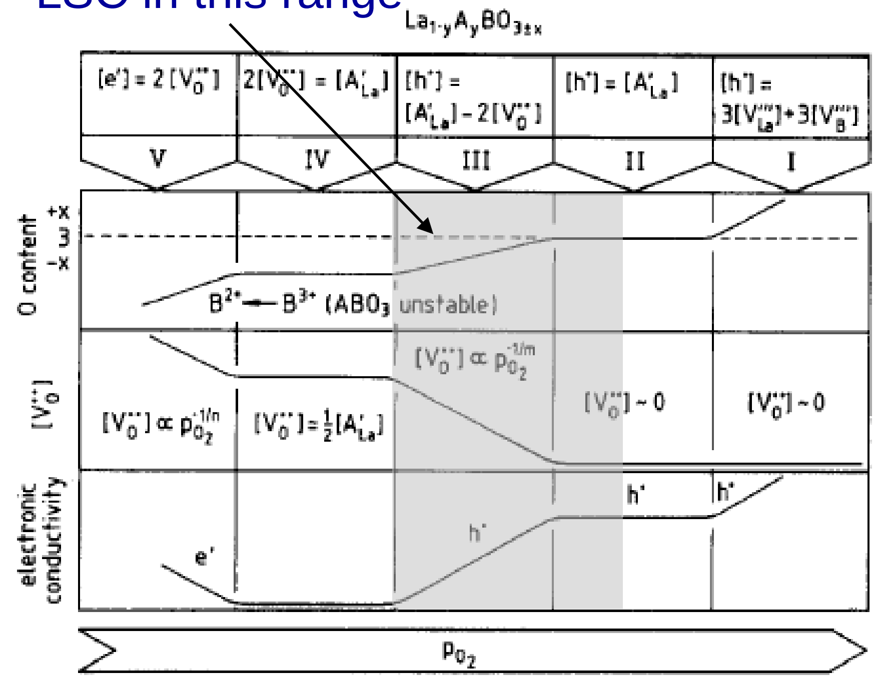


Sr increases conductivity and induces metallic behaviour

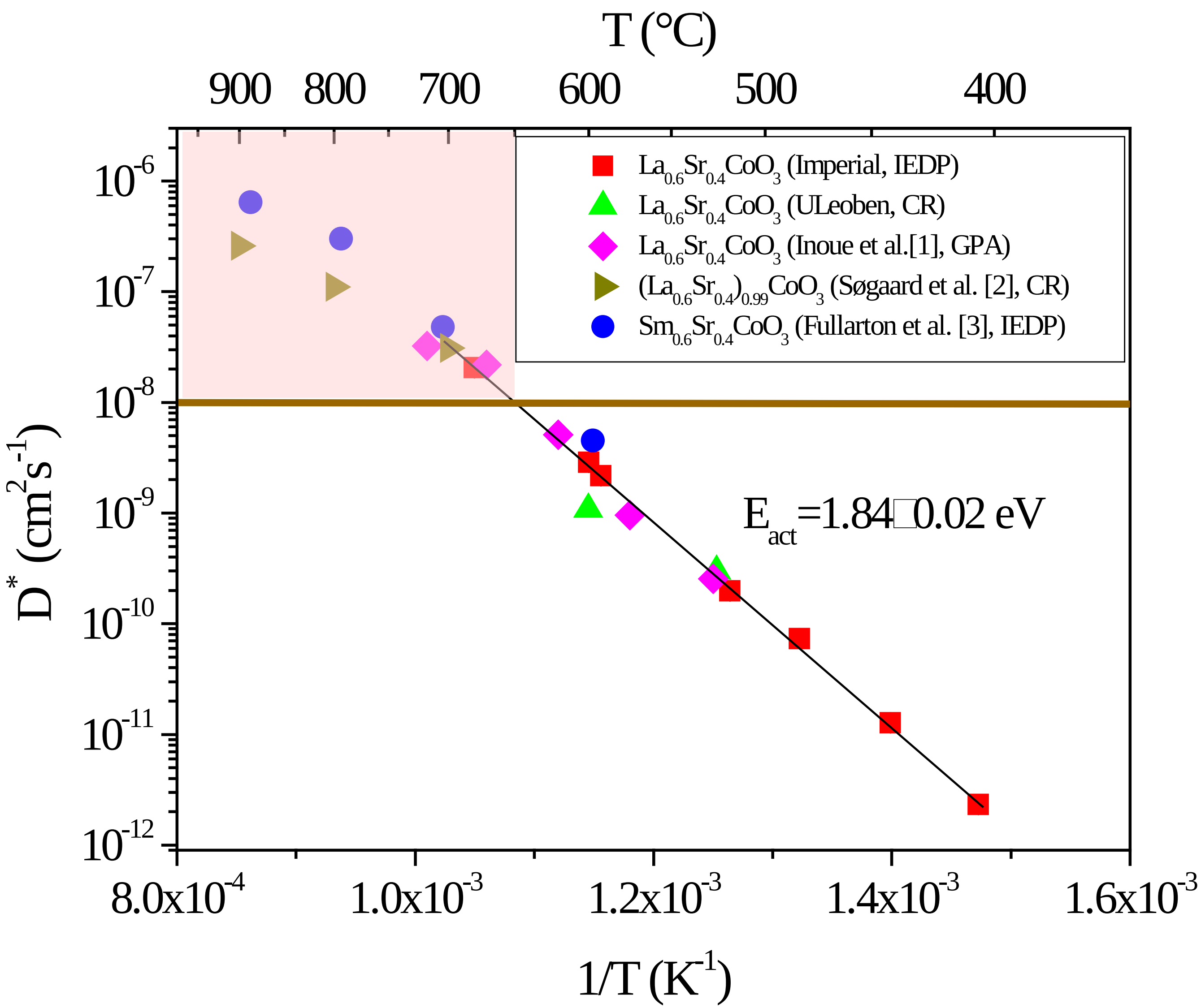
A.N. Petrov et al., Solid State Ionics (1995)



LSC in this range



Oxygen diffusion in $La_{0.6}Sr_{0.4}CoO_3$ at p_{O2}=0.21 atm

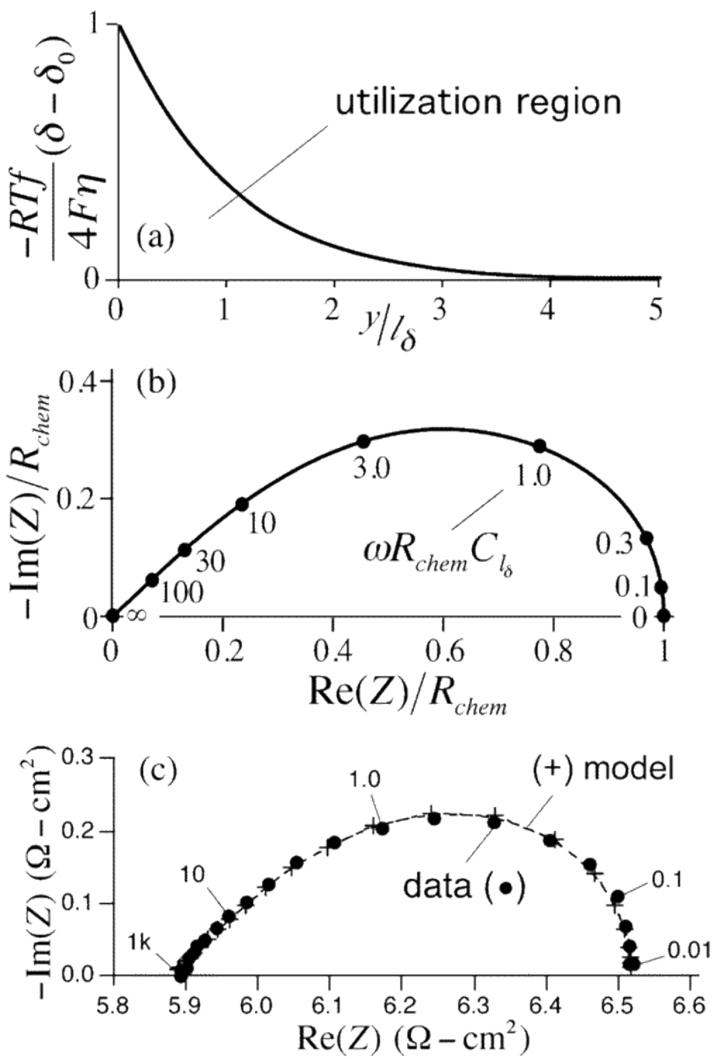


(1) Inoue, T., Kamimae, J., Ueda, M., Eguchi, K. & Arai, H. *Journal of Materials Chemistry 3, 751 - 754 (1993).*

(2) Sogaard, M., Hendriksen, P. V., Mogensen, M., Poulsen, F. W. & Skou, E. *Solid State Ionics 177, 3285-3296 (2006).*

(3) Fullarton, I. C., Kilner, J. A., Steele, B. C. H. & Middleton, P. H. in *2nd International Symposium on Ionic and Mixed Conducting Ceramics (eds. Ramanarayanan, T. A., Worrell, W. L. & Tuller, H. L.) 9-26 (The Electrochemical Soviety, San Francisco, 1994).*

ALS model for MIEC porous electrode



$$l_\delta = \sqrt{\frac{D^*}{k^*}\frac{(1-\varepsilon)}{a\tau}}$$

Effective cathode thickness increases with D and decreases with k and is usually < 10 μm

$$Z_{chem} = R_{chem}\sqrt{\frac{1}{1 + j\omega R_{chem} C_{chem}}}$$

"Gerischer impedance"

$$t_{chem} = \frac{c_V}{c_O A}\frac{(1-\varepsilon)}{a}\frac{1}{k^*}$$

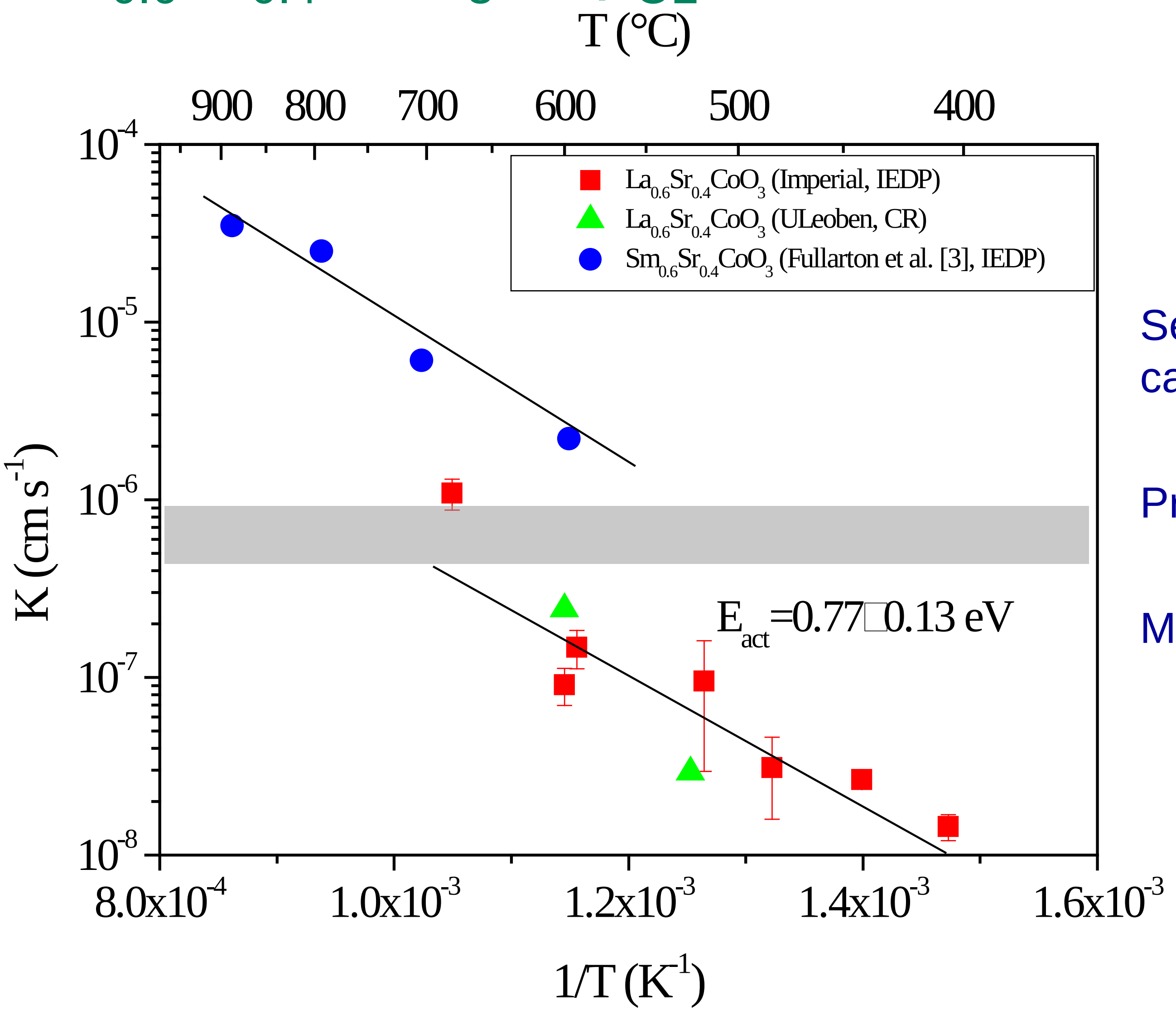
$$C_{chem} = \frac{2F^2(1-\varepsilon)}{ART} c_V l_\delta$$

Large chemical capacitance controlled by deviation from stoichiometry, c_V (e.g.1F/cm^2)

A is a thermodynamic factor for defects and is close to unity

Data for $La_{0.6}Ca_{0.4}Co_{0.2}Fe_{0.8}O_3$ on SDC at 700°C (Adler et al. J. Electrochem Soc., 1996)

Surface exchange in $La_{0.6}Sr_{0.4}CoO_3$ and $Sm_{0.6}Sr_{0.4}CoO_3$ at p_{O2}=0.21 atm

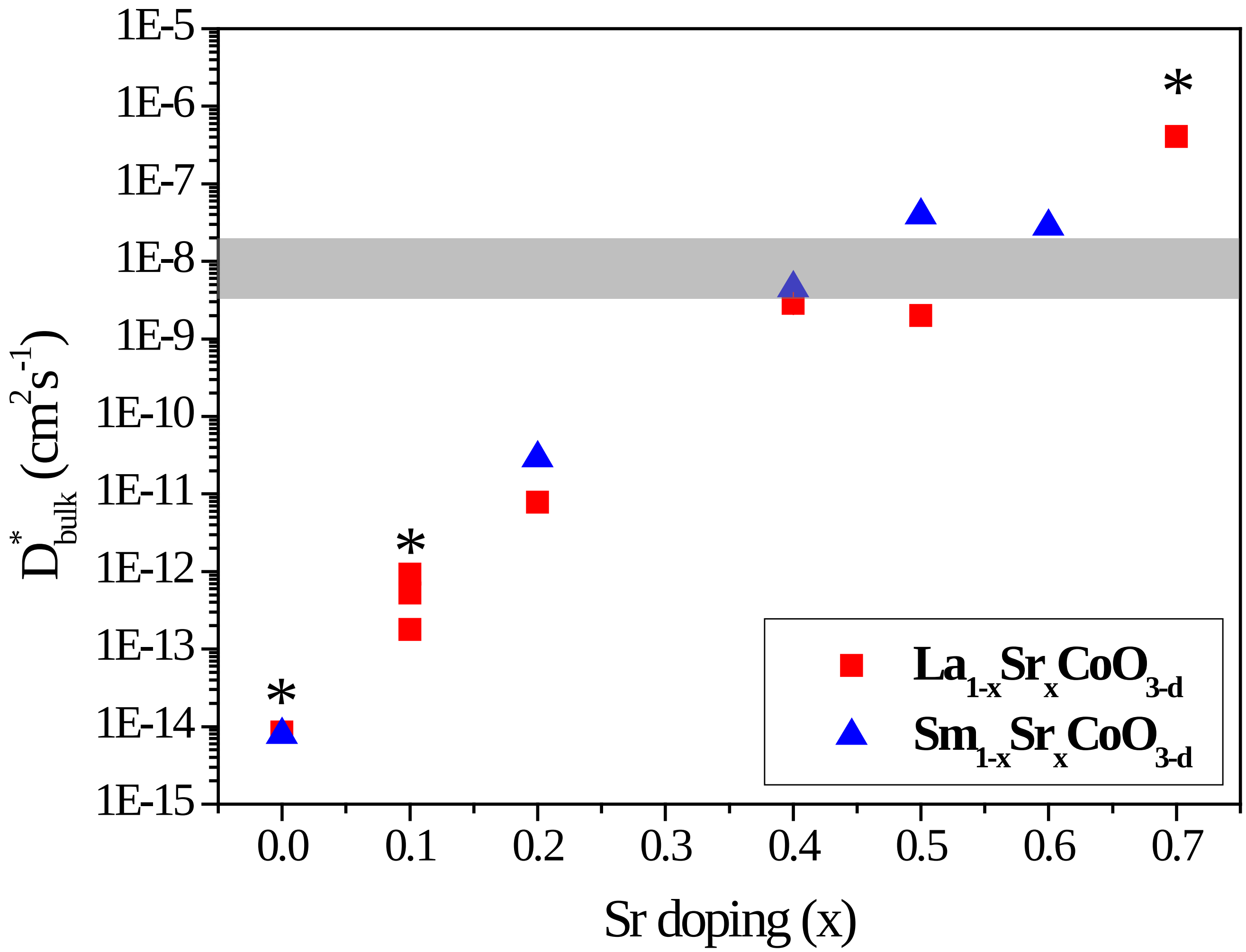


Sensitive to rare-earth cation

Predicted E_a for R_p=1.4eV

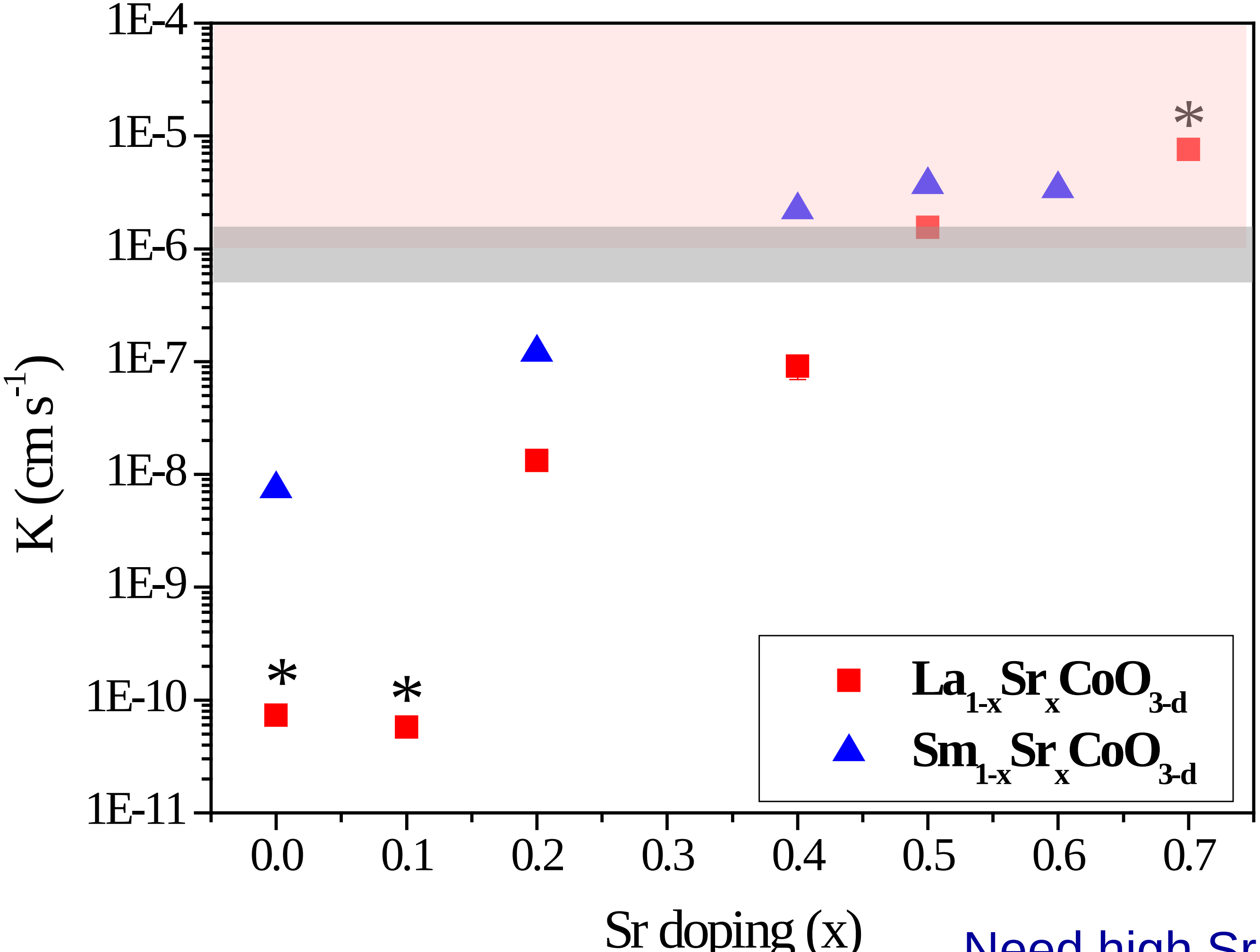
Measured is 1.1eV

D* in LSC at 600°C



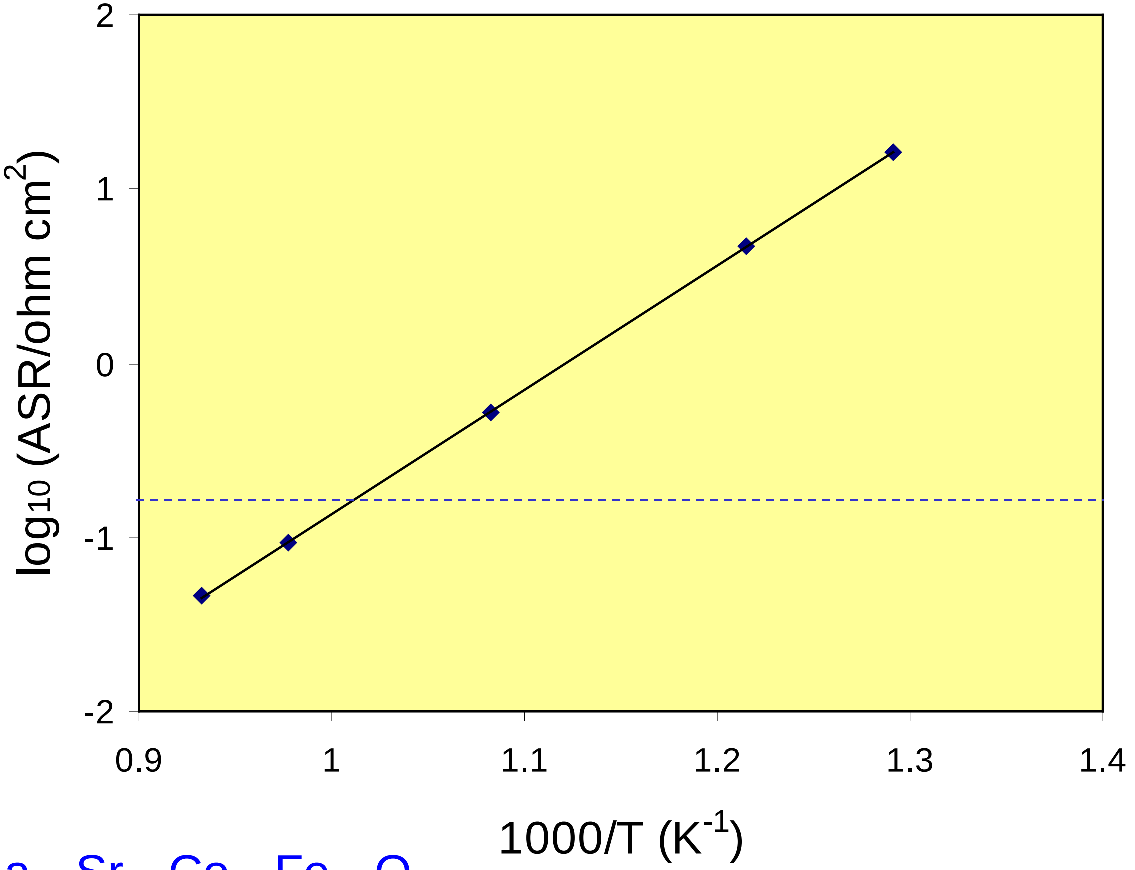
* Extrapolated from higher T

k* at 600°C



Need high Sr content

Low temperature composite cathodes



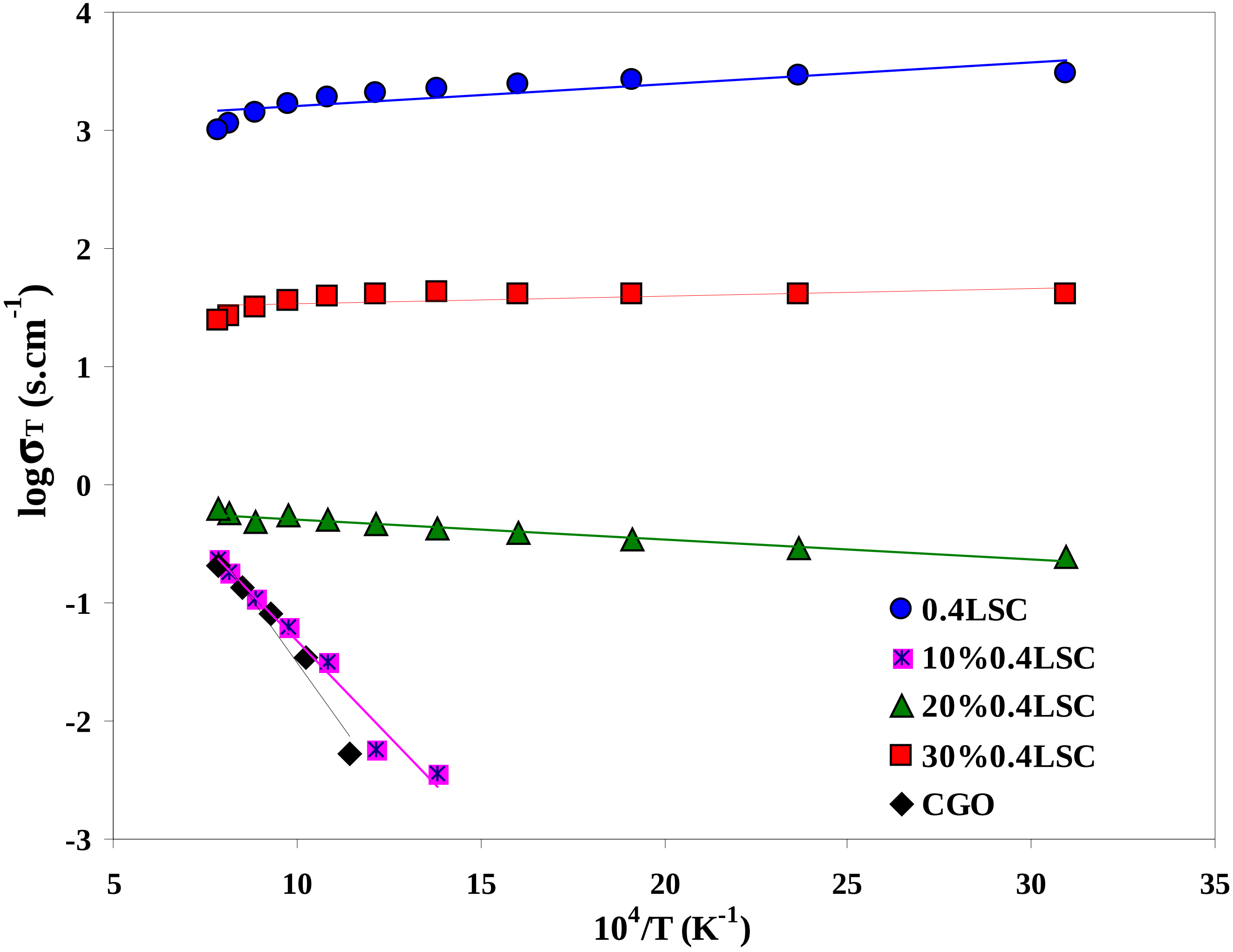
70% $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$

30% $Ce_{0.8}Gd_{0.2}O_2$

Composite

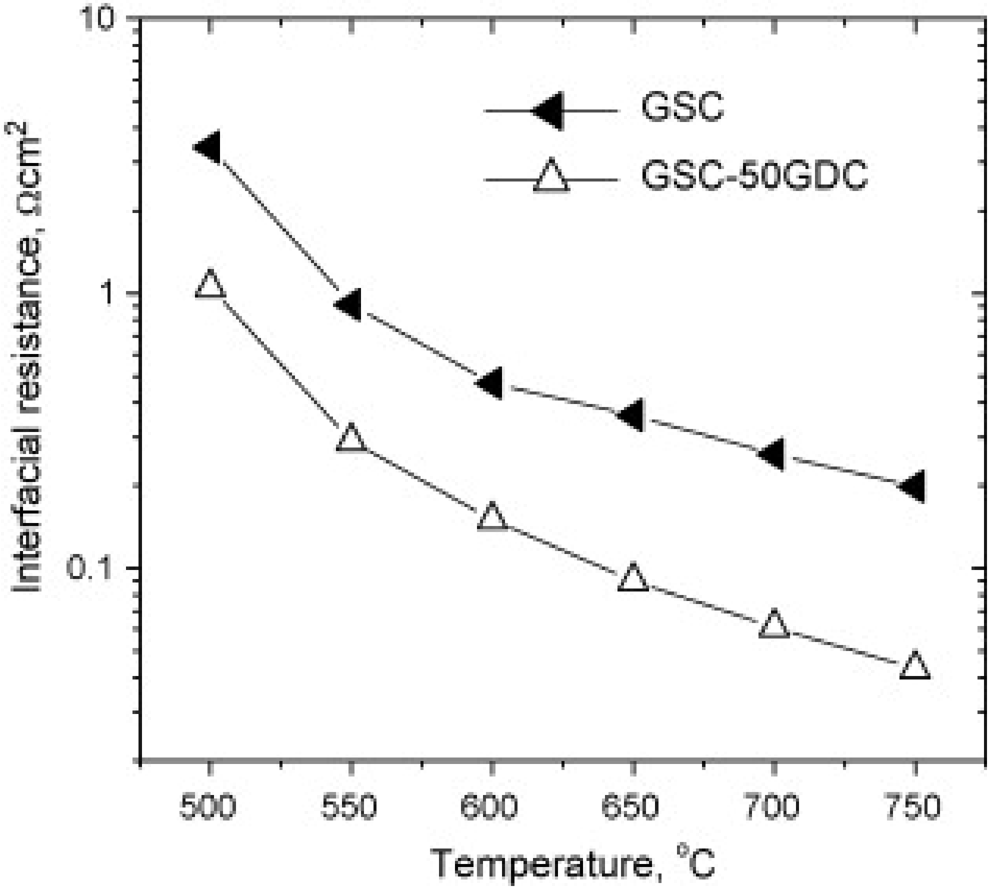
Esquirol, Kilner and Brandon, Solid State Ionics, 2004

Conductivity of LSC/CGO composites



Material	CTE ppm/K
CGO	12.5
20%LSC /CGO	13.7
30%LSC /CGO	14.8
LSC	20.4

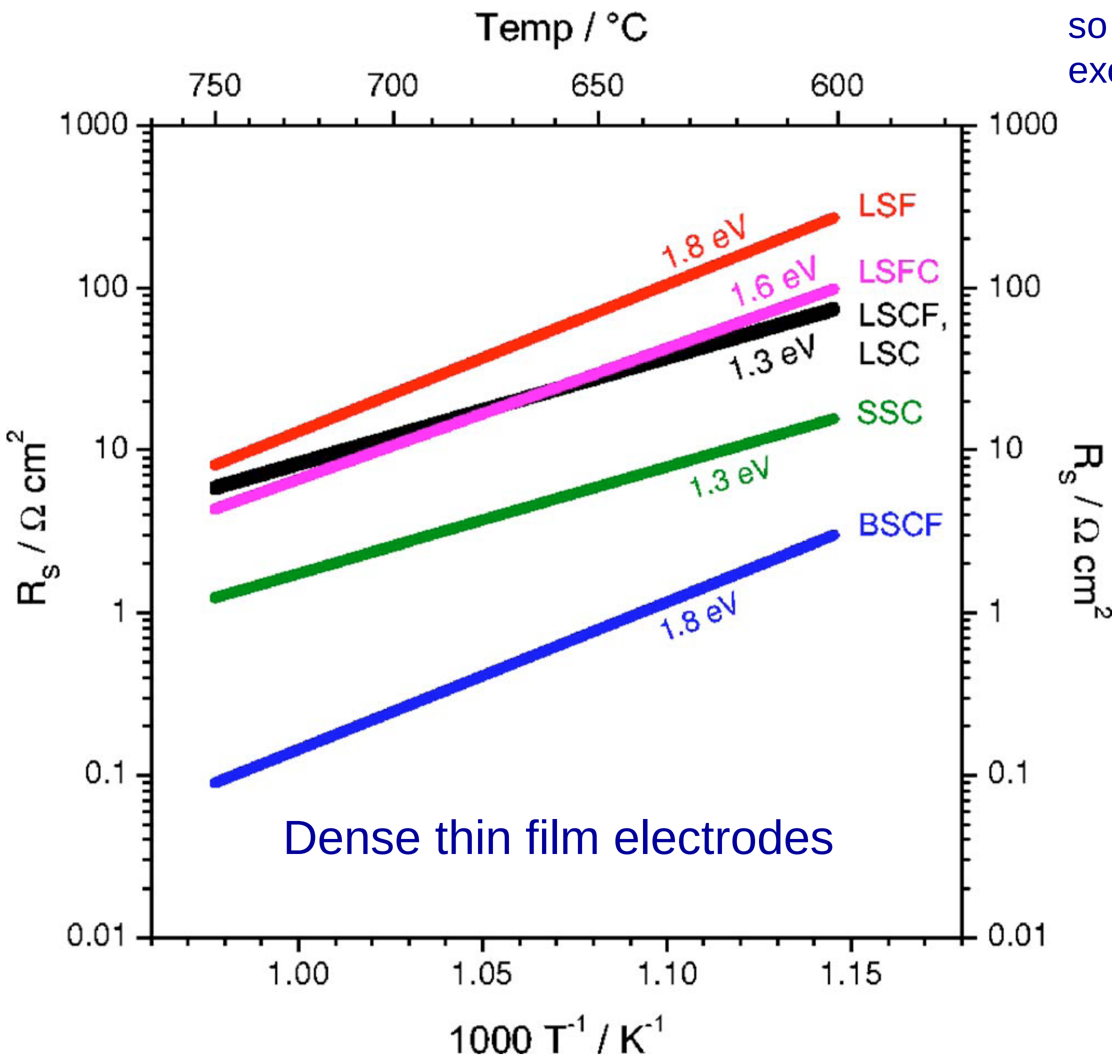
Low temperature composite cathodes



50% $Gd_{0.8}Sr_{0.2}CoO_3$
50% $Ce_{0.9}Gd_{0.1}O_2$
Composite

Huang et al. J. Power Sources (2008)

Oxygen surface exchange on thin film cathode materials



F.S. Baumann et al., J Electrochem. Soc. (2007)

Thickness is much less than D*/k*, so rate is controlled by surface exchange

$$k = \frac{RT}{4F^2 R_s c_{\mathrm{O}}}$$

- **BSCF** cathodes have excellent initial performance but degrade rapidly in air

- Surface carbonation forming $BaCO_3$ is a major problem

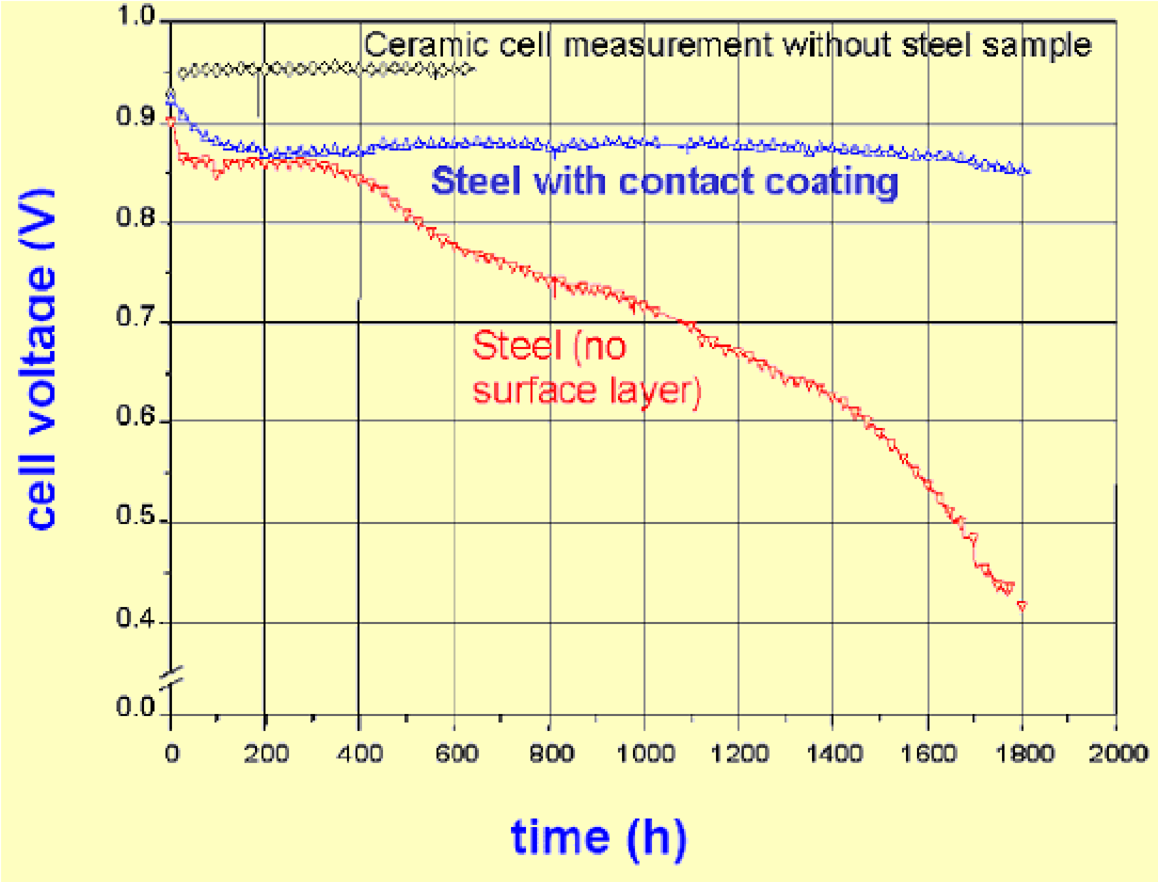
Cr poisoning

Cr released from steel components as $CrO(OH)_2$ vapour

At cathode this is reduced to Cr_2O_3: $2CrO(OH)_2 + 2e^- \rightarrow Cr_2O_3 + 2H_2O + O^{2-}$

Reacts with Sr in cathode to give $SrCrO_4$

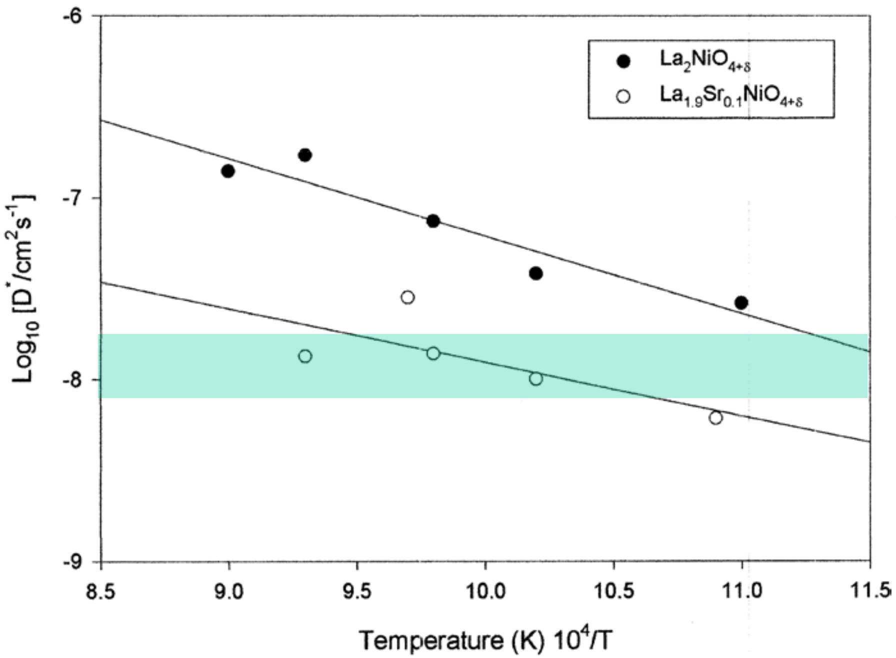
Need coating on steel to prevent Cr evaporation



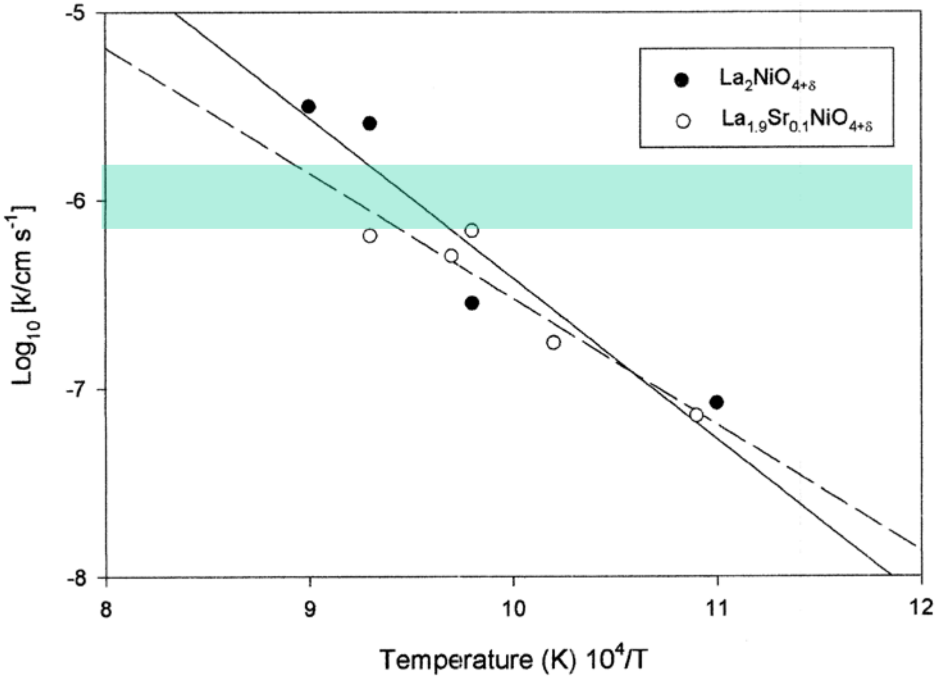
I. Vinke, SOFC IX, 2007

"K_2NiF_4" -structured oxides with oxygen excess

Oxygen diffusion



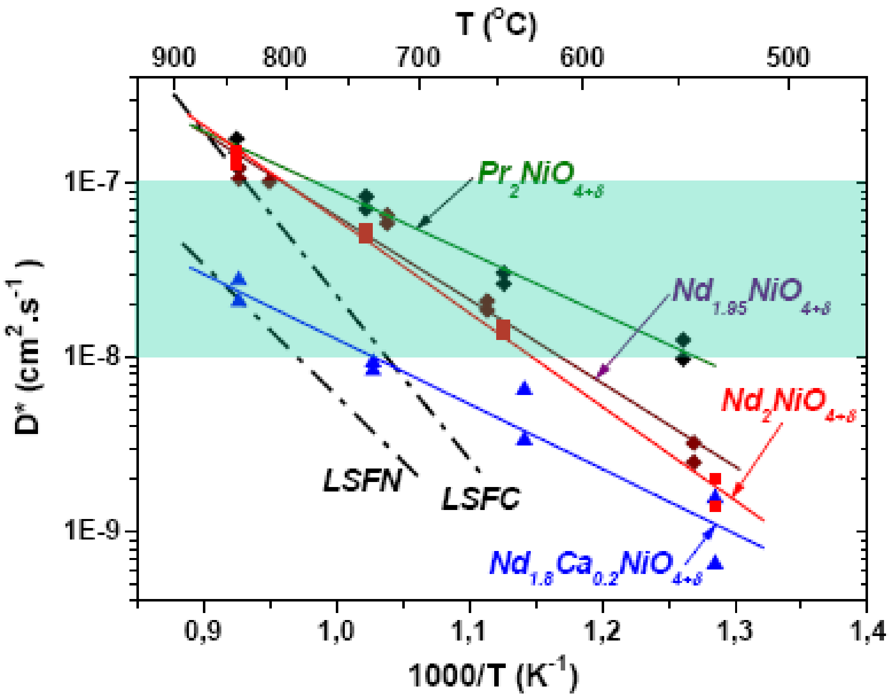
Oxygen surface exchange

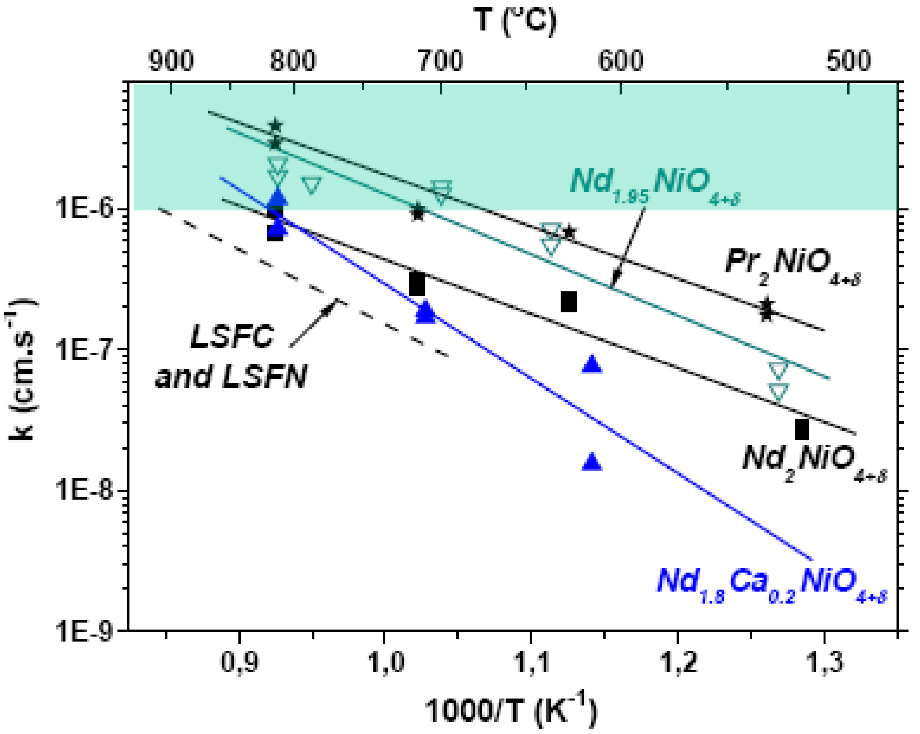


S.J. Skinner and J.A. Kilner, Solid State Ionics 135 (2000)709.

- With no Sr or Ba hope to avoid some of the degradation issues
- Because defects are oxygen interstitials performance under polarisation is not enhanced (as it is with oxygen deficient oxides)

"K_2NiF_4" -structured oxides with oxygen excess (2)

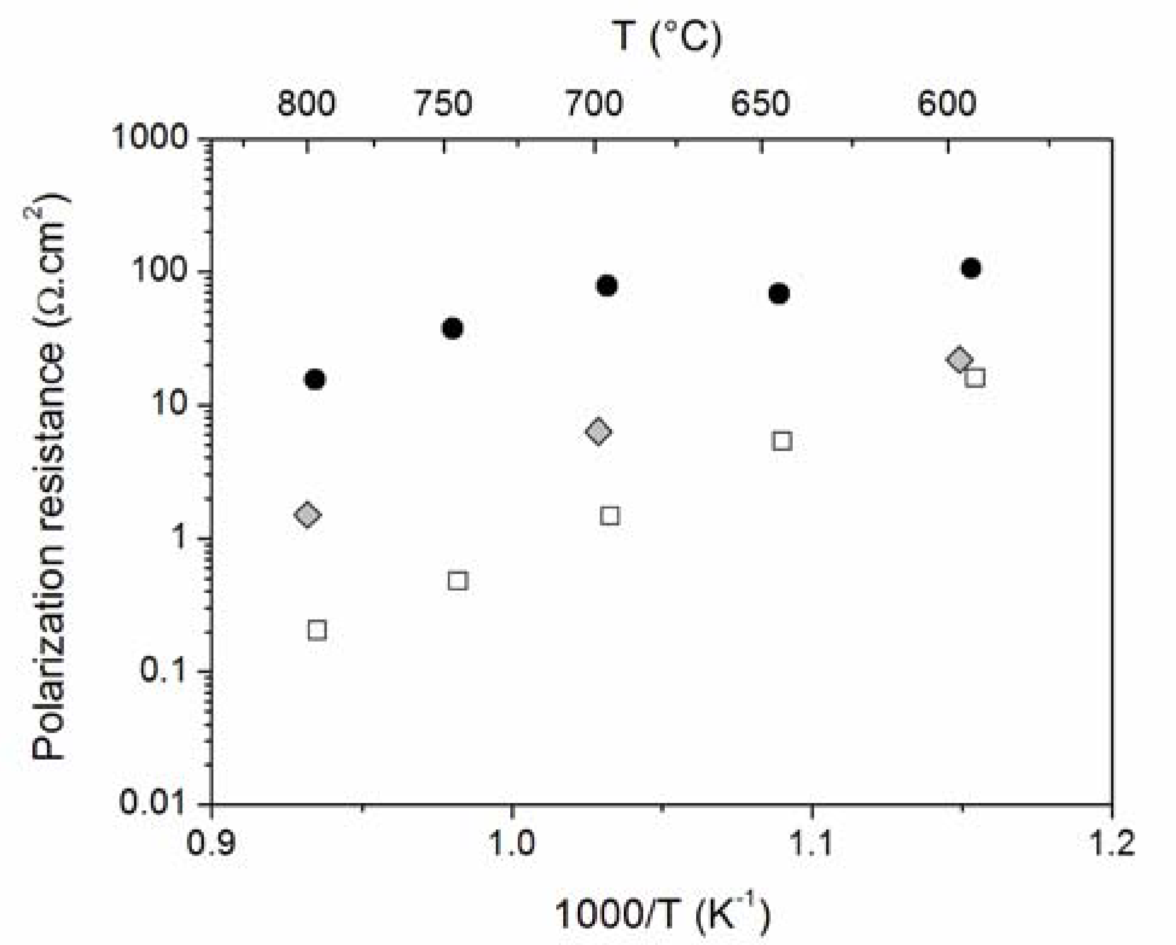




Boehm et al., Solid State Ionics 176 (2005) 2717

Performance of LNO cathodes

F. Chauveau et al, ECS Transactions, 25, 2557 (2009)



• LSM

◊ $Nd_2NiO_{4+\delta}$

□ $La_2NiO_{4+\delta}$

Final comments on cathodes

- LSM needs ionic conductor (YSZ) to give composite with TPBs and percolating ionic pathways.
  - LSM composites good for higher T (e.g. > 800 C)
- Transition metal perovskites good mixed conductors and some can be used as single phase cathodes
  - E.g. LSCF (with CGO barrier layer) at T > 700 C.
  - Below 700 C needs composite to boost ionic conductivity
- Composites also allow better CTE matching
- In general, the higher the intrinsic activity the lower the stability (chemical and mechanical)
  - High Ba, Sr and/or Co contents bring problems
- Would like better tolerance of Cr, H_2O and CO_2

Thank you for your attention!

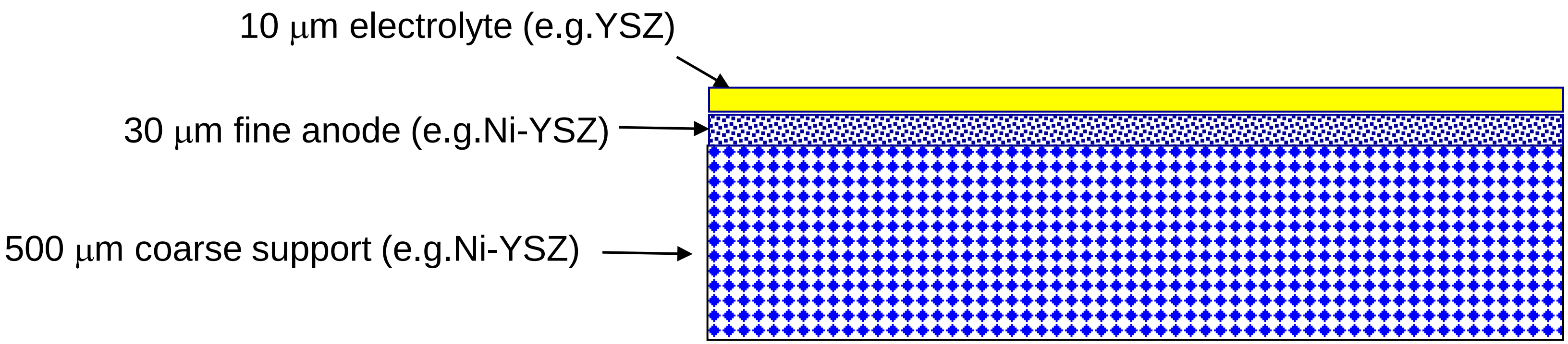
Questions on cathodes?

Supports and contact/protective layers

Cell supports

- Requirements
  - Mechanical support for cell structure
  - Sufficient gas transport to electrode (conflicts with previous)
  - Sufficient electronic conductivity
  - CTE match to cell
  - Stable to chemical changes in environment
  - Easy and cheap to manufacture
- Options
  - Anode
  - Cathode
  - Electrolyte
  - Interconnect (metal)
  - Inert material

Anode support (Ni-based)

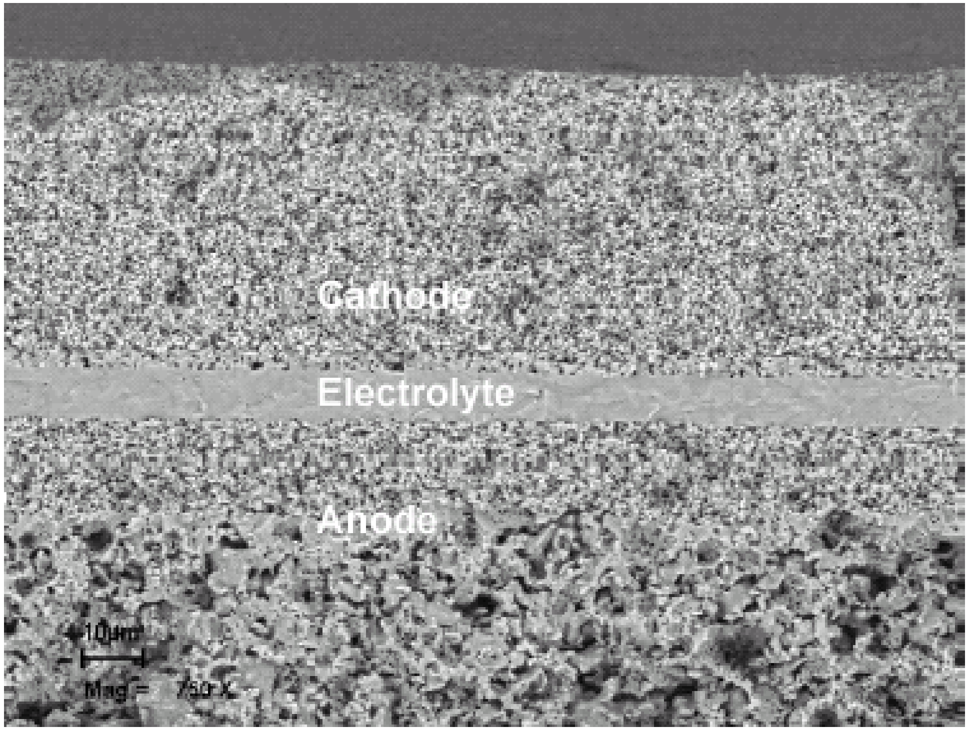


Advantages

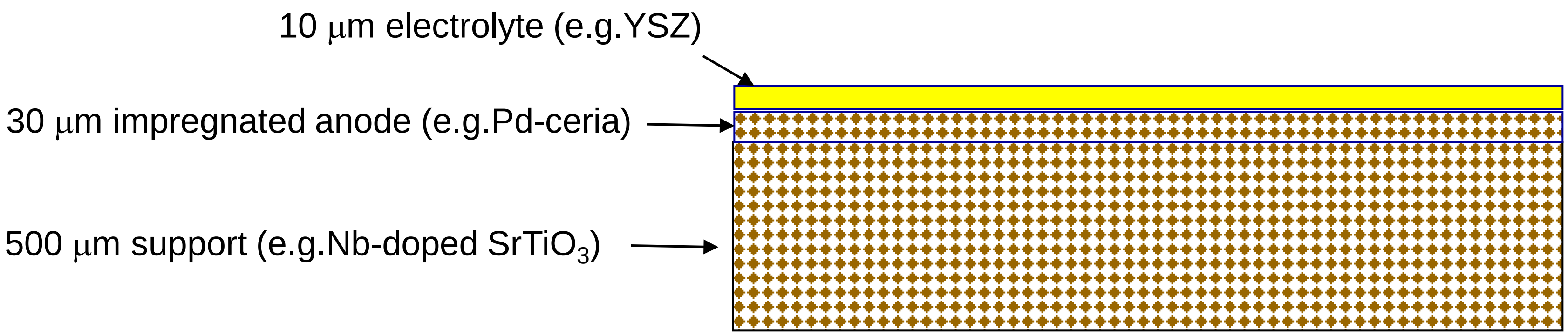
- Popular (e.g. Juelich, Versa, Topsoe)
- Good performance
- Internal reforming

Disadvantages

- Expensive Ni content (but better than cathode support)
- Poor redox tolerance
- C-deposition problems

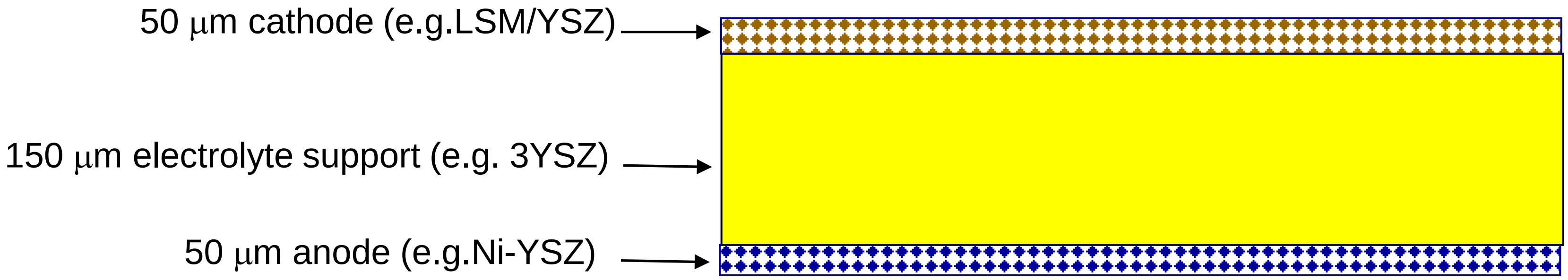


Anode support (ceramic)



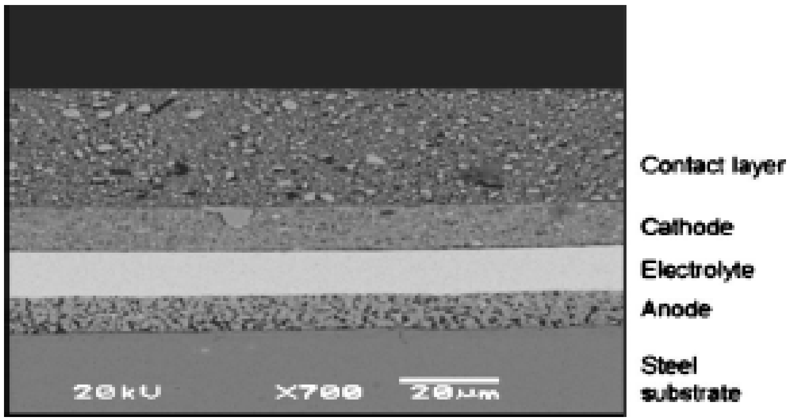
- Advantages
  - No redox or C-deposition problems
- Disadvantages
  - Poor electronic conduction (difficult current collection)
  - Unreliable impregnation of catalyst
  - Still at research stage

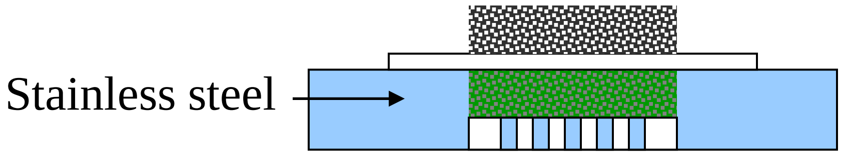
Electrolyte support (e.g. Hexis)



- Advantages
  - Flexible choice for anode
  - Some redox tolerance even with Ni-based anodes
- Disadvantages
  - Limited to high operating T (e.g.900C)
  - Fragile
  - Expensive interconnector (e.g. CrFeY)

Metallic support (e.g. Ceres Power, DLR)

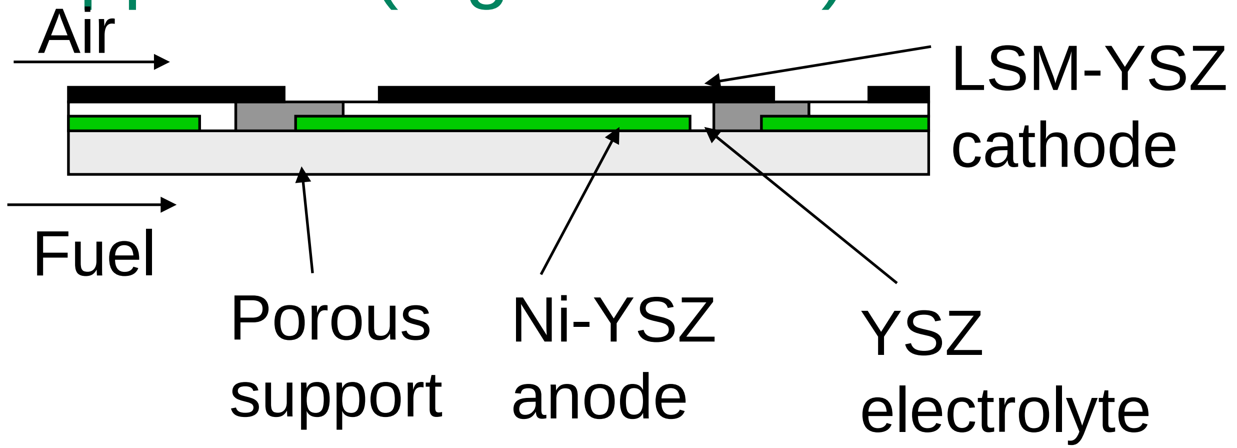




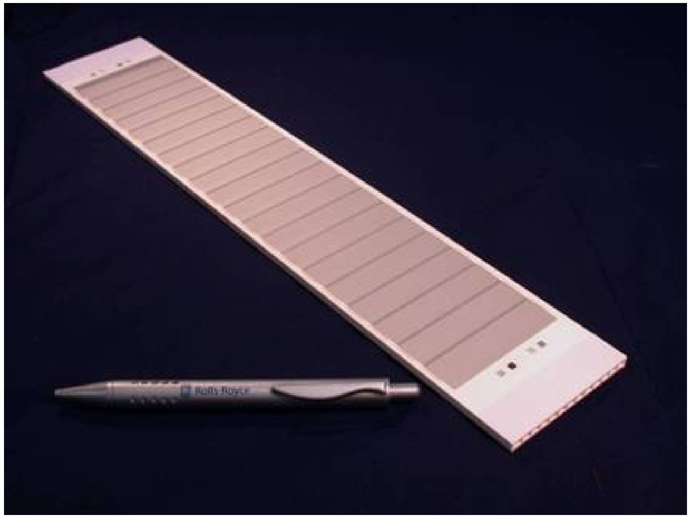
Stainless steel-supported

- Advantages
  - Mechanically robust
  - Cheap material
  - Good for lower temperatures
  - Easy to seal
- Disadvantages
  - Tricky processing

Inert supported (e.g. LGFCS)

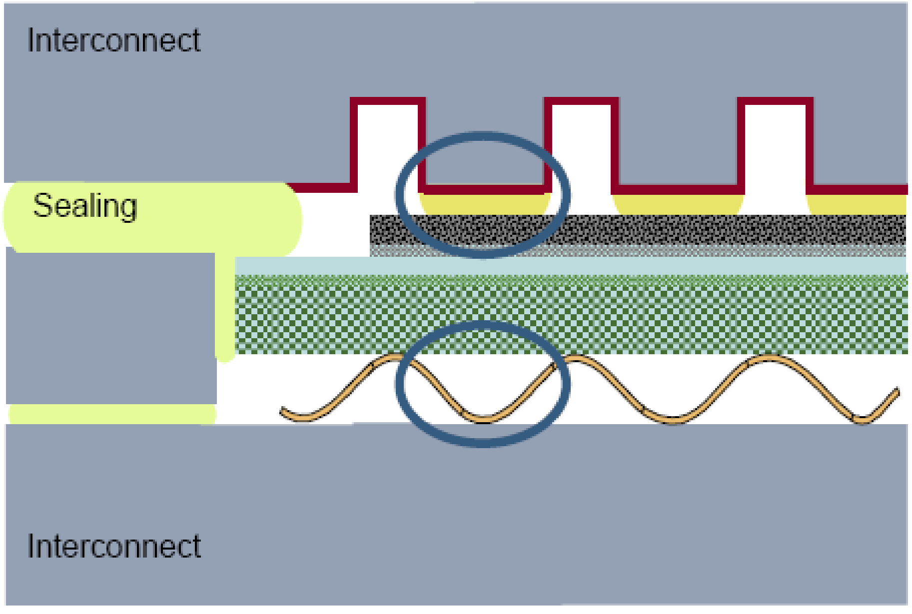


- Advantages
  - Cheap material
  - Some redox tolerance
- Disadvantages
  - In-plane design has difficult current collection



Need for contact and protective coatings

- Used with metallic interconnects/bipolar plates
- To improve (lower) contact resistance between metal and cathode
  - Target contribution to ASR < 20 mΩ cm^2
  - Corresponds to approx. 1% reduction in power density
- To reduce contamination of cathode by Cr-containing vapour evaporating from metal
  - Target for cathode ASR to increase by < 1%/kh
- Applied as a coating(s) on the interconnect on cathode side

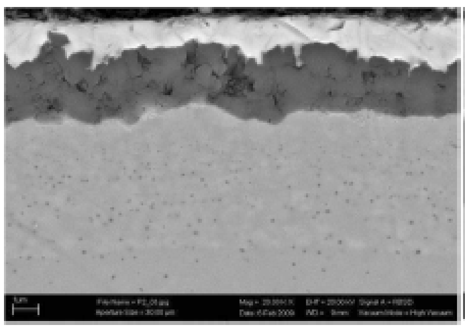


Juelich cell cross-section

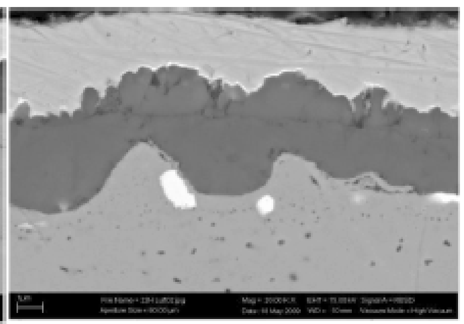
Corrosion scales on interconnect alloys

	Fe	Cr	Mn	Ti	Si	Al	Nb	Andere
F18TNb	78	19,4	0,12-0,5	0,12	0,46	0,02	0,17	Mo 1,7
ITM	70	26			0,02	0,02		Y 0,06
Crofer 22APU	Rest	20-24	0,3-0,8	0,2	0,5	0,5		Cu 0,5
Crofer 22 H	Rest	20-24	0,3-0,8	0,2	0,1-0,6	0,1	0,2-1,0	W 1,0-3; La 0,04-0,2; Cu 0,5; S 0,006

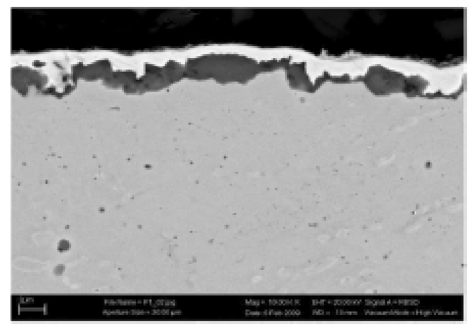
Crofer APU



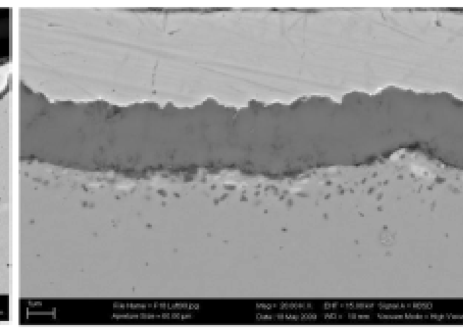
Crofer H



ITM



F18TNb



After 1000hrs exposure in air at 800°C all interconnects form a **Cr and/or (Cr,Mn) oxide** layer

Often there are 2 layers: inner Cr_2O_3 and outer $(Mn,Cr)_3O_4$ spinel

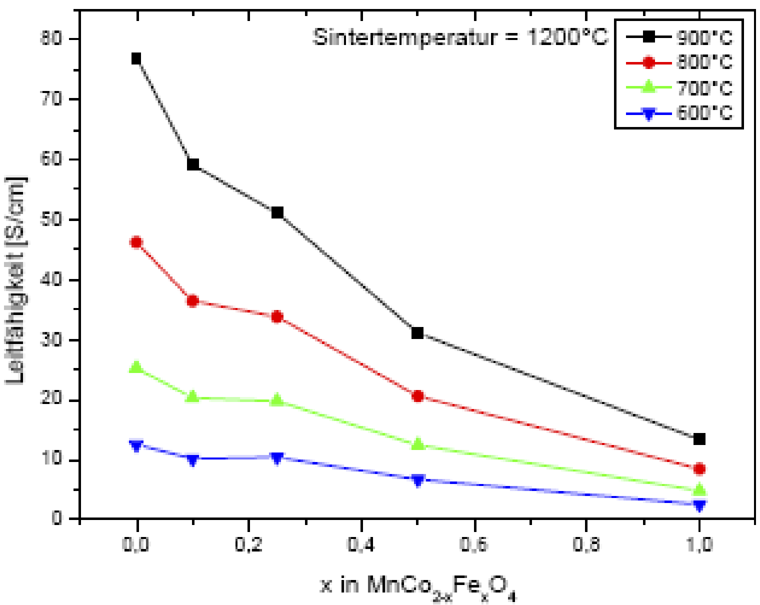
Evaporation of Cr species poisons cathode

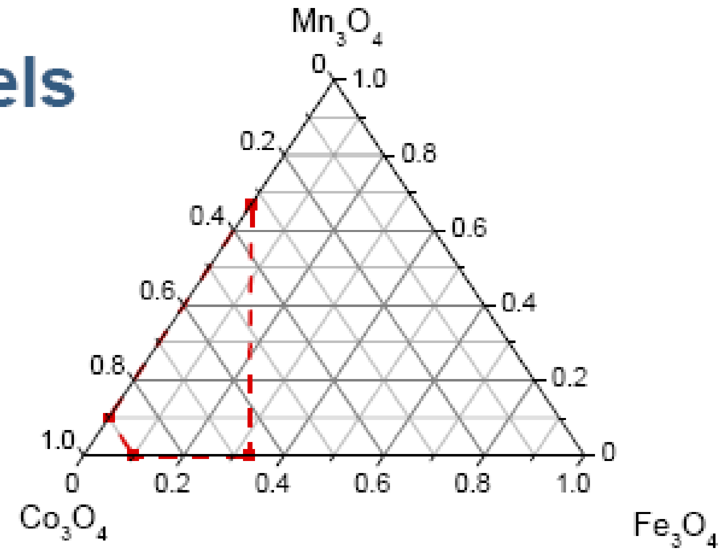
M. Zahid

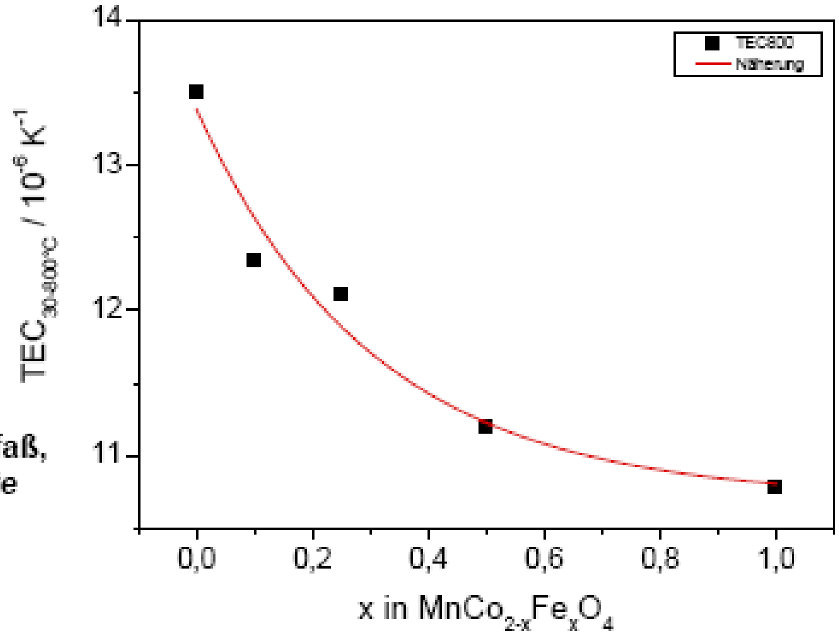
Protective coatings

Physical properties of spinels

Thermal expansion & conductivity







T. Kiefer, M. Zahid, F. Tietz, D. Stöver, H.-R. Zerfaß, Proc. *26th Risø Int. Symp.Mater. Sci.: Solid State Electrochemistry*, eds.: S. Linderoth et al., Roskilde, Denmark (2005), 261-266

Application of Mn-Co-O spinels as protective layer

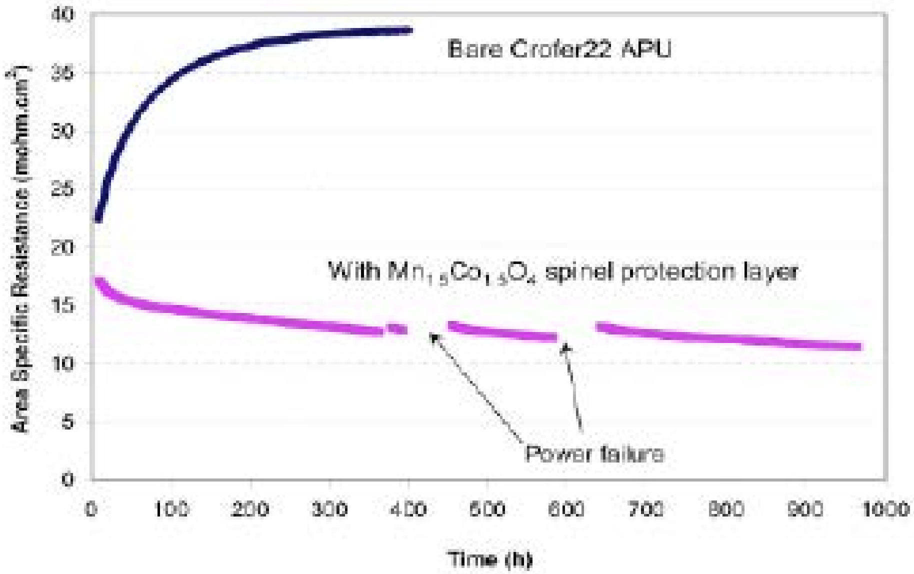
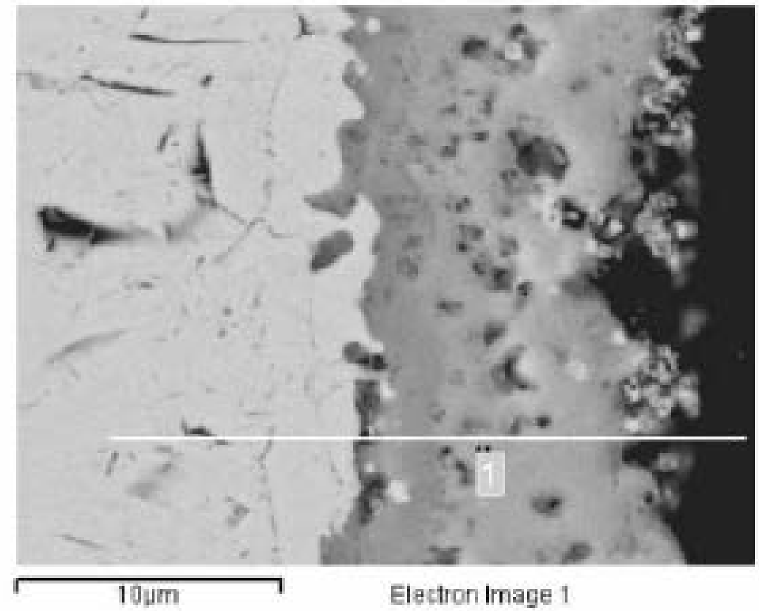
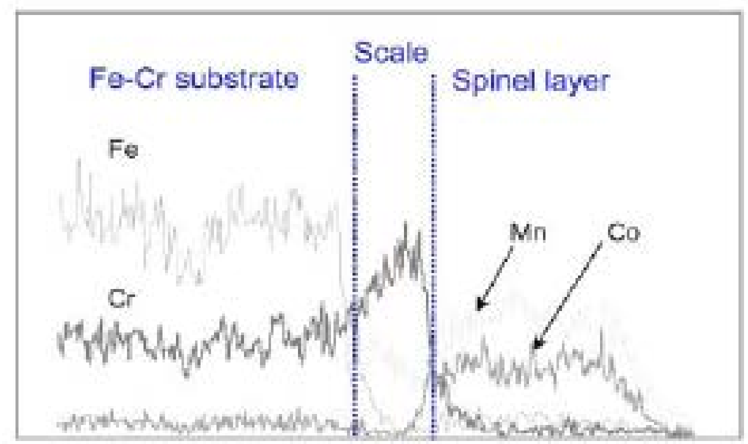


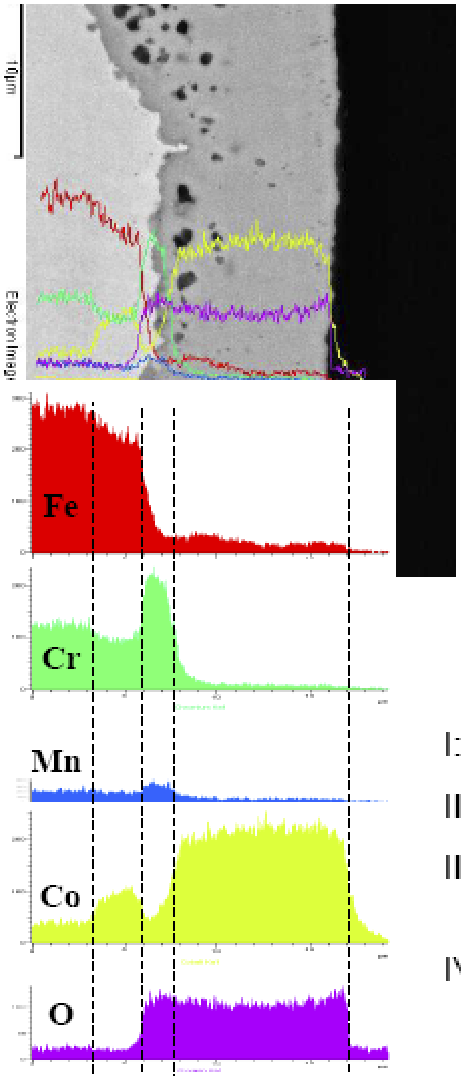
Figure 2. Interfacial ASR between a LSF cathode and a coated Crofer22 APU interconnect as a function of time at 800°C in air, in comparison with that between a LSF cathode and a bare Crofer22 APU interconnect under the same test conditions.

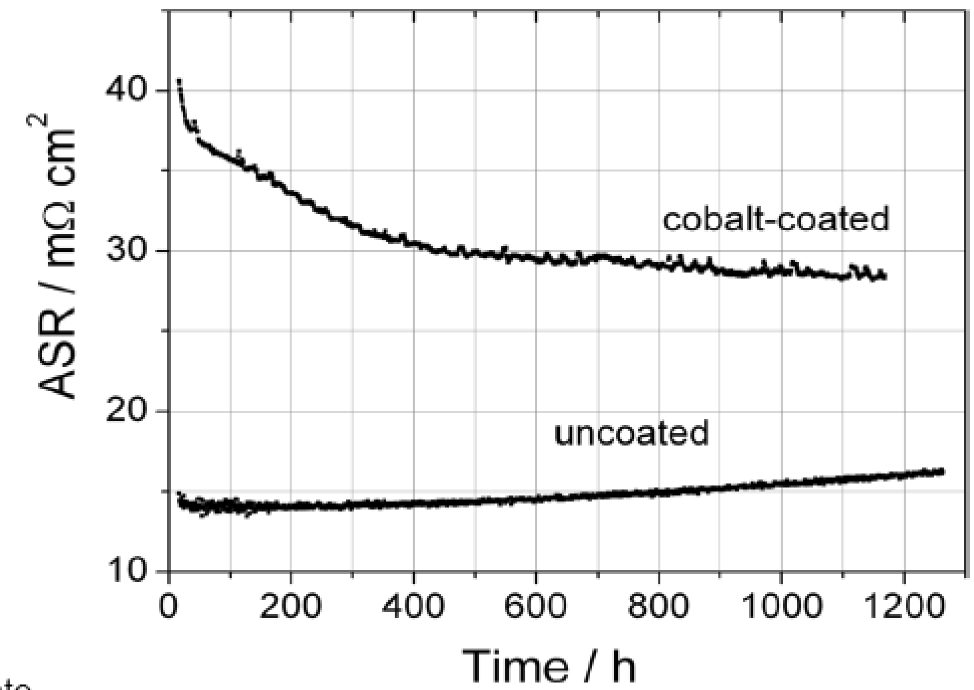




Z. G. Yang, G. G. Xia, J. W. Stevenson, Electrochem. Solid State Lett. 8 (2005) A168-A170

Electroplated or PVD Co coating on interconnect





I: steel substrate

II: Co diffusion layer

III: Cr_2O_3 layer containing little Fe, Mn and Co

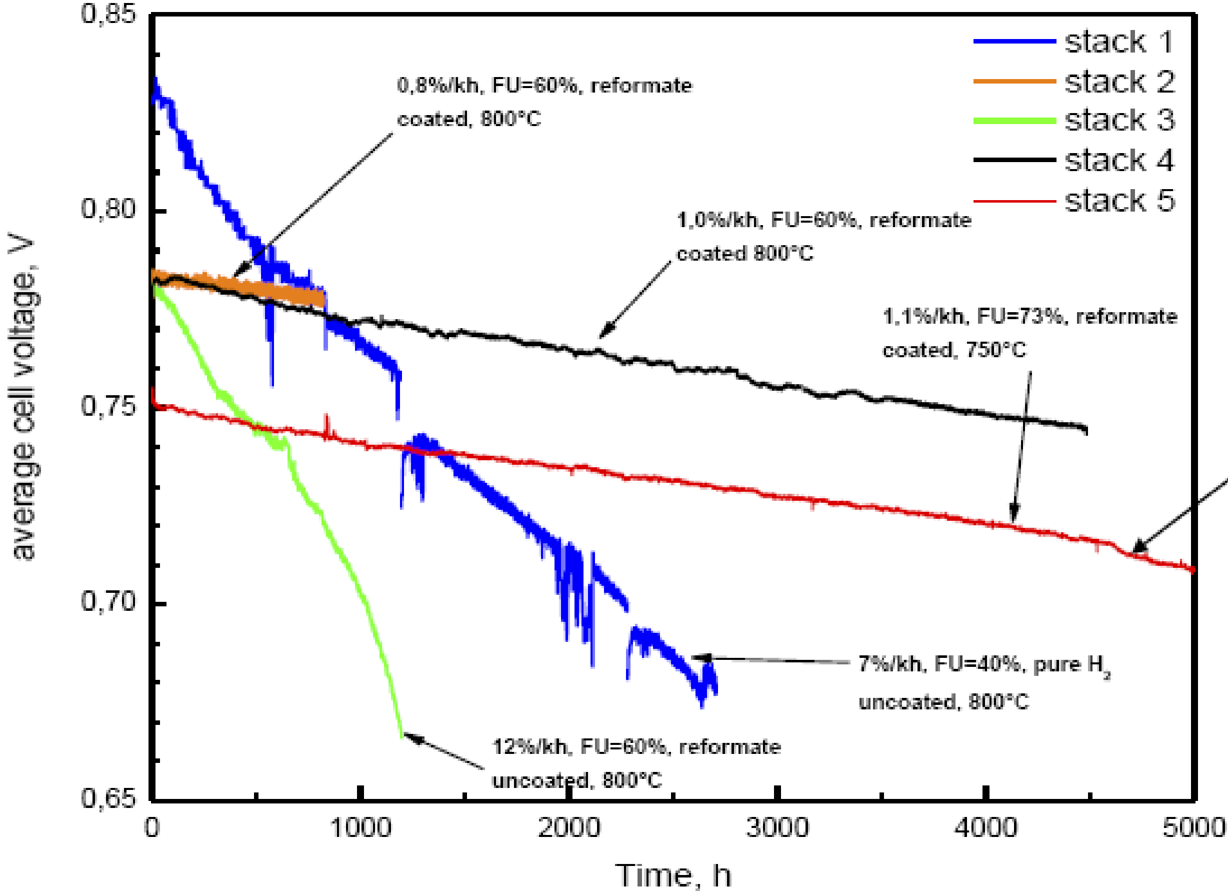
IV: Co_3O_4 top layer

Q.-X. Fu, et al., Solid State Ionics (2010)

Available commercially as Sandvik Sanergy HT

Coatings improve performance

$MnCo_{1.9}Fe_{0.1}O_4$ protective coating on Crofer 22APU



10000 hrs with constant degradation rate achieved!

Final comments on coatings

- Protective and contact coatings need to be optimised for particular interconnect alloys and cathodes
- Protective coatings
  - Ideally should be dense
  - Should be able to absorb Cr in solid solution
  - Can reduce alloy corrosion rates
  - Should not react to produce insulating phases
  - Transition metal spinels currently favoured for stainless steel interconnects
  - If not used, then need Cr-tolerant cathodes
- Contact coatings
  - Ideally should be porous (compliant)
  - Transition metal perovskites currently favoured

Thank you for your attention!

Questions on supports and coatings?