23rd Annual SOFC/SOEC Project Review Meeting

Reactivation of Chromia Poisoned SOFC Cathodes by Controlled Surface Acidity

Han Gil Seo, Anna Staerz, Clement Nicollet, Dino Klotz, Dennis Kim, James LeBeau, **Harry L. Tuller**

Department of Materials Science and Engineering

Massachusetts Institute of Technology (MIT)

DE-FOA-0001853 - Dr. Debalina Dasgupta

Day 1 – October 25, 2022, Pittsburgh

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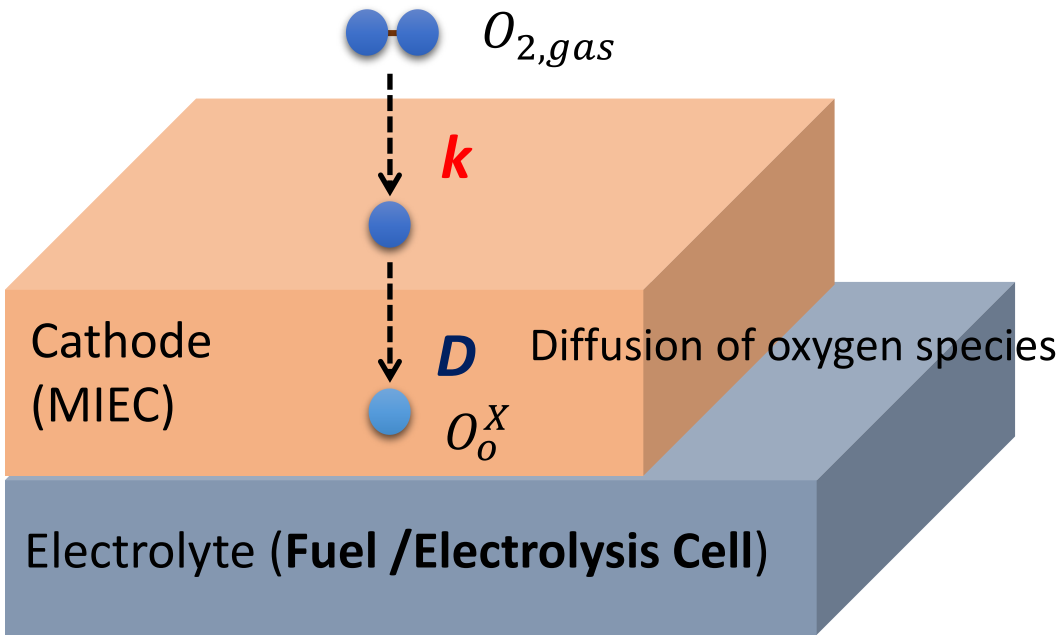
Surface Oxygen Exchange Kinetics in Mixed Conducting Oxides

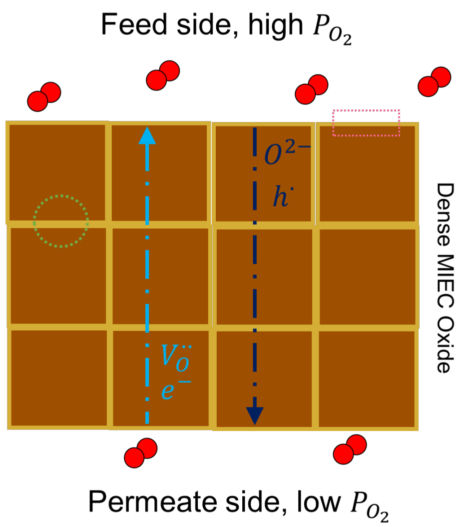
$$1/2\, O_2 + V_O^{\cdot\cdot} + 2e^- \leftrightarrow O_O^X$$

k – Surface exchange reaction coefficient

$$j_O = -k_O(C_{O,\text{atmosphere}} - C_{O,surface})$$

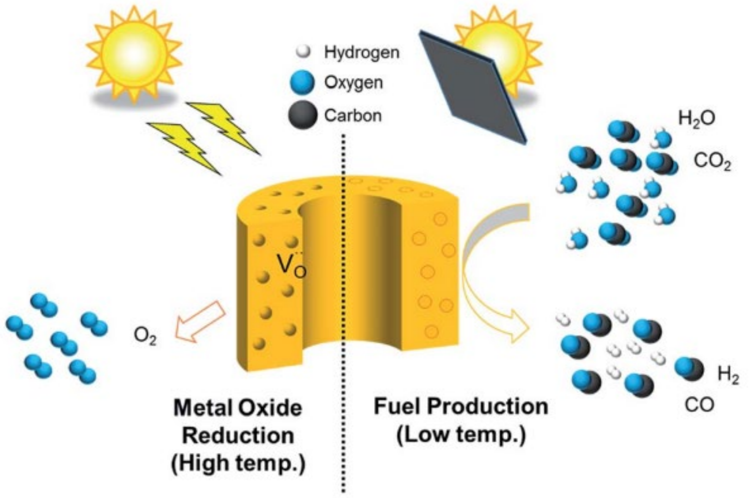


Oxygen permeation membrane



*Staerz et al., J. Mater. Chem. A, **2022**, 10, 2618–2636*

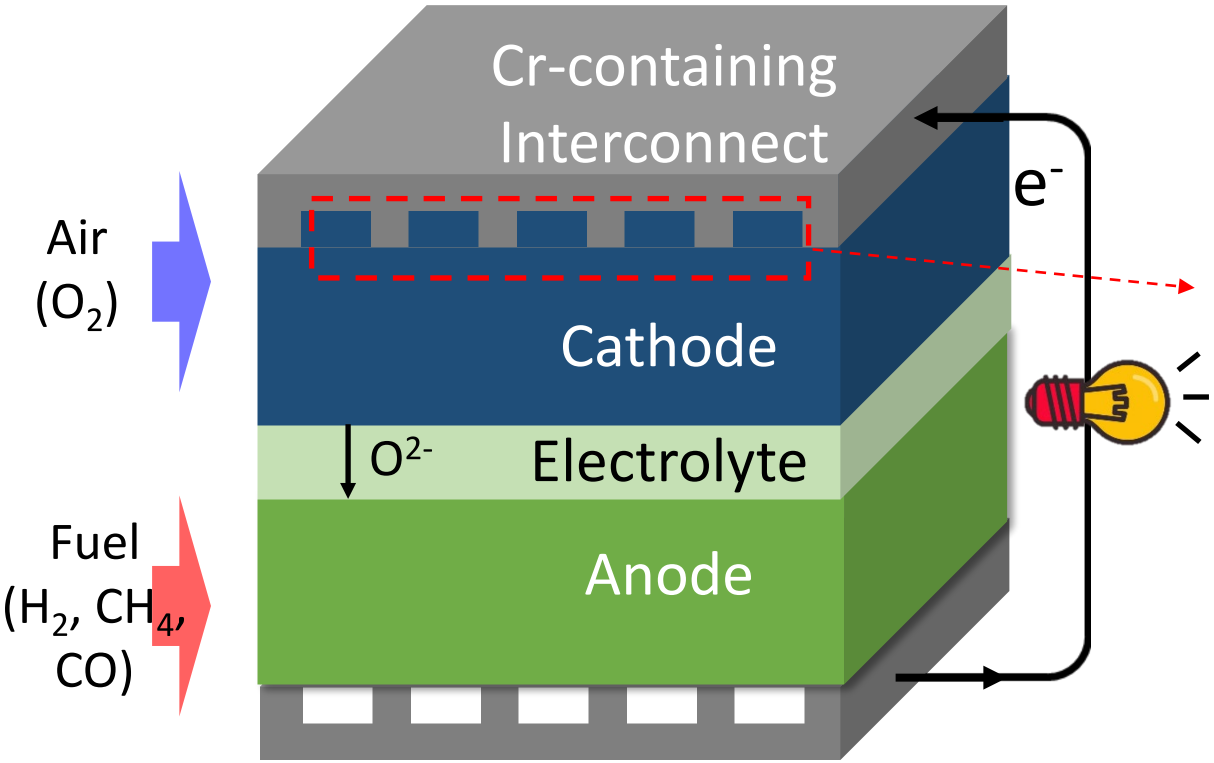
Solar thermochemical reaction

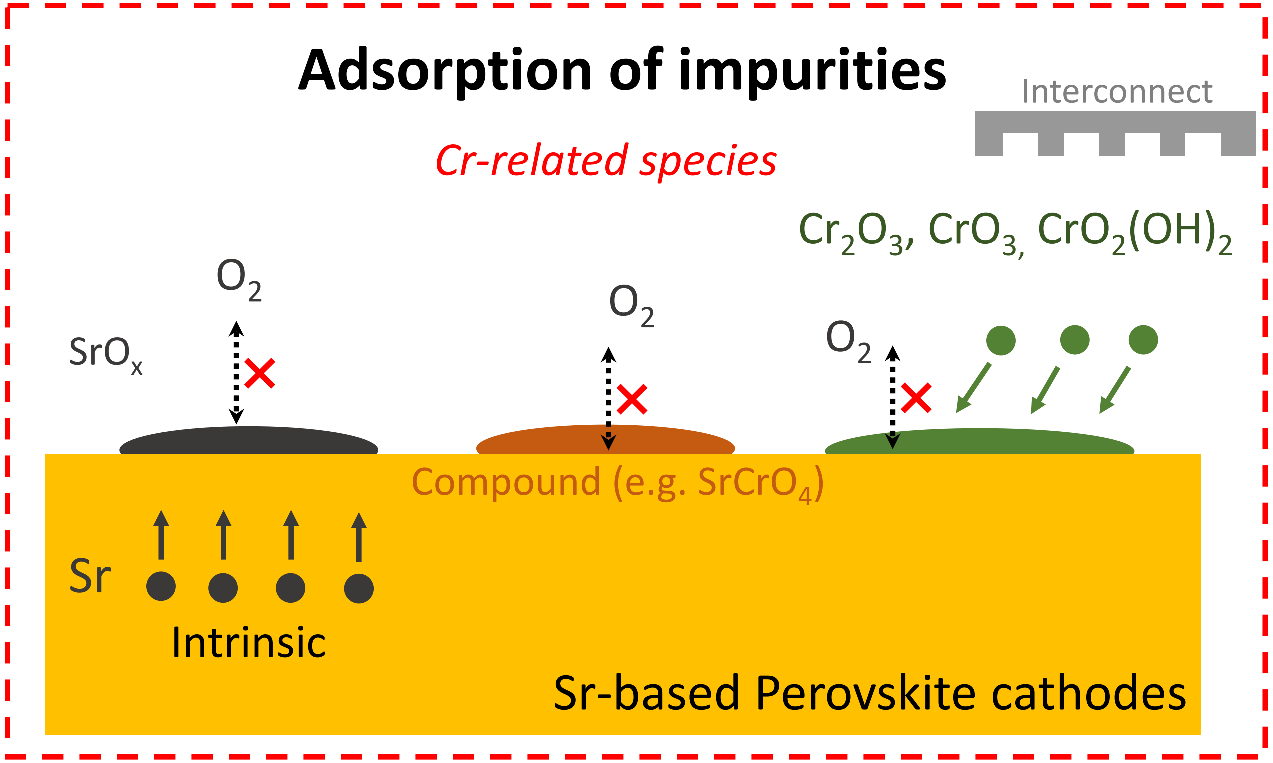


*Kim et al., J. Mater. Chem. A, **2018**, 6, 13082–13089*

Oxygen exchange kinetics are key to many energy-related technologies!

Solid Oxide Fuel Cells (SOFCs) and Cr-poisoning





Jung et al., Energy Environ. Sci., ***2012****, 5, 5370–5378.,*
Chen et al., Faraday Discuss., ***2015****, 182, 457-476*

- Cr-containing interconnects
- Chemical degradation by Cr-impurities

To date, the main source of Cr-induced degradation remains controversial.

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DOE Targets on SOFCs

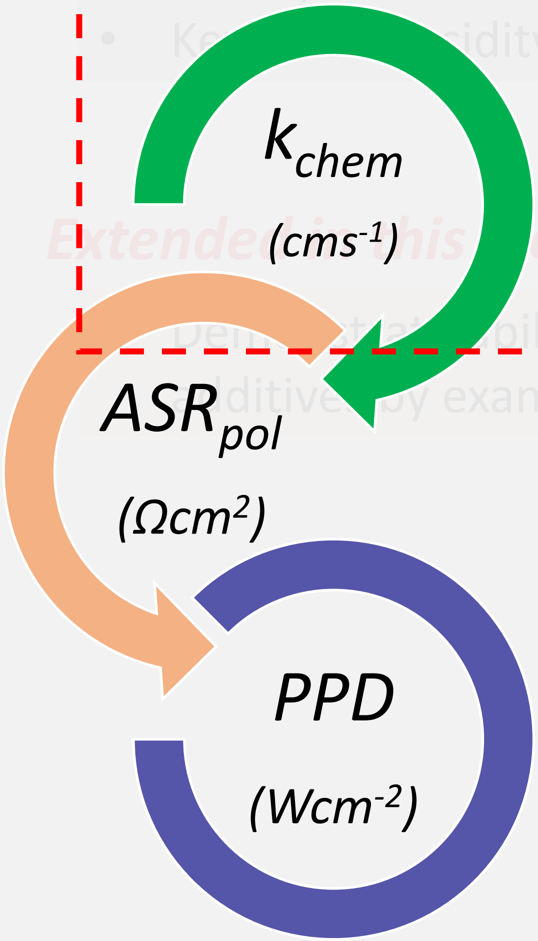
Metric	Current	2020 Target	2025/2030 Target
System Cost (100 kW- 1MW)	>$12,000/kWe	$6,000/kWe	$900/kWe
Single Cell Degradation	0.2 - 0.5% per 1,000 hrs		
Cell Manufacturing Approach	Batch	Semi- Continuous	Continuous
System Degradation	1 – 1.5% per 1,000 hrs	0.5 - 1.0% per 1,000 hrs	<0.2% per 1,000 hrs
Fuel Reformation	Primarily external natural gas conditioning/reforming	100% integrated natural gas reformation inside cell stack	[illegible]
Durability	[illegible]	[illegible]	[illegible]
Platform	[illegible]	[illegible]	DG: Commercial [illegible]
Configuration	Breadboard/Integrated systems	Fully packaged	Fully packaged
Fuel	Natural gas	Natural gas Simulated syngas	Natural gas Coal-derived syngas
Demonstration Scale	50 kWe – 200 kWe	200 kWe – 1 MWe	DG: MWe-class Utility-scale: 10 – 50 MWe

If not resolved, high degradation rates are potentially show stoppers for SOFC technology to be broadly *accepted*

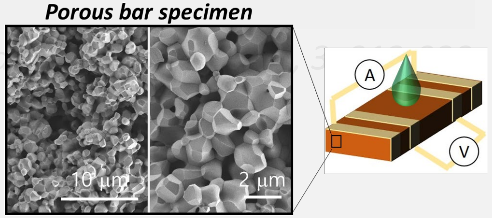
Table: Dr. Shailesh Vora, "U.S. DOE Office of Fossil Energy Solid Oxide Fuel Cell (SOFC) Program", 2019 Fuel Cell Seminar and Exposition

Outline

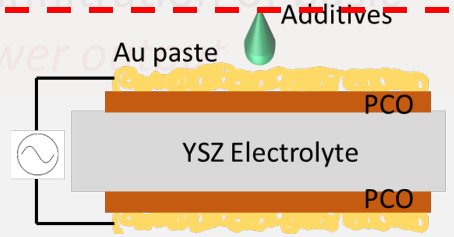
Approach



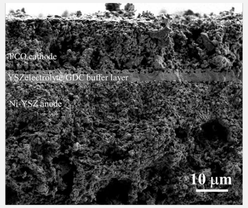
- Conductivity relaxation measurements (ECR)
- *Porous bar*

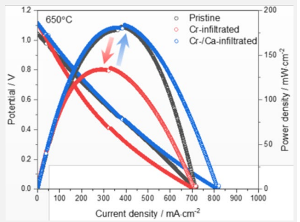


- Electrochemical impedance spectroscopy (EIS)
- *Distribution of relaxation time (DRT)*
- *Screen-printed symmetric cells*

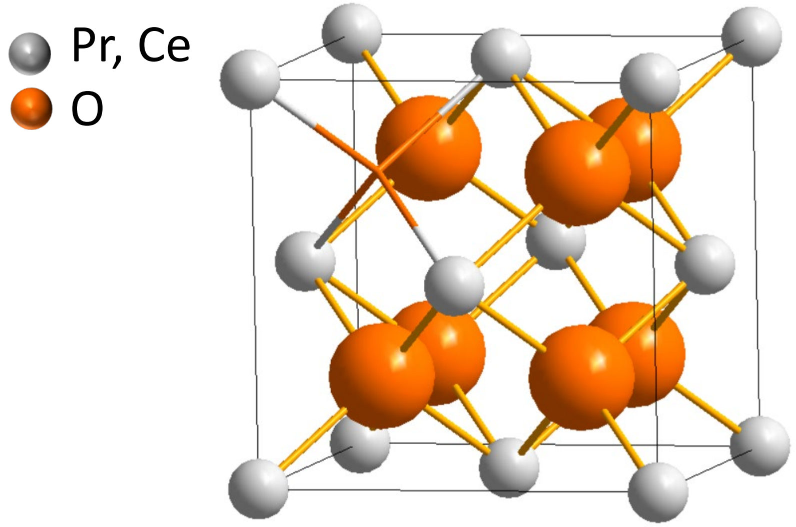


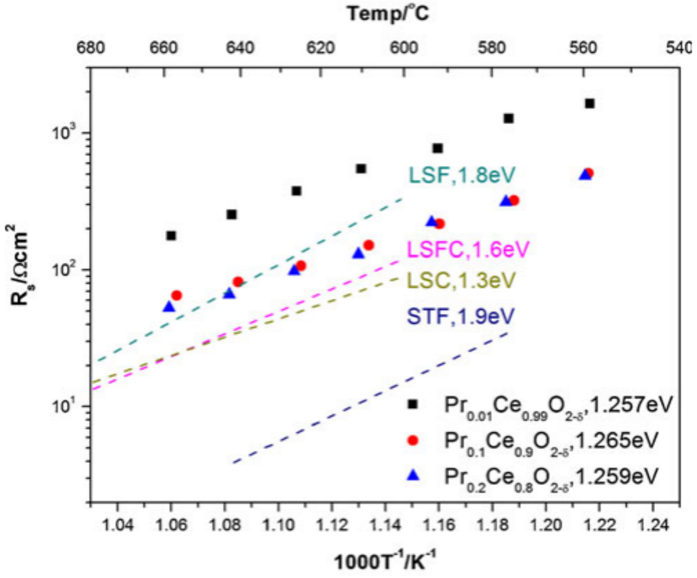
- Current-Voltage-Power curves (I-V-P)
- *Anode-supported single cells*





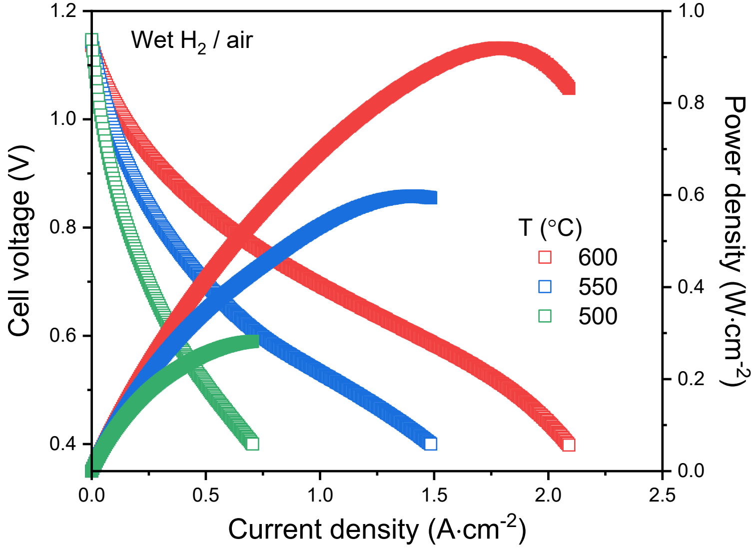
Model Pr-doped CeO_2, $Pr_xCe_{1-x}O_{2-\delta}$ (PCO)





Chen et al., J. Electroceram., **2012**, 28, 62-69.

0.92 Wcm^{-2} @600°C



H.G. Seo *et al., Adv. Energy Mater.* ***2022***

- *Fluorite structure*
- *High oxygen reduction reaction (ORR) activity*
- *Mixed ionic and electronic conductivity in air*
- *Compatible with ceria-based solid electrolytes*
- *Free of Sr segregation in typical SOFC cathodes*

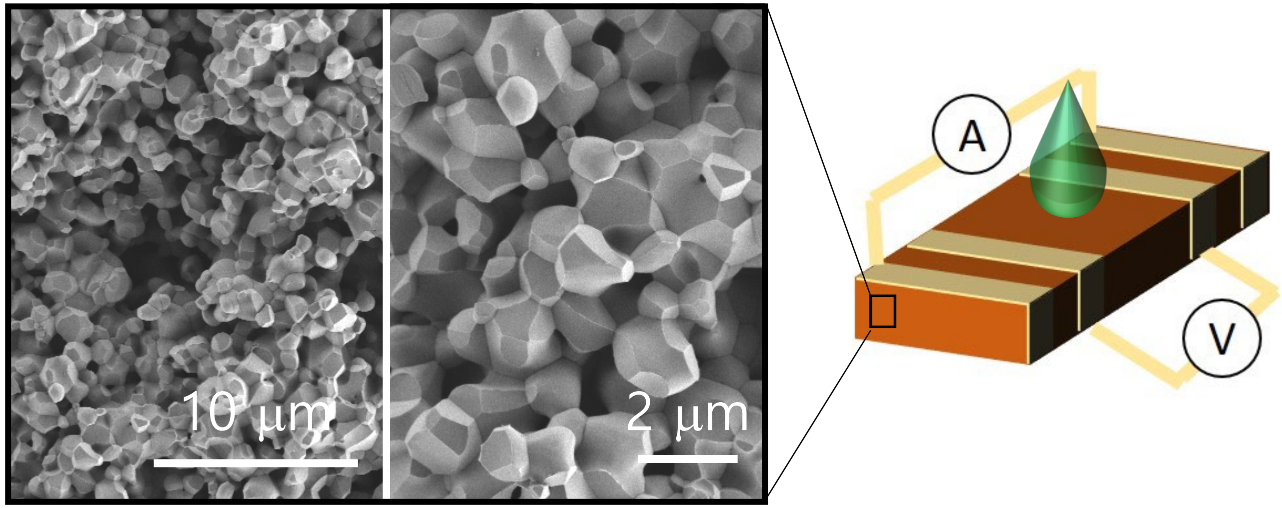
Possible to isolate cause of degradation by ***extrinsic impurities.***

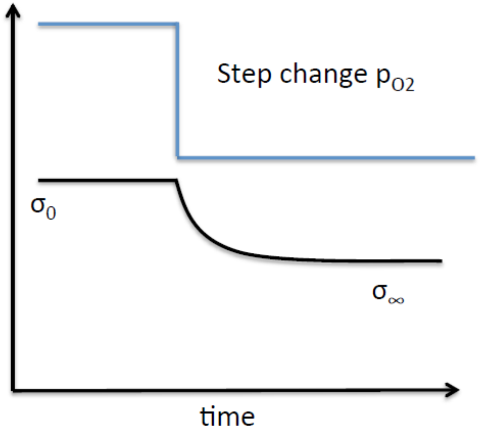
Bishop et al., J. Mater. Res., ***2012****, 27, 2009.,*
Bishop et al., Phys. Chem. Chem. Phys., ***2011****, 13, 10165-10173,*

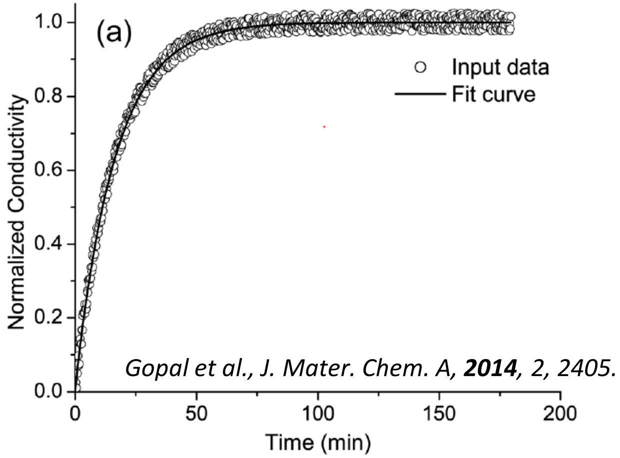
Conductivity Relaxation Measurements: Porous Bars

Monitoring bulk conductivity upon abrupt change in surrounding environment
→ Measure D (chemical diffusion coefficient) and k (oxygen exchange coefficient)

Porous bar specimen







Gopal et al., J. Mater. Chem. A, ***2014****, 2, 2405.*

- ~1 μm grain size: much shorter than critical thickness *(Surface reaction limited process → k)*
- *Allow for liquid infiltration protocol*
- Temperature: 250 °C – 600 °C
- *p*O_2 step: 0.1 ↔ 0.2 atm

$$g(t) = \frac{\sigma(t)-\sigma_0}{\sigma_\infty-\sigma_0} = 1 - exp(-\frac{t}{\boldsymbol{\tau}})$$

$$= 1 - ex\,p\left(-\boldsymbol{k_{chem}}\frac{A}{V}t\right)$$

$\boldsymbol{\tau}$*: time constant*
$\sigma(t), \sigma_0, and\ \sigma_\infty$: conductivity at time t,0, infinite
A/V: geometric factor (surface area to volume ratio)

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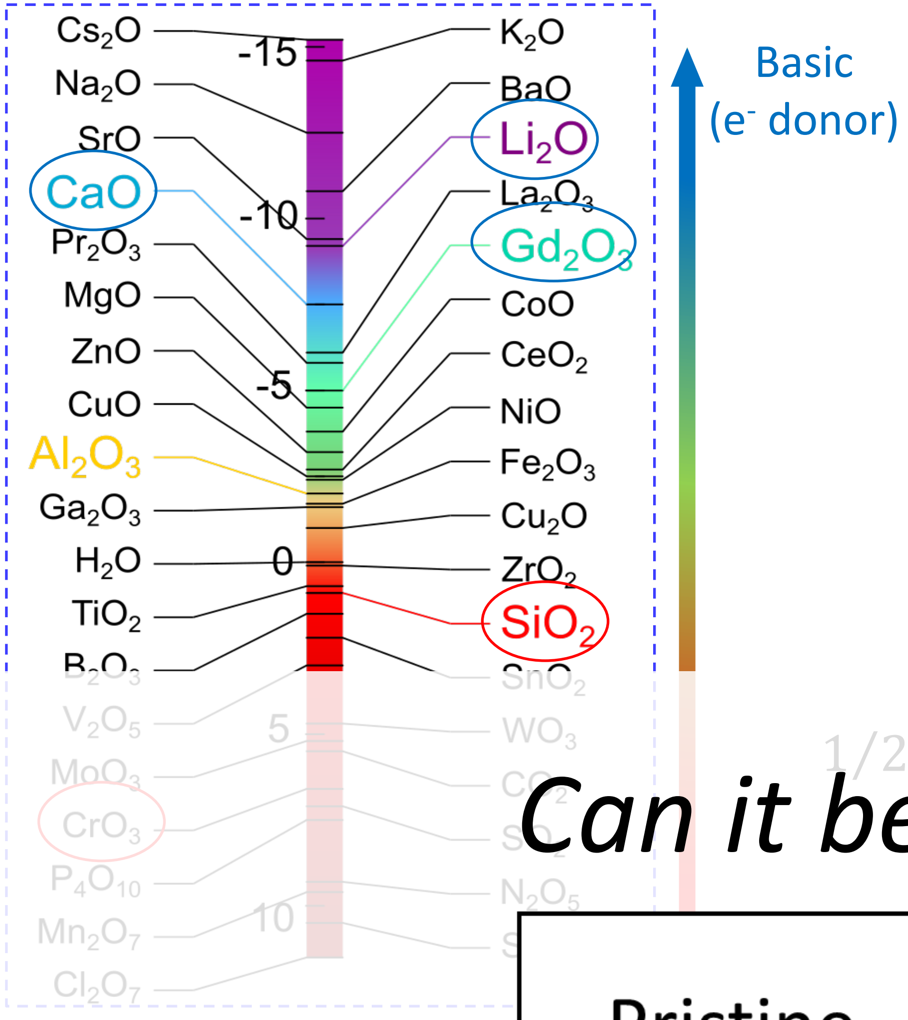
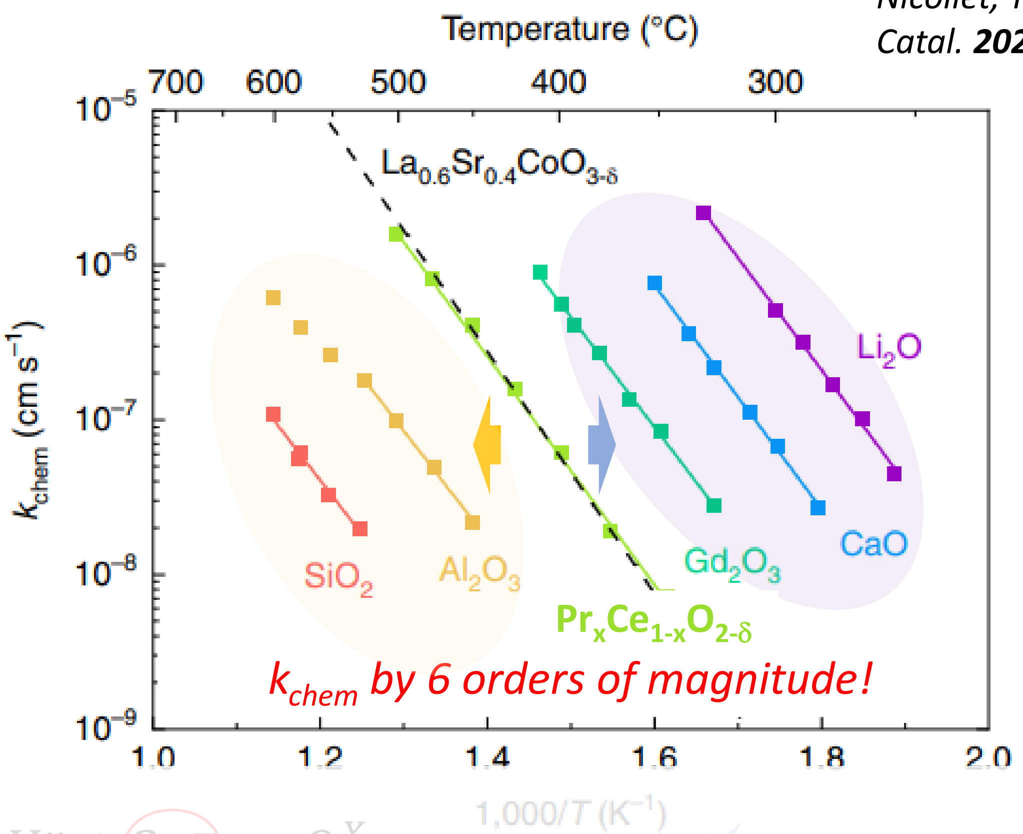
Identified Descriptor: Acidity of Surface Additives

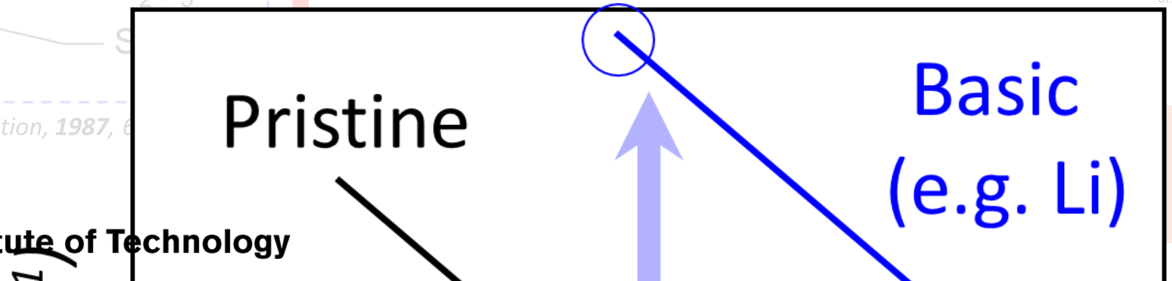
Nicollet, Tuller, et al., Nat. Catal. ***2020****, 3, 913-920*

Acidity scale for binary oxides





Can it be reactivated ?



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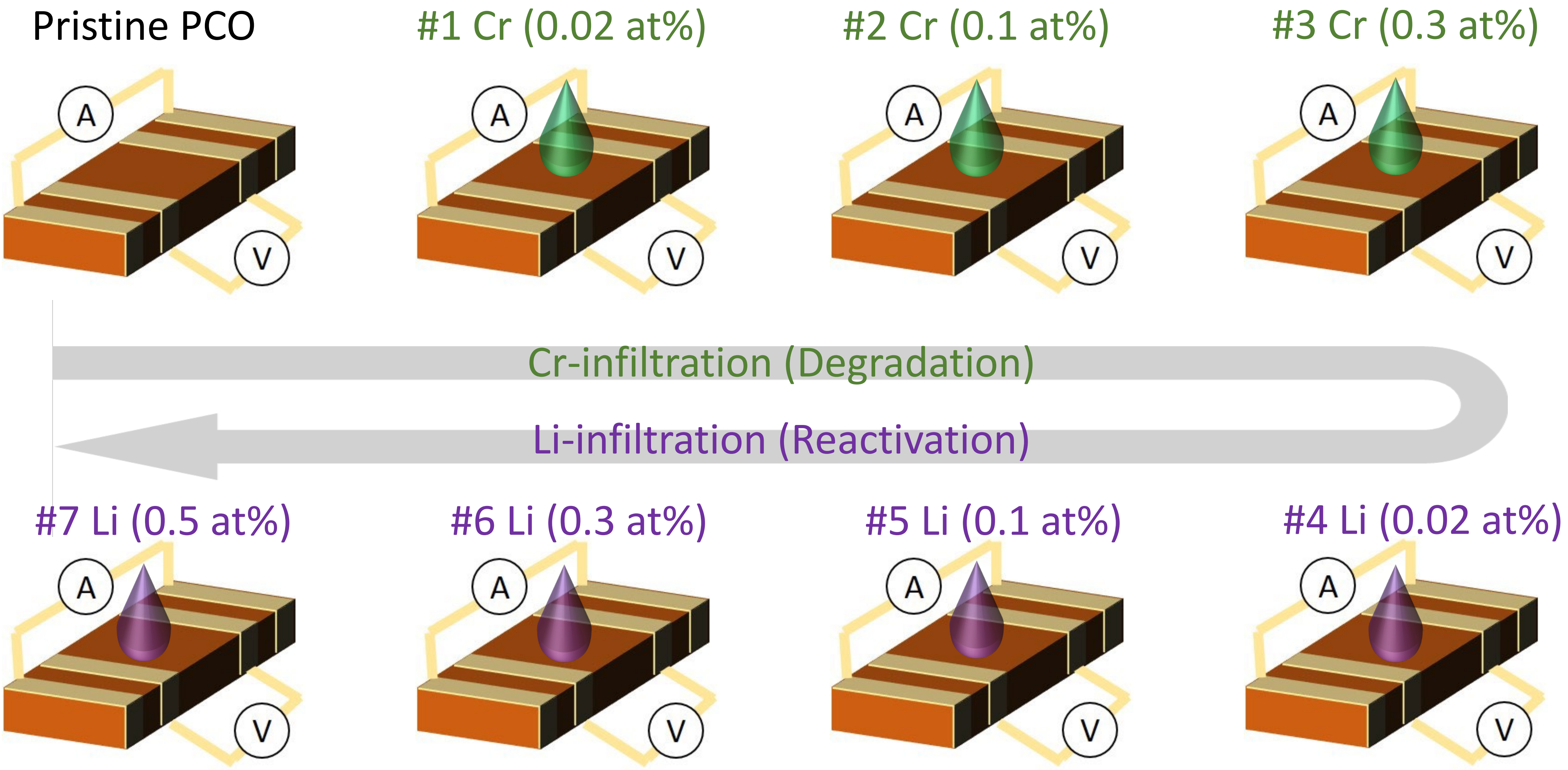
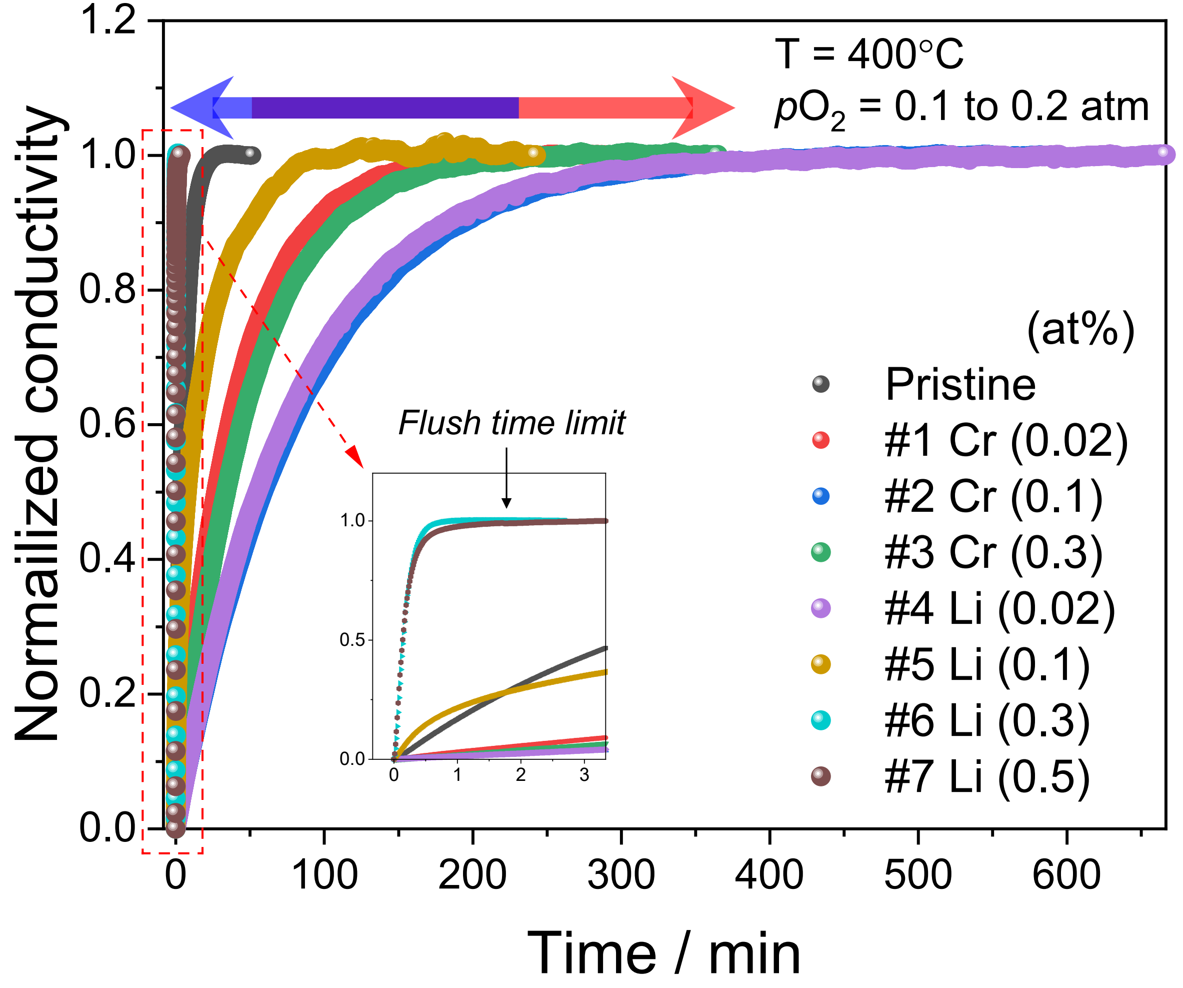
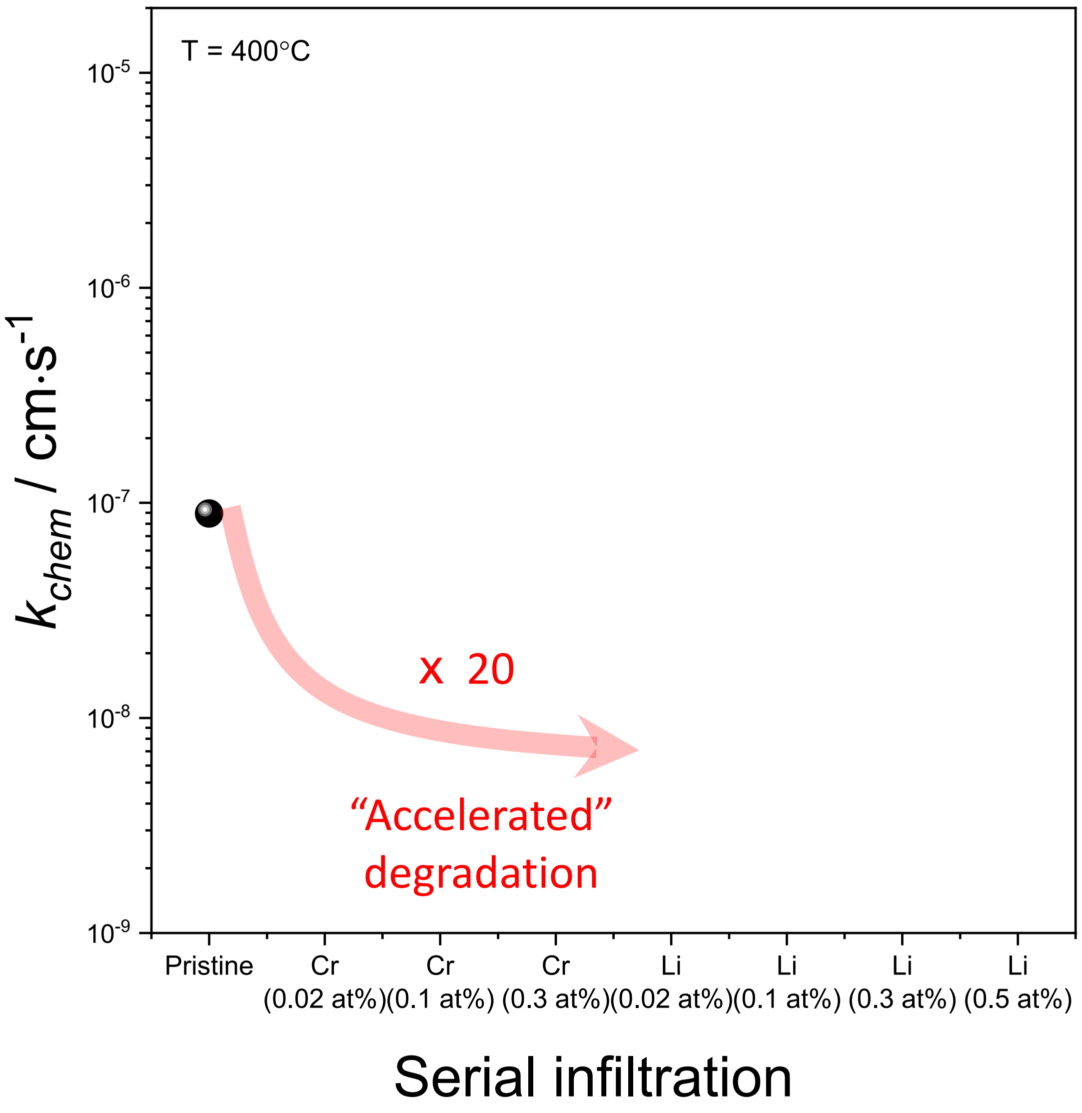
Sequence of Conductivity Relaxation Measurements



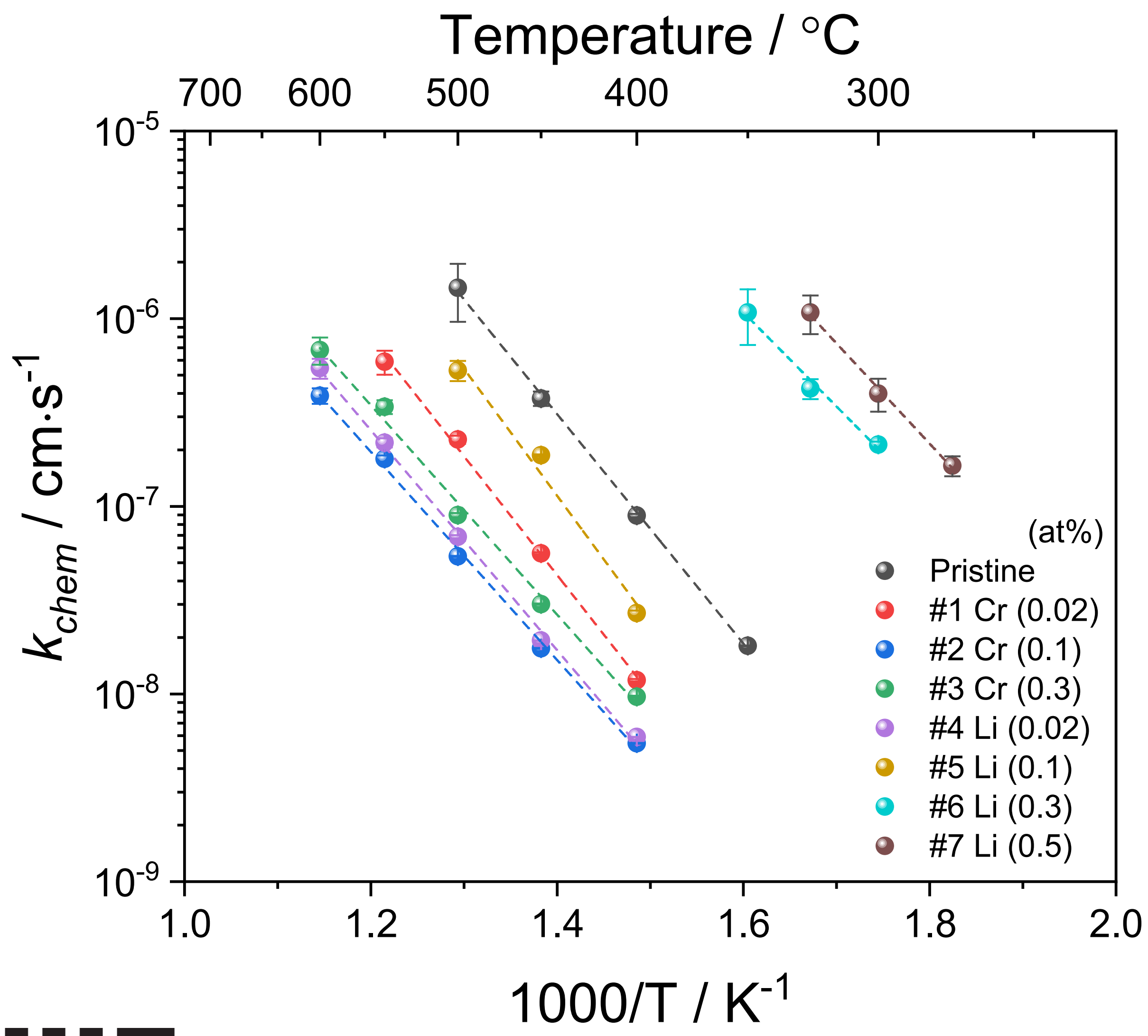
Cr-Poisoning and Recovery by Serial Infiltration with Li





<u>H. G. Seo, H.L. Tuller</u> *et al., Energy Environ. Sci.,* ***2022****, 15, 4038-4047* ***Patent Pending***

Temperature Dependence of k_{chem}



$$k_{chem} = A\exp\left(-\frac{E_a}{k_b T}\right)$$

A: Pre-exponential factor
E_a: Activation energy

- *Activation energy (E_a): 1.16 ± 0.11 eV*
- *E_a: little dependence on infiltration*
- *A: largely controlled by acidity/basicity of additives*

Controlling relative surface acidity can recover performance.

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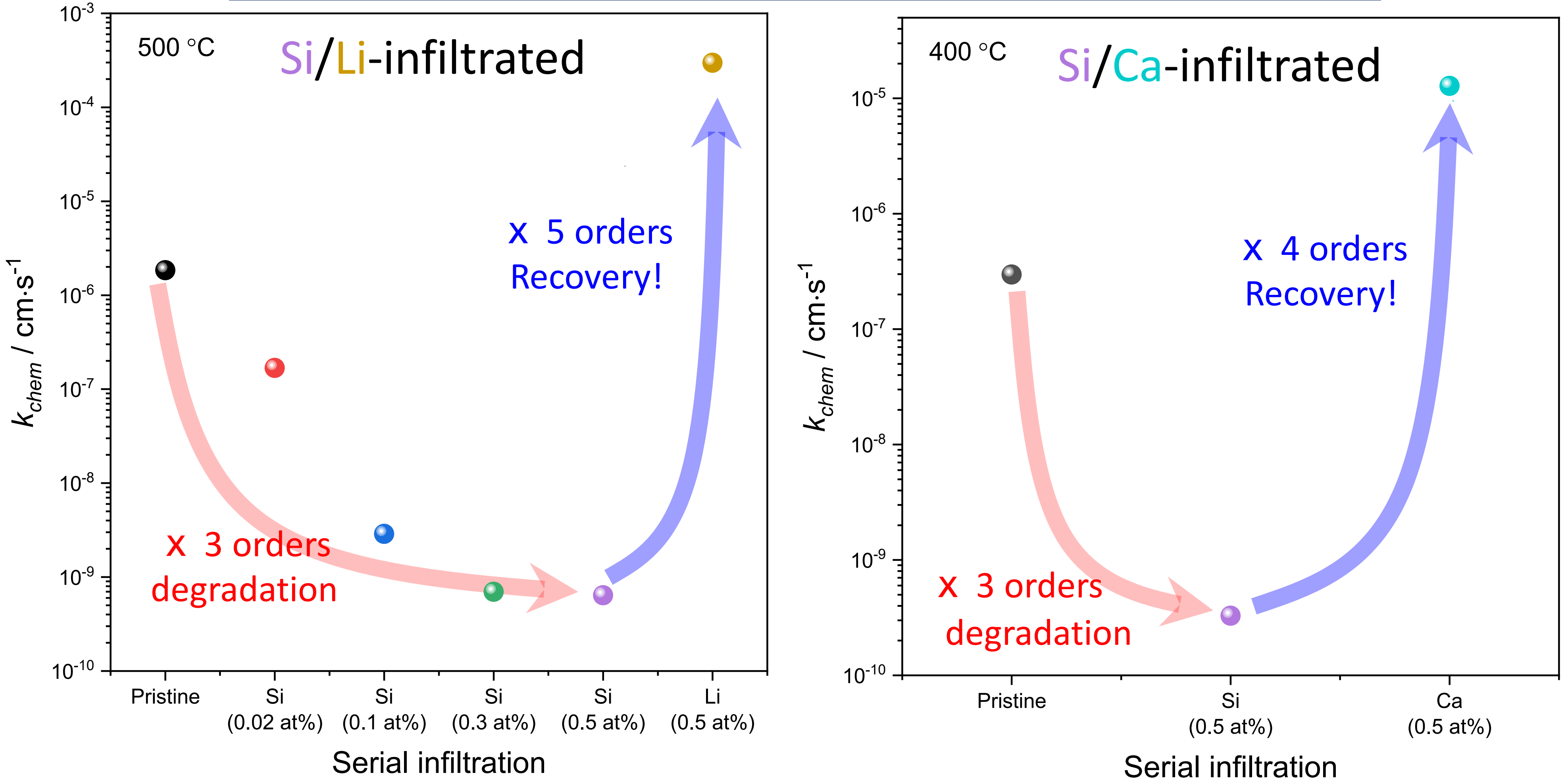
H. G. Seo, H.L. Tuller *et. al., Energy Environ. Sci.,* ***2022****, 15, 4038-*

Patent Pending

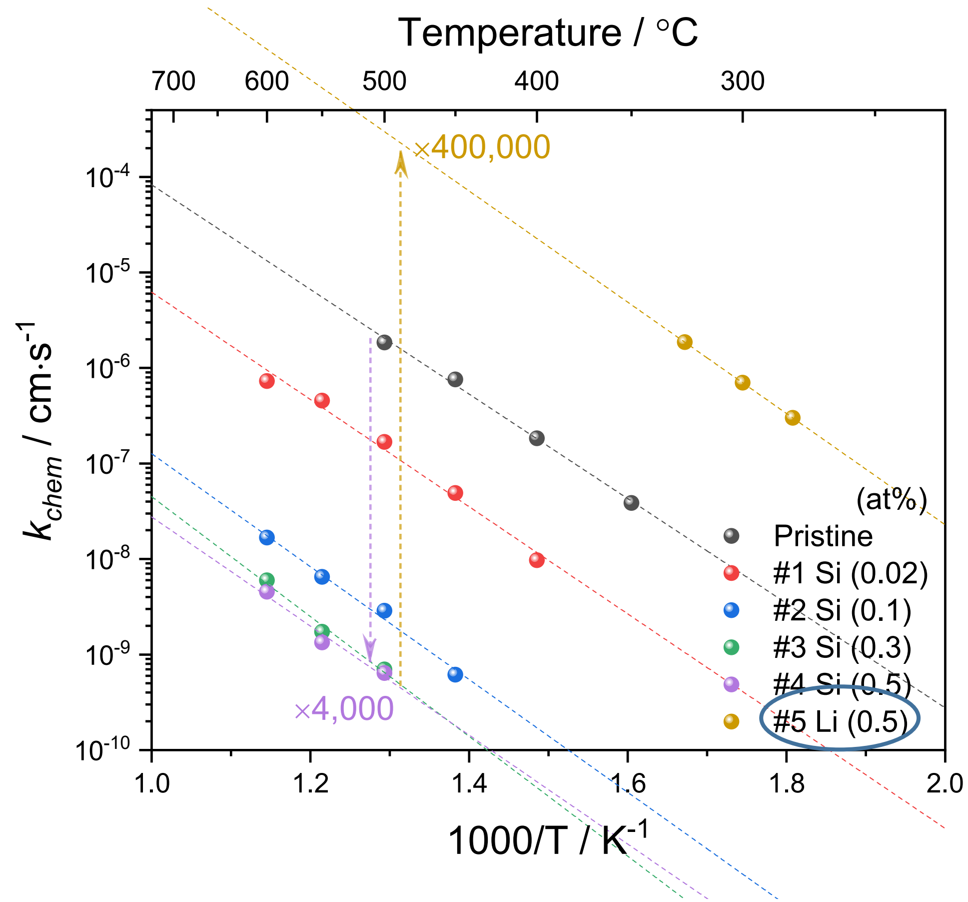
Beyond Cr-Poisoning, can it be Generalized to Other Acidic (Si vs Cr) /Basic (Ca vs Li) Additives?

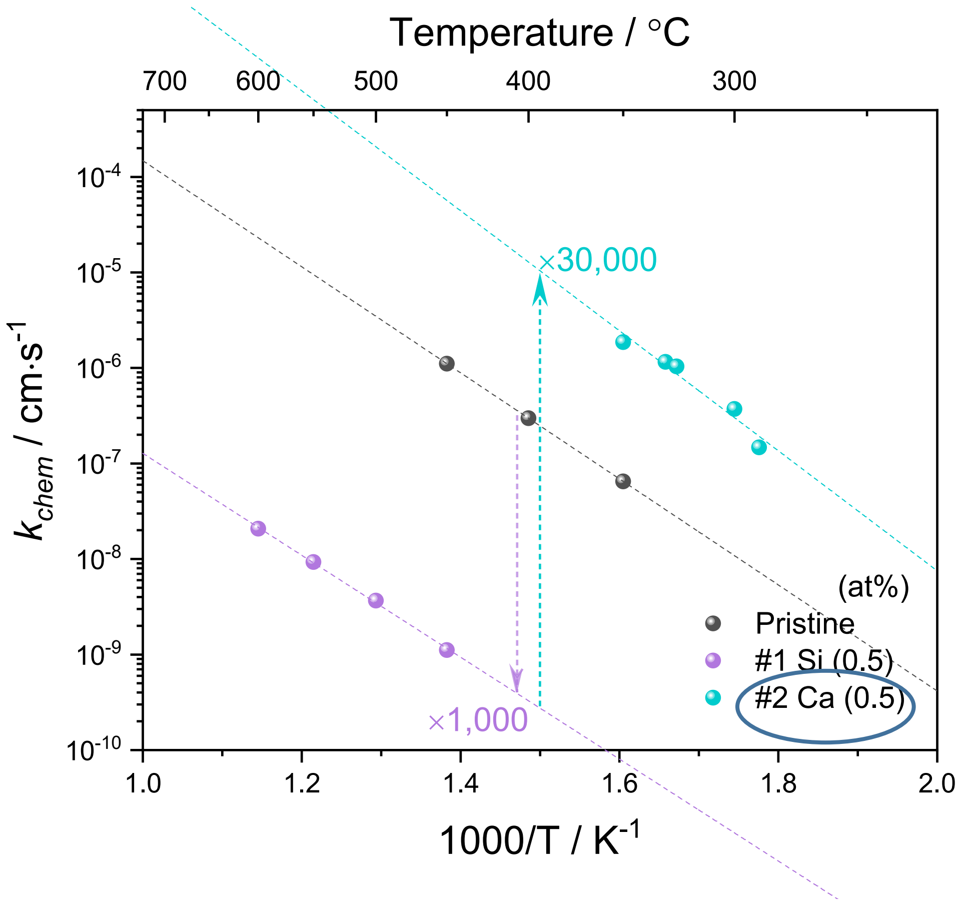
Silica can be a more dangerous poison than chromia!



*<u>H. G. Seo, H.L. Tuller</u> et al., Advanced Materials, In Revision **2022***   ***Patent Pending***

Si-Poisoning and Recovery by Basic Additives (Li,Ca)

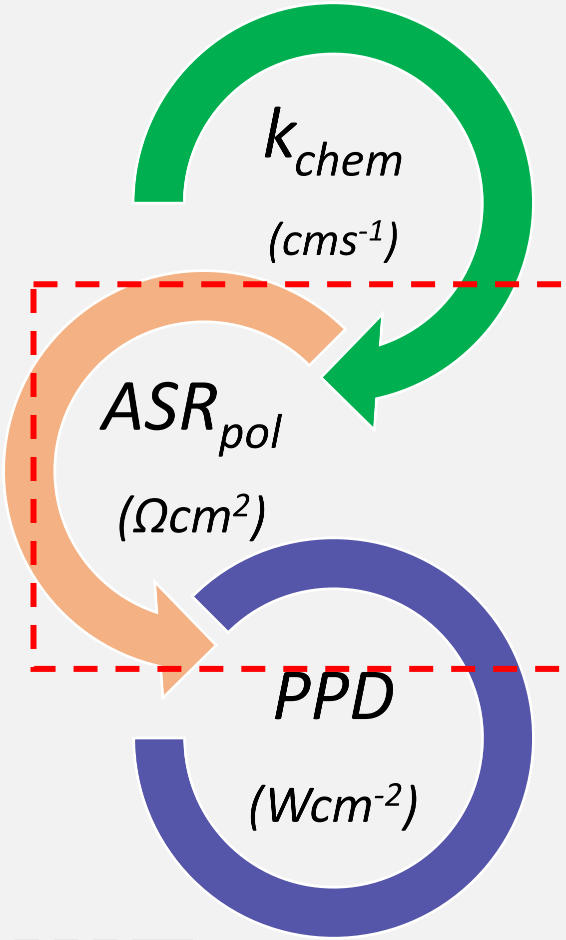




As observed in Cr/Li-infiltrated sample, acidity/basicity has a significant impact on pre-exponential factor (A), not E_a.

Impact of Additives on Polarization Resistances

Approach



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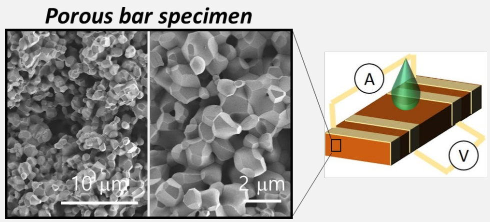
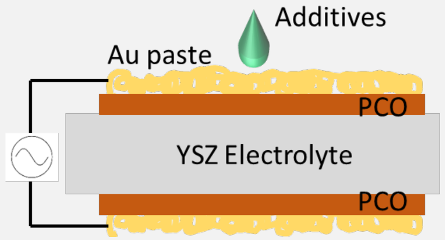


- Electrochemical impedance spectroscopy (EIS)
- Distribution of relaxation time (DRT)
- Screen-printed symmetric cells



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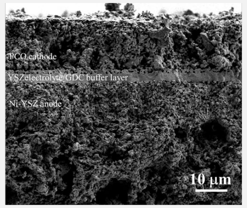
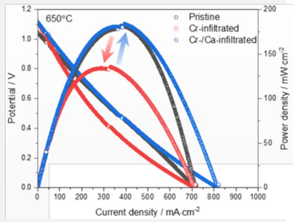
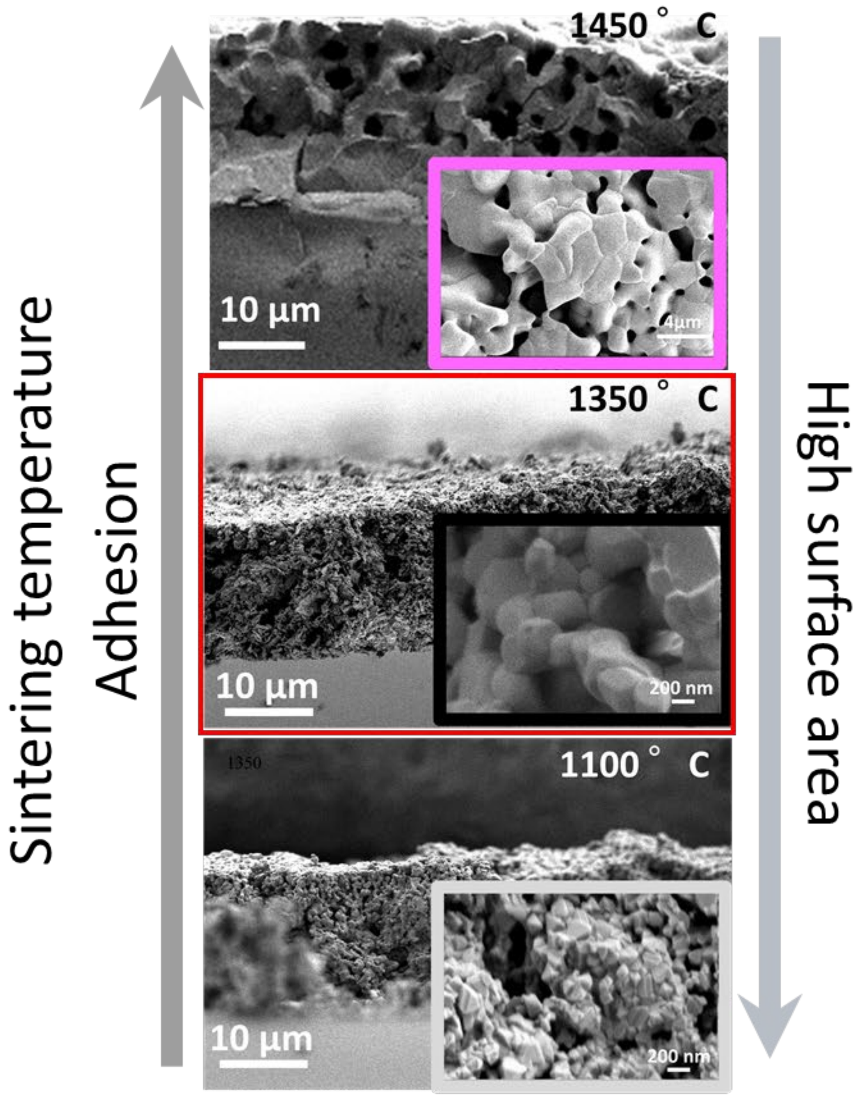
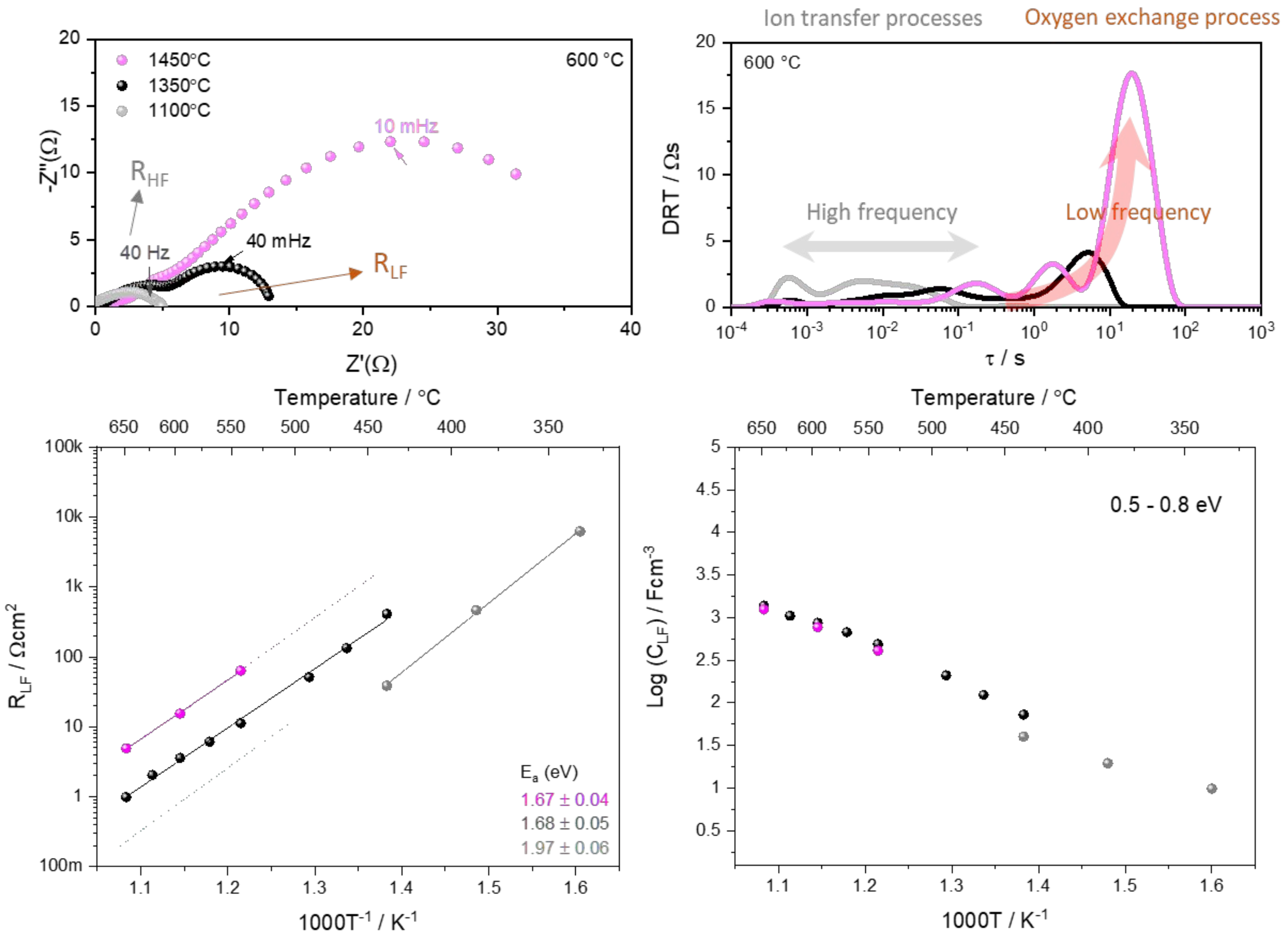




Microstructural Optimization of Symmetric Cells

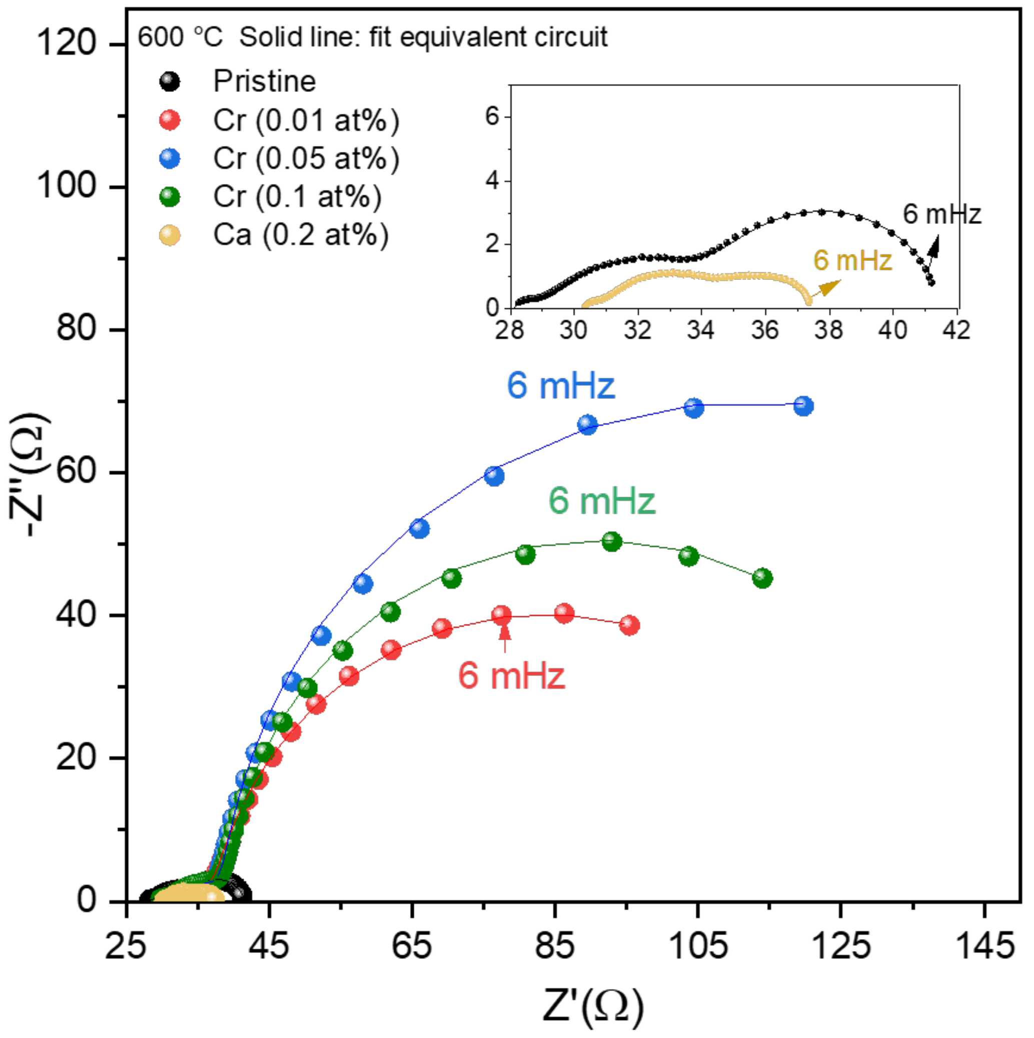


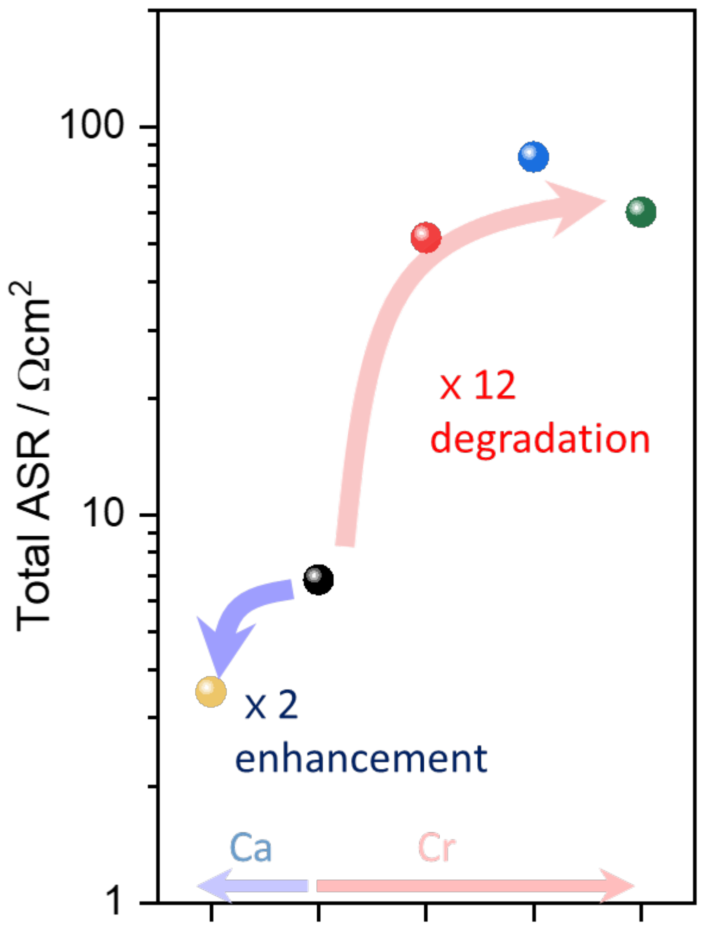


A. Staerz, H. G. Seo, H.L. Tuller, et al., J. Electrochem. Soc., ***2022****, 169, 044530*

Surface Additive-Induced ORR Activity

Non serial infiltration





A. Staerz, H. G. Seo, H.L. Tuller, et al., J. Electrochem. Soc., ***2022****, 169, 044530*

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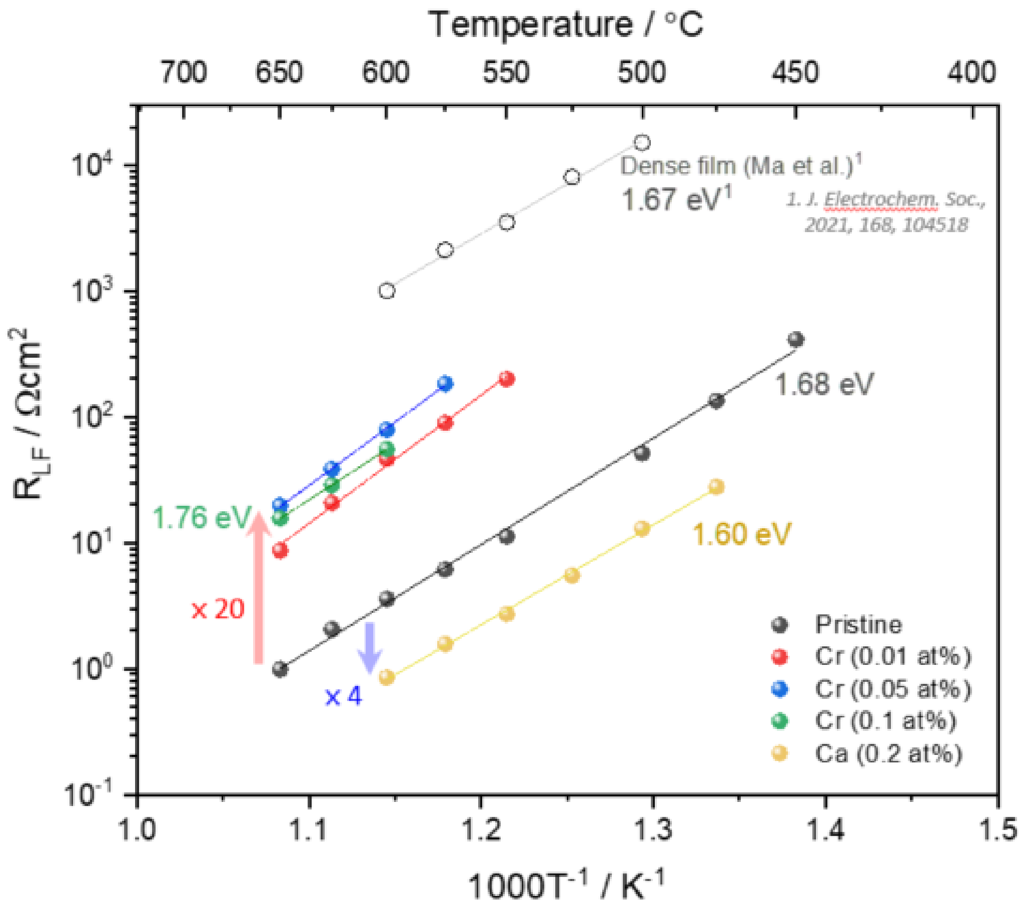
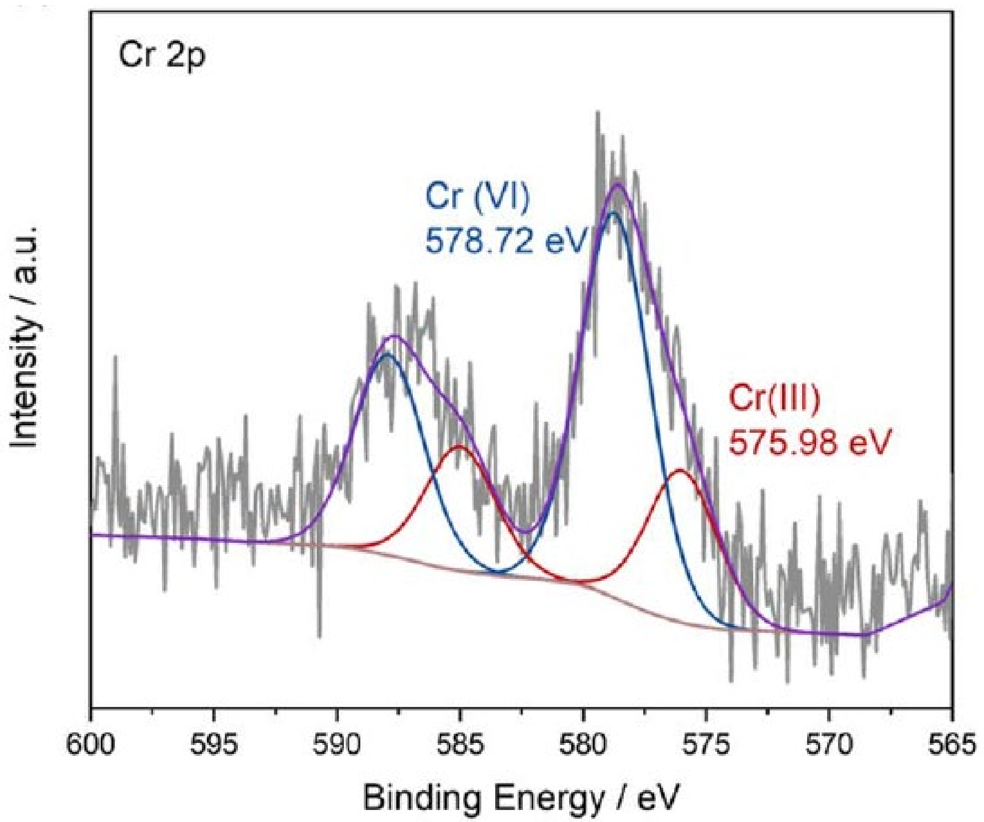


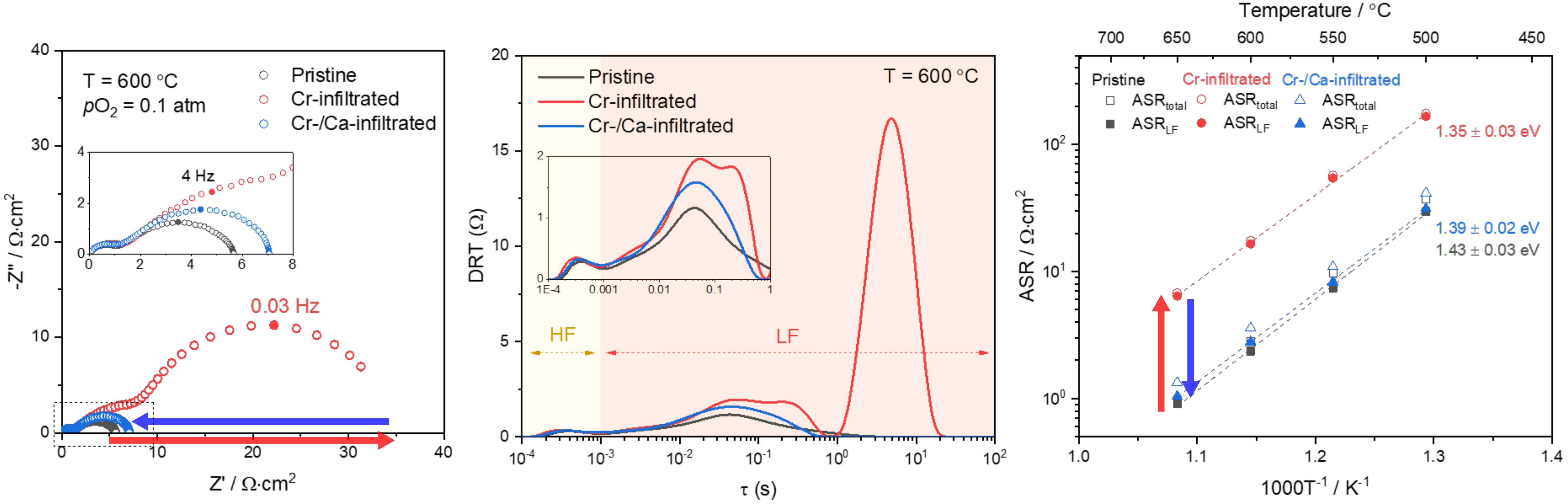


Similarly, acidity/basicity show little dependence on activation energy (E_a).
Mixture of Cr(III) and Cr(VI) valence is detected.

A. Staerz, H. G. Seo, H.L. Tuller, et al., J. Electrochem. Soc., **2022**, 169, 044530

Can Ca-Additives Reactivate Cr-Poisoned Surface?

Symmetric cells

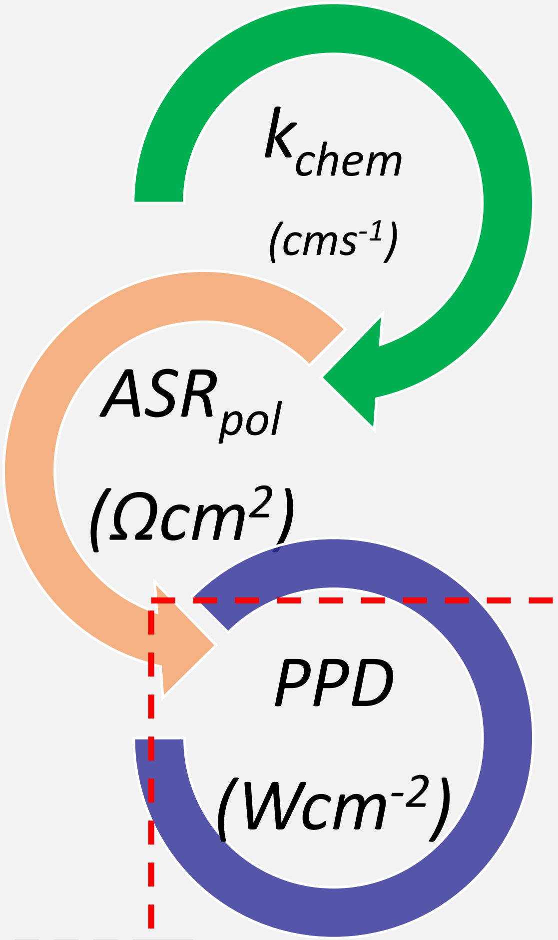


Cr-additives significantly impeded rate of oxygen reduction, leading to increases in ASR.
Remarkedly, degraded ASR can be recovered by addition of Ca-additives.

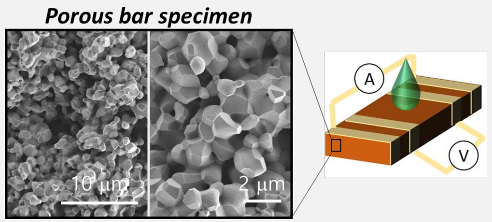
H. G. Seo, H.L. Tuller, *et al., J. Power Sources., Under review* ***2022***

Impact of Additives on Power Outputs

Approach



- Conductivity relaxation measurements (ECR)
- Porous bar



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- Distribution of relaxation time (DRT)
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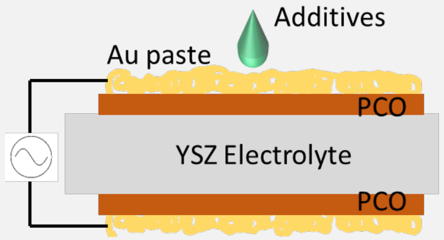
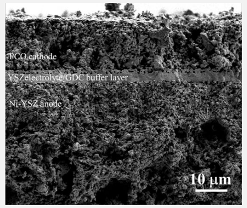
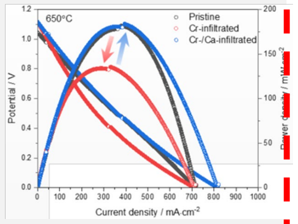
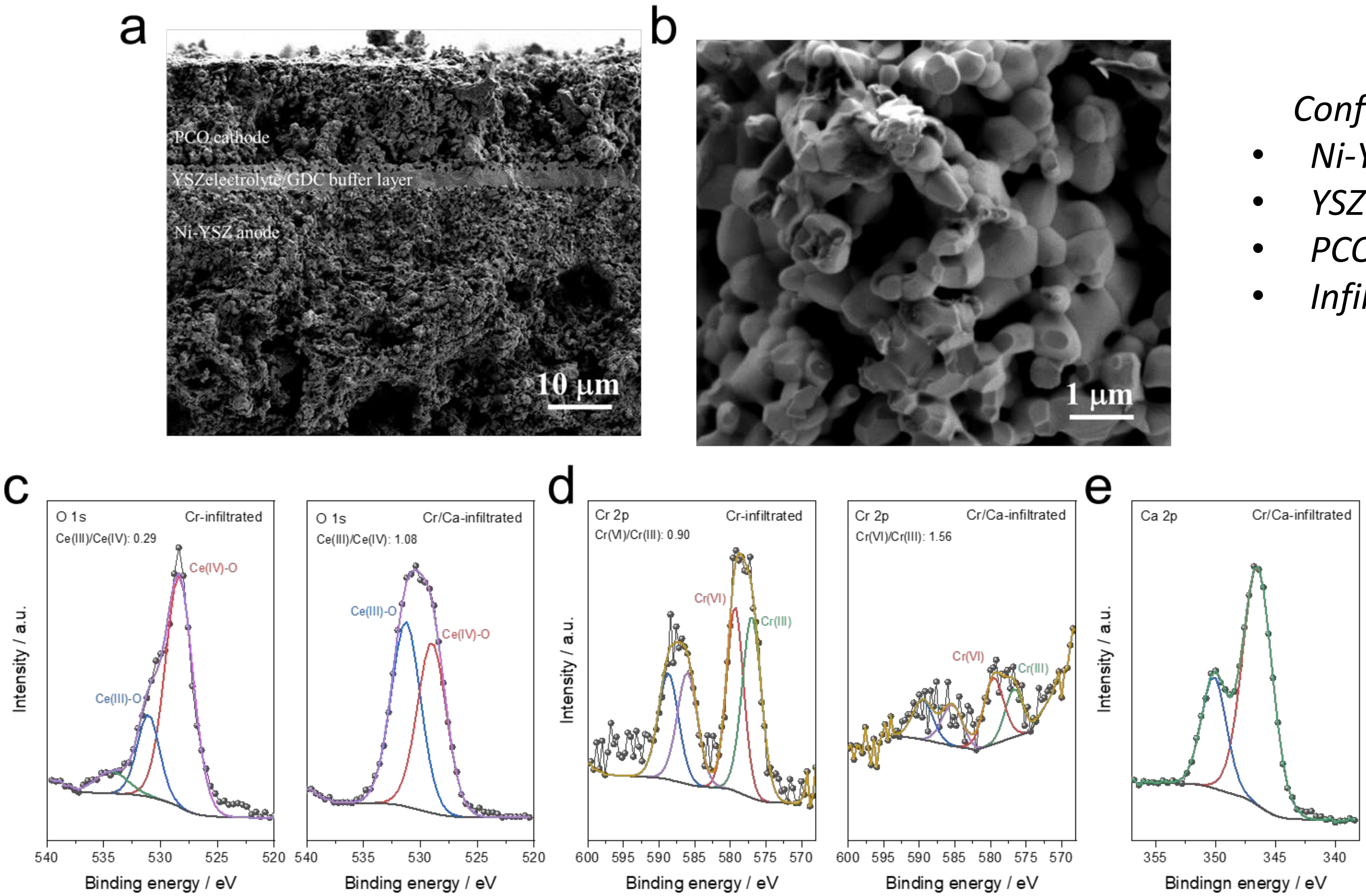


- Current-Voltage-Power curves (I-V-P)
- Anode-supported single fuel cells





Anode-Supported Fuel Cells with PCO Cathode with Additives



Configuration of anode-supported cells

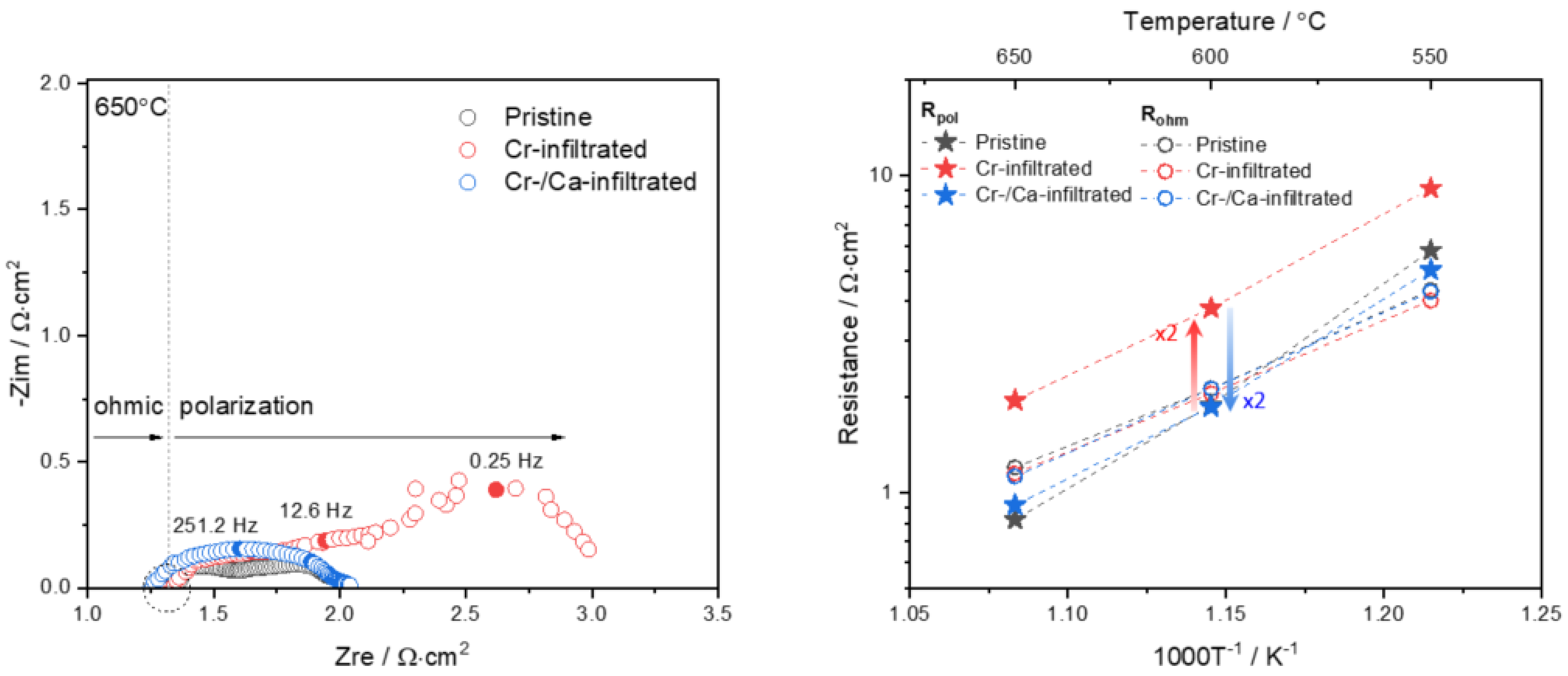
- *Ni-YSZ anode*
- *YSZ electrolyte (GDC buffer layer)*
- *PCO cathode*
- *Infiltration of Ca and Cr*

Addition of Ca on Cr-poisoned cell

- *Expectation of compensation for electron depletion at PCO surface ($Ce^{4+} \rightarrow Ce^{3+}$)*
- *Enhancement of Cr^{6+}/Cr^{3+} ratio possibly due to $CaCrO_4$ formation*

H. G. Seo, H.L. Tuller, *et al., J. Power Sources., Under review* ***2022***

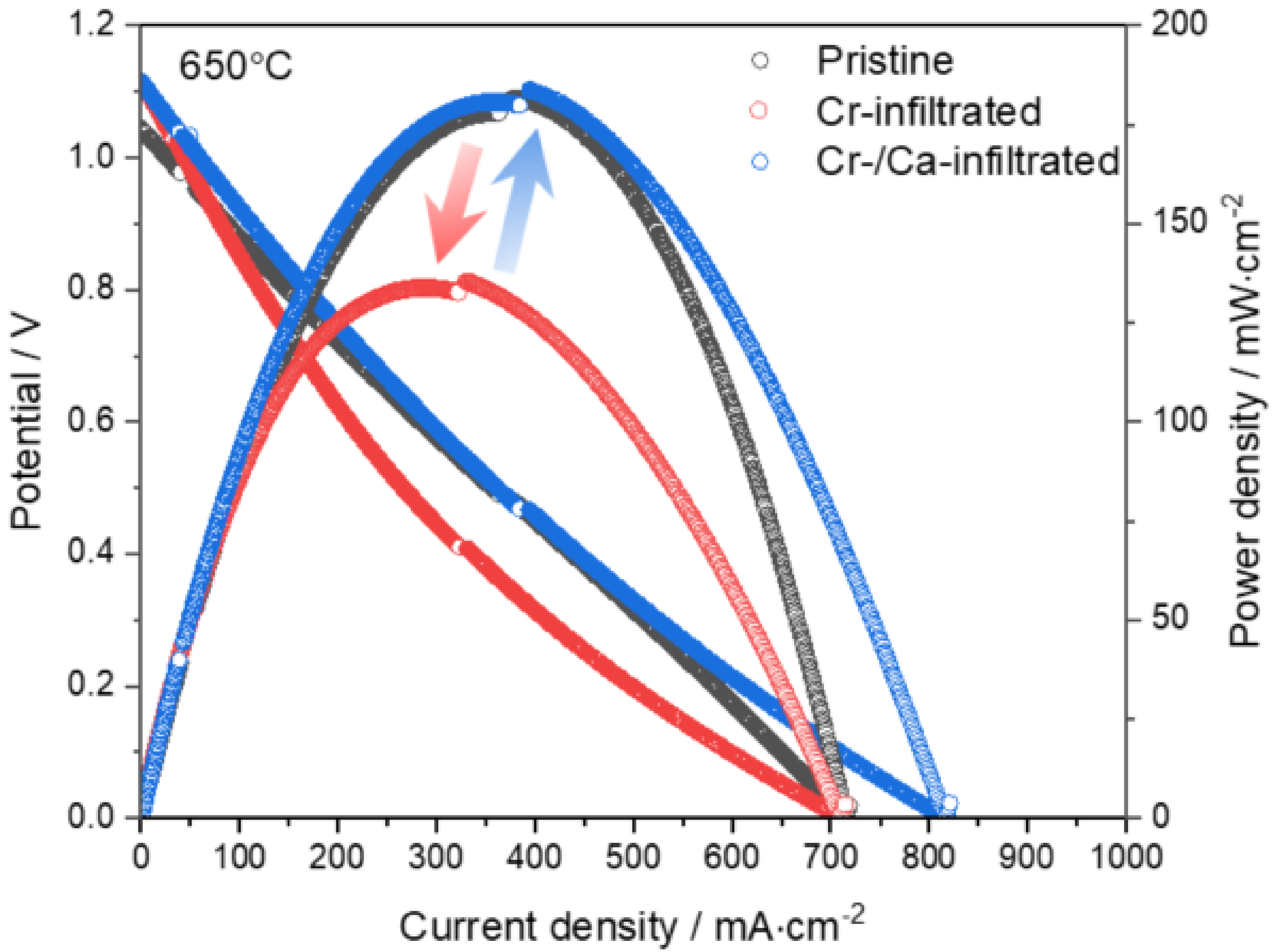
Demonstration of Cell Performance with Controlled Acidity



While ohmic resistances show little dependence on additives, polarization resistances at low frequency are significantly influenced by infiltration, as expected.

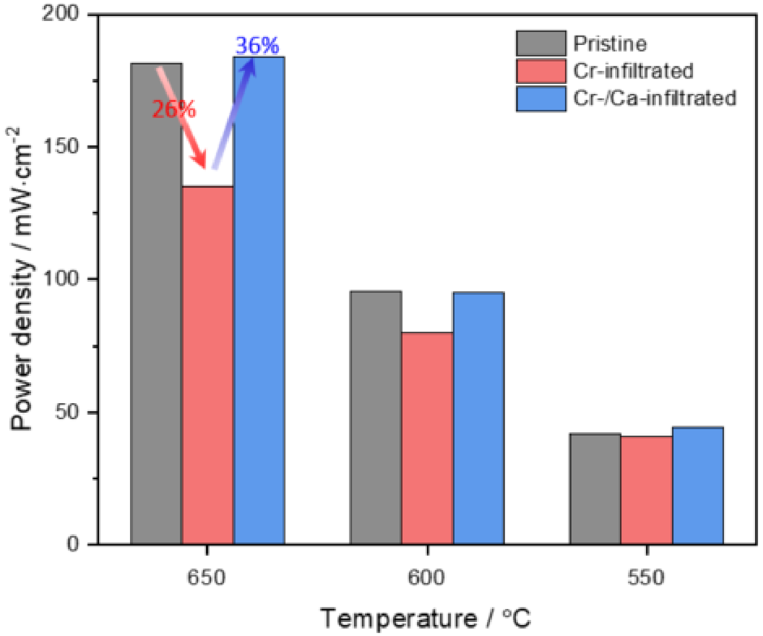
H. G. Seo, H.L. Tuller, *et al., J. Power Sources., Under review* ***2022***

Demonstration of Cell Performance with Controlled Acidity



Measurement conditions

- *Humidified H_2 at anode*
- *Synthetic air at cathode*
- *Temperature: 650-550°C*



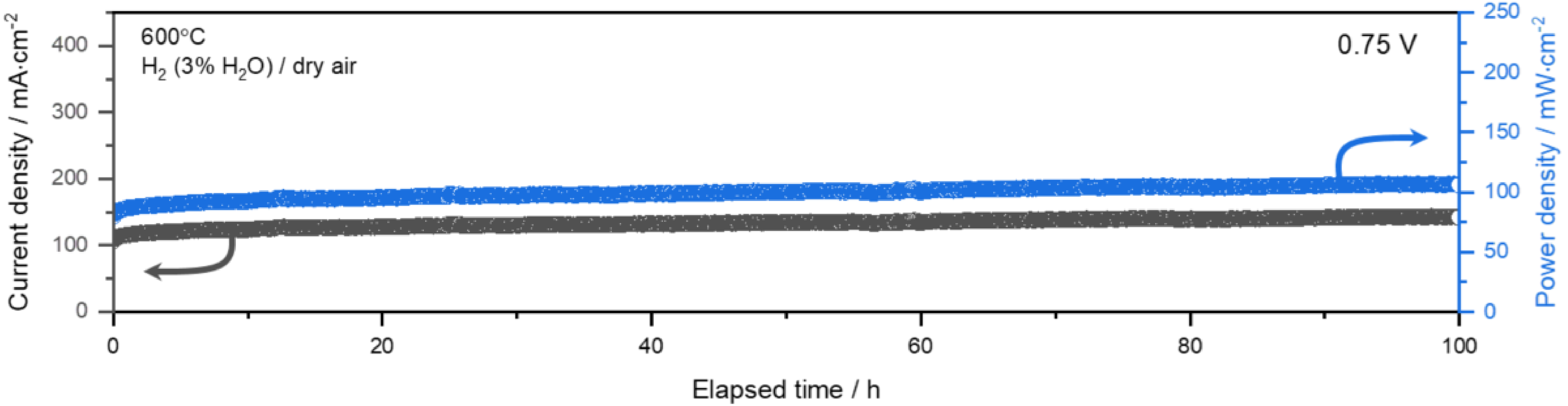
✓ More than 35% recovery of degraded power density!

H. G. Seo, H.L. Tuller, *et al., J. Power Sources., Under review* ***2022***

Stability of Cell Performance with Controlled Acidity

Measurement conditions

- *Temperature: 600°C*
- *Constant voltage: 0.75 V*



No notable performance degradation observed following 100 h of operation.

H. G. Seo, H.L. Tuller,** et al., J. Power Sources., Under review **2022

Recall DOE Targets on SOFCs

Metric	Current	2020 Target	2025/2030 Target
System Cost (100 kW- 1MW)	>$12,000/kWe	$6,000/kWe	$900/kWe
Single Cell Degradation	0.2 - 0.5% per 1,000 hrs		
Cell Manufacturing Approach	Batch	Semi- Continuous	Continuous
System Degradation	1 – 1.5% per 1,000 hrs	0.5 - 1.0% per 1,000 hrs	<0.2% per 1,000 hrs
Fuel Reformation	Primarily external natural gas conditioning/reforming	100% integrated natural gas reformation inside cell stack	
Durability	<2,000 hrs	5,000 hrs	5 years
Platform	Proof-of-Concept	Prototype/Pilot	DG: Commercial Utility-scale: Pilot
Configuration	Breadboard/Integrated systems	Fully packaged	Fully packaged
Fuel	Natural gas	Natural gas Simulated syngas	Natural gas Coal-derived syngas
Demonstration Scale	50 kWe – 200 kWe	200 kWe – 1 MWe	DG: MWe-class Utility-scale: 10 – 50 MWe

Table: Dr. Shailesh Vora, "U.S. DOE Office of Fossil Energy Solid Oxide Fuel Cell (SOFC) Program", 2019 Fuel Cell Seminar and Exposition

*Given long-standing degradation problem with SOFCs, our findings support a **practical** solution for considerably extending device lifetimes!*

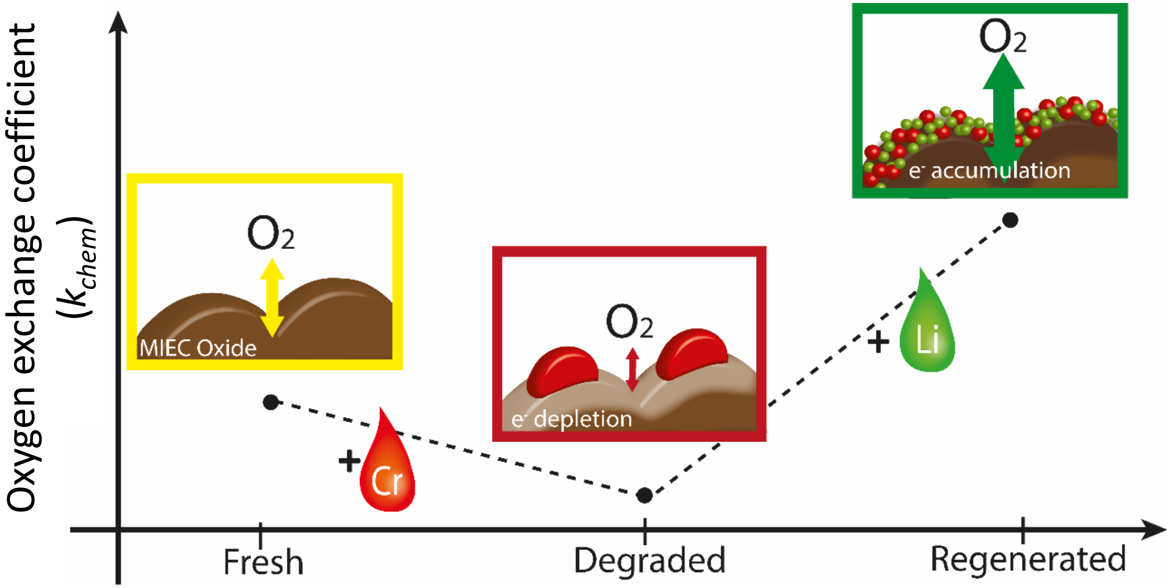
Conclusions

- Demonstrated for first time ability to reactivate electrocatalytic surfaces by controlled acidity/basicity via

  1) conductivity relaxation, 2) electrochemical impedance, and 3) power output measurements.

  (*Not only Cr-induced poisoning of SOFCs, but other potential poison sources such as Si detected, applicable to many applications*)

- Confirmed cause of performance degradation related to electronic coupling between additives and host oxide.



Demonstrated with controlled acidity:

- *Enhanced performance*
- *Extended life*

"IMPACT": Accelerate ability to bring wide range of technologies to market!

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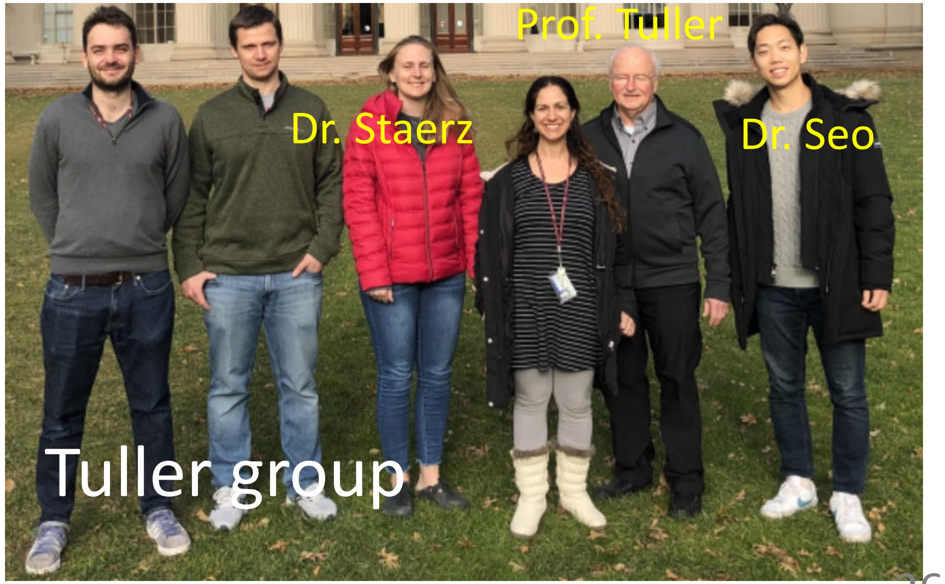
Acknowledgement

- Title: “Robust highly durable solid oxide fuel cell cathodes – Improved materials compatibility & self-regulating surface chemistry”
- Funding Opportunity Number: DE-FOA-0001853; Dr. Debalina Dasgupta
- Specific FOA area of interest: AOI 1 – Solid Oxide Fuel Cells (SOFC) Core Technology Research: Cell and stack degradation
- Collaboration with Prof. James M. LeBeau, Prof. Bilge Yildiz, and Dr. Dennis S. Kim at MIT

NATIONAL ENERGY TECHNOLOGY LABORATORY

Dr. Nicollet



Thank you for your attention!!

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