Durable and High-Performance SOECs Based on Proton Conductors for Hydrogen Production

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Project manager: **Evelyn Lopez**

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Outline

- Background & Challenges
- Project Objectives
- Technical Approach
- Highlights of Accomplishments to Date
- Recent Progress
  - Development of catalysts to enhance catalytic activity and durability
  - Understanding the mechanism of electrode processes
  - Rational selection of dopants for better electrode & catalyst materials
- Summary and Future Work
- Acknowledgment

Challenges for Proton Conductors

- $BaZr_xCe_{0.8-x}Y_{0.2-y}Yb_yO_{3-\delta}$ (BZCYYb)
  Performance is limited by a tradeoff between stability & conductivity
- $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb1711)
  - Achieves high conductivity and t_H
  - But questionable long-term stability during electrolysis
  - BZCYYb4411 is more stable but less conductive
- $BaHf_{0.8}Yb_{0.2}O_{3-\delta}$ (**BHY82**)
  - Excellent stability against high concentration of H_2O/CO_2
  - But relatively low conductivity
- The optimal composition for bulk and surface should be different.

  The bulk is optimized for conductivity while the surface is for stability.

Objectives

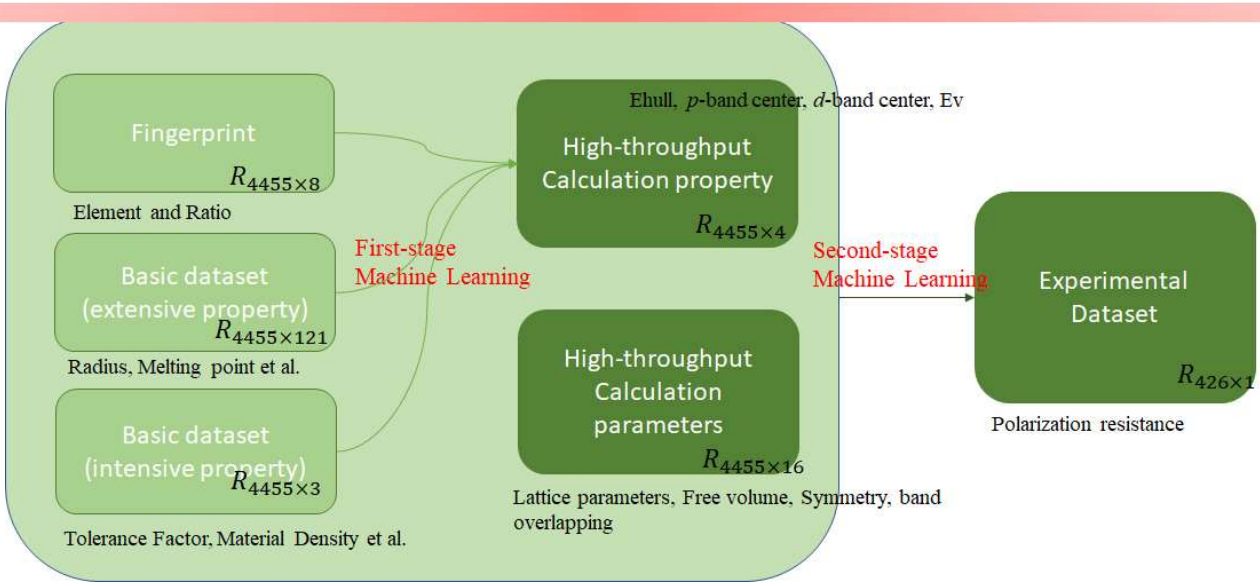
- To develop and optimize a surface modification process (sputtering, SSG, ALD) for deposition of conformal coatings on electrolyte/electrode surface with controlled composition and morphology
- To characterize the electrochemical properties of surface-modified electrolyte/electrodes under typical operating conditions and correlate the properties with the microscopic features of the coating
- To develop and optimize surface modification layers that greatly enhance stability while maintaining high electrochemical performance
- To synthesize the information in order to establish the scientific basis for rational design of ***durable*** electrolytes, electrodes, and catalysts for rSOCs

Technical Approach

Accelerating Materials Discovery via Machine Learning

- Rationally select dopants for better electrode & catalyst materials
- Unravel the mechanisms of transport and electrode processes

A Two-Stage Machine Learning Model



The 1st stage involves predicting the high-throughput calculation property based on the chemo-physical properties of 4,455 different materials.

The 2nd stage: data obtained through computational methods are included as input to predict the polarization resistance.

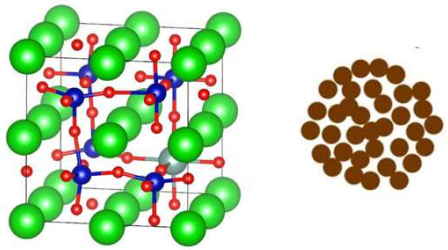
Current status: collected polarization resistances of **426** materials for the second-stage machine learning

Xueyu Hu's Poster on **Preliminary Results**

- Successfully predicted E_{hull}, *p*-band center, *d*-band center, and Ev using the combination of high-throughput calculation and machine learning models.
- Notably, the *d-p* band overlapping area is identified as a critical factor influencing the polarization resistance.
- The predicted promising materials, e.g., X-doped PBC, displayed outstanding performance as an oxygen cathode for rSOCs.

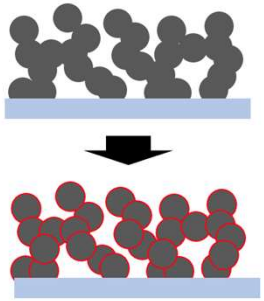
Technical Approach

New Materials Development



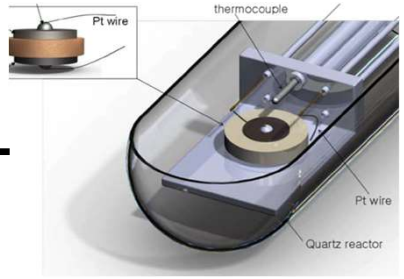
Designing and Synthesis

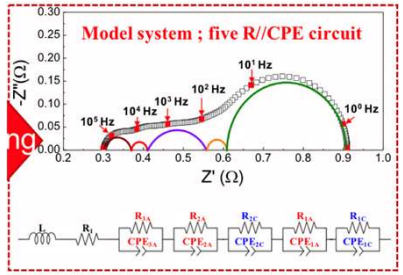
Surface Modification



Optimization of surface morphology

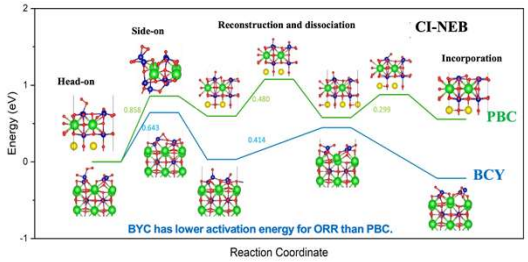
Electrochemical Characterizations





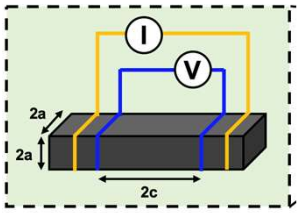
Characterization of performance and durability

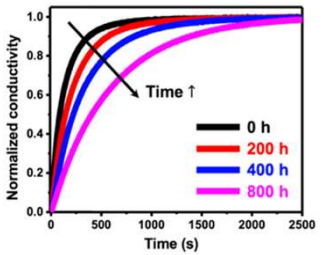
DFT calculations



Prediction of E_a and ORR kinetics for better electrodes

Oxygen Transport Kinetics





Investigation of surface kinetics

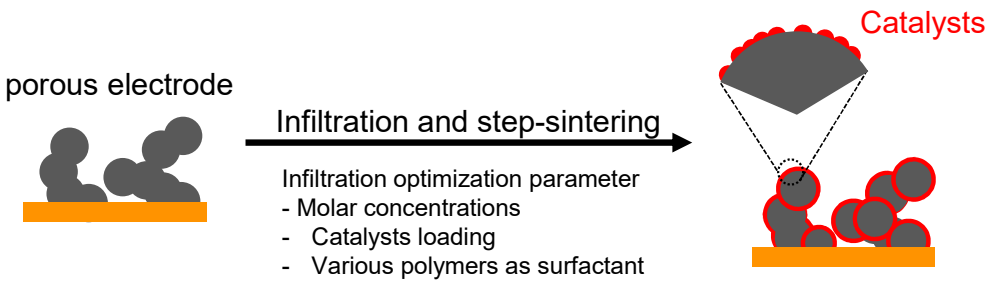
Cell Design and Fabrication

porous PBCC air electrode

dense SDC electrolyte

symmetric cell configuration

- Porous electrode layered prepared by tape-casting
- Symmetric cells fabricated with co-sintering process



- Surface-decorated catalysts on the porous electrode

2a=2b<<2c

Bar-type air electrode

- Well-polished the electrode surface
- Relative density (> 97%) of bar-type sample

○ Contaminants (H_2O and Cr)

- Steam concentrations: 3% to 30% H_2O
- Cr source: Crofer 22

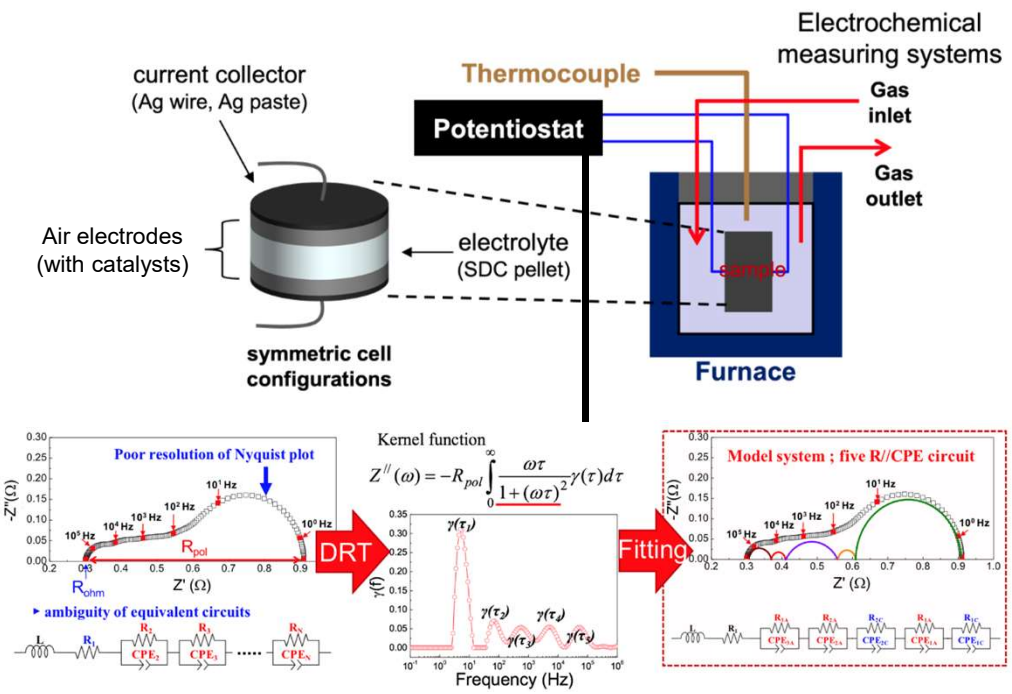
○ Model Cells

1) Fresh sample
   - As-prepared PBCC bar

2) Annealed sample
   - at 600 °C with 30% H_2O with Cr for 50h and 100 h

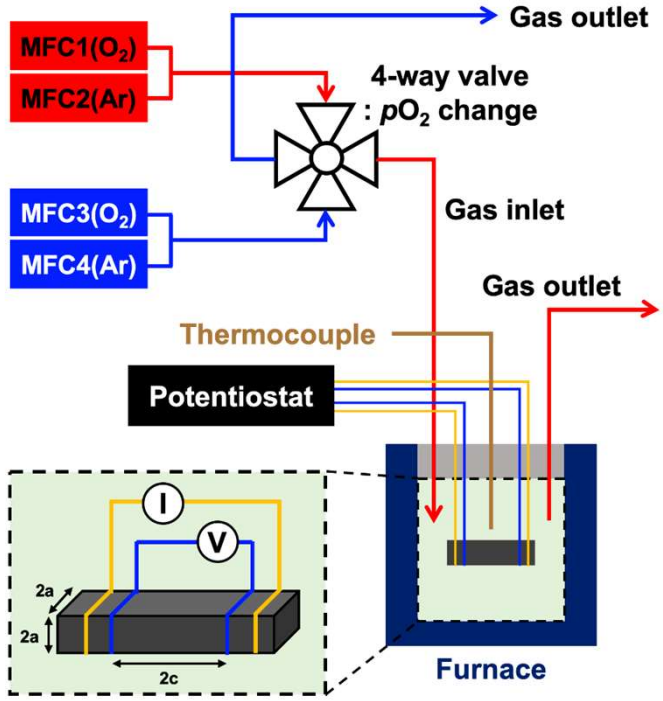
Testing Cell and Characterizations Set-up

Electrochemical Characterization for Performance and Stability under wet air (3-30% H_2O) with Cr



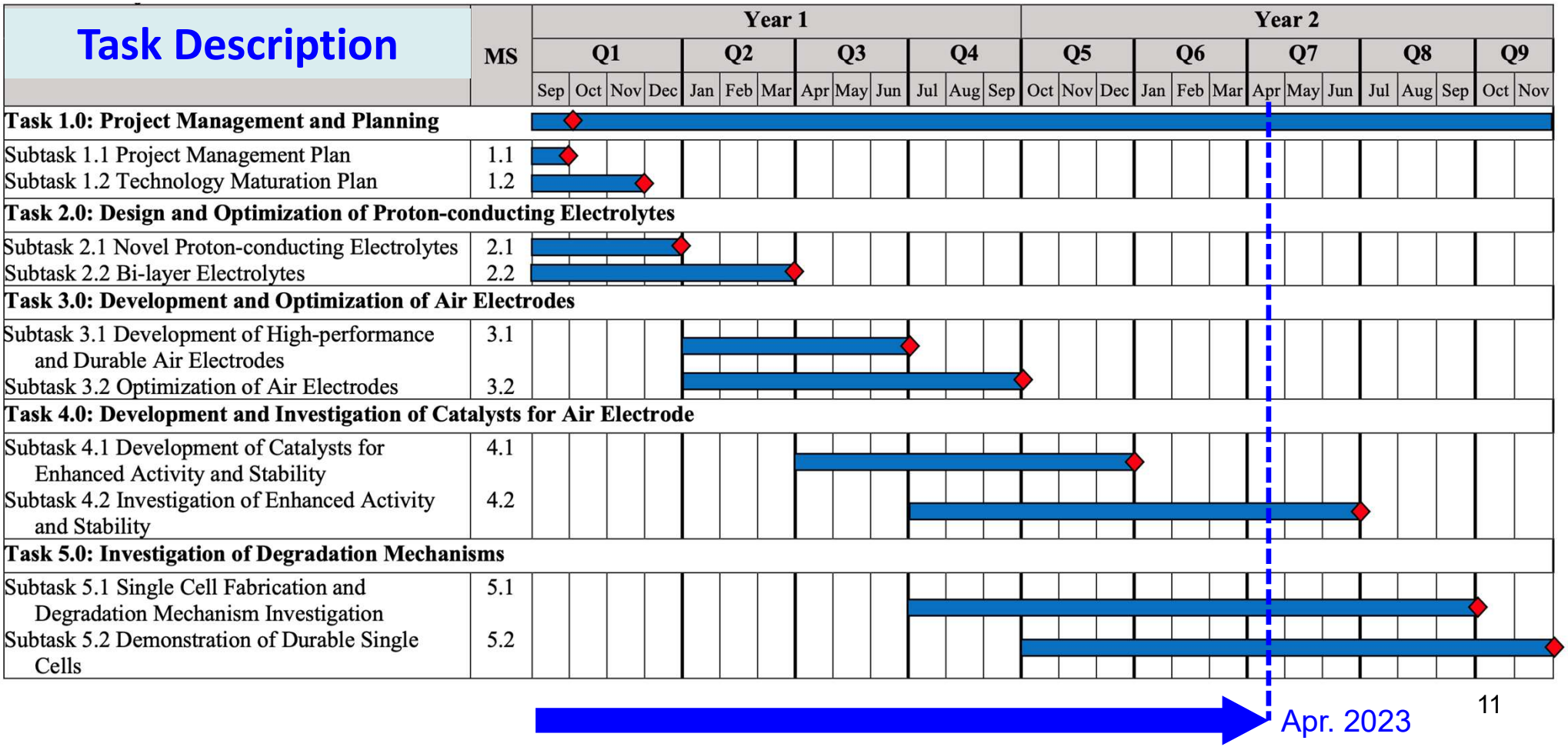
Electrochemical Impedance Spectroscopy (EIS) with Distribution of Relaxation Time (DRT) method

Quantification of Oxygen Transport Kinetics (k_{chem} and D_{chem}) with Cr



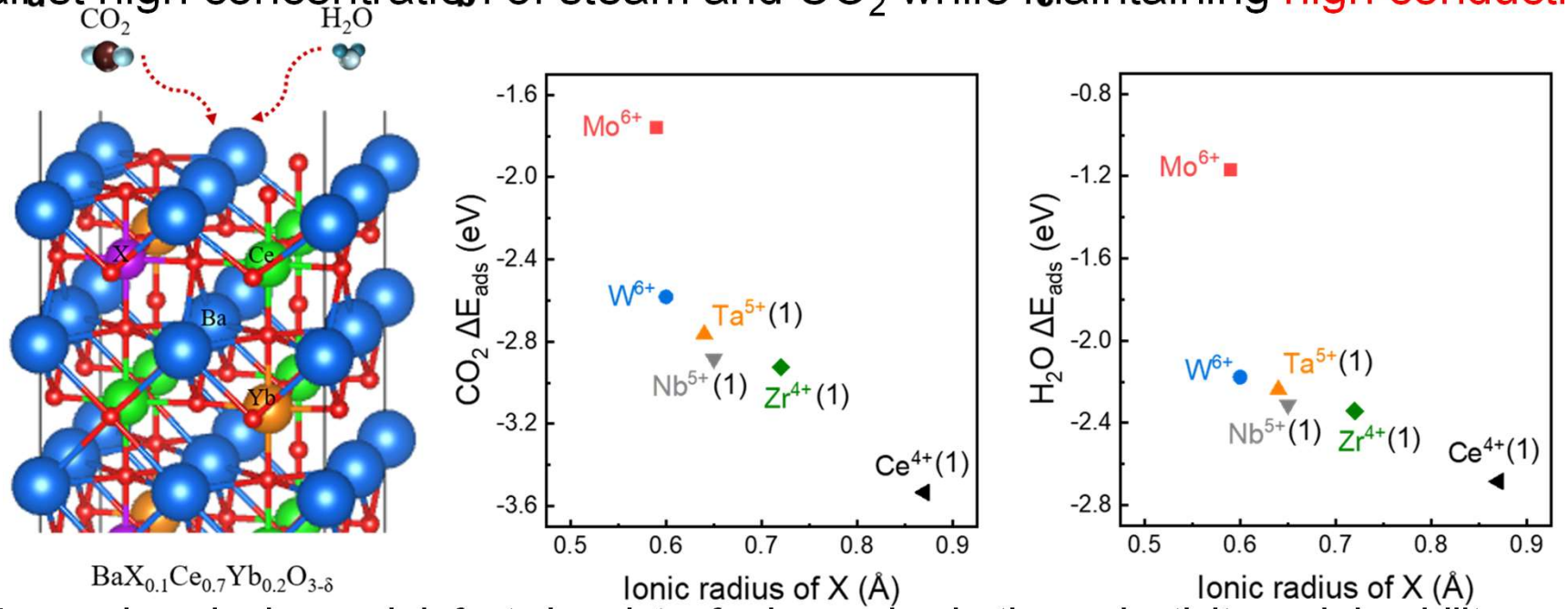
Electrical Conductivity Relaxations (ECR) Measurement Set-up

Tasks and Project Schedule



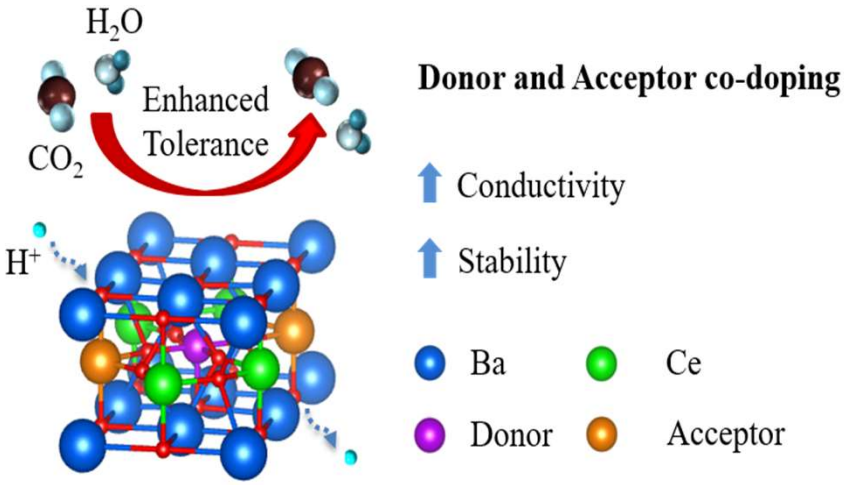
Highlight of Accomplishments to date: Electrolyte

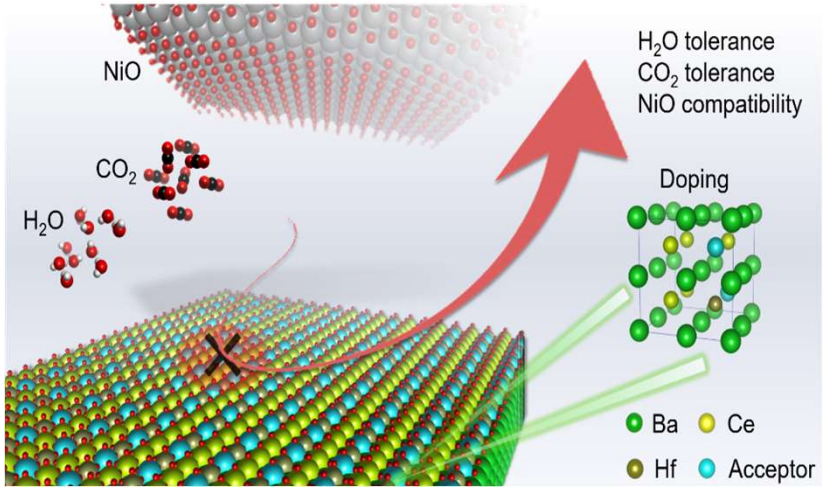
Developed a new set of proton-conducting electrolytes with excellent stability against high concentration of steam and CO_2 while maintaining high conductivity



- Engineered co-doping and defect chemistry for improving both conductivity and durability against high concentration of steam
- Identified co-doped proton conductors with enhanced stability and minimal reaction towards NiO; compatibility with Ni-based electrode is critical to performance

Zheyu Luo's Poster on Electrolyte Development





Luo, Z., Zhou, Y., Hu, X., Kane, N., Li, T., Zhang, W., Liu, Z., Ding, Y., Liu, Y., & Liu, M. (2022). *Energy & Environmental Science, 15*, 2992-3003

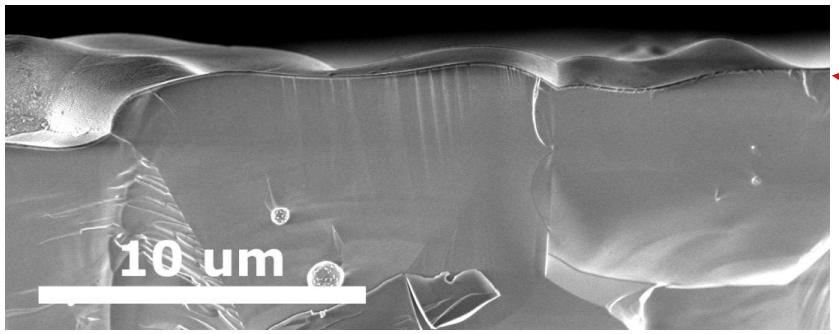
Luo, Z., Zhou, Y., Hu, X., Kane, N., Zhang, W., Li, T., Ding, Y., Liu, Y., & Liu, M. (2022). *ACS Energy Letters*, *7*, 2970-2978.

Luo, Z., Zhou, Y., Hu, X., Wang, W., Ding, Y., Zhang, W., Li, T., Kane, N., Liu, Z., & Liu, M. (2023). *Small*, 2208064

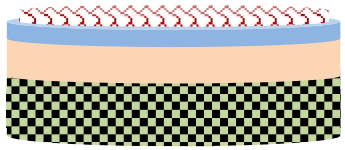
Highlight of Accomplishments to date: Bi-layer Electrolyte

- Demonstrated that a protective coating is effective to enhance stability while the ASR of the bi-layer electrolyte is still sufficiently low.

Well adhered and continuous over the entire electrolyte

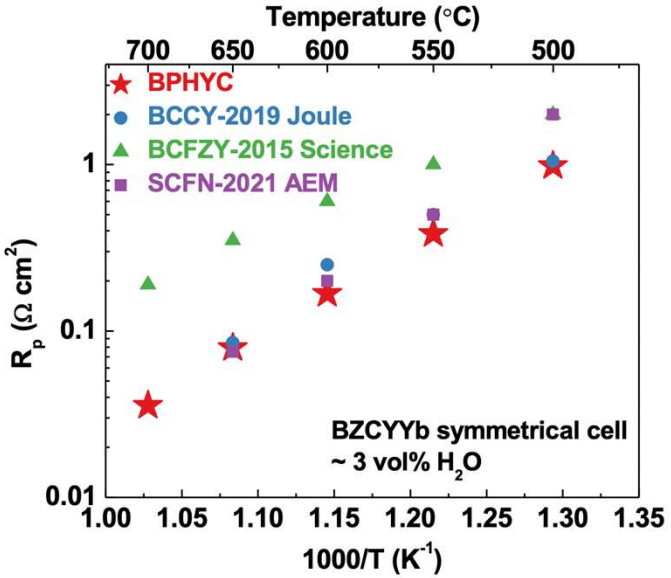


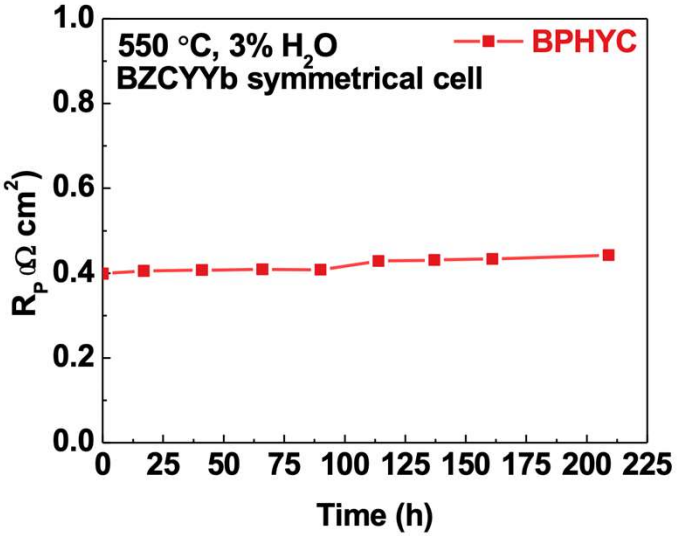
Anode-supported Single Cell



Accomplishments to date: Electrode Materials

- Developed a composite oxygen electrode material (BPHYC) with high electro-catalytic activity and durability



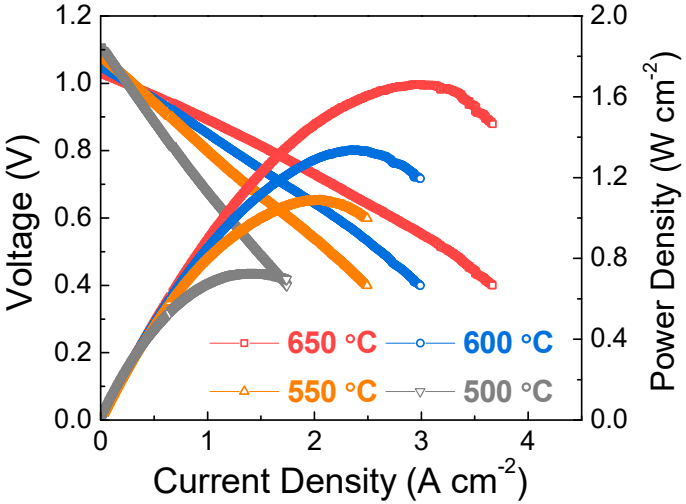


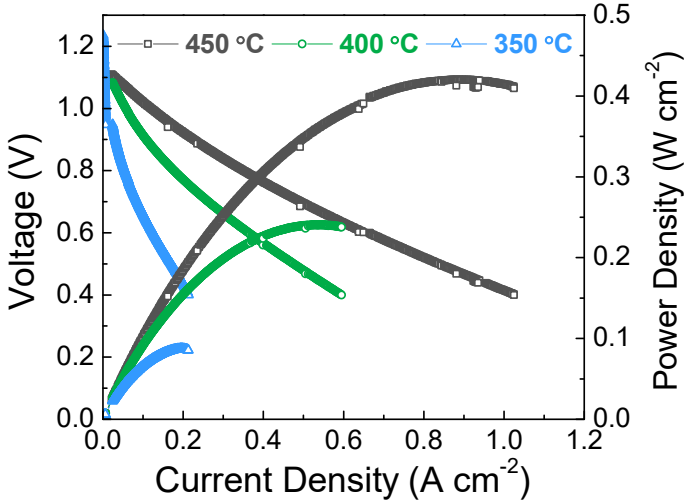
- **Electrode polarization resistance: < 0.2 Ω cm^2 at 600 ºC**
- **Good stability in humified air**

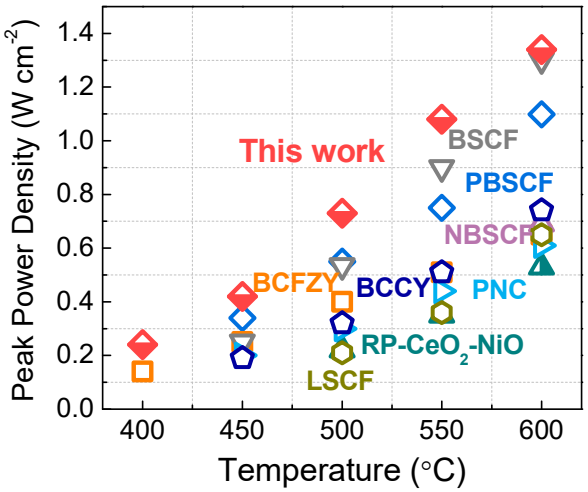
Accomplishments to date: **Cell Performance in the Fuel Cell Mode**

- Demonstrated high performances in fuel cell mode:

  Peak power density of ~1.34 W cm^{-2} at 600 ºC, ~ 0.4 W cm^{-2} at **450ºC**



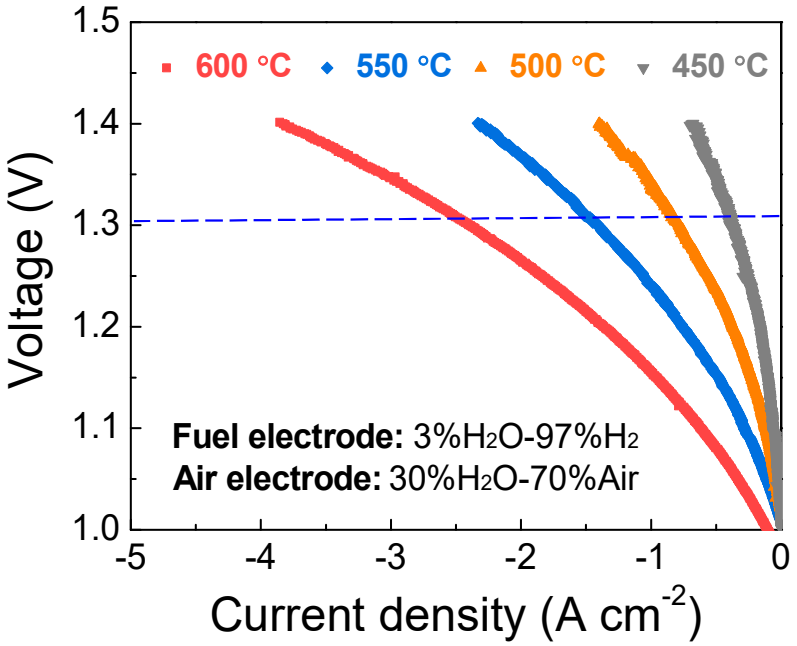


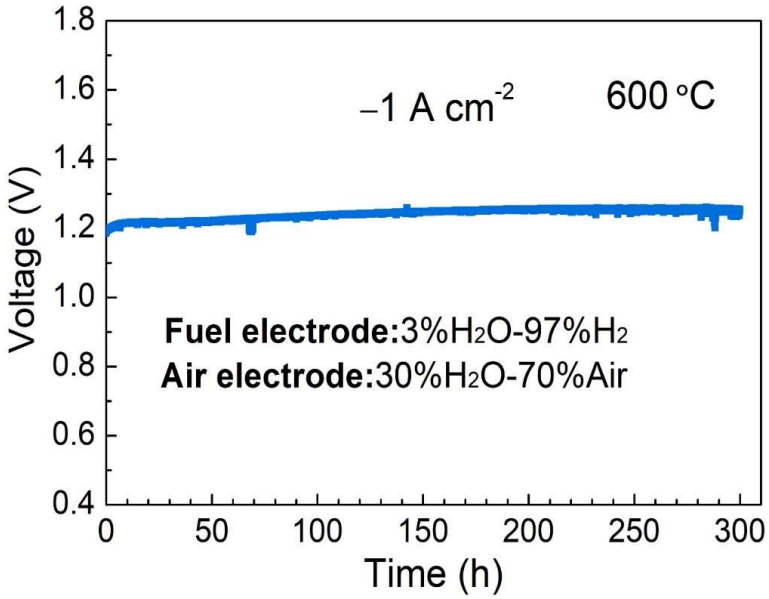


- **Very high performance even at relatively low temperatures**

Accomplishments to date: **Cell Performance in the Electrolysis Mode**

At **1.3 V**, achieved 2.4 A cm^{-2} at **600 °C**, ~0.8 A cm^{-2} at **500 °C**, minimal degradation over 300 h operation at 600 °C





Status of Milestones

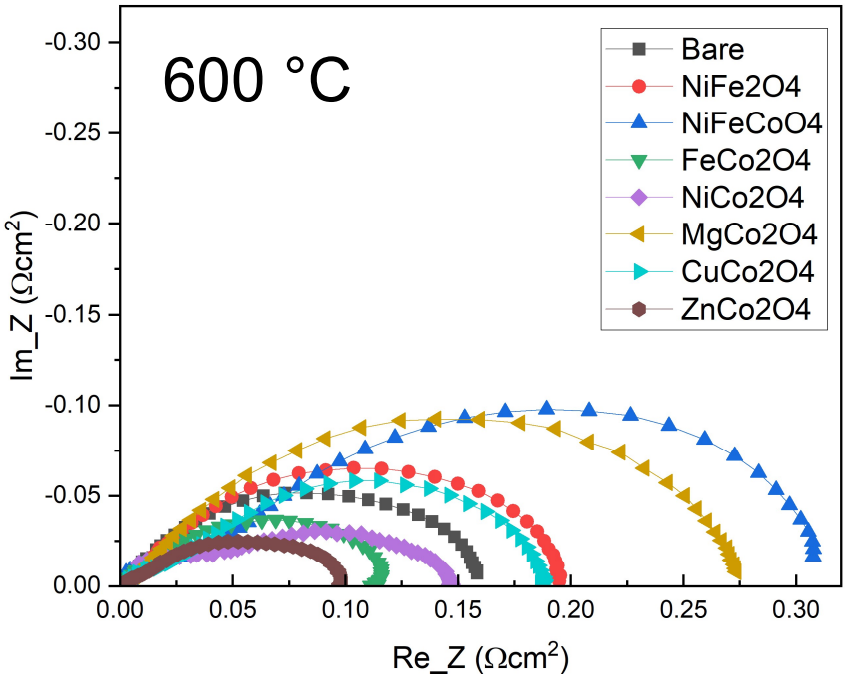
Date	Milestone	% Complete
12/21	Complete electrolyte development with conductivity >0.01 S cm^{-1} in Ar (3%H_2O) and ionic transference numbers >0.95 at 600 ºC.	100
03/22	Complete bi-layer electrolyte development with the durability of at least 500 h with a degradation rate of <0.5% per 1,000 h.	100
06/22	Complete air electrode development with a R_p of <0.3 Ω cm^2 at 600 ºC in Air (3%H_2O).	100
09/22	Complete air electrode optimization with a R_p of <0.2 Ω cm^2 at 600 ºC in Air (3%H_2O).	100
12/22	Complete the catalyst modification of the air electrode with a R_p of <0.15 Ω cm^2 at 600 ºC in Air (3%H_2O), and the durability evaluation for at least 500 h with a degradation rate of <0.5% per 1,000 h under the presence of contaminations (e.g., H_2O and Cr).	100
06/23	Complete *in situ* and *ex situ* characterization of surface morphology and surface species using experimental and modeling work to determine the activity and stability of the cells as a function of contaminant presence, relevant operating conditions, and catalyst content.	70
09/23	Complete the fabrication of button cells with a current density of >1.8 A cm^{-2} at 1.3 V in electrolysis mode at 600 °C and **≥75% roundtrip efficiency** in both SOFC and SOEC modes at ≤ 650 °C.	30
12/23	Complete the long-term durability evaluation of button cells for at least 500 h with a degradation rate of <0.5% per 1,000 h.	5

Recent Progress

- **Developed catalysts to enhance electro-catalytic activity and durability**
- **Unraveling the mechanism of electrode processes**
  - Deduced reaction sequence and rate-determining steps from phenomenological modeling, impedance spectroscopy, and DRT analysis
  - Estimated surface exchange rate and diffusivity from ECR measurement
  - Correlated electrochemical performance directly with surface morphology and surface chemistry (Raman)
- **Accelerating materials discovery via machine learning**
  - Rational selection of dopants for better electrode & catalyst materials

Recent Progress: Catalysts Development

- Symmetric cell configurations (**PBCC@catalysts | SDC | PBCC@catalysts**)
- Nyquist plots of various Spinel-based catalysts coated on bare air electrode in wet air at 600 °C

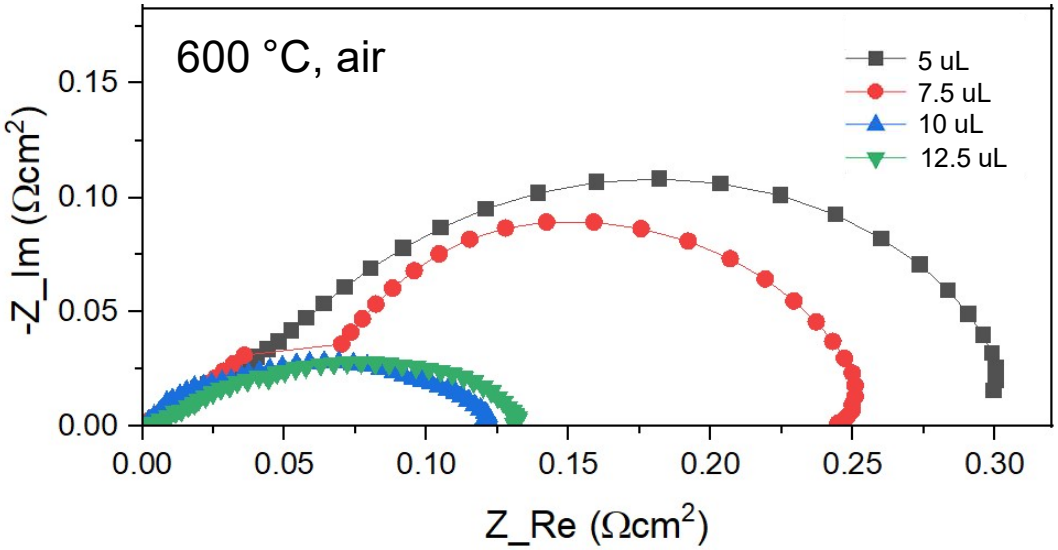


Spinel-Catalysts	R_p (Ω-cm²)	Performance Enhancement (%)
Bare	0.1584	-
$CuCo_2O_4$	0.1882	-19
$NiFe_2O_4$	0.1949	-23
$NiFeCoO_4$	0.3076	-95
$MgCo_2O_4$	0.2734	-28
$NiCo_2O_4$	**0.1474**	**7**
$FeCo_2O_4$	**0.1112**	**30**
$ZnCo_2O_4$	**0.0968**	**38**

➢ Spinel-based $NiCo_2O_4$, $FeCo_2O_4$, and $ZnCo_2O_4$ catalysts showed good catalytic performances

Optimization of Amount of Catalysts

- Symmetric cell configurations (PBCC@$NiCo_2O_4$ | **SDC** | PBCC@$NiCo_2O_4$)
- Nyquist plots of $NiCo_2O_4$ catalysts as function of various amount of nitrate solution at 600 °C

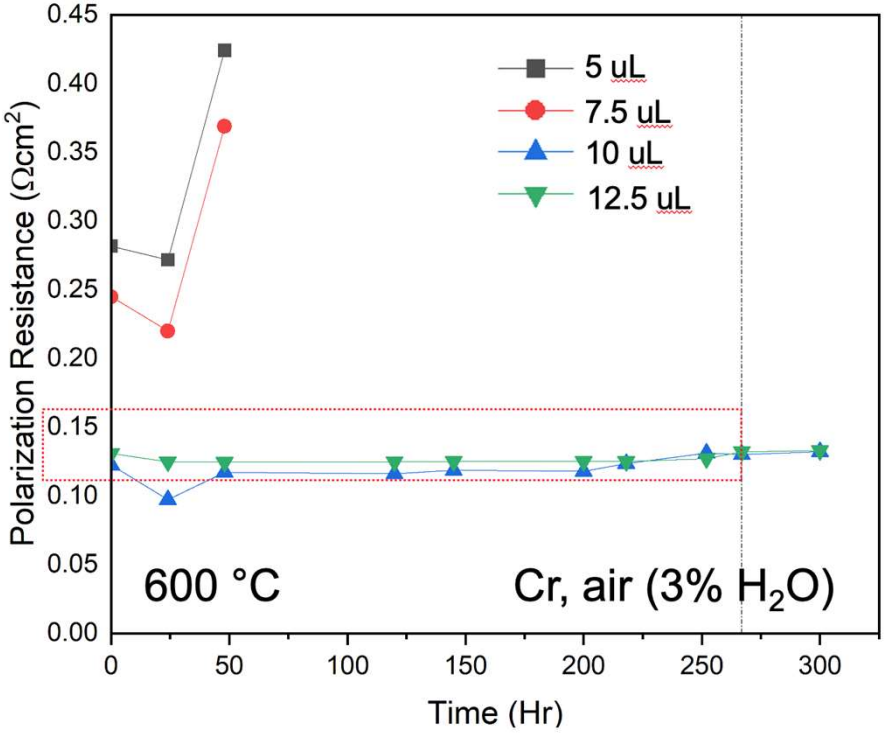


Amount of Infiltrate (uL)	R_p (Ω-cm²)
5	0.29974
7.5	0.24486
10	0.1225
12.5	0.1309

- The effect of the amount of infiltration solution on the cell performance was investigated.
- The 10 uL of infiltration solution for $NiCo_2O_4$ catalysts showed the lowest electrode resistances.

Stability Against Cr (Spinel Catalysts)

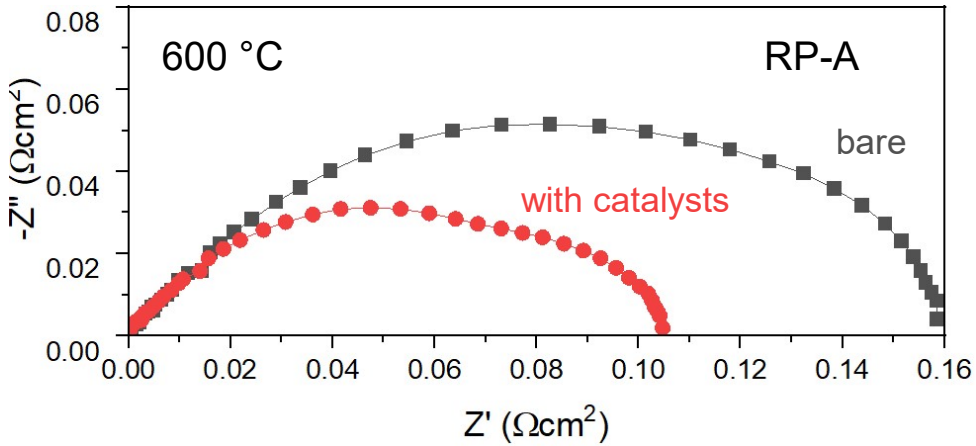
- Symmetric cell configurations (PBCC**@$NiCo_2O_4$ | SDC |** PBCC **@$NiCo_2O_4$**)
- ASRs of $NiCo_2O_4$ catalysts for long-term operation at 600 °C in the presence of Cr with 3% H_2O



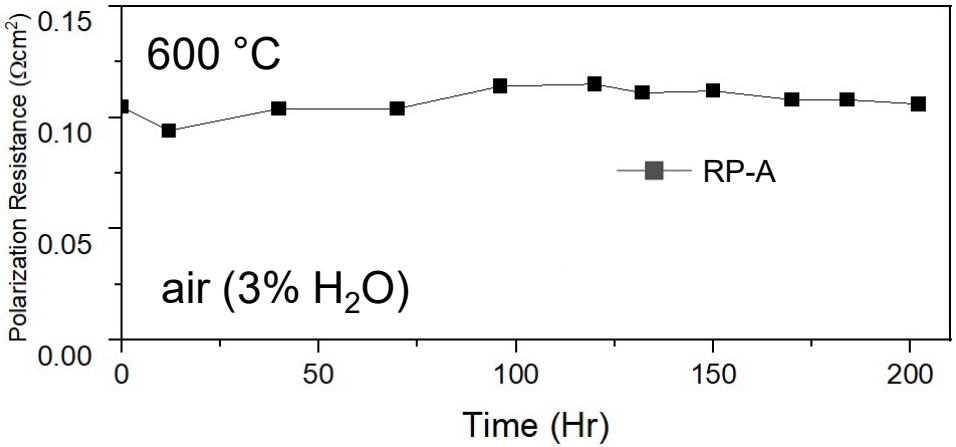
- Tested Bare@$NiCo_2O_4$ in the presence of Cr in 3% steam
- There were insufficient catalyst amounts for 5 and 7.5 µL of $NiCo_2O_4$
- The degradation rate was <0.5% for catalyst derived from 12 µL $NiCo_2O_4$.

Development of Ruddlsden-Popper(RP) Phase Catalysts

- Symmetric cell configurations (PBCC**@RP-A | SDC |** PBCC**@RP-A**)
- Nyquist plots of Ruddlsden-Popper phase catalysts in air at 600 °C
- ASRs of catalysts for operation in wet air (3% H_2O) at 600 °C



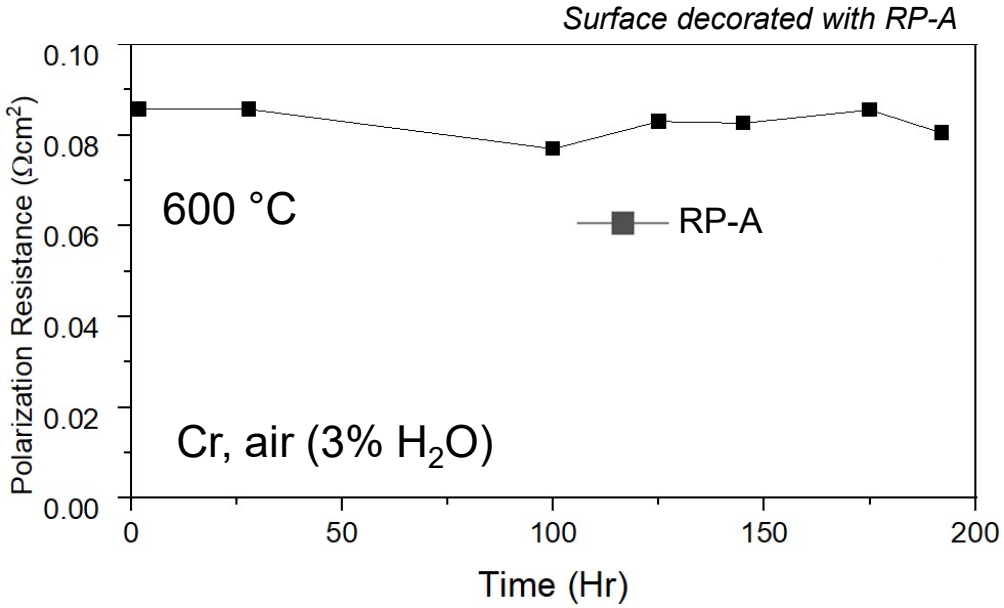
Surface decorated with RP-A



- The polarization resistance of RP-A catalysts was ~0.11 Ω · cm^2 at 600 °C.
- The degradation rate of RP-A catalysts was below 1% in wet air for 200 h operations.

Stability Against Cr (RP-A catalysts)

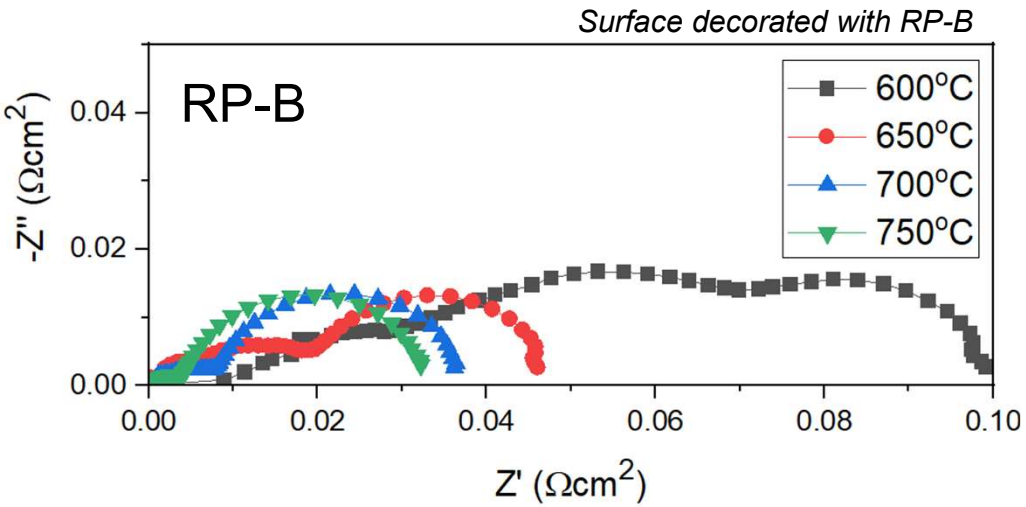
- Symmetric cell configurations (PBCC **@RP-A | SDC |** PBCC**@RP-A**)
- ASRs of catalysts for long-term operation at 600 °C in the presence of Cr with 3% steam concentration



➢ When exposed to Cr in 3% steam, the La_2NiO_4 catalyst showed no degradation in over 200 h operations.

Development of Ruddleden-Popper Catalysts

- Symmetric cell configurations (PBCC**@RP-B | SDC |** PBCC**@RP-B**)
- Nyquist plots of Ruddlsden-Popper phase catalysts in air at 600 °C
- ASRs of catalysts for long-term operation at 600 °C in wet air (3% H_2O)

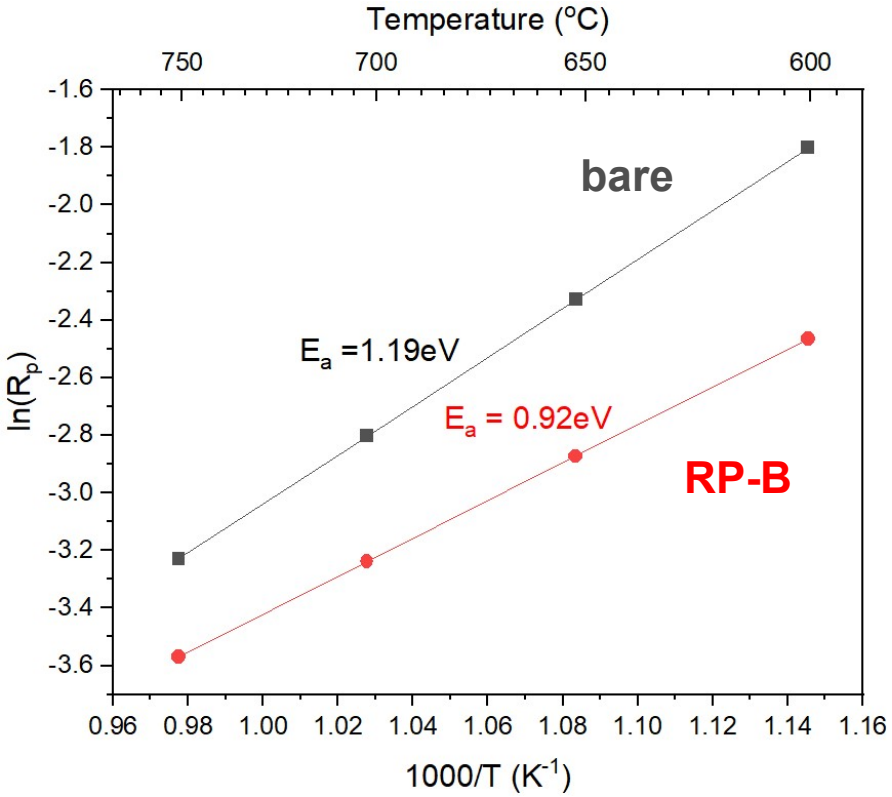


Temperature (°C)	Polarization Resistance (Ωcm$^{2)}$	
	Bare	Bare@RP-B
600	**0.170**	**0.0992**
650	0.0948	0.0460
700	0.0584	0.0362
750	0.0411	0.0322

➢ Surface coating RP-B reduces the polarization resistances of bare air electrodes (0.17 Ω-cm^2 → 0.09 Ω · cm^2 @600)

Electrochemical Performances of RP-B Catalysts

- Symmetric cell configurations (PBCC**@RP-B | SDC |** PBCC**@RP-B**)
- Arrhenius plots of PBCC and RP-B infiltrated PBCC samples



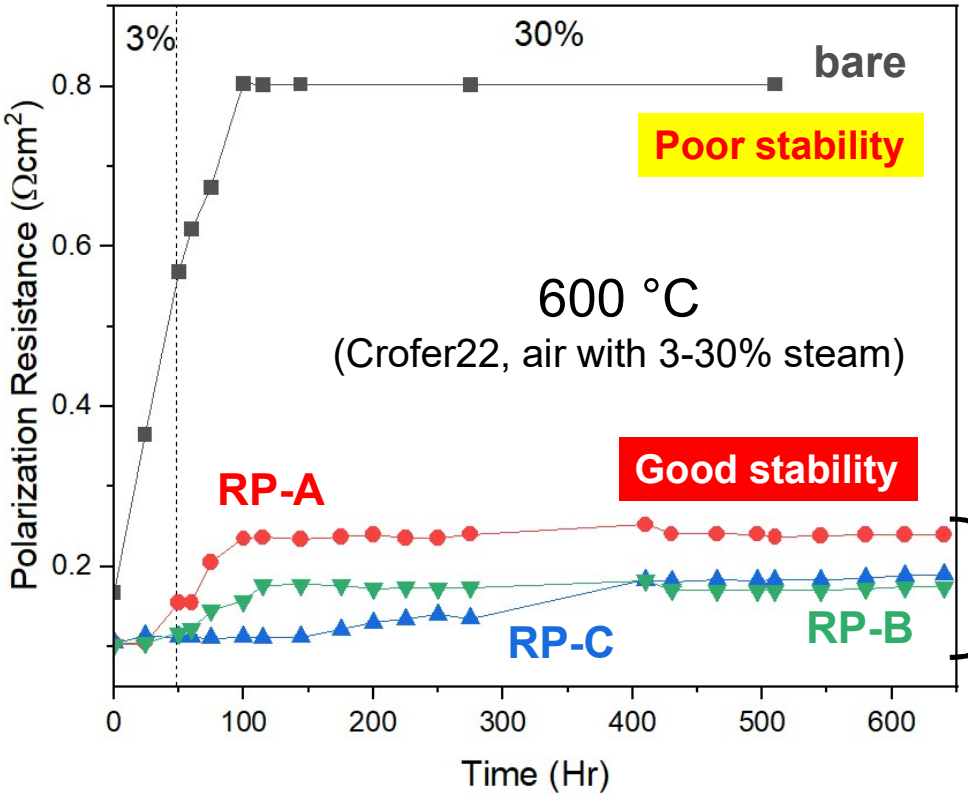
Surface decorated with RP-B

Materials	Activation Energy (eV)
Bare	1.19
Bare@RP-B	0.92

➢ Calculated activation energy of infiltrated cell and compared it with bare cell activation energy.

Stability Against Cr (RP-B catalysts)

- Symmetric cell configurations (PBCC**@RP-B | SDC |** PBCC**@RP-B**)
- ASRs of catalysts at 600 °C in the presence of Cr with 3 to 30% steam concentrations

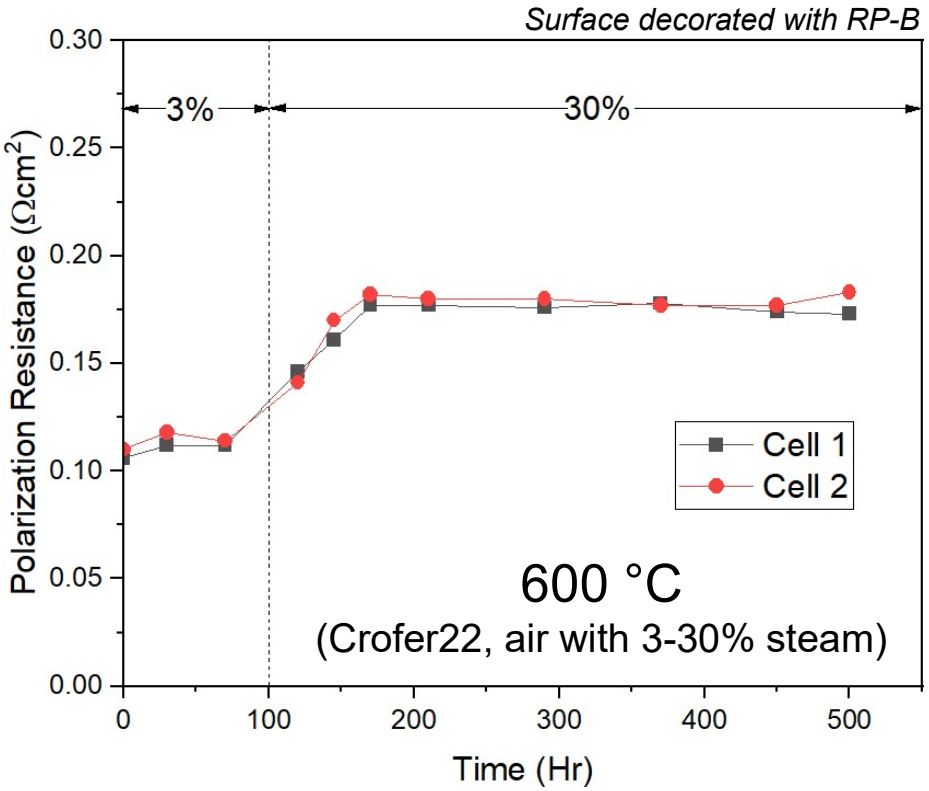


- RP-A catalysts show expected behavior – rapid degradation in 30% steam before stabilizing around ~0.25 Ω-cm^2.
- RP-C initially showed good performance, but the stability is poor.
- RP-B showed the best electrochemical performance and stability when exposed to Cr in 30% steam.

Surface decorated with RP catalysts

Reproducibility of Cr-tolerance (RP-B catalysts)

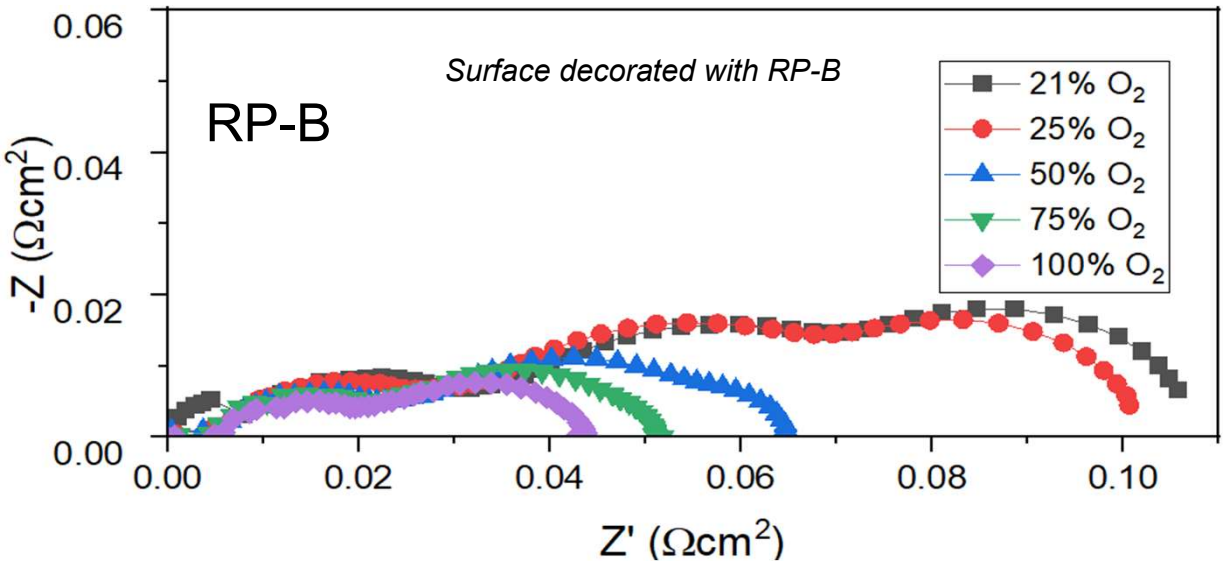
- Symmetric cell configurations: PBCC**@RP-B | SDC |** PBCC**@RP-B**
- ASRs of catalyst-coated PBCC exposed to Cr in 3 to 30% steam at 600 °C



- The R_p values for the two cells are relatively close, indicating good reproducibility.
- The stability test is still on-going to complete 500 h test in 30% steam, indicating the RP-B catalyst enhanced the tolerance to Cr poisoning.

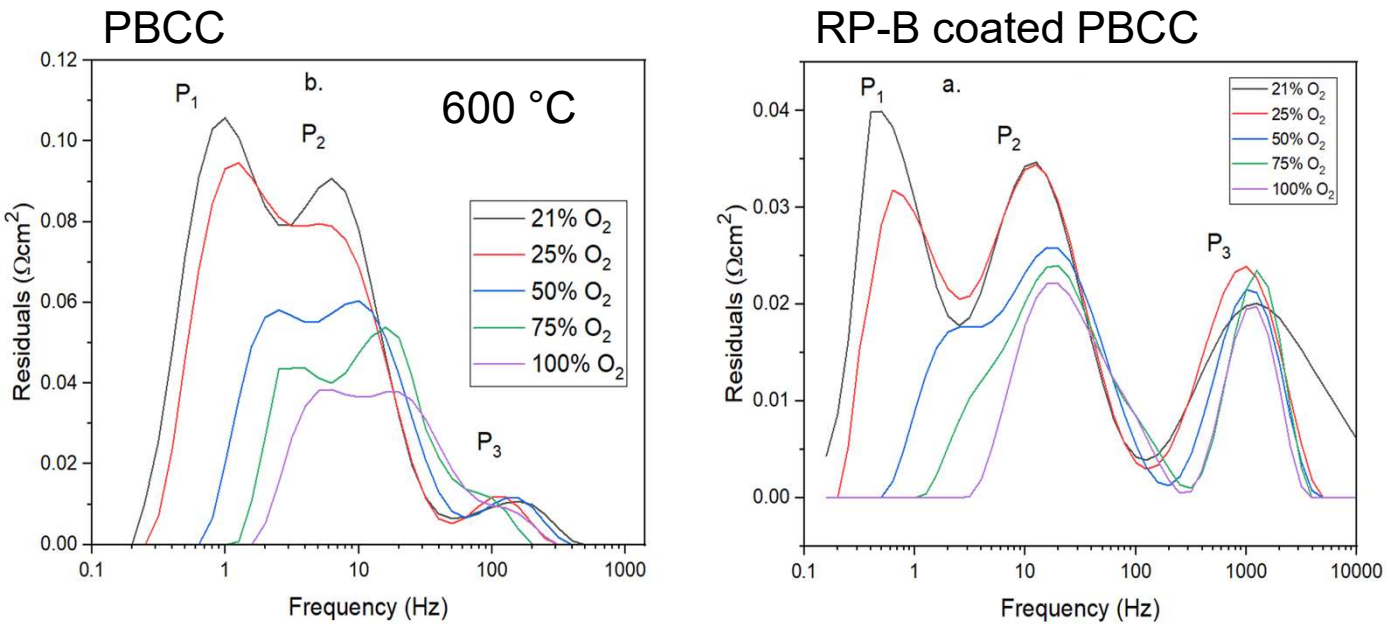
pO_2-dependence ASRs (RP-B catalysts)

Symmetric cell configurations: PBCC**@RP-B | SDC |** PBCC**@RP-B**
Dependence of polarization resistance R_p on oxygen partial pressure pO_2



pO_2	Polarization Resistance (Ωcm^2)	
	Bare	PBCC@RP-B
21%	0.1601	0.106
25%	0.140	0.101
50%	0.0881	0.0648
75%	0.0697	0.0517
100%	0.0522	0.0428

pO_2-dependence of Impedance Spectra



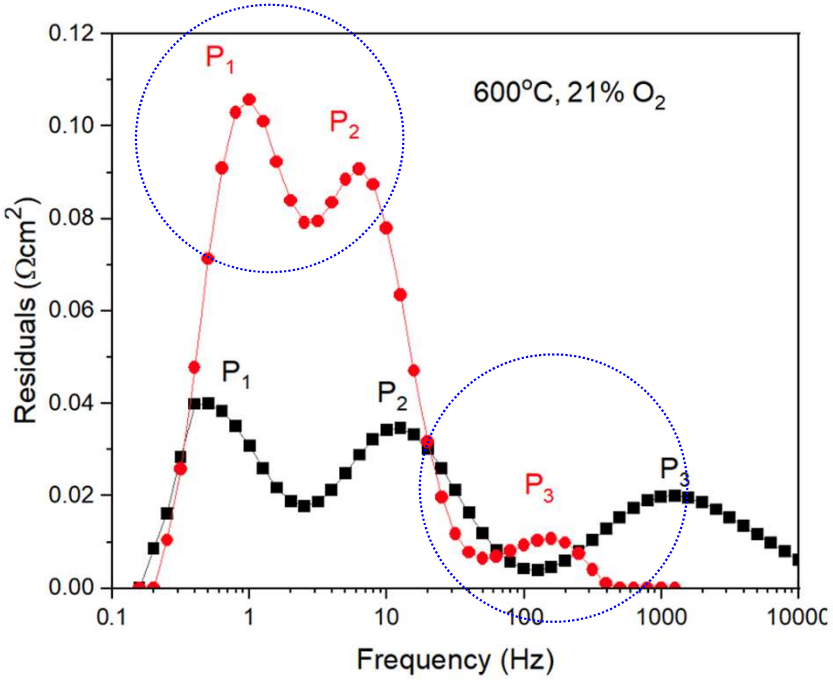
- The impedance for P1 and P2 are greatly reduced with pO_2.
- The impedance for P3 is relatively independent of pO_2.

Correlation between Impedance and pO_2

$$\mathrm{ASR} = k(pO_2)^{-n}$$

Peak	Slope		Process	Ref
	Bare			
P_1	0.805	0.92	diffusion & Mass transfer	[1][2][3][4]
P_2	0.492	0.303	Dissociative adsorption & Oxygen reduction	[2][3][4]
P_3	0.029	0.023	Oxide ion incorporation into electrolyte	[2][3][4][5]

1. *International Journal of Hydrogen Energy* 46.58 (2021): 30101-30111
2. *Journal of Power Sources* 283 (2015): 464-477.
3. *J. Electrochem. Soc.* **148** A433
4. *Journal of Materials Chemistry A* 10.16 (2022): 8798-8806.
5. J. Electrochem. Soc. 143 3554



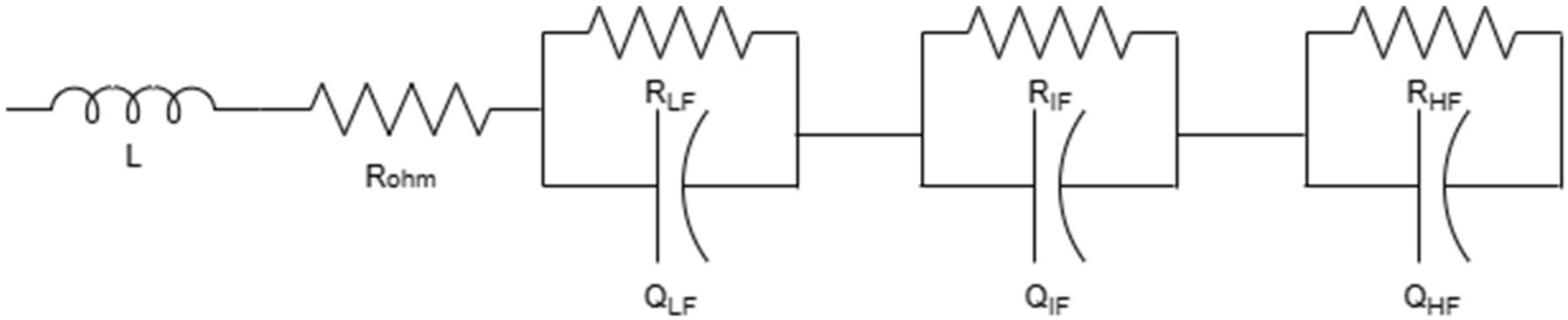
P1: corresponding likely to **mass transfer**

P2: dissociative adsorption & reduction of O_2

P3: transfer of oxide ions across interface

Proposed Equivalent Circuit Model

- The individual steps of the electrode processes



Series inductor – represents high frequency inductance of the cell or lead wire

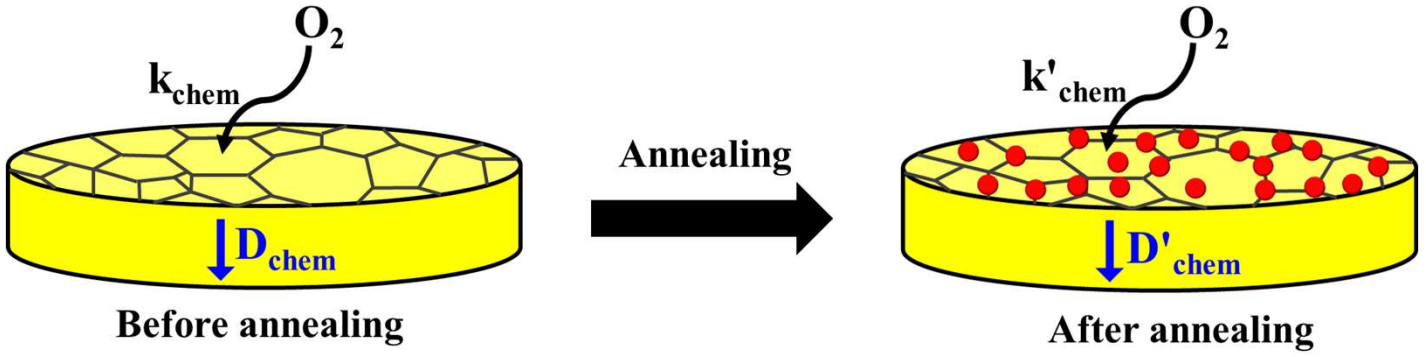
Series resistor – ohmic resistance of the electrolyte

RLF & QLF – mass transfer process

RIF & QIF – reduction process

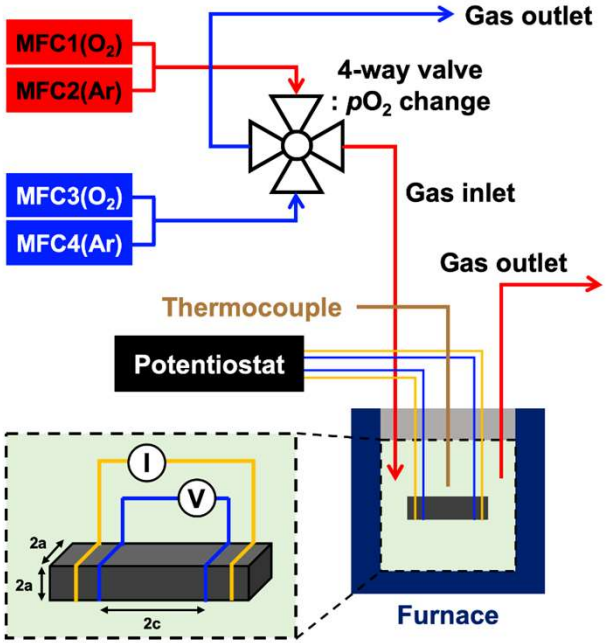
RHF & QHF – interfacial charge transfer process

Characterization of Catalytic/Transport Properties

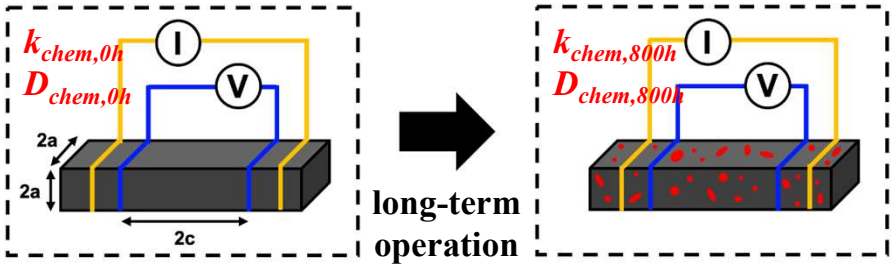


- Surface exchange coefficient (k_{chem}) and diffusion coefficient (D_{chem}) were estimated from electrical conductivity relaxation (ECR) measurement.
- Surface chemistry from Raman spectroscopy

Electrical Conductivity Relaxation (ECR) Measurement



ECR measurement system



Initial state (0h) **Final state**

- Normalized conductivities need to be fitted by **Crank Equations**

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

$$=1-\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\sum_{l=1}^{\infty}\frac{2L^2\exp(-\beta_n^2 D_{chem}t/a^2)}{\beta_n^2(\beta_n^2+L_a^2+L_a)}\times\frac{2L^2\exp(-\beta_m^2 D_{chem}t/b^2)}{\beta_m^2(\beta_m^2+L_b^2+L_b)}\times\frac{2L^2\exp(-\beta_l^2 D_{chem}t/c^2)}{\beta_l^2(\beta_l^2+L_c^2+L_c)}$$

If c>>a, (Sample dimension: 2a*2a X 2c)
Diffusion along c can be neglected and conductivity is expressed:

$$\frac{\sigma(t)-\sigma(0)}{\sigma(\infty)-\sigma(0)}=1-\left[\sum_{n=1}^{\infty}\frac{2L^2\exp\left\{-\frac{\beta_n^2 D_{chem}(t-t_0)}{a^2}\right\}}{\beta_n^2(\beta_n^2+L^2+L)}\right]^2$$

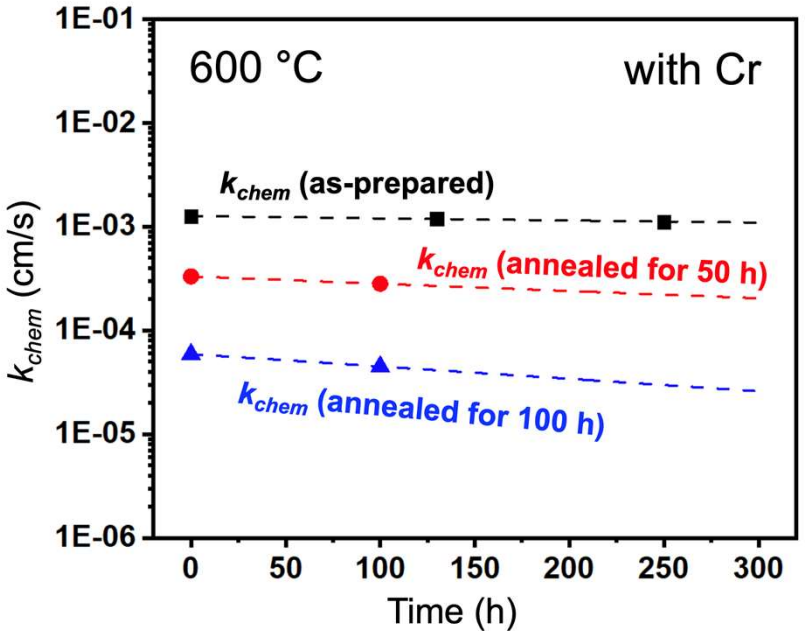
Where β_ns are positive roots of $L=\beta_n\tan\beta_n$ and $L=a\cdot\frac{k_{chem}}{D_{chem}}$

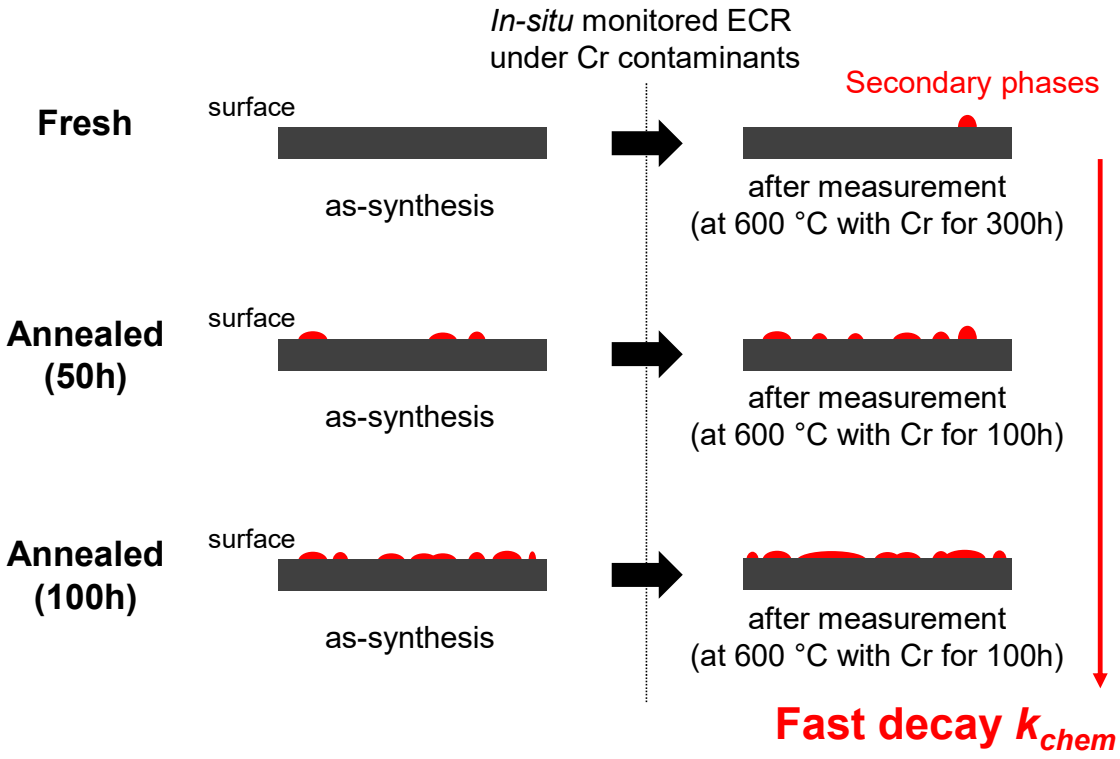
Crank Equation fitting

J. Crank, *The Mathematics of Diffusion, 2nd ed.*, Clarendon Press, Oxford, UK, 1975, p. 60

Characterization of Electrode Degradation (Cr)

For the bare electrode without catalyst





- K_{chem} decreased with steam concentration and the length of exposure, suggesting an acceleration of degradation with time in higher concentration of steam.

Summary

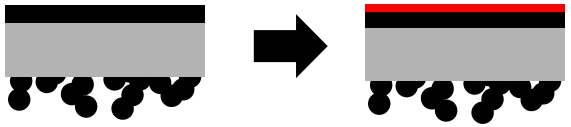
- ✓ Developed highly active and durable ***catalysts*** against high concentration of steam and Cr poisoning
  - → Reduced electrode resistance by ~50%
  - → Minimal degradation over 500 h against 30% H_2O with Cr
- ✓ Characterized ***electrode kinetics*** of surface-decorated electrodes
  - → Surface exchange coefficients and diffusivity estimated from ECR
  - → Deduced possible reaction steps and mechanism from DRT, impedance analyses
- ✓ *in-situ* monitored oxygen transport kinetics under Cr contaminants
  - → High steam concentration appears to be an important factor that influences the rate of electrode degradation
- ✓ Designed and fabricated ***model cells*** for mechanistic studies
  - → A platform for direct correlation between macroscopic features and electrochemical performance

Future Work

A platform for surface characterization

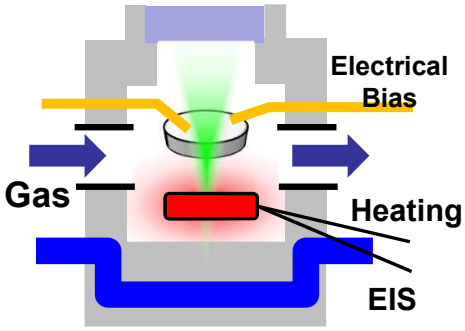
Bare

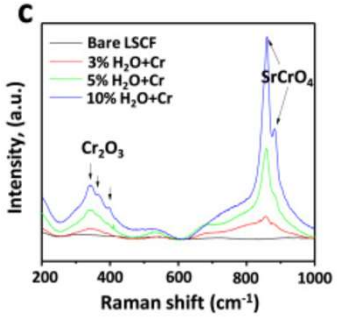
surface-decorated



Fabrication of catalysts-coated model cells

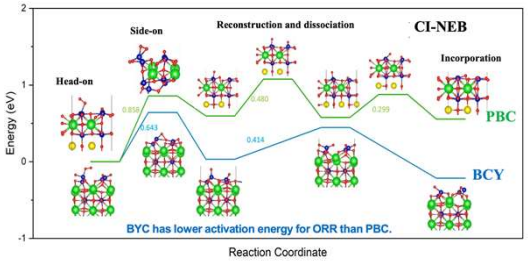
In-situ/ex-situ Raman analysis





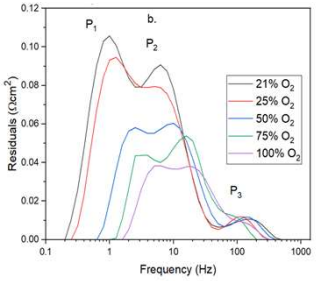
Investigation of surface species and incipient phases

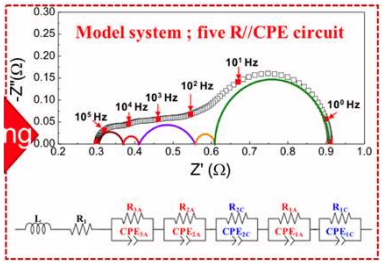
DFT calculations



Searching for suitable material candidates

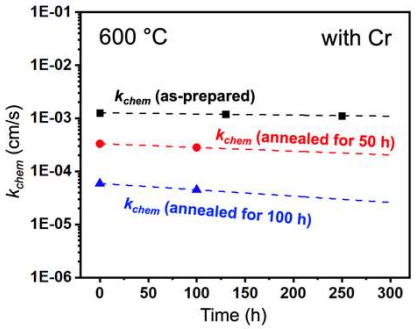
Electrochemical Characterizations





In-depth characterization of electrode mechanisms

Surface Kinetic Properties



Investigation of surface kinetics

Future Work

Date	Brief Description	%Complete
06/30/23	Complete in situ and ex situ characterization of surface morphology and surface species using experimental and modeling work to determine the activity and stability of the cells as a function of contaminant presence, relevant operating conditions, and catalyst content.	**70**
09/30/23	Complete the fabrication of button cells with a current density of >1.8 A cm^{-2} at 1.3 V in electrolysis mode at 600 °C and ≥75% roundtrip efficiency in both SOFC and SOEC modes at ≤ 650 °C.	**30**
12/31/23	Complete the long-term durability evaluation of button cells for at least 500 h with a degradation rate of <0.5% per 1,000 h.	**5**

End of Project Goal:	Demonstrate a current density of >1.8 A cm^{-2} at 1.3 V in electrolysis mode at 600 °C and ≥75% roundtrip efficiency in both SOFC and SOEC modes at ≤ 650 °C. Complete >500-h operation with a degradation rate of <0.5% per 1,000 h.	FY23

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and other DOE management team members

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Award No. FE0032115

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