Improved Cathode Performance via Infiltration

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Outline

- **Major Conclusions**
- **Motivation: Economic Merit & Benefit**
- **Objectives and Technical Approach**
- **Results and discussion**
  - Isolation of surface properties
    - The use of dense film electrode to eliminate effects of microstricture
    - Elimination of mass transfer limitations
  - Surface limitation of LSCF
    - Cells with dense LSCF films prepared by sputtering
  - Cells with surface-modified LSCF (sputtering and infiltration)
    - Improved performance and stability
- **Conclusions**
- **Questions to be Answered**
- **Acknowledgment**

Major Conclusions

- Demonstrated the feasibility that the stability and catalytic properties of LSCF-based cathodes can be enhanced by infiltration of a catalytically active coating.
- Developed a platform for reliably evaluating the surface catalytic properties of cathode materials.

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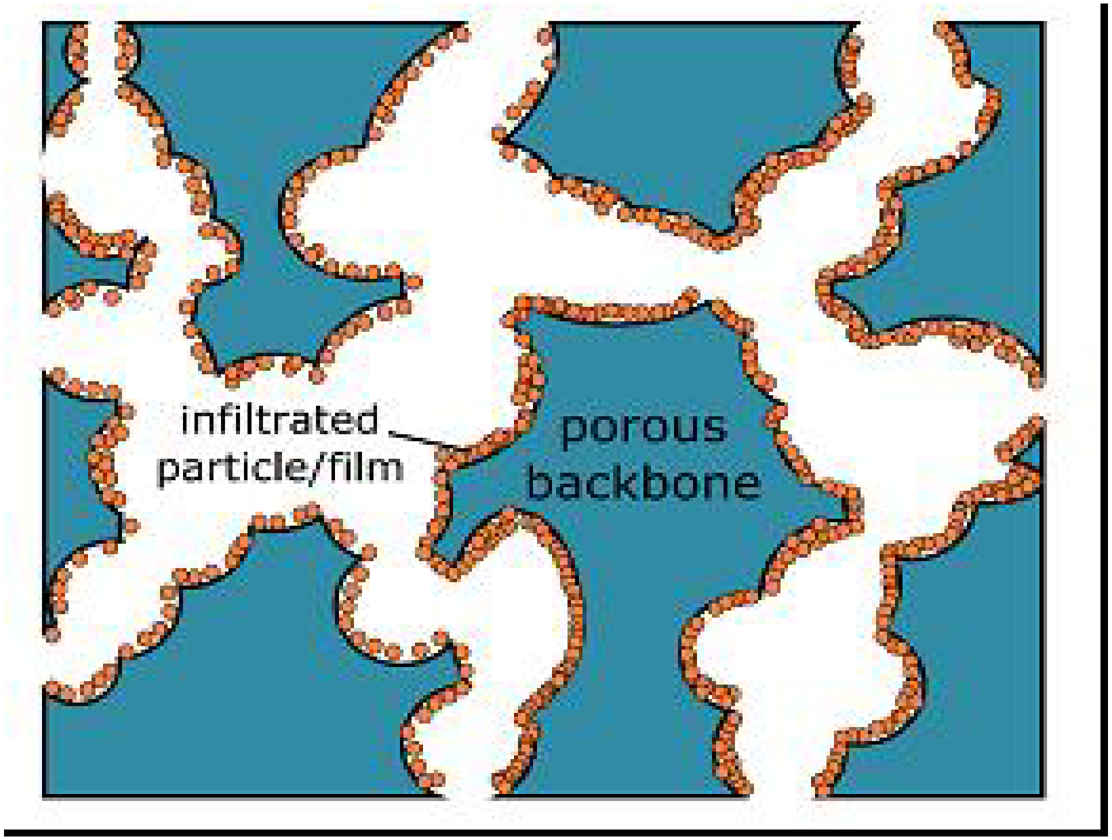
- Developed a platform for reliably evaluating the surface catalytic properties of cathode materials.

Motivation

- Since performance/reliability of SOFCs depends critically on the cathodes (more so at lower operating temperatures), reduction in cathode polarization resistance and improvement in stability will reduce the cost of SOFCs and help to meet **DOE cost goals**.
- **Benefits**
  - **Reduce the ASR** of the cathode to further enhance the performance and reduce the losses on cathodes
  - **Improve the stability** and operational life of cathodes and SOFCs
  - Reduce the sensitivity to contaminants poisoning (using a coating with tolerance to poisoning)
  - Develop new approaches to high performance cathodes through new design of cathode architecture

Characteristics of an ideal cathode material

- High catalytic activity
- Fast Transport of ionic and electronic species



A porous MIEC backbone with a thin film coating of catalytically active materials for oxygen reduction

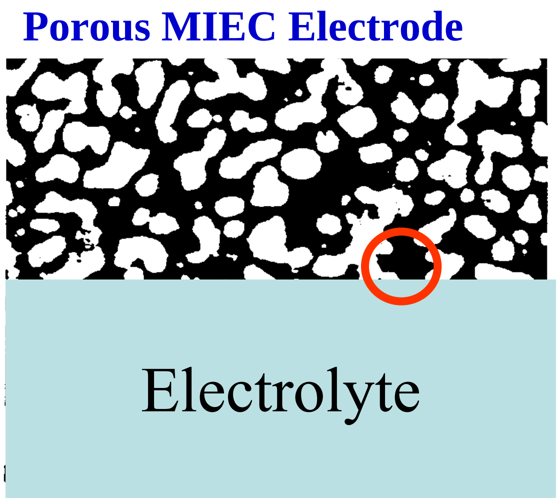
Objectives

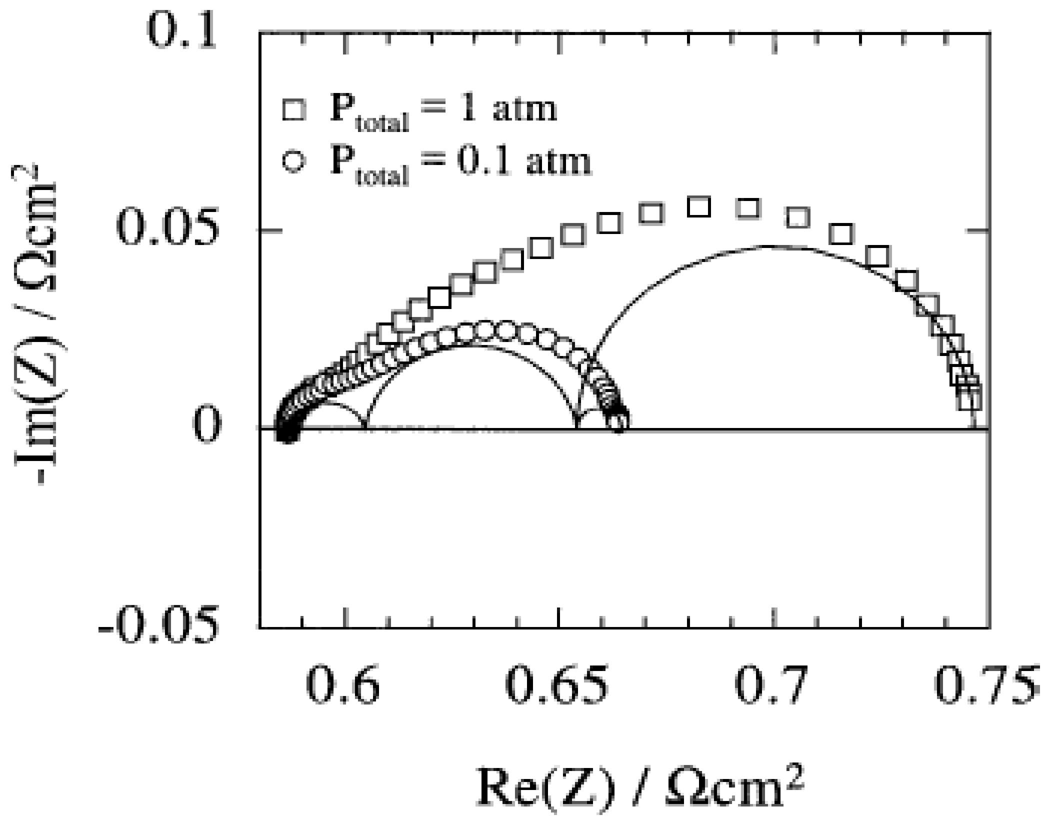
- To demonstrate the concept feasibility that a highly conductive backbone coated with a catalytically active material makes a more efficient electrode;
- To determine if the surface catalytic property and/or stability of a state-of-the-art LSCF cathode can be enhanced by a catalytically active coating; and
- To gain insight into rational design of better or more efficient electrode structure or microstructure.

Technical Approach

- To develop a strategy for reliable testing of surface catalytic properties of a thin film cathode material without the limitation of geometry/microstructure of the electrodes;
- To modify the surface of an LSCF backbone (having high ionic and electronic conductivity) by a thin coating of a stable and catalytically active material for O_2 reduction;
- To select and modify the detailed microstructure of backbone and catalyst materials that create a better performing cathode.

How to determine the catalytic property of an electrode?





Little can be learn from the impedance spectra.

Factors Influencing R_P

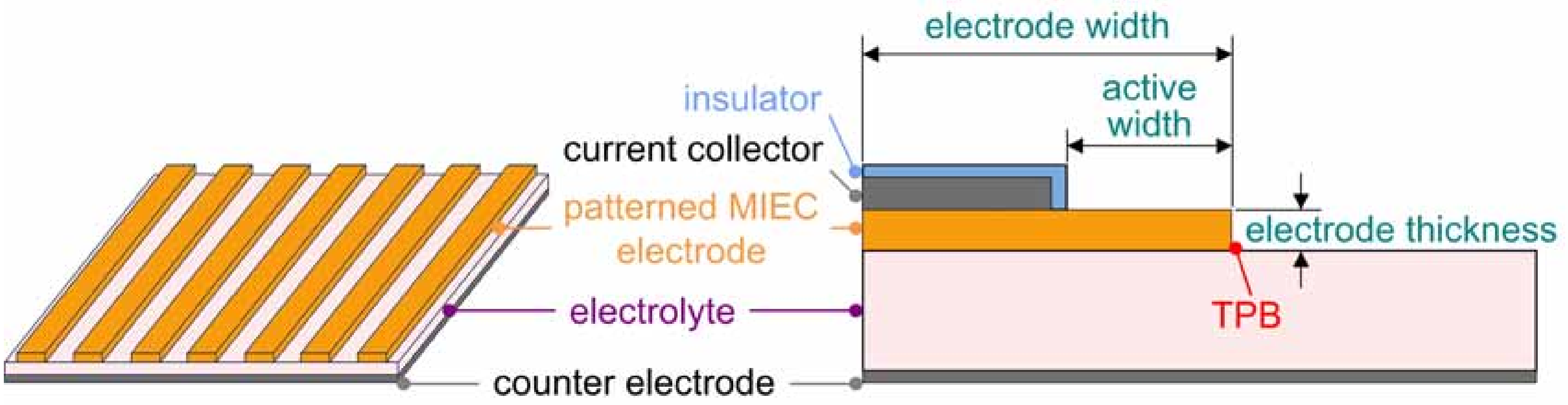
	Intrinsic Properties	Extrinsic (influenced by microstructure/geometry)	Electrode Polarization Resistance R_P
Surface **catalytic** properties	$i_o, k^o, \alpha_a, \alpha_c$	Specific surface area	$R_{surface,ct}$
Ionic and electronic **Transport** in bulk and along surfaces	$\sigma_{V,} D_V$	Phase distribution, Connectivity for v transport	R_V
	$\sigma_{e,} D_e, \sigma_h, D_h$	Connectivity for e, h transport	R_{sheet}
Gas Transport		Porosity, pore size, connectivity	R_{gas}
	DFT calculations	Microscopic Characterization	Electrochemical Measurements
	Continuum modeling		

← may involve multiple steps

Challenges

- How to determine the intrinsic properties or how to eliminate the effect of electrode microstructure?
- How to separate charge transfer from the mass transfer processes?
- How to isolate different reaction sites and sort out the reaction sequence and mechanisms?
- How to extract the characteristic parameters of electrode materials?

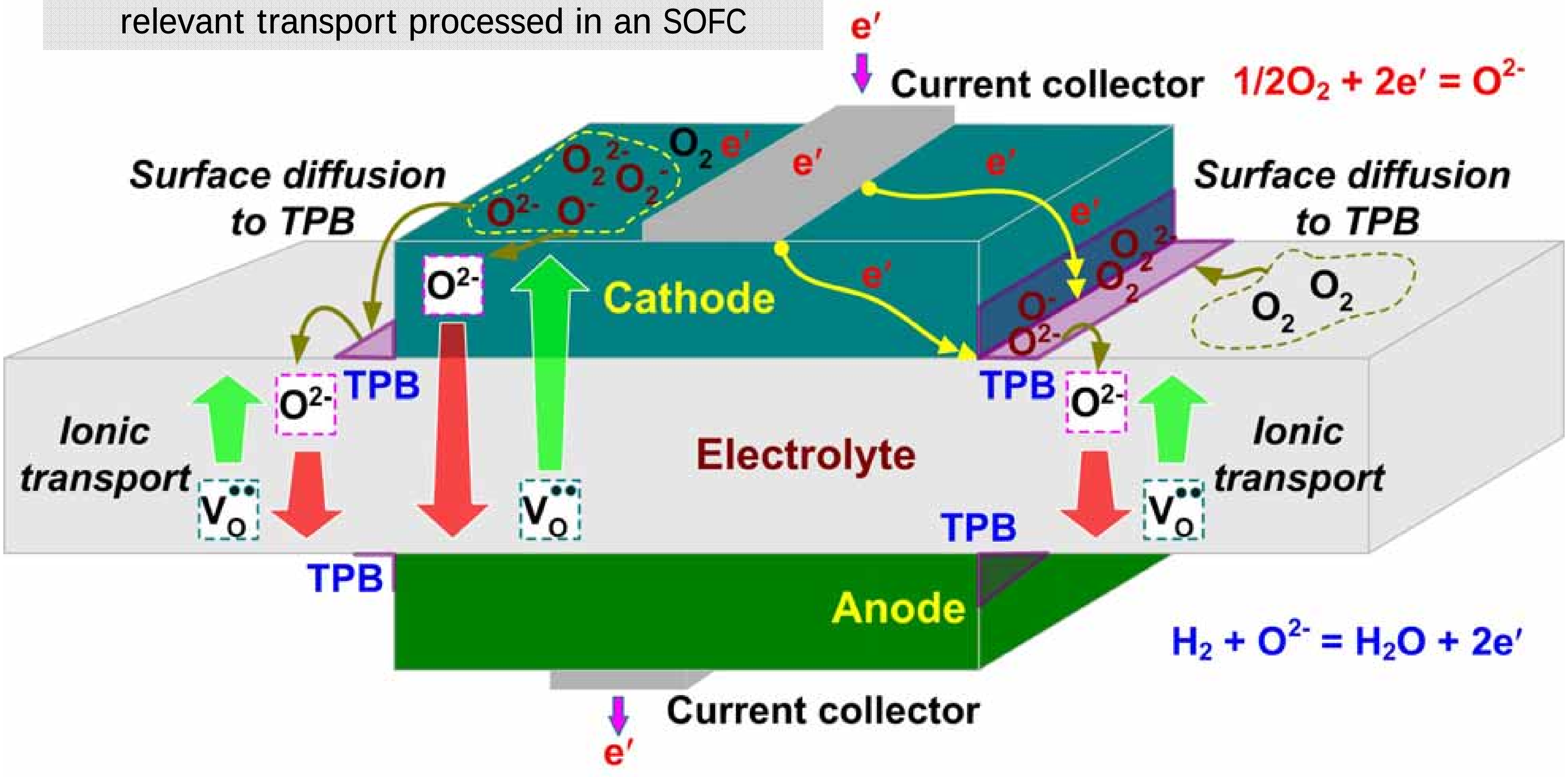
Electrode of well-controlled geometry



- To eliminate the effect of microstructure of porous electrodes (or to decouple intrinsic from extrinsic properties)
- To correlate electrochemical performance with specific reaction sites (TPB, surfaces, etc…)

Processes Relevant to Continuum Modeling

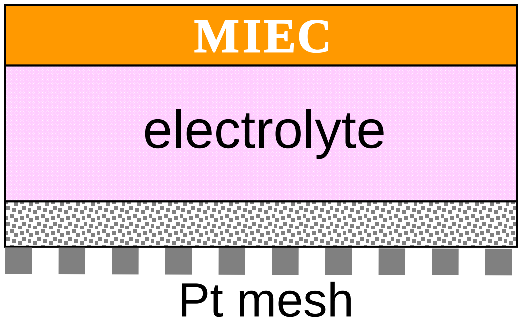
Schematic of oxygen reduction and the relevant transport processed in an SOFC



Choi, Mebane, and Liu, Topics in Catalysis, 46, (2007), p.386.

Factors Influencing R_P

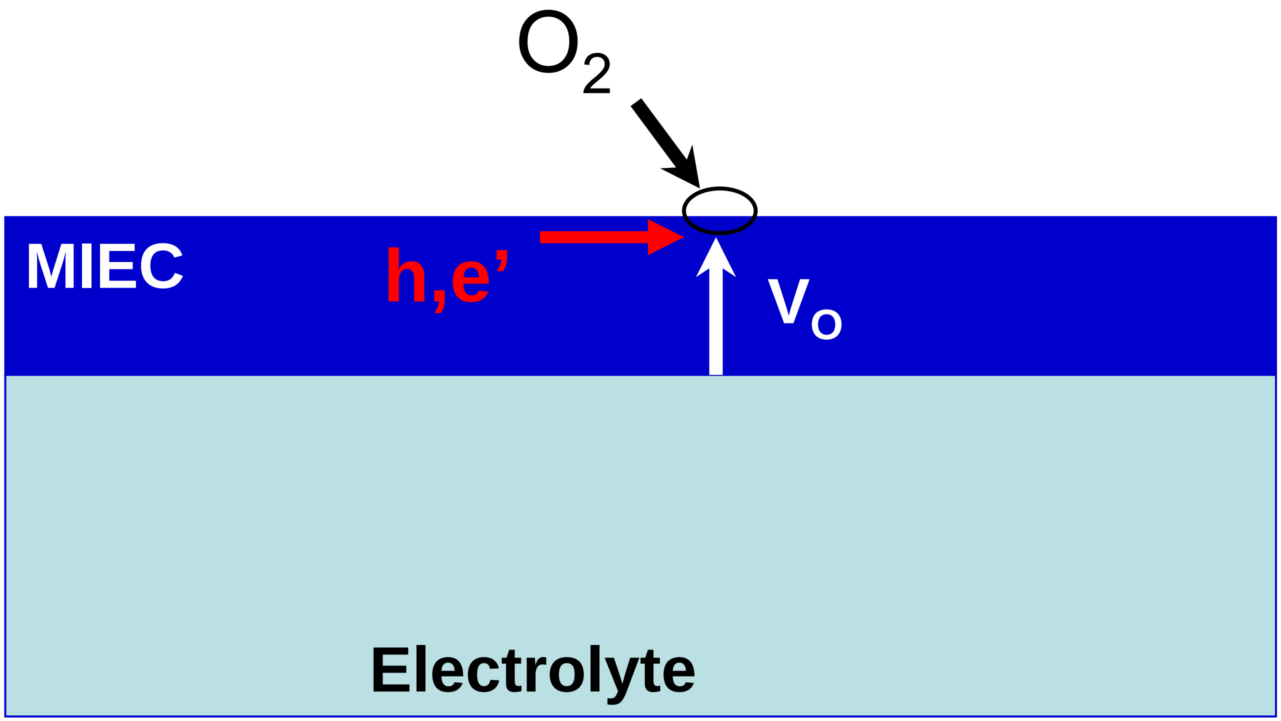
- The use of **dense MIEC films**



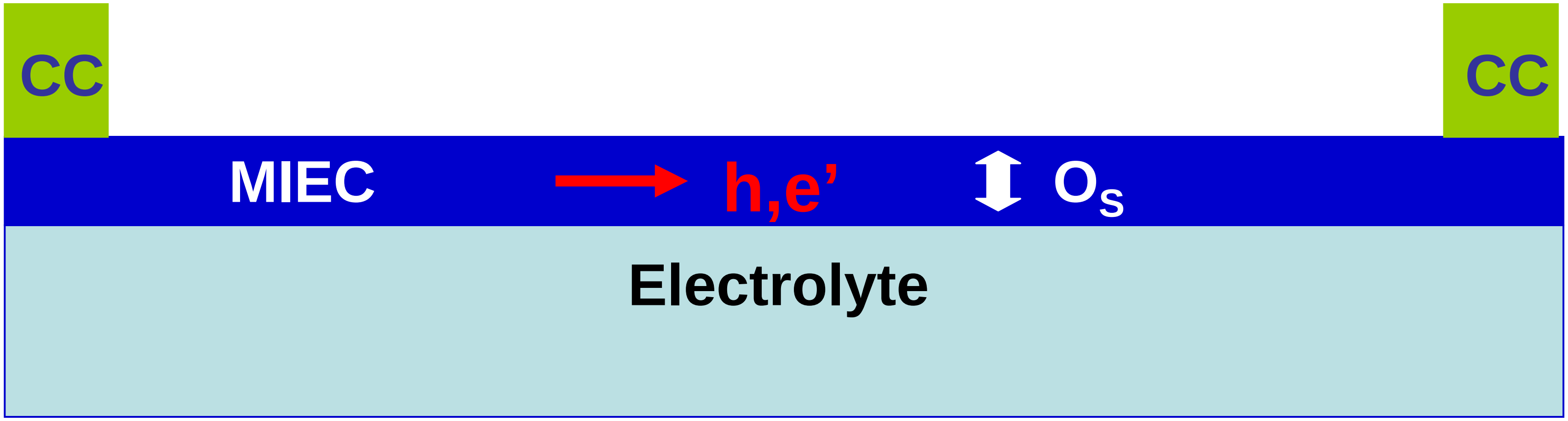
	Intrinsic Properties	Extrinsic (influenced by microstructure/geometry)	Electrode Polarization Resistance R_P
Surface **catalytic** properties	$i_o, k^o, \alpha_a, \alpha_c$	→	$R_{surface,ct}$
Ionic and electronic **Transport** in bulk and along surfaces	$\sigma_{V,} D_V$	→	R_V
	$\sigma_{e,} D_e, \sigma_h, D_h$	→	R_{sheet}
Gas Transport			R_{gas}
	DFT calculations		Electrochemical Measurements
	Continuum modeling		

The Simplest Case:

Surface reactions on a dense MIEC electrode



Activity of the Bulk MIEC



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MIEC → h,e' ↕ O_S

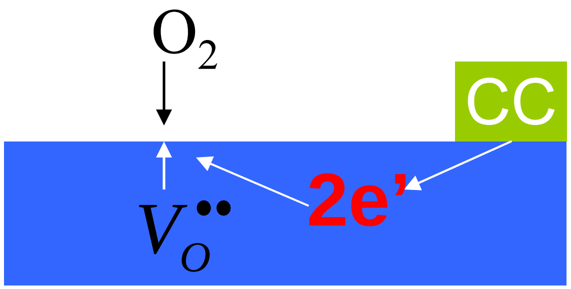
Electrolyte

Two competing influences:

- Top-to-bottom vacancy transport: $R_{V_O^{\bullet\bullet}} \propto L$ =thickness
- Lateral transport of electrons/holes: $R_{sheet} \propto \frac{1}{L}$

As the thickness of the MIEC, L, decreases,
ionic transport gets easier while electronic transport gets harder.

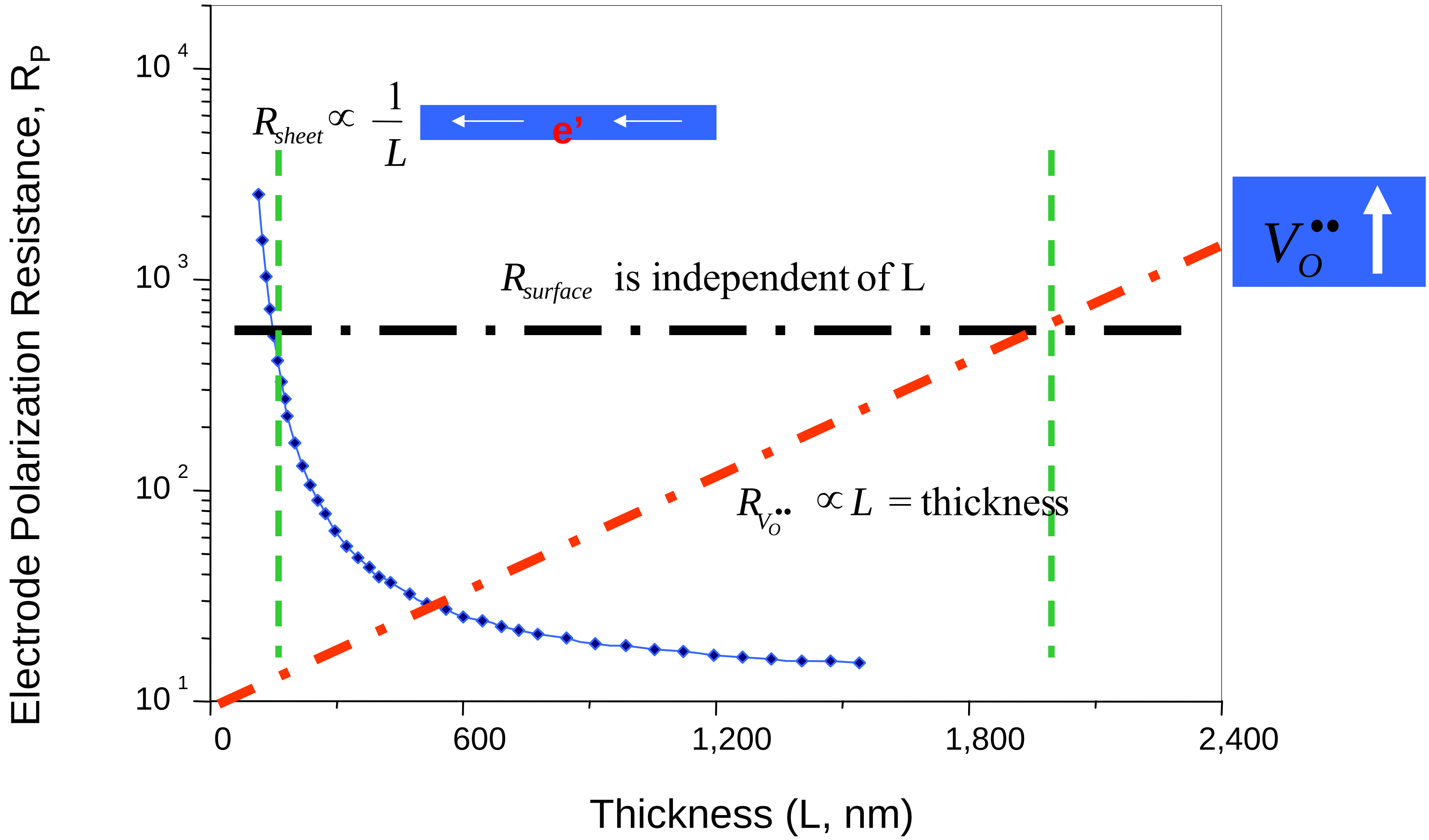
How to decouple charge transfer from mass transfer?



O_2 reduction involves electron and vacancy transport as well as surface reactions across the MIEC-air interface; thus, R_p depends on R_{sheet}, R_v, and $R_{surface}$.

- By changing the thickness of the dense MIEC electrode

Effect of L on R_{sheet} , R_V, $R_{surface}$



$R_{sheet} \propto \frac{1}{L}$

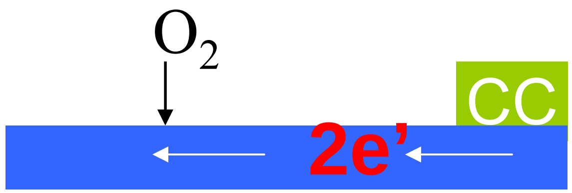
$R_{surface}$ is independent of L

$R_{V_O^{\bullet\bullet}} \propto L =$ thickness

$V_O^{\bullet\bullet}$ ↑

Factors Influencing R_P

- The use of a <u>**dense MIEC film**</u> of <u>**sufficiently thin**</u>



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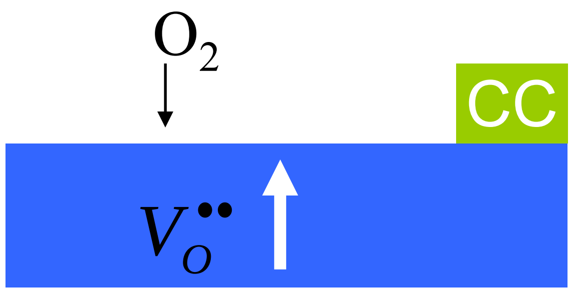
Surface **catalytic** properties			
Ionic and electronic **Transport** in bulk and along surfaces	$\sigma_{e,} D_e, \sigma_h, D_h$	$\longrightarrow$	R_{sheet}
Gas Transport			
	DFT calculations		Electrochemical Measurements
	Continuum modeling		

Factors Influencing R_P

- The use of **dense MIEC film** of sufficiently **thick**



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Gas Transport			
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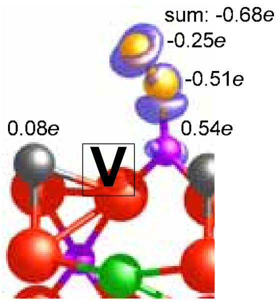
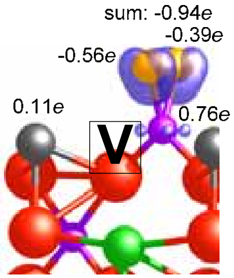
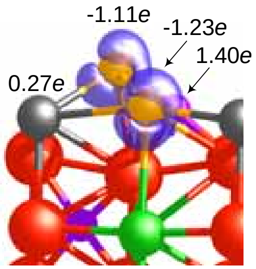
Factors Influencing R_P

- The use of **dense MIEC film** of **proper thickness**







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Surface **catalytic** properties	$i_o, k^o, \alpha_a, \alpha_c$	→	$R_{surface,ct}$
Ionic and electronic **Transport** in bulk and along surfaces			
Gas Transport			
	DFT calculations		Electrochemical Measurements
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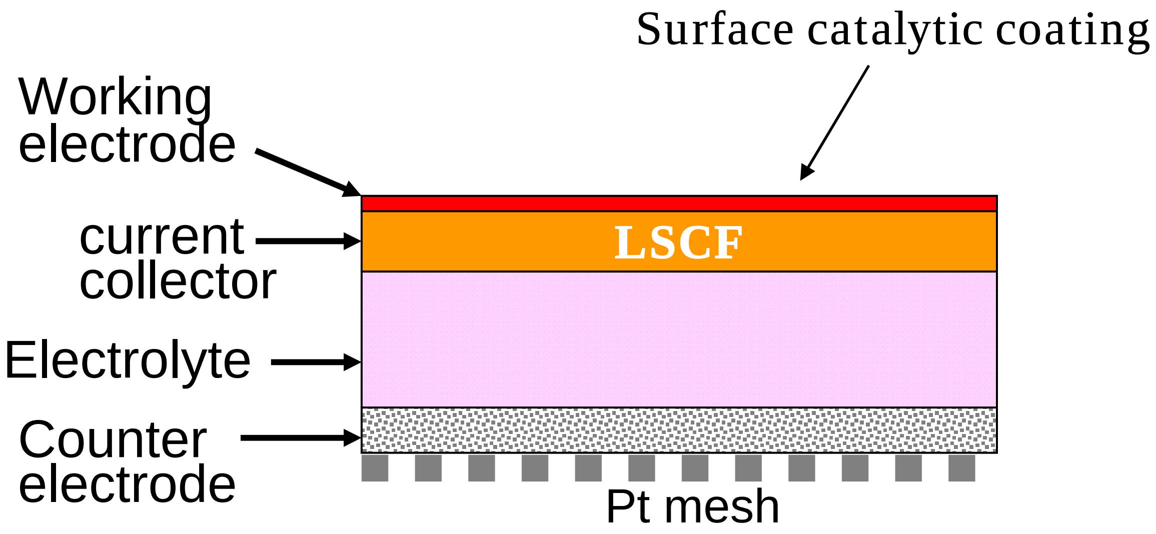
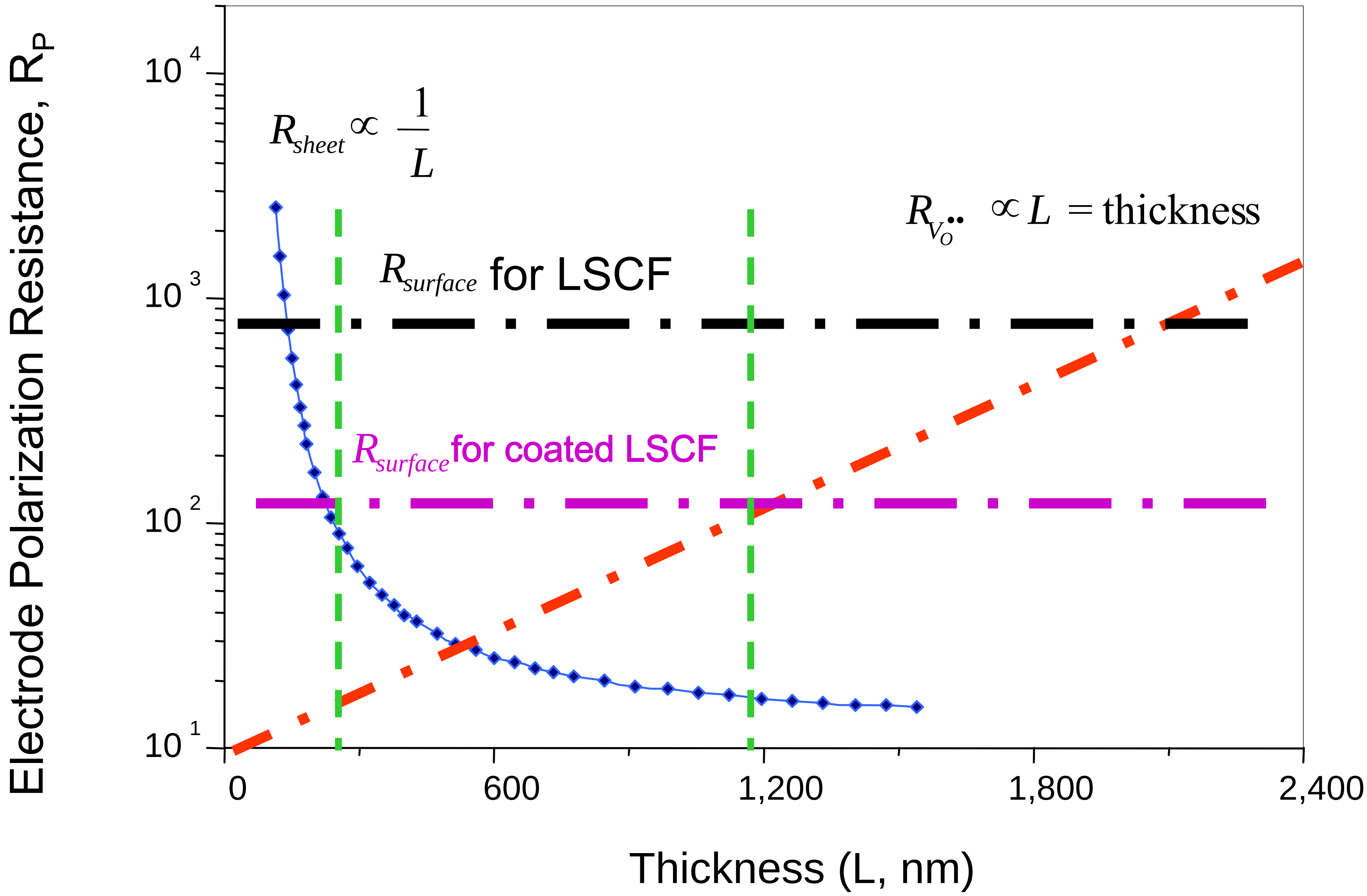
Test Cell: Cross-sectional view



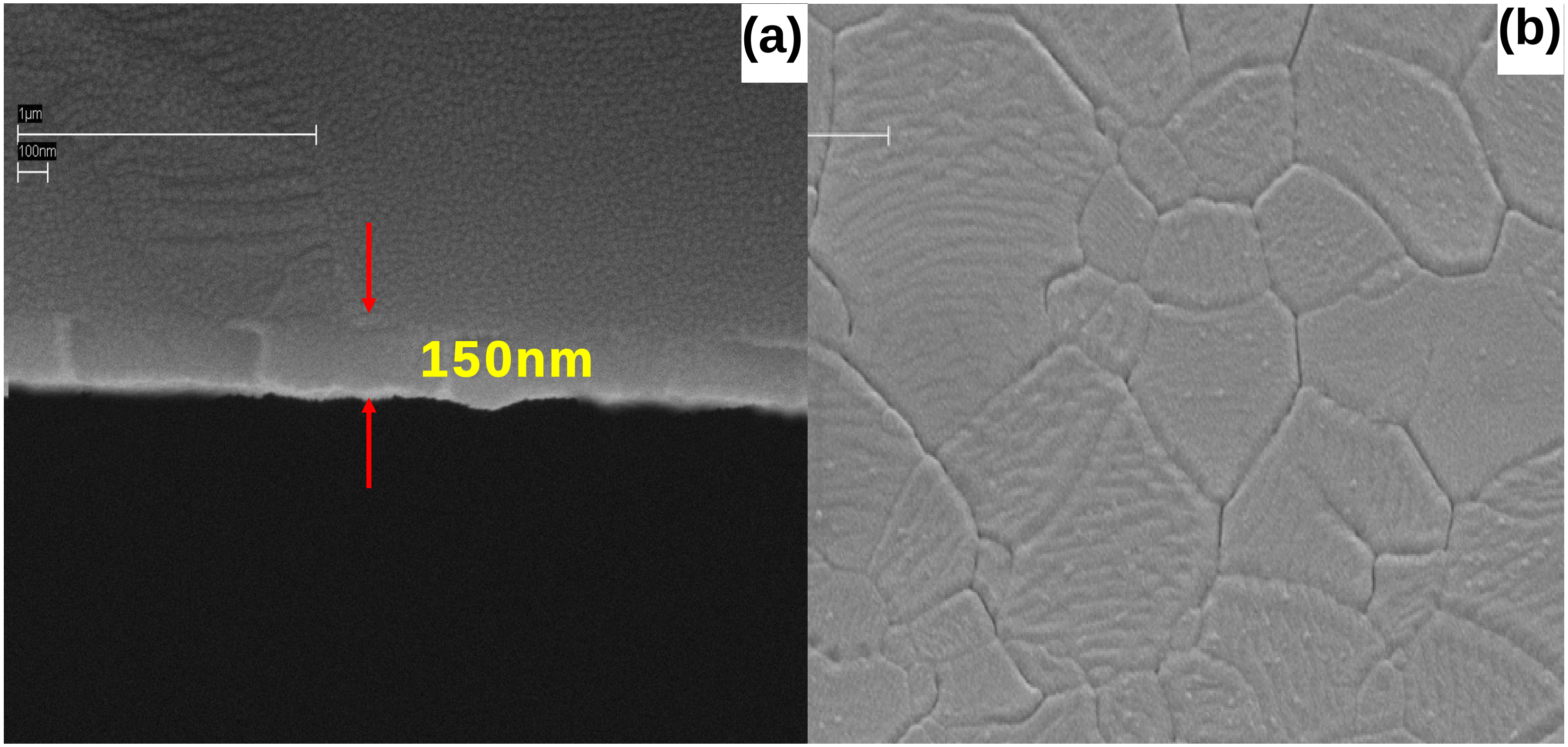
Step 1: The optimal thickness of LSCF can be determined from its effect on cell performance → thickness window for surface study

Step 2: A cell with proper thickness of LSCF as the current collector can then be used to evaluate the surface catalytic properties of the surface coating

Effect of L on R_{sheet} , R_V, $R_{surface}$

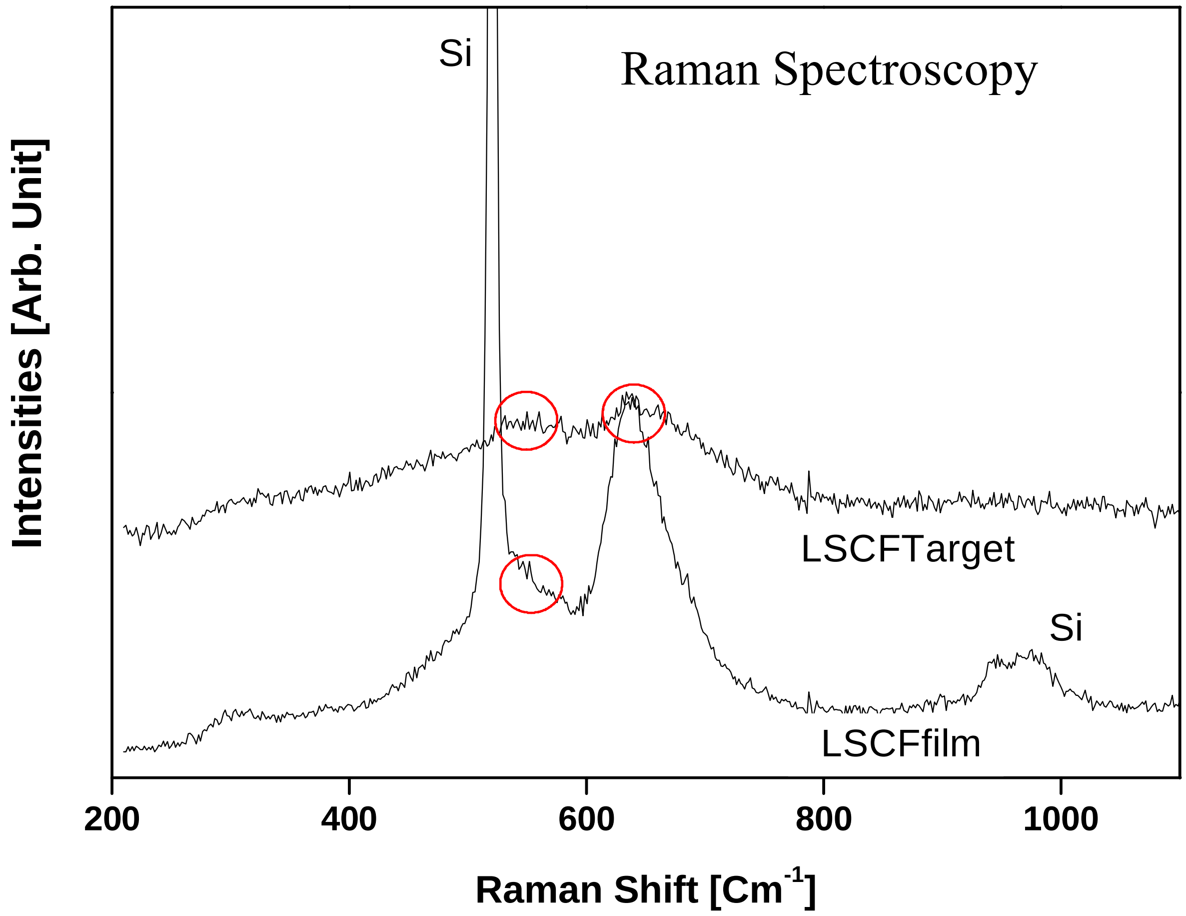


Morphology and thickness of LSCF

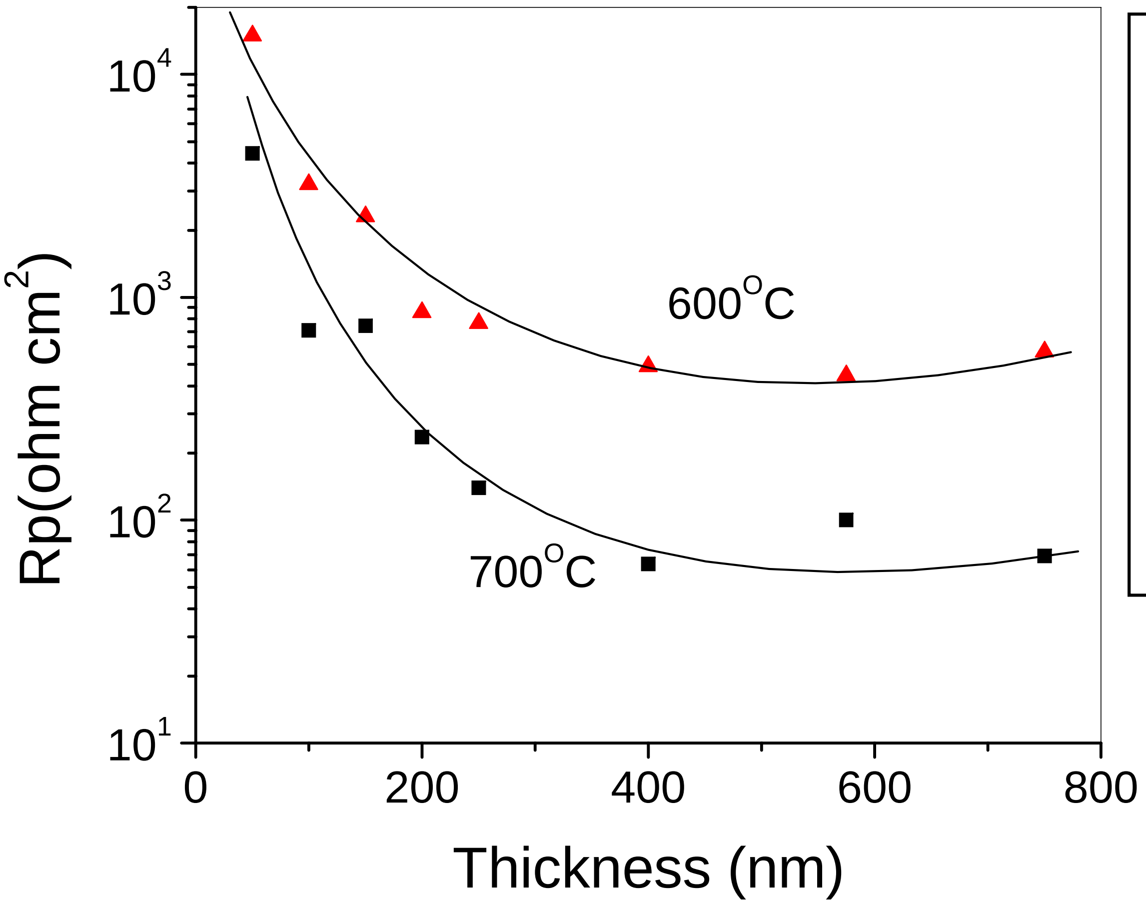


Annealed at 800°C for 1 hour; the desired phase was confirmed by XRD and Raman spectroscopy.

Raman spectra of LSCF



Dependence of R_p on LSCF film thickness



The electrode polarization resistance, R_P, is determined by

$$R_{V_O^{\bullet\bullet}} \propto L = \text{thickness}$$

$$R_{sheet} \propto \frac{1}{L}, \text{ and}$$

$R_{surface}$ is independent of L

The sheet resistance is no longer rate-limiting for LSCF films thicker than ~400 nm, where R_P is limited by surface catalytic activity

Dependence of R_P on pO_2 - Theory

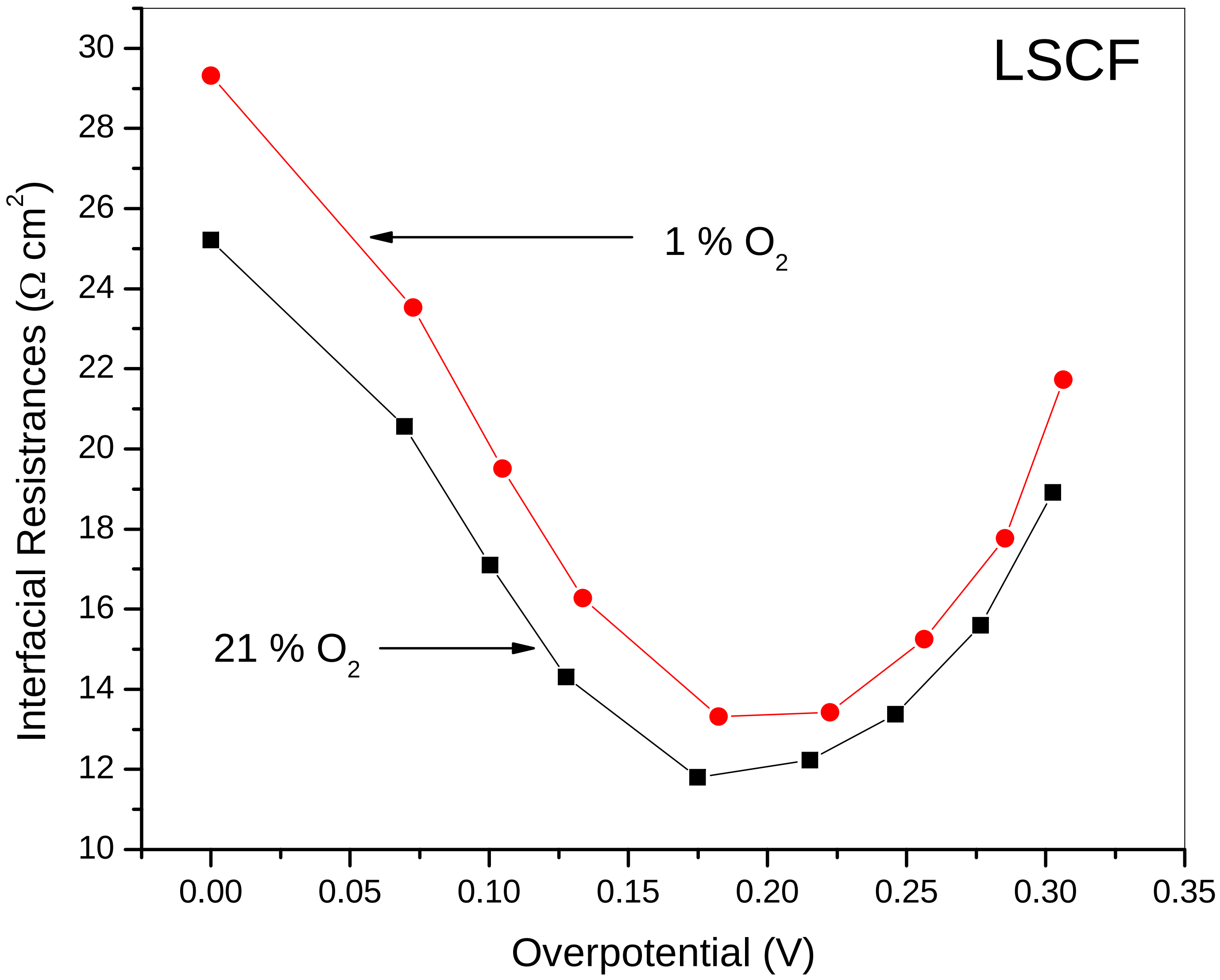
In General

$$R_{ct,surface} = \frac{1}{(\alpha_a + \alpha_c) i_o}\left(\frac{RT}{4F}\right) \propto \frac{1}{p_{O_2}^{\gamma}} \downarrow with \uparrow p_{O_2}; \quad strong$$

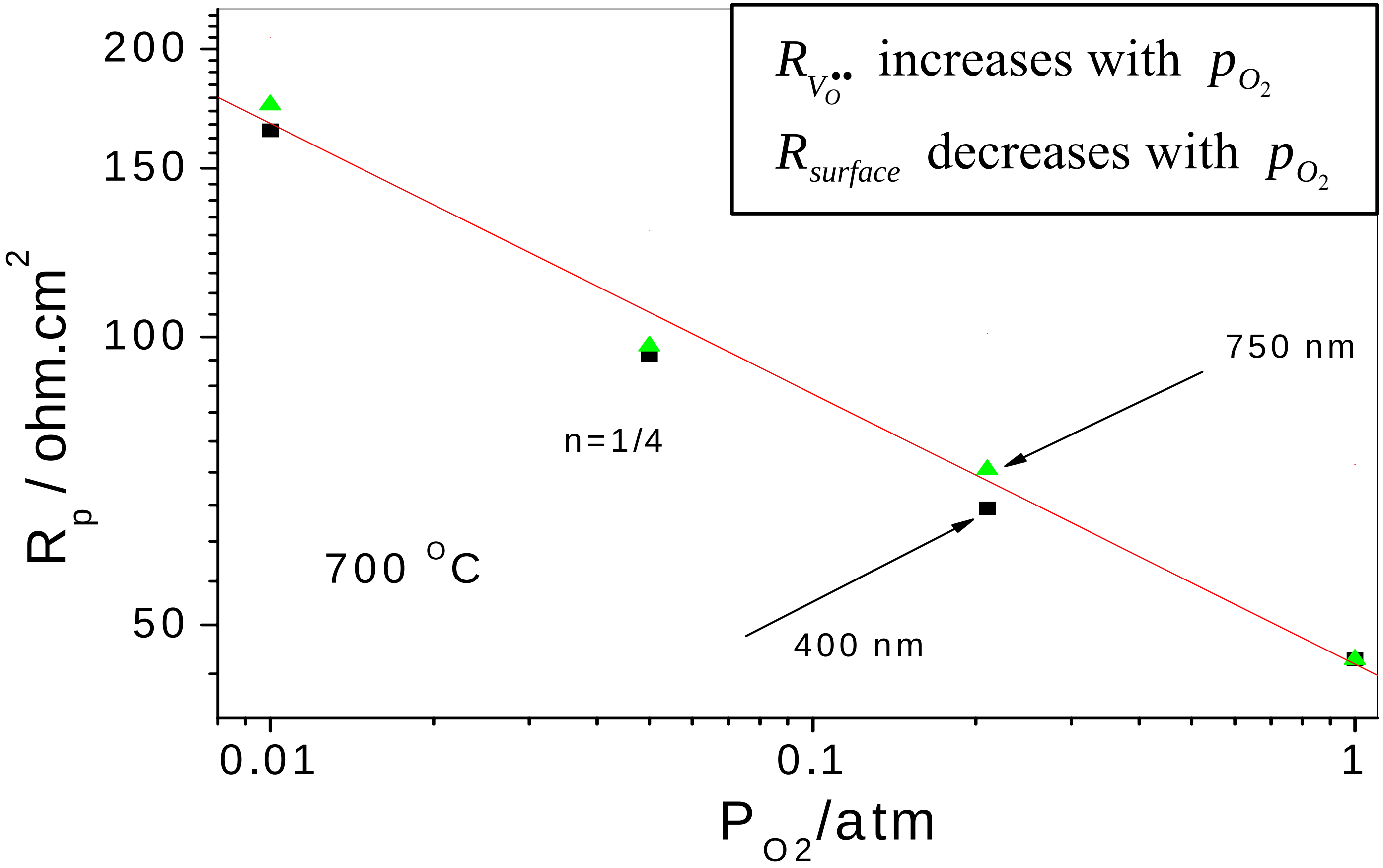
$$R_{V_O^{\bullet\bullet}} \propto p_{O_2}^{\gamma} \;\sin ce \;\; \left[V_O^{\bullet\bullet}\right] \uparrow with \uparrow p_{O_2}; \quad week$$

$$R_{sheet} little \quad dependence \quad on \quad p_{O_2}; \quad very \quad week$$

Dependence of RP on *p*O2 - Results

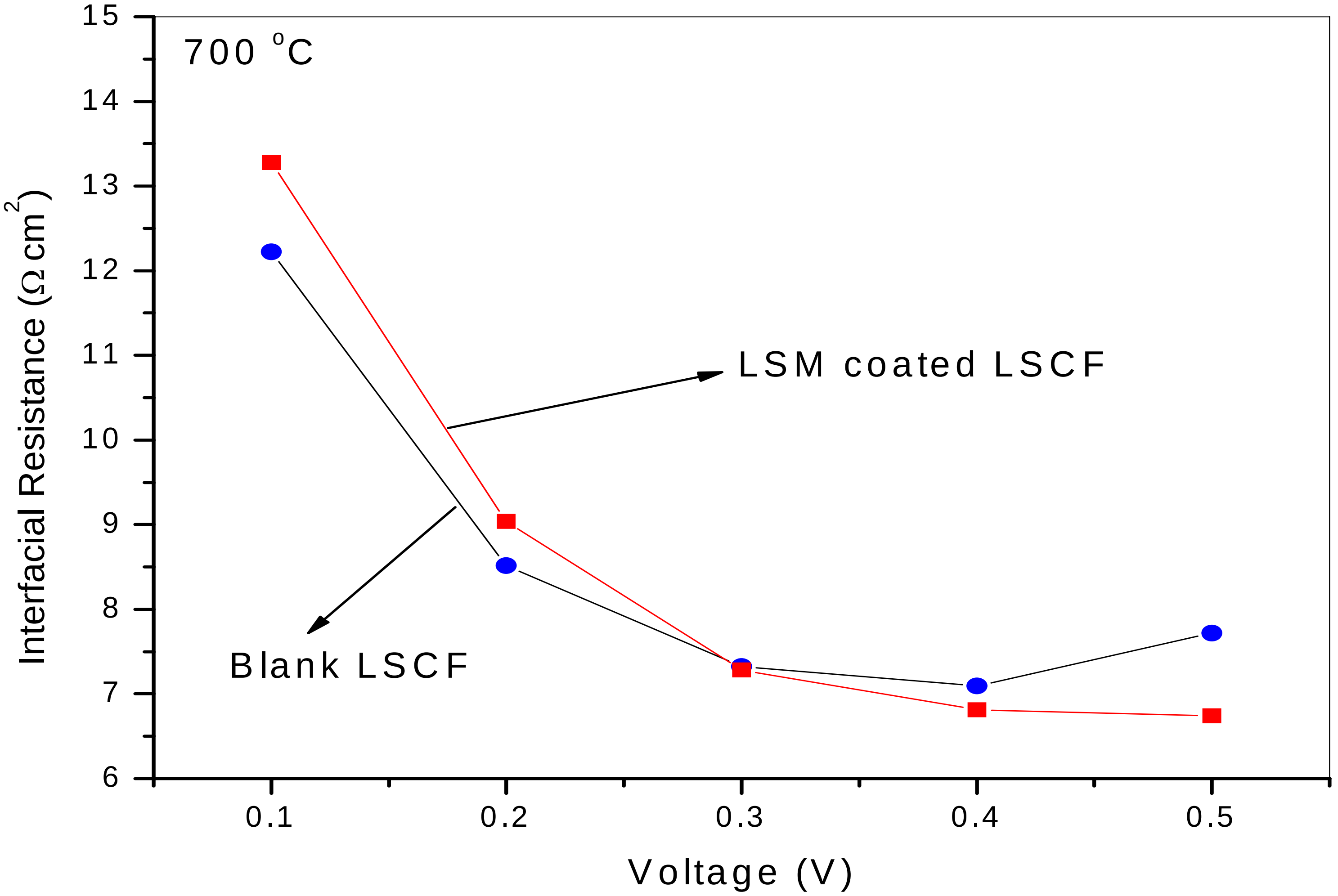


Dependence of R_p on pO_2 at OCV

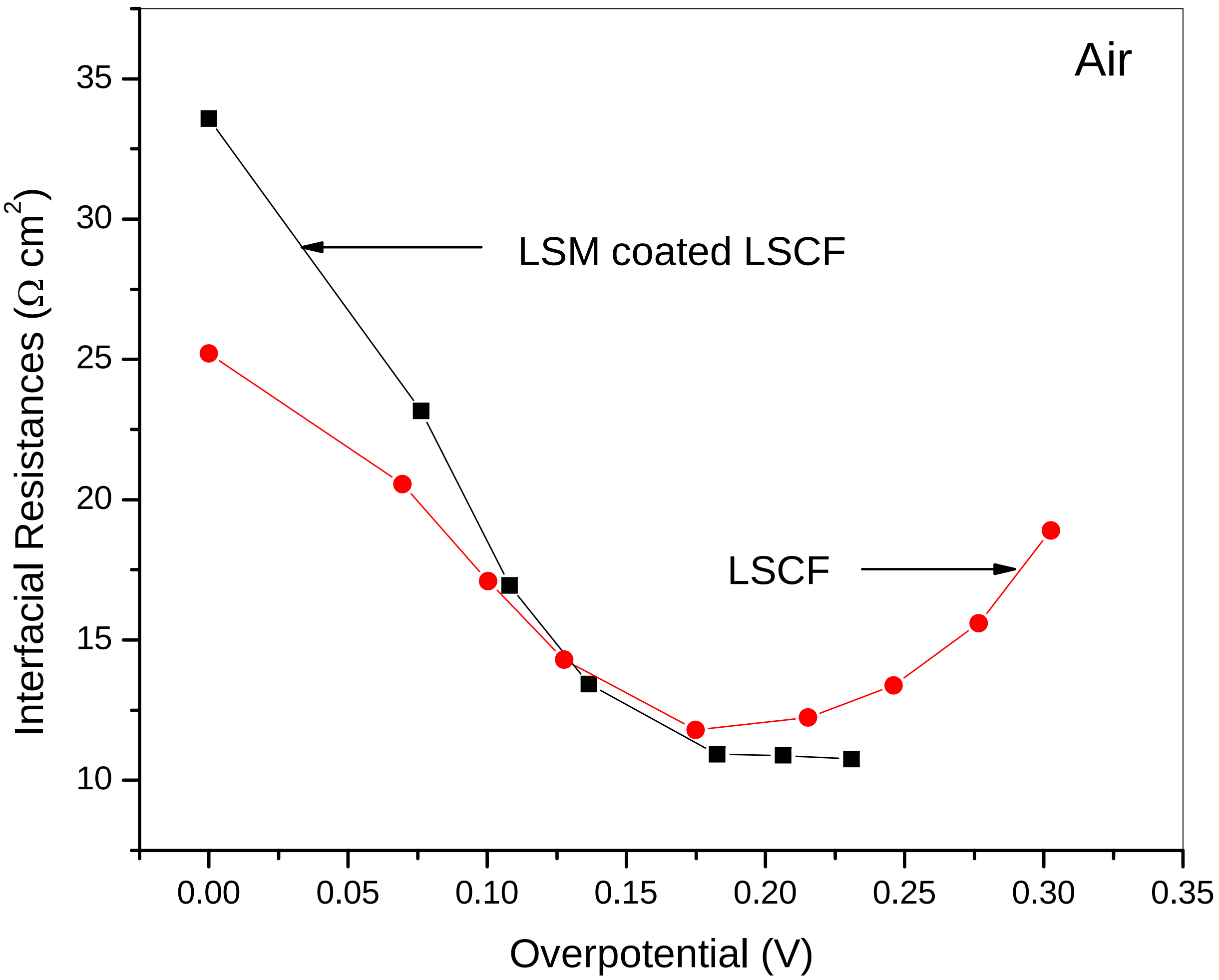


The R_P appears to be limited by the surface catalytic activity, not by the bulk transport property for both 400 and 750 nm thick LSCF films; otherwise, R_P should increase with p_{O_2}.

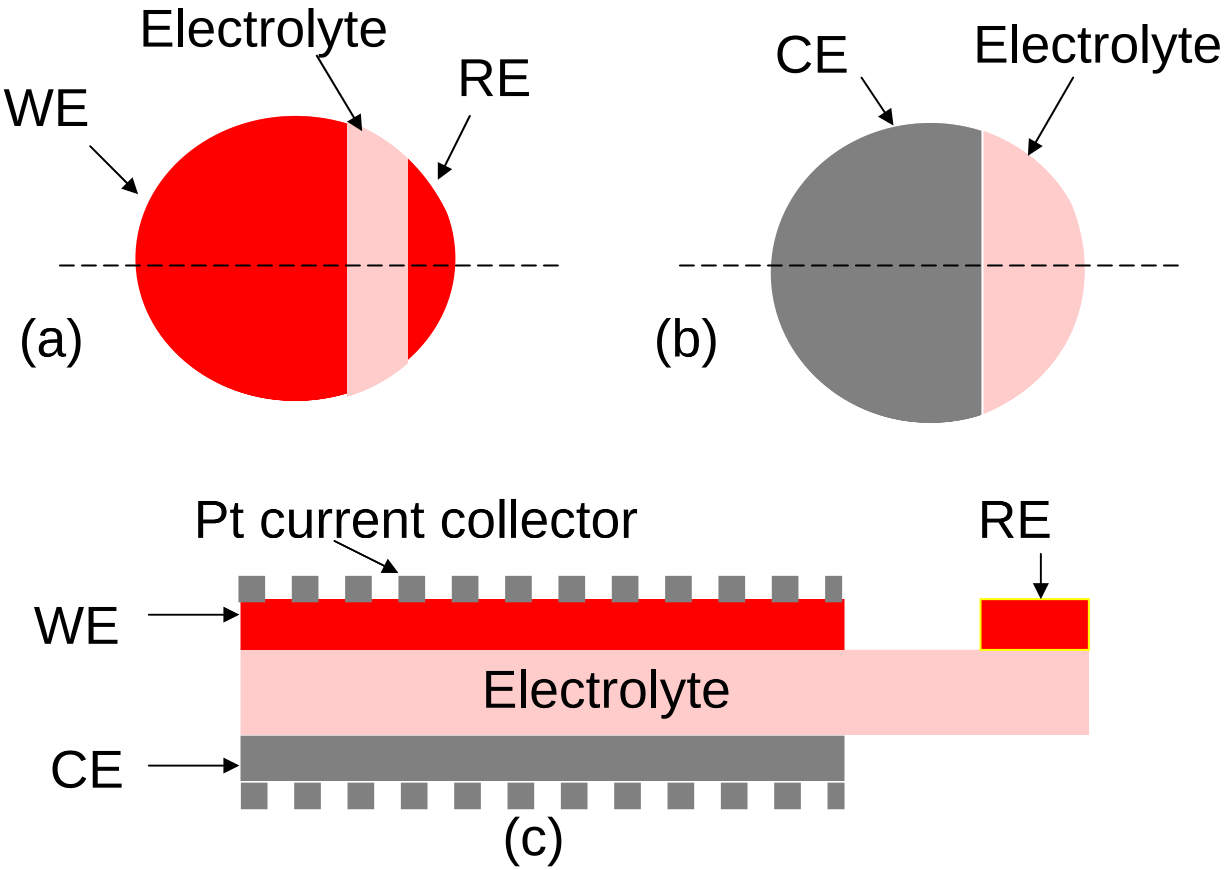
Effect of surface modification



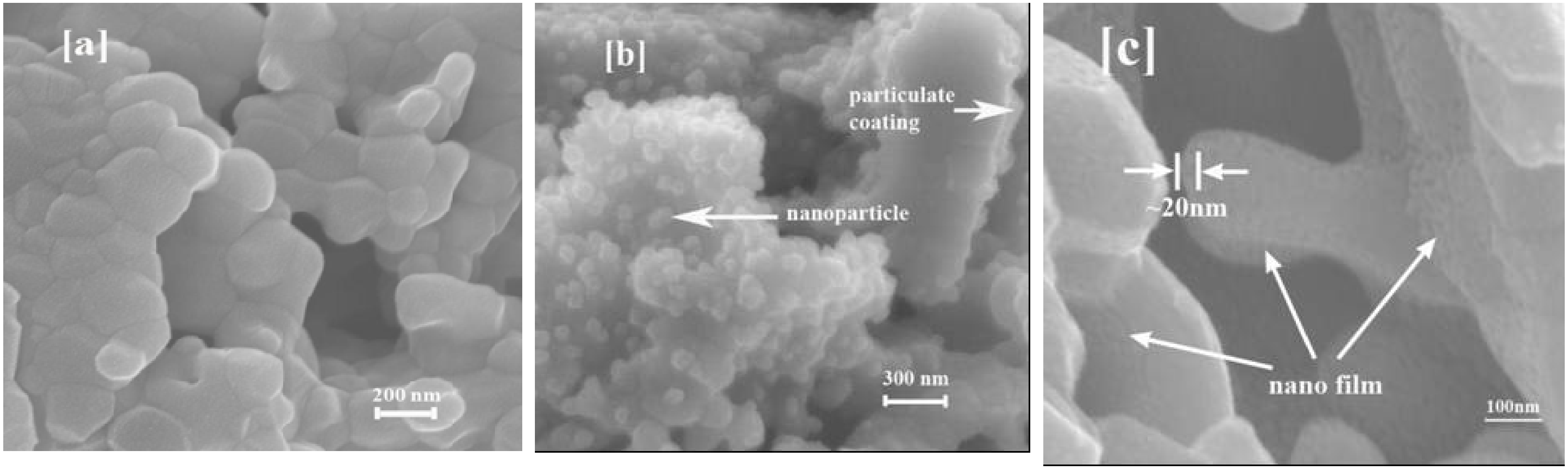
Effect of surface modification



Cell for performance evaluation

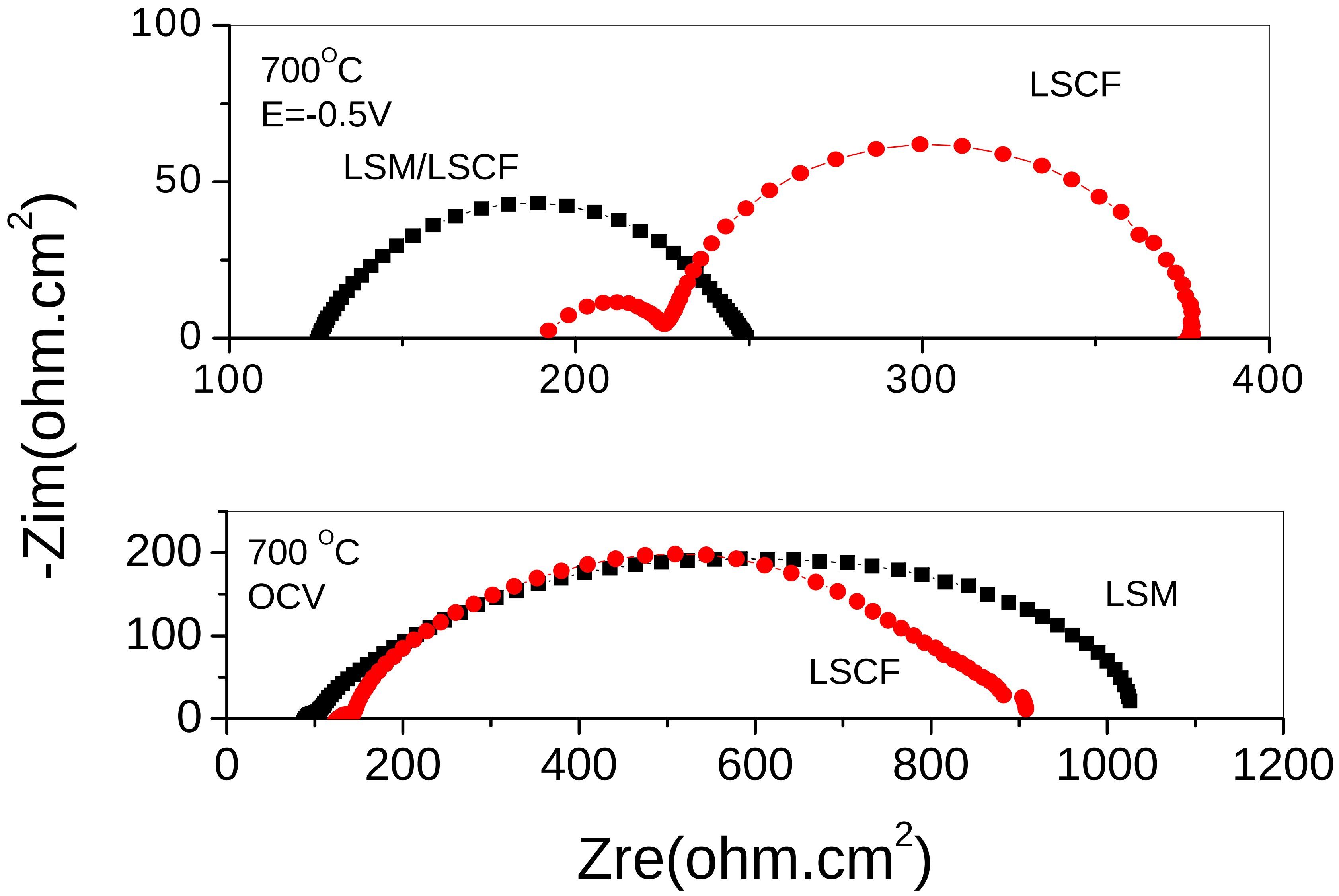


LSM-Infiltrated LSCF

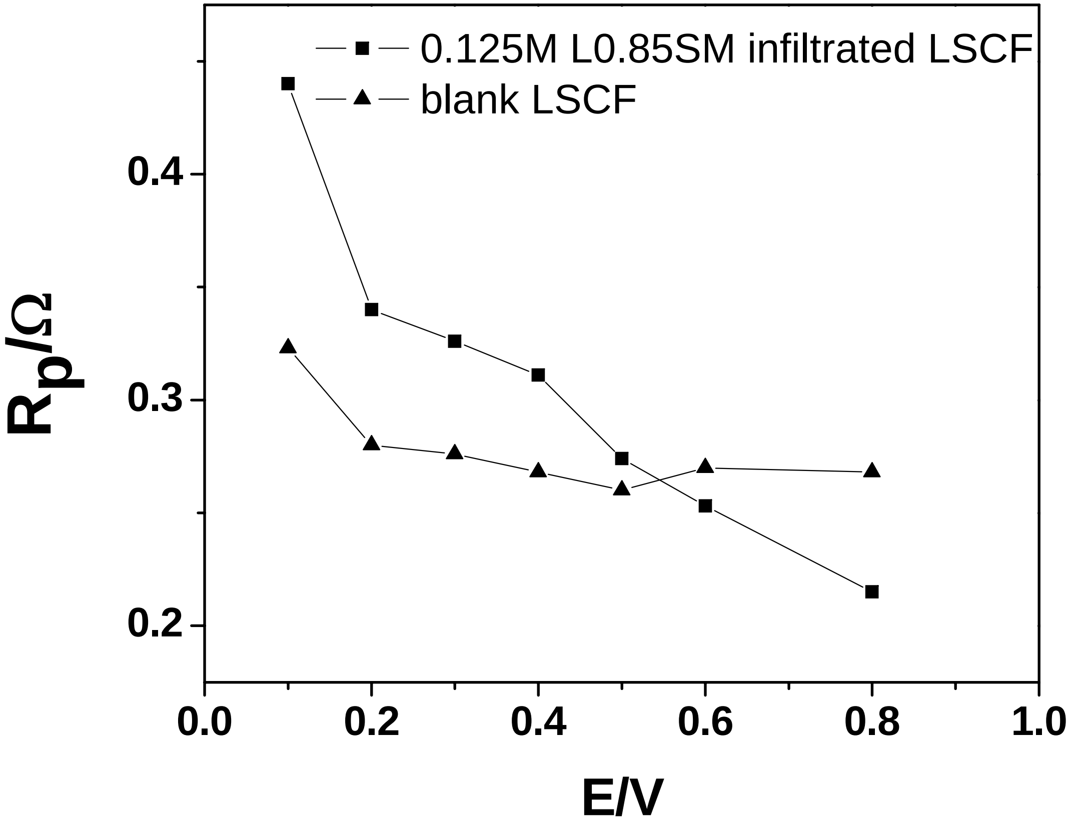


Cross-sectional views of porous LSCF cathodes: (a) blank LSCF, (b) infiltrated with SSC (concentration of SSC solution: 1.44 mol/L), and (c) infiltrated with LSM (concentration of LSM solution: 0.0312 mol/L). 850ºC/ 1hr

Typical Impedance Spectra

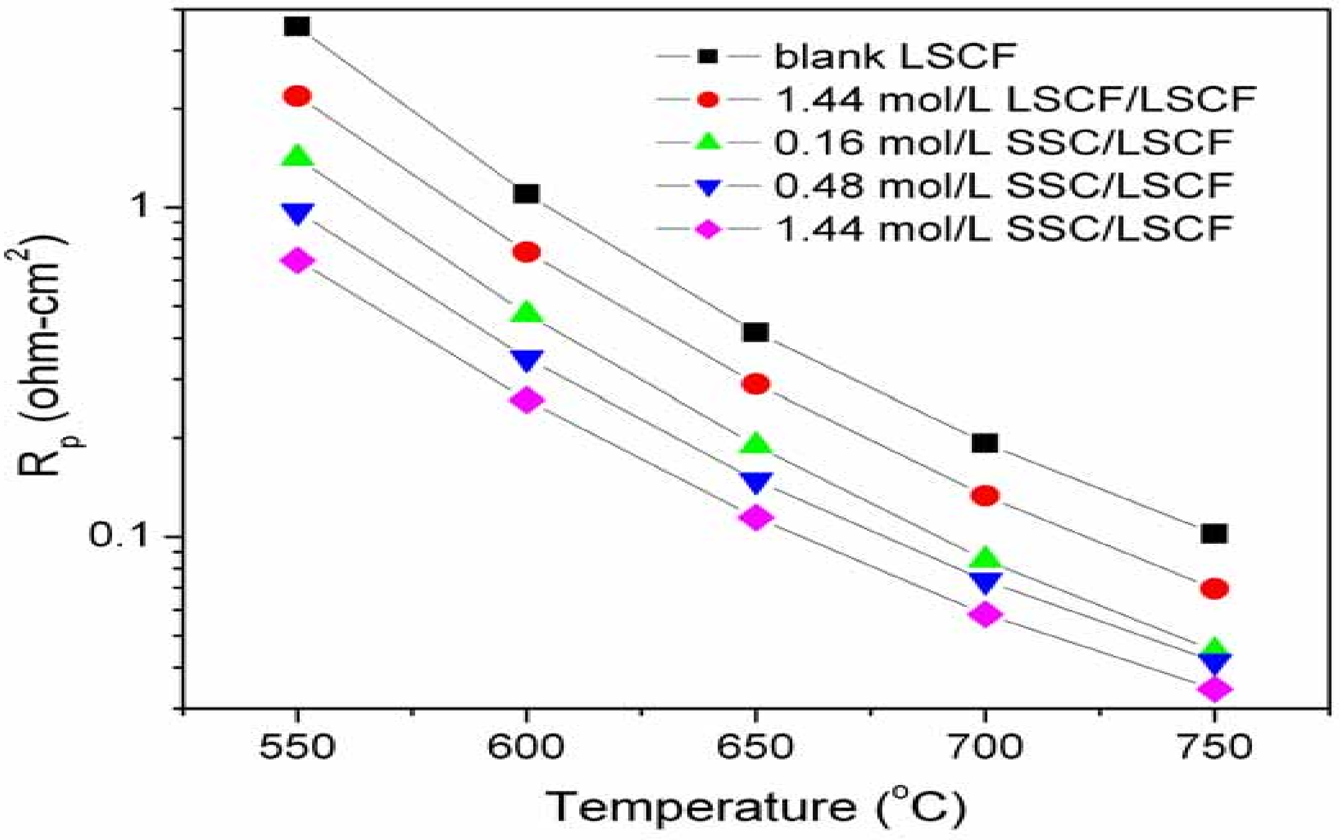


Effect of polarization on R_p



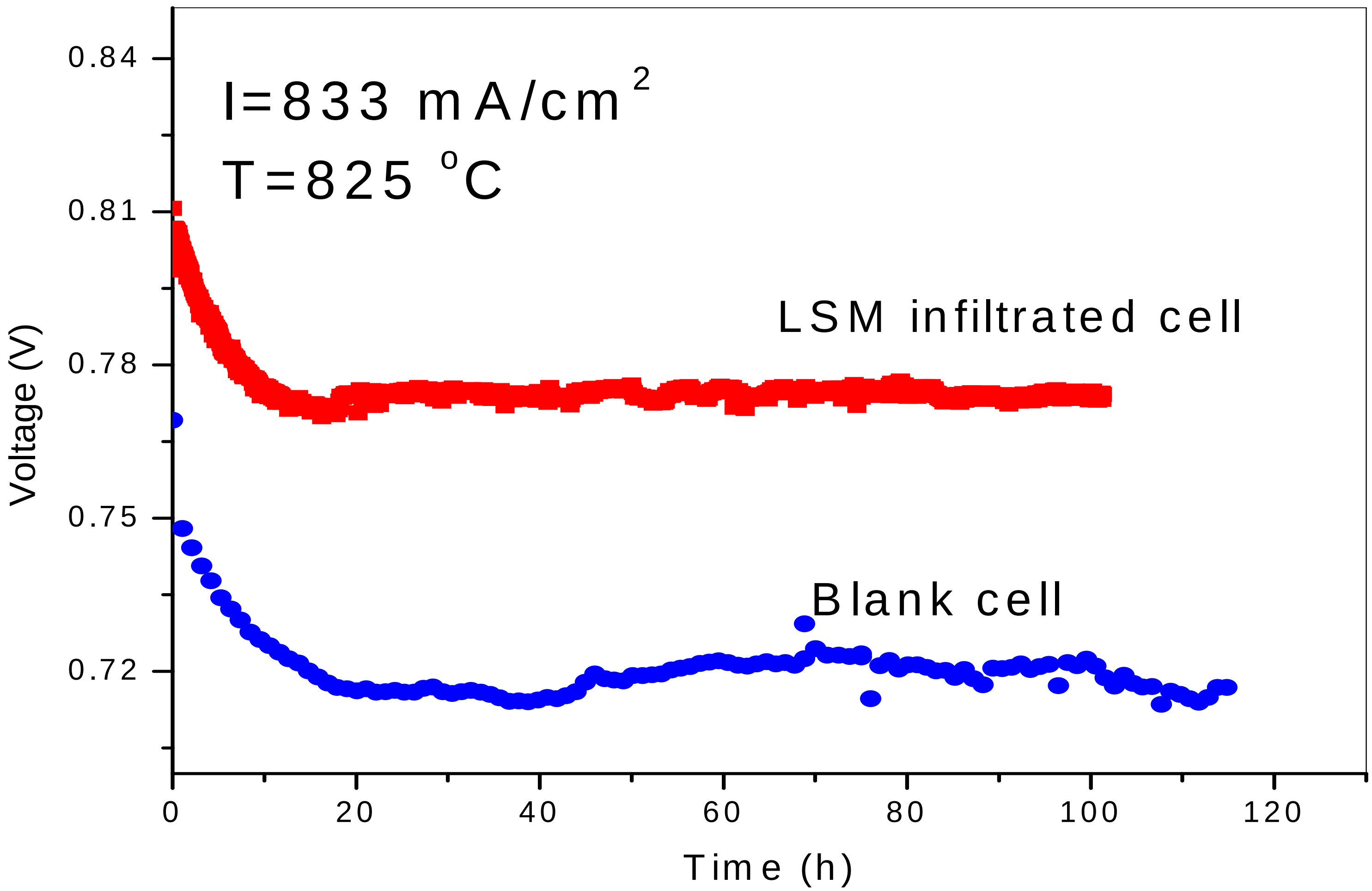
- Polarization resistance of porous LSCF and LSM infiltrated LSCF electrode

$Sm_{0.6}Sr_{0.4}CoO_{3-\delta}$ (SSC) infiltrated LSCF-6428

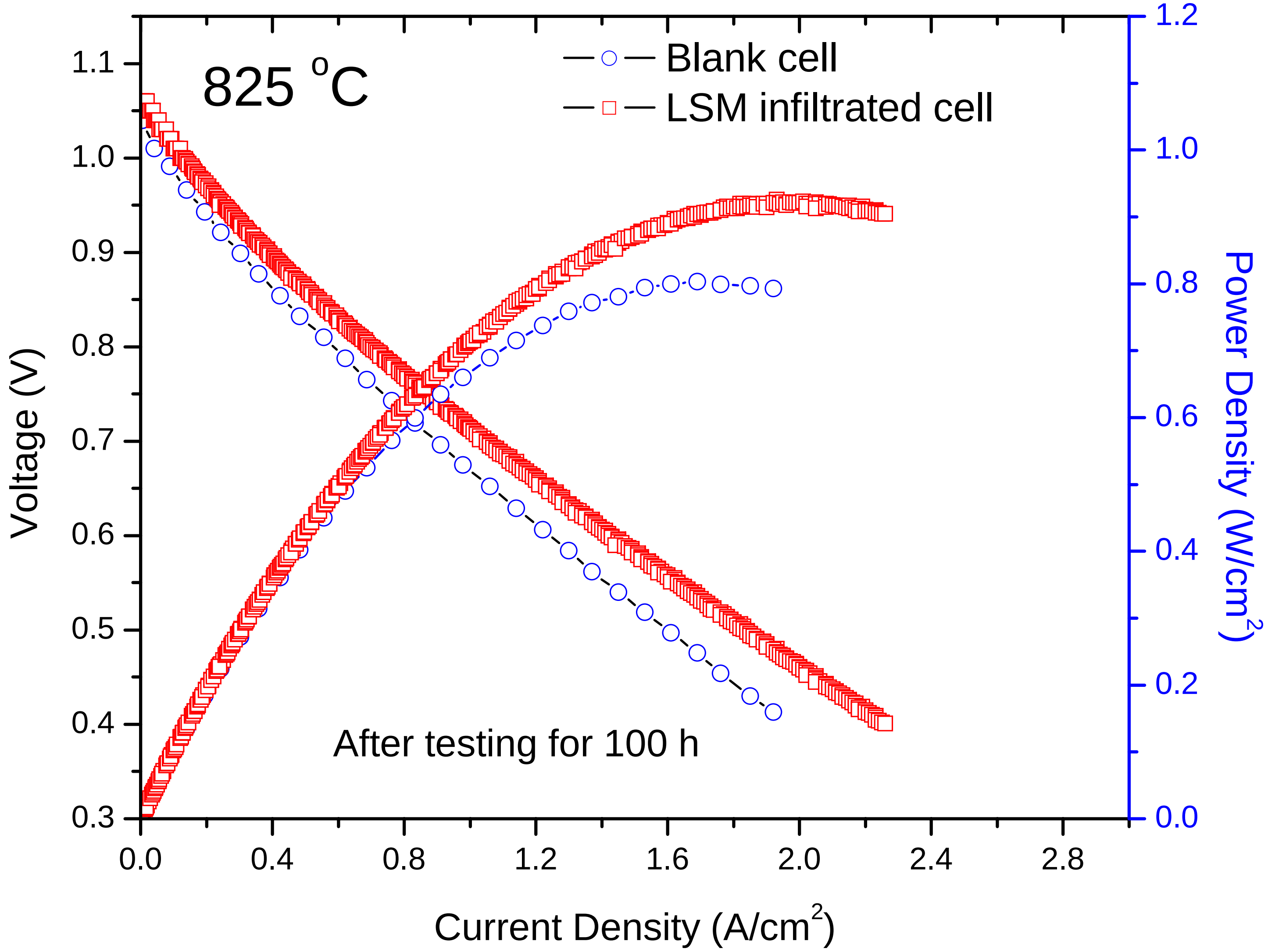


- Comparison of polarization resistance (R_p) of the blank, LSCF infiltrated, and SSC infiltrated LSCF/GDC/LSCF symmetrical cells.

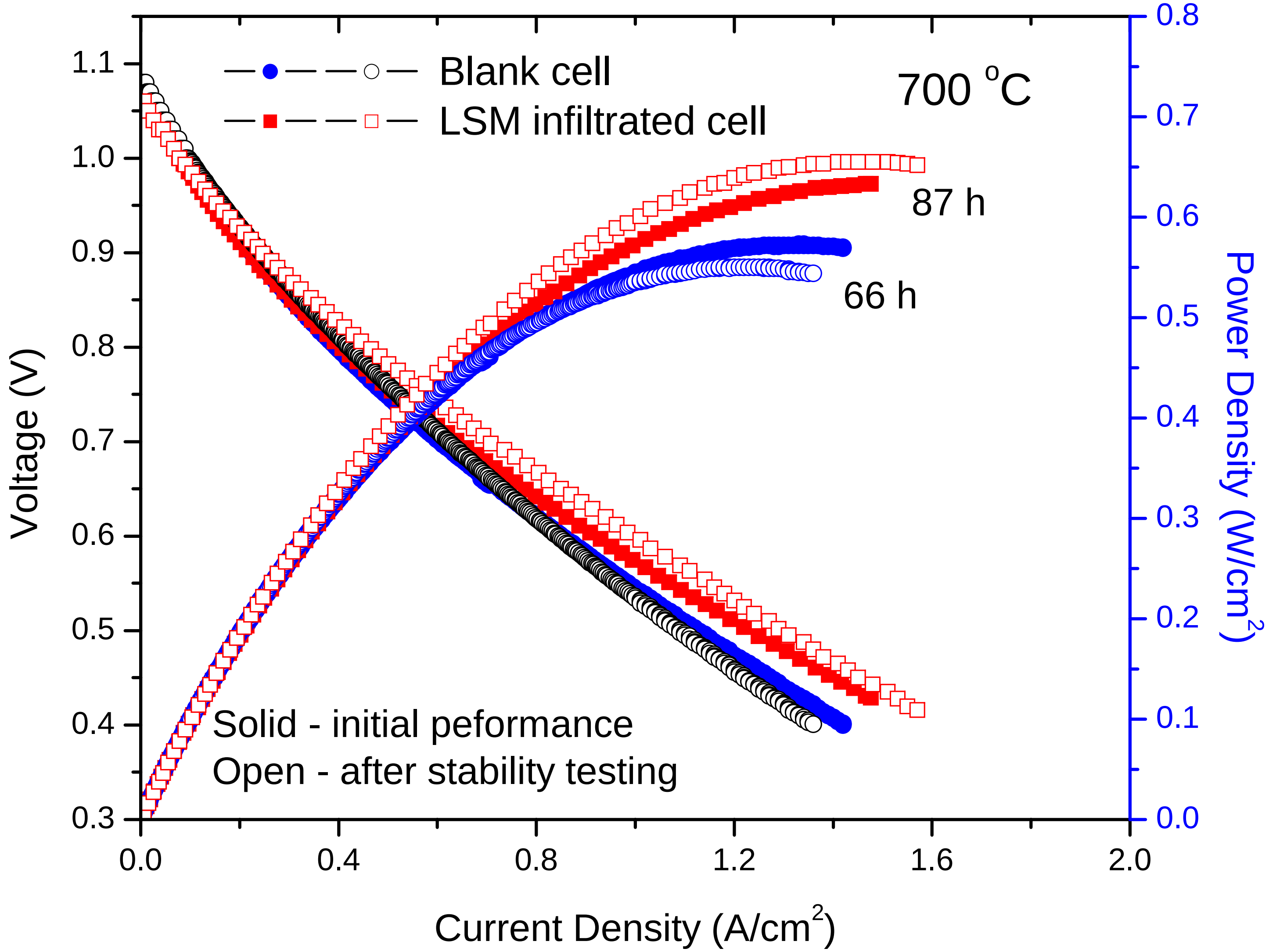
Performance stability of LSM/LSCF



Current-Voltage Characteristics



Cell performance



Conclusions

- Developed a platform for reliably evaluating the surface catalytic properties of cathode materials;
- Fabricated high quality thin films of cathode materials for evaluating their intrinsic catalytic activities
- Confirmed that the surface catalytic activity limits the performances of LSCF-based cathodes;
- Enhanced the stability and performance of LSCF-based cathodes by infiltration of a catalytically active coating (such as LSM and SSC); and
- Demonstrated the concept feasibility of the novel cathode design - highly conductive backbone coated with a highly active catalyst.

Questions yet to be Answered

Several fundamental questions still remain:

- Why are the degradation rates of LSCF cathodes relatively high? What is the degradation mechanism?
- Why does a LSM coating improve the stability of LSCF cathodes? What is the mechanism?
- Are there other catalytically more active materials for the catalyst or more effective matrixes as the backbone?
- The long-term stability of the interfaces (e.g., LSM/LSCF) is yet to be determined.

Other questions to be Answered

- How the surface morphology, composition, and thickness of the coatings change under operating conditions?
- How these changes influence the electrochemical behavior of the cathodes?
- How to control the microscopic details of the coatings in order to optimize the performance?

Acknowledgement

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