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New Concept Composite Cathodes for SOFC

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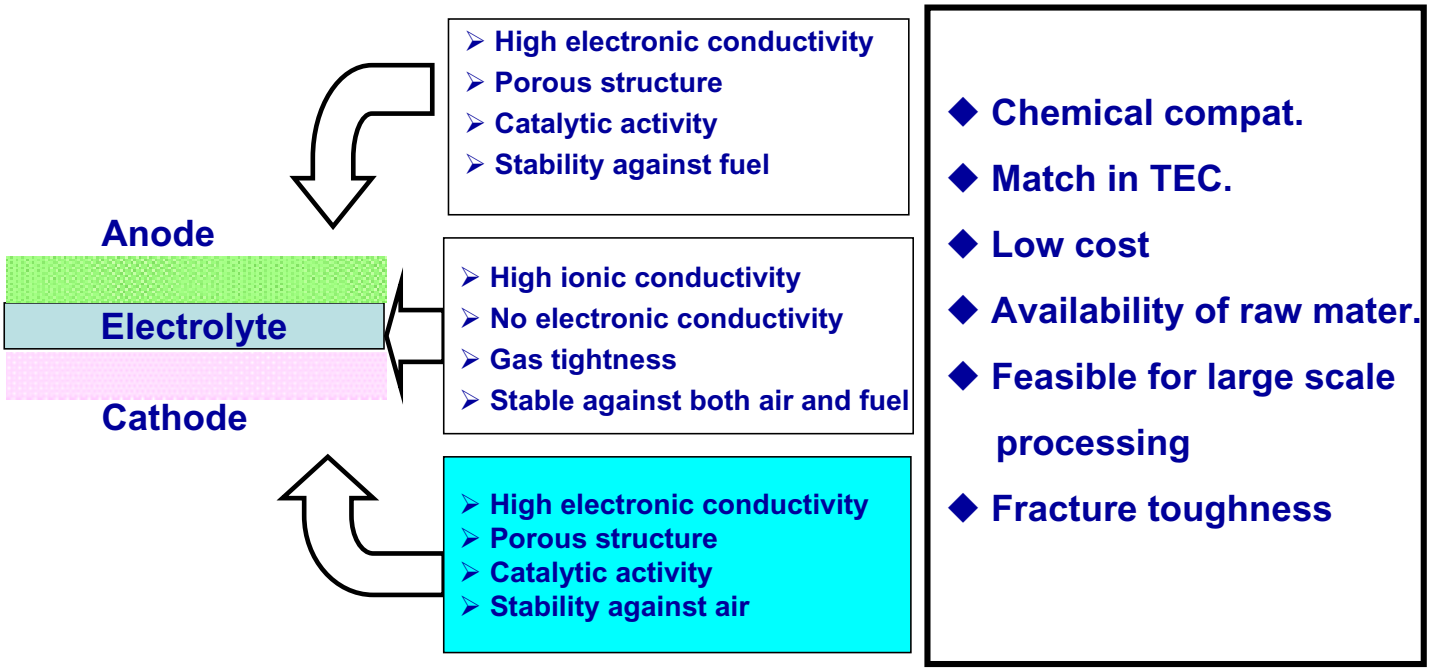
1. Introduction

➢Materials and multilayered structure

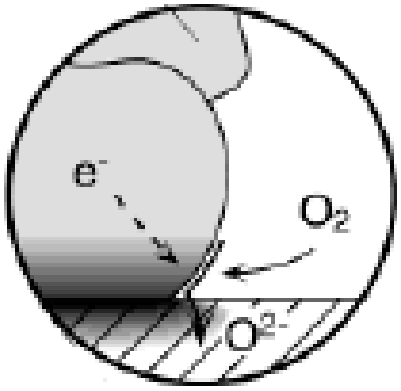


➢Main types of cathode materials

Cathode Materials	TEC 10^{-6} K^{-1}	Electronic conductivity S/cm	Oxide conductivity S/cm	Compatibility with electrolyte	Operation Temperature °C
LSM	12.3	2.01	$1.7x10^{-4}$	(+) YSZ	750−1000
LSC	20.5	3.2	0.22	(+) CeO_2 (-) YSZ	650−800
LSCF	14.8	1.94	0.04	(+) CeO_2,LSGM (-) YSZ	650−800
SSC	21.5	2.47	0.133	(+) CeO_2,LSGM (-) YSZ	500−650
BSCF	18.53	1.63	_	(+) CeO_2,LSGM (-) YSZ	500−650

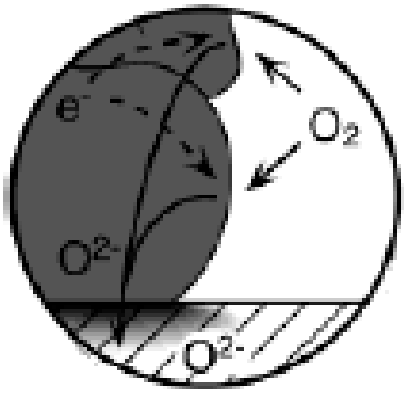
➢Differences in reaction paths for oxygen reduction

LSM



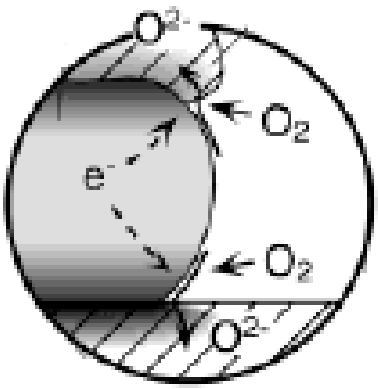
Electronic conductor

LSC



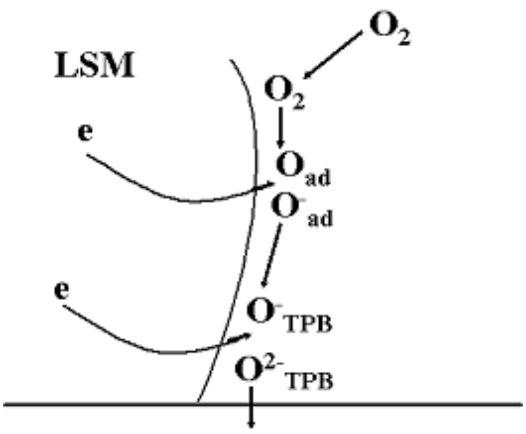
Mixed conductor

LSM-YSZ



Composite of electronic and ionic phase

➢Oxygen reduction over LSM cathode



Step 1 $O_2(bulk) \rightarrow O_2$ (interface)

Step 2 $O_2(interface) \rightarrow 2O_{ad}$

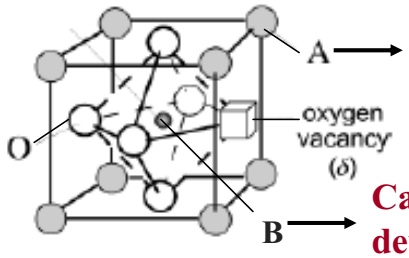
Step 3 $O_{ad} + e^- \rightarrow O^-_{ad}$

Step 4 $O^-_{ad} \rightarrow O^-_{TPB}$

Step 5 $O^-_{TPB} + e^- \rightarrow O^{2-}_{TPB}$

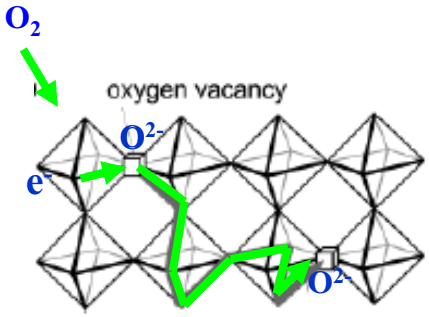
Step 6 $O^{2-}_{TPB, LSM} + V_{ö, YSZ} \rightarrow O^x_{O, YSZ}$

➢Oxygen reduction on perovskite surfaces



The valence state of B-site cations, oxygen vacancies are changed after doping in A sites. → Tuning of catalytic activity, electrical conductivity, TEC, stability and so on.

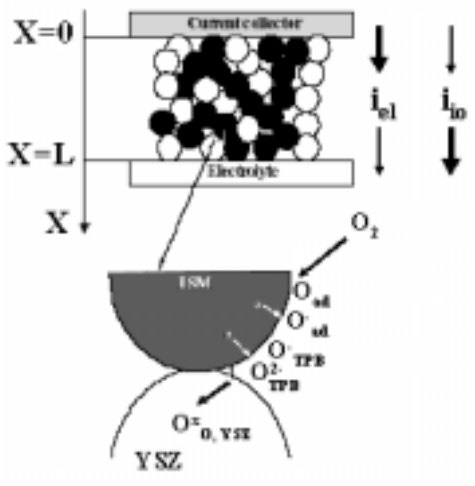
Catalytic activity is largely dependent on the properties of transitional metal on B sites Co>Ni>Mn>Fe>Cr



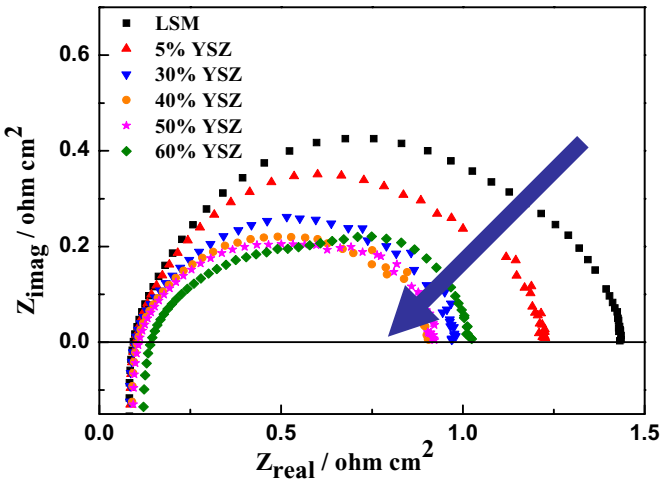
Reactions over MIEC

- ➢Diffusion to surface
- ➢Adsorption onto surface
- ➢Charge transfer reaction
- ➢Diffusion of oxygen anions on surface or in bulk
- ➢Diffusion into electrolyte

➢Variation of polarization resistance with YSZ content in the LSM-YSZ composite cathodes

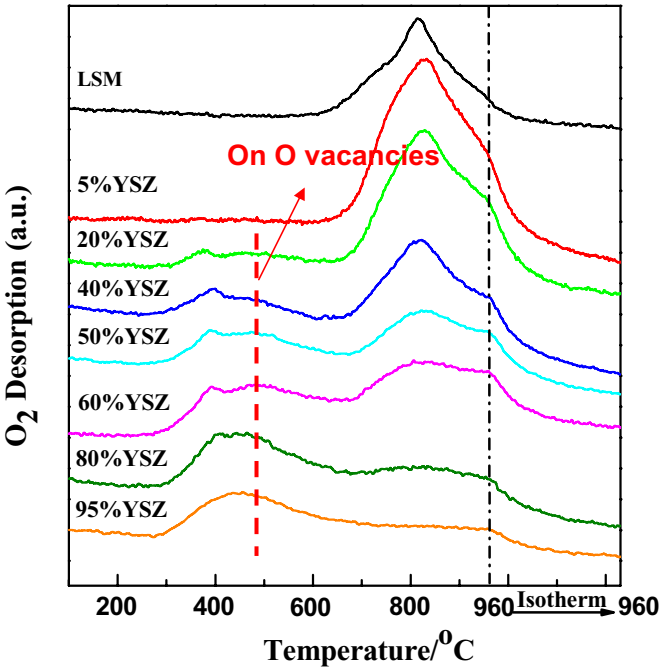


Extended TPB



- ➢The LF arc is depressed in the LSM-YSZ composite;
- ➢YSZ=40%-50%, R_p is lowest;
- ➢YSZ≥60%, R_{ohmic} decreases.

➢O_2-TPD of LSM-YSZ composites



✓**Oxygen vacancies form at the interfaces between LSM and YSZ electrolyte**

$$O^{x}_{O,LSM} + 2Mn^{g}_{Mn,LSM} + V^{gg}_{O,YSZ} + 2e' \rightarrow V^{gg}_{O,LSM} + 2Mn^{x}_{Mn,LSM} + O^{x}_{O,YSZ}$$

$$O^{x}_{O,LSM} + 2Mn^{x}_{Mn,LSM} + V^{gg}_{O,YSZ} + 2e' \rightarrow V^{gg}_{O,LSM} + 2Mn'_{Mn,LSM} + O^{x}_{O,YSZ}$$

2. New Cathode Designs

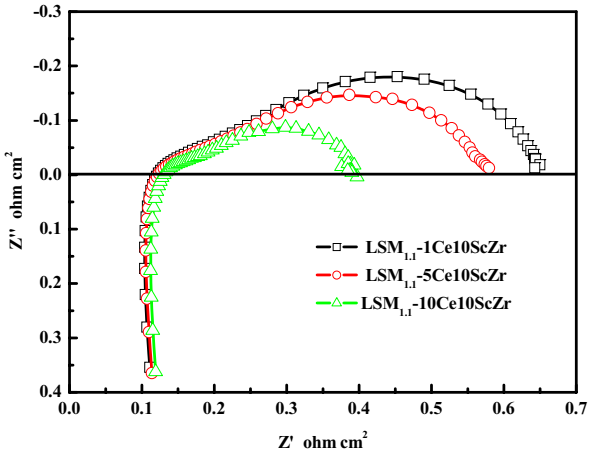
2.1 Cathode with a high oxide conductivity electrolyte

2.2 Cathode with two different electrolyte components

2.3 Cathode with a modified electrolyte/cathode surface

2.4 Cathode with two different perovskite oxide catalysts

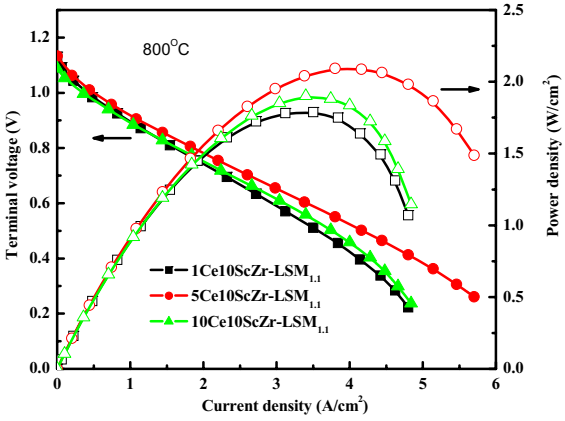
2.1Composite cathode with a high oxide conductivity electrolyte -Impedance spectra

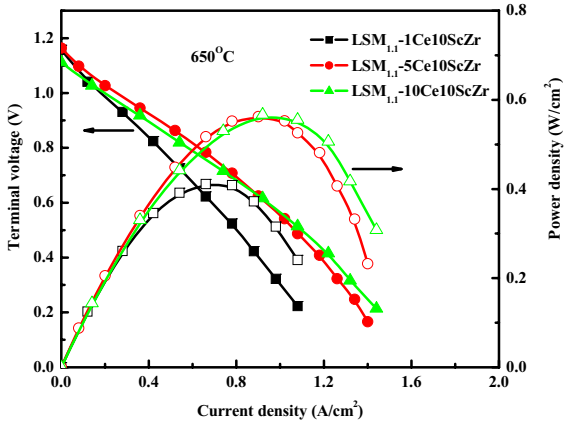


	$LSM_{1.1}$-1Ce10ScZr	$LSM_{1.1}$-5Ce10ScZr	$LSM_{1.1}$-10Ce10ScZr
R0 (ohm cm^2)	0.120	0.123	0.131
R1 (ohm cm^2)	0.093	0.073	0.046
R2 (ohm cm^2)	0.444	0.385	0.218

✓The adsorption, surface diffusion and charge-transfer reaction of oxygen are promoted with the increase of CeO_2 content.

2.1Composite cathode with a high oxide conductivity electrolyte --Effect of ScSZ composition

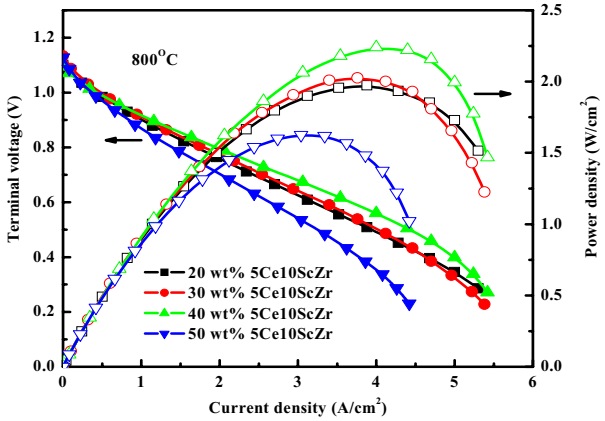


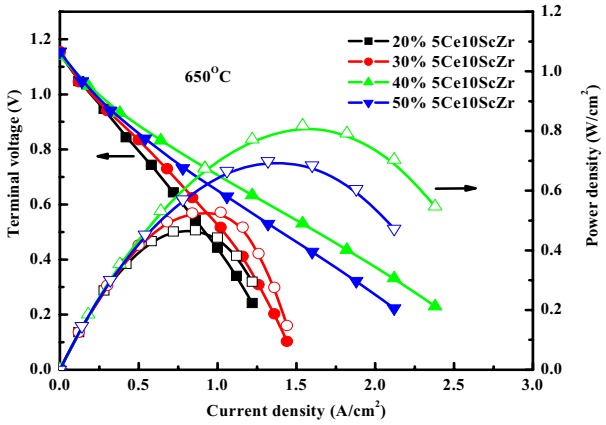


✓ Best ScSZ electrolyte for cathode : 5Ce10ScZr

2.1Composite cathode with a high oxide conductivity electrolyte

- Effect of 5Ce10ScZr content

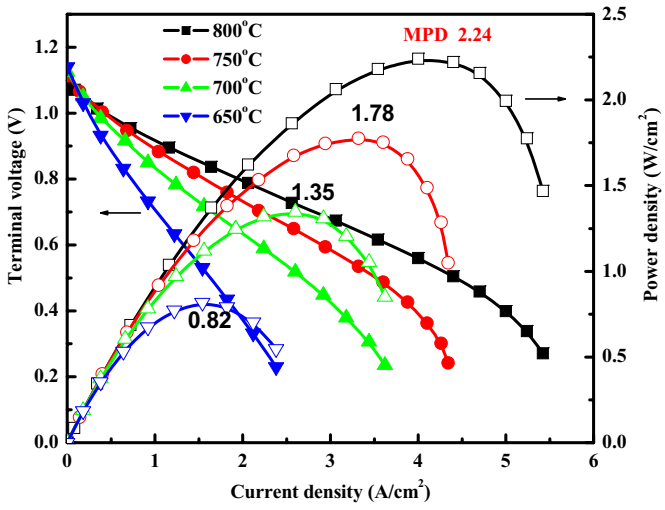




- ✓ **Optimum content: 40 wt%**
- ✓ **800°C MPD：40%>30%>20%>50%**
- ✓ **650°C MPD：40%>50%>30%>20%**

2.1 Composite cathode with a high oxide conductivity electrolyte

- Cell performance with the optimum cathode



I-V curves

Cell performance(W/cm²)

Temp/°C	800	750	700	650
0.7V	1.96	1.52	1.15	0.70
MPD	2.24	1.78	1.35	0.82

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2.2 Cathode with two different electrolyte components

2.3 Cathode with a modified electrolyte/cathode interface

2.4 Cathode with two different perovskite oxide catalysts

2.2 Cathode with two different electrolyte components

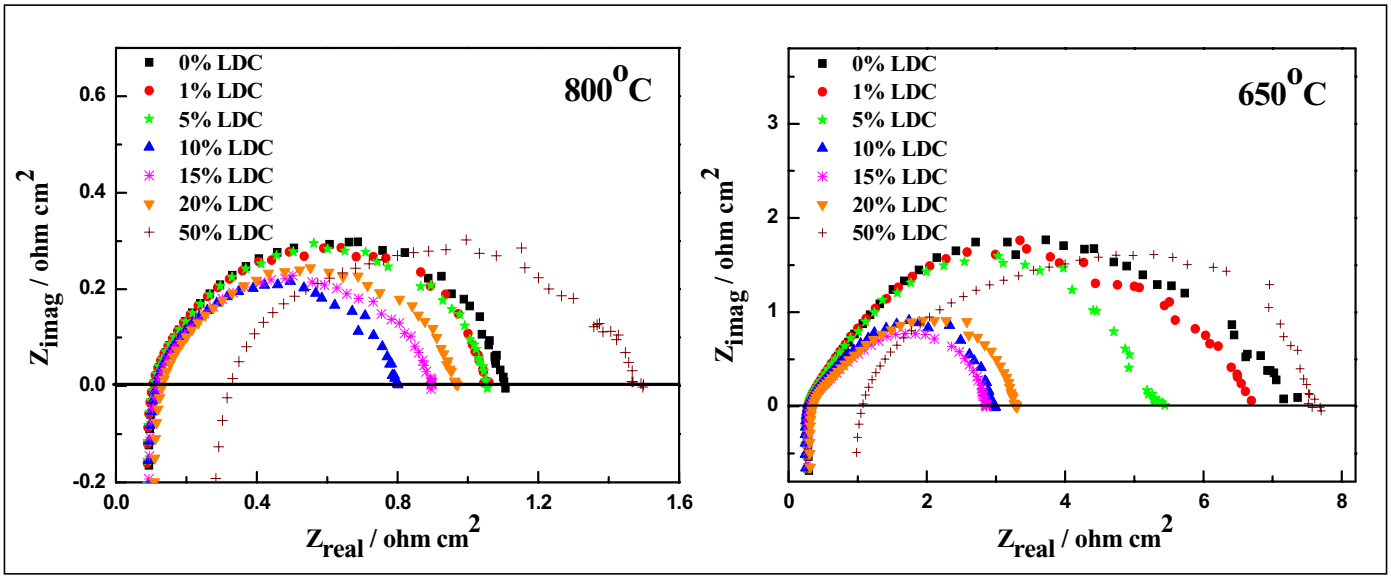
- Cell performance with LDC-YSZ-LSM cathodes

LDC content	Maximum Power Density (W cm^{-2})			
	800°C	750°C	700°C	650°C
0%LDC	1.29	0.85	0.43	0.18
1%LDC	1.35	0.84	0.49	0.19
3%LDC	1.41	0.97	0.52	0.19
5%LDC	1.39	0.92	0.58	0.23
10%LDC	1.47	1.01	0.73	0.50
15%LDC	1.43	1.05	0.76	0.51
20%LDC	1.17	0.86	0.62	0.39
50%LDC	0.77	0.54	0.38	0.25

At 650°C，the cell with a 10%LDC-LSM-YSZ cathode gives a the MPD of 2.8 times of the MPD of the unmodified cell.

2.2 Cathode with two different electrolyte components

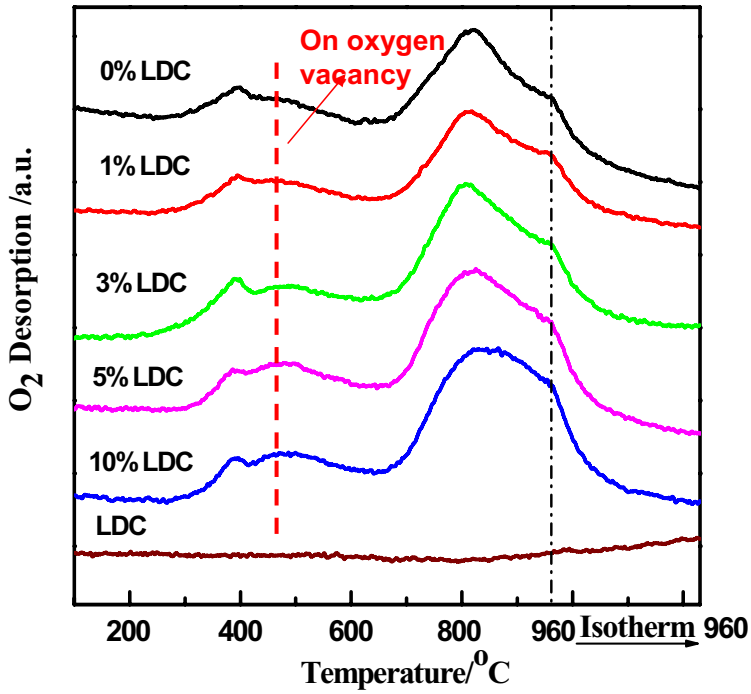
-Impedance spectra of the cells with LDC-YSZ-LSM cathode



✓**With the increase of LDC content, the arc at LF decreases at low LDC content and increases at high LDC content and shows a minimum at LDC content of 10-15 %。**

2.2 Cathode with two different electrolyte components

-- O_2-TPD profiles of LDC-LSM-YSZ composites



The introduction of LDC creates more oxygen vacancies on the composite surfaces.

2.2 Cathode with two different electrolyte components

-LSM-YSZ/LSM-LDC bi-layered cathode

➢Fundamentals：

•LSM-LDC

High electrochemical activity

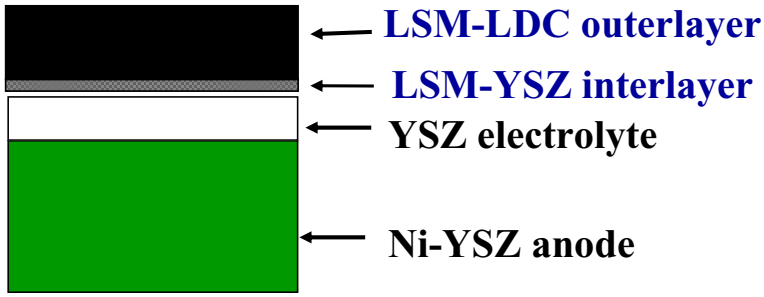
Bad chemical and thermal-mechanical compatibility with YSZ

•LSM-YSZ:

Good compatibility with YSZ

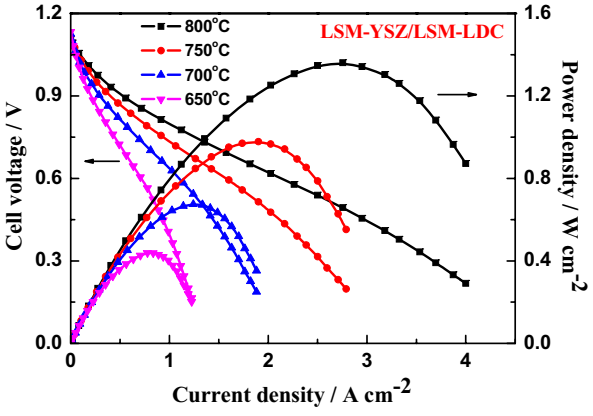
Low electrochemical activity

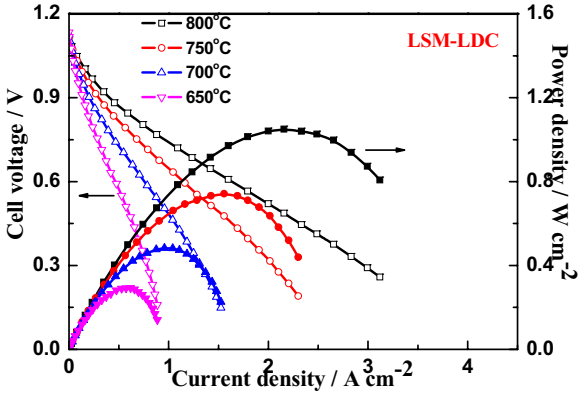
➢Solutions: LSM-YSZ/LSM-LDC bi-layered cathode

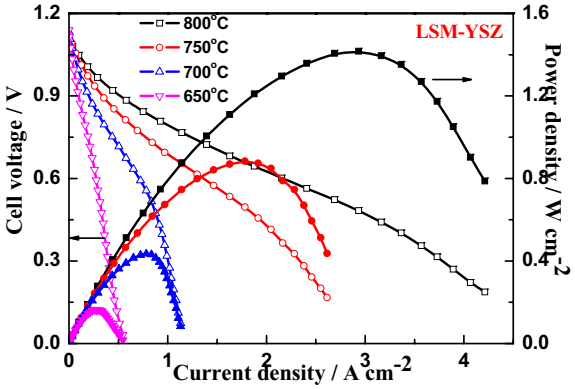


2.2 Cathode with two different electrolyte components

-Performance of cells with LSM-YSZ/LSM-LDC bi-layered cathodes







MPD at 650°C

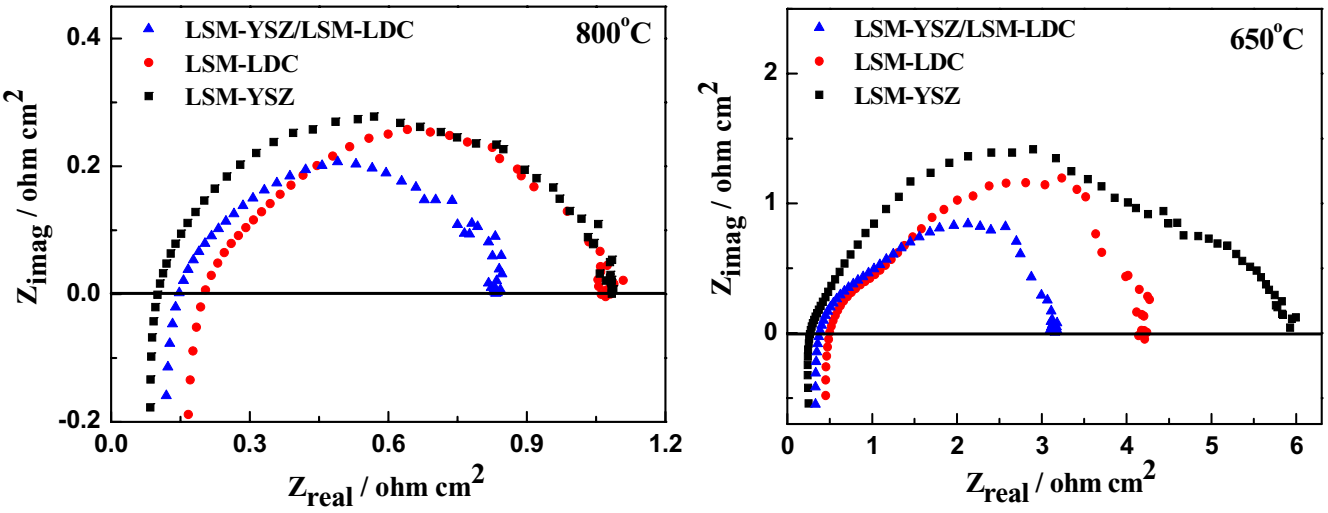
Bi-layered cathode: 0.44 W cm^{-2}

LSM-YSZ cathode: 0.16 W cm^{-2}

LSM-LDC cathode: 0.29 W cm^{-2}

2.2 Cathode with two different electrolyte components

- Impedance of cells with bi-layered cathodes



➢**Ohmic resistance:**

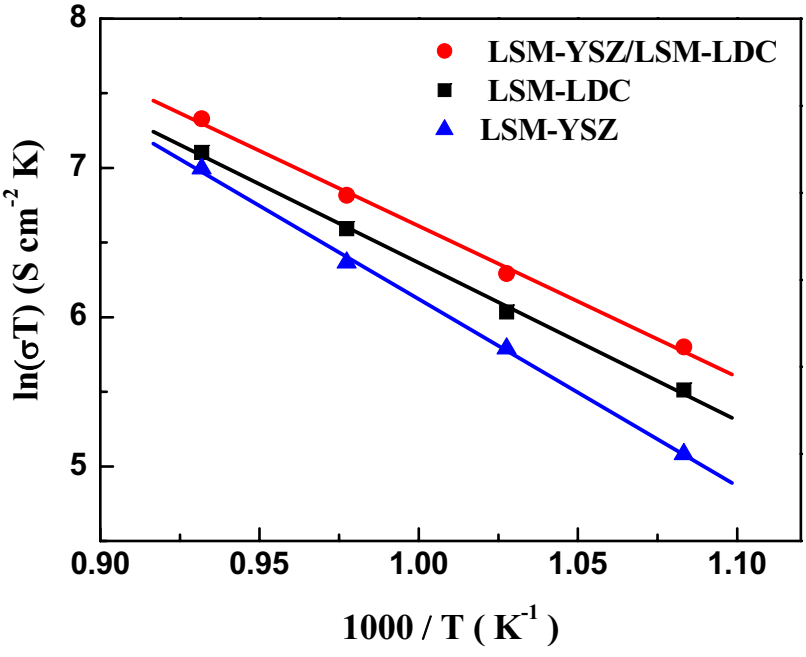
$$Cell_{LSM\text{-}YSZ} < Cell_{Bi\text{-}layered\ cathode} < Cell_{LSM\text{-}LDC}$$

➢**Polarization resistance:**

$$Cell_{Bi\text{-}layered\ cathode} < Cell_{LSM\text{-}LDC} < Cell_{LSM\text{-}YSZ}$$

2.2 Cathode with two different electrolyte components

- Activation energy of polarization resistance of cells with bi-layered cathodes



➢Ea (kJ mol^{-1}):

✓Bi-layered cathode : 82

✓LSM-LDC: 84

✓LSM-YSZ: 104

Arrhenius curves

2. New Cathode Designs

2.1 Cathode with a high oxide conductivity electrolyte

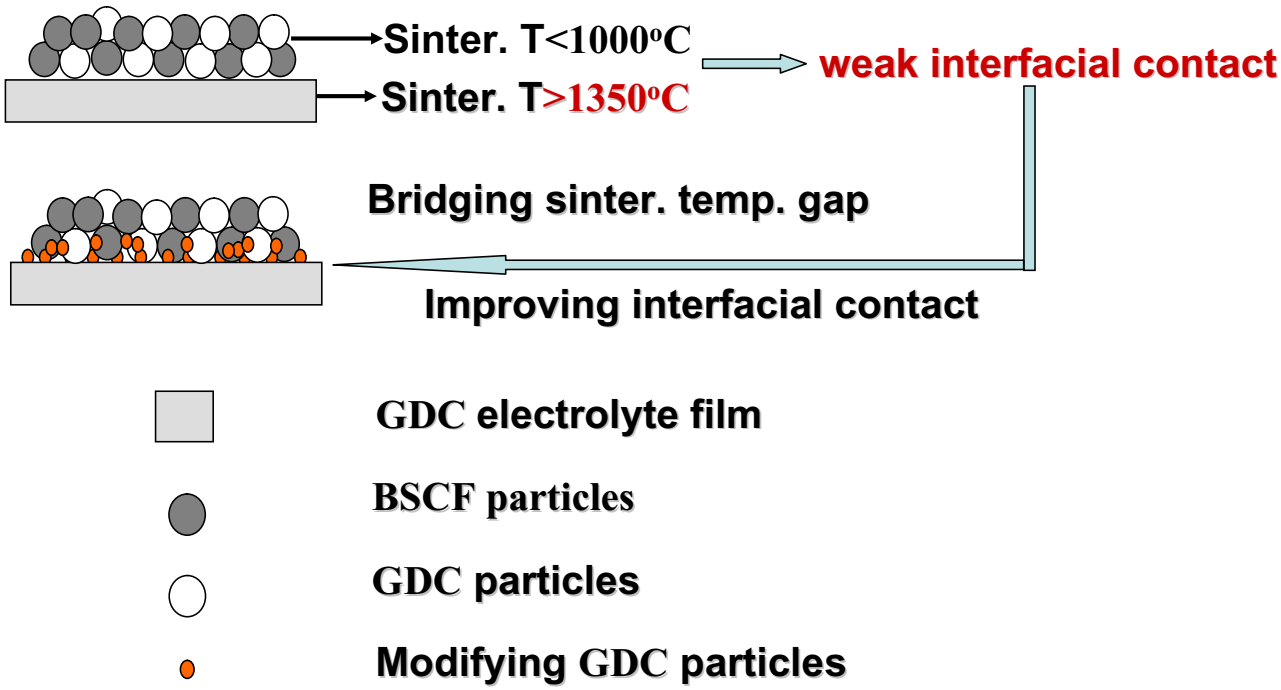
2.2 Cathode with two different electrolyte components

2.3 Cathode on a modified electrolyte/cathode interface

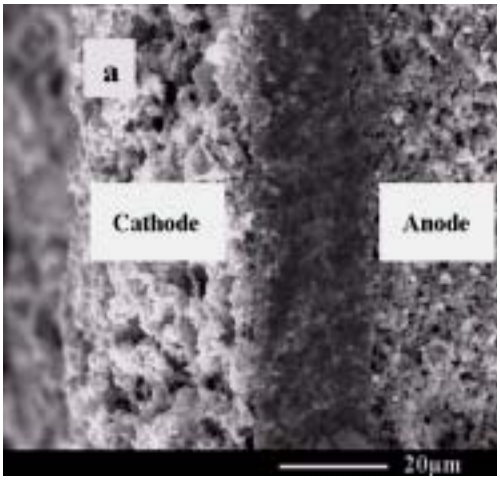
2.4 Cathode with two different perovskite oxide catalysts

2.3 Cathode with a modified electrolyte/cathode interface

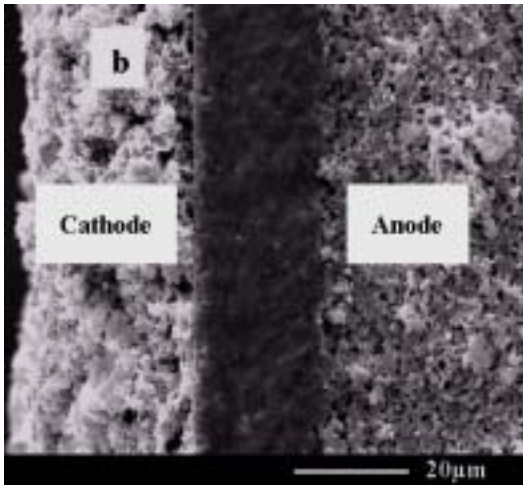
-LT cell with the same electrolyte modified surface



2.3 Cathode with a modified electrolyte/cathode interface - LT cell with a same electrolyte modified surface



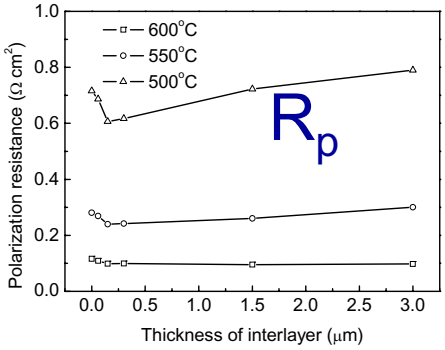
(a) Cell with a GDC modifying layer (0.15 μ m)

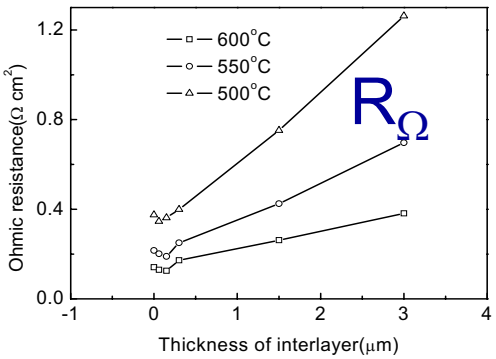


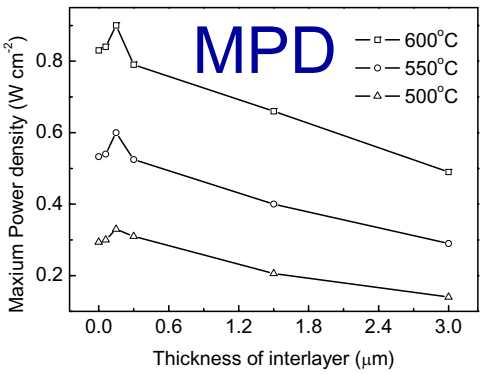
(b) Cell without a GDC modifying layer

The modifying GDC layer strengthens the contact between electrolyte and cathode

2.3 Cathode with a modified electrolyte/cathode interface - LT cell with a same electrolyte modified surface

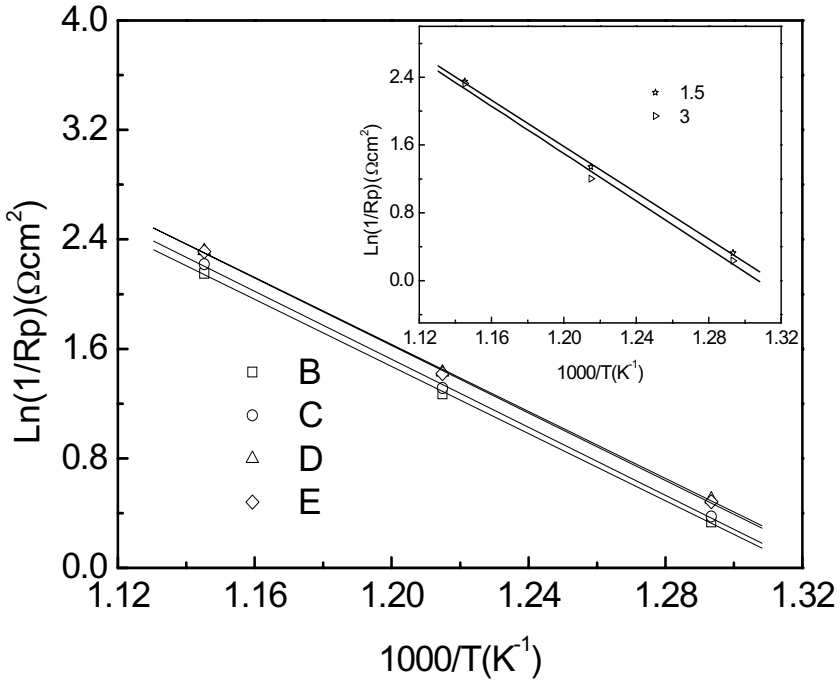






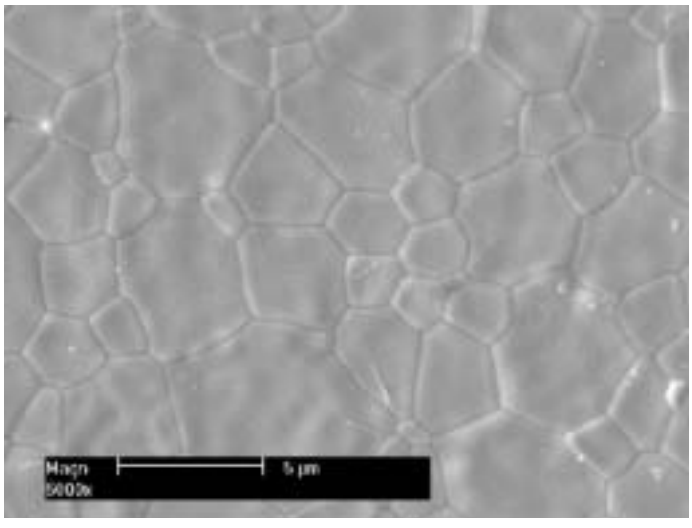
The optimum thickness of the GDC layer is 0.15 μ m

About mechanism

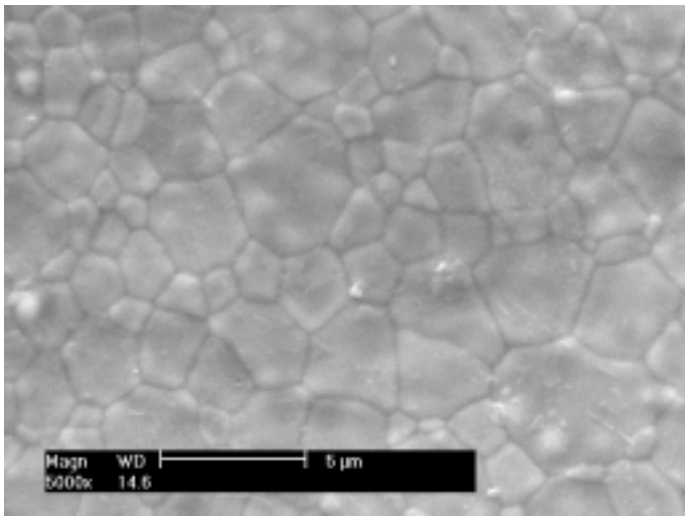


The same Ea and different A value suggest that the modifying change only the number of active sites.

2.3 Cathode with a modified electrolyte/cathode interface
- Modified with a high ionic conductivity electrolyte

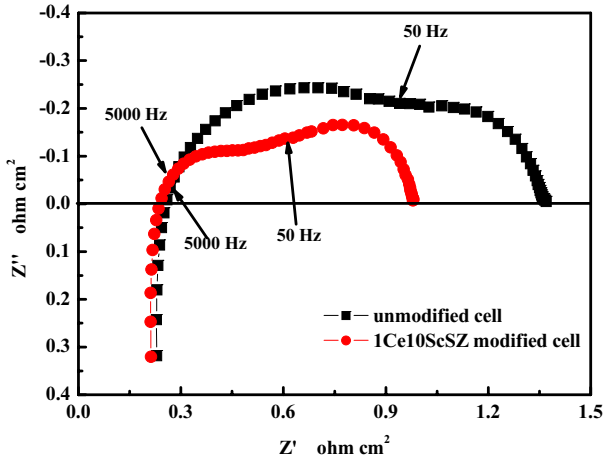


YSZ electrolyte film

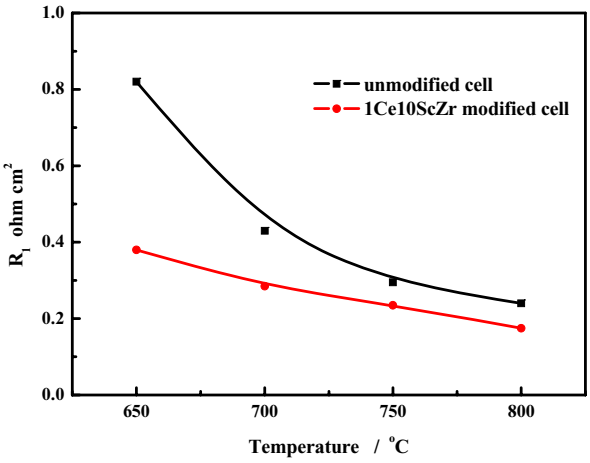


ScSZ modified YSZ electrolyte film

2.3 Cathode with a modified electrolyte/cathode interface - Modified with a high ionic conductivity electrolyte



EIS



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2. New Cathode Designs

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2.2 Cathode with two different electrolyte components

2.3 Cathode with a modified electrolyte/cathode interface

2.4 Cathode with two different perovskite oxide catalysts

2.4 Cathode with two different perovskite oxide catalysts

BSCF

- New MIEC materials
- High oxygen reduction activity at low temp.
- Low sintering temp.

LSM

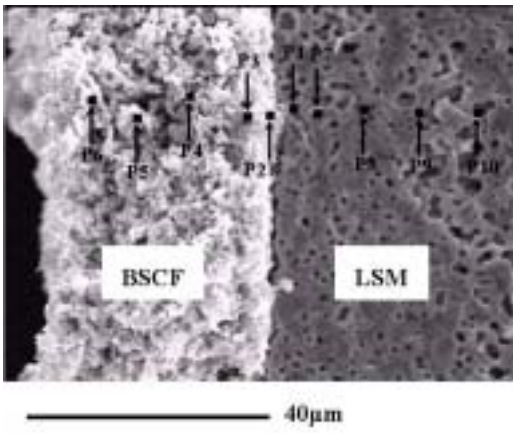
- High electron conductivity
- Low oxide conductivity
- Low oxygen reduction activity at low temp.
- High sintering temp.

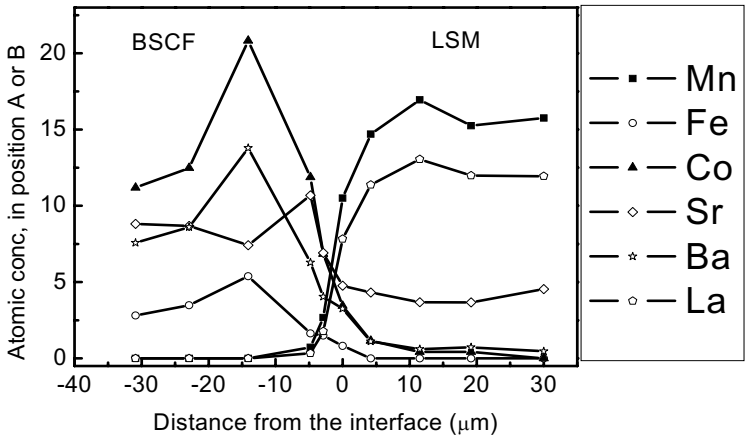
How to take advantages of the two materials ?

2.4 Cathode with two different perovskite oxide catalysts

LSM transition layer to bridge sintering temp. gap

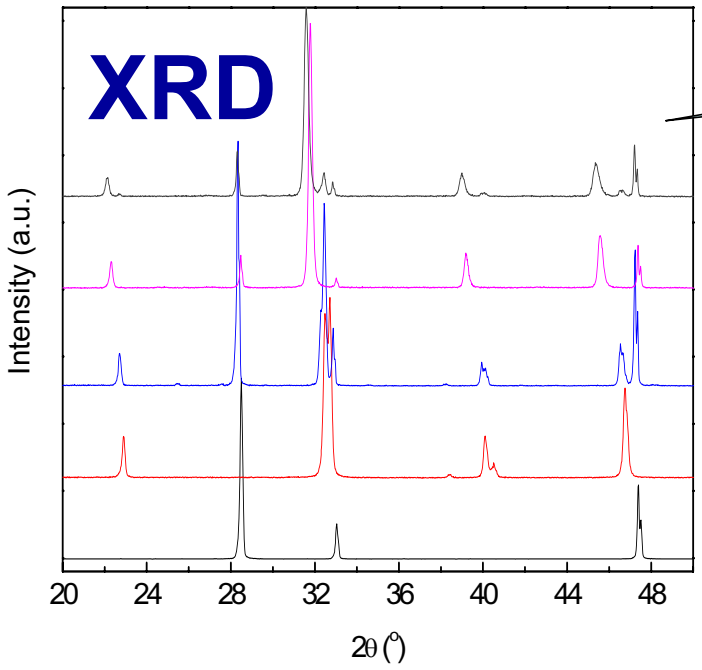
EDX of LSM/BSCF bi-layered assembly





2.4 Cathode with two different perovskite oxide catalysts

LSM/BSCF-GDC



Inter-diffusions between the LSM layer and the BSCF layer

BSCF fired onto LSM film at 950°C

BSCF fired onto GDC electrolyte membrane at 950°C

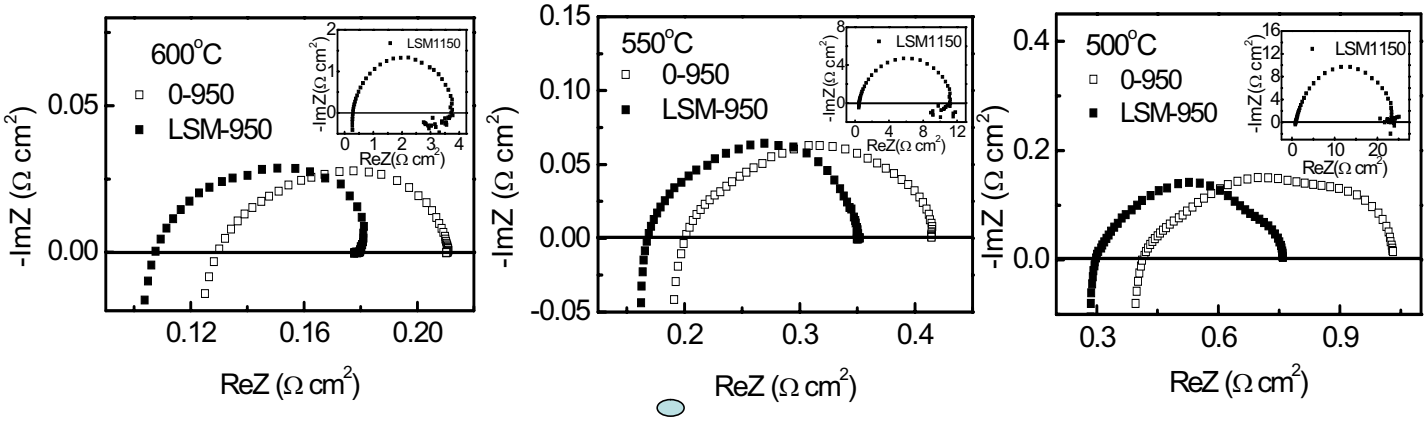
LSM transition layer fired onto GDC electrolyte membrane at 1300°C

LSM powder

GDC electrolyte membrane

2.4 Cathode with two different perovskite oxide catalysts

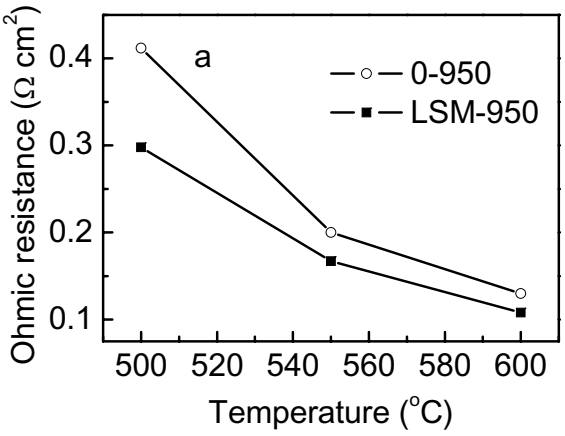
Impedance of cell with LSM/BSCF-GDC

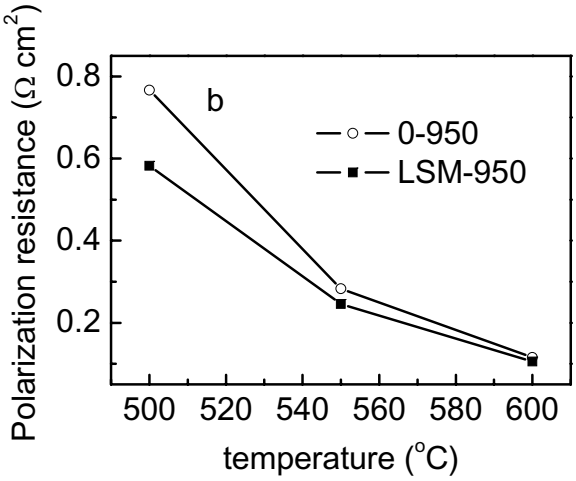


The LSM transition layer reduces both ohmic resistance and polarization resistance

2.4 Cathode with two different perovskite oxide catalysts

Polarization resistance

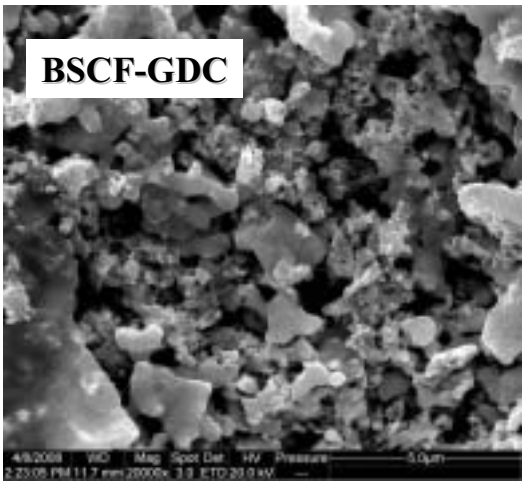


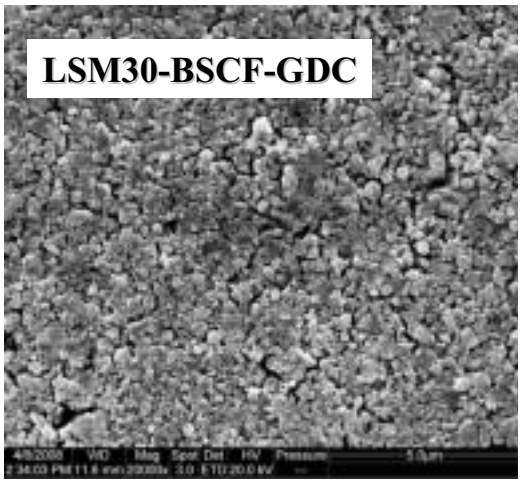


The LSM transition layer not only improves interfacial contact but also accelerates oxygen reduction, especially at low temp.

2.4 Cathode with two different perovskite oxide catalysts

LSM-BSCF-GDC -microstructure



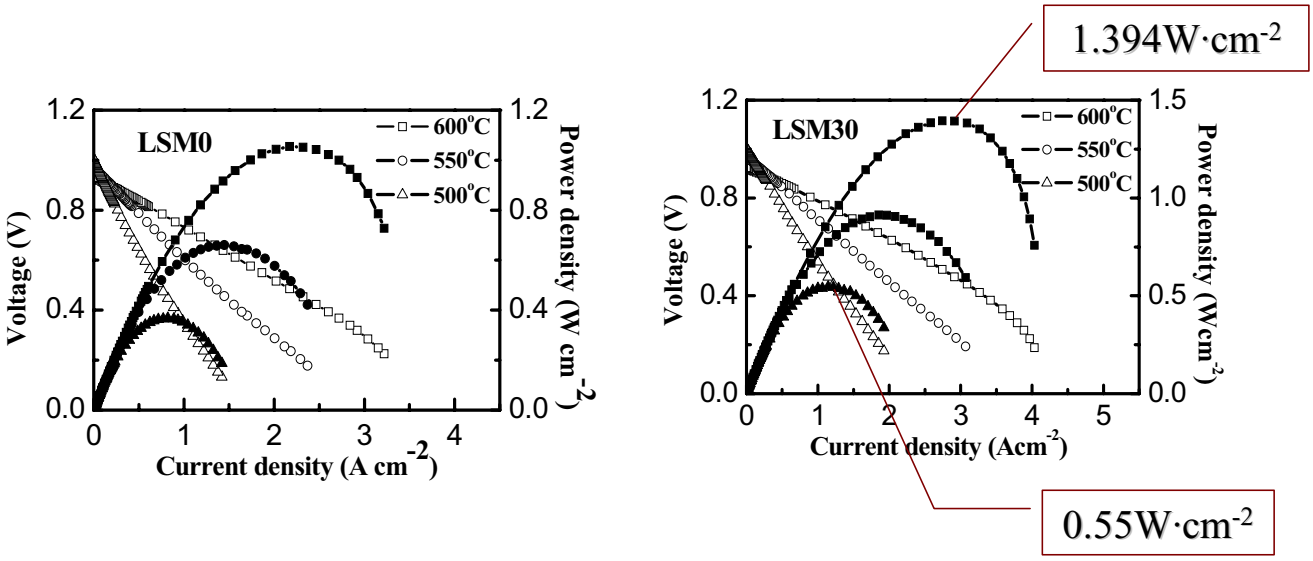


SEM pictures

The LSM-BSCF-GDC cathode shows a better microstructure than the BSCF cathode.

2.4 Cathode with two different perovskite oxide catalysts

- LSM-BSCF-GDC, Cell performance



The cell with a 30wt% LSM cathode exhibits the best cell performance attains a MPD of 1.394 and0.55 $W \cdot cm^{-2}$ at 600 and 500°C respectively.

3. Summary

Four types of new cathodes have been fabricated and investigated at DICP for SOFC.

- Cathode with high oxide conductivity electrolyte
- Cathode with two different electrolytes
- Cathode with a modified electrolyte/cathode interface
- Cathode with two different perovskite oxide catalysts

All the cells with new composite cathodes show better performance than the unmodified one, especially at lower temperatures.

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