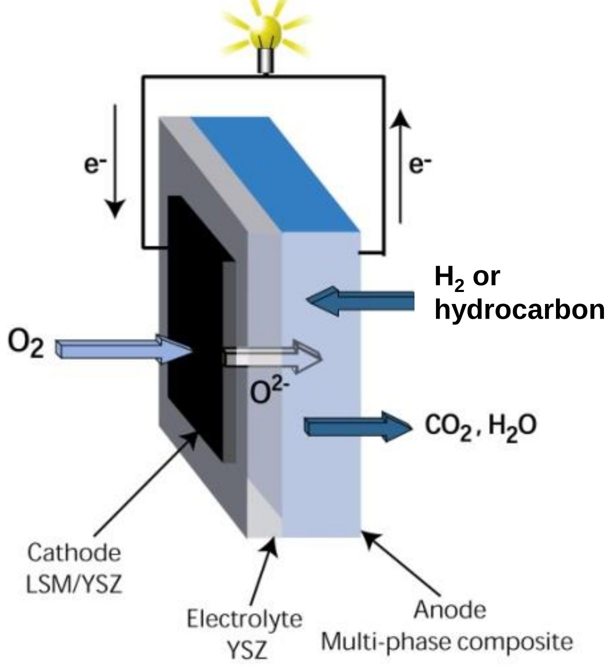
Enhancing Coking Tolerance and Stability of SOFC Anodes using Atomic Layer Deposition (ALD) of Oxide Thin Films

Raymond J. Gorte, John M. Vohs
University of Pennsylvania
and
Steve McIntosh
Lehigh University

Wensheng Wang, Praveen Cheekatamarla
Atrex Energy

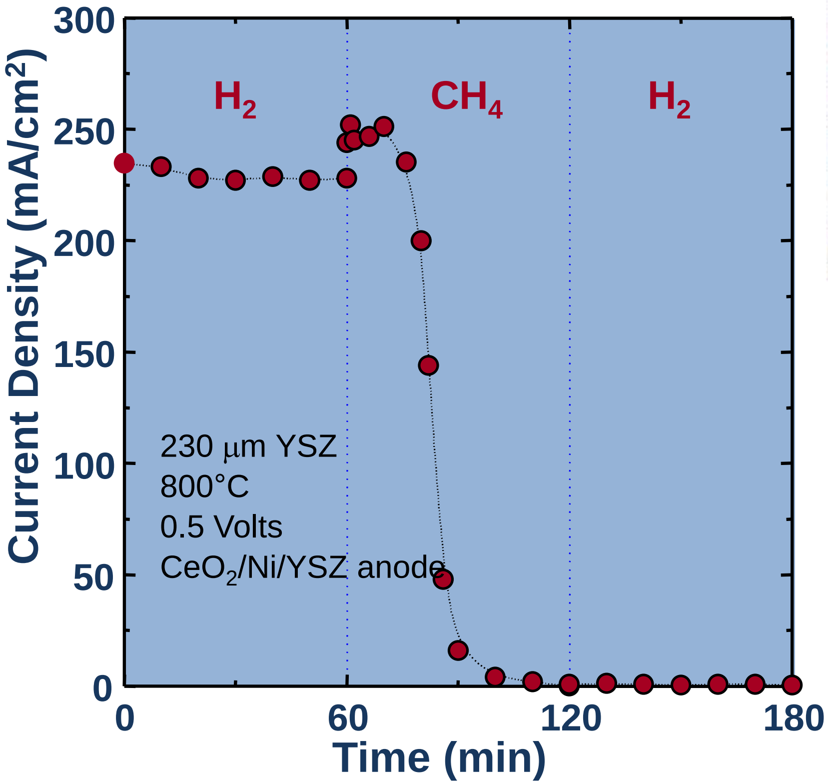
Background

Solid Oxide Fuel Cell

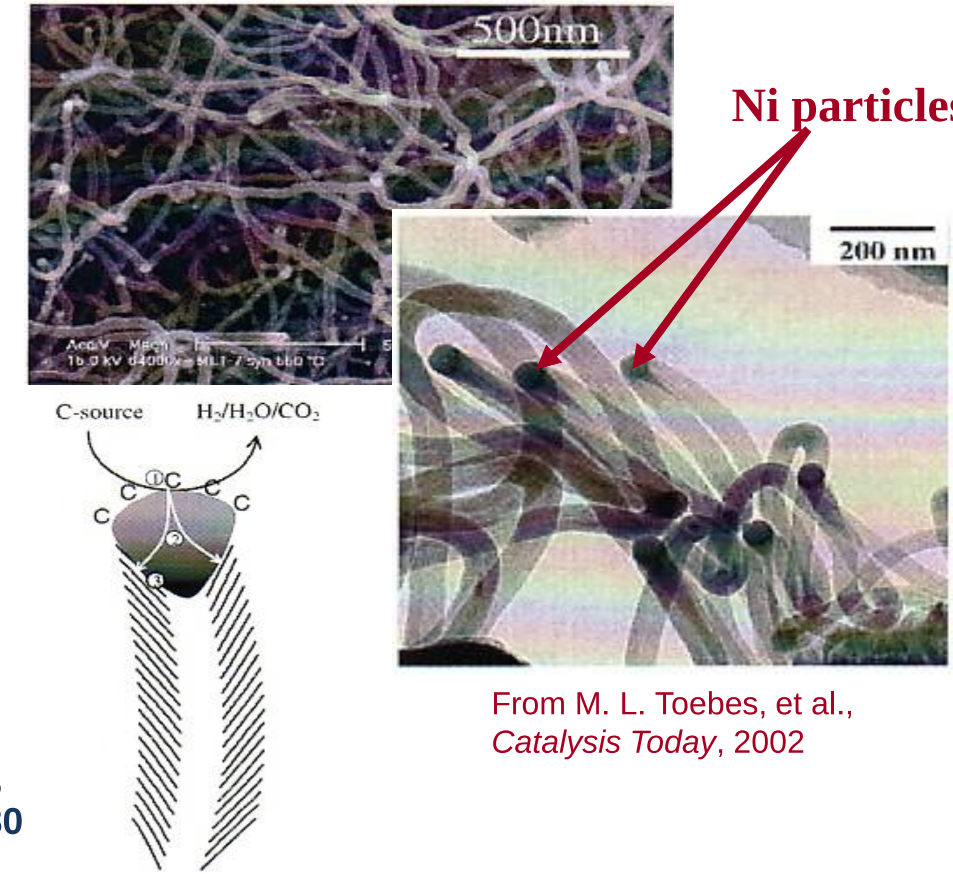


- **Ni-YSZ cermets are generally considered to be the state of the art anode for SOFCs.**
- **In spite of years of development they still have some limitations including:**
    - Loss of surface area which degrades performance over time
    - Low fuel flexibility due to propensity to coke when exposed to hydrocarbons
    - Susceptible to deactivation when exposed to common fuel impurities such as sulfur

Background - Hydrocarbon Tolerance of Ni-YSZ Anodes



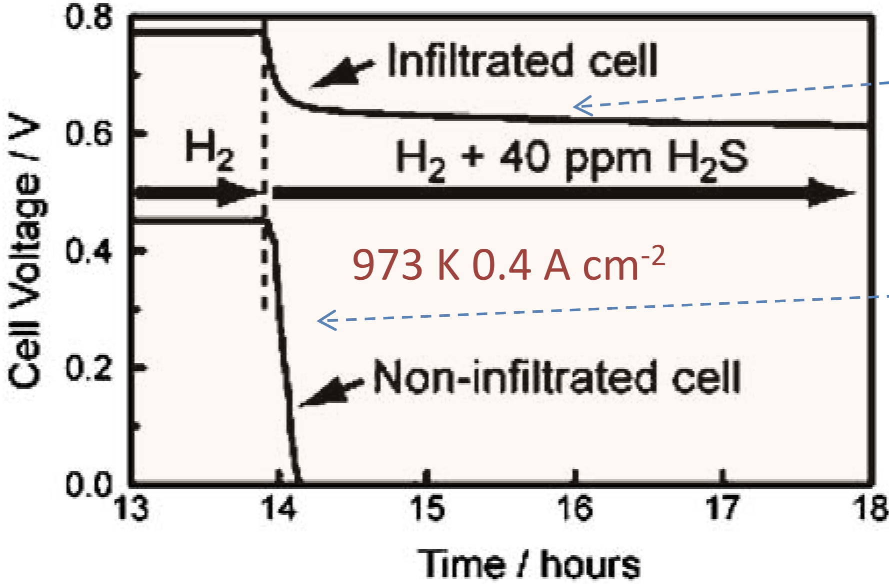
Ni exposed to 20% CO,7% H_2 at 550°C.



From M. L. Toebes, et al., *Catalysis Today*, 2002

- **Carbon deposition rapidly degrades cell performance**
- **Is an issue even for reformed natural gas where excess steam must be used to suppress coking**

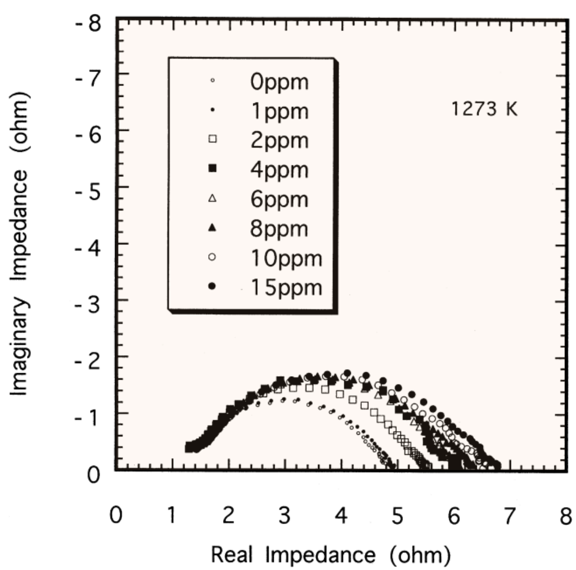
Background - Sulfur Tolerance of Ni-YSZ Anodes



LSM-YSZ/YSZ/CeO_2-Ni-YSZ Cell

LSM-YSZ/YSZ/Ni-YSZ Cell

From Visco et al., *Elec. Solid State Lett.*, **10** (2007) B135.



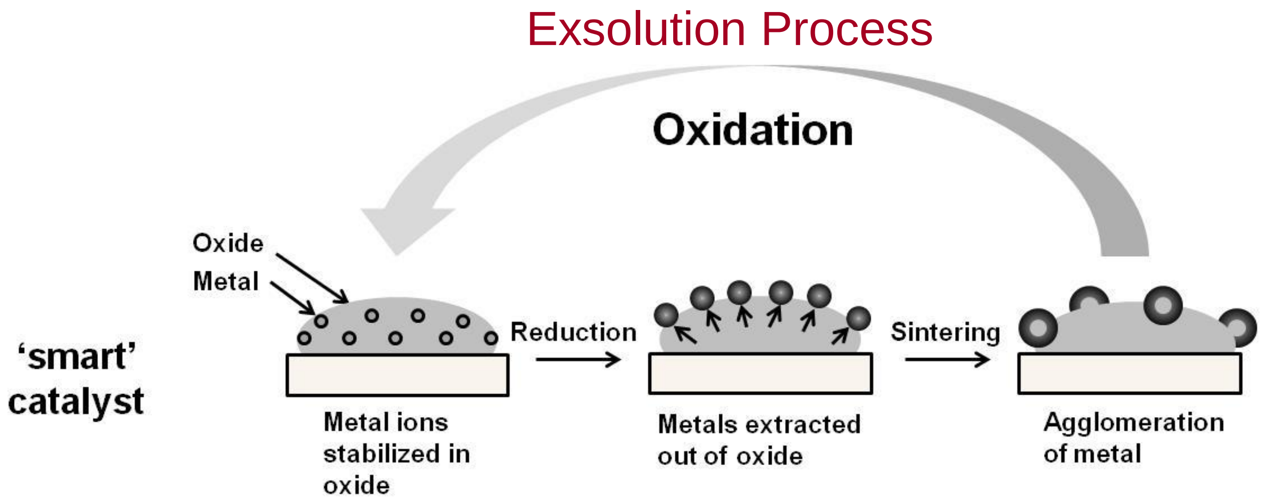
Ni-YSZ Anode – 1273 K

H_2 + x ppm H_2S

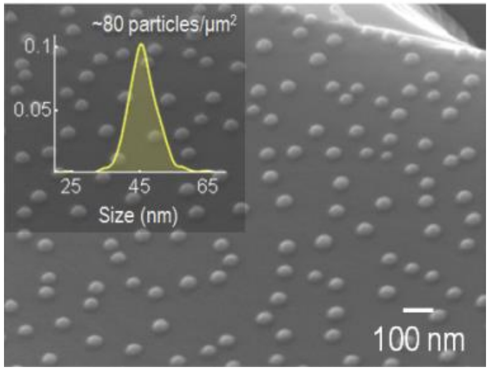
From Matsuzaki and Yasuda, *Solid State Ionics*, **132** (2000) 261.

Sulfur levels as low as 1 ppm adversely affect performance

Background - Exsolution



- **Pd-doped perovskite regenerable catalysts first developed for automotive emissions control systems by researchers at Daihatsu and Toyota (Nishihata et al. *Nature* 418 (2002) 164)**
- **Many conducting perovskites have been shown to exhibit this exsolution behavior**

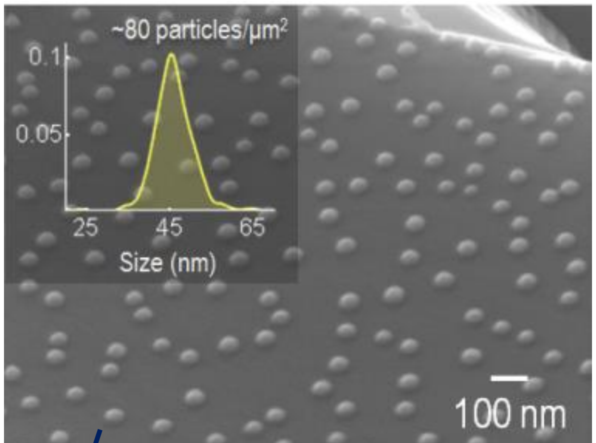


Ni particles exsolved from $La_{0.4}Sr_{0.4}Ni_{0.03}Ti_{0.97}O_{3-\delta}$

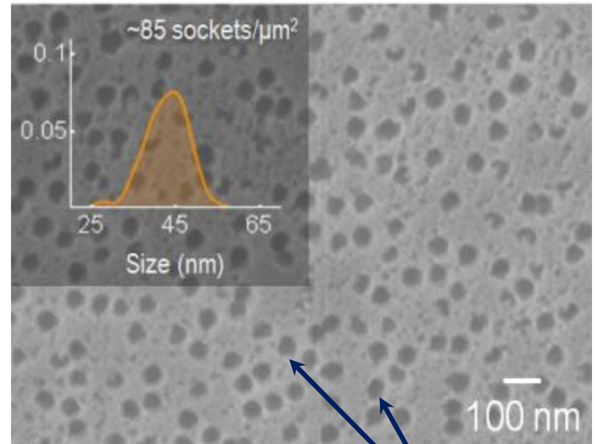
Background - Exsolution produces “socketed” metal particles

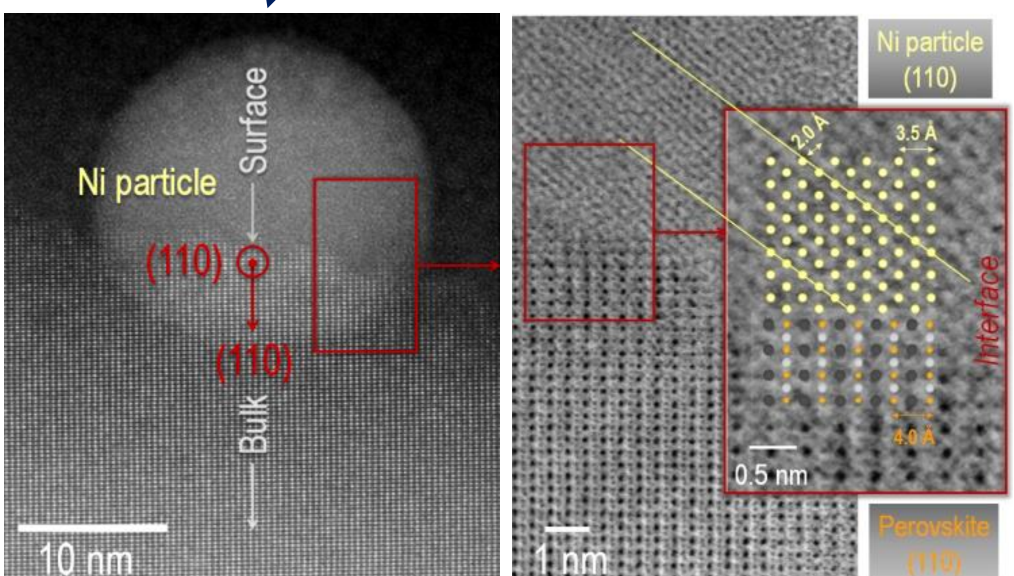
$La_{0.4}Sr_{0.4}Ni_{0.03}Ti_{0.97}O_{3-\delta}$

Reduced in H_2

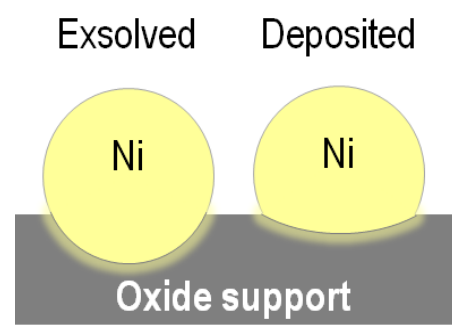


Etched in HNO_3



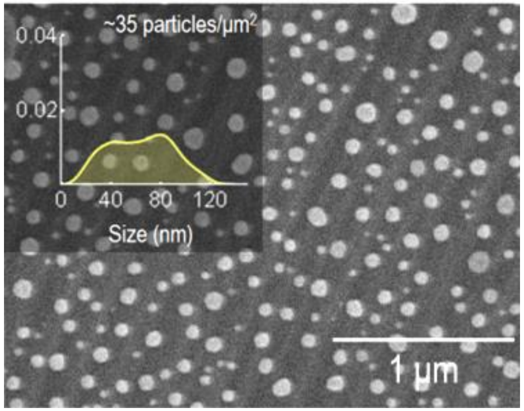


Surface pits that remain after etching away the Ni

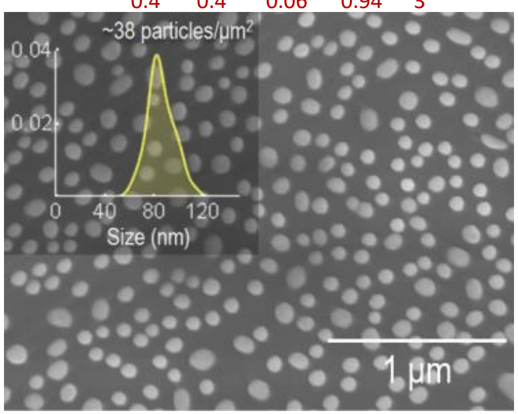


Background - Socketed exsolved particles have high coking resistance

Vapor deposited Ni particles on $La_{0.4}\,Sr_{0.4}\,TiO_3$

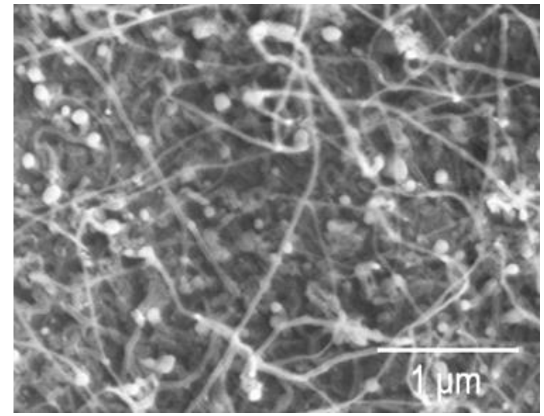


Exsolved Ni particles On $La_{0.4}\,Sr_{0.4}\,Ni_{0.06}\,Ti_{0.94}\,O_3$

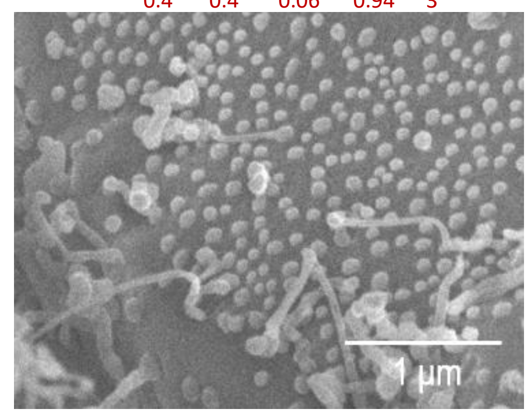


20% CH_4
80% H_2
800˚C
4hr

Vapor deposited Ni particles on $La_{0.4}\,Sr_{0.4}\,TiO_3$



Exsolved Ni particles On $La_{0.4}\,Sr_{0.4}\,Ni_{0.06}\,Ti_{0.94}\,O_3$



- Can we effectively use the unique properties of exsolved metal particles in SOFC anodes?
- Sulfur tolerance of exsolved metal particles?

Background - BaO surface modifier to enhance coking resistance

Yang et al. *Nature Comm.* 2011, DoI: 10.1038/ncomms1359

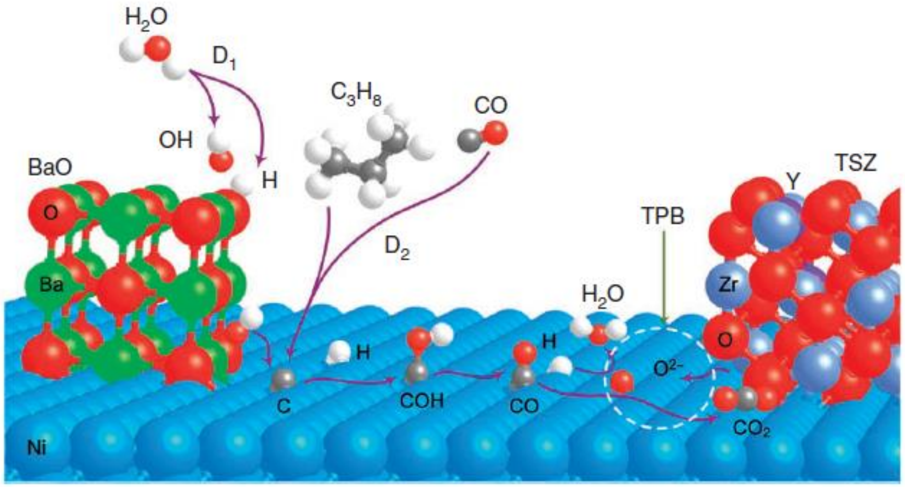


Figure 7 | Proposed mechanism for water-mediated carbon removal on the anode with BaO/Ni interfaces. Large balls in Brandeis blue, green, red, blue grey and purple are Ni, Ba, O of BaO or YSZ, Zr and Y, respectively, whereas small balls in red, white and grey are O from H_2O, H and C, respectively. D_1 is the dissociative adsorption of H_2O, whereas D_2 is the dehydrogenation of hydrocarbons or the CO disproportionation reaction.

It has been proposed that BaO enhances coking tolerance by providing sites at BaO-Ni interfaces that preferentially adsorb H_2O that can then react with and help gasify nearby carbon deposits

Can this function be engineered into SOFC anodes using BaO or other reducible oxide modifiers?

Overall Project Goals

Goals

- **Engineer the aforementioned ideas, including coking and sulfur tolerant exsolved metal particles and reducible oxides that promoter carbon removal, into sate-of-the-art Ni-YSZ anodes**

- **Determine if oxide coatings can also enhance the redox stability of Ni-YSZ anodes**

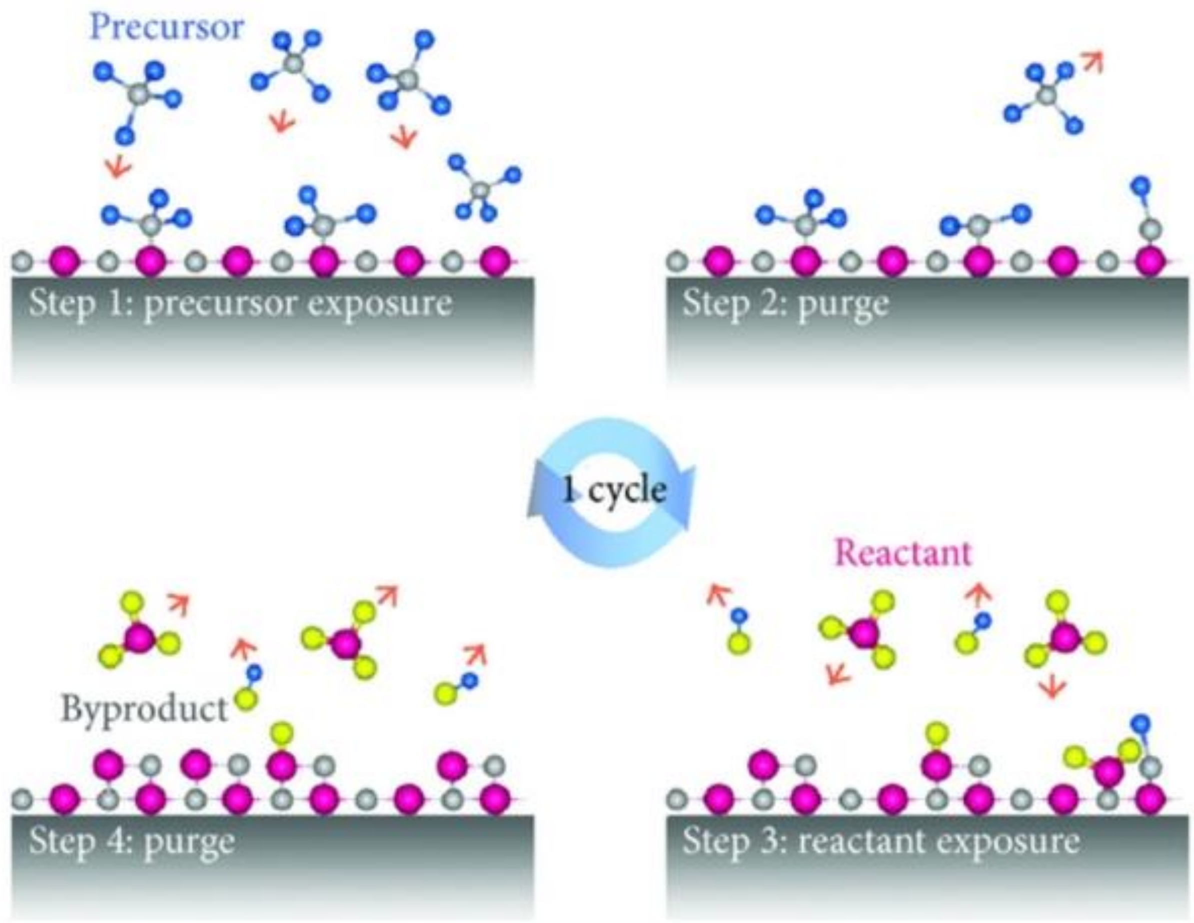
- **Transfer the most promising technologies to Atrix and test on commercial scale cells.**

Technical Approach

- **Use atomic layer deposition (ALD) to selectively deposit oxide thin films including perovskites and reducible oxide modifiers, such as BaO, on Ni-YSZ anodes**

- **Perform detailed characterization of the surface composition and structure of oxide modified Ni-YSZ anodes and correlate with performance measurements.**

Technical Approach - **Atomic Layer Deposition (ALD)**

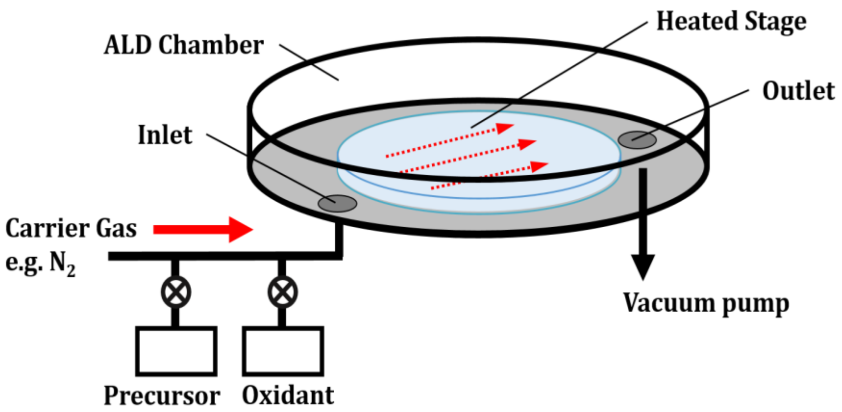


We have demonstrated the ALD growth of perovskite thin films

Technical Approach - Atomic Layer Deposition (ALD)

Issues With ALD Modification of Electrodes:

- ALD equipment is expensive
- Cost of precursors with ALD in flow systems would be prohibitive
- Current commercial ALD equipment not designed for film growth on highly porous substrates such as SOFC electrodes

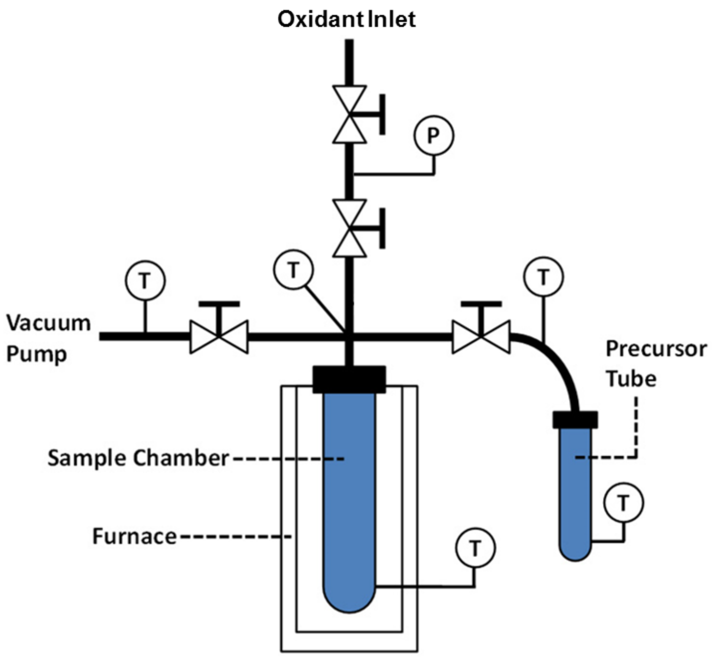


Conventional ALD is done using a flow system that is not amenable to the growth of thin films on highly porous substrates

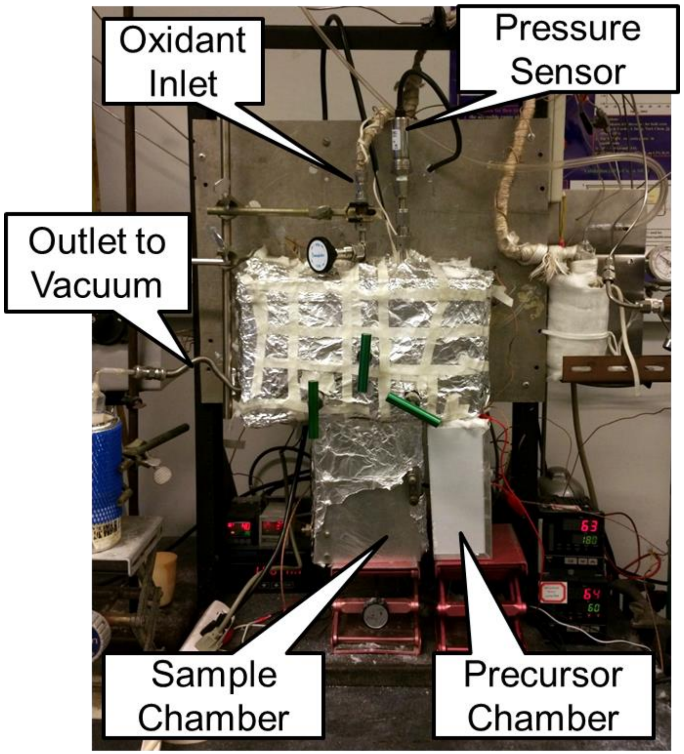
Technical Approach - Atomic Layer Deposition (ALD)

We have developed vacuum ALD as an effective method for oxide film growth on porous substrates

- Fast pulsing not required! No need for many cycles
- Vacuum (millitorr) more effective than carrier gas
- Easily applied to large cells

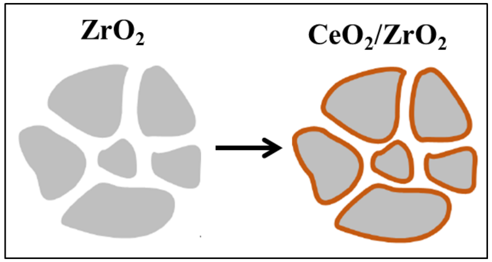


Vacuum-ALD Apparatus



ALD growth rates can be measured gravimetrically

Example: Coating ZrO_2 with 1 nm CeO_2 film

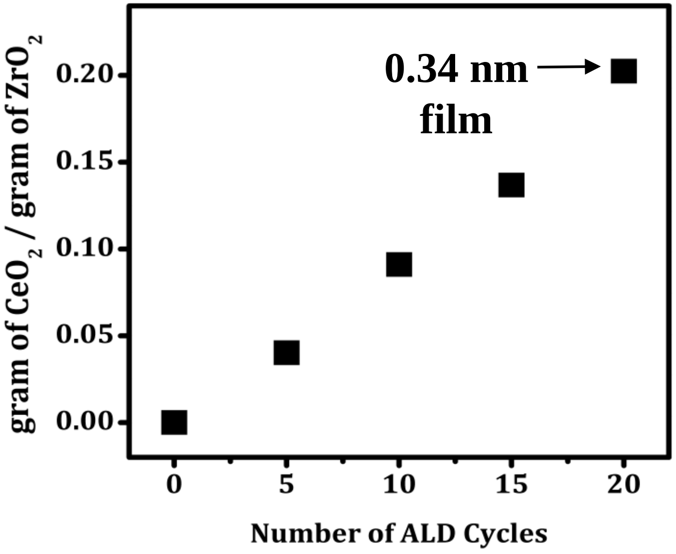


ALD of CeO_2 on 84 m^2/g ZrO_2

Basis: 1 m^2/g Al_2O_3

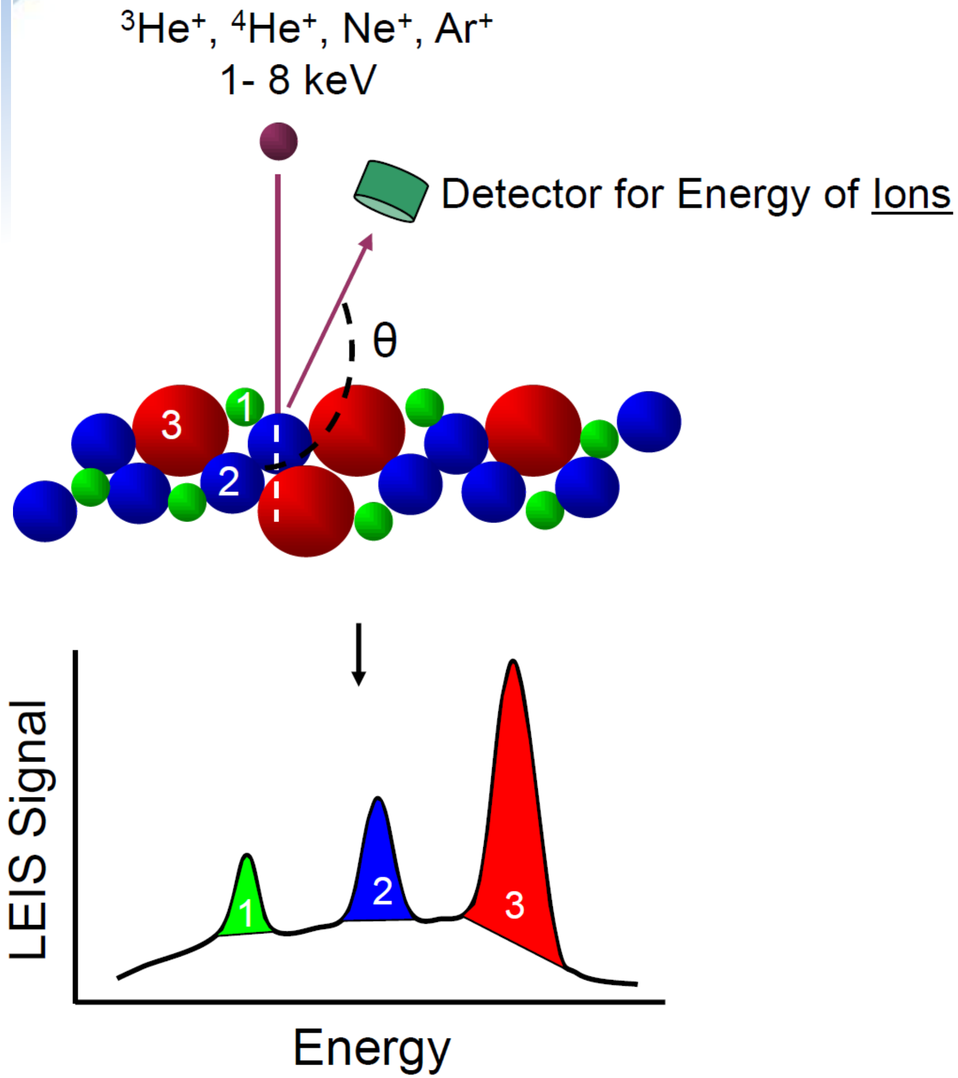
$10\ m^2/g * 10^4\ cm^2/m^2 * 10^{-7}\ cm = 0.01\ cm^3\ CeO_2/g\ ZrO_2$
$0.01\ cm^3\ CeO_2/g\ ZrO_2 * 7.22\ g/cm^3 = 0.072\ g\ CeO_2/g\ ZrO_2$

1-nm film equals 4.2-wt% CeO_2.



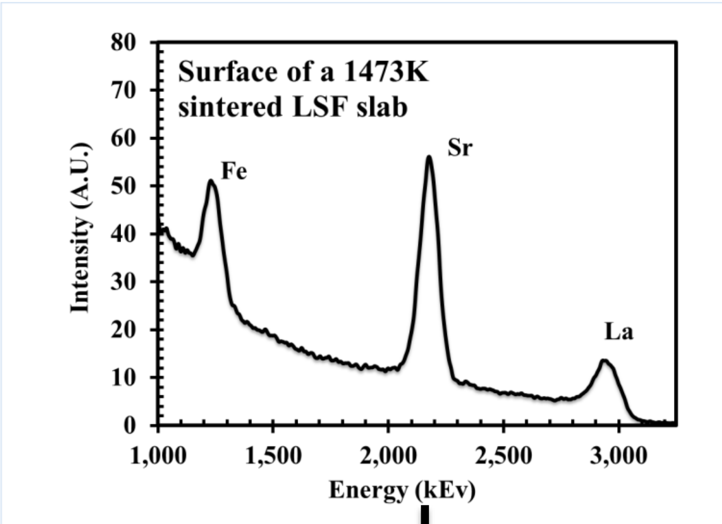
Technical Approach - High Sensitivity - Low Energy Ion Scattering (HS-LEIS)

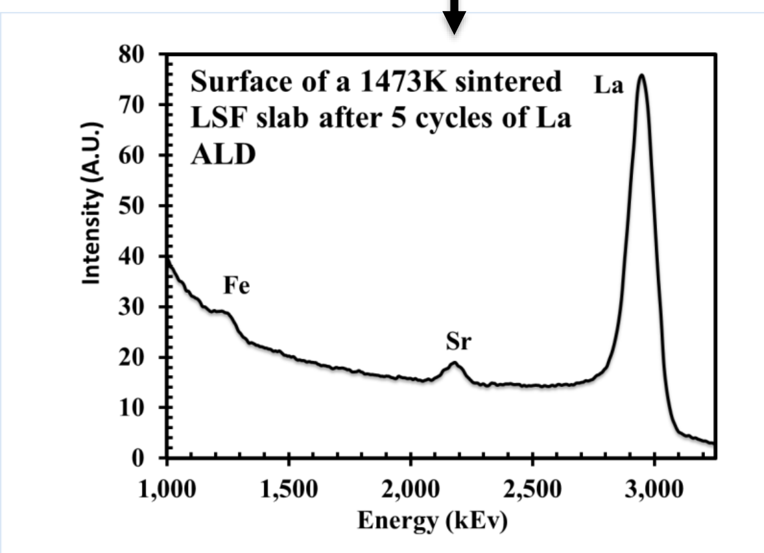
Detailed characterization of surface composition and structure needed to correlated oxide modifier function with anode performance



- Provides atomic composition of the outermost atomic layer
- Quantifies the surface coverage of each element with no matrix effect.
- Standards can be utilized to give absolute coverage of each element.
- Detection limits down to <0.05% of a monolayer.
- Can be coupled with sputtering to produce depth profiles.

Example HS-LEIS data for ALD of La onto an LSF slab





- Initial surface composition shows the expected Sr enrichment.
- 5 cycles of La forms an almost complete atomic monolayer of La on the slab surface.

Project Structure

- **Task 1.0: Project management and planning.**

- **Task 2.1: Set up and cell fabrication.**
  - Prepare batches of Ni-YSZ anode-supported SOFC button cells.
  - Attache LSCF cathodes.
  - Construct dedicated ALD system.

- **Task 2.2: BaO and CeO_2 films.**
  - Use ALD to deposit BaO and/or CeO_2 films on Ni-YSZ powders.
  - Use ALD to deposit BaO and/or CeO_2 films on the anodes.
  - Gravimetric characterization of film growth
  - Structural characterization using BET surface area and XRD as a function of the number of ALD cycles.
  - Impedance measurements between 700 and 800°C

Project Structure

- **Task 2.3: Perovskite films.**
  - Use ALD to deposit perovskite films on the anode (CatiO_3, $SrTiO_3$, and $BaZrO_3$ Ni-YSZ powders .
  - Structural characterization using BET surface area and XRD as a function of the number of ALD cycles.
  - Impedance measurements between 700 and 800°C

- **Task 3.1: Testing of CeO_2- and BaO-modified button cells for carbon deposition.**
  - Electrochemical performance measurements in H_2O-CH_4 mixtures to determine optimal H_2O:CH_4 ratios.
  - Carbon deposition amounts determined using oxygen titration.

- **Task 3.2: Testing of perovskite-modified button cells for carbon deposition.**
  - Testing of perovskite-modified button cells for carbon deposition.
  - Carbon deposition amounts determined using oxygen titration.

Project Structure

- **Task 3.3: Redox measurements of modified cells.**
  - Effect of ALD films from Task 2.3 on redox stability measured using temperature-programmed oxidation.
  - Electrochemical fuel-cell measuremnts to verify performance at high H_2O:H_2 ratios.

- **Task 3.4: Characterization of ALD films by HR-LEIS.**
  - Measure surface composition of films as a function of the number of ALD cycles using HR_LEIS.
  - Near surface depth profiling to examine phase stability at oxide-oxide interface.
  - Near ambient pressure XPS for in situ measurement of oxidation states of cations in ALD films.

- **Task 4.0: Transfer of results to Atrex.**
  - Results from Tasks 3.2 and 3.3 will be transferred to Atrex Energy. Atrex cells will be modified for them as requested.

Project Schedule

Task	Task Description	1	2	3	4	5	6	7	8
1	Task 1.0: Project management								
2	Task 2.0: ALD modification of cells Task 2.1 Set up and cell fabrication Task 2.2 BaO and CeO_2 ALD Films Task 2.3 Perovskite ALD Films								
3	Task 3.0: Cell characterization Task 3.1 Coking testing of BaO and CeO_2 systems Task 3.2 Coking Testing of perovskite systems Task 3.3 Redox Testing Task 3.4 HS-LEIS Cell Characterization								
4	Task 4.0 Tech transfer to Atrex								
	Progress Milestone								

Project Budget

Budget Information - Non Construction Programs

OMB Approval No. 0348-0044

Section A - Budget Summary

Grant Program Function or Activity (a)	Catalog of Federal Domestic Assistance Number (b)	Estimated Unobligated Funds Federal (c)	Estimated Unobligated Funds Non-Federal (d)	New or Revised Budget Federal (e)	New or Revised Budget Non-Federal (f)	New or Revised Budget Total (g)
1. Budget Period 1				$252,876.00	$63,748.00	$316,624.00
2. Budget Period 2				$247,124.00	$61,252.00	$308,376.00
3. Budget Period 3				$0.00	$0.00	$0.00
4.						
5. Totals				$500,000.00	$125,000.00	$625,000.00

Section B - Budget Categories

6. Object Class Categories	Grant Program, Function or Activity: Budget Period 1	Budget Period 2	Budget Period 3		Total (5)
a. Personnel	$57,621.00	$56,840.00	$0.00		$114,461.00
b. Fringe Benefits	$7,931.00	$7,373.00	$0.00		$15,304.00
c. Travel	$1,400.00	$1,400.00	$0.00		$2,800.00
d. Equipment	$0.00	$0.00	$0.00		$0.00
e. Supplies	$2,000.00	$2,000.00	$0.00		$4,000.00
f. Contractual	$152,627.00	$160,744.00	$0.00		$313,371.00
g. Construction	$0.00	$0.00	$0.00		$0.00
h. Other	$27,786.00	$28,776.00	$0.00		$56,562.00
i. Total Direct Charges (sum of 6a-6h)	$249,365.00	$257,133.00	$0.00		$506,498.00
j. Indirect Charges	$67,259.00	$51,243.00	$0.00		$118,502.00
k. **Totals** (sum of 6i-6j)	$316,624.00	$308,376.00	$0.00		$625,000.00
7. Program Income					$0

Project Budget - subcontracts

SOPO Task #	Sub-Recipient Name/Organization	Purpose and Basis of Cost	Budget Period 1	Budget Period 2	Budget Period 3	Project Total
2,4	**EXAMPLE!!!** XYZ Corp.	Partner to develop optimal lens for Gen 2 product. Cost estimate based on personnel hours.	$48,000	$32,000	$16,000	**$96,000**
3	Lehigh University	Researchers at Lehigh will be using LEIS to investigate the growth, coverages, and stability of ALD films on the Ni anodes. They will further use LEIS to determine whether there are differences in the growth of ALD films on Ni and YSZ. Cost estimate based on budget proposed.	$144,744	$148,627		**$293,371**
						$0
						$0
						$0
						$0
						$0
		Sub-total	**$144,744**	**$148,627**	**$0**	**$293,371**

SOPO Task #	Vendor Name/Organization	Purpose and Basis of Cost	Budget Period 1	Budget Period 2	Budget Period 3	Project Total
6	**EXAMPLE!!!** ABC Corp.	Vendor for developing robotics to perform lens inspection. Estimate provided by vendor.	$32,900	$86,500		**$119,400**
4	Atrex, Inc.	They will test cells modified by ALD by the group at Penn.	$10,000	$10,000		**$20,000**
						$0
						$0
						$0
						$0
		Sub-total	**$10,000**	**$10,000**	**$0**	**$20,000**

Project Management Plan

- The experimental work at Penn will be carried out by students, under the direction of Profs. Gorte and Vohs.
- The experimental work at Lehigh will be carried out by students, under the direction of Prof. McIntosh.
- Dr. Cheekatamarla will direct efforts at Atrex Energy.
- Close collaborations between the groups will be facilitated by frequent tele/video conferences.

Project Management Plan – Risk Assessment/Management

- Overall risk of the project is mitigated by the fact that the basic concepts have already been proven, although not necessarily within the context of an SOFC anode.
- While we have expertise in ALD growth of oxide films on porous substrates, we have yet to do this for BaO and for several of the perovskite-type oxides. Some optimization of growth conditions will be required and this may take longer than allotted in the project schedule.
- To help mitigate this risk we are building an additional ALD apparatus which will allow us to sample different reaction conditions more rapidly.
- The team has significant experience in SOFC fabrication and testing so the potential risk of this part of the project is low.
- To insure adherence to timeline, unforeseen technical hurdles will be identified as early as possible and the PI (Gorte) will maintain close contact with the Co-PIs (Vohs and McIntosh) as well as the project manager at DOE.