

Project Review for DE-FE32116

Heterostructured Cr Resistant Oxygen Electrode for SOECs



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Outline

- Background
- Proposed novel La₂NiO₄-LaCoO₃ heterostructure
- Critical Factors to consider
- Overall Approach & Objectives
- Updates on Tasks

Background: Cr in SOC Stack



High P_{02} in SOEC lead to increased P_{cr} relative to SOFC

Cr from metallic part in the stack

 $SrO + CrO_3(g) \rightarrow Cr - Sr - O(nuclei)$

 $Cr - Sr - O(nuclei) + CrO_3(g) \rightarrow Cr_2O_3(s)$

 $Cr - Sr - O(nuclei) + SrO + CrO_3(g) \rightarrow SrCrO_4(s)$

Alkaline-earth element - Sr is the triggering factor

Background: Cr to Poison Benchmark LSCF



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Previous Results From WPI on La₂NiO₄





No apparent secondary phase formation

LNO is stable with the exposure to Cr

Previous Results From WVU: La₂NiO₄-LaCoO₃ Heterostructure



Interstitial oxygen defects in LNO to provide high ion conductivity in high P_{O2}



Infiltration to abruptly improve the performance

Proposed Novel La₂NiO₄-LaCoO₃ Heterostructure



Sr-free, fast O-conducting LNO backbone plus active OER LCO surface coating as Cr-resistant, high performing oxygen electrode

Critical Factors to consider

- CF1. Cr Resistance: It is well known that Sr is the main reason for the Cr poisoning due to the formation of SrCrO₄. The new oxygen electrode candidate should not have Sr;
- **CF2. Oxygen Ionic Conductivity:** R-P phases and perovskites have totally different oxygen ionic conduction mechanisms. Dopant choice and interface engineering is needed to achieve excellent bulk conductivity and interfacial ion exchange;
- **CF3. Interfacial Stability:** The infiltration with LCO-based perovskites will introduce the interfaces with LNO and LDC barrier layer respectively. Dopant choice is needed to control the bulk and interfacial phase stabilities;
- **CF4. Long-Term Degradation Mechanism:** Accelerated test will be carried out to simulate the long-term degradation performance. However, it is imperative to validate the accelerated test mechanism is identical to which under the real operation conditions.

Overall Approach & Objectives



When fully optimized, this oxygen electrode material will target to an INTRINSIC long-term degradation rate of less than 0.3%/1000 hrs at 700°C. By the end of the first year, it is expected to reach the $0.8A/cm^2$ current density at 1.4V applied potential. By the end of the project, we will reach 1A/cm² current density.

(1) LCO-based Materials



s (e.g. Ni, Cu, Mn) as

(2) Chemical Stabilities Under Cr-Containing Gas Impurity Conditions



LNO backbone



(3) Electrical Conductivity and Conductivity Relaxation Experiments

(a) 1 2 (b) 3 4 (b) C_1 C_2 C_3 LCO-based perovskite

ECR sample configuration for OER kinetics on the heterostructured interface. (a) sample top view, (b) sample cross section



ECR on porous sample to evaluate the oxygen surface exchange coefficient

Solution for D&k co-control scenario

$$\frac{\partial C}{\partial t} = \tilde{D} \frac{\partial^2 C}{\partial x^2} \quad -l \leq x \leq l \tag{1}$$

$$-\tilde{D} \frac{\partial C(x,t)}{\partial x} \bigg|_{x=\pm l} = k_{\text{chem}} [C_0 - C_s(t)] \quad t > 0 \tag{2}$$

$$g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma_{\infty} - \sigma(0)} = \frac{C(t) - C(0)}{C_0 - C(0)} = \frac{M(t)}{M_{\infty}} = 1$$

$$-\sum_{n=1}^{\infty} \frac{2L^2 \exp(-\beta_n^2 \tilde{D} t/l^2)}{\beta_n^2 (\beta_n^2 + L^2 + L)} \tag{3}$$

$$\beta_n \tan \beta_n = L$$

 $L = \frac{lk_{\text{chem}}}{L} = \frac{l}{L}$

(5)

Solution for k control scenario

$$S_{\rm V}k_{\rm chem}[C_{\rm o} - C(t)]dt = (1 - V_{\rm v})dC(t)$$
(1)

$$\frac{C_{\rm o} - C(t)}{C_{\rm o} - C(0)} = \exp\left[-\frac{t}{\left(\frac{1 - V_{\rm v}}{S_{\rm V}k_{\rm chem}}\right)}\right] = \exp\left[-\frac{t}{\tau_{\rm r}}\right]$$
(2)
$$g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma_{\infty} - \sigma(0)} = 1 - \exp\left[-\frac{t}{\tau_{\rm r}}\right] = 1 - \exp\left[-\frac{t}{\left(\frac{1 - V_{\rm v}}{S_{\rm V}k_{\rm chem}}\right)}\right]$$
(3)

Average sample particle size $<< I_{cr}$



Synthesis of Sr-free perovskite surface coating materials



Pure phase achieved for each perovskite material at 800C

Chemical compatibility between LNO backbone and coating materials



Fittings for samples with Heat: for 0.8atm-1.0atm at 600°C



K-Values for the pure samples at different Oxygen partial pressure and varying temperatures



K-Values for samples with Heat at different Oxygen partial pressure and varying temperatures



K-Values for samples with Cr at different Oxygen partial pressure and varying temperatures



Summary:

The chemical compatibility between LNO(r-p phase) and LCO-based perovskites were confirmed.

ECR tests were carried out in the following three conditions:

- After doping (coating as is)
- After heat treatment (aged at 700C for 200h)
- After exposure to Cr (exposed to Cr source at 700C for 200h)

The following candidates worth the further experimental and modeling verification

- LNO
- LCO
- LMNO
- LNCO

Task 3. Simulation on Oxygen Electrode Stabilities

• Interfacial stability of LNO/LCO heterostructure interface



Interfacial Energy

R-p phase

Perovskite

 $\gamma_{A/B} = (N_{\text{int}}E_{A/B} - (N_A E_A + N_B E_B))/2A$

 $N_{\rm int}$: The number of atoms for the interfacial structure

 N_A : The number of atoms for phase A in the interfacial structure

 N_B : The number of atoms for phase B in the interfacial structure

A: The area of the interface

Task 3. Simulation on Oxygen Electrode Stabilities Examples Interface #1 Interface #1





254 atom-La₂NiO₄/LaCoO₃ interfacial structure:

□ Calculation of interfacial energy of all the

structures

Find the one that shows the lowest interfacial energy

Task 3. Simulation on Oxygen Electrode Stabilities



Task 3. Simulation on Oxygen Electrode Stabilities

Dopant energy

Task 4 Simulations on the Oxygen Electrode Conductivity NEB approach

24/23

Introduction: Wet-Impregnation of Nano-Catalyst for SOFCs/SOECs

Objective: to deposit full phase, LaCoO₃ (and similar) nano-catalyst via controlled deposition throughout a porous structure of the electrode at temperatures <800 °C.

Proposed Solution: use of poly-norepinephrine (pNE) and other catechol-like surfactants to properly chelate the complex higher-order nano-oxides in orderly, non-agglomerated fashion.

Lanthanum Cobaltite Powder Study: Alternative Surfactant Study

A study has been in process to deposit $LaCoO_3$ nano-oxide powder at lower temperatures. The below surfactants were chosen due to similarities to previously proven pNE and lower cost.

Procedure: Combined lanthanum nitrate, cobalt nitrate, ethanol/water. Added surfactant powder to form a solution. Mixture dried by stirring at 75°C until gel-like, and then further dried in oven at 200°C.

Each of these were formed into 0.01M and 0.1M solutions, and then split into batches to fire at 600 °C, 700 °C, and 800 °C. X-ray diffractometry was completed to determine powder composition.

Lanthanum Cobaltite Powder Study: 800 °C pNE XRD Results

Initial Nano-Catalyst Deposition: AFM Images

- The above CoO nano-oxides on single crystal substrates were studied preliminarily to analyze effectiveness of surfactants and to analyze both grain size and nanoparticle distribution of similar nano-oxides.
- These results were obtained with the poly norepinephrine surfactant at 1mg/ml, and fired to 750 °C.

Nano-Catalyst Deposition in Symmetrical Cells: SEM Imaging

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Thank You!

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