Scalable Nano-Scaffold Architecture On the Internal Surface of SOFC Anode For Direct Hydrocarbon Utilization

Xueyan Song

Department of Mechanical and Aerospace Engineering
West Virginia University

National Energy Technology Laboratory
DOE Award – FE0026167

Program Manager: Briggs White

Overview

➢ Scientific and Technical Merit

- State-of-the-art Ni/YSZ anode, and its degradation with H_2 fuel
- Direct hydrocarbon utilization: Principle and challenges

➢ Project Objective and Tasks To Be Performed

- Objective
- Tasks

➢ Approaches

- Ni/YSZ surface multi-functional nano-scaffold, facilitated by multiple heterostructured interfaces
- Uniqueness of ALD and its technical challenge for SOFC applications

➢ Preliminary Results

- Single phase discrete nano crystals of oxide conductor on Ni/YSZ
- Single phase of electro-catalysts on Ni/YSZ
- Dural phase nano-composite consisting oxide conductor and nano catalyst on Ni/YSZ

Overview

➢ Scientific and Technical Merit

- State-of-the-art Ni/YSZ anode, and its degradation with H_2 fuel
- Direct hydrocarbon utilization: Principle and challenges

➢ Project Objective and Tasks To Be Performed

- Objective
- Tasks

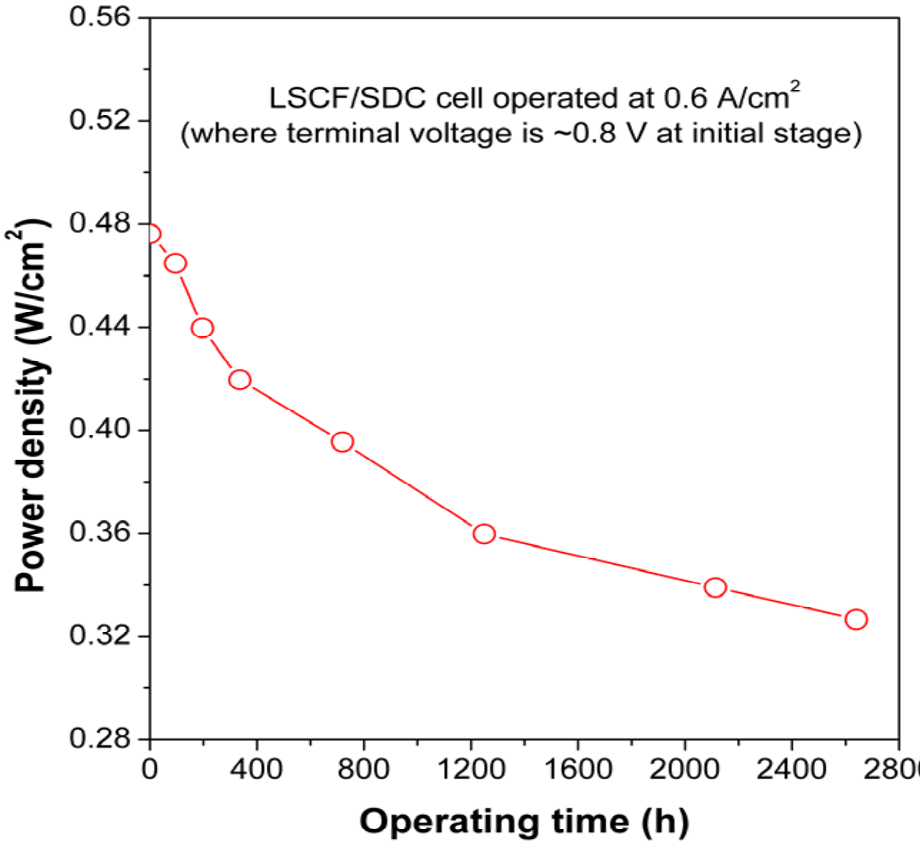
➢ Approaches

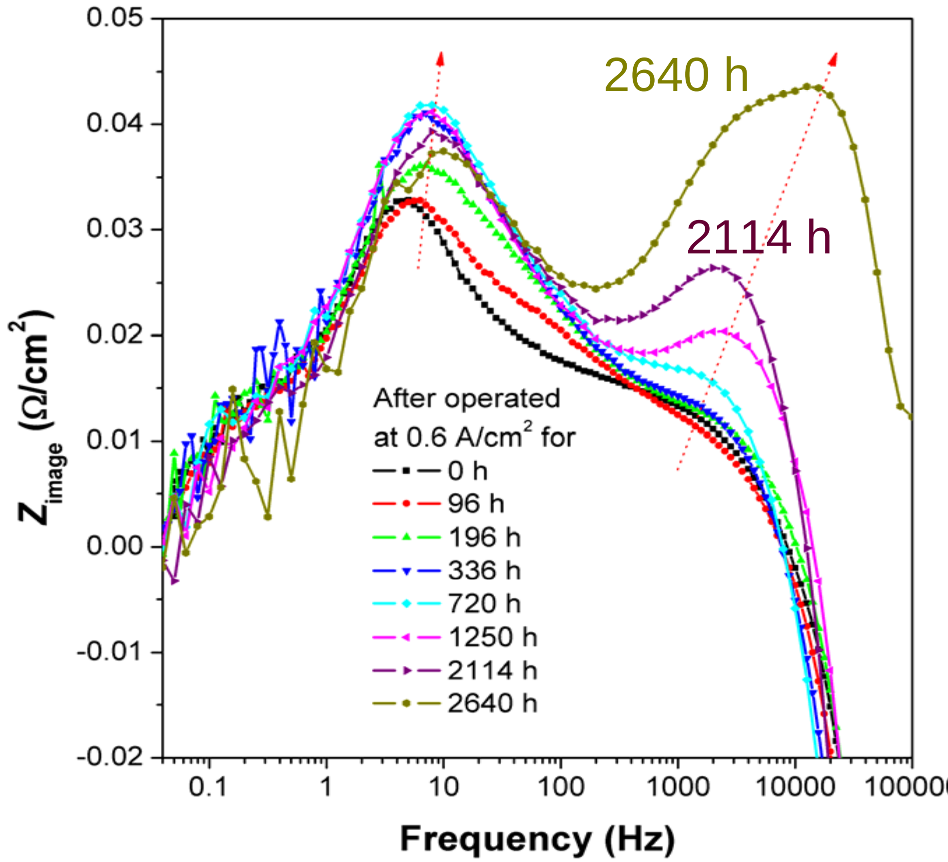
- Ni/YSZ surface multi-functional nano-scaffold, facilitated by multiple heterostructured interfaces
- Uniqueness of ALD and its technical challenge for SOFC applications

➢ Preliminary Results

- Single phase discrete nano crystals of oxide conductor on Ni/YSZ
- Single phase of electro-catalysts on Ni/YSZ
- Dural phase nano-composite consisting oxide conductor and nano catalyst on Ni/YSZ

Background: State-of-the-art Ni/YSZ anode and its degradation





- Commercial button cell, operated at 750C, at current density of $0.6A/cm^2$, for 2640 hours.
- Upon the operation, significant increase of resistance in the frequency range of 10^3 to $2x10^4$ Hz. Such increase could be related to the **anode degradation**.

*[J Electrochemical Society, **157** B234 (2010), J Power Sources 106, 160 (2002)].*

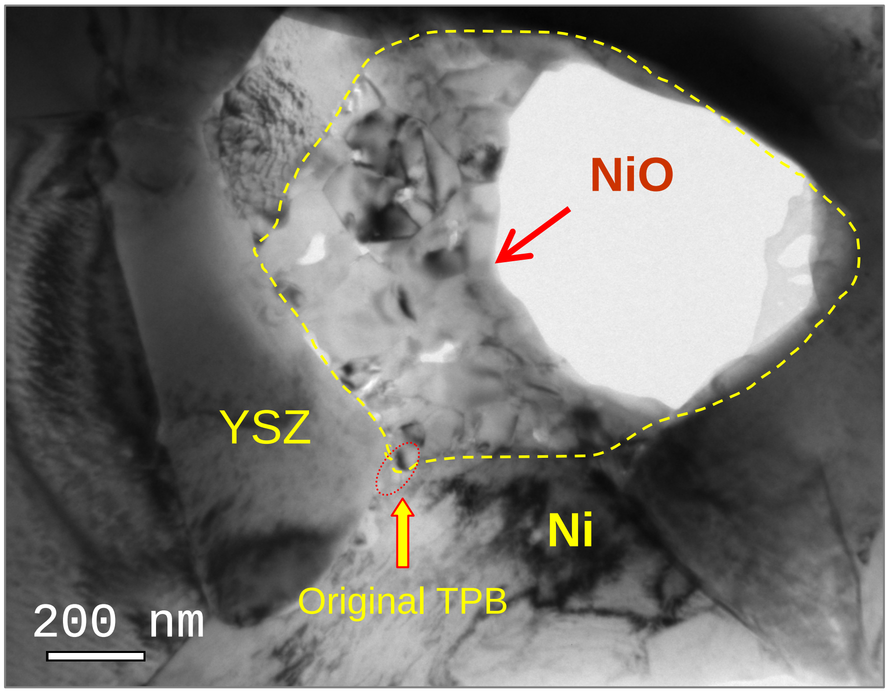
Y. Chen, X. Song, K. Gerdes, et al, Degradation of YSZ as SOFC Ionic Conductor upon Long Term Electrochemical Operation (to be submitted).

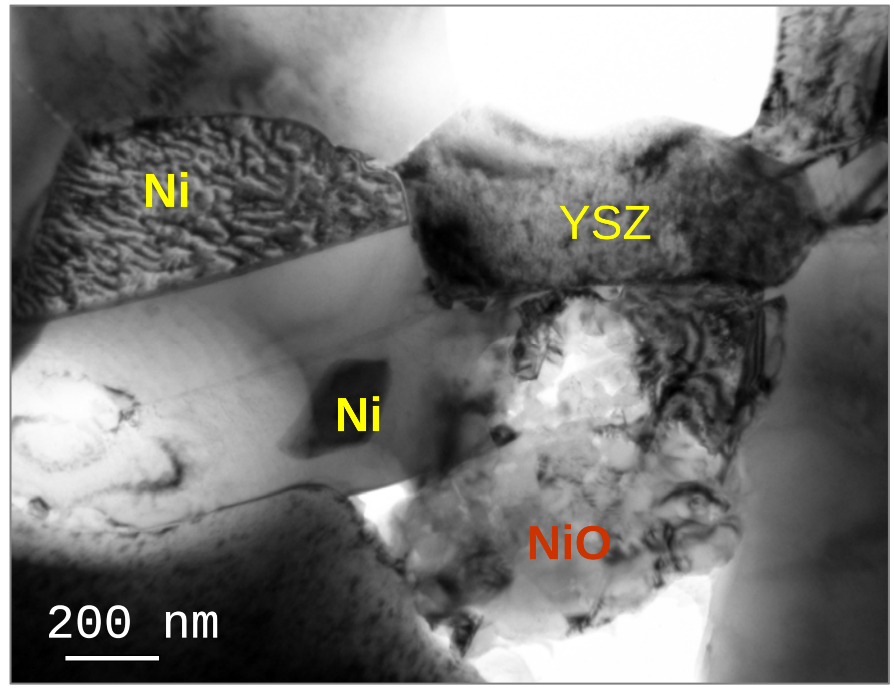
Background: Ni/YSZ anode and Ni degradation

Significant resistance increase from the anode.

Anode performance degradation **is rooted from the anode nanostructure degradation.**

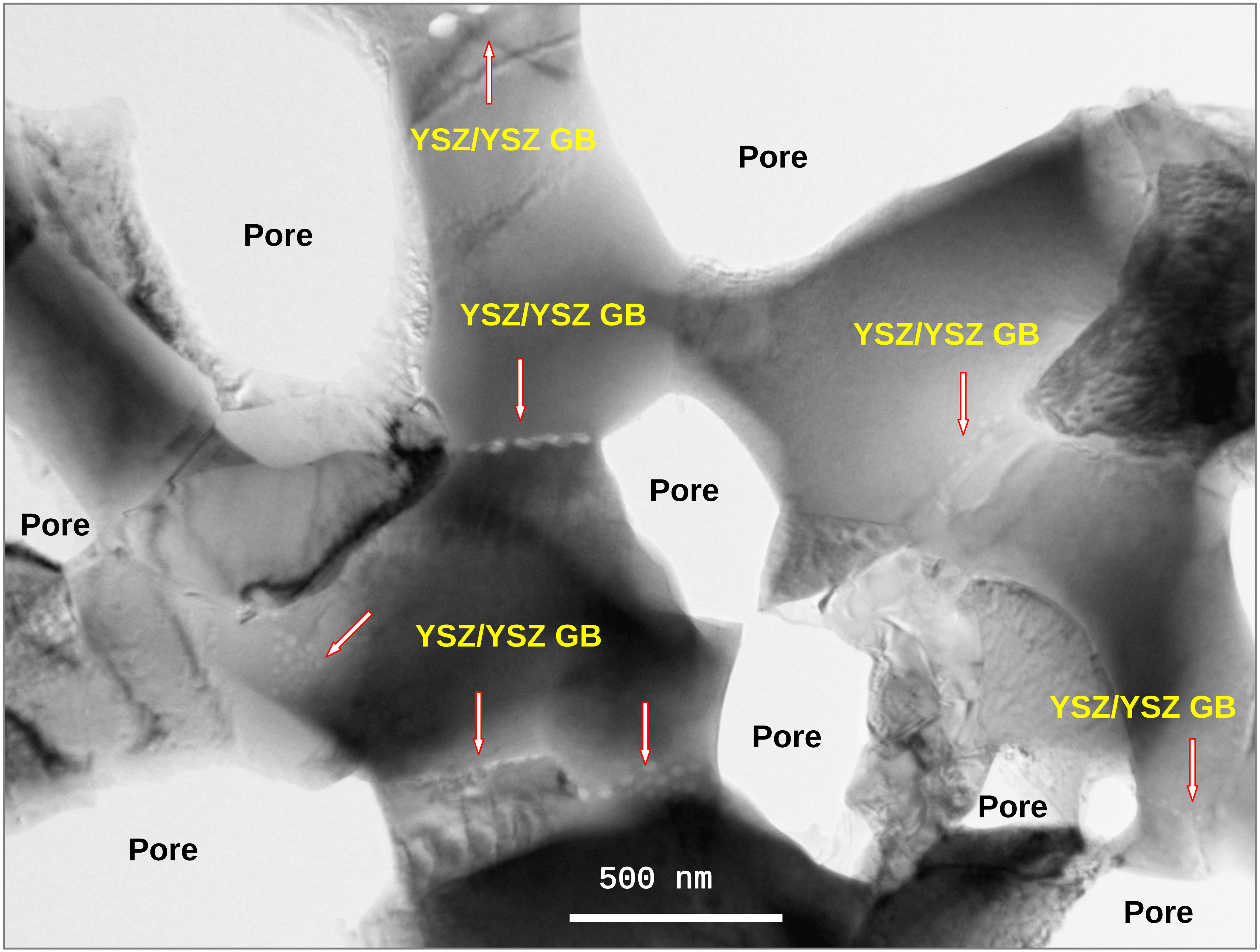
Anode degradation **is on both the Ni and YSZ.**



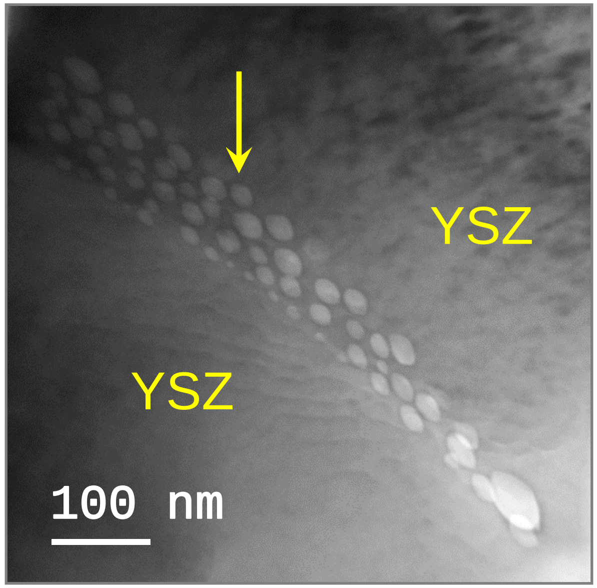


- Co-existence of Ni and NiO in the anode.
- Ni redox instability, and formation of NiO in the original pore regions.
- NiO, formed during the reactions, block the original TPBs.

Background: Ni/YSZ anode and YSZ/YSZ GB degradation

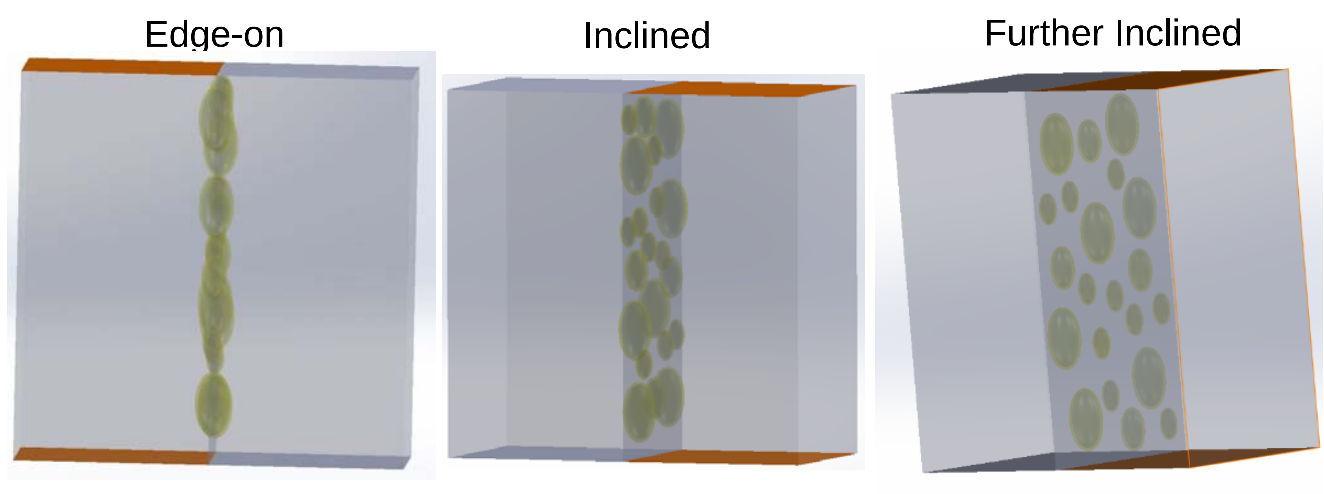


Background: Ni/YSZ anode and YSZ/YSZ GB degradation



- **Degradation at YSZ/YSZ GBs**
- **Oval shaped along the GB plane.**
- **~20-50 nm in dimension.**
- **2-3 nm shell region.**
- No other contamination elements.
- Y depleted**, low mass in cores.**

Atomic%	Nano-sphere Cores	Adjacent YSZ Grain	Adjacent YSZ Grain
O K	53.73	59.39	58.82
Ni K	-	0.77	0.47
Y L	-	4.82	4.98
Zr L	46.27	35.02	35.73



Y. Chen, X. Song, K. Gerdes, et al, Degradation of YSZ as SOFC Ionic Conductor upon Long Term Electrochemical Operation (to be submitted).

Overview

- **Scientific and Technical Merit**
  - State-of-the-art Ni/YSZ anode, and its degradation with H_2 fuel
  - Direct hydrocarbon utilization: Principle and challenges
- **Project Objective and Tasks To Be Performed**
  - Objective
  - Tasks
- **Approaches**
  - Ni/YSZ surface multi-functional nano-scaffold, facilitated by multiple heterostructured interfaces
  - Uniqueness of ALD and its technical challenge for SOFC applications
- **Preliminary Results**
  - Single phase discrete nano crystals of oxide conductor on Ni/YSZ
  - Single phase of electro-catalysts on Ni/YSZ
  - Dural phase nano-composite consisting oxide conductor and nano catalyst on Ni/YSZ

Background: Internal reforming - Direct hydrocarbon utilization

Steam reforming:

Steam reforming reaction **CH_4+H_2O <-> $CO+3H_2$** (endothermic ΔH^o_{298} = 206 kJ mol^{-1})
Water gas shift reaction **$CO+H_2O$ <-> CO_2+H_2** (exothermic ΔH^o_{298} = -41 kJ mol^{-1})

Advantages: (1) Waste heat (electrochemical reactions and ohmic heating) is directly used for the endothermic reforming reaction. (2) Equipment costs are lower if proper control of the catalytic activity is achieved.

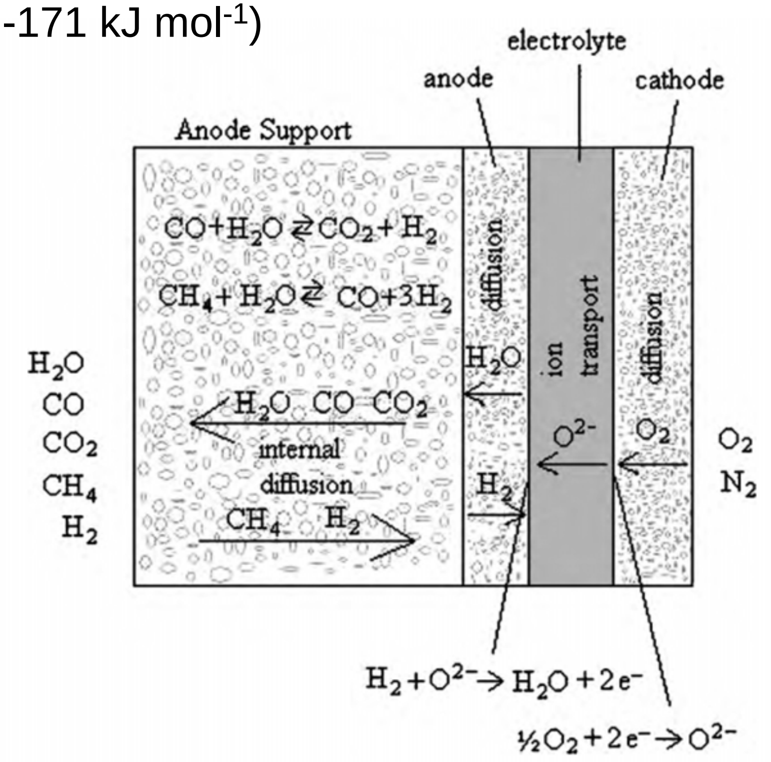
Side reactions:

Methane decomposition/cracking (MD) **CH_4 <-> $C(s)+2H_2$** (ΔH^o_{298} = 75 kJ mol^{-1})
Boudouard reaction (BR) **$2CO$ <-> $C(s)+CO_2$** (ΔH^o_{298} = -171 kJ mol^{-1})

Disadvantage: carbon deposition, and internal steam reforming is much faster than the electrochemical reactions and induce thermal stress.
Goal for optimizing internal steam reforming: is to lower the reaction rate of steam reforming, while maintaining high electric conductivity and high reactivity of the electrochemical reactions.

Approaches: (1) operating temperatures (2) adjust steam/hydrocarbon ratio (3) **anode surface modifications**.

[D Mogensen et al. J Power Sources, 196(2011)25]



Background: Internal reforming - Direct hydrocarbon utilization

Dry reforming:

Extremely endothermic reaction **CH_4+CO_2 <-> $2CO+2H_2$** (ΔH^o_{298} = +247 kJ mol^{-1}),
Reverse water gas shift reaction **$CO+H_2O$ <-> CO_2+H_2** (exothermic ΔH^o_{298} = -41 kJ mol^{-1})

Side reactions:

Methane decomposition (MD) **CH_4 <-> $C(s)+2H_2$** (ΔH^o_{298} = 75 kJ mol^{-1})
Boudouard reaction (BR) **$2CO$ <-> $C(s)+CO_2$** (ΔH^o_{298} = -171 kJ mol^{-1})

Advantage: (1). Dry reforming has a 20% lower operating cost compared to the other reforming processes. *[Ross Catal. Today 2005 100, p.151]*. (2).Reactants CO_2 and CH_4 are both greenhouse gases.

Disadvantage: coking, and high temperatures (~ 830ºC) are required to reach high conversions. ***Goal for optimizing internal dry reforming:*** is to reduce carbon deposition and attain high conversions and high H_2/CO yield. [*Pakhare and Spivey, Chem Soc Rev 2014, 43, p.7813*]

Approaches: (1) operating temperatures (2) **anode surface modifications**.

Overview

- **Scientific and Technical Merit**
  - State-of-the-art Ni/YSZ anode, and its degradation with H_2 fuel
  - Direct hydrocarbon utilization: Principle and challenges
- **Project Objective and Tasks To Be Performed**
  - Objective
  - Tasks
- **Approaches**
  - Ni/YSZ surface multi-functional nano-scaffold, facilitated by multiple heterostructured interfaces
  - Uniqueness of ALD and its technical challenge for SOFC applications
- **Preliminary Results**
  - Single phase discrete nano crystals of oxide conductor on Ni/YSZ
  - Single phase of electro-catalysts on Ni/YSZ
  - Dural phase nano-composite consisting oxide conductor and nano catalyst on Ni/YSZ

Project Objectives

This project will design and modify internal surfaces of Ni/YSZ anodes from currently commercial available SOFCs.

Three dimensional (3-D) nano scaffold architectures with both nano-catalysts and nanoscale oxides will be applied on Ni/YSZ surface.

The surface architecture will be ***multi-functional and nano-scaled, facilitated by multiple heterostructured interfaces that will significantly enhance the power density and anode durability***. The objective will be achieved by:

1. Increasing the electrochemical reaction sites to enhance the hydrogen/hydrocarbon oxidation reactions;
2. Promoting the internal reforming capabilities especially for natural gas application;
3. Enhancing tolerance to carbon formation;
4. Mitigating coarsening of the backbone Ni phase and the oxidation attack of Ni from oxidants (e.g. H_2O, CO_2);
5. Accelerating anode reactions thereby decreasing the over-potential;
6. Mitigating YSZ degradation.

Tasks To Be Performed

3-D nano scaffold architectures will be applied to the internal surfaces of entire porous SOFC anode, using Atomic Layer Deposition (ALD).

- **Task 2.0**: Design and fabricate single phase porous nano-grained conductor network on the surface of the composite anodes of Ni/YSZ.
- **Task 3.0**: Develop a single phase electro-catalytic network on surface of Ni/YSZ anode.
- **Task 4.0**: Develop a dual-phase nanostructured porous nano scaffold on surface of Ni/YSZ anodes

Nano-scale architecture/scaffold: The formation of the engineered nano-scale architecture/scaffold on the surface of SOFC cathode will be analyzed by TEM.

Performance Characterization: Commercial anode support full cells.

- Cells will be tested at different temperatures 700^{o}C and 750^{o}C.
- Constant current density of 0.3 A/cm^2.
- Operated for >500 h and impedance will be taken periodically.

Overview

- **Scientific and Technical Merit**
  - State-of-the-art Ni/YSZ anode, and its degradation with H_2 fuel
  - Direct hydrocarbon utilization: Principle and challenges
- **Project Objective and Tasks To Be Performed**
  - Objective
  - Tasks
- **Approaches**
  - Ni/YSZ surface multi-functional nano-scaffold, facilitated by multiple heterostructured interfaces
  - Uniqueness of ALD and its technical challenge for SOFC applications
- **Preliminary Results**
  - Single phase discrete nano crystals of oxide conductor on Ni/YSZ
  - Single phase of electro-catalysts on Ni/YSZ
  - Dural phase nano-composite consisting oxide conductor and nano catalyst on Ni/YSZ

Overview

- **Scientific and Technical Merit**
  - State-of-the-art Ni/YSZ anode, and its degradation with H_2 fuel
  - Direct hydrocarbon utilization: Principle and challenges
- **Project Objective and Tasks To Be Performed**
  - Objective
  - Tasks
- **Approaches**
  - Ni/YSZ surface multi-functional nano-scaffold, facilitated by multiple heterostructured interfaces
  - Uniqueness of ALD and its technical challenge for SOFC applications
- **Preliminary Results**
  - Single phase discrete nano crystals of oxide conductor on Ni/YSZ
  - Single phase of electro-catalysts on Ni/YSZ
  - Dural phase nano-composite consisting oxide conductor and nano catalyst on Ni/YSZ

Approaches: Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD):

- ALD is a method for depositing *thin films* onto various substrates with atomic scale precision.
- Principle is similar to chemical vapor deposition except that ALD reactions are separated into two half reactions by keeping the precursor materials separate during the reactions
- ALD film growth is self limited and based on surface reactions. Therefore, film thickness control can be as fine as monolayer.

A sequential chemical vapor deposition technique allowing processing of one mono-atomic layer after another.

Steven M George, Atomic Layer Deposition: An Overview, Chemical review, 2010, 110, 111-131

Nicola Pinna, Mato Knez , Atomic Layer Deposition Of Nanostructured Materials, Wiley, 2011

Approaches: ALD Growth Procedure and Applications

Self-limiting **film growth via alternate exposure/*saturative* of chemical species in *layer by layer* manner.**

1) Metal ***precursor*** exposure.
2) Purging of the precursors and any byproducts from the chamber.
3) Exposure of the ***other reactant species*** (non-metal precursor).
4) Purging of the reactants and byproduct molecules from the chamber.

- **Protective coatings**
- **Optics**
- **Magnetic recording heads**
- **Microelectronics**
- **MEMS**
- **Photovoltaics**
- **Catalyst**

J. Mater. Chem. C, 2014, 2, 5805

Approaches: Advantages of ALD

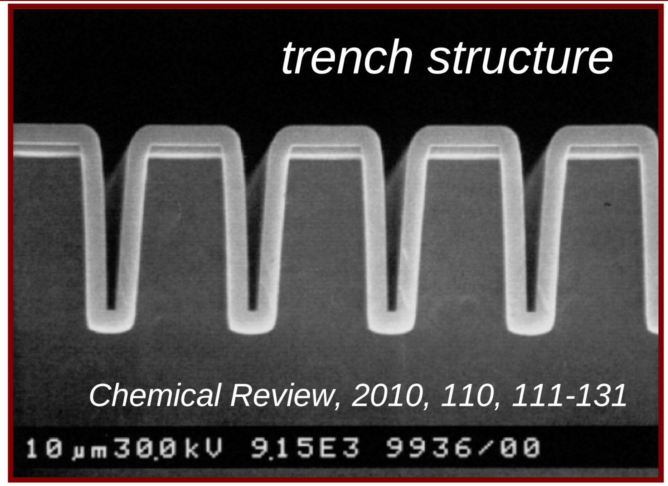
ALD is unique in processing of films

When substrate are:

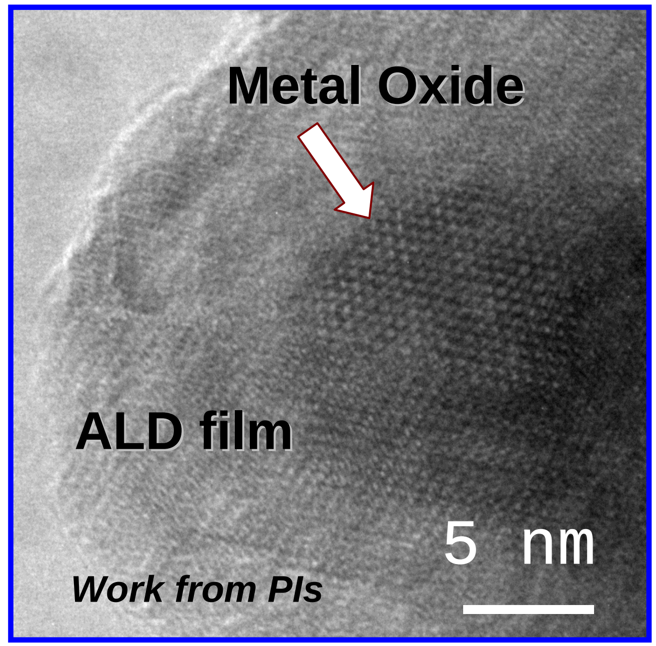
- ❖ Large surface area.
- ❖ Porous.
- ❖ Complex shaped.
- ❖ Ultra high aspect ratio.

When films need to be:

- ✓ *Thin.*
- ✓ *Controlable thicknesses to atomic level.*
- ✓ *Uniform over entire substrate.*
- ✓ *Conformal in deep trenches.*
- ✓ *High quality.*
- ✓ *Reproducible.*
- ✓ *Easy scale-up.*



~300 nm Al_2O_3 ALD film on Si substrate



~5 nm ALD film on oxide particle

Uniqueness and Challenge of ALD for SOFC Applications

ALD is unique in processing of films.

When substrate are:

- *Large surface area.*
- *Porous.*
- *Complex shaped.*
- *Ultra high aspect ratio.*

When films need to be:

✓*Thin.*

✓*Controllable thicknesses to atomic level.*

✓*Uniform over entire substrate.*

✓*Conformal in deep trenches.*

✓*High quality.*

✓*Reproducible.*

✓*Easy scale-up.*

SOFCs:

Performance strictly depending on the surface properties of electrodes.

Electrodes are with:

- *Large surface area.*
- *Porous active structure.*
- *Complex 3D topographies.*
- *High aspect ratio.*

Technical challenges:

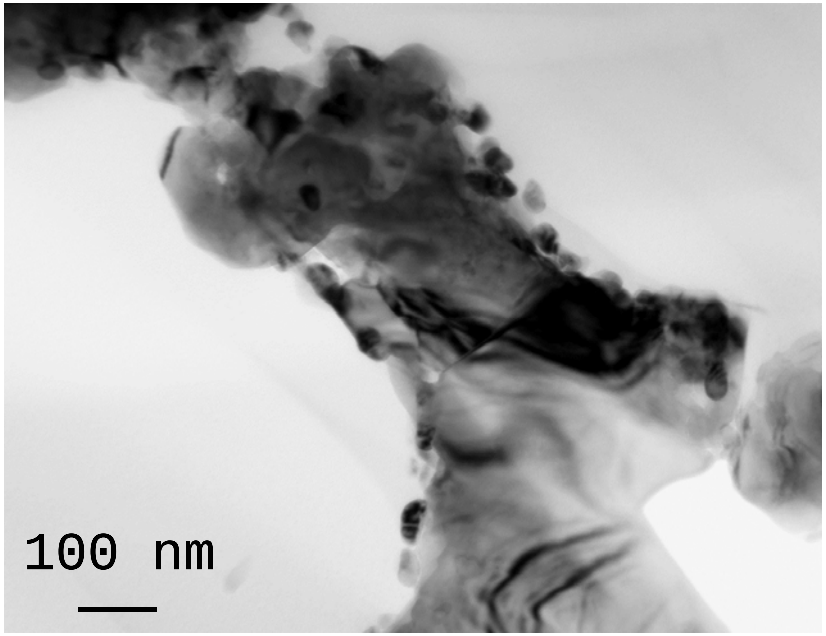
✓*ALD possesses significant promise for SOFC. Insufficient research to assure success in commercial applications.*

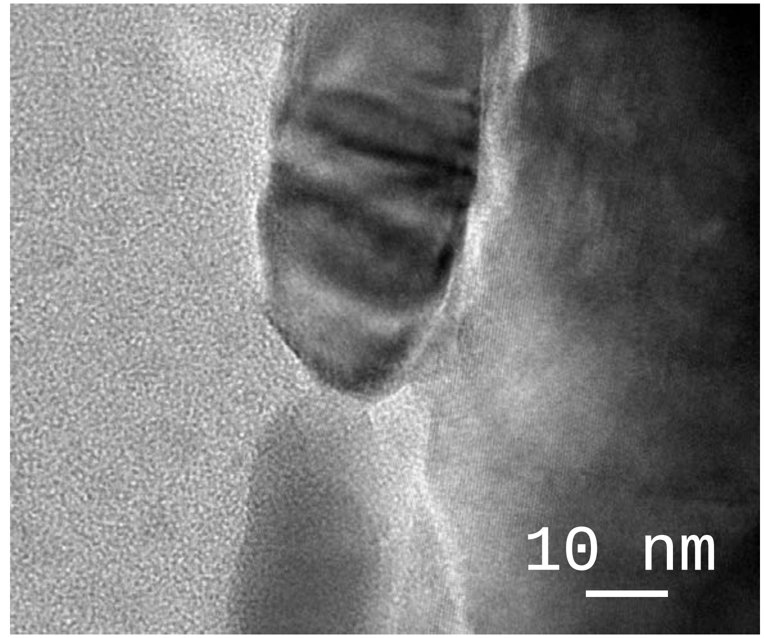
✓*No ALD work reported on the commercial SOFCs.*

Overview

- **Scientific and Technical Merit**
  - State-of-the-art Ni/YSZ anode, and its degradation with H_2 fuel
  - Direct hydrocarbon utilization: Principle and challenges
- **Project Objective and Tasks To Be Performed**
  - Objective
  - Tasks
- **Approaches**
  - Ni/YSZ surface multi-functional nano-scaffold, facilitated by multiple heterostructured interfaces
  - Uniqueness of ALD and its technical challenge for SOFC applications
- **Preliminary Results**
  - Single phase discrete nano crystals of oxide conductor on Ni/YSZ
  - Single phase of electro-catalysts on Ni/YSZ
  - Dural phase nano-composite consisting oxide conductor and nano catalyst on Ni/YSZ

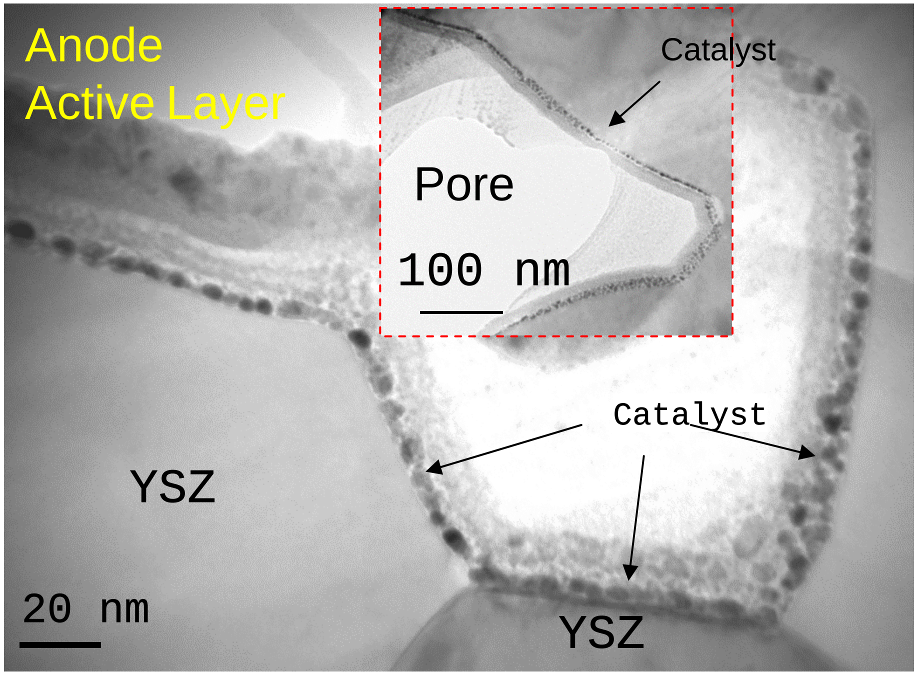
Preliminary Results: Single Layer Oxide Conductor on Electrode

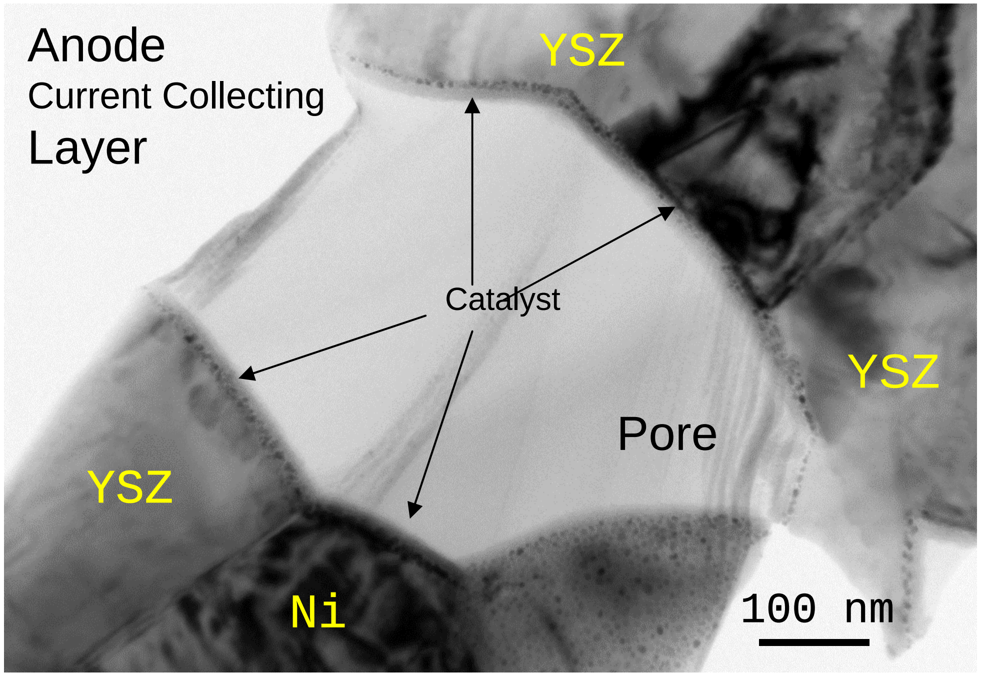




- Conformal coating on the surface of porous electrode.
- Layer thickness is uniform throughout the sample.

Preliminary Results: Catalyst on the Internal Surface of Ni/YSZ





- Catalyst is infiltrated/coated on both the YSZ and Ni grain surface.
- Catalyst is conformal on both anode active layer and anode current collecting layer

Overview

➢ Scientific and Technical Merit

- State-of-the-art Ni/YSZ anode, and its degradation with H_2 fuel
- Direct hydrocarbon utilization: Principle and challenges

➢ Project Objective and Tasks To Be Performed

- Objective
- Tasks

➢ Approaches

- Ni/YSZ surface multi-functional nano-scaffold, facilitated by multiple heterostructured interfaces
- Uniqueness of ALD and its technical challenge for SOFC applications

➢ Preliminary Results

- Single phase discrete nano crystals of oxide conductor on Ni/YSZ
- Single phase of electro-catalysts on Ni/YSZ
- Dural phase nano-composite consisting oxide conductor and nano catalyst on Ni/YSZ

Acknowledgements

National Energy Technology Laboratory

DOE Award – FE0026167

Program Manager: Briggs White