Developing High Performance and Stable Hetero-structured Cathodes and Fundamental Understanding of Oxygen Reduction and Reaction Behavior

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Outline

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  - SOFC Cathode Degradation
  - Functions of Cathode Infiltration
  - Fundamental Issues in Infiltrated Cathodes
- Project Objectives & Benefits
- Technical Approaches
- Technical Accomplishments
  - ORR Characterizations
  - Development of LNO Infiltrated LSCF Cathode
  - Long-term stability
- Summary and Future work

Background - SOFC Cathode Degradation

- Microstructural changes (loss effective TPB area)
  - Grain growth
  - Coarsening of the particles
  - Surface re-construction
- Chemical reaction with YSZ electrolyte.

$$La_2O_3(s) + 2ZrO_2(s) \rightarrow La_2Zr_7O_3(s)$$

$$SrO(s) + ZrO_2(s) \rightarrow SrZrO_3(s)$$

- Strontium segregation related issues

$$2Sr_{La}^{'} + V_{O,LSCF}^{\bullet\bullet} + 2O_O^x \leftrightarrow 2SrO(s) \qquad SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$$

$$SrO(s) + H_2O(g) \rightarrow Sr(OH)_2(s)$$

- Poisoning of the cathode (e.g. by chromium species etc.)
- Etc.

Background - Function of Cathode Infiltration

- Enhancement of ORR kinetics
  - ➢ Improving electrochemical catalytic performance

    (noble metal Pt/Ag/Pd-infiltrated cathode)
  - ➢ Enlarging the TPB

    (LSM - infiltrated YSZ, GDC-infiltrated LSM & LSCF, self-infiltration)
- Improvement of chemical and thermal stability
  - ➢ Avoiding electrolyte/electrode reaction
  - ➢ Alleviating the TEC mismatch problem

    (LSC-infiltrated YSZ cathode)

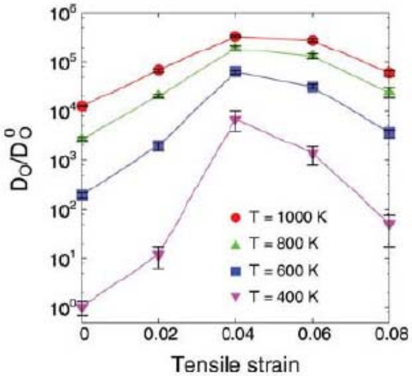
Background - Fundamental Issues in Infiltrated Cathode

Take Home Message

- Infiltrants
  - Surface Exchange Rate Limiting Step
  - Strain Effect
  - Size vs. Characteristic Length
- Hetero-Interface
  - Nature of the Interface
  - Oxygen Transport Mechanisms
- Stability Issues
  - Backbone
  - Reaction between Backbone and Infiltrants
  - Infiltrants growth
- Overall ORR Kinetics

Future study recommendations:

- Further investigation for the hetero interface
- Atomic packing
- Chemical composition
- In-situ electrochemical study
- Infiltrated/cathode backbone/atmosphere interface investigation
- 3-D Model
- Long term stability investigation



Lattice strain effects on oxygen diffusivity for YSZ (calculated with Kinetic Monto Carlo method)

Project Objectives

- **The primary objectives of this project**
  - To develop the fundamental understanding of the oxygen reduction and reaction (ORR) mechanisms, especially the oxygen exchange behavior between the hetero-structured surface (nickelate) and bulk (perovskite) of the cathode through systematic experimental investigations and theoretical modeling.
  - To develop cathodes with hetero-structured surfaces that demonstrate high performance and stability, via low-cost infiltration method.

- **Meeting SECA program goals**
  - This project directly addresses the key goal of the Topic Area 1 – Electrochemical Performance Enhancement Activity of the FOA " to acquire fundamental knowledge and understanding of cell interfaces to facilitate research and development in electrochemical performance enhancement while meeting SECA cost, stability, and lifetime targets",
  - The research areas of interest of the Topic Area 1 "include cell interface evaluation and modifications as well as the development of more stable and higher performance materials morphologies, including, but not limited to, cathode enhancements via infiltration techniques".

Project Benefits

- Develop a new generation of hetero-structured cathode having both high performance and stability, while still be compatible with current industrial practice of making LSCF cathode.

- Provide the guidance on the scientific design and derive experimental methodologies towards advanced IT SOFC cathodes that are in line with the SECA's objectives for next-generation cost-competitive and reliable power output from coal energy source.

Technical Approaches

Advantages of LSCF

- Mixed ionic and electronic conductor
- High electrochemical activity of oxygen reduction at IT range

Concerns of LSCF

- Sr segregation during SOFC operation

$$2Sr_{La}^{'} + V_{O,LSCF}^{\bullet\bullet} + 2O_O^x \leftrightarrow 2SrO(s)$$

- ORR kinetics limited by surface reaction process

$$1/2O_2 + V_{LSCF}^{\bullet\bullet} \Rightarrow O_{O,LSCF}^x + 2h^{\bullet}$$

LNO with Ruddlesden-Popper (RP) Structure

- **$La_2NiO_{4+\delta}$ containing perovskite layer and salt layer alternatively**
- **Good oxygen transport properties via ionic paths of interstitial and vacancy**
- **Rapid surface oxygen exchange**
- **Compatible TEC with solid electrolytes**

Technical Approaches

- LNO as Sr acceptor, improving electronic conduction properties of LNO and stability of LSCF

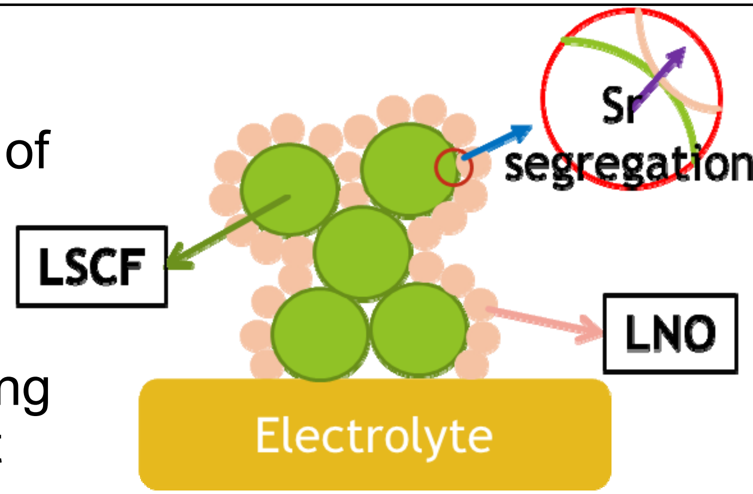
$$SrO + Ni_{Ni}^{x} \leftrightarrow Sr_{La}^{'} + Ni_{Ni}^{'} + O_{O}^{x}$$

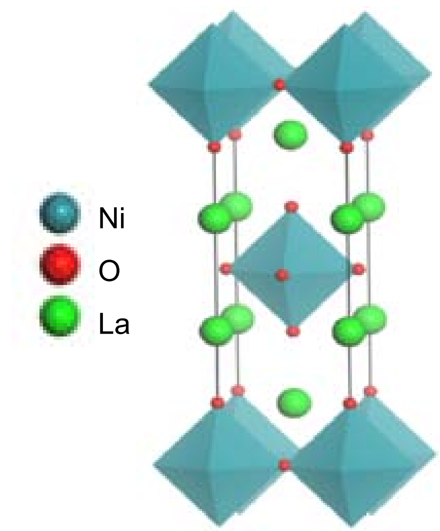
- Enhanced hetero-structure interface, leading to high stability and good oxygen transport properties of infiltrated cathode materials

$$O_{i,LNO}^{''} + V_{O,LSCF}^{\bullet\bullet} \Rightarrow O_{O,LSCF}^{x}$$

- Increased surface adsorption kinetics, resulting from high K value of LNO

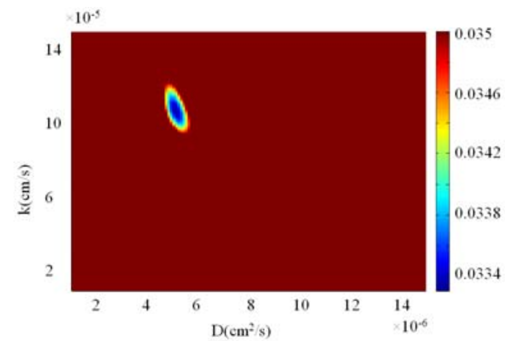
- Increased 3PB reaction areas and change of surface reaction/polarization





- Assume a small oxygen partial pressure changing step:

$$\frac{\mathrm{C}(t)-\mathrm{C}(0)}{\mathrm{C}(\infty)-\mathrm{C}(0)}=\frac{\delta(t)-\delta(0)}{\delta(\infty)-\delta(0)}=\frac{\sigma(t)-\sigma(0)}{\sigma(\infty)-\sigma(0)}$$



$$f=\sqrt{\frac{F_1^2}{T_1}+\frac{F_2^2}{T_2}}$$

- Diffusion equation and solution:

$$\frac{\partial\phi}{\partial t}=\mathrm{D}\frac{\partial^2\phi}{\partial x^2}$$

$$-D\partial C/\partial x\big|_{x=\pm a}=k[C(\infty)-C(t)]$$

$$k=k_1P_{O_2}^{1/2}+k_2$$

C(∞): is in equilibrium surface concentration under certain oxygen pressure

C(t): real time surface concentration

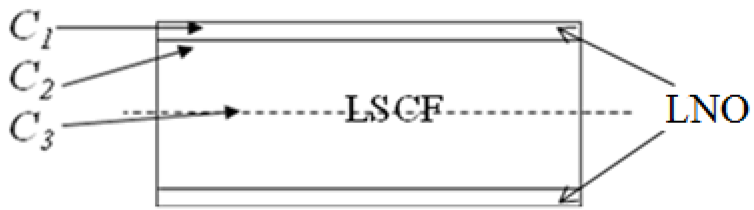
$$\frac{C(\mathrm{t})-C(0)}{C(\infty)-C(0)}=1-\sum_{n=1}^{\infty}\frac{2L^2\exp(-\beta_n^2Dt/a^2)}{\beta_n^2(\beta_n^2+L^2+L)}$$

$$L=\frac{ak}{D}=\frac{a}{l_c}=\beta_n\tan\beta_n$$

Characteristic length

Fundamental ORR Characterization by ECR

- Characterize oxygen exchange coefficient at infiltrated/cathode backbone interface

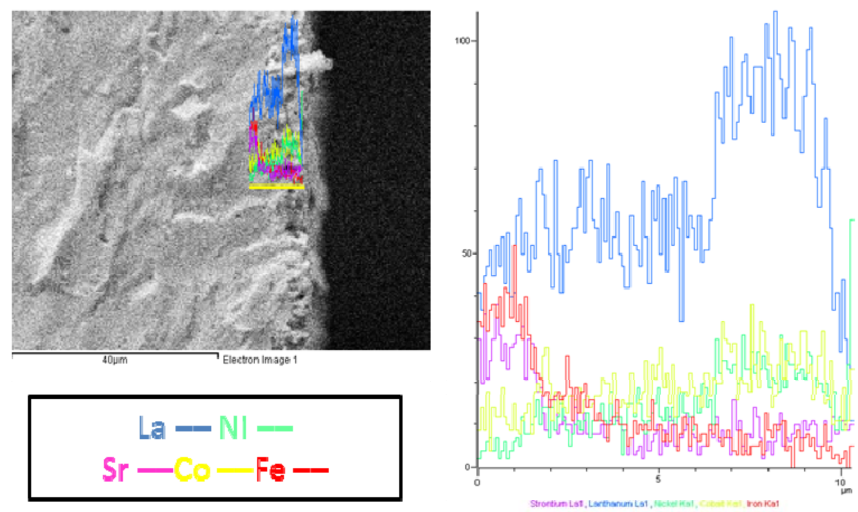


$$C_1 - C_{\infty}' = \frac{J}{k_{surface}}$$

$$C_2 - C_{\infty} = \frac{J}{k_{interface}}$$

$$C_3 - C_2 = \frac{Ja}{D}$$

$$\frac{1}{k} = \frac{1}{k_{interface}} + \frac{1}{k_{surface}}$$



•LNO layer obtained by spin coating

•Thickness about 5-10µm

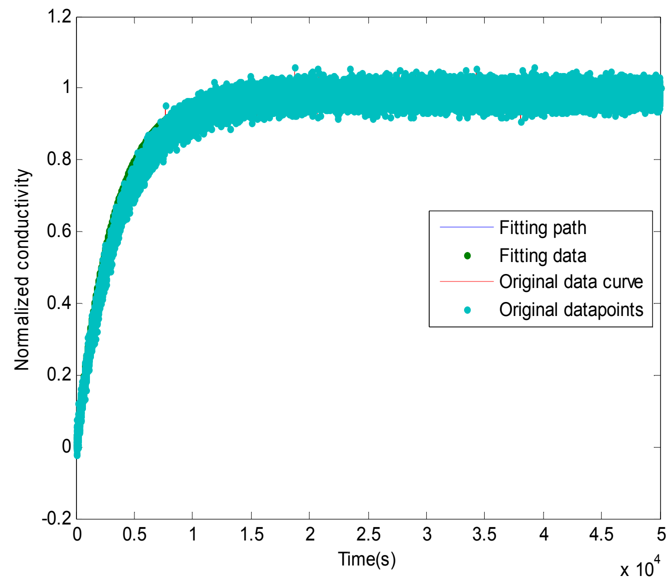
•Small amount of Co diffusion shows in EDXs

Fundamental ORR Characterization by ECR

- Higher LNO-LSCF surface and interface oxygen exchange properties than that of pure LSCF surface (hetero-structured interface)

- k value slightly gets decrease as small amount of Sr loading increases.

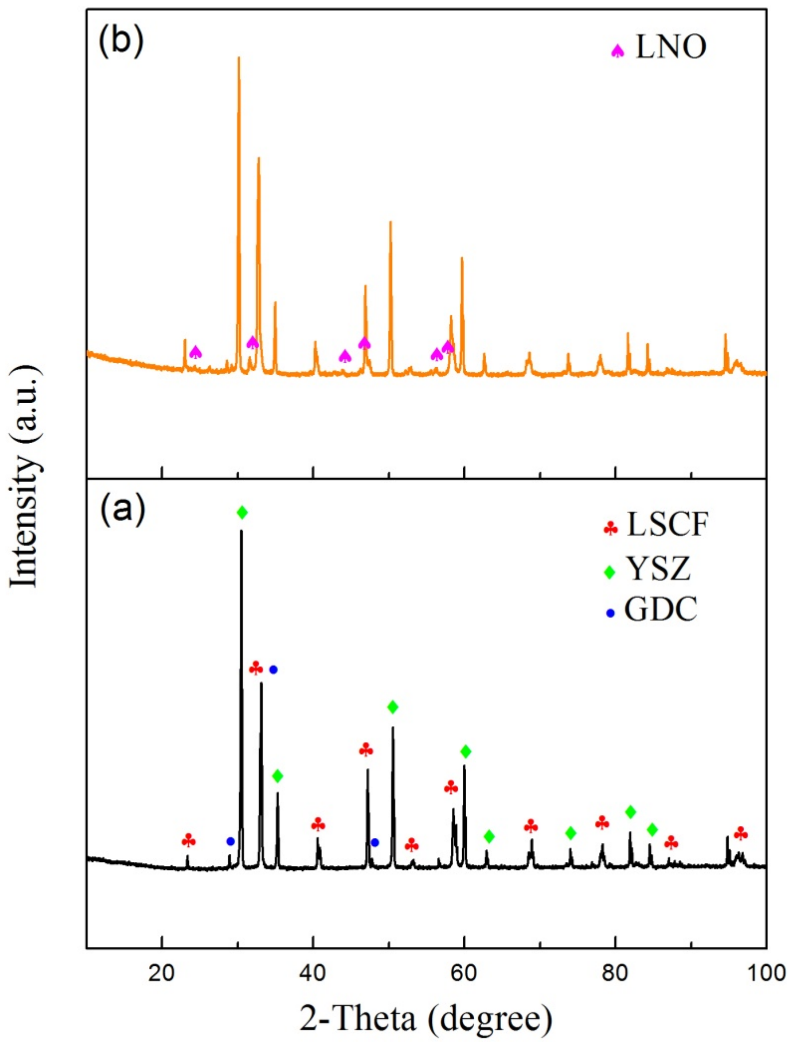
- D value decreases with the increase of Sr loading. but *lc* is still hundreds of microns.



Po2(0.2atm)	D(cm2/s)	k(cm/s)
LNO	3.98E-06	4.38E-05
Sr10	3.41E-06	4.22E-05
Sr20	2.66E-06	4.41E-05
Sr40	8.91E-07	5.12E-05

Po$_2$(0.2atm)	*k*(cm/s)
LSCF	4.21E-05
LNO-LSCF$_{total}$	5.03E-05
LNO-LSCF$_{inter}$	8.32E-05

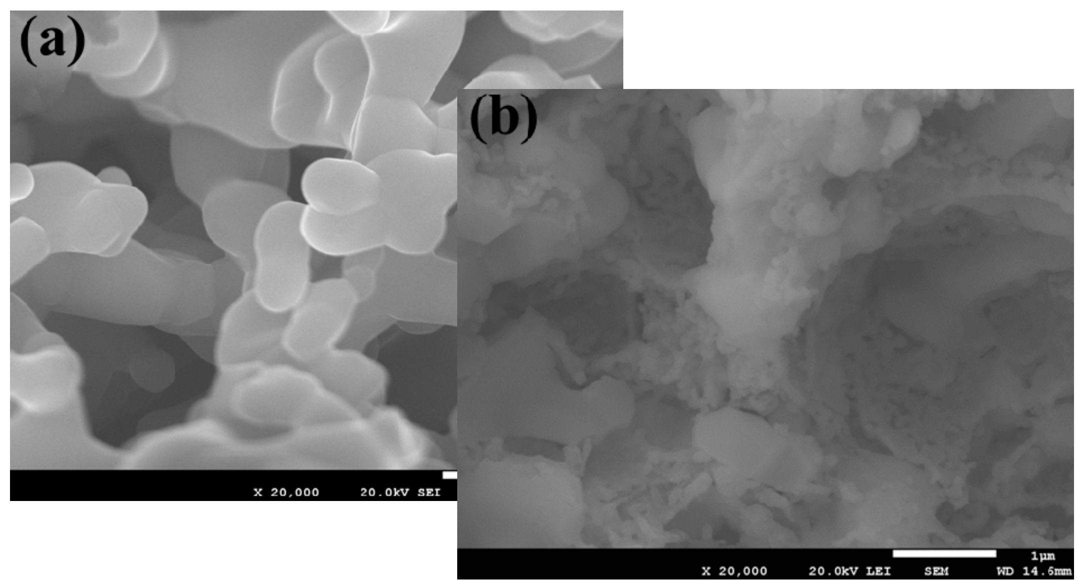
Developing high performance cathode



1mol/L LNO infiltration solution

Sintering at 900^{o}C ⟶ Ruddlesden-Popper Phase

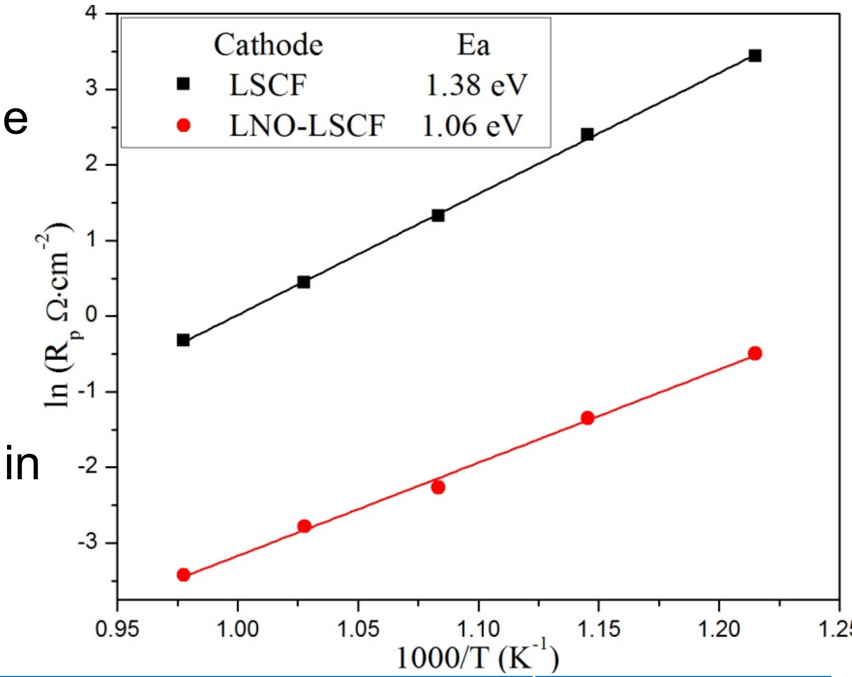
Loading ≈15 wt.%



Xinxin Zhang; Hui Zhang; **Xingbo Liu***: High Performance $La_2NiO_{4+<delta>}$-Infiltrated $(La_{0.6}Sr_{0.4})_{0.995}Co_{0.2}Fe_{0.8}O_{3-\delta}$ Cathode for Solid Oxide Fuel Cells, *Journal of Power Sources 269 (2014) 412-417.*

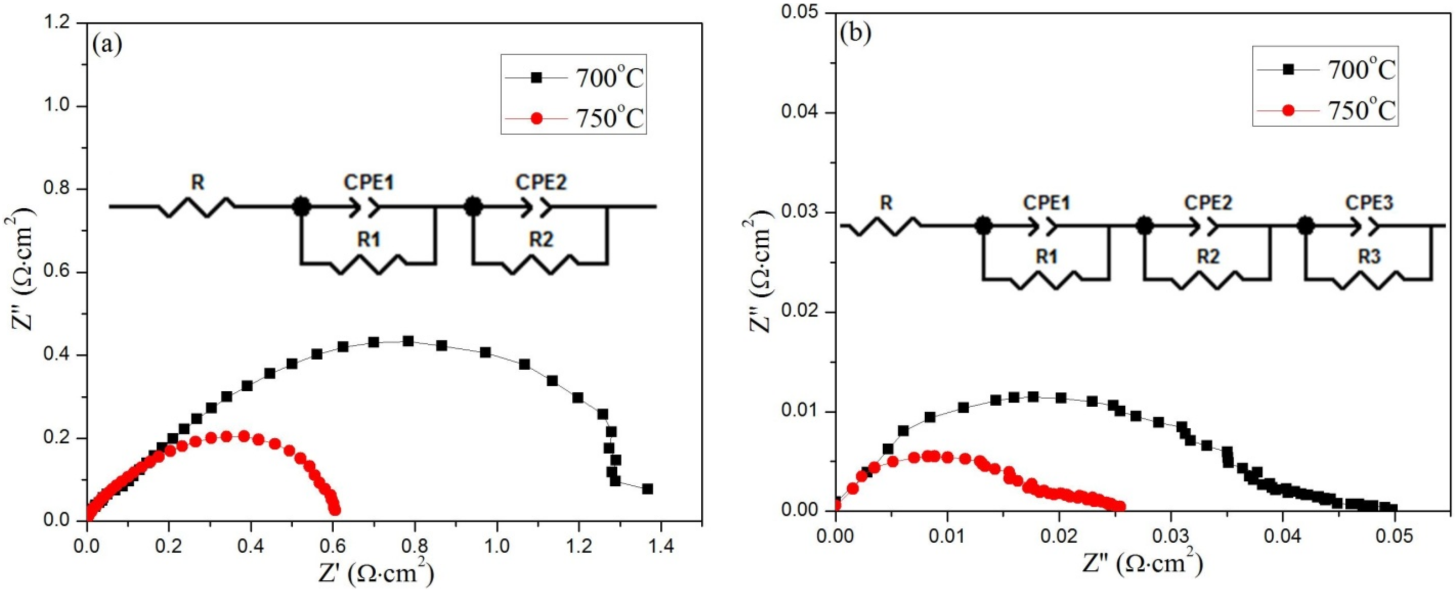
Electrochemical Performance of LNO-infiltrated LSCF by EIS

- LNO infiltration decreases the polarization resistance by more than one order of magnitude at 750°C.
- The activation energy also decreases dramatically.
- Higher polarization resistance for pure LSCF in our work possibly related with higher sintering temperature.



	R (Ωcm²) at different T in air				Ea (eV)
	600°C	650 °C	700 °C	750 °C	
LSCF	9.34	3.48	1.35	0.62	1.38
LSCF [Ref]	----	----	0.6-0.3	0.3-0.1	
LNO-LSCF	0.20	0.079	0.042	0.023	1.06

Rate-limiting Step Analysis



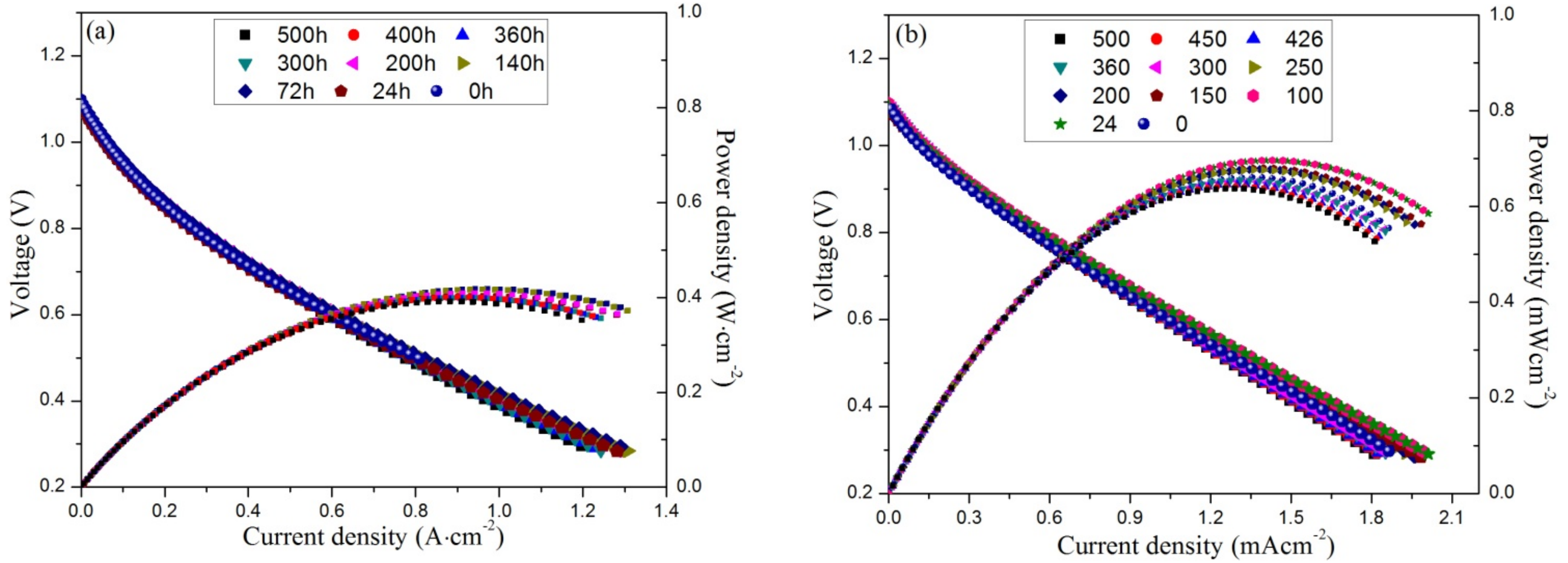
Surface charge transfer

Surface process

Diffusion process

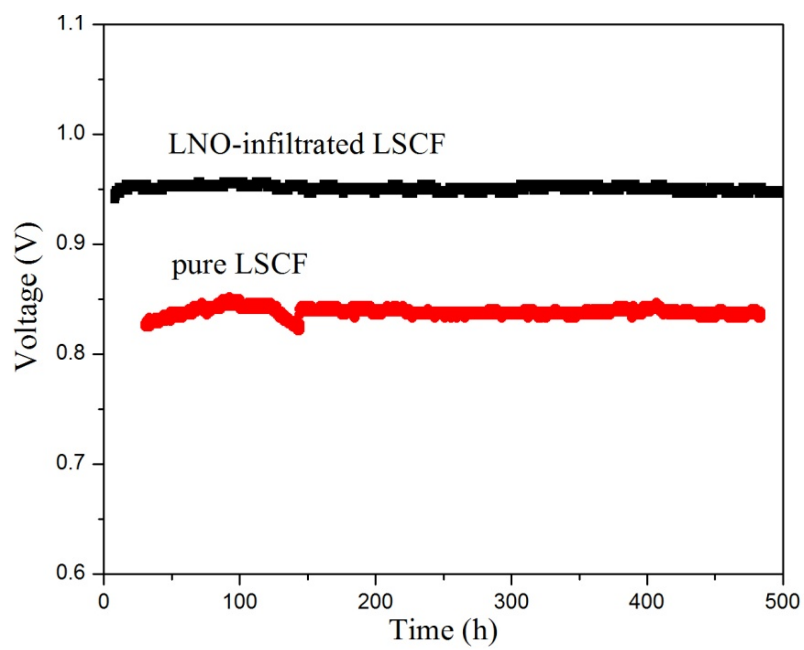
	Intermediate-frequency arc 1		**Intermediate-frequency arc 2**		**low frequency arc 3**	
	R_1 (Ωcm^2)	C_1(Fcm^{-2})	R_2(Ωcm^2)	C_2(Fcm^{-2})	R_3(Ωcm^2)	C_3(Fcm^{-2})
LSCF	0.67	$4.1*10^{-3}$	0.68	$2.0*10^{-2}$	-----	-----
LNO-LSCF	0.020	$6.4*10^{-3}$	0.016	$7.0*10^{-2}$	0.0061	2.9

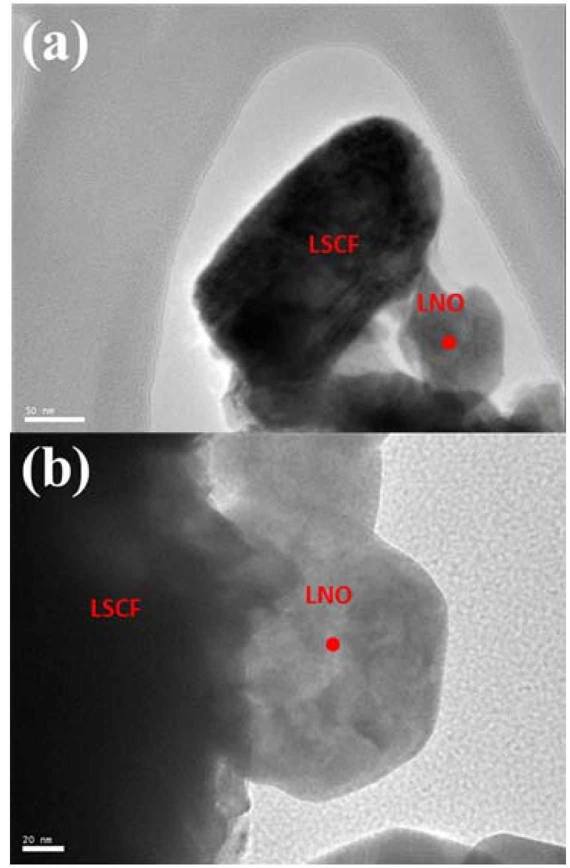
Long-term stability



	LSCF cathode		**LNO-infiltrated LSCF cathode**	
	140h	**500h**	**24h**	**500h**
Ohmic (Ωcm^2)	0.37	0.39	0.29	0.30
Non-ohmic (Ωcm^2)	0.39	0.41	0.19	0.21
Max Power Density ($mWcm^{-2}$)	418	392	697	637

Long-term stability





- Similar degradation for pure LSCF and LNO-LSCF, although nano-particles growth and aggregation exist in LNO infiltration.
- Favorable cations Sr/Co diffusion shows in EDXS analysis.

Degradation:

- Pure LSCF: 0.841-0.839 V to 0.839-0.836 V **0.36% (~400 hours)**
- LNO-LSCF:0.952-0.949 V to 0.949-0.946 V **0.39% (~500 hours)**

Summary

- LNO infiltration enhances the electrochemical properties of LSCF electrode. Rp decreases by one order magnitude and a 67% higher power density is obtained after LNO infiltration;

- Similar long-term stability for LSCF and LNO-LSCF is obtained, although nano-particles growth and aggregation exist after testing for LNO infiltration.

- LNO-coated LSCF has a higher oxygen surface and interface exchange coefficient , as compared to pure LSCF materials, which would responsible for the decrease of cathode polarization of LSCF electrode.

- Favorable cations Sr/Co diffusion shows in EDXS analysis, which would enhance the long-term stability and high electrochemical performance. More accurate elements diffusion analysis needs to be done in future.

Future Work

- High Performance and Stability Issues
  - Improve the uniformity of infiltrated layer
  - Optimize the cathode performance
  - Extend long-term stability testing
  - Analyze elements diffusion in hetero-structured interface
- Hetero-structured Interface
  - Structure and Elements State of the interface
  - Oxygen Transport Mechanisms
- Overall ORR Kinetics
  - In-situ Monitor oxygen transport properties under different conditions.
  - Establish ORR model for infiltration cathode

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