Integrated Energy Systems

Cathy Riddle	Synthesis of Nanocomposite Polymer Material for Thermal Storage
Gorakh Pawar	A fundamental investigation of the current leakage mechanism and relevant harsh environmental chemistries in solid oxide materials
John Klaehn	Modular Designs for Facilitated Transport Membranes in Olefin Production
Meng Shi	Sulfate Double Salts: Using Recycled Ni and Co Sources to Produce Cathodes in Lithium-ion Batteries
Qiang Wang	Recovery of High Purity Critical Elements from Spent Lithium Ion Batteries without Waste Emission
Rebecca Fushimi	Methane Upgrading Using Dynamic Energy Supply
Rebecca Fushimi	Continuous Syngas Production from a New Chemical Looping Concept to Balance Power Dynamics in Integrated Energy System
Victor Walker	Deep Reinforcement Learning and Decision Analytics for Integrated Energy Systems

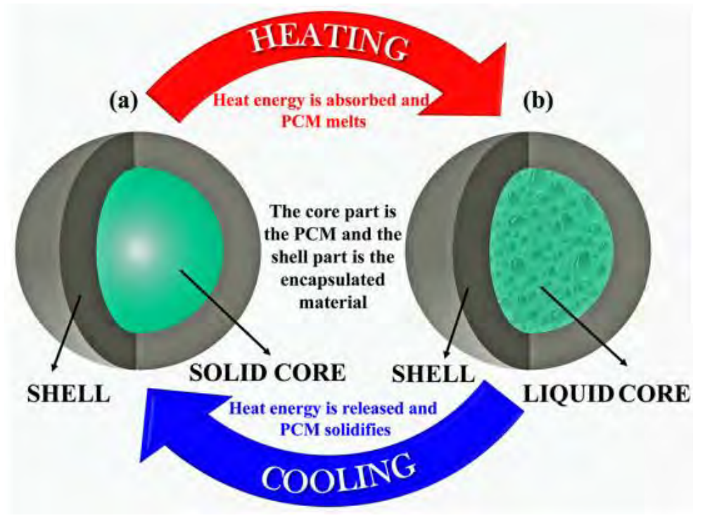
Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517."

Smart Rocks and Thermogenic Cement Material for Thermal Energy Storage

Catherine Riddle and Joshua McNally

Smart Rocks & Thermogenic Cement (TGC)

- Thermogenic Cement (TGC) and Smart Rocks have been designed to address needs for technologies in energy demand and thermal controls.
- TGC and Smart Rocks can store heat for electricity, residential heating, engine security, and energy loss protection.
- TGC and Smart Rocks outperform industry standards, such as basalt and basalt glass, by more than 60%.
- TGC and Smart Rocks are environmentally friendly, non-hazardous, stable (no thermal runaway as seen in Li-ion batteries), and no fire or explosive hazard.



Basalt rock test material

From left – right, Thermogenic Cement spheres, before heating (silver), after heating (dark grey), and the core material without metal casing.

Large Commercial Operation

- TGC is useful for large sensible heat storage, a process where energy is stored as heat within a physical body.
- TGC consists of a cement core, an inner coating, and a steel alloy shell.
  - The Cement functions as the main heat storage medium, water within the structure enhances specific heat and the inner coating prevents water from escaping the internal system.
- Smart Rocks material can be used for smaller more compact applications as a PCM.
  - Incorporation of inorganic nanoparticles into the Smart Rock core matrix significantly and positively affects the properties of the matrix resulting improved thermal, mechanical, rheological, electrical, catalytic, fire retardant and non-hazardous properties.

Current thermal storage technology

Siemens Gamesa volcanic rock TES

TGC could reduce the footprint of thermal energy storage from the size of a silo to that of a Ford F-150 truck.

Thermogenic Cement prototype design.

Development & Testing

Carbon steel sphere with cement core along side.

- Steel spheres were used as a basis into which a plaster coating and cement or paraffin core were applied.
- Thermal Gravimetric Analysis was used to determine mass loss from heating, and specific heat.
- Furnaces were used to heat TGC and Smart Rocks to operational temperature of 800 and 100°C, respectively. Rate of cooling was measured to extrapolate thermal performance.

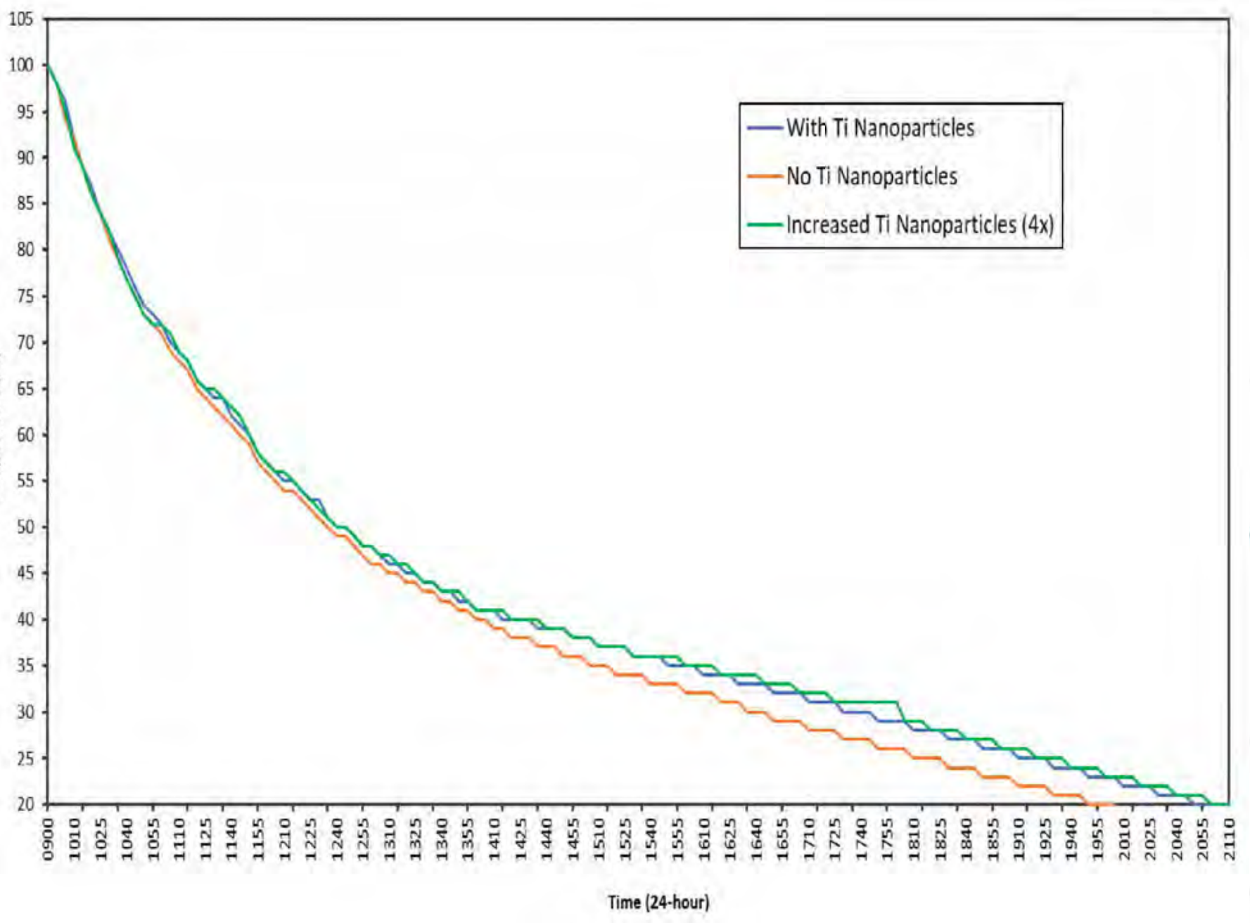
Smart Rocks phase change material (PCM)

TGC and Smart Rock sphere after heating cycle

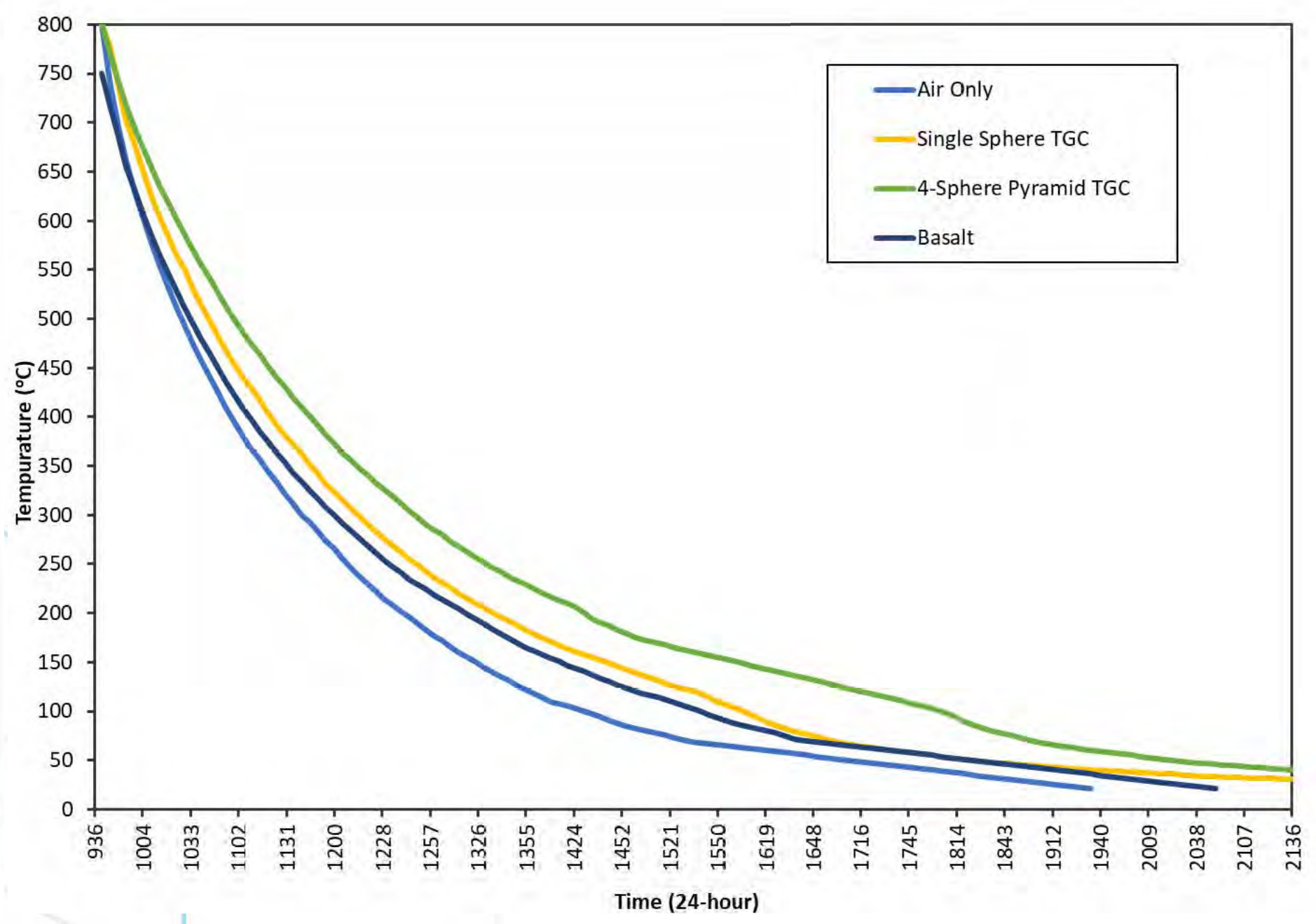
Results

- TGC: Refractory cement saturated with water has a large specific heat capacity. Increasing water content decreases the rate at which heat energy can be released but increases the amount of heat energy present. The presence of plaster assists cement in retaining water concentration.
- SR: Addition of Ti nanoparticles increases thermal retention and extends thermal load time.

Smart Rocks



Thermogenic Cement (TGC)



Conclusion

- Thermogenic Cement and Smart Rocks show promise as novel systems with benefits from replaceable parts allowing for versatility in function.
- The binding of water in the TGC cement allows for a much greater Specific Heat capacity. Smart Rocks Ti nanoparticles increase PCM stability and thermal retention.
- The steel alloy shells provide a structurally consistent design which makes engineering the material simple, fast, and inexpensive to mass produce.
- Patent pending on both technologies and current interest in licensing by energy industry and technology startup company partners for TGC.

Thermal Energy Storage material	Energy Density J/(kg · °C)
TGC	$3.0E^6$
Smart Rocks	$2.9E^6$
Basalt	$1.8E^6$

Special thanks to interns Evelyn Andrade and Tyler Reed for their hard work advancing this work.

Project Number: 21A1050-002FP

LRS Number: INL/JOU-22-69661

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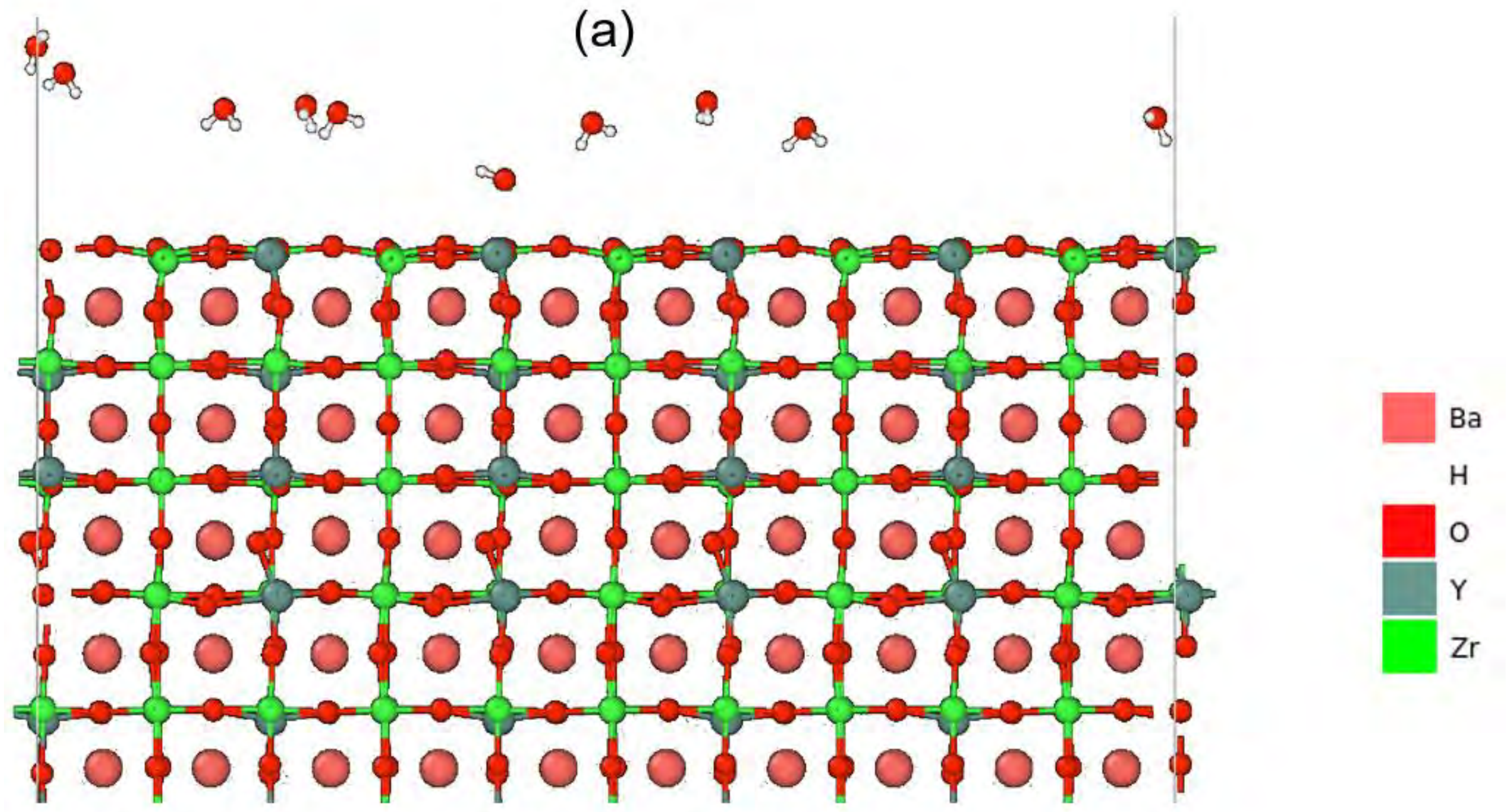
Idaho National Laboratory

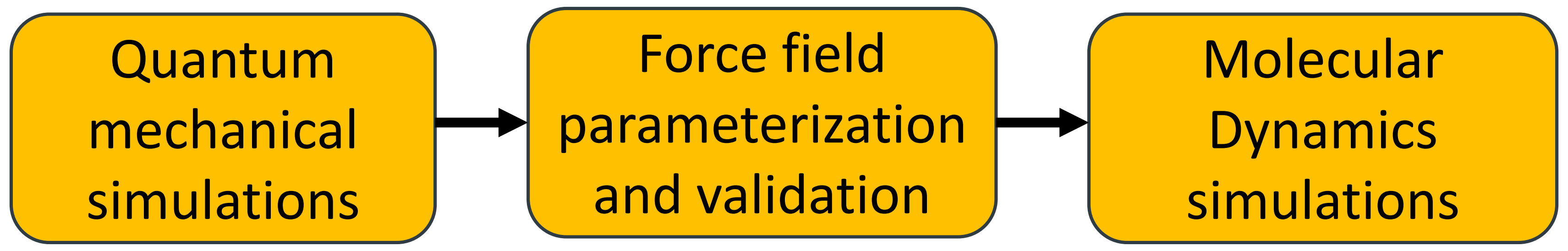
Motivation

- **What:** Low faradaic efficiency of SOECs affects the costs per kilogram of H_2 and the large-scale adoption of H_2 as a fuel.
- **Why:** Addressing the fundamental issues surrounding the low faradaic efficiency can pave the way for a better SOEC design.

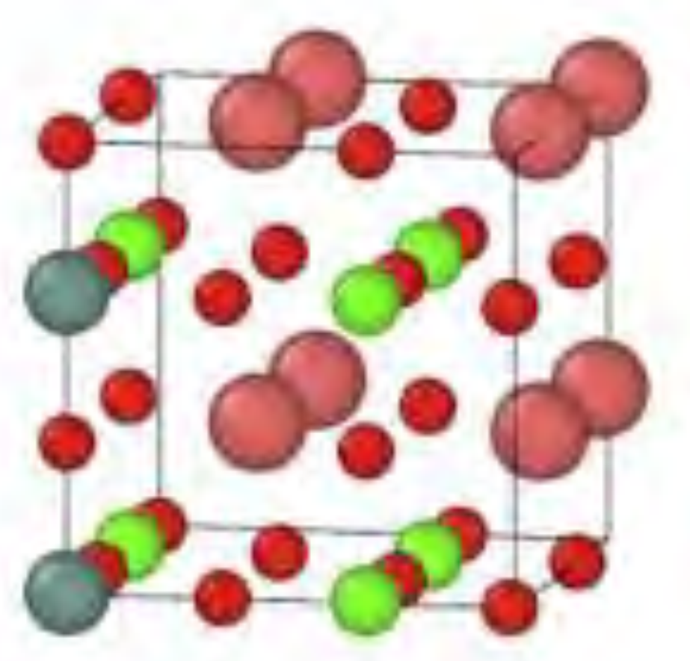


Methodology

R&D workflow to unlock the intrinsic SOEC chemistries

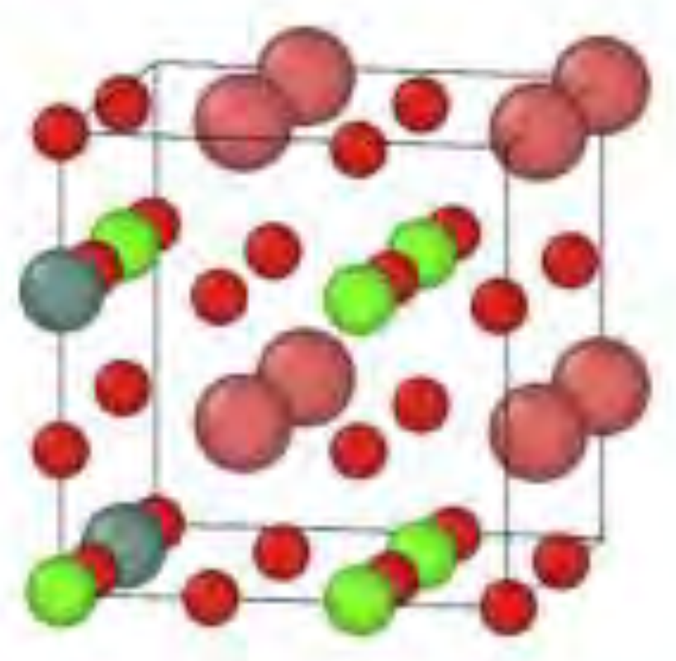


Quantum mechanical simulations → Force field parameterization and validation → Molecular Dynamics simulations



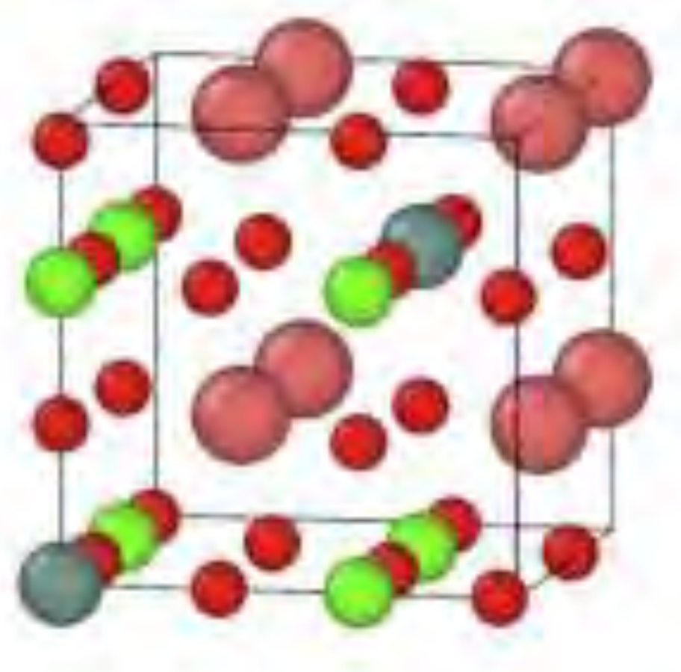
BZY20 1st form of Y doping

Energy (kcal/mol):
eReaxFF 5.09
DFT 5.30



BZY20 2nd form of Y doping

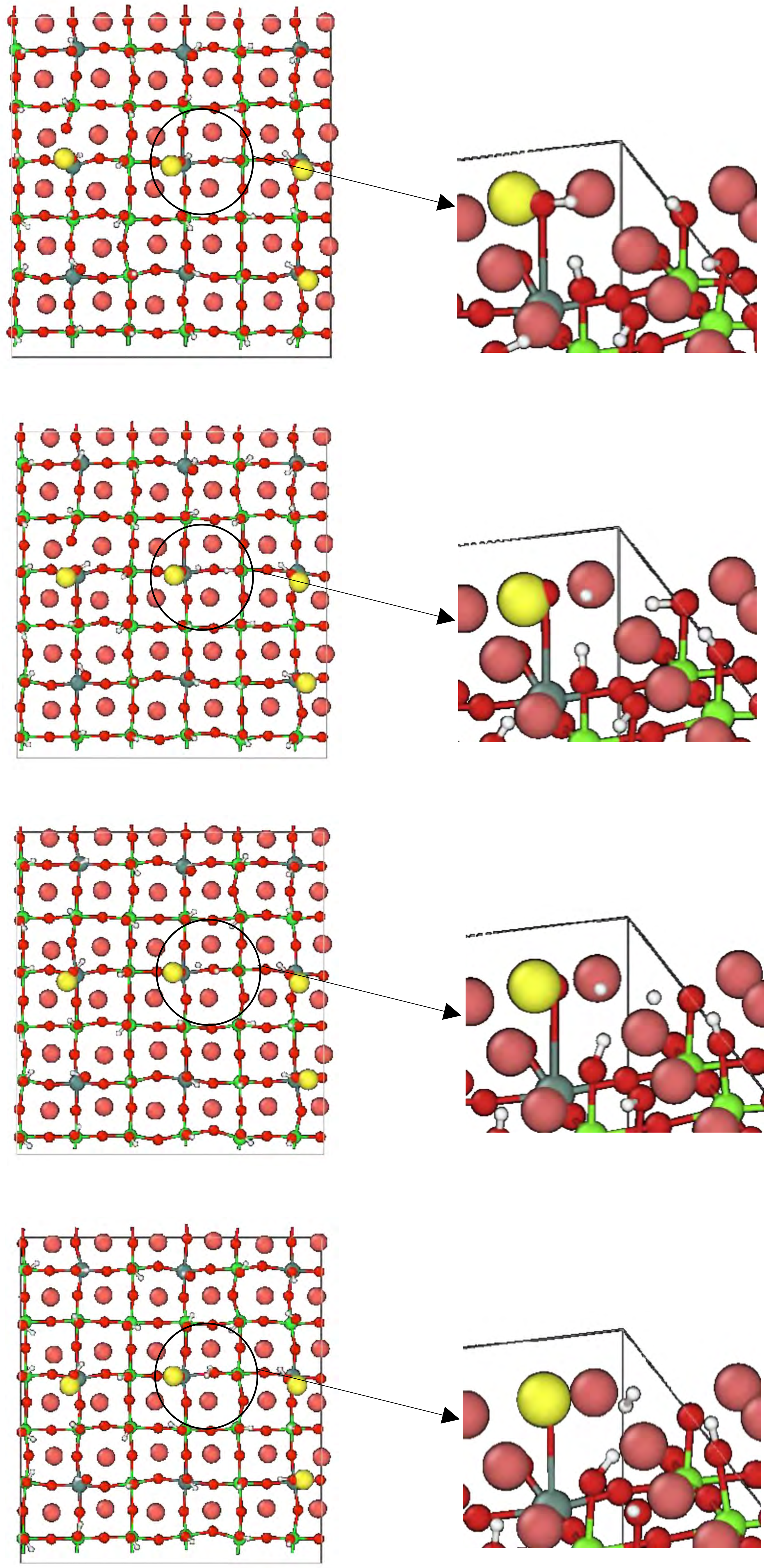
Energy (kcal/mol):
eReaxFF 1.59
DFT 1.38



BZY20 3rd form of Y doping

Energy (kcal/mol):
eReaxFF 0
DFT 0

Results



Evolution of complex H_2 generation reaction

Major takeaways

- A deep-dive into the fundamentals of SOEC operation under realistic provided various **intriguing insights**.
- **Oxygen vacancy concentrations and distribution** hold a key in electron migration and efficient hydrogen production.
- **Doping** could be an effective strategy to modify the SOEC surface properties and the electron mobility.
- eReaxFF force-field-based approach sets the stage to simulate electron conductivity, **electron leakage and other non-zero-voltage effects** in SOECs.

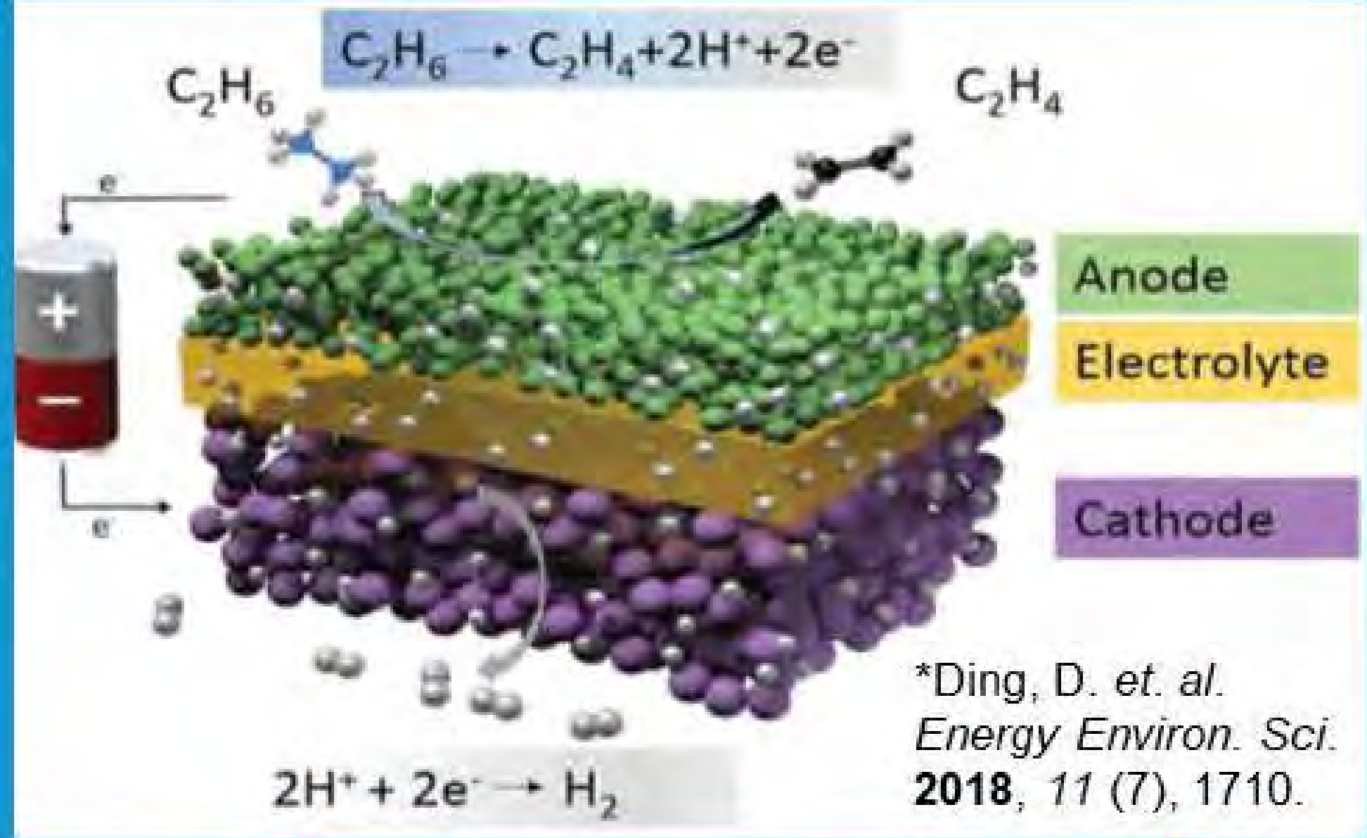
Research output and impact

- **Scientific advances**: Four manuscripts and one conference paper. Journal includes NPJ Computational Materials (Nature)
- **STEM pipeline development**: 4 early career staff members, 1 postdoc, 2 graduate interns who competed for INL's distinguished postdoc positions, lab techs, and other support staff
- **Research collaborations:** 1 Distinguished professor, 1 associate research professor, 3 graduate students, Frontiers of Energy Science seminar for INL researchers
- **External grant applications competed:** EFRC, EERC, BES, CMI

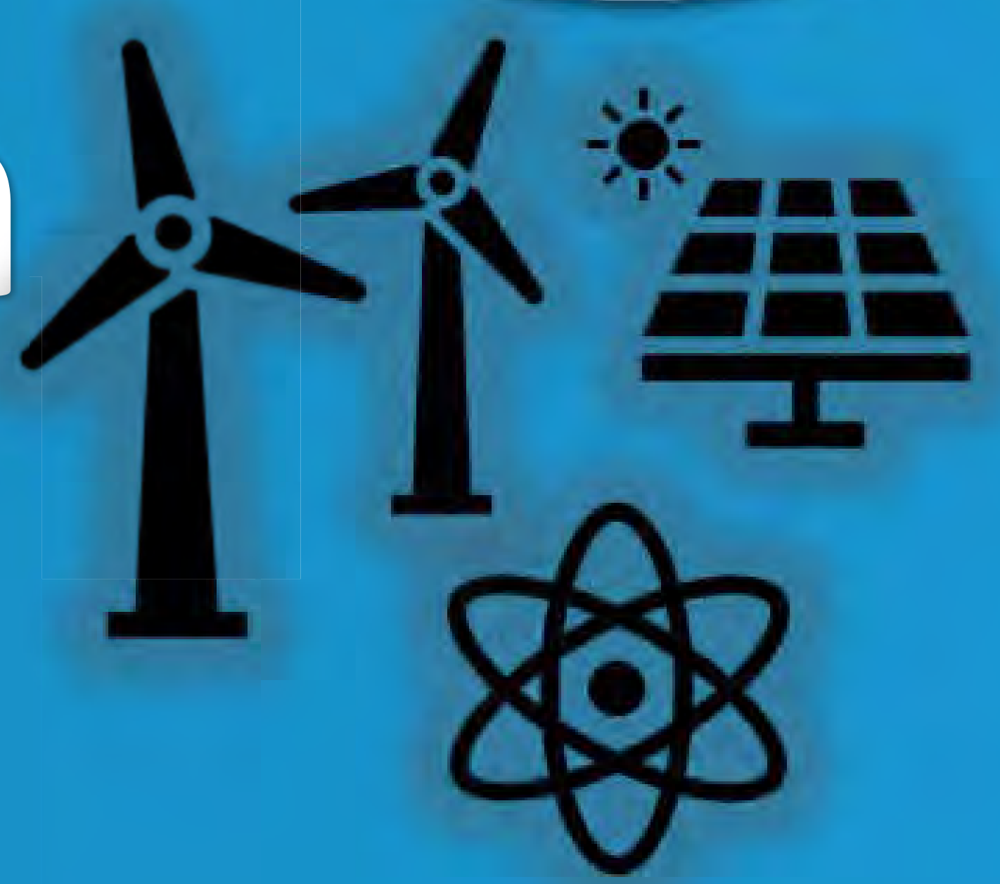
Project tracking number: 21A1050-131FP
Presenter: Gorakh Pawar
LRS number: INL/MIS-23-74216

Work supported through the INL Laboratory Directed Research& Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517

Robust and Scalable Membranes for Effective Ethylene Recovery from Point Source Generators



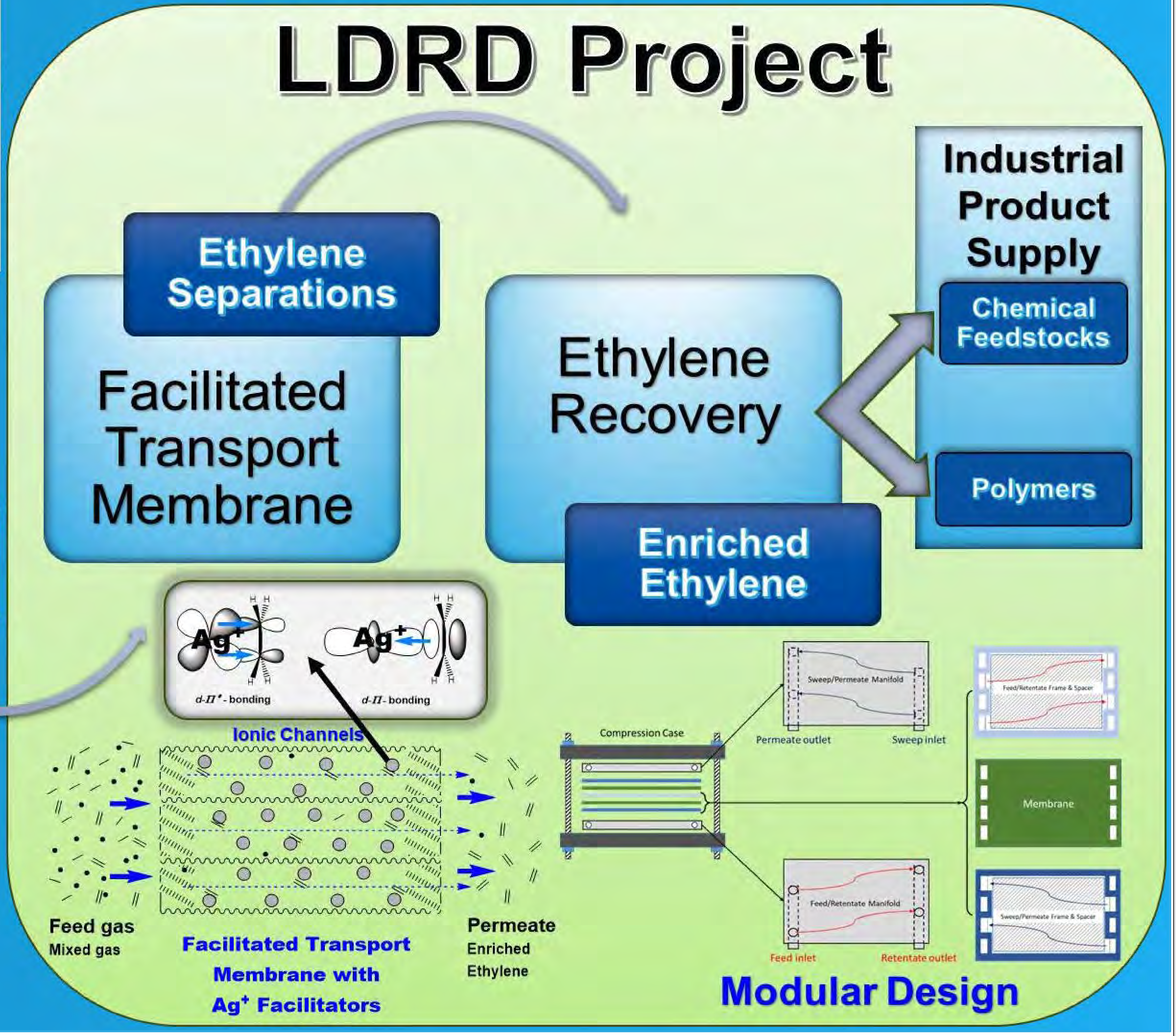
*Ding, D. *et. al.* *Energy Environ. Sci.* **2018**, *11* (7), 1710.



Electrical Overgeneration

Point Source Generation of Ethylene

Electrocatalytic Ethylene Production



LDRD Project

Ethylene Separations

Facilitated Transport Membrane

Ethylene Recovery

Enriched Ethylene

Industrial Product Supply

Chemical Feedstocks

Polymers

Facilitated Transport Membrane with Ag^+ Facilitators

Modular Design

Title: Modular Designs for Facilitated Transport Membranes in Olefin Production

John R. Klaehn[1],, Christopher J. Orme[1], Luis A. Diaz-Aldana[1], G. Glenn Lipscomb[2]*

[1]Idaho National Laboratory (INL); [2]University of Toledo (UToledo)

Needs: New applications for electricity during periods of overgeneration.

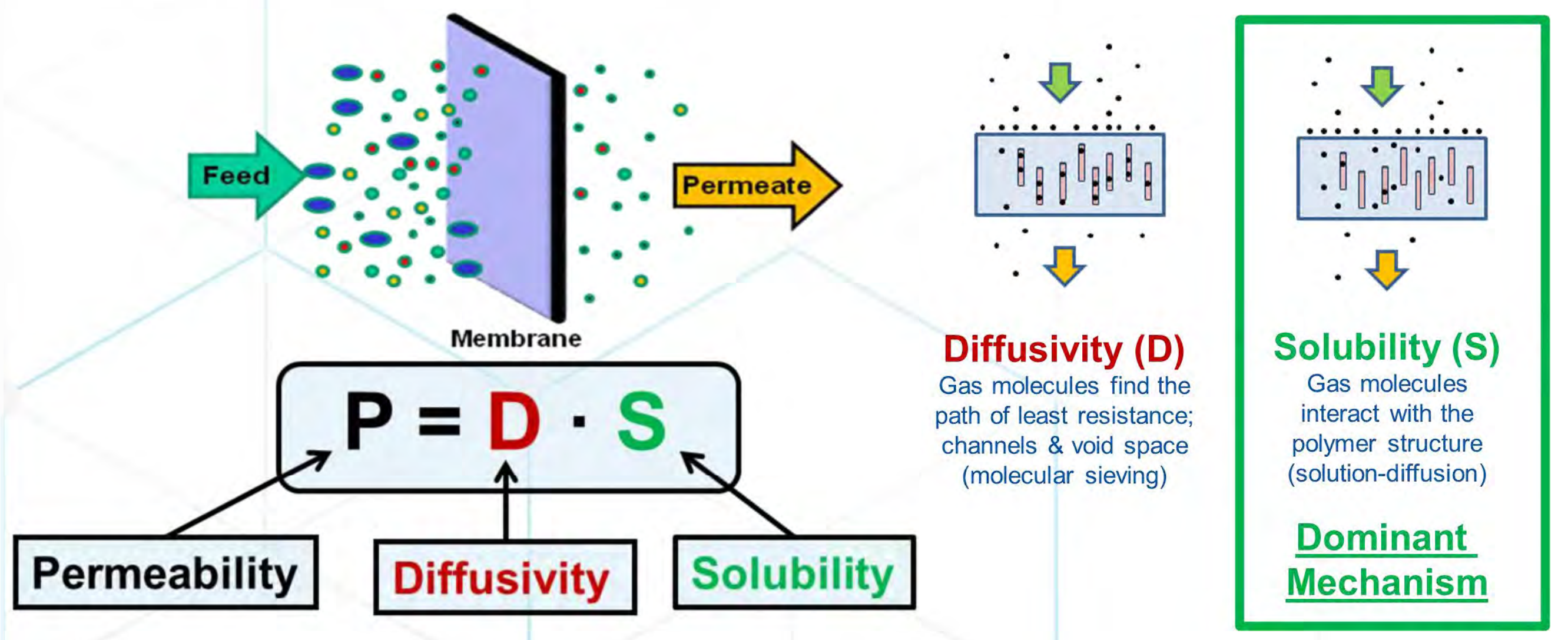
Application: Point-source generation and purification of ethylene (electrocatalytic processes).

Challenge: Ethylene production is not selective. Thus, a downstream separation process is required to obtain a purified product. Current industrial processes, such as cryogenic separations, require long ramp-up time and energy to achieve temperatures for ethylene separations. This prevents their use with intermittent energy source (or for associated load leveling applications).

Solution: Separations with minimal operation delay time to collect ethylene.

METHODS

Facilitate Transport Membrane (FTM) assembly and module fabrication were analyzed with mixed-gas permeability using GC.



Diffusivity (D)
Gas molecules find the path of least resistance; channels & void space (molecular sieving)

Solubility (S)
Gas molecules interact with the polymer structure (solution-diffusion)

Dominant Mechanism

50/50 Ethane-Ethylene ~200 hrs exposure

Membrane After Gas Permeability Testing

RESULTS

- Silver(I) salts were added with PDMS to form the FTM for ethylene (C_2H_4).
- Is easily fabricated and potentially scaled.
- Gas permeability with the PDMS FTM can switch among gas mixes and still maintain C_2H_4 production with CO_2, CO, CH_4, N_2, C_2H_6 and H_2.
- C_2H_4 separation ratio is up to 150 for C_2H_4 over C_2H_6, and C_2H_4 permeation up to 200 GPU for 50 vol%, 10 vol% and 2 vol% ethylene gas mixtures.
- Water vapor does not affect C_2H_4 transport.
- Ag FTM remains active for ethylene ***after 30 days***, while exposed to various gas mixtures.
- Larger scale module designs were made by UToledo and tested. (*INL IDR – BA-1307*)

Project Number: 21A1050-072FP

LRS Number: INL/PRO-20-57362

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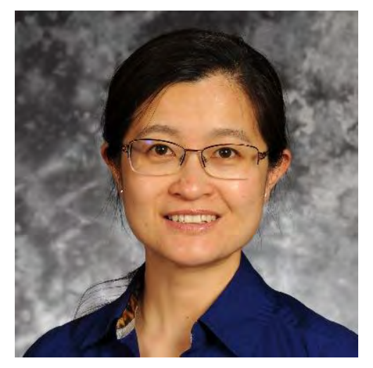
Sulfate Double Salts:
Using Recycled Nickel and Cobalt Sources to Produce Cathodes in Lithium-ion Batteries



PRESENTER:

Meng Shi

Bor-Rong Chen, Pete L. Barnes,
Luis A. Diaz Aldana, John R. Klaehn,
Tedd E. Lister

Idaho National Laboratory (INL)

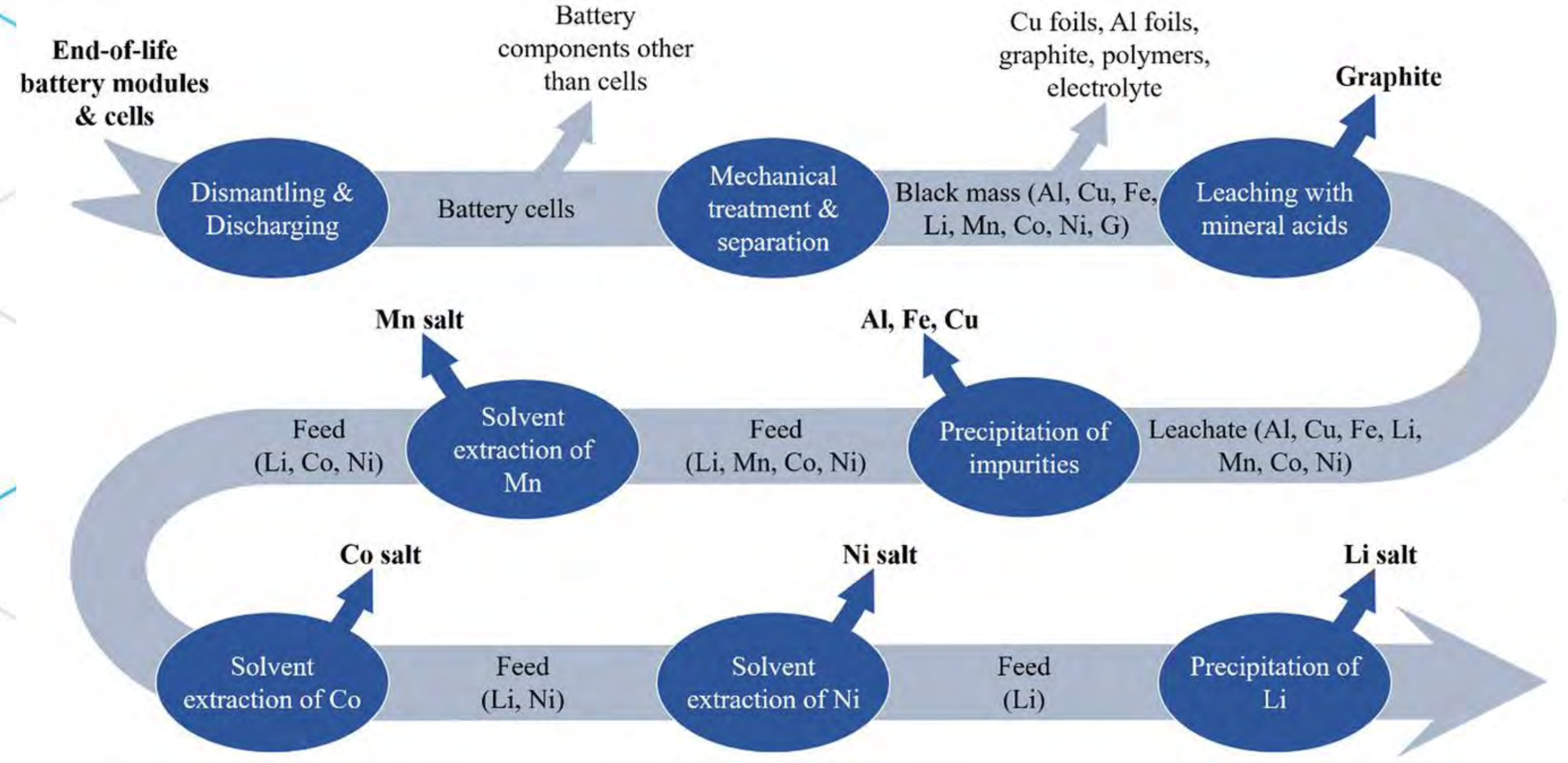
BACKGROUND:

- Ni and Co are costly elements in NMC cathode.
- Global supply chains have been unsecured.

To secure domestic Co and Ni resources

→ Recycle and reuse batteries

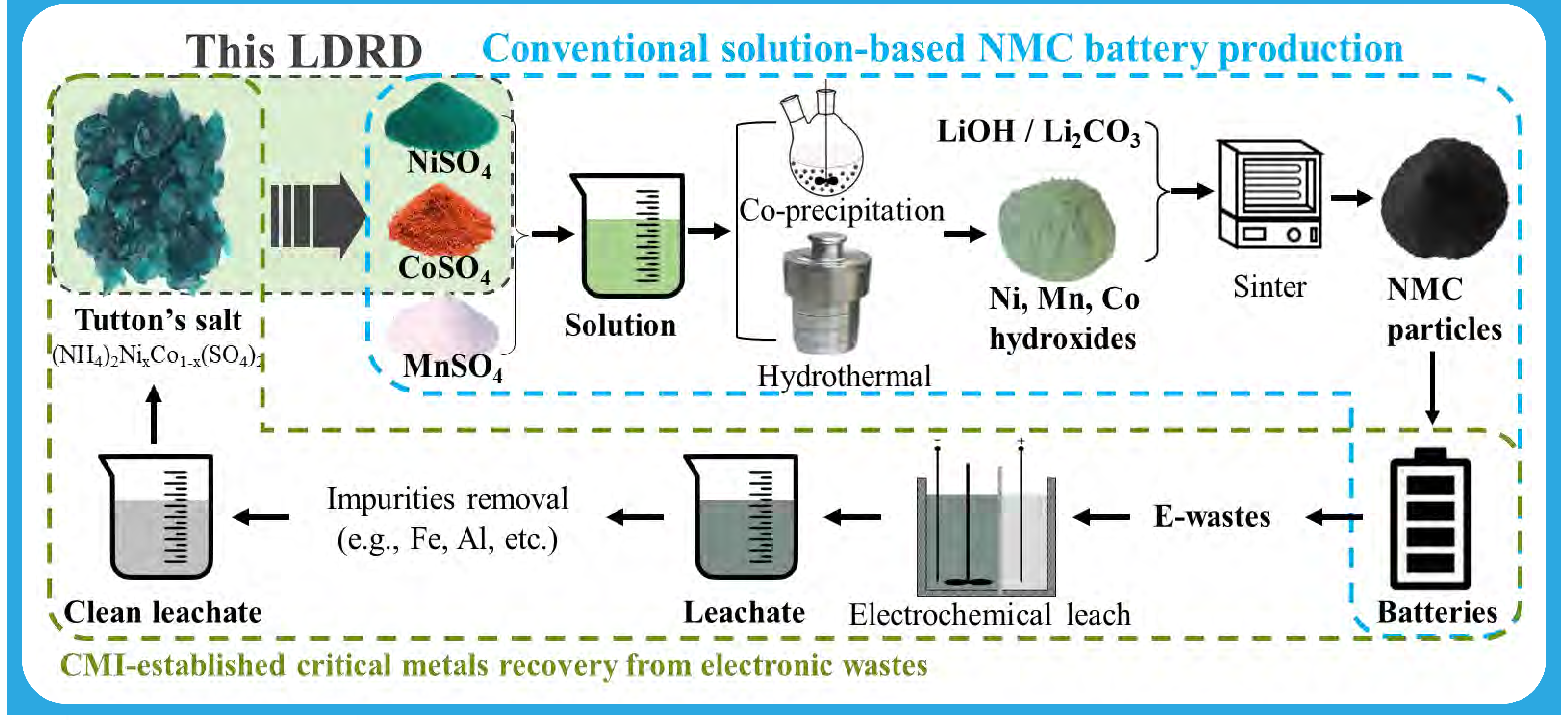
- Traditional hydrometallurgical processing is complicated.



Neumann, J., et al., Advanced Energy Materials, 2022. 12(17): p. 2102917.

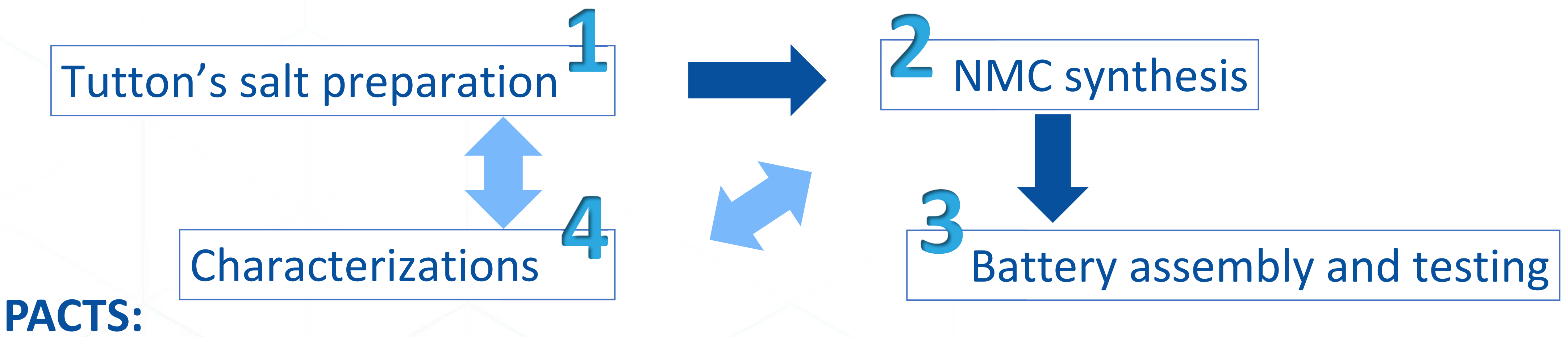
- INL developed a key technology in Ni and Co co-recovery through a fast and cheap process.
- There is no previous study on battery manufacturing using **Tutton's salt** **$(NH_4)_2Ni_xCo_{1-x}(SO_4)_2{\cdot}6H_2O$**.

This project bridges a technology gap by synthesizing new cathodes with isolated metals from recycled lithium-ion batteries.



METHODS:

Use commercial Tutton's salt as the surrogate

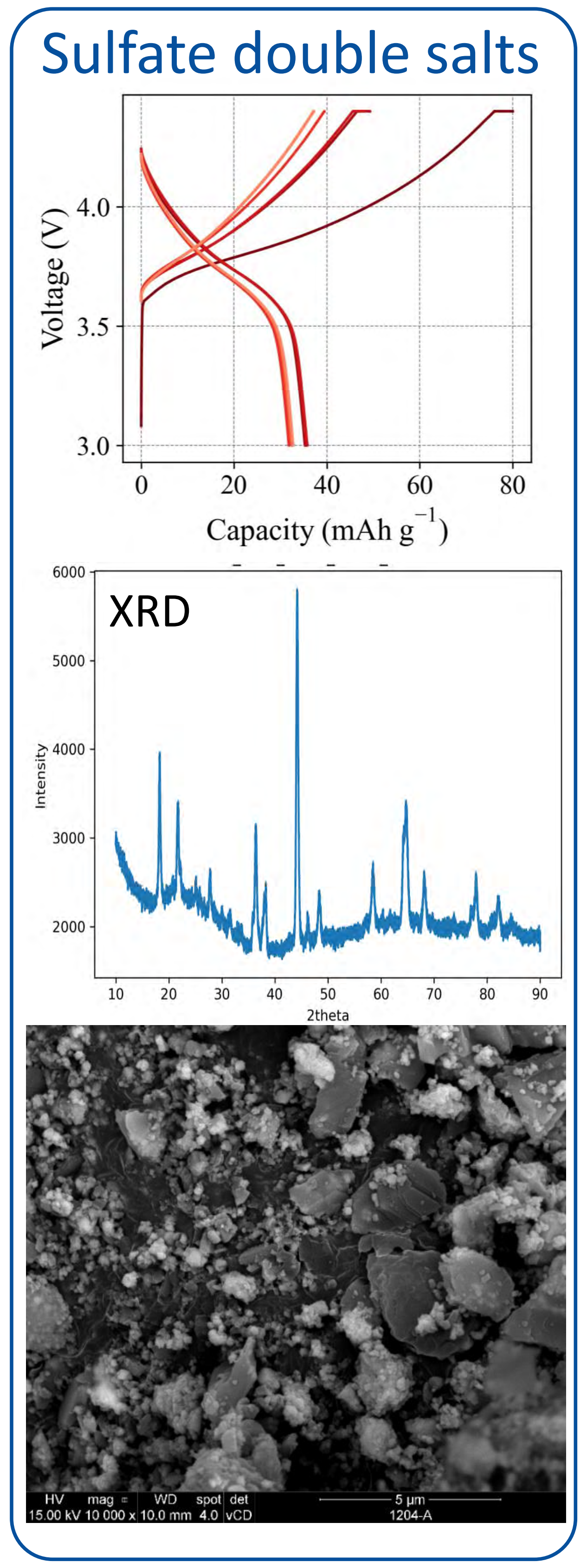


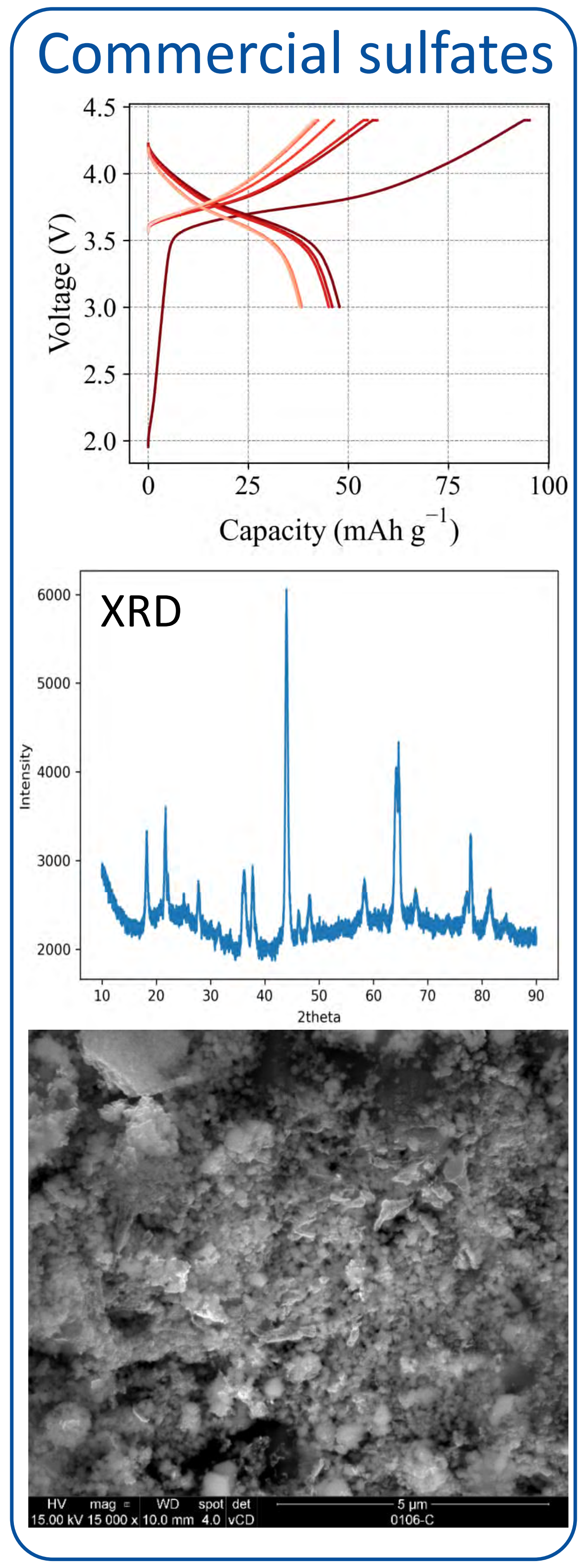
IMPACTS:

- Develop new manufacturing methodology for NMC cathodes
- Provide a pathway to digest spent Li-ion batteries
- Simplify battery recycle process
- Secure the Co and Ni sources

RESULTS:

- **Proof of concept:** A new NMC battery cathode can be made from recycled Tutton's salts, which diversifies the supply chain of critical materials and closes the loop of lithium-ion battery recycling process
- Similar battery performances for conventional and non-conventional transition metal sources





Project Number: 22P1071-018FP

LRS Number: INL/PRO-22-67659

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Idaho National Laboratory

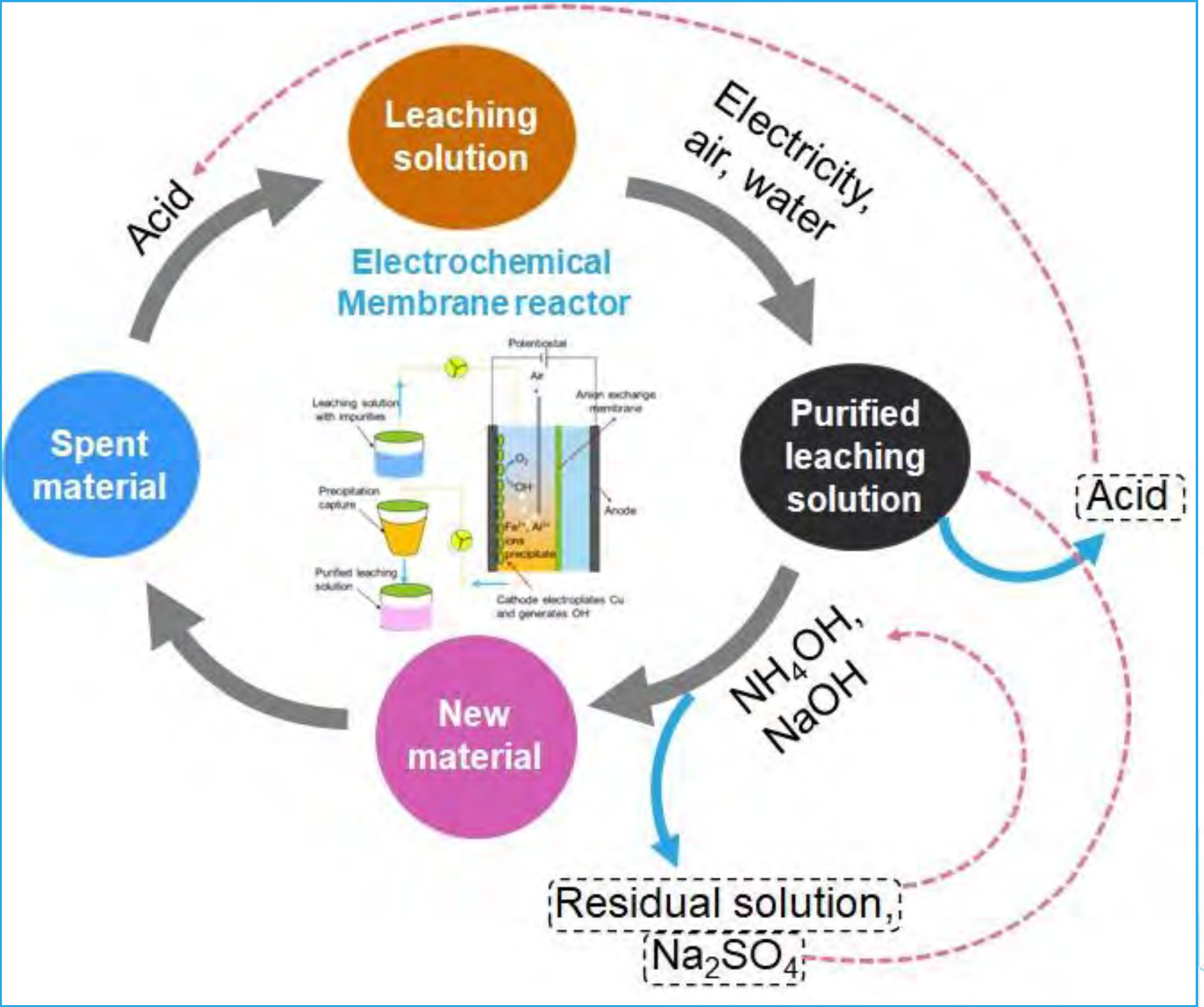
Recovery of High Purity Critical Elements from Spent Lithium-Ion Batteries (LIB) without Waste Emission

PRESENTER

Qiang Wang, Robert V. Fox

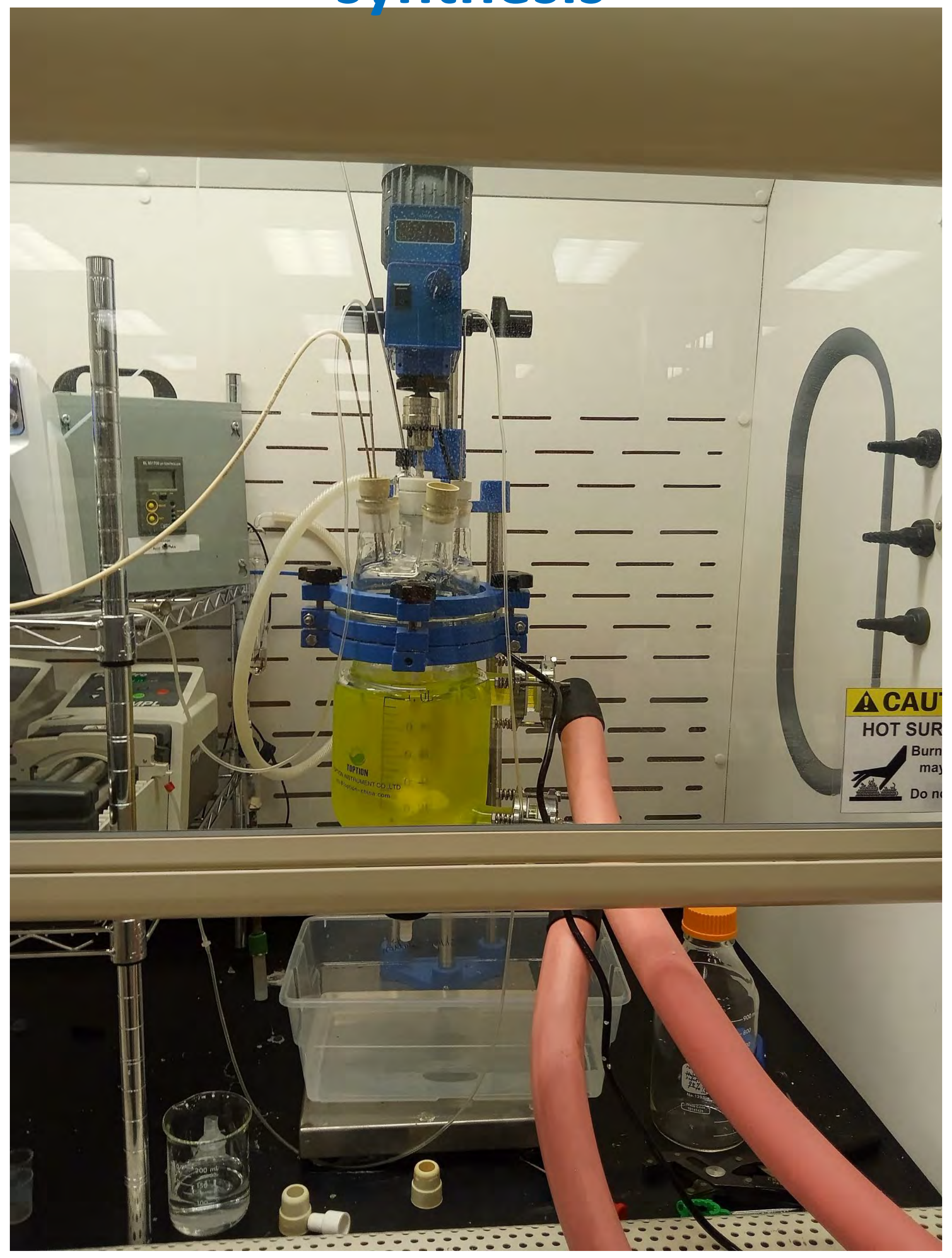
Background

In the process of close-loop recycling LIB, purified leaching solution is applied to synthesize $Ni_xMn_yCo_z(OH)_2$ precursor, generating residual solution, being rich in Na_2SO_4 and NH_4OH. Can the solution be re-used as NH_4OH resource? How Na_2SO_4 influences $Ni_xCo_yMn_z(OH)_2$ precursor co-precipitation?

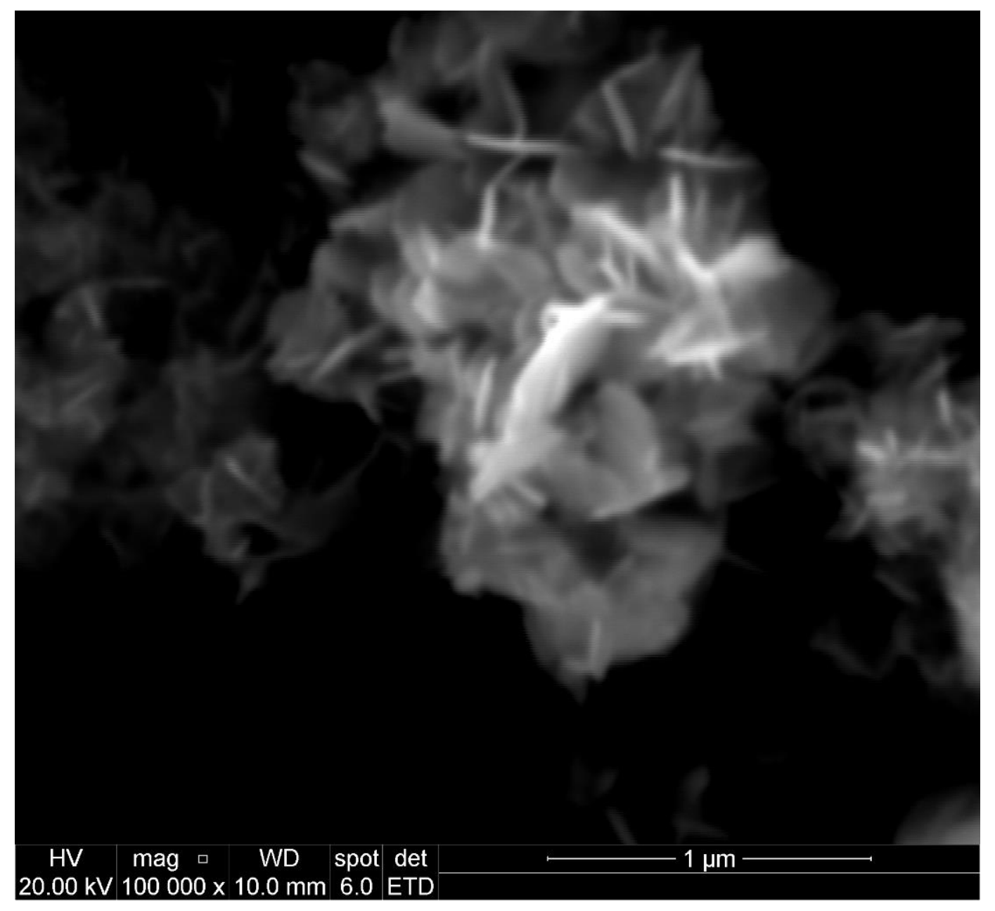


A flowsheet to achieve a high atom economy and no waste emission to close-loop recycling spent LIB

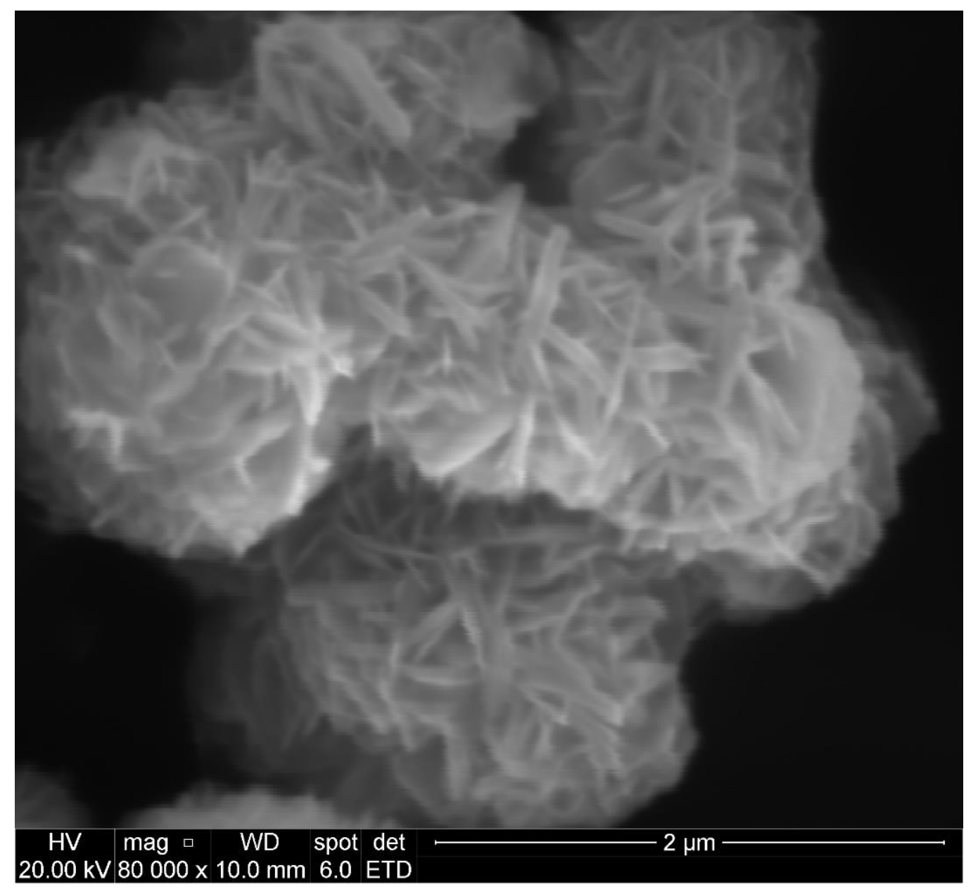
Hydro-thermal reactor for $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ precursor synthesis



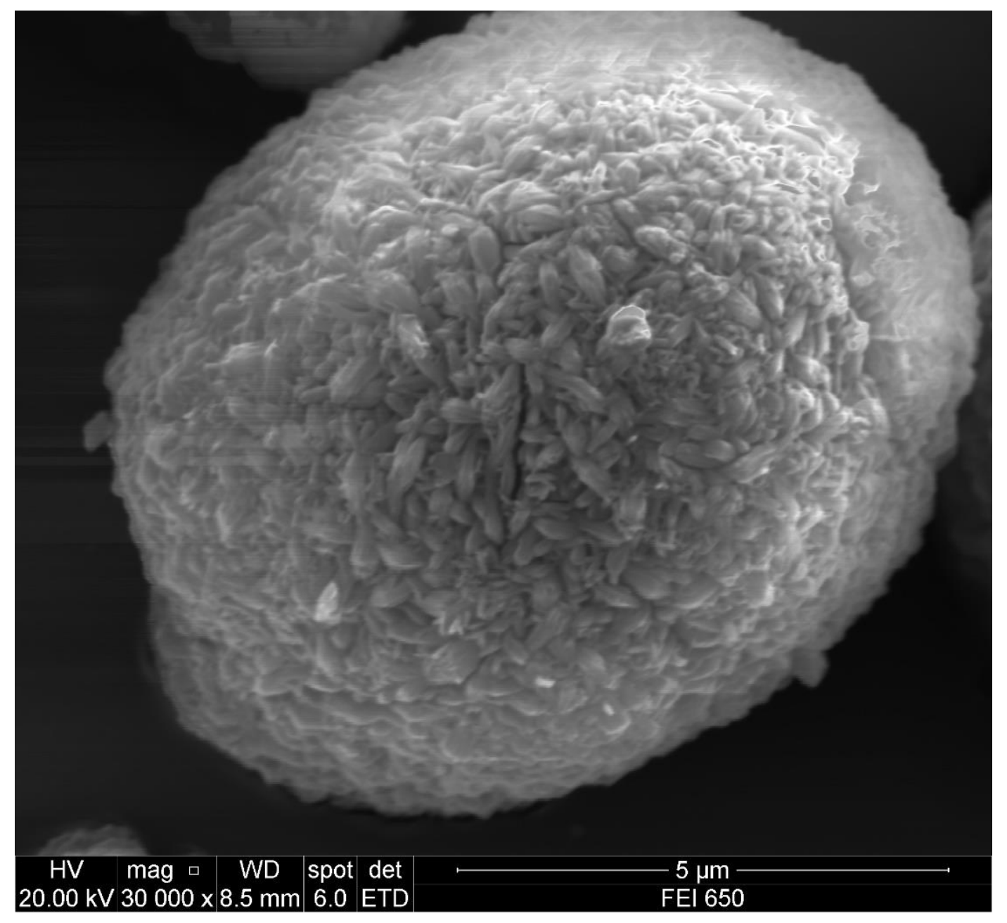
$Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ precursor Crystallization mechanism



Signal crystal to cluster

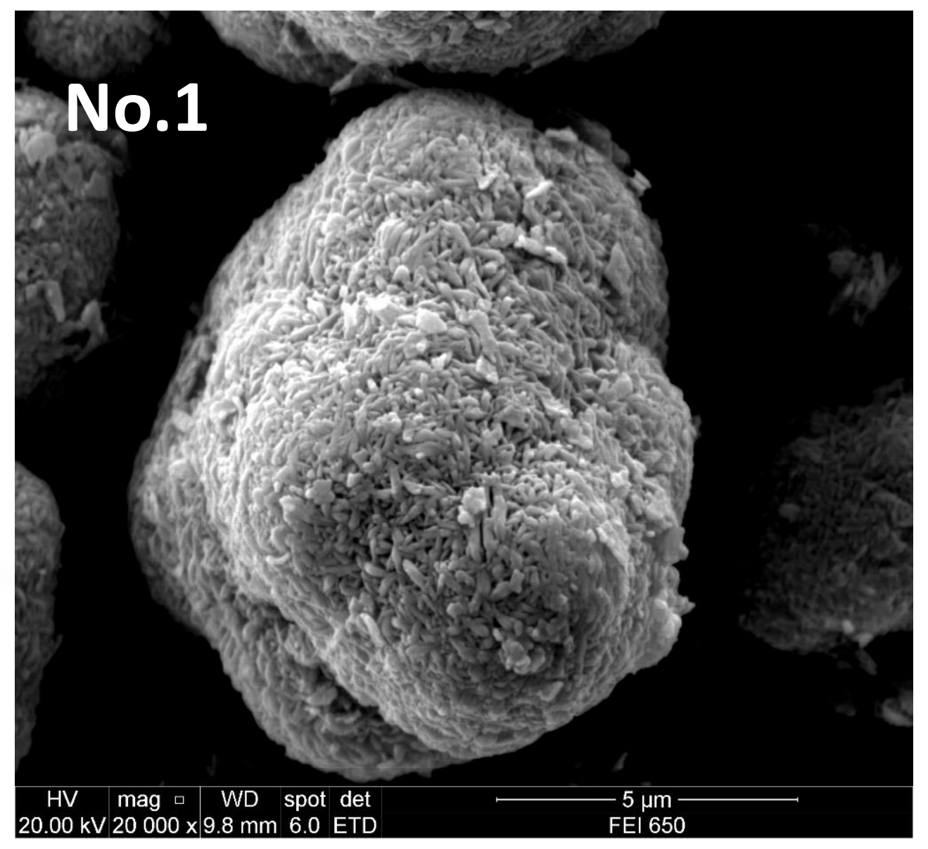


Cluster aggregation



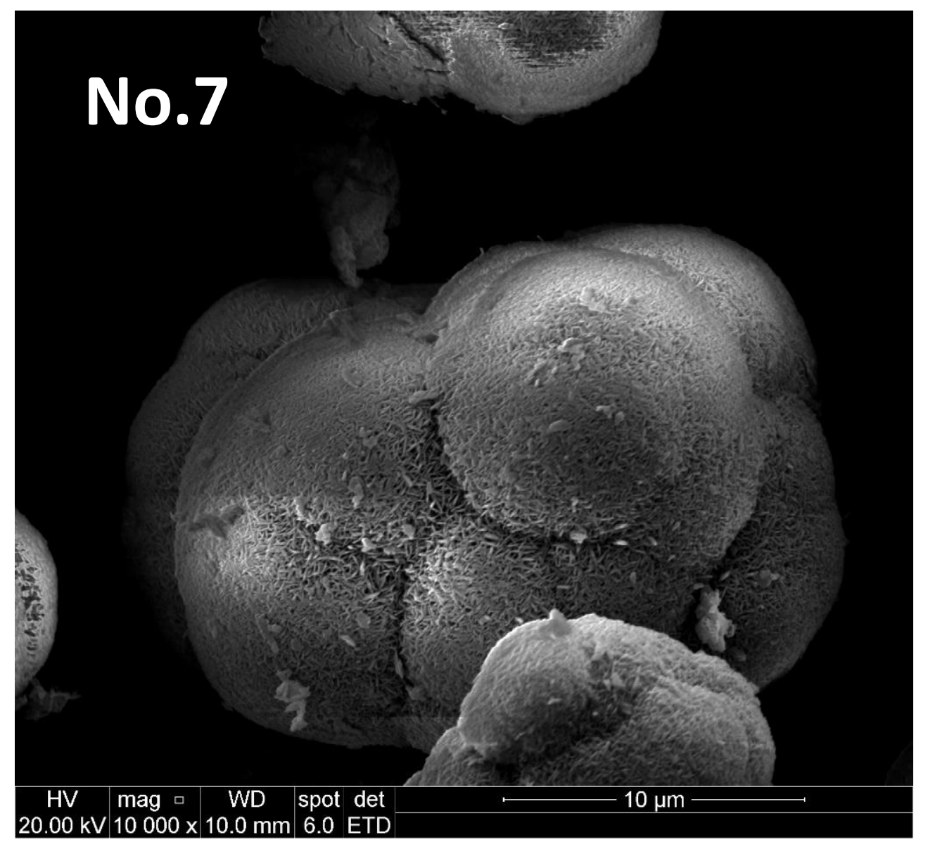
Aggregation plumping

No.1



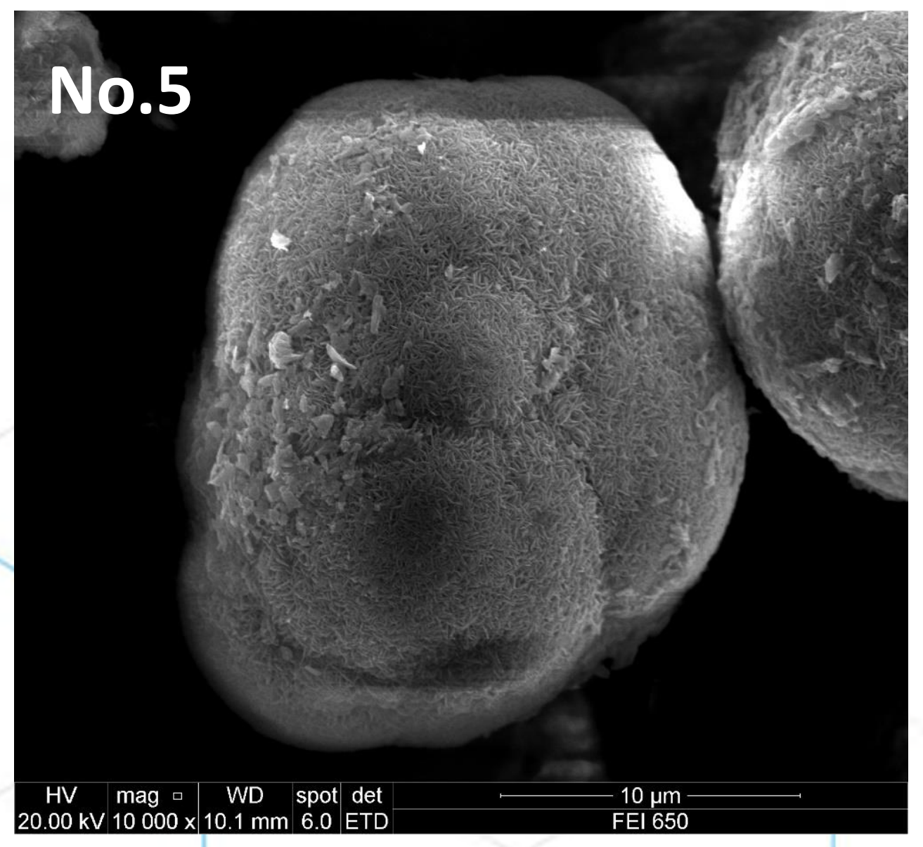
Dense surface, aspherical secondary particle

No.7



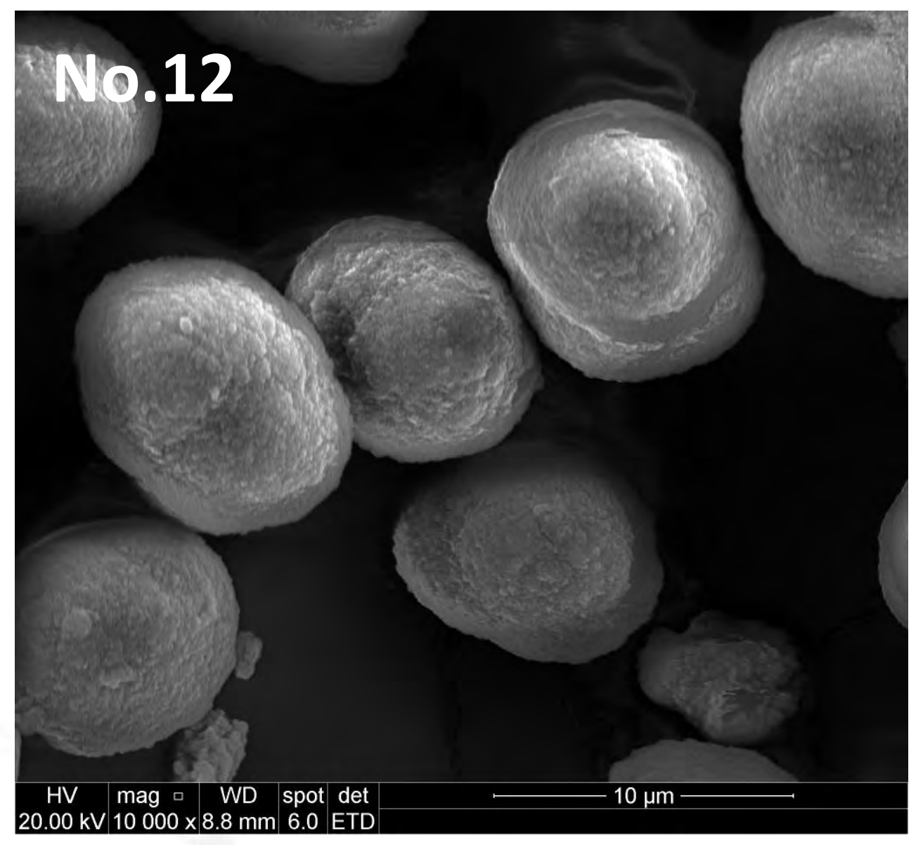
Thin flake primary particle, aspherical secondary particle

No.5



Thin flake primary particle

No.12



Dense surface, spherical secondary particle

Limited Influence from Na_2SO_4 impurity on precipitation

Exp No.	Temperature	Reaction time	NH_4OH/Metal ratio	pH	Impurity	Tape Density
1	xx °C	xx hours	xx	xx	no	1.81 g·cm^{-3}
2	xx °C	xx hours	xx	xx	no	1.89 g·cm^{-3}
3	xx °C	xx hours	xx	xx	no	1.92 g·cm^{-3}
4	xx °C	xx hours	xx	xx	no	1.81 g·cm^{-3}
5	xx °C	xx hours	xx	xx	no	1.79 g·cm^{-3}
6	xx °C	xx hours	xx	xx	no	1.85 g·cm^{-3}
7	xx °C	xx hours	xx	xx	no	1.62 g·cm^{-3}
8	xx °C	xx hours	xx	xx	no	1.69 g·cm^{-3}
9	xx °C	xx hours	xx	xx	no	1.86 g·cm^{-3}
10	xx °C	xx hours	xx	xx	no	1.94 g·cm^{-3}
11	xx °C	xx hours	xx	xx	no	1.99 g·cm^{-3}
12	xx °C	xx hours	xx	xx	Na_2SO_4	1.98 g·cm^{-3}

Conclusion: Through investigating synthesis conditions systematically, an optimized condition was found to be able to synthesize $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ precursor with tap density 1.99 g·cm^{-1} > literature reported value 1.91 g·cm^{-1}. Applying this synthesis condition, metal sulfate solution with high Na_2SO_4 impurity was able to synthesize high quality precursor with tap density 1.98 g·cm^{-1}. The residual solution was evidenced to be able to re-use as NH_4OH resource for precursor synthesis, eliminating waste.

Project Number: 22P1071-027FP

LRS Number: RPT-23-74315

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Idaho National Laboratory

Methane Upgrading Using Dynamic Energy Supply

PRESENTER:

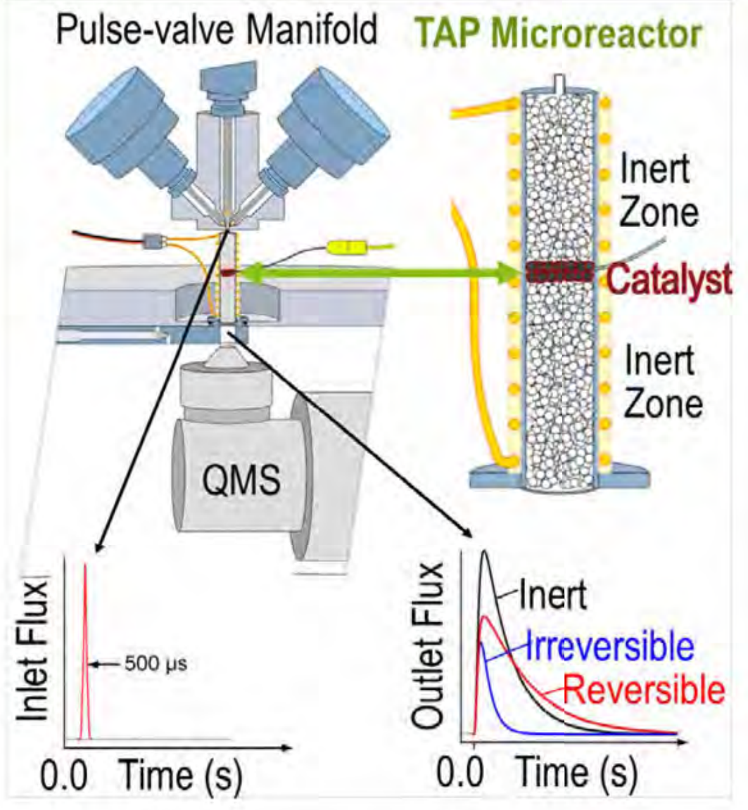
Debtanu Maiti

Rebecca Fushimi[1], Erin Sobchinsky[1,2], Debtanu Maiti[1], Yixiao Wang[1], Zongtang Fang[1], Rakesh Batchu[1]

[1] Catalysis and Transient Kinetics Group, Idaho National Laboratory

[2] Lehigh University

Methods



TAP investigation of methane dehydroaromatization

- State altering pulses to probe transient evolution of active sites
- Characterization of redox states of MoO_xC_y-clusters

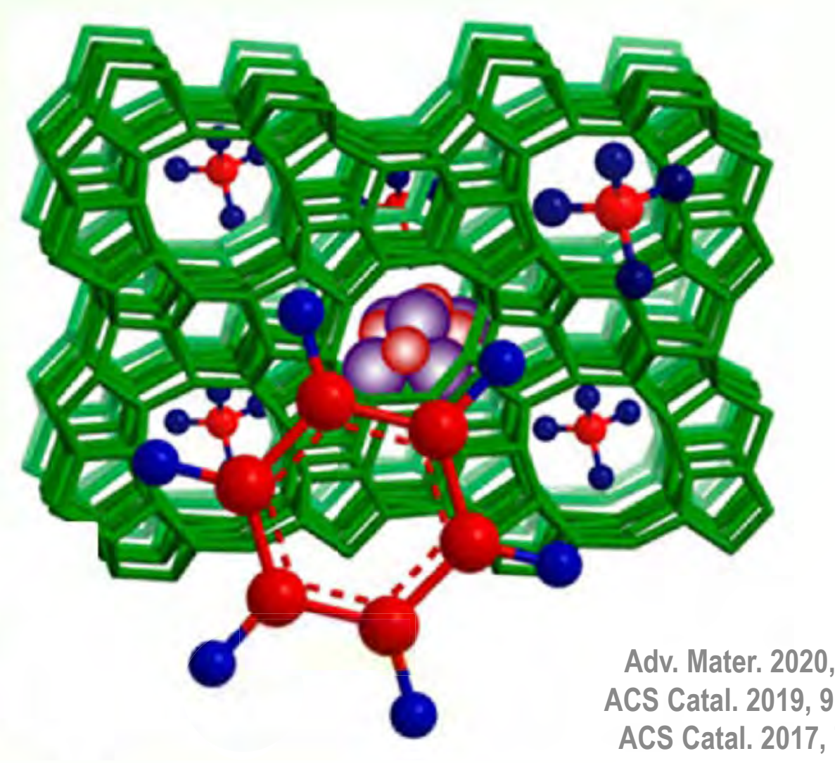
Temporal Analysis of Products (TAP) Reactor

Key advantages

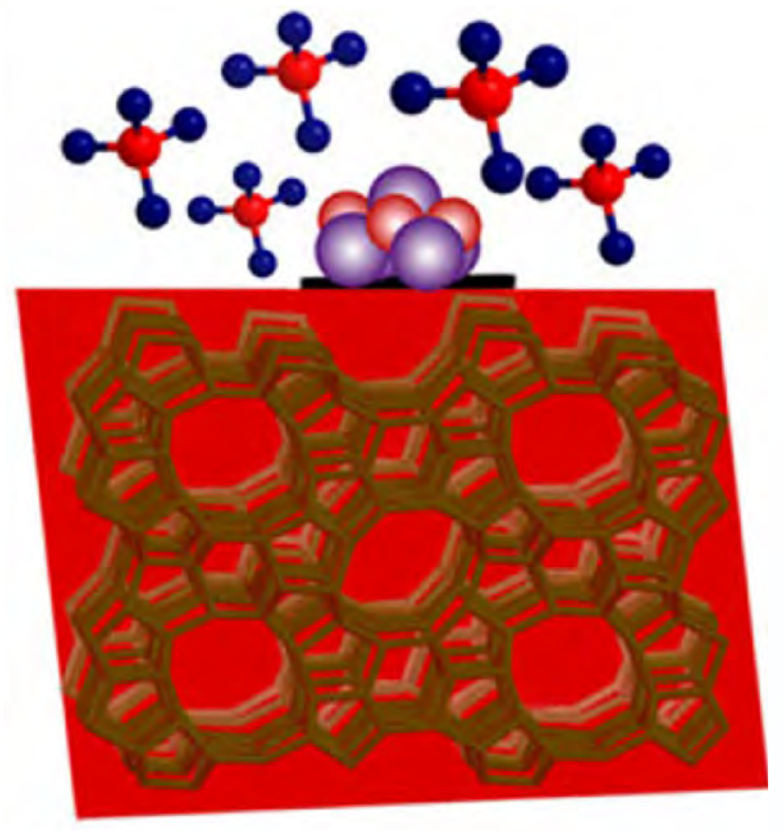
- Nanomole size pulses (Knudsen) – state defining experiments
- In situ kinetic characterization of catalysts at reaction temperatures
- Gas-gas interactions eliminated; Insight of only gas-solid interactions

Material Characteristics

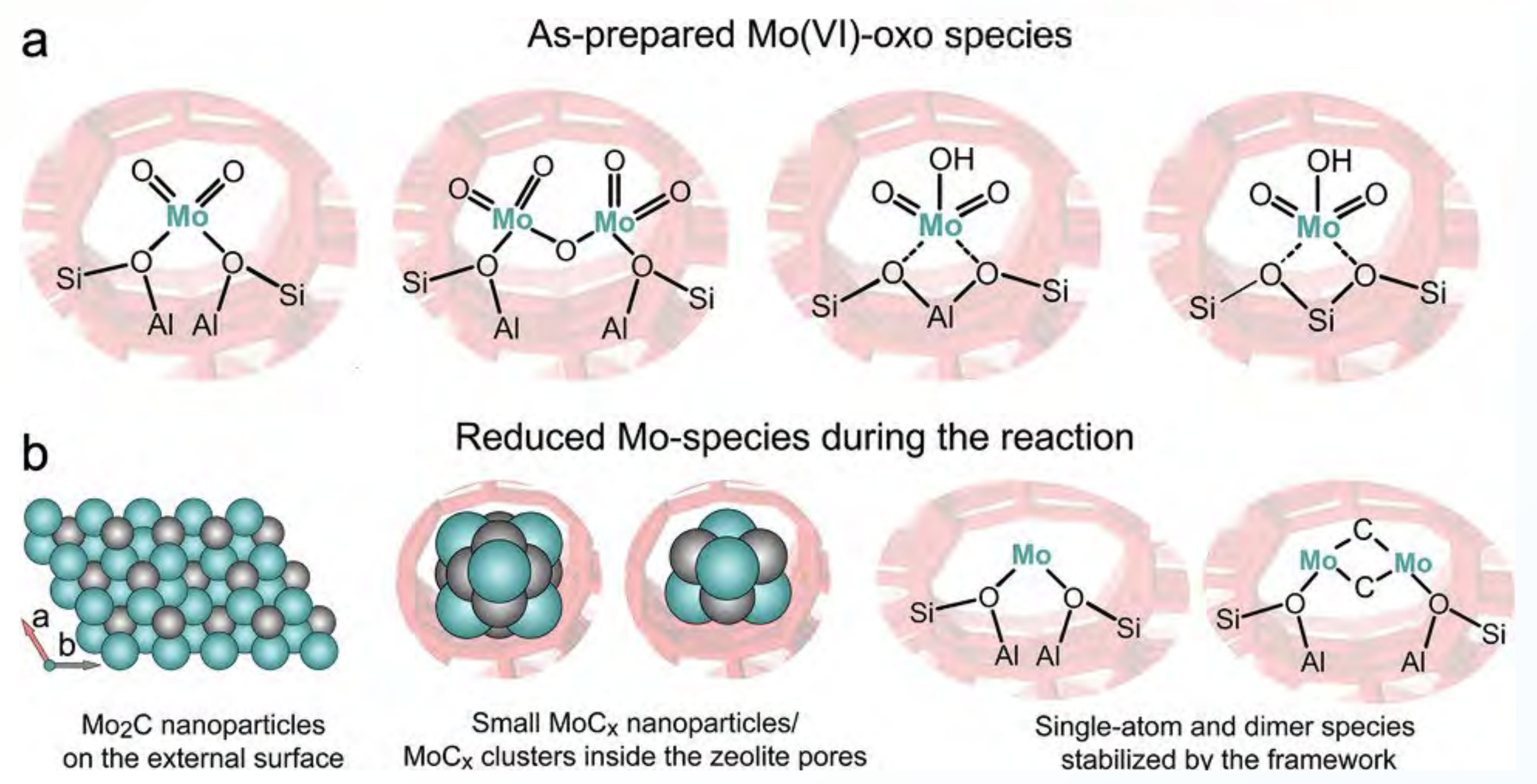
MoC_x inside zeolite pores



MoC_x outside zeolite pores



Adv. Mater. 2020, 32, 2002565;
ACS Catal. 2019, 9, 9, 8731–8737;
ACS Catal. 2017, 7, 1, 520–529;



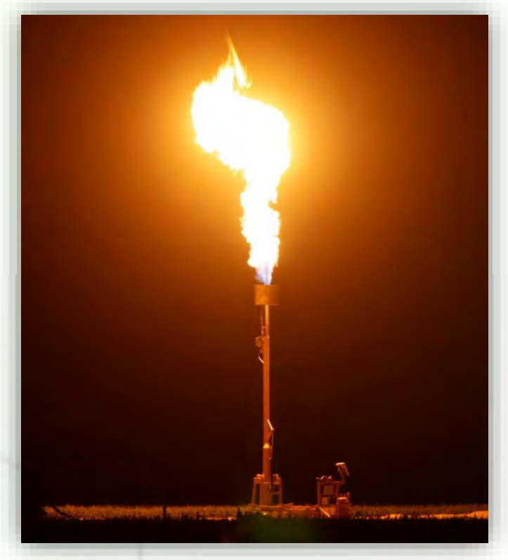
Mo2C nanoparticles on the external surface

Small MoCx nanoparticles/ MoCx clusters inside the zeolite pores

Single-atom and dimer species stabilized by the framework

Background

Vast abundance of U.S. Natural Gas (CH_4)

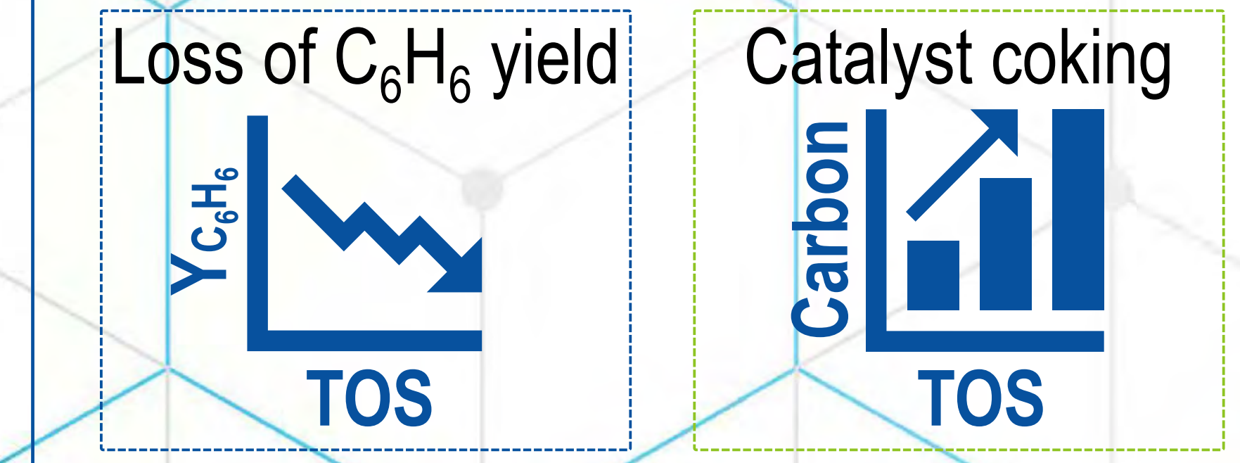


CH_4 flaring → Greenhouse gas emissions

Global benzene market size
USD 22.4 Billion (2021)

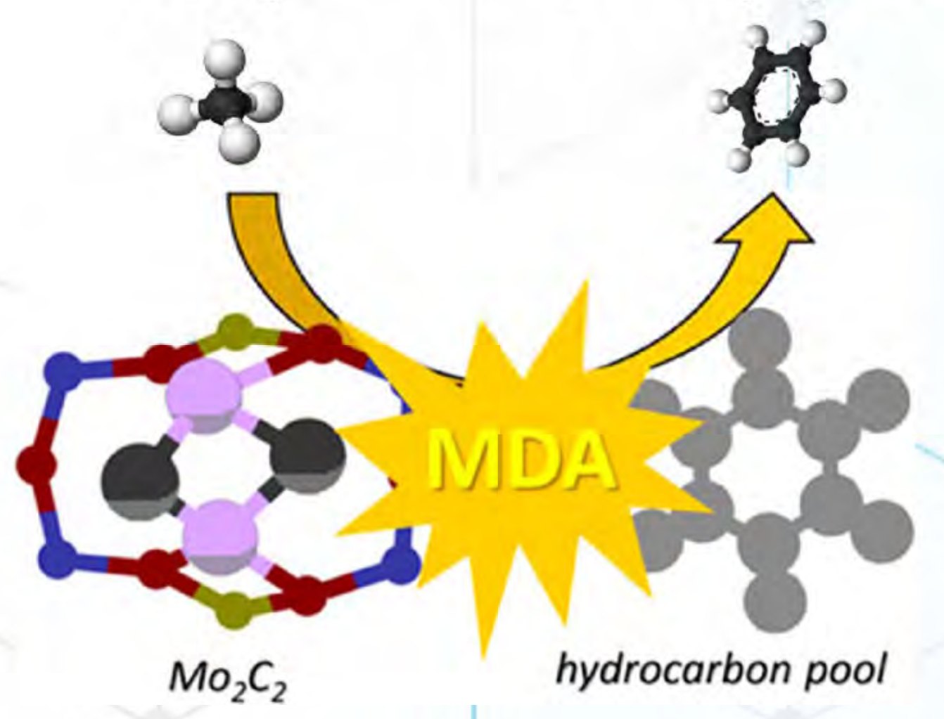
Methane Dehydroaromatization (MDA) can directly convert abundant domestic methane to more valuable benzene and hydrogen. A key challenge is rapid deactivation of the Mo-ZSM5 catalyst by carbon deposition. An intensified process with periodic reaction/regeneration was investigated.

Time-on-stream (TOS) trends:

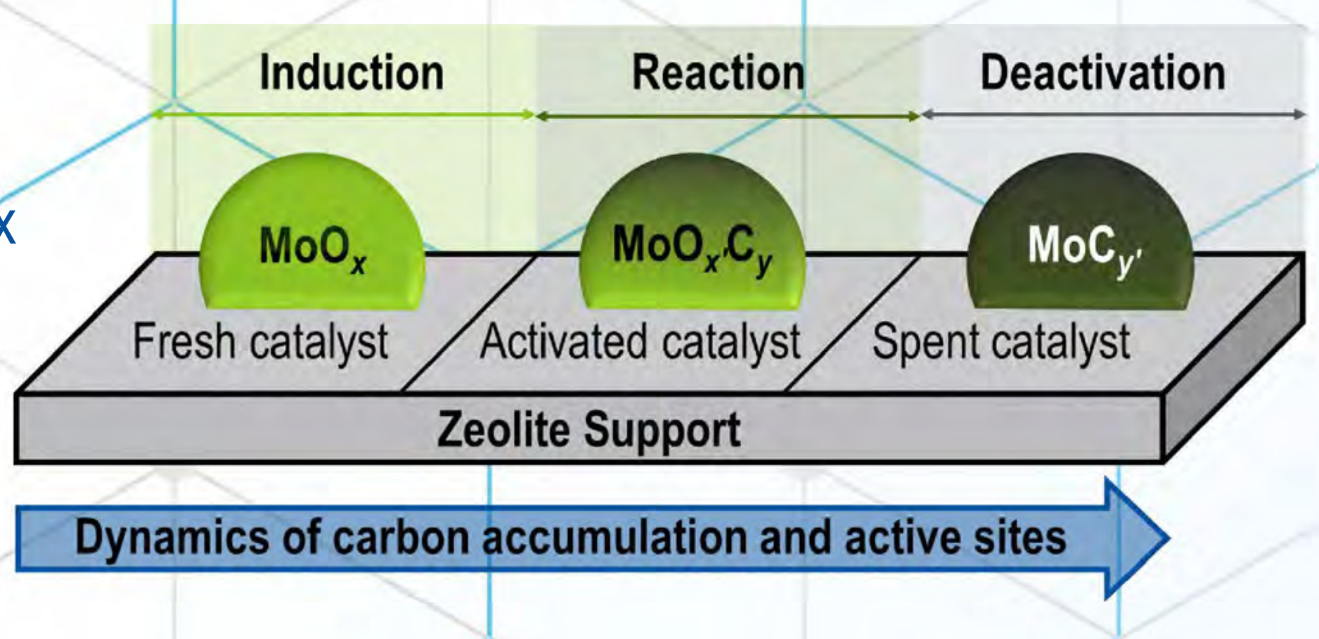


Catalytic non-oxidative pathway

$$6\,CH_4 \longrightarrow C_6H_6 + 9\,H_2$$



- **Goal:** high yield of C_6H_6, with high selectivity
  mitigate coking of active sites
- **Challenge: dynamic nature of active sites** –
  metal (Mo) dispersion, redox state of Mo-sites, Mo-anchoring sites, Brønsted acidity of zeolites



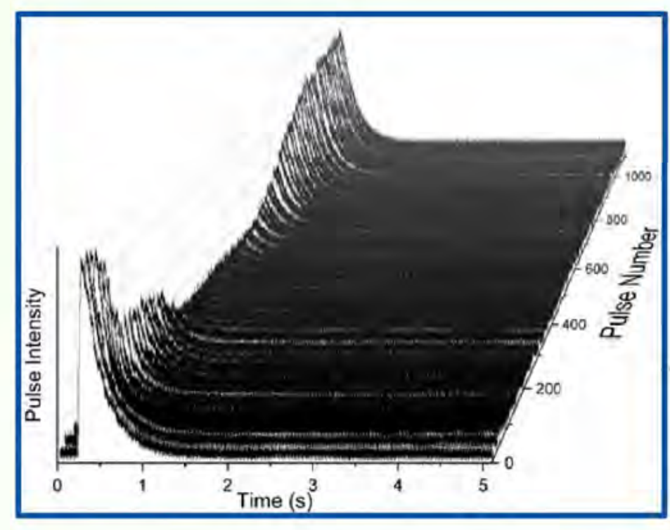
Effect of Reduction Pretreatment

As-synthesized catalyst

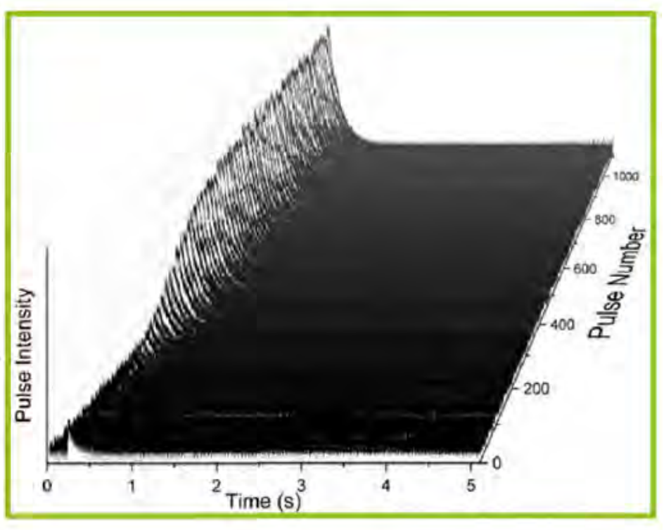
Reduced catalyst

Ethane pulsing to probe dehydroaromatization

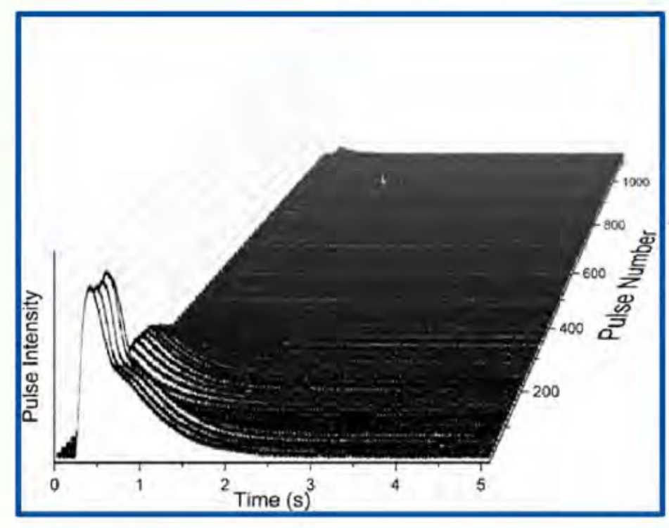
Increased ethane uptake on reduced catalyst



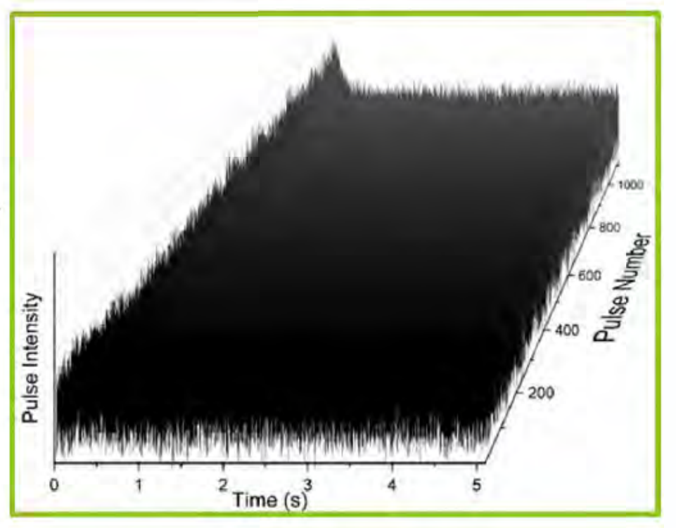
AMU 27 (C_2H_6)

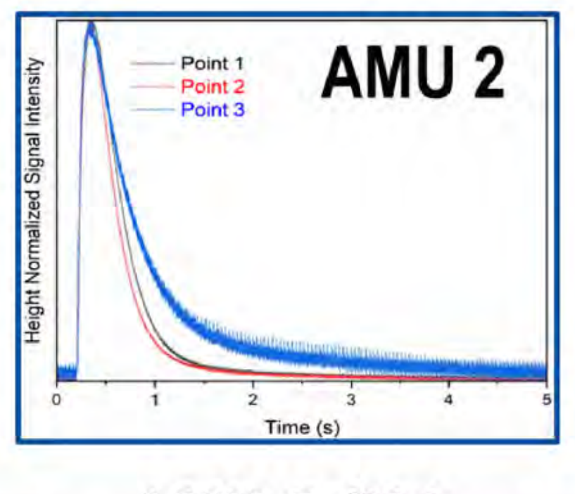


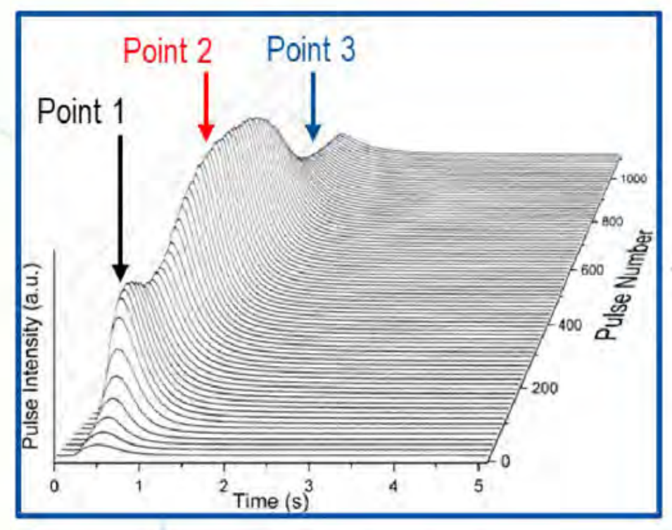
Ethane oxidation by MoO_x species, as detected by CO_2 formation



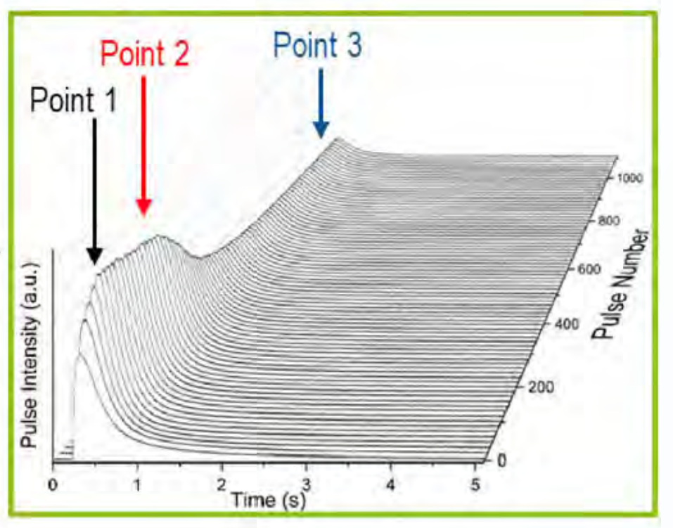
AMU 44 (CO_2)



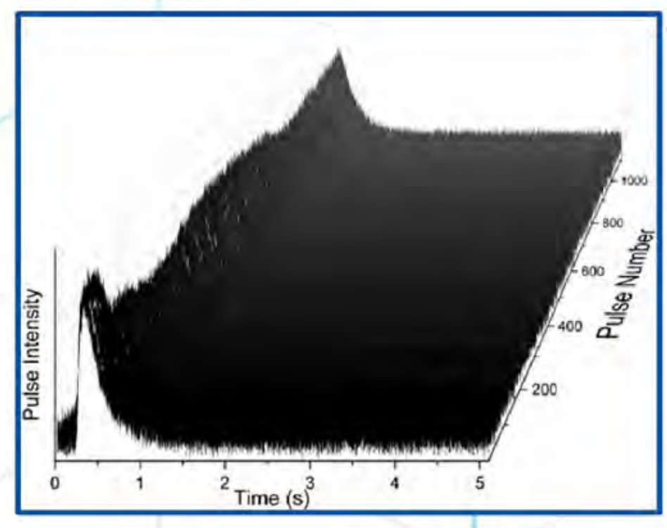




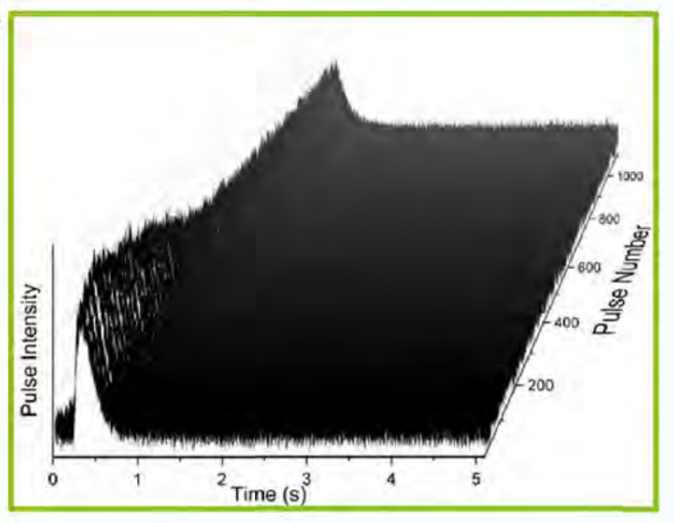
AMU 2 (H_2)

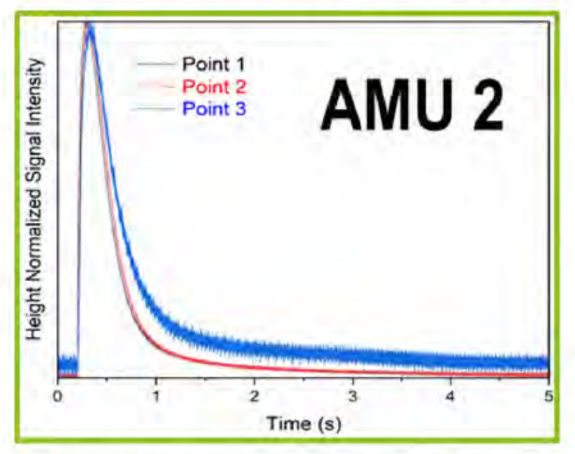


Ethane cracking and/or dehydroaromatization

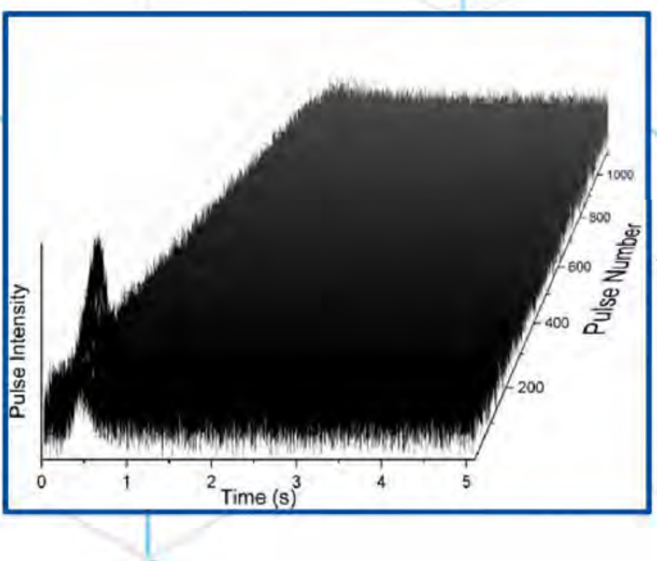


AMU 41 (C_3-C_4)

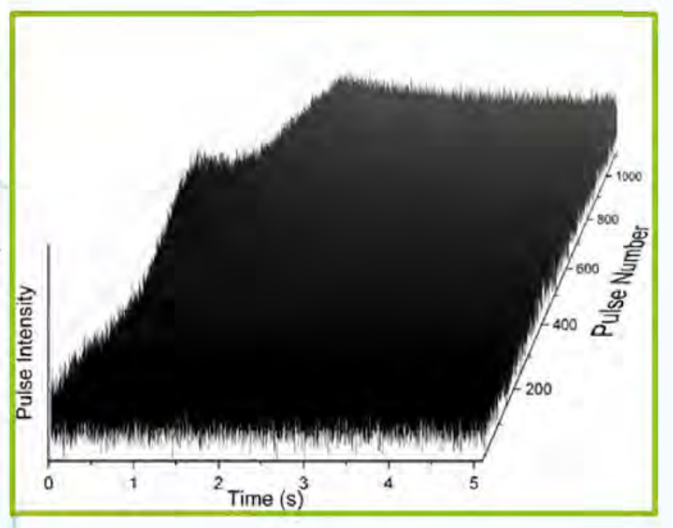




Oxidative reaction on as-synthesized catalyst



AMU 78 (C_6H_6)

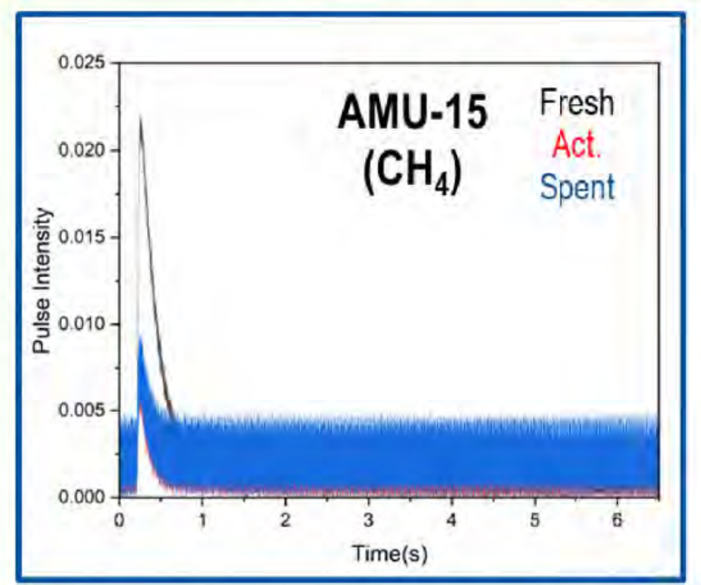


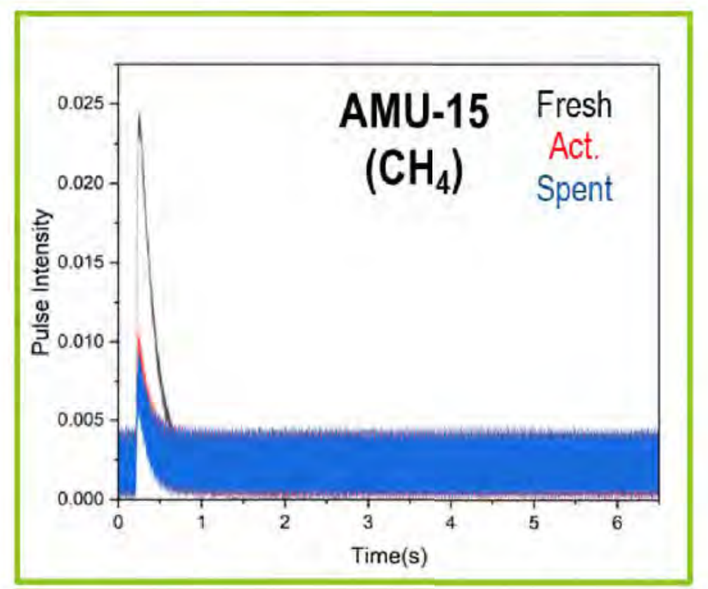
Non-oxidative dehydroaromatization on reduced catalyst

Effect of Brønsted Site Blocking

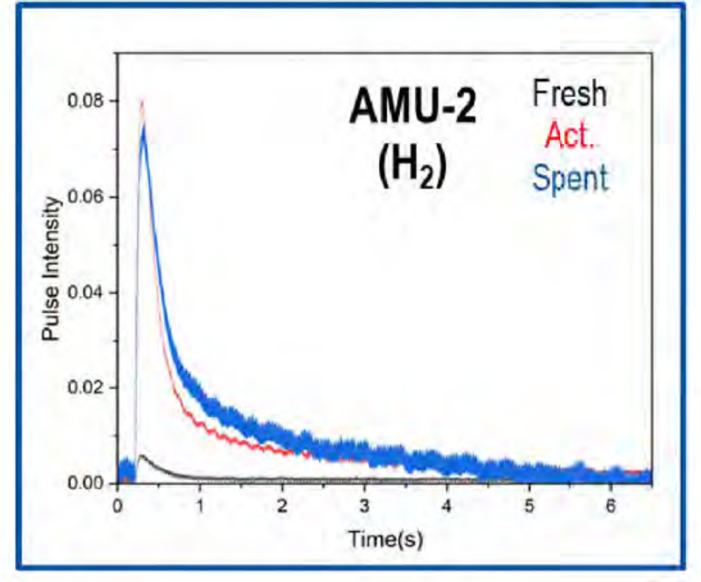
Mo/HZSM-5

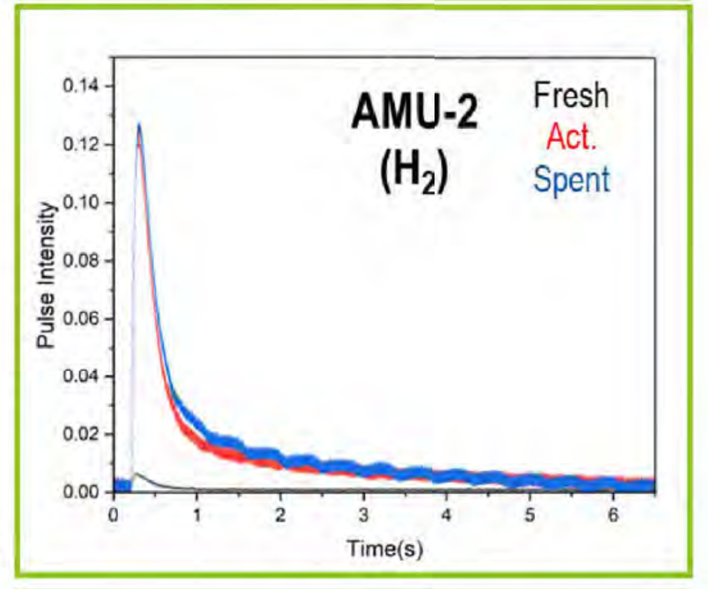
Mo-Si/HZSM-5



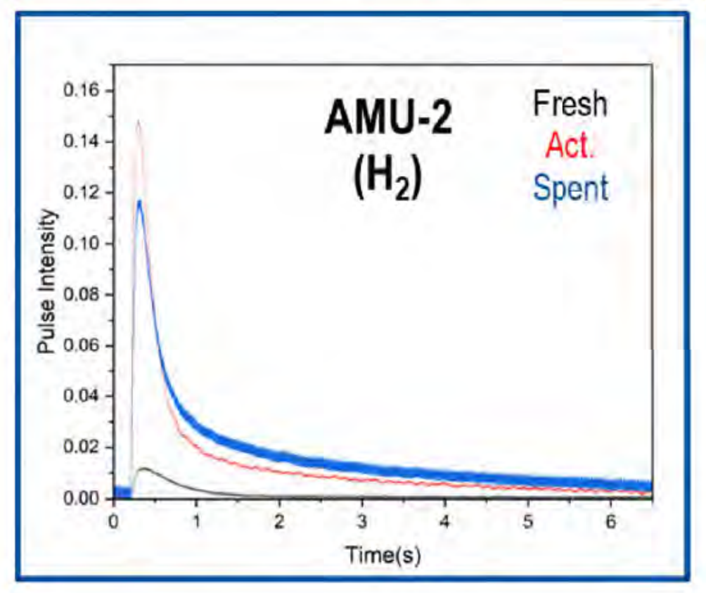


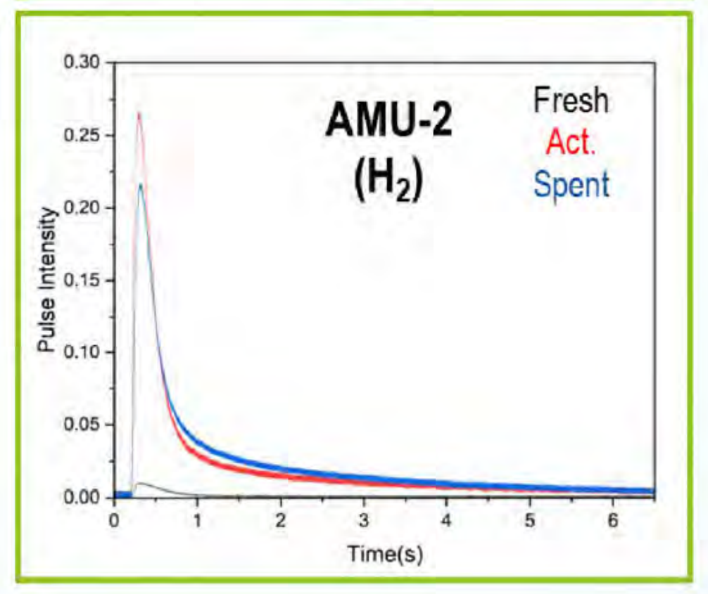
Methane, and ethane pulsing over fresh, activated, and spent catalysts





More methane, and ethane conversion on activated, and spent catalysts





Silicated samples induce more methane or ethane cracking and/or dehydro-aromatization: an indication of varying MoO_xC_y cluster size, and location

Project Number: 21A1050-062

LRS Number: INL/CON-23-73077

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Idaho National Laboratory

Continuous Syngas Production from a New Chemical Looping Concept to Balance Power Dynamics in Integrated Energy System

PRESENTER:

Debtanu Maiti

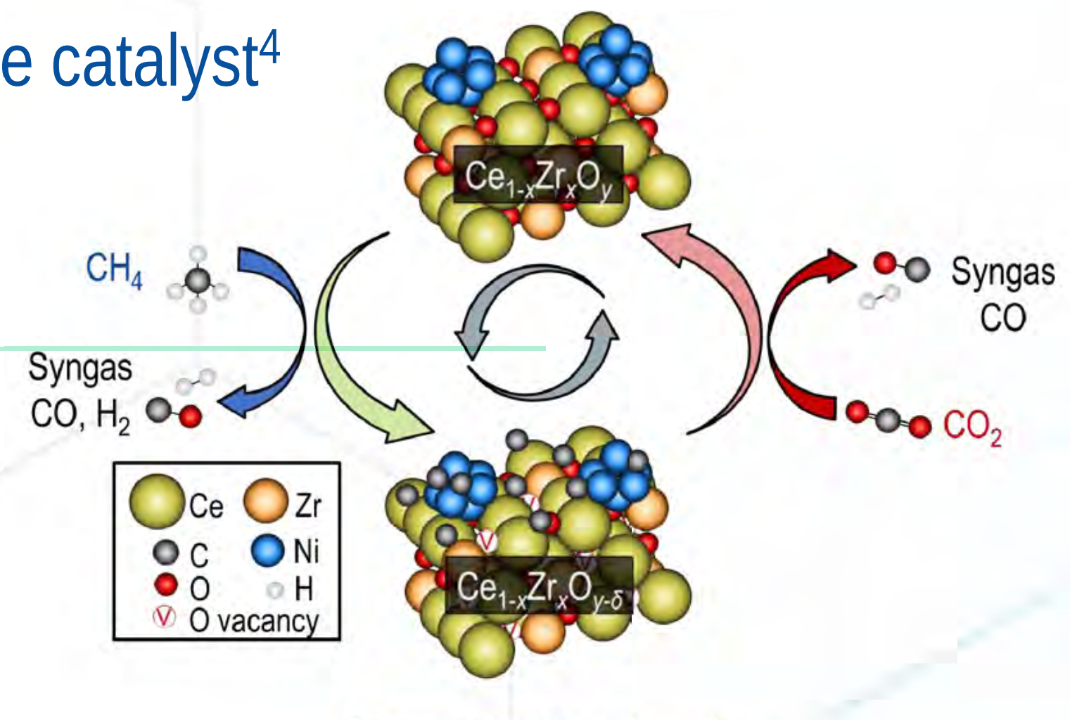
Rebecca Fushimi[1], Debtanu Maiti,[1] Zoe Benedict[1,2], Birendra Adhikari[1]
[1] Catalysis and Transient Kinetics Group, INL [2] University of Maine

Background

- CH_4 and CO2: greenhouse gases (GHGs)

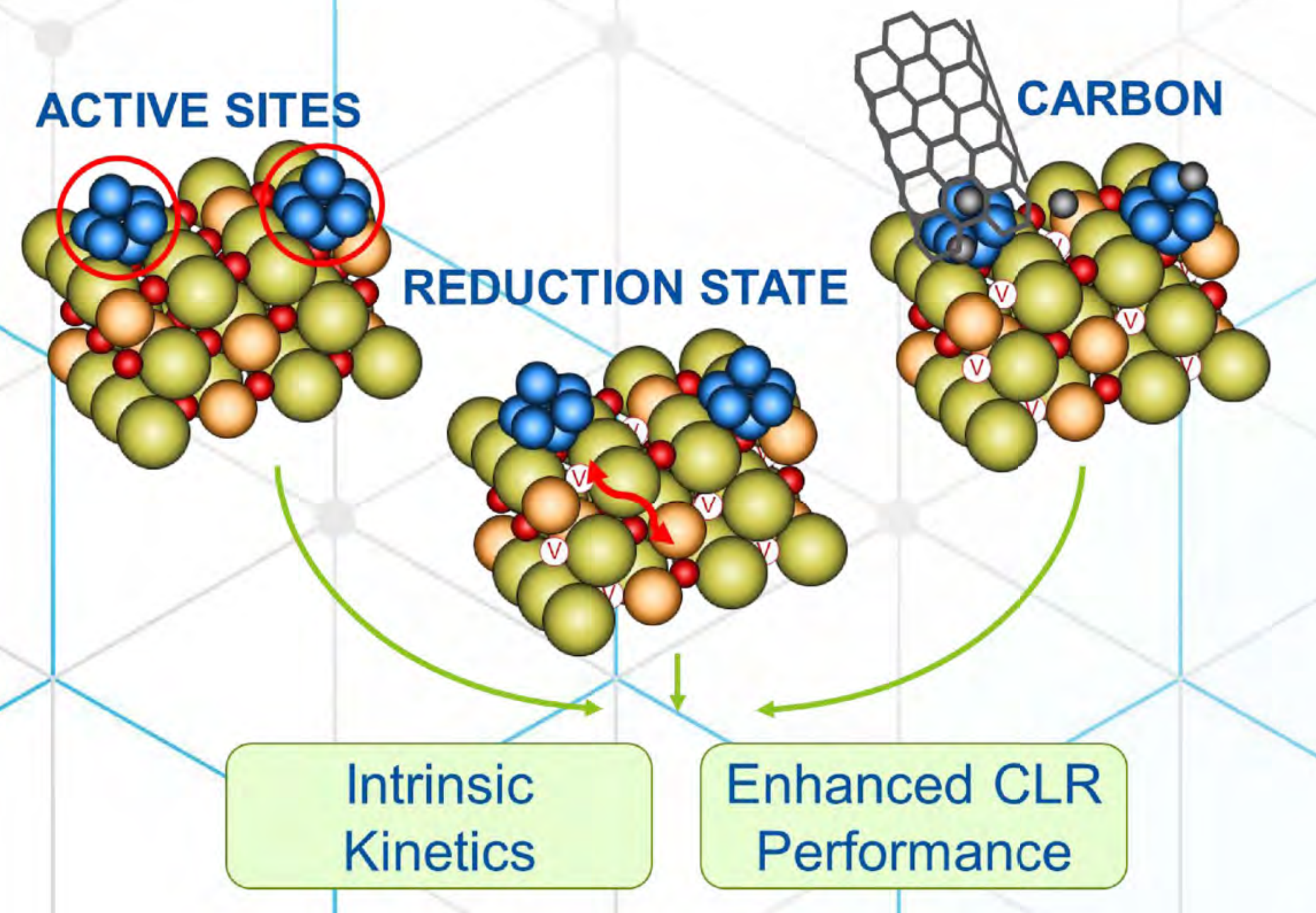
  Catalytic ↓ conversion

- Syngas (CO, H2) → chemicals and fuels[1]
- Chemical looping reforming (CLR): continuous production of syngas over a metal oxide catalyst[2]
- Ni/Ce1-xZrxO2: common catalyst, good oxygen storage capacity, and good CH4 partial oxidation[3]
- CH4 $\xrightarrow{\text{crack}}$ surface C → deactivate catalyst[4]



Chemical looping schematic

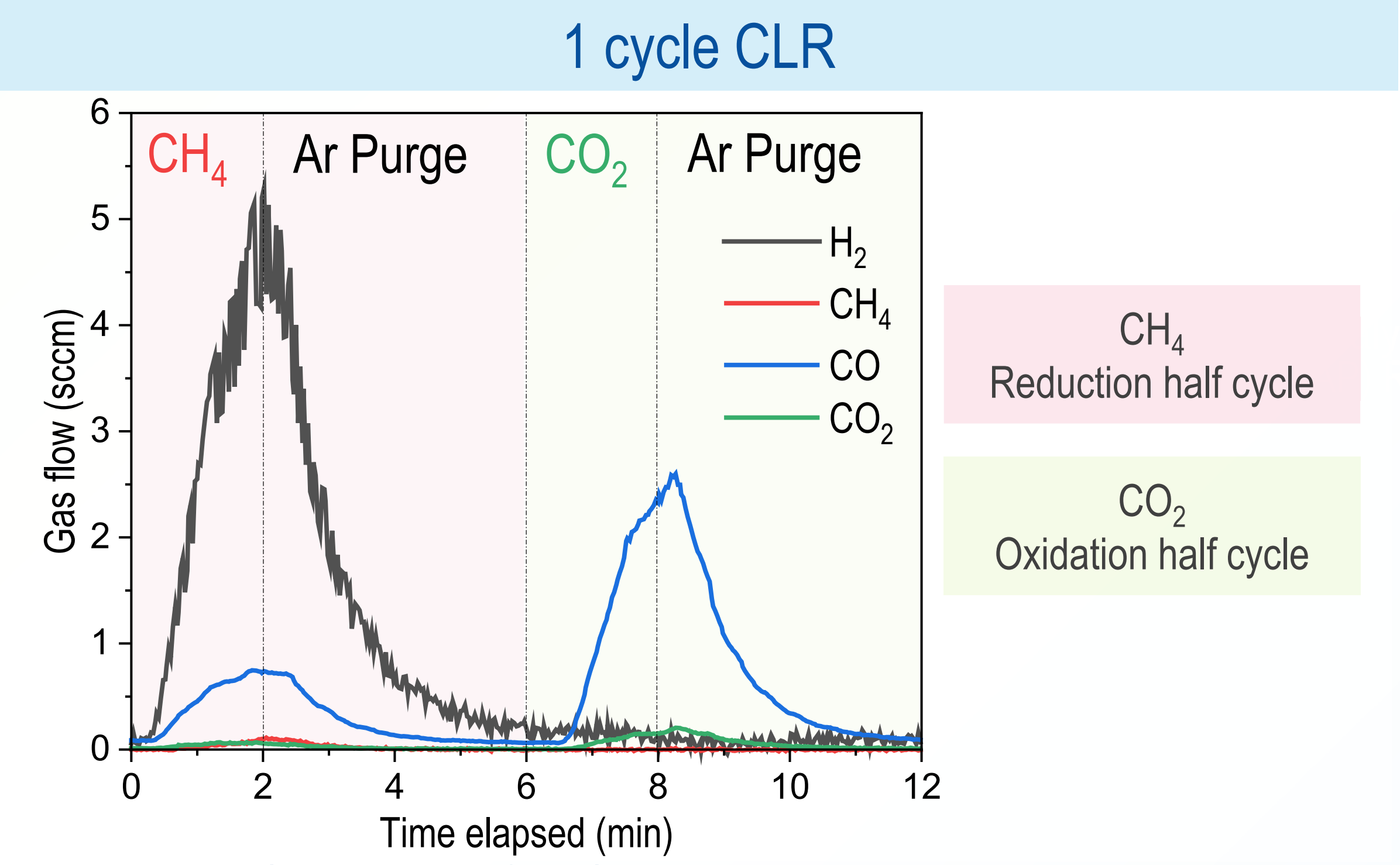
Objective



Improve reaction strategies to control C formed for best reaction kinetics with stable catalyst

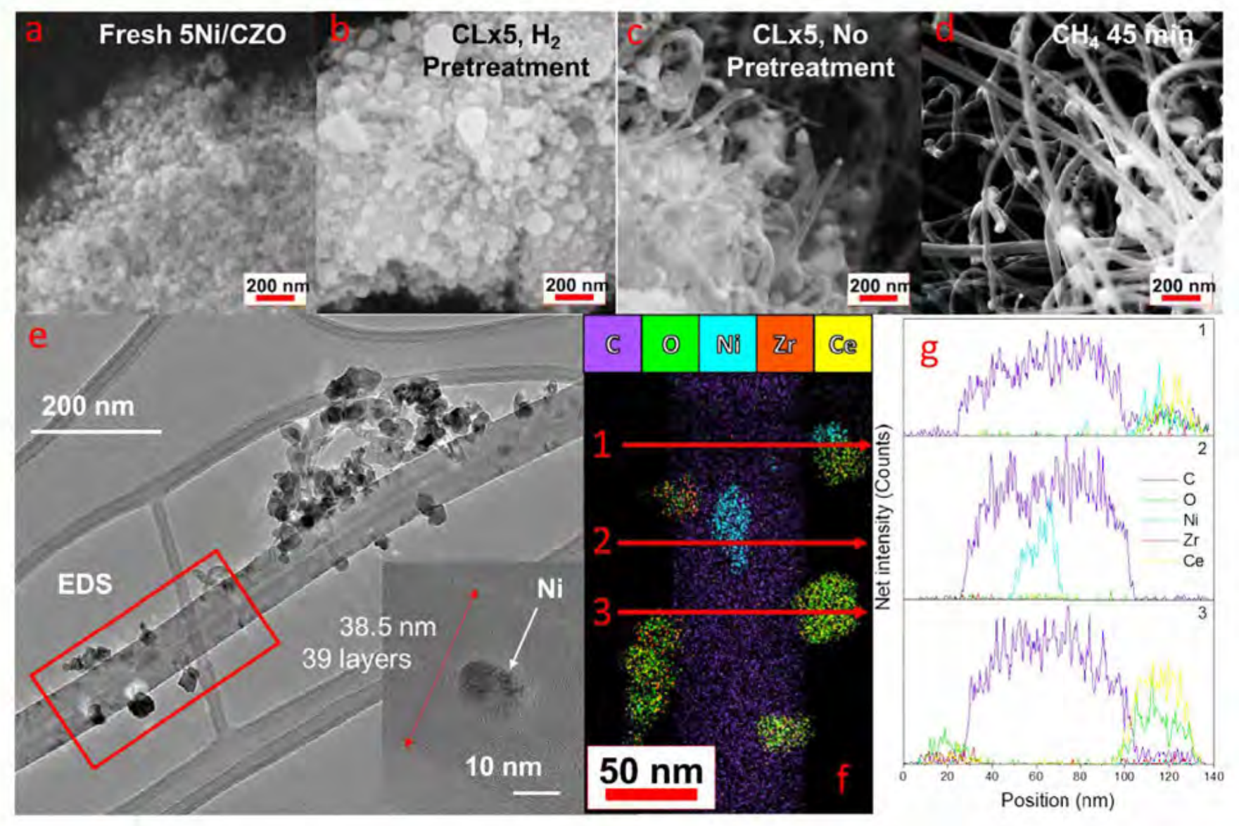
Methods

- CZO wet impregnated with 5 wt.% Ni loading (5Ni/CZO)
- Catalyst performance (10 cycles) CLR in fixed-bed reactor (700 °C, 108 h^{-1} GHSV, 10% pp in Ar)

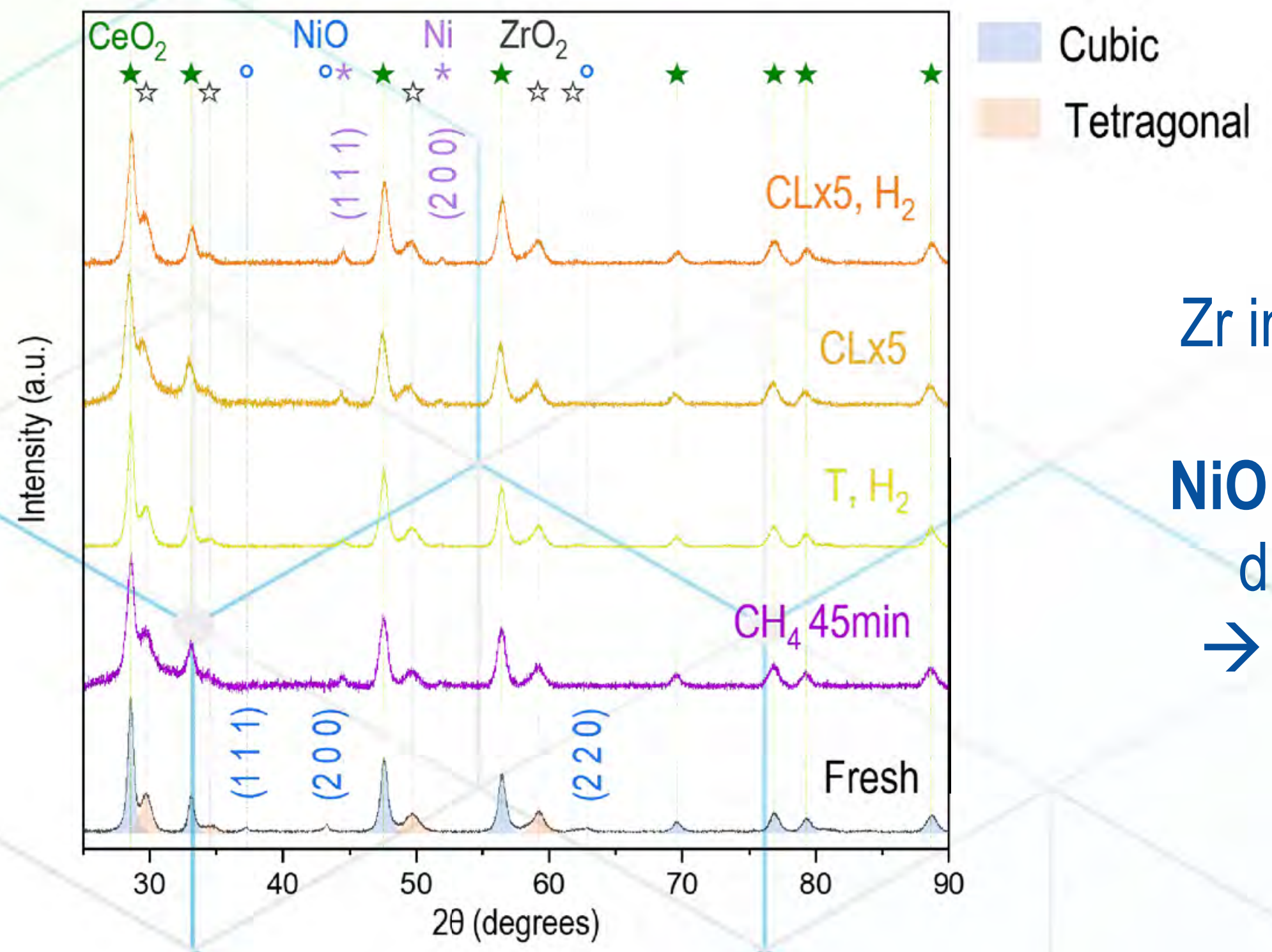


- Dynamic evolution (5 cycles CLR) probed with *in situ* Fourier transform spectroscopy
- CH_4 reduction (5, 15, 30, and 45 min)
- Bulk, surface, carbon characterization by electron microscopy, X-ray diffraction, and *ex situ* Raman

Catalyst Evolution

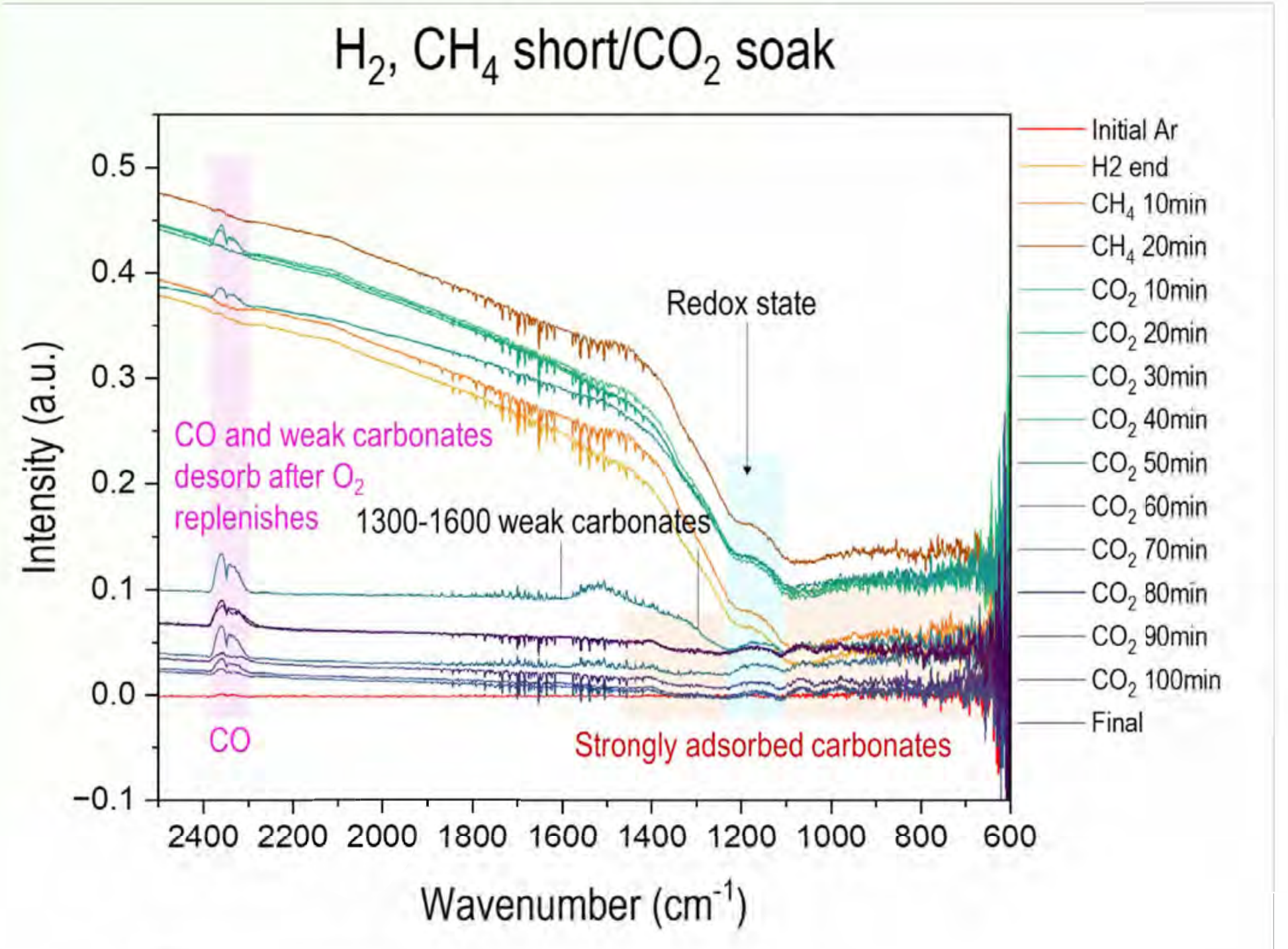


Amorphous and CNT carbon during CL without H_2
Ni catalyzed MWCNTS (tip growth)
Ruptured support material

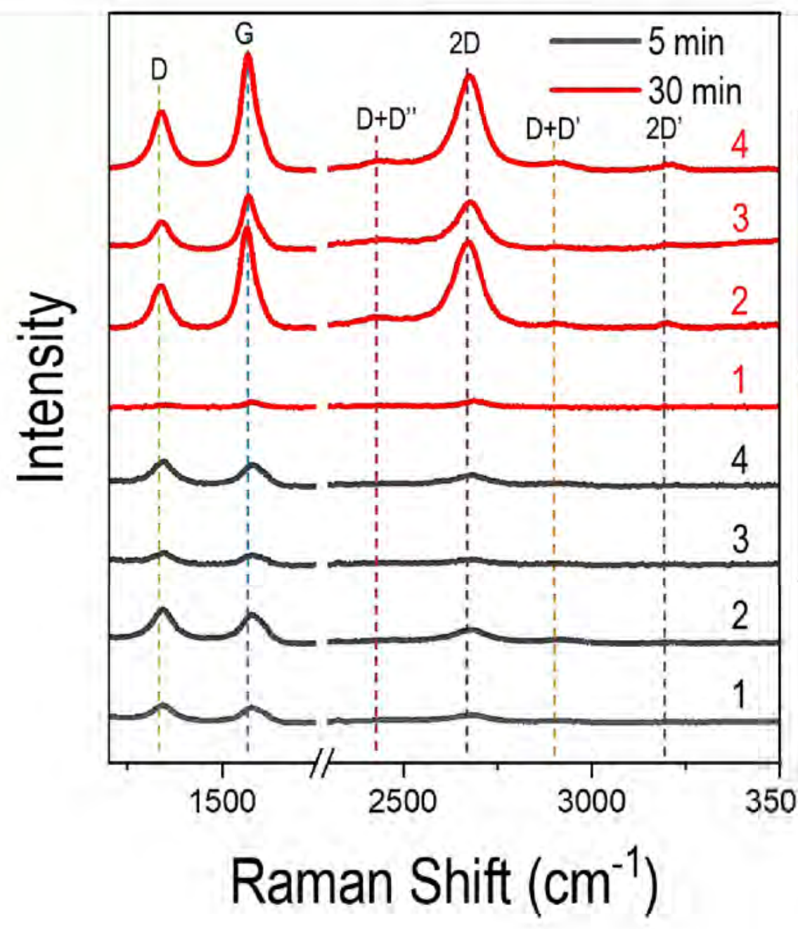


Zr incorporated into CeO_2 lattice
NiO irreversibly forms Ni during CH_4 reduction
→ Decreases strongly adsorbed carbon

Carbon Characterization



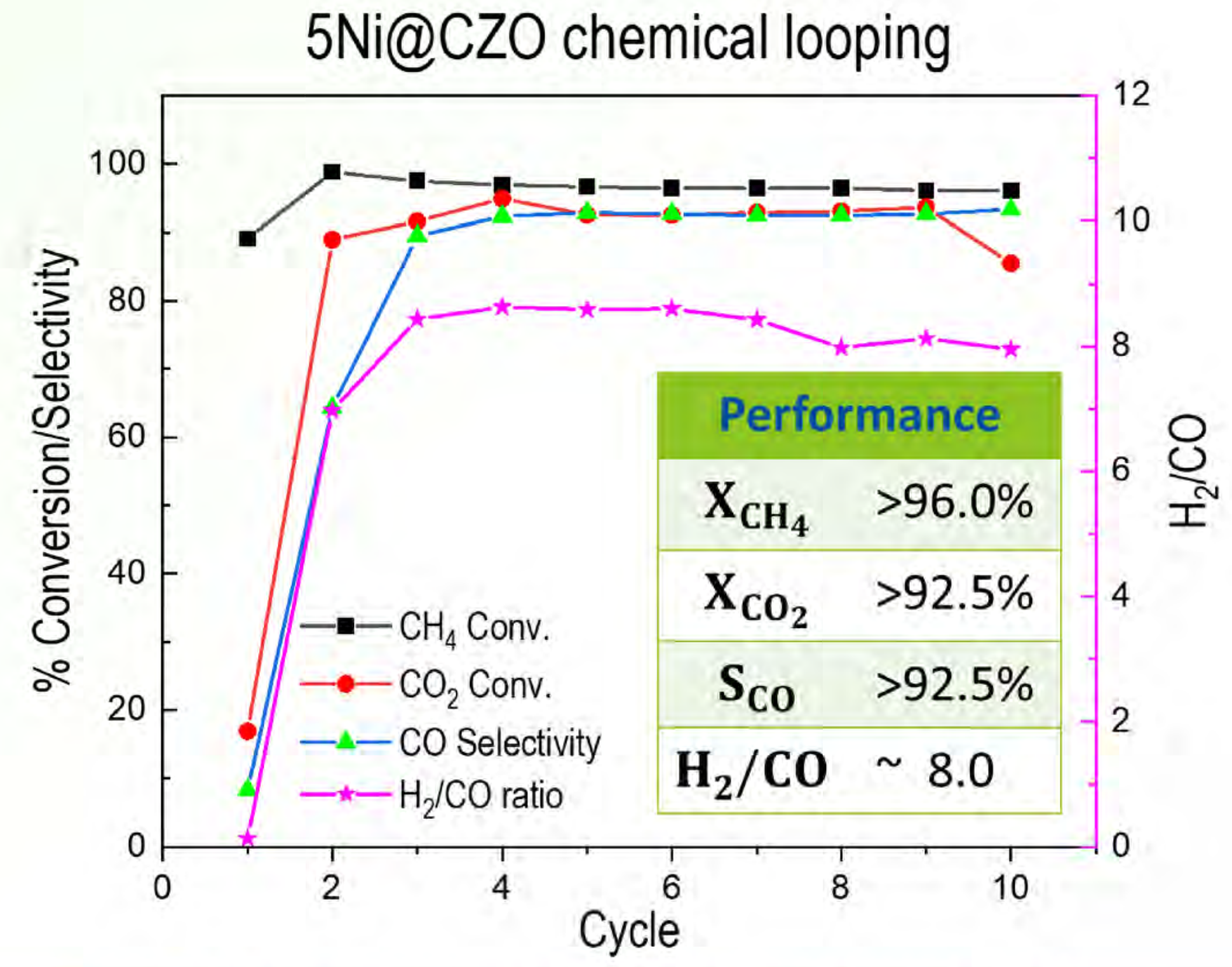
Irreversible reduction
Easily oxidized amorphous C, hard to oxidize graphitic C



Cluster		$I_{D/G}$	D cm^{-1}	G cm^{-1}
30 min CH_4	4	0.49	1339	1568
	3	0.48	1340	1570
	2	0.42	1351	1575
	1	0.44	1351	1575
5 min CH_4	4	1.02	1346	1580
	3	1.01	1346	1580
	2	1.09	1344	1579
	1	1.01	1341	1582

Increasingly graphitic with TOS CH_4
→ Harder to oxidize

Performance



Performance	
X_{CH_4}	>96.0%
X_{CO_2}	>92.5%
S_{CO}	>92.5%
H_2/CO	~ 8.0

Good performance of 5Ni/CZO in CH_4/CO_2 CLR

Conclusions

- Redox optimization of half cycles to establish higher yield, selectivity and catalyst stability:
  - Understanding of graphitic vs amorphous surface carbon optimization for improved continuous CLR
- Reduced Ni promotes more easily oxidized surface carbon forms
  - More stable catalyst

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LRS Number: INL/CON-23-72360

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Idaho National Laboratory

Title: Deep Reinforcement Learning for Integrated Energy Systems

Effectively balancing production with profit

PRESENTER:

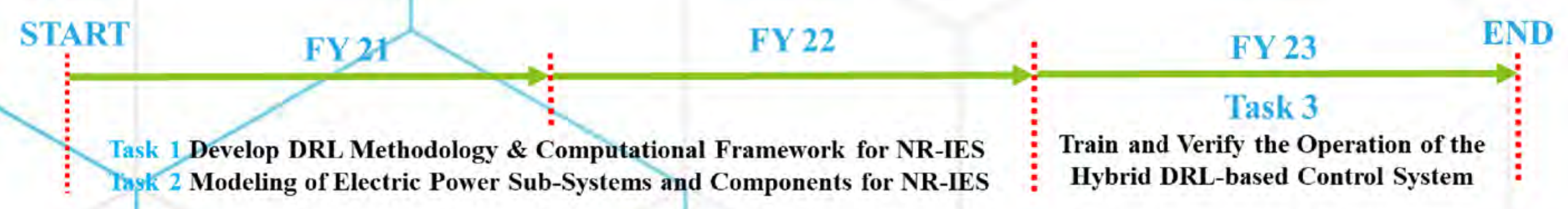
Victor Walker

BACKGROUND:

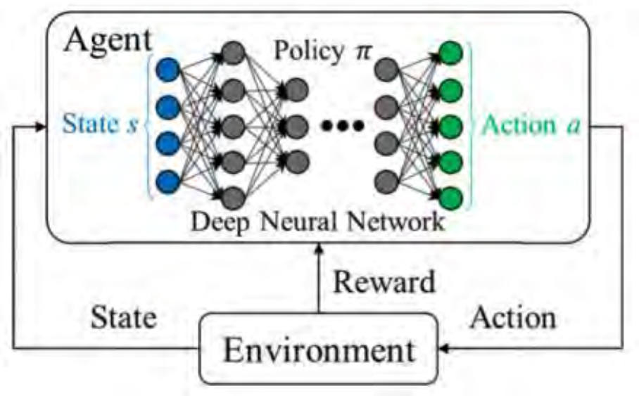
Integrated Energy Systems (IES) offer increased ability, but also increased complexity and scale. Intelligent control using AI systems may be critical to success in uncertain markets.

Success involves building novel frameworks and new model capabilities.

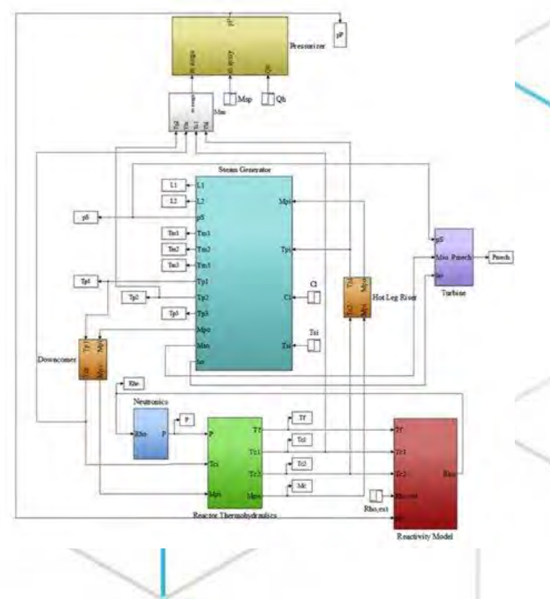
METHOD:



1. **Develop DRL methodology for IES**

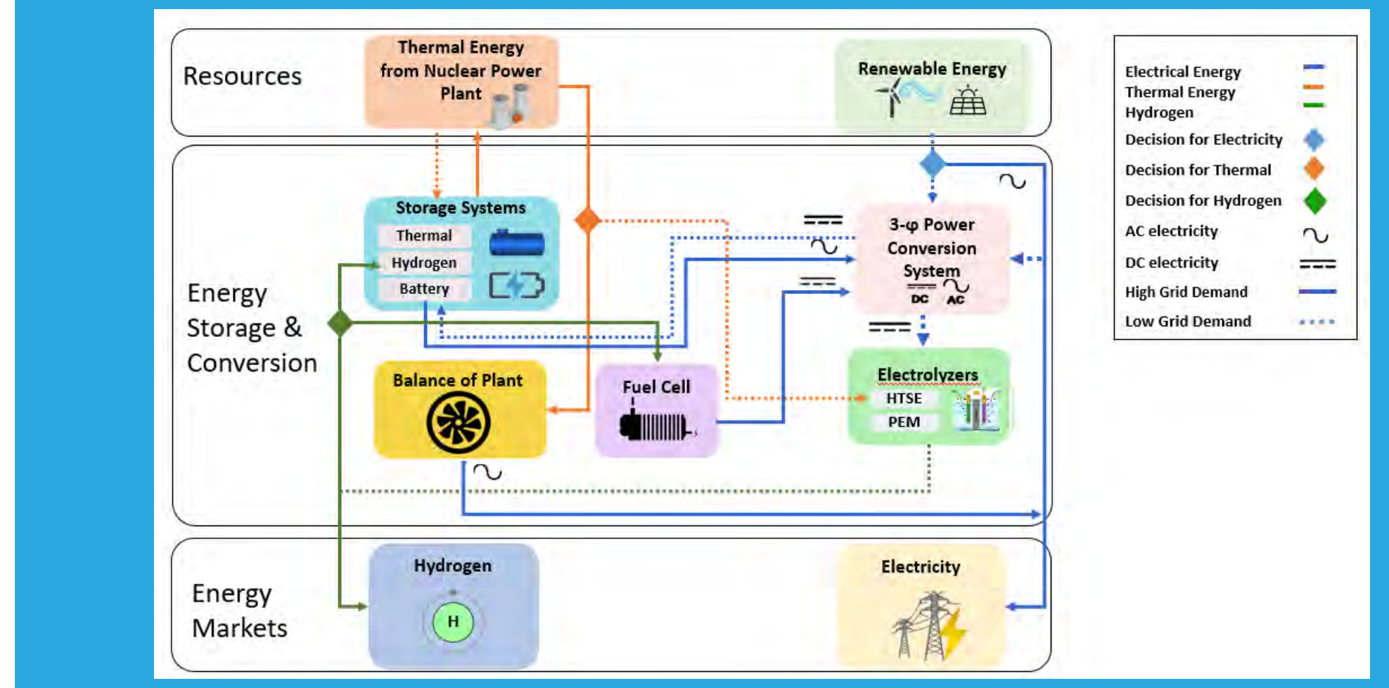


2. **Model power sub-systems for IES**

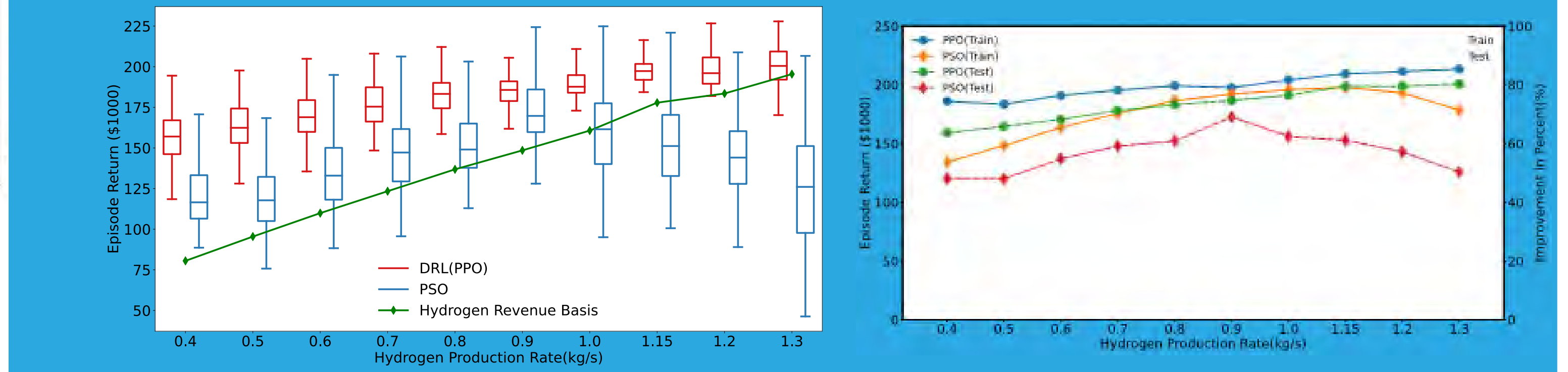


Deep Reinforcement Learning can effectively learn to control an integrated energy system

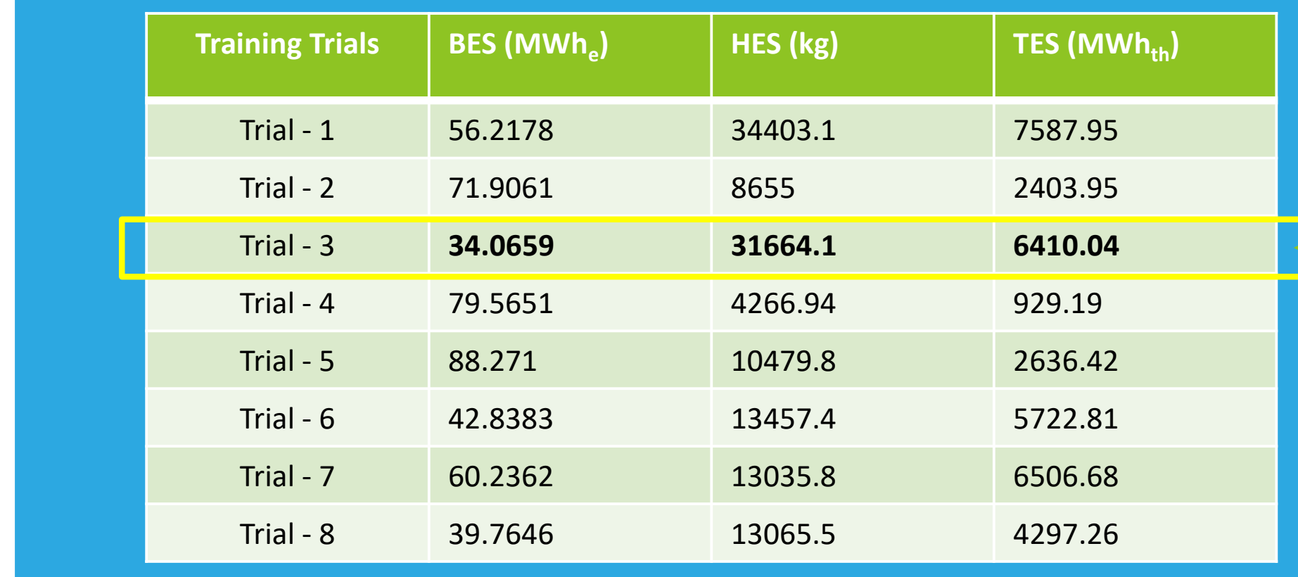
Integrated Energy System models demonstrate interdependancies



Deep Reinforcement Learning methods show improved responses to different dynamics



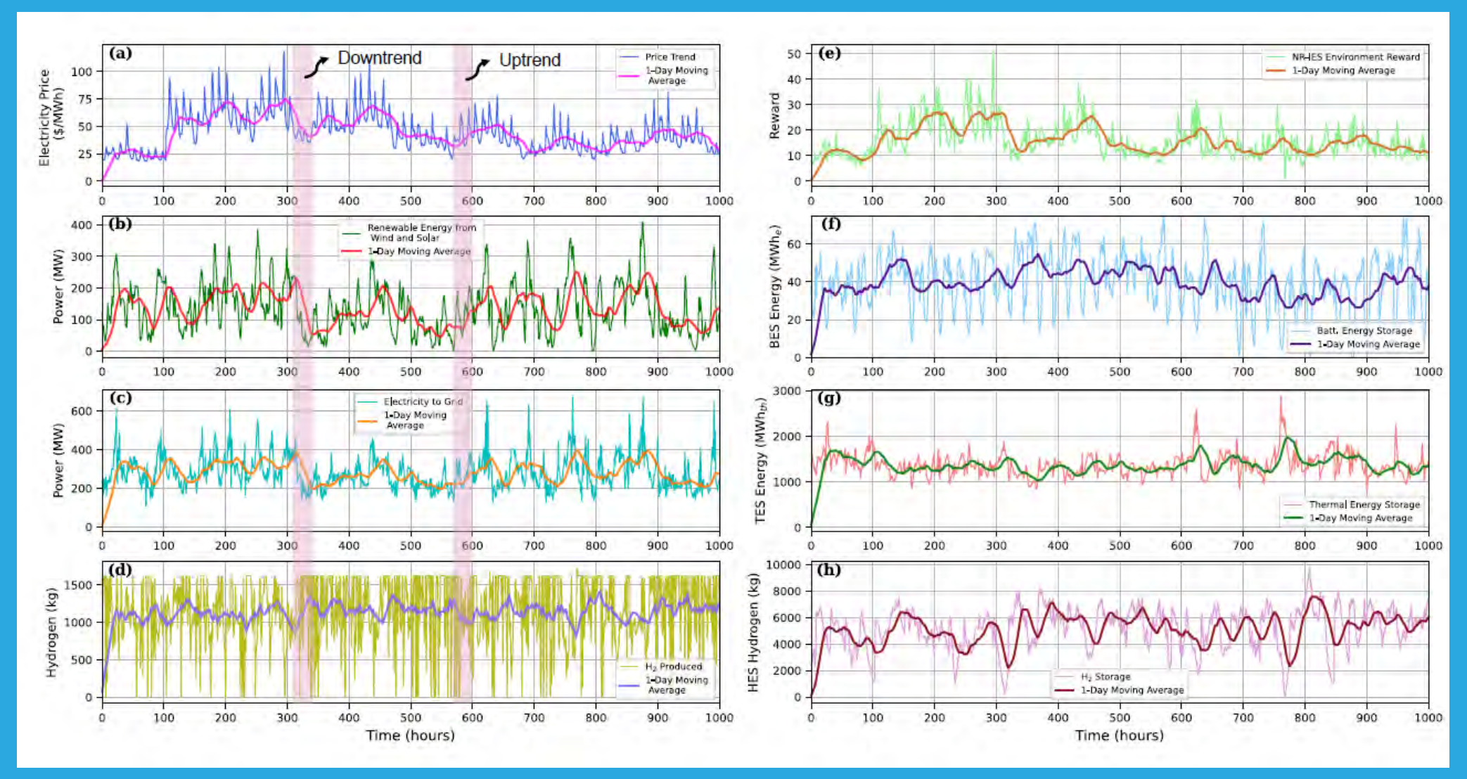
Hyperparameter tuning provides a more optimal configuration



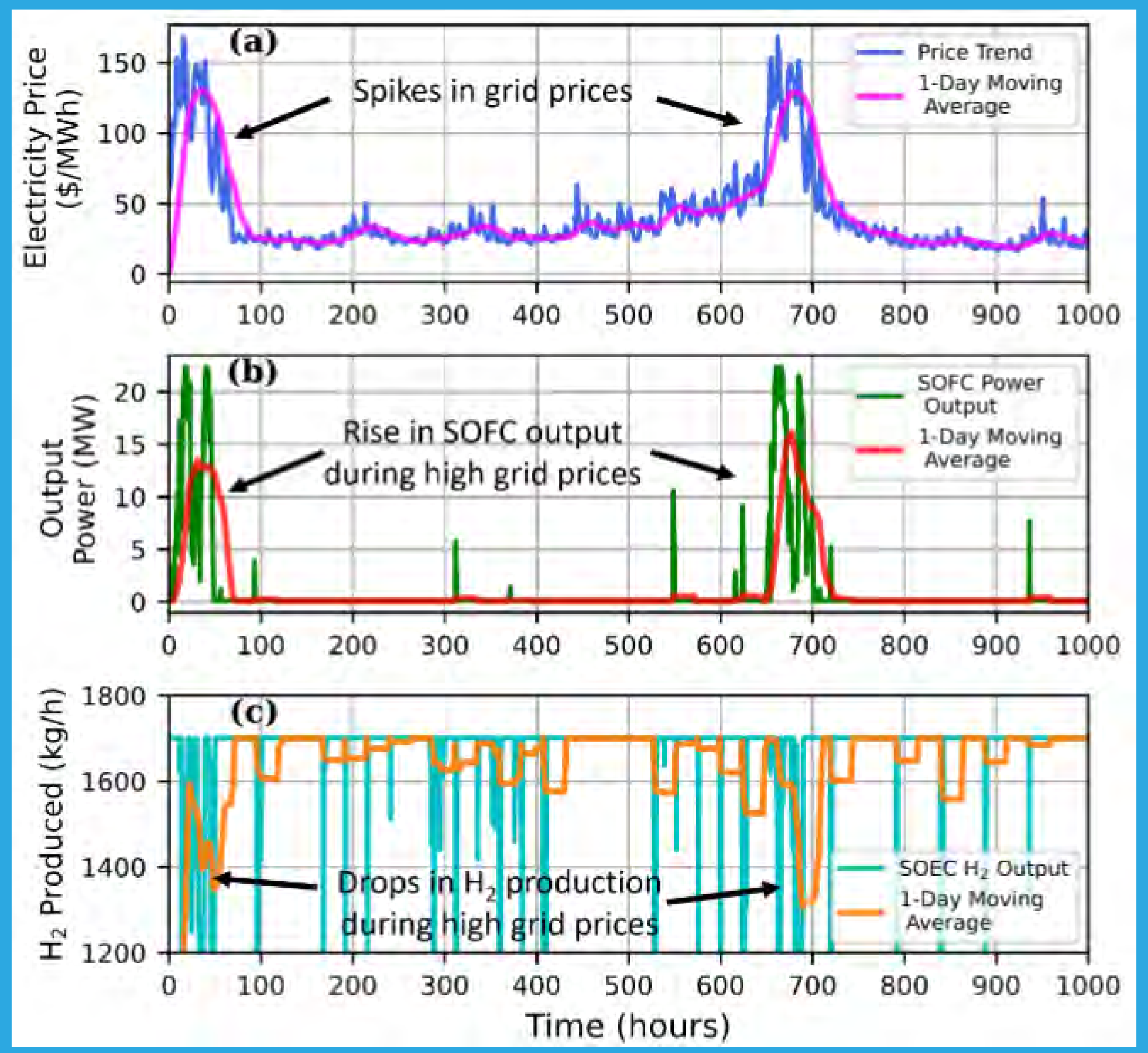
Training Trials	BES (MWh_e)	HES (kg)	TES (MWh_{th})
Trial - 1	56.2178	34403.1	7587.95
Trial - 2	71.9061	8655	2403.95
Trial - 3	**34.0659**	**31664.1**	**6410.04**
Trial - 4	79.5651	4266.94	929.19
Trial - 5	88.271	10479.8	2636.42
Trial - 6	42.8383	13457.4	5722.81
Trial - 7	60.2362	13035.8	6506.68
Trial - 8	39.7646	13065.5	4297.26

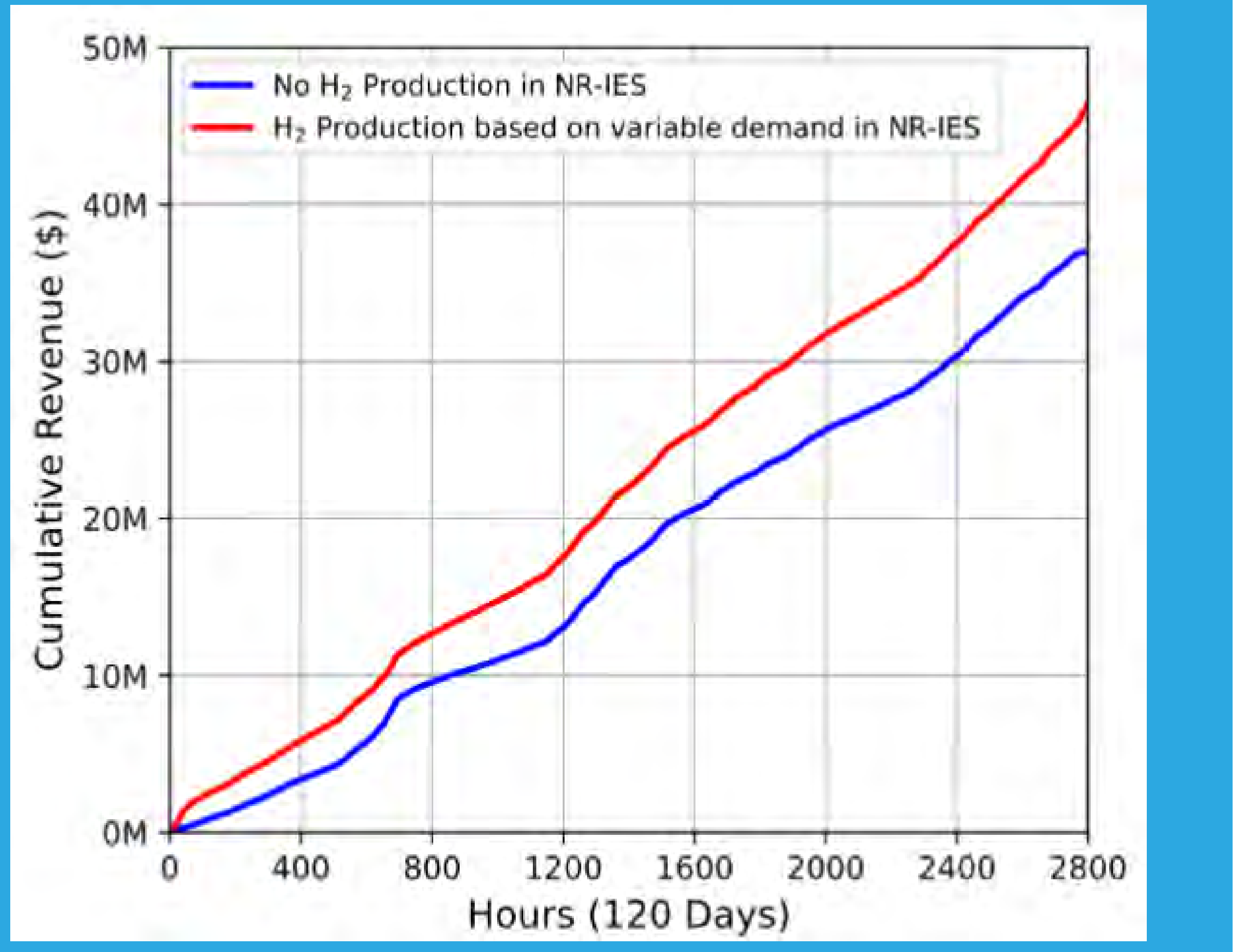
Best case

Full model learns improved interaction between many energy systems



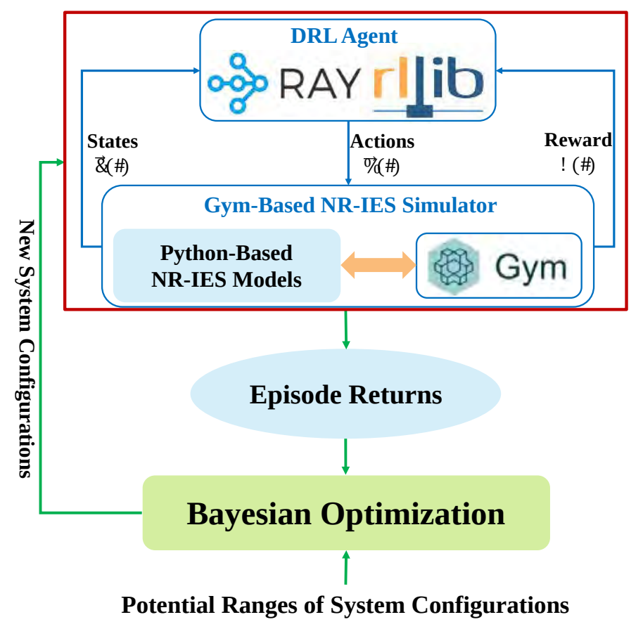
System learned to improve revenue by 25% over 120 days



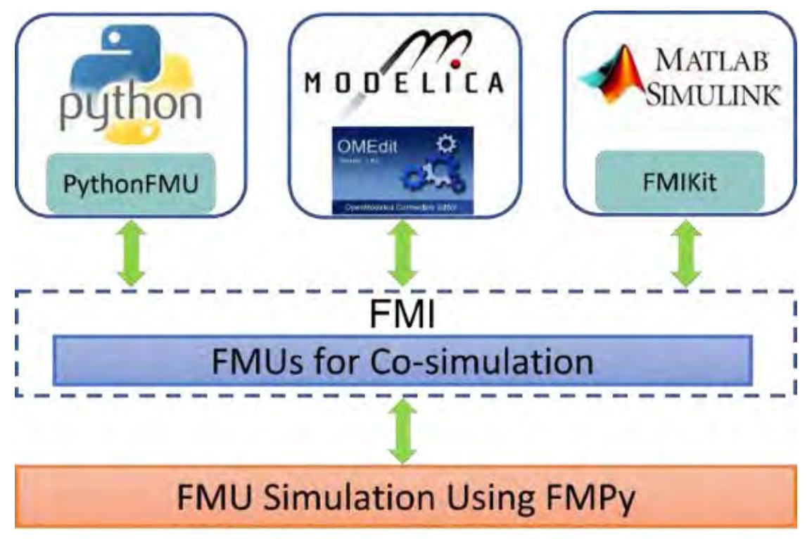


METHOD (Continued):

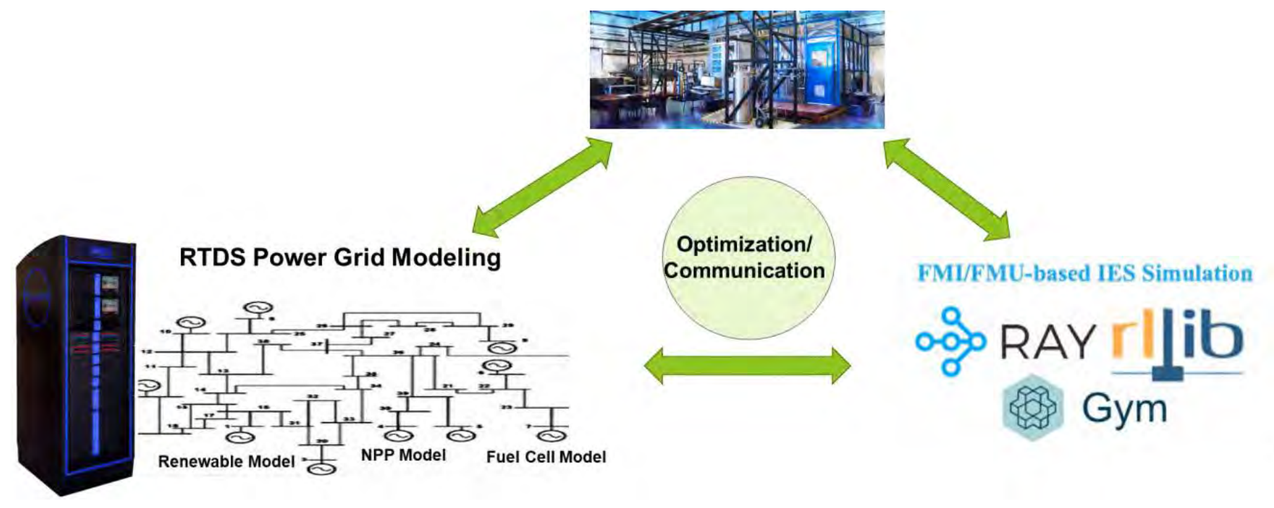
3. **Optimize sub-system configurations using DRL**



4. **Create method for integrating models using Functional Mock-up Interfaces and Units (FMI/FMU)**



5. **Test DRL system with a Hardware-in-Loop System**



INL:
Zonggen Yi, Tyler Westover, Congjian Wang, Han Boa, Anudeep Medam, Temitayo Olowu, Victor Walker
University of Toledo:
Raghav Khanna, Ahmad Javaid, Michael Heben, Many Awesome Students

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LRS Number: INL/EXP-23-74354

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