Highly-Active and Contaminant-Tolerant Cathodes for Durable Solid Oxide Fuel Cells

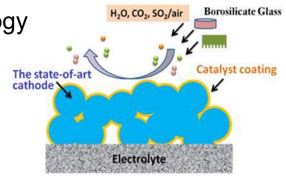
DOE Project Manager: **Joseph Stoffa**

PI: **Meilin Liu**

Team: **Yu Chen, Nicholas Kane, Kai Pei, Yucun Zhou**

Georgia Institute of Technology

May 1, 2019



2019 DOE Hydrogen and Fuel Cells Program Review **FE21**

1

Outline

- **Project Information**
  - **Motivation, objectives, technical Approaches**
- **Accomplishments**
  - **Characterized electrochemical behavior** of LSCF cathodes exposed to various contaminates
  - **Fabricated *catalyst-coated electrodes*** with well controlled composition, structure, and morphology
  - **Probed surface species** of electrodes using *in operando Raman spectroscopy*
  - **Developed efficient catalysts** for enhancing **ORR activity** and **durability**
- **Summary**
- **Acknowledgement**

2

U.S. DEPARTMENT OF ENERGY

2

Motivation

- **Cathodic polarization** causes significant energy loss.
- The state-of-the-art SOFC cathode materials are **susceptible** to degradation due to inherent instability and contaminants poisoning.
- Cathode **durability** is critical to long-term reliable SOFC performance for commercial deployment.
- Mitigating the issues by **catalyst coatings** will reduce the cost of SOFCs and help to meet both **cost and performance goals**.

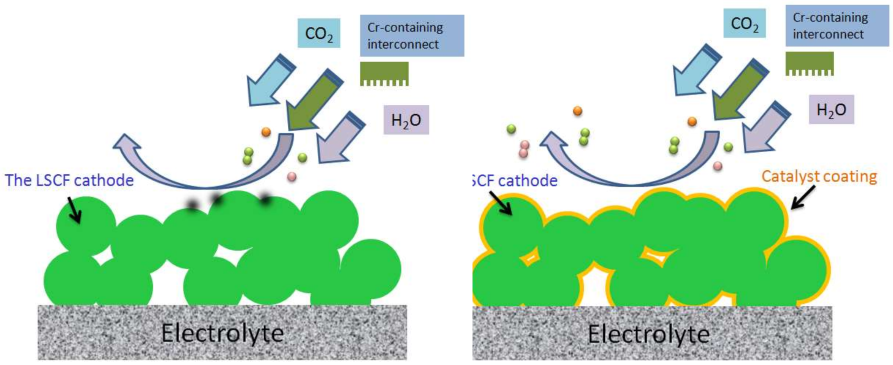
U.S. DEPARTMENT OF ENERGY

Contaminant-tolerant electrodes

3

Strategy to Durability

- ❑ Limit the sources of contaminants
- ❑ Reduce the exposure to contaminants: use of getters
- ❑ **The last defense**: **contaminant-resistant** electrode



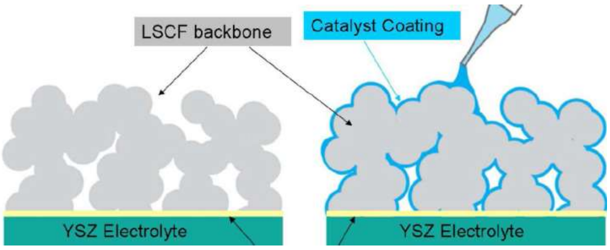
U.S. DEPARTMENT OF ENERGY

Contaminant-tolerant electrodes

4

Surface Modification

- To develop **a conformal catalyst coating** that may (1) suppress Sr segregation or enrichment[1,2] and (2) enhance the tolerance to contaminants



- The catalysts must be **inherently more stable**, **electro-catalytically active**, yet **less sensitive to contaminants**

1. EES, **2011**, 4, 2249; 2. AEM, **2013**, 3, 1149; EES, **2014**, 7,

5

Project Objectives

- To characterize the **electrochemical behavior** of LSCF exposed to contaminants under realistic operating conditions (ROC);
- To probe **the surface species/phases** of LSCF cathodes exposed to contaminants under ROC using *in situ* and *ex situ* measurements performed on specially-designed cathodes;
- To unravel the **degradation mechanism** of LSCF cathodes by correlating the changes in performance with the surface chemistry, microstructure, and morphology under ROC;
- To establish **scientific basis for rational design** of new catalysts of high tolerance to contaminants;
- To validate the **long term stability of modified LSCF** cathodes in commercially available cells under ROC.

6

U.S. DEPARTMENT OF ENERGY

Highly Active and Durable SOFC Cathodes

6

Tasks and Schedule

Task 1: Project Management and Planning

Task 2: Charactering the EC Behavior of Catalyst-Coated LSCF under Realistic Conditions

Task 3: Understanding the Mechanism of Contamination Tolerance

Task 4: Development of Low-cost and Applicable Deposition Techniques for Cathode

Task 5: Development of Catalyst Coating on Porous Cathodes of Large Commercial Cells

Task 6: Verification of Catalyst Coating in a Subscale Stacks of Fuel Cell Energy

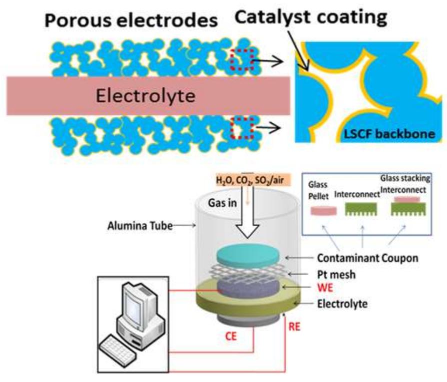
Task	FY2017	FY2018				FY2019		
	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3
1	→							
2	→	→	→					
3		→	→	→	→			
4				→	→	→	→	
5						→	→	→
6							→	→

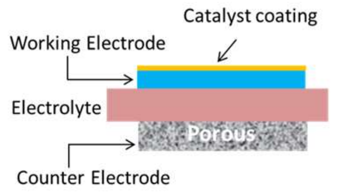
U.S. DEPARTMENT OF ENERGY

Highly Active and Durable SOFC Cathodes

7

Symmetric and Model Cells

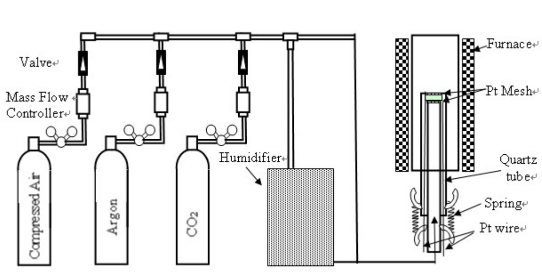


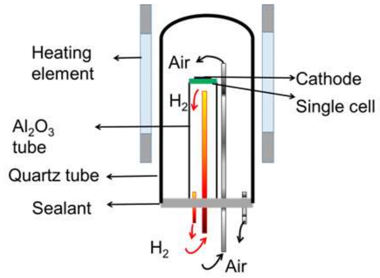


- Symmetrical cells of porous LSCF cathode with 2-electrode configuration to determine the sensitivity of cathode performance to the type and concentration of contaminants (S, B and Cr) under various testing conditions
- Model Cells with thin-film dense LSCF electrode to facilitate the interface analysis and correlate the degradation mechanism with the geometric factors, revealing the major path of surface reaction on the cathodes

8

Electrochemical Testing





Symmetrical/model cell ***Full*** cell

- ❑ Oxidant composition can be well controlled;
- ❑ Contamination can be introduced easily.

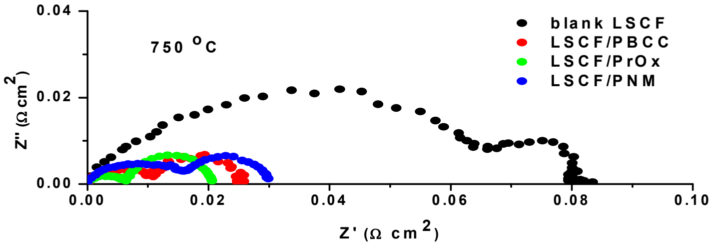
U.S. DEPARTMENT OF ENERGY

Contaminant-tolerant electrodes

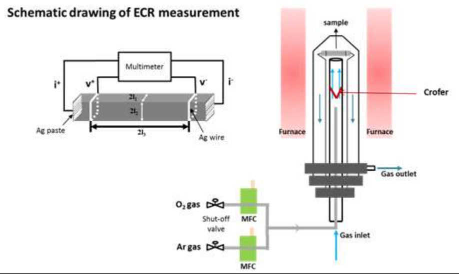
9

ORR Activity of Catalyst-infiltrated LSCF

- **R_P determined from EIS**

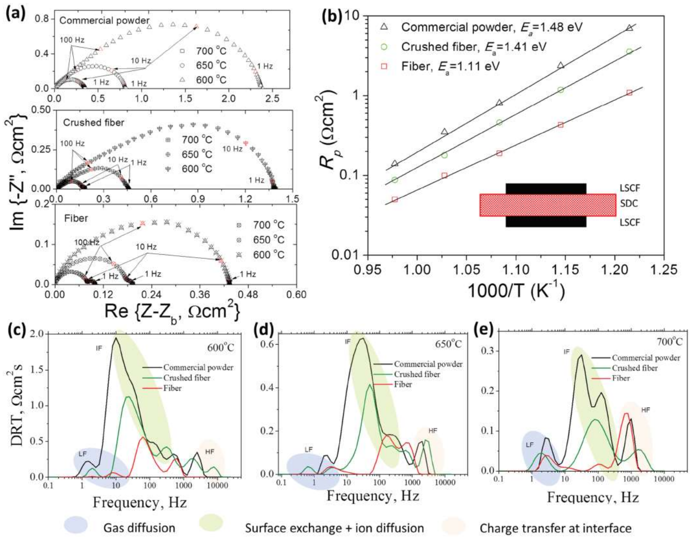


- **k determined from ECR**



10

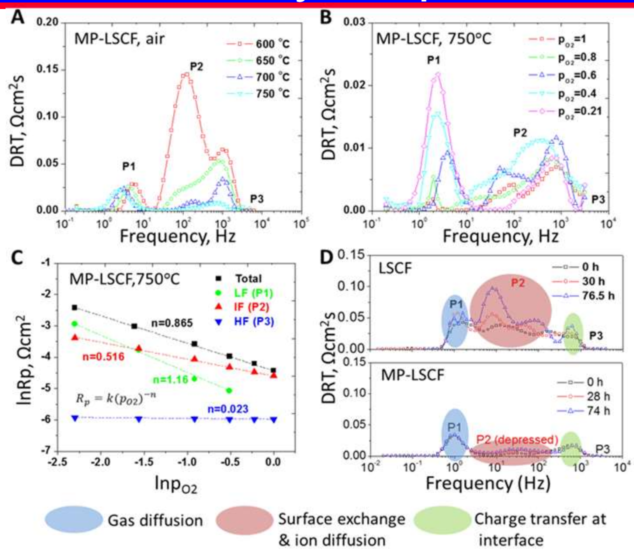
Distribution of Relaxation Time (DRT)



- DRT is a powerful tool for deconvoluting the impedance data of the complex ORR reactions, helping us to separate or isolate some of the key steps involved in the electrode reactions.

11

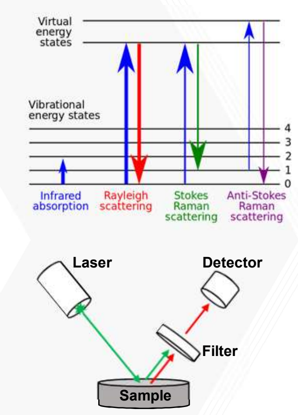
DRT of Catalyst-Cpated LSCF



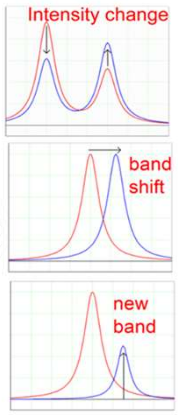
- DRT is a powerful tool for deconvoluting the impedance data of the complex ORR reactions, helping us to separate or isolate some of the key steps involved in the electrode reactions.

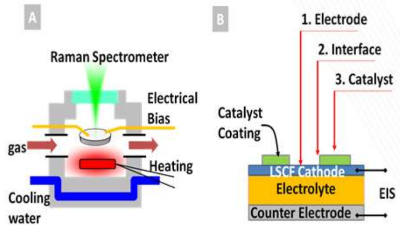
12

Raman Spectroscopy



$$Raman\ shift = \omega_{incident} - \omega_{scattered}$$





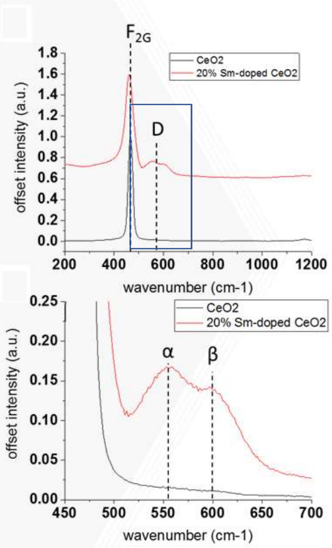
- Inelastic scattering of light due to interaction with vibration modes
- Energy of photon changes after interaction, *shifting* the frequency of the scattered light.
- In situ compatable

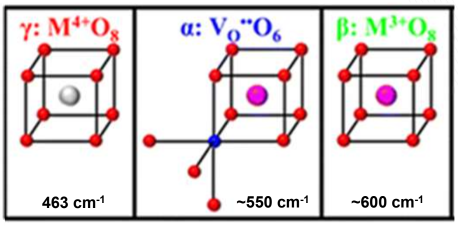
Georgia Tech
CREATING THE NEXT

13

13

Probing Oxygen Vacancies





$$Sm_2O_3 \rightarrow 2Sm'_{Ce} + V_O^{**} + 3O_O^x$$

$$2Ce_{Ce}^x + O_O^x \rightarrow 2Ce'_{Ce} + V_O^{**} + \frac{1}{2}O_2$$

- Strong Raman modes reveal presence of oxygen vacancies and M^{3+} dopants

Georgia Tech
CREATING THE NEXT

14

14

Accomplishments and Progress

- Characterized **electrochemical behavior** of LSCF cathodes exposed to contaminates (such as Cr, SO_2, CO_2 and B) under ROC;
- Identified some **efficient catalysts** for enhancing **ORR activity** and **durability;**
- Fabricated model cells with a **thin-film LSCF electrode** and characterized the **model cells** (w/o catalyst) in different contaminants;
- Probed **surface species** of LSCF using *in operando* **SERS**; and
- Developed the low-cost and applicable deposition techniques for large cathodes (~1 inch diameter).

15

15

Accomplishments and Progress

- Characterized **electrochemical behavior** of LSCF cathodes exposed to contaminates (such as Cr, SO_2, CO_2 and B) under ROC;
- Identified some **efficient catalysts** for enhancing **ORR activity** and **durability;**
- Fabricated model cells with a **thin-film LSCF electrode** and characterized the **model cells** (w/o catalyst) in different contaminants;
- Probed **surface species** of LSCF using *in operando* **SERS**; and
- Developed the low-cost and applicable deposition techniques for large cathodes (~1 inch diameter).

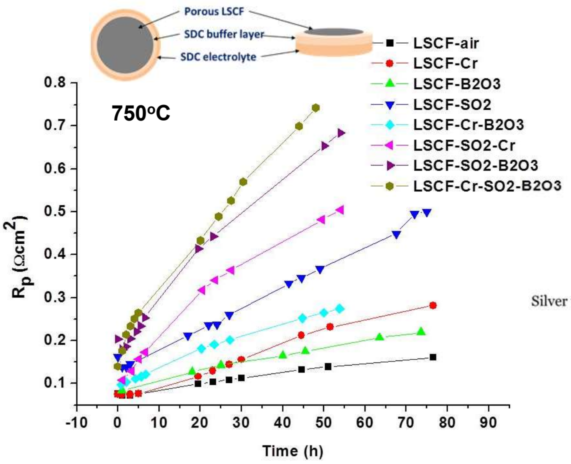
16

16

Performance of LSCF

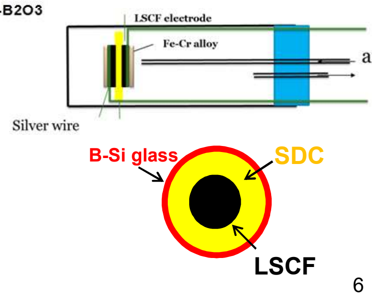
exposed to different contaminants

- Cr, B, or S alone can cause severe LSCF degradation
- Combination of contaminants exacerbates the degradation effect



Rp of LSCF exposed to different contaminants

- ✓ LSCF I **SDC** I LSCF
- ✓ SDC: dry-pressed & fired at 1450°C
- ✓ LSCF: on SDC fired at 1080°C/2h
- ✓ Rp: determined from EIS at OCV
- ✓ Cr: Direct contact in dry air
- ✓ SO_2: 27 ppm in air
- ✓ B: on the edge of SDC pellet



6

17

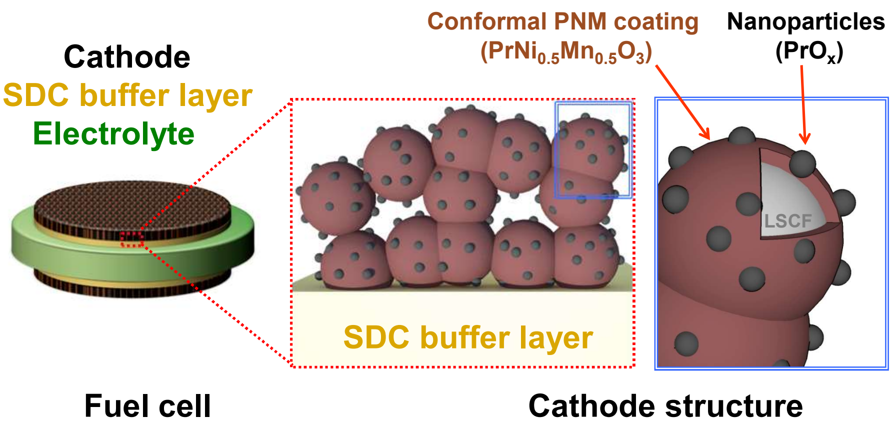
Accomplishments and Progress

- Characterized **electrochemical behavior** of LSCF cathodes exposed to contaminates (such as Cr, SO_2, CO_2 and B) under ROC;
- Identified some **efficient catalysts** for enhancing **ORR activity** and **durability;**
- Fabricated model cells with a **thin-film LSCF electrode** and characterized the **model cells** (w/o catalyst) in different contaminants;
- Probed **surface species** of LSCF using *in operando* **SERS**; and
- Developed the low-cost and applicable deposition techniques for large cathodes (~1 inch diameter).

18

18

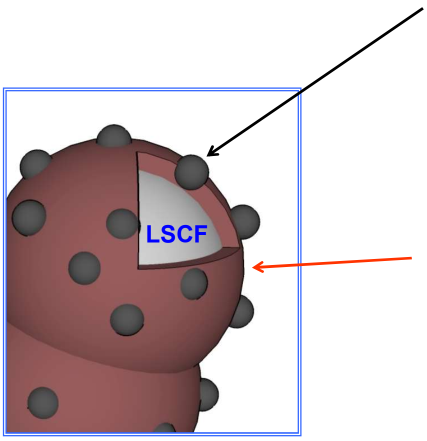
Schematics of a conformal PNM coating with exsoluted PrOx nano-particles



Chen. *et al.*, **Energy Environ. Sci**. ***2017***, 10, 964.

19

Candidate Catalyst Materials



Exsoluted Nanoparticles

- PrO_x
- $Sm_{0.2}Ce_{0.8}O_2$ (SDC)

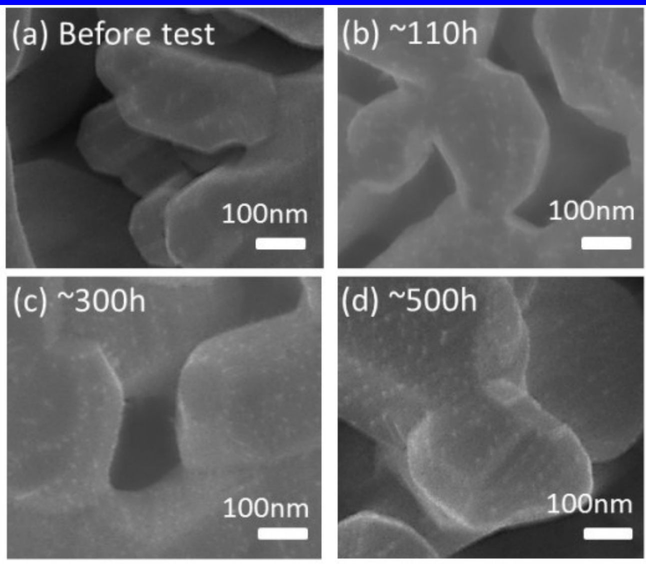
Catalytically active and stable!

Conformal coating:

- ❑ $Sm_{0.5}Sr_{0.5}CoO_{3-x}$ (SSC)
- ❑ $PrBa_{1-x}Ca_xCo_2O_{5+x}$ (PBCC)
- ❑ $Pr_2Ni_{0.5}Mn_{0.5}O_{4+x}$ (PNM)
- ❑ $Ba_xCo_yO_z$ (BCO)
- ❑ $Pr_xCo_yO_z$ (PCO)

20

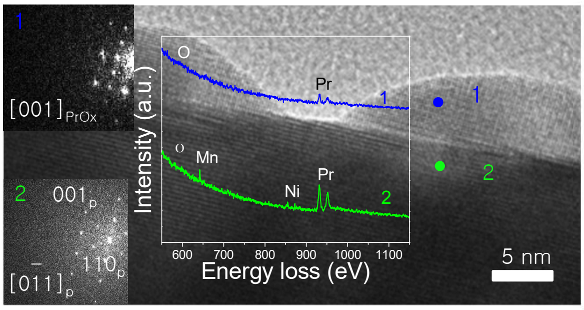
Morphology/composition evolution of porous LSCF

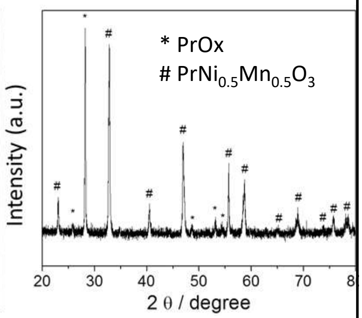


More PrOx particles exsolved overtime, leading to performance enhancement.

21

Micro-analysis of PNM-LSCF





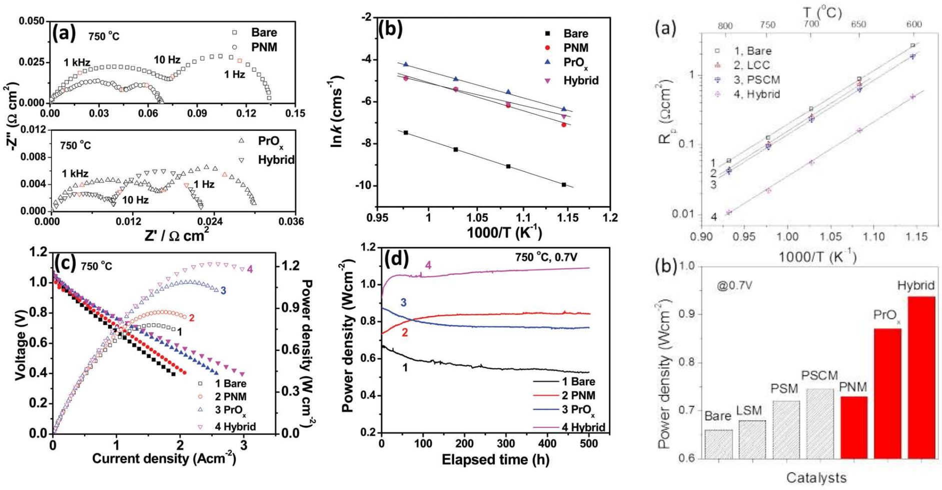
A high-resolution TEM image showing two PrOx particles on a conformal PNM coating deposited on an LSCF grain. The insets are the FFT patterns from the nanoparticles (point 1) and the conformal PNM coatings (point 2); and the EELS spectra from point 1 and 2, suggesting that the nanoparticles are mainly PrOx (point 1) while the conformal coating is PNM (point 2).

- **PNM is a composite with possible composition of PrO_x and $PrNi_{0.5}Mn_{0.5}O_3$;**
- **LSCF was covered by a conformal coating and exsoluted nanoparticles;**

Energy Environ. Sci. 2017, 10, 964.

22

Electrochemical performance of catalyst coated-LSCF

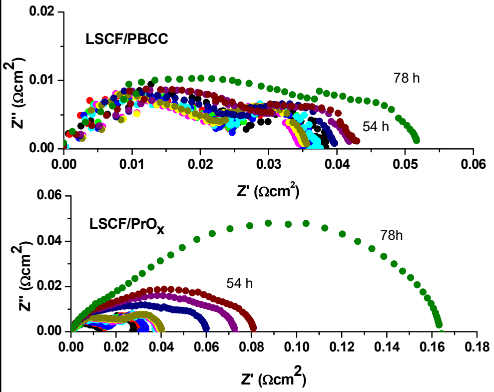


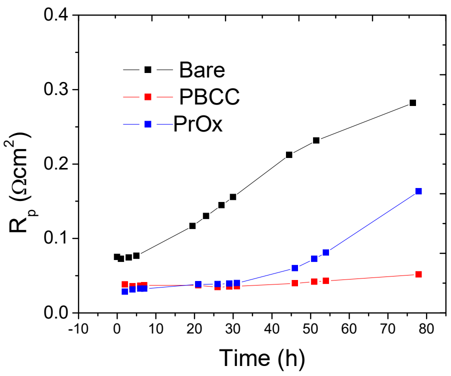
- **PNM shows best performance (activity and durability) among catalysts we studied;**
- **PrOx facilitated the surface exchange process; $PrNi_{0.5}Mn_{0.5}O_3$ enhance durability.**

23

Surface coating to enhance durability: Cr poisoning

Experimental condition
- **Temperature: 750 °C**
- **Contaminants: Cr**



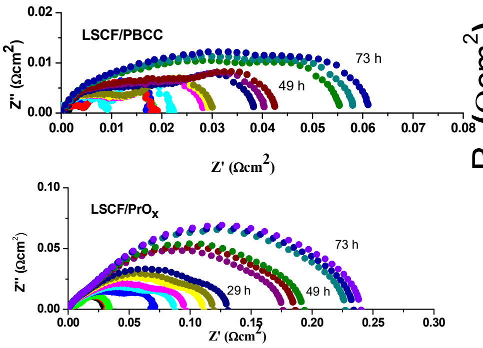


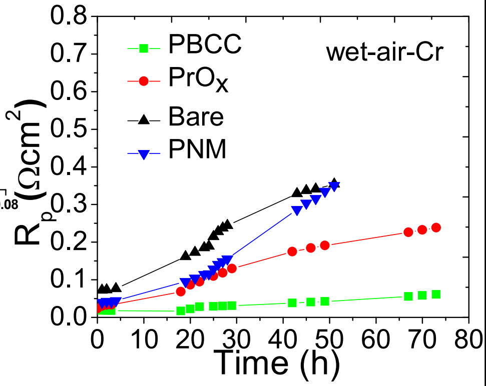
- **Blank LSCF shows significant degradation when exposed to Cr alloy;**
- **Catalyst of PBCC or PrOx can enhance the durability.**

24

Surface coating to enhance durability: Cr+ H2O poisoning

Experimental condition
- **Temperature: 750 °C**
- **Contaminants: Cr, H_2O (3%)**



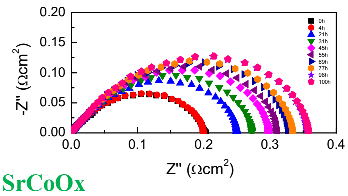


- ❖ Blank LSCF shows significant degradation when exposed to Cr alloy and H2O;
- ❖ Catalyst of PBCC or PrOx can enhance the durability.

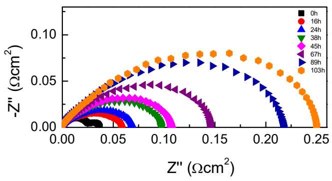
25

SrCoOx and BaCoOx

BaCoOx

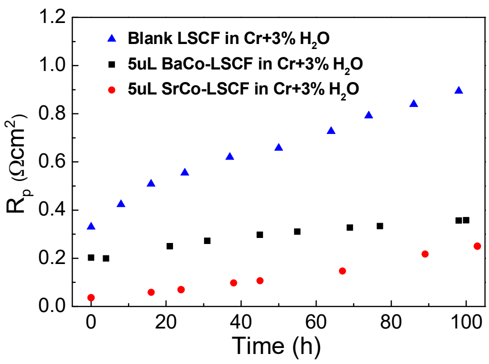


SrCoOx



5μL	LSCF	BaCoOx-LSCF	SrCoOx-LSCF
Initial Rp	0.1121	0.2024	0.0362
Final Rp	0.9491	0.3582	0.2501

EIS results of catalyst infiltrated LSCF
- ➢ Catalyst: **5uL BaCoO fired 900°C, 5uL SrCoO fired 900°C**
- ➢ Temperature: **750°C 100hr**
- ➢ Condition: **3%vt H_2O +Cr**



U.S. DEPARTMENT OF ENERGY

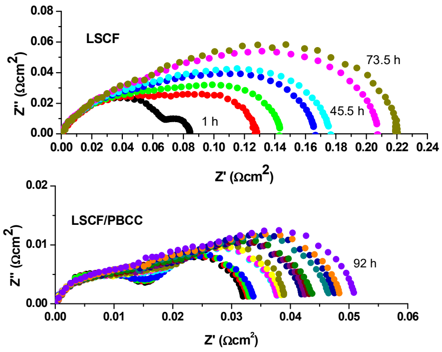
In Operando SERS of Electrode Surfaces

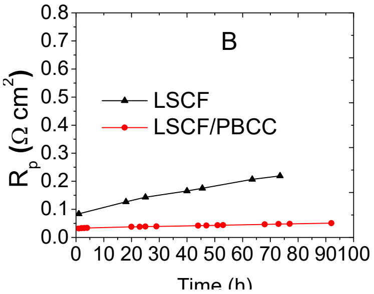
26

Surface coating to enhance durability: B poisoning

Experimental condition

- **Temperature: 750 °C**
- **Contaminants: B_2O_3**

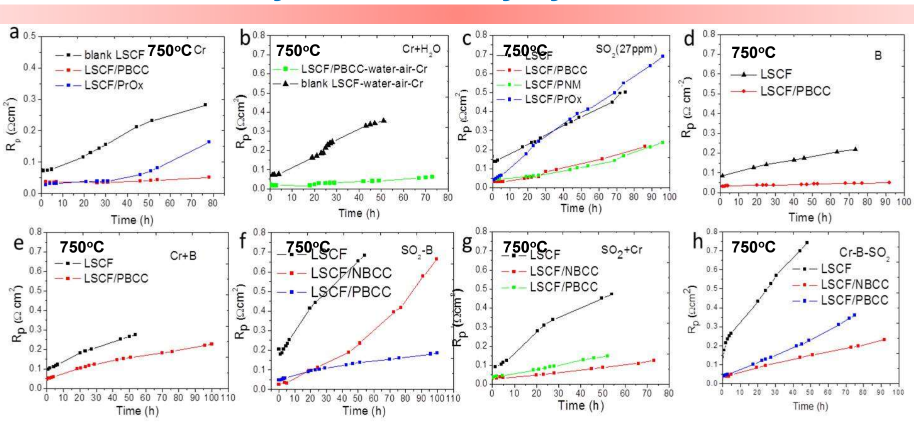




❖ Blank LSCF shows significant degradation when exposed to B;
❖ Catalyst of PBCC can enhance the durability.

27

Increased activity and durability by surface modification



- PBCC, PNM, and PrO_x coating significantly reduced the Rp of cathode;
- PBCC-LSCF cathode showed remarkable tolerance to Cr, B_2O_3, and improved tolerance to SO_2 in contrast to the bare LSCF or PrOx-LSCF;
- PBCC- and NBCC-infiltrated LSCF cathodes showed better tolerance and resistance to combinations of Cr, B_2O_3, and SO_2.

✓ LSCF I SDC I LSCF
✓ SDC: dry-pressed & fired at 1450°C
✓ LSCF on SDC, fired at 1080°C/2h
✓ Rp: from EIS of cells at OCV
✓ Cr: Direct contact in dry air
✓ SO_2: 27 ppm in air
✓ B: on the edge of SDC pellet

28

28

Accomplishments and Progress

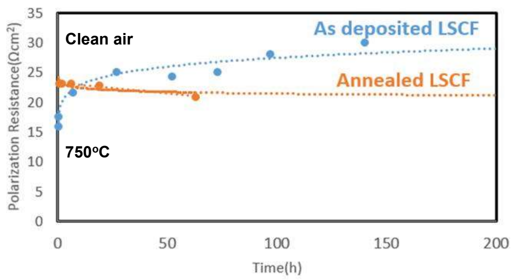
- Characterized **electrochemical behavior** of LSCF cathodes exposed to contaminates (such as Cr, SO_2, CO_2 and B) under ROC;
- Identified some **efficient catalysts** for enhancing **ORR activity** and **durability;**
- Fabricated model cells with a **thin-film LSCF electrode** and characterized the **model cells** (w/o catalyst) in different contaminants;
- Probed **surface species** of LSCF using *in operando* **SERS**; and
- Developed the low-cost and applicable deposition techniques for large cathodes (~1 inch diameter).

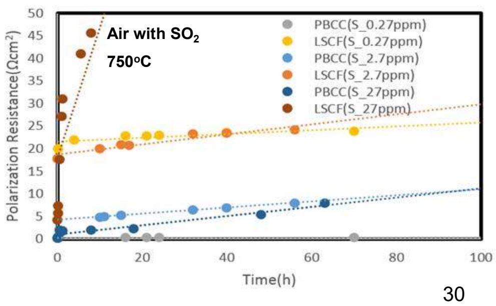
29

29

Thin-film electrodes

LSCF thin film l SDC l porous LSCF
SDC: dry-pressed & fired at 1450°C
Porous LSCF on SDC fired at 1080°C/2h
Rp determined from EIS at OCV
Rp of porous the LSCF was negligible
SO_2: 27 ppm in air





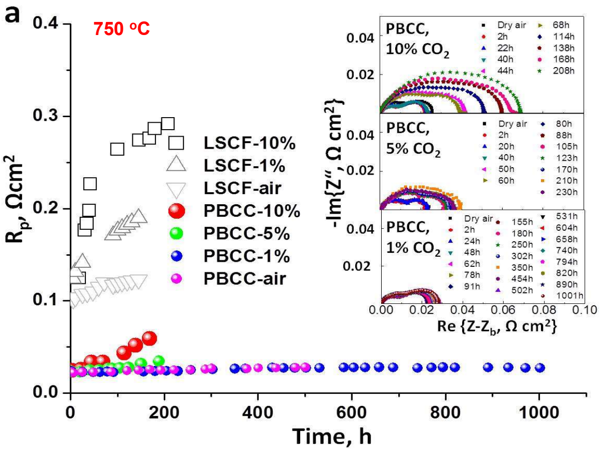
- Thin film electrodes have been successfully fabricated by **PLD or** RF **sputtering**
- Annealed LSCF behavior shows very stable up to 60 hrs without additional degradation.
- Sulfur caused degradation; degradation rate increases with concentration.
- PBCC Catalyst helps to enhance durability.

30

30

PBCC: excellent CO_2 tolerance

Energy Environ. Sci., 11 (2018) 2458.



- ✓ LSCF I SDC I LSCF;
- ✓ PBCC I SDC I PBCC
- ✓ SDC dry-pressed/fired at 1450°C;
- ✓ LSCF or PBCC on SDC fired at 1080°C/2h
- ✓ Rp: from EIS of cells at OCV
- ✓ CO_2 content: 1%, 5%, and 10%

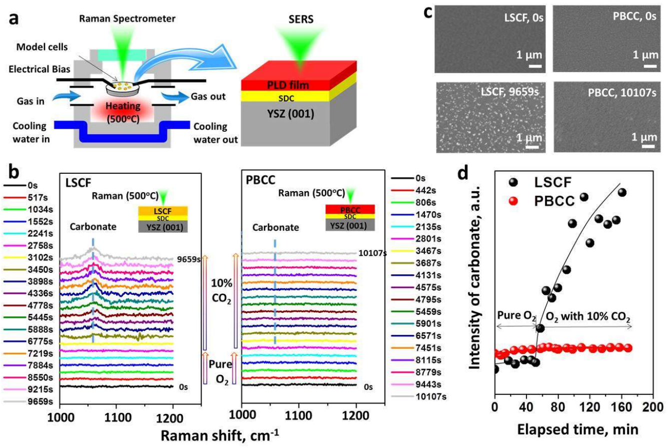
- ❖ LSCF or PBCC showed degradation in air with different concentration of CO_2: higher cause faster degradation;
- ❖ However, PBCC remains active in air with CO_2 up to 5%.

31

31

Probing surfaces by *In situ* SERS

Energy Environ. Sci., 11 (2018) 2458.



- **Model cells**: LSCF thin film on YSZ single crystal;
- LSCF or PBCC thin film by PLD
- *In situ Raman* performed in a chamber with O_2 or air with 10% CO_2 at 500 °C

b. The surface species of CO_2 poisoning are carbonate, as indicated from the Raman spectra.
c,d. - LSCF showed faster degradation than PBCC in air with 10% CO_2 : rougher surface compared with PBCC;

32

32

Development of low-cost and applicable
Thin-Film deposition Process

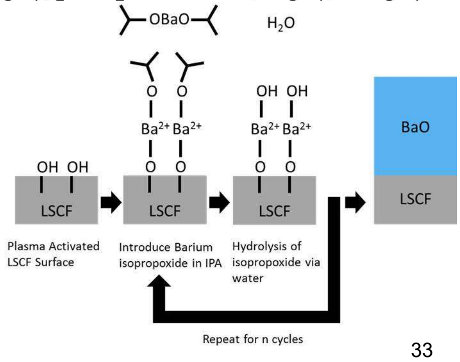
Surface Sol Gel Process

- ✓ Layer by layer growth via two alternating self limiting reactions:

1. Metal alkoxide reacts with hydroxyl groups on surface
2. Hydrolysis via water to form oxide
3. Repeat for n cycles

- ✓ Achieves highly conformal coating
- ✓ Precise thickness control
- ✓ Low cost compared to ALD

$$Ba(OC_3H_7)_2 + H_2O \rightarrow HOBa(OC_3H_7) + C_3H_7OH$$

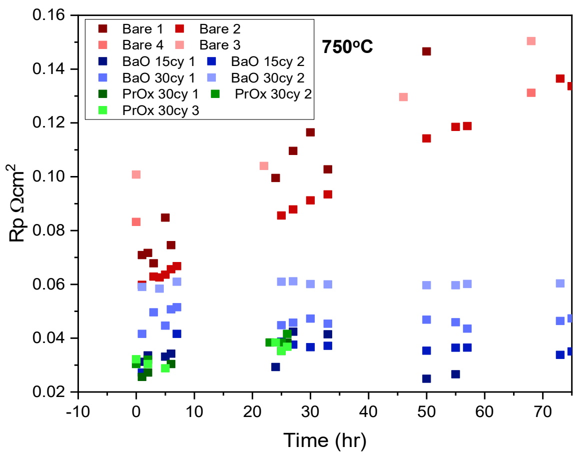


33

33

Coatings from Surface Sol-Gel

Rp of bare LSCF and LSCF coated with catalyst derived from a surface sol-gel process



LSCF I SDC I LSCF
SDC: dry-pressed & fired at 1450°C;
LSCF on SDC, fired at 1080°C/2h;
Catalysts: from surface sol-gel;
Rp: from EIS of cells at OCV acquired at 750°C.

- ❑ Surface sol-gel has better control over morphology & thickness.
- ❑ Catalyst-coated cathode showed higher activity and stability.
- ❑ The effect is similar to that of solution infiltration.

34

34

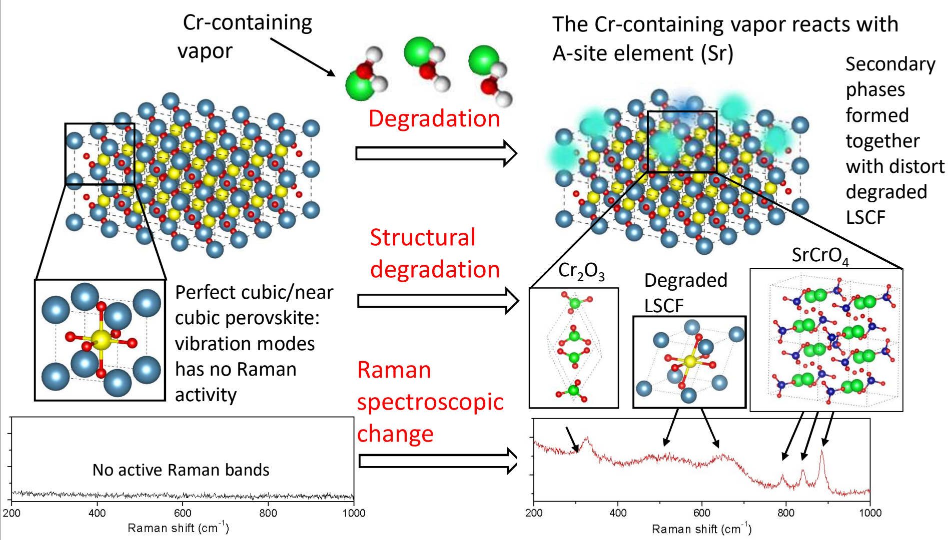
Accomplishments and Progress

- Characterized **electrochemical behavior** of LSCF cathodes exposed to contaminates (such as Cr, SO_2, CO_2 and B) under ROC;
- Identified some **efficient catalysts** for enhancing **ORR activity** and **durability;**
- Fabricated model cells with a **thin-film LSCF electrode** and characterized the **model cells** (w/o catalyst) in different contaminants;
- Probed **surface species** of LSCF using *in operando* **SERS**; and
- Developed the low-cost and applicable deposition techniques for large cathodes (~1 inch diameter).

35

35

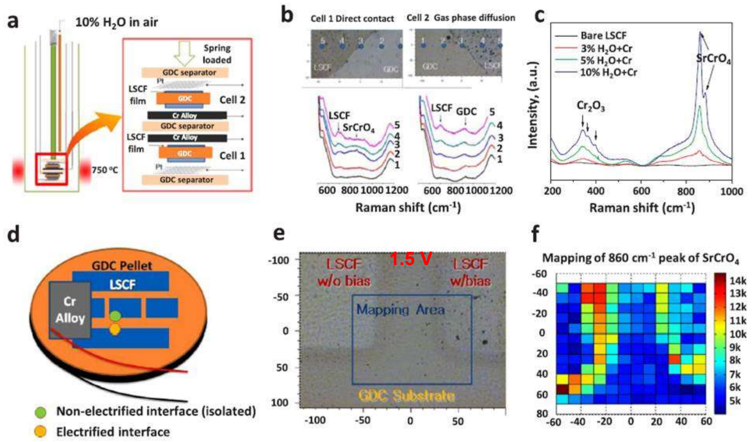
Effects of Cr on LSCF Raman spectra



36

36

$SrCrO_4$ concentrates on LSCF-GDC boundary



- **a**: Cr poisoning was studied in **two modes**: direct and indirect contact;
- **b**: Raman spectra indicated that $SrCrO_4$ concentrates mainly on boundary;
- **c**: Water exacerbated the formation of $SrCrO_4$;
- **d,e,f**: bias exacerbated formation of $SrCrO_4$.

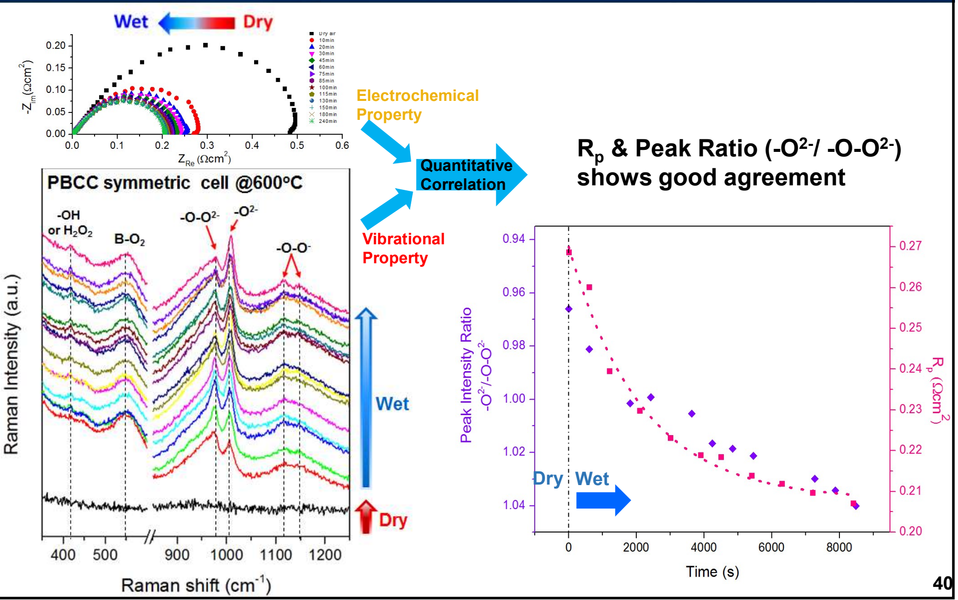
- ✓ LSCF thin film I SDC I LSCF thin film
- ✓ GDC dry-pressed & fired at 1450°C
- ✓ LSCF: RF sputtered
- ✓ Cr: Direct or indirect contact in wet air
- ✓ Bias: 1.5 V
- ✓ *in situ Raman* at 550°C

Nano Energy, 47 (2018) 474-480

37

37

Quantitative correlation: Raman and EIS



40

38

Summary

- **Developed** **an effective strategy** (in operando characterization and computation) for enhancing the tolerance to contaminants poisoning of electrodes

- **Identified** a number of **new catalysts** with high electro-catalytic activity and excellent durability for surface modification of electrode, demonstrating better tolerance to H_2O, CO_2, Cr, B_2O_3 and SO_2.

39

Acknowledgement

Discussions with Joseph Stoffa and Arun Bose, and other DOE management team members

DOE Solid Oxide Fuel Cell Program (Grant No. DE-FE0031201)

U.S. DEPARTMENT OF ENERGY

In Operando SERS of Electrode Surfaces

40