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Technological implementation of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ as porous cathode in SOFCs

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Abstract

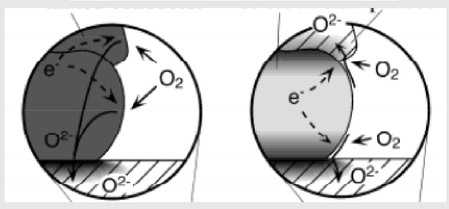
Strontium substituted lanthanum cobaltite, $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) is a perovskite-type oxide with high electro-catalytic activity towards oxygen reduction at elevated temperatures which makes fabrication of oxygen electrode for solid oxide fuel cells (SOFC) with very low *polarisation resistance* (R_P) possible. LSC is also a good mixed electronic and oxide ion conductor (MIEC) which is believed to reduce R_P even further as it expands the catalytically active area of the electrode beyond the triple phase boundary (TPB) i.e. where the electrode and electrolyte meet the gas phase. Further, the high conductivity of LSC reduces losses associated with current collection and current constriction.
However, the use of LSC as a cathode on Yttria Stabilised Zirconia (YSZ) is problematic due to the high thermal and stoichiometric expansion coefficient of LSC when compared to that of 8% Y2O3 stabilised ZrO2 (8YSZ). Also ionic and electronic blocking reaction products ($SrZrO_3$, $La_2Zr_2O_7$) inhibit the direct use of LSC on YSZ electrolyte at high temperatures and necessitates the use an interdiffusion barrier of rare earth doped Ceria (CGO). In this paper we will report on our efforts to fabricate and implement $La_{0.6}Sr_{0.4}CoO_3$ (LSC40) as oxygen electrode in our anode supported SOFCs and discuss advantages and challenges.

Motivation

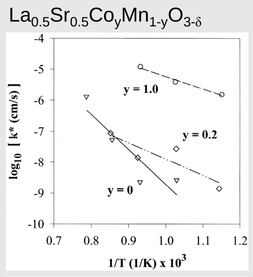
Electronic conductivity at 800 C of common SOFC cathode materials

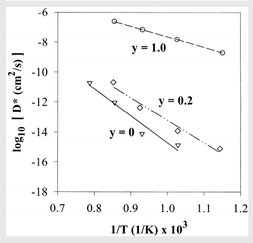
Cathode	σ [Scm^{-1}]
LSM25[2]	~200
LSCF6482[3]	~300
LSC[4]	~2000

LSC LSM:YSZ



$La_{0.5}Sr_{0.5}Co_yMn_{1-y}O_{3-\delta}$





- The oxygen surface exchange (k*) and oxygen diffusion coefficient (D*) is substantially higher in LSC as compared to LSM.[5,6]
- High electro-catalytic activity towards oxygen reduction results in a low R_P.
- High electronic conductivity ease cathode contacting.

Challenges

Thermal expansion coefficient (TEC) of common SOFC cathode materials

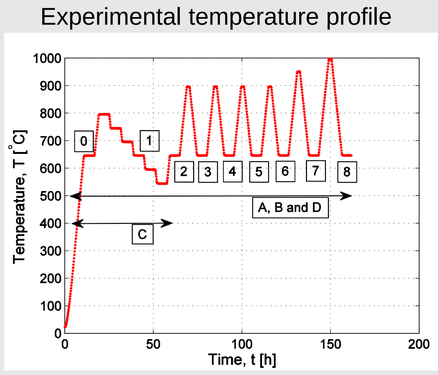
Material	TEC [K^{-1}]
8YSZ[7]	~10.8 *10-6
LSC[5]	~20*10-6

- Expansion mismatch between the LSC40 cathode and the rest of the cell → mechanical rupture.
- High Sr diffusivity and activity →reacts with YSZ to form the highly insulating $SrZrO_3$ phase.
- Low thermodynamic stability at high T/low P_{O2} → cathode decomposition and degradation.[8]

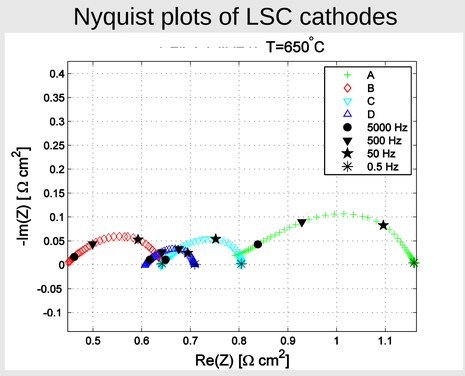
1. *Per Hjalmarsson, Solid State Ionics, Volume 180, Issue 26-27,19 October 2009, Pages 1395-1405*
2. *A. Berenov, et. al. Solid Oxide Fuel Cells 10 (SOFC-X), (2007) 1173-1181.*
3. *L.W. Tai, et. al. Solid State Ionics, 76 (1995) 273-283.*
4. *Per Hjalmarsson, Solid State Ionics, Volume 179, Issues 17-18, July 2008, Pages 636-646*
5. *R. De Souza, Solid State Ionics, 126 (1999) 153-161.*
6. *R. De Souza, Solid State Ionics, 106 (1998) 175-187.*
7. M. Mori et. al. *J. Am. Ceram. Soc.* **84** (2001) (4), pp. 781–786
8. A Petrov et. al. J. of Solid State Electrochemistry 10 (2006) pp 517-537

Electrochemical characterization – symmetrical cell testing

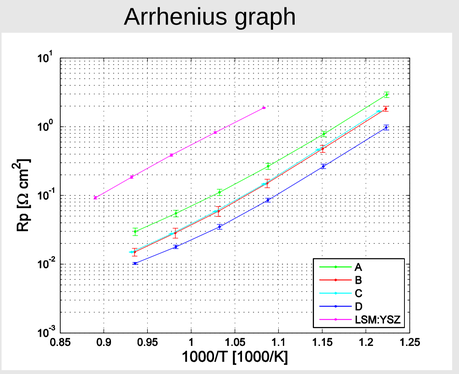
Experimental temperature profile



Nyquist plots of LSC cathodes

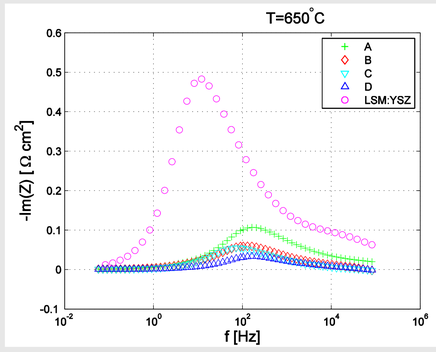


Arrhenius graph

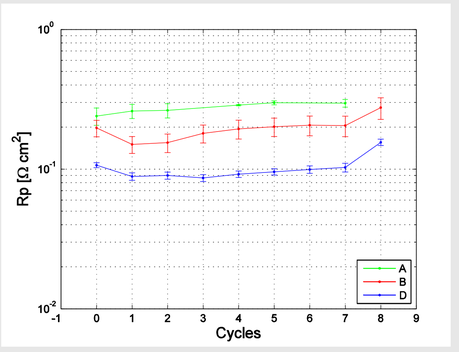


- Cathode A-C consist of different raw powder but are processed similarly.
- Cathode C and D consist of the same raw powder but are processed using different binders.
- R_P of electrodes depends largely on processing.
- Processing does not affect the frequency at which the electrochemical response occurs.
- R_P appears to be relatively independent on thermal cycling below T_{MAX}=1000 °C.

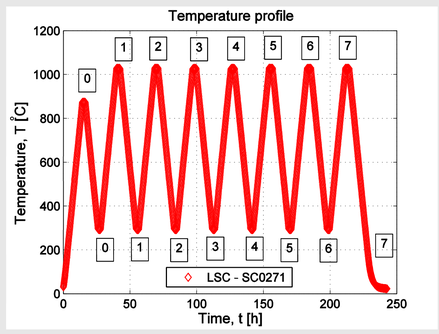
Bode plot of LSC and LSM:YSZ cathodes



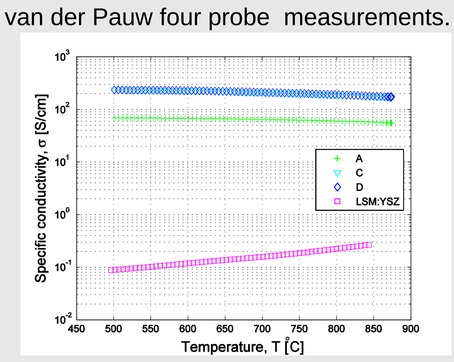
R_P at 600 °C during thermal cycling



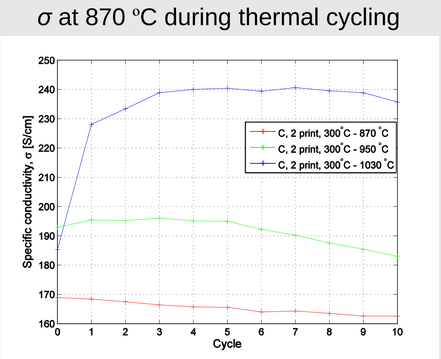
In plane electric al conductivity



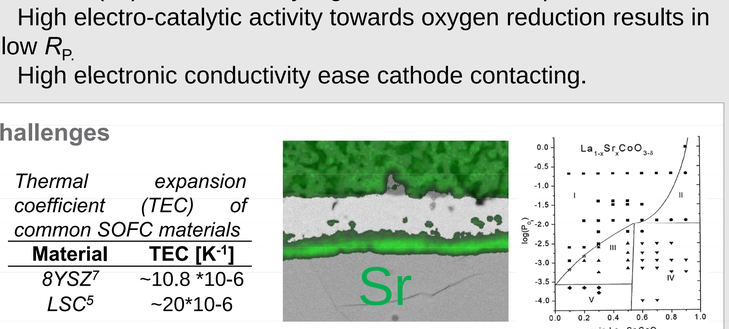
van der Pauw four probe measurements.



σ at 870 °C during thermal cycling



Processing

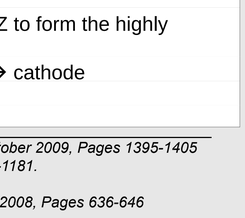


Poor cathode print

Powder properties:
- Phase purity
- Chemical Homogenity
- Impurities
- Particle size distribution
- Agglomerates
- Surface area
- Surface morphology
- Etc.

Ink properties:
- Viscosity
- Shear thinning
- Thixotropic

Good cathode print

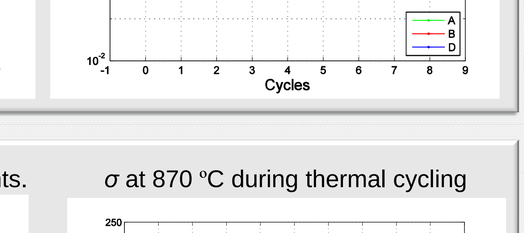


Electrochemical characterization – single cell testing

Cell architecture

Screen printed	LSC
Screen printed	CGO
	YSZ
	Ni+YSZ

- LSC cathodes decrease both R_S and R_P and thus overall ASR_{CELL}.
- The LSC cathode impedance response is highly resolved from the anode making detailed anode studies easier.



Conclusions

- Oxygen electrodes based on powder of LSC40 ($La_{0.6}Sr_{0.4}CoO_3$) can be manufactured with good microstructure and high electrochemical performance as a result.
- Oxygen electrodes of porous LSC40 has substantially better electronic conductivity than conventional LSM:YSZ reducing serial resistance and contacting issues.
- The LSC electrode can withstand thermal cycling reasonably well despite its comparably high TEC.

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