Final Scientific/Technical Report

Scalable Nano-Scaffold SOFC Anode Architecture Enabling Direct Hydrocarbon Utilization

DE-FE0026167

Recipient: West Virginia University Research Corporation
October 1, 2015, to July 31, 2021
Principle Investigator: Xueyan Song, Ph.D.,
Professor,
George B. Berry Chair of Engineering
Department of Mechanical and Aerospace Engineering,
West Virginia University
Tel: 304-293-3269,
Email: xueyan.song@mail.wvu.edu

1 Abstract

This project is based on WVU's pending patents, technology and aims to design and modify the internal surfaces of the Ni/YSZ anode from currently commercially viable Solid Oxide Fuel Cells (SOFCs) using the additive manufacturing process of Atomic Layer Deposition (ALD). The surface architecture/scaffold added onto the internal surface of the anode possesses an engineered nanostructure but it features only commonly-used oxide conductors and electro-catalyst materials. The surface layer possesses a minimum thickness of ~2-40 nm and is solely designed to control the surface reforming reactions and to increase catalytic activity. Three-dimensional (3D) nano scaffold architectures with the noble metal nano-catalyst, low-cost bimetallic catalytic alloys, and nano-scale ionic conducting oxide fully compatible with the state-of-the-art Ni/YSZ anode, were applied to the internal surface of the entire porous SOFC anode using ALD. In the present work, the surface scaffold architecture is essentially multi-functional at the nano-scale, facilitated by the multiple heterostructured interfaces. It will significantly enhance the power density and cell durability for direct hydrocarbon utilization by (1) increasing the number of electrochemical reaction sites to enhance the hydrogen/hydrocarbon oxidation reactions; (2) reducing carbon formation; (3) mitigating the coarsening of backbone Ni phase and the oxidation attack of Ni from oxidants (e.g., H_2O, CO_2); and (4) promoting the internal reforming capabilities, especially for natural gas applications. ALD is employed to generate stable anode surface architectures that are uniform, precisely controllable at the atomic scale, and accurately repeatable for processing. The engineered anode surface nano-scaffold architecture was cataloged and analyzed using High-resolution Transmission Electron Microscopy (TEM), and cell power/durability performance assessed via comprehensive electrochemical performance testing with commercial specimens and relevant environments using hydrocarbon fuels.

To the best of our knowledge, this project is the First Report on ALD of Ni/YSZ. The actual achievement of this Project includes (1). Successful demonstration of 7 types of ALD layers on Ni/YSZ anode, including mono-catalysts and multi-functional nano-composite. (1). Conformal coating and subsequently spontaneously pinning the discrete nano-catalyst,. Those nano-catalysts on the ionic-conducting YSZ provided excellent sites for promoting internal reforming; (2). Demonstrated ALD coating increased both catalytic activity and conductivity of Ni/YSZ. Conformal coating provided dopants and introduced additional electrical conducting pathways on the YSZ ionic conductor. The doped surface layer of YSZ with mixed conductivity thus further introduces the active triple phase boundaries adjacent to the ALD-coated nano-catalysts that are pinned on the YSZ surface. The nano-composite ALD coating on Ni/YSZ anode has significantly increased cell durability; and (3). ALD coating of Ni/YSZ anode increased the power density of the entire cell by 300%.

For a long time, the SOFC performance, such as the power density, was deemed hindered by the cathode. The sluggish oxygen reduction reaction (ORR) in the cathode was deemed as hindering the power density of the SOFCs. For the anode-supported commercial SOFCs, the cell performance is considered to be limited by the cathode's performance.

For the first time in the field of SOFC, this project has demonstrated that (1). the performance of commercial SOFCs can be further increased by the ALD coating on Ni/YSZ anode backbone. (2). ALD coating on Ni/YSZ fuel electrodes results in the enhancement of power density, and increased reliability, robustness, and endurance of SOFCs, for their application using both hydrogen and hydrocarbon fuels over the entire operating temperature range of 650-800ºC for the inherently functional commercial cells. (3). ALD coating provides alternative approaches of exsolutions for introducing the stable catalyst onto the internal surface of the Ni/YSZ electrode. ALD coating could be much more versatile than exsolution in employing the catalysts with various chemistries onto the various backbones. (4). Due to the negligible amount of ALD materials coated onto the internal surface of the porous cathode of the as-fabricated cells, a peak power density increase up to 300 % induced by ALD coating was simultaneously achieved in terms of both power density and specific power. (5). The ALD coating developed through this project was applied to both the SOFC and Solid Oxide Electrolysis Cells (SOEC). SOEC's face a similar but more demanding need to improve the fuel electrode's performance. It opens further research directions for electrocatalytic surface nanoionics with a wide range of chemistry. It will **revolutionize our ability to render the formation of a nanostructured electrode** that has been constantly pursued yet barely achieved for practical SOFC/SOEC applications. The research is also immediately transformative since both the preliminary data and the proposed work are on the direct implantation of nanoionics into the state-of-the-art inherently functional SOCs. It **represents an immediate impact on the commercial sectors** in SOC technology since the applied ALD processing is computer-controlled ALD coating using the commercial ALD systems, and it is scalable to both the single cells and SOC stacks.

Table of Contents

1 Abstract 3
2 Executive Summary 8
3 Comparison of The Actual Accomplishment with the Goals and Objectives 10
  3.1 Proposed goals and objectives 10
  3.2 Actual Accomplishment 10
  3.3 References cited 12
4 Internal Surface Modification of Ni/YSZ Electrode, ALD and Uniqueness of This Project 13
  4.1 Ni/YSZ Fuel Electrode In SOFCs and Its Related Degradation 13
    4.1.1 Degradation on Ni-Based anode due to Redox Instability 17
    4.1.2 Degradation on Ni-Based anode due to Carbon Deposition 21
    4.1.3 Mitigation of Ni/YSZ Electrode Degradation and Carbon Deposition on Fuel Electrode 25
  4.2 ALD Coating of Ni/YSZ, its Advantages and Technical Challenges 31
  4.3 Uniqueness of ALD developed from this project: Ni/YSZ Anode Only and deep penetration .. 32
  4.4 References cited 34
5 ALD-Enabled Spontaneously Pinned Nano-Catalyst on the Internal Surface of Ni/YSZ 39
  5.1 ALD Mono-Metallic and Bi-Metallic Electrocatalyst onto the Internal Surface of Ni/YSZ 39
  5.2 Experimental Section 39
  5.3 Results and Discussion-ALD coating pinned catalyst on YSZ surface 41
    5.3.1 Minute amount of ALD Coating onto the Ni/YSZ of Anode Active Layer 41
    5.3.2 Performance Enhancement 43
    5.3.3 Spontaneously Pinned Nano-Catalyst on the Internal Surface of Ni/YSZ 43
    5.3.4 Impact of Pinned Nano-Catalyst on Ni/YSZ on Electrochemical Performance 46
  5.4 Results and Discussion-ALD Nano Catalyst and Formation of Catalytic Alloy 49
  5.5 Results and Discussion-ALD Coating Nano Ni-catalyst on YSZ 51
  5.6 Results and Discussion- Design of the ALD Coating Layer with Composite 53
  5.7 Summary 56
  5.8 References Cited 58
6 Patentable Materials: Simultaneously Enhancing Both the Conductivity and Catalytic Activity 59
  6.1 Introduction: ALD coating on the nanostructure and Conductivity of Ni/YSZ 59
  6.2 Experimental Section 61
  6.3 Results and Discussions: ALD coating of dual layer on Ni/YSZ 63
  6.4 Summary 79
  6.5 References Cited 81
7 Patentable Materials: ~300 % Increase of the Power Density of SOFC by ALD Nano-Catalyst 83
  7.1 Introduction: Potential large performance enhancement of Catalytic Activity SOFC Anode 83
  7.2 Experimental Section 84
  7.3 Results and Discussions 85
    7.3.1 As-deposited ALD layer on Ni/YSZ 85
    7.3.2 Ultra-Thin Layer of ALD-coating applied on Ni/YSZ 88

7.3.3 Electrochemical performance of ~ 300 % increase of cell peak power density 89
7.3.4 Nanostructure Evolution of ALD Nano-Catalyst upon electrochemical operation 95
7.3.5 Nanostructrure and Thermodynamic Origin of the Large Cell Performance Enhancement 96
7.4 Summary 100
7.5 References Cited 102
8 Patentable Materials: ALD coating of Ni/YSZ for Dramatically Increased Coking Resistance 103
8.1 Introduction-Coking of Ni/YSZ Electrodes 103
8.2 Experimental Section 106
8.3 Results and Discussions 108
8.4 Summary 115
8.5 References Cited 117
9 Technical Effectiveness of ALD, Project Conclusion and Product 120
9.1 Target community of beneficiaries: 120
9.2 State-Of-The-Art Solution Based Infiltration and its Technical Barrier 121
9.3 Uniqueness of ALD and its Technical Challenge for SOFC Applications 121
9.4 Technical Effectiveness and Economic Feasibility of ALD Developed Through This Project 122
9.5 Project Conclusion and Product 123
9.6 References Cite 124

Scalable Nano-Scaffold SOFC Anode Architecture Enabling Direct Hydrocarbon Utilization

2 Executive Summary

This project is based on West Virginia University (WVU)'s patent-pending technology and aimed to design and modify the internal surfaces of the Ni/YSZ anodes from currently commercially viable Solid Oxide Fuel Cells (SOFCs) using the additive manufacturing process of Atomic Layer Deposition (ALD). The surface architecture/scaffold added onto the internal surface of the anode possesses an engineered nanostructure but it features only commonly-used oxide conductors and electro-catalyst materials. The surface layer possesses a minimum thickness of ~2-40 nm and is solely designed to control the surface reforming reactions and increase catalytic activity. Three-dimensional (3D) nano scaffold architectures with noble metal nano-catalyst, low-cost bimetallic catalytic alloys, and nano-scale ionic conducting oxide that are fully compatible with the state-of-the-art Ni/YSZ anode, were applied to the internal surface of entire porous SOFC anode, using ALD. In the present work, the surface scaffold architecture were essentially multi-functional at the nano-scale, facilitated by the multiple heterostructured interfaces, and significantly enhanced the power density and cell durability for direct hydrocarbon utilization by (1) increasing the electrochemical reaction sites to enhance the hydrogen/hydrocarbon oxidation reactions; (2) reducing the carbon formation; (3) mitigating the coarsening of backbone Ni phase and the oxidation attack of Ni from oxidants (e.g. H_2O, CO_2). (4) promoting the internal reforming capabilities, especially for natural gas application; ALD is employed to generate stable anode surface architectures that are uniform, precisely controllable at the atomic scale, and accurately repeatable for processing. The engineered anode surface nano-scaffold architecture was cataloged and analyzed using High-resolution Transmission Electron Microscopy (TEM), and cell power/durability performance assessed via comprehensive electrochemical performance testing with the commercial specimen and relevant environments using hydrocarbon fuels.

To the best of our knowledge, this project is the First Report on ALD of Ni/YSZ. The actual

achievement of this Project includes (1). Successful demonstration of 7 types of ALD layers on Ni/YSZ anode, including mono-catalyst and multi-functional nano-composite. (2). Demonstrated ALD coating increasing both the catalytic activity and conductivity of Ni/YSZ. (3). ALD coating of Ni/YSZ anode increased the power density of the entire cell by 300%. (4). ALD coating of nano-composite on Ni/YSZ anode has significantly increased cell durability. (5). For the anode-supported commercial cells, the SOFC performed is deemed limited by the cathode's performance. For the first time in the field of SOFC, this project has demonstrated that the commercial SOFC performance can be further and dramatically increased by the ALD coating of Ni/YSZ anode. Due to the negligible amount of ALD materials coated onto the internal surface of the porous cathode of the as-fabricated cells, the peak power density increase of up to 300 % induced by ALD coating was simultaneously achieved in terms of both power density and specific power.

Overall, this project has successfully developed and demonstrated that for the inherently functional commercial cells, ALD coating of Ni/YSZ fuel electrode results in the enhancement of power density, and increased reliability, robustness, and endurance of SOFCs, for their application using both hydrogen and hydrocarbon fuels over the entire operating temperature range of 650-800ºC. It opens new research directions in terms of the fundamental design of the internal surface of the fuel electrode, including both the well-developed Ni/YSZ and emerging ceramic anodes for SOFC electrochemical reactions at elevated temperatures.

3 Comparison of The Actual Accomplishment with the Goals and Objectives

3.1 Proposed goals and objectives

Our target material systems are commercial Ni/YSZ anodes, and our emphasis is on direct hydrocarbon utilization for SOFC at cell operation temperatures of 650-800 ºC. The research objectives are (1) Objective 1: Optimize the ALD capping layer on YSZ to promote the performance of SOFC when fueled with hydrocarbon. (2) Objective 2: Design a low-cost bimetallic catalyst to promote hydrocarbon utilization. (3). Objective 3: Design a nano-composite consisting of low-cost bimetallic catalyst and oxide conductor to increase the carbon resistance, optimize the rate of internal reforming and promote the electrochemical reactions. (4). Objective 4: Apply the designed ALD coating to evaluate its feasibility of achieving 50% greater power density for commercial operation using hydrocarbon fuel at 650-800 ºC and of achieving increased durability for long term operation.

3.2 Actual Accomplishment

The following key aspects make the proposed work relevant to the SECA industry teams and produced a significant impact on the DOE-SOFC program's technical development and objectives. (1). Modifying the internal surface of Ni/YSZ **from commercial cells for direct hydrocarbon utilization**. (2). **Highly repeatable and controllable (to atomic scale) manufacturing processing of ALD**. (3). **Cost-effective processing**. The surface architecture/scaffold possesses an engineered nanostructure but only employs commonly used oxide conductors and electro-catalyst materials. The surface layer possesses a minimum thickness of ~2-40 nm and is solely designed to control the surface reforming reactions and increased catalytic activity. (4). **Simple one-step gas/vapor automatic infiltration is time-efficient**. ALD processing is fully automatic. For a 40 nm ALD single or multiple layers, one can finish deposition within several hours. (5). **Scale-up ready**. ALD systems for large-scale SOFC stack processing are commercially available and capable of processing of cells and stacks. Overall, the proposed surface architectures added into the Ni/YSZ anode are expected to result in significant enhancement of electrochemical performance and durability for the commercial anodes, without materials set changes of the cells, and leading to an immediate impact on industry commercialization.

In terms of the chemistry of the ALD layer, this project has employed a commercially relevant electrolyte, electrocatalyst, and noble metal materials set. Such materials are fully compatible with the commercial fuel cells, and this project has developed a special nanostructure on the surface of the commercial composite cathodes. Under the support of this award, the following has been achieved:

Accomplishment -1: Spontaneous Pinned Nano-Catalysts on the Surface of Fuel Electrode

Accomplishment -2: Simultaneously Increased Conductivity and Catalytic Activity

Accomplishment -3: Significantly Increased Catalytic Activity and Power Density Induced by ALD Coating

For the anode-supported commercial cells, it is well agreed that the cell performance and cell power density is limited by the cathode performance. For the first time in the field of SOFC, the present work demonstrated that the ALD coating of the electrocatalyst on the Ni/YSZ electrode alone significantly reduced the ohmic resistance and dramatically increased the entire cell power density. Such a large cell power density increase was confirmed at both 700 and 650C. The cell power density increase was more significant at the lower temperature of 650C, and ALD coated cells increased up to 300% the original baseline power density

Accomplishment -4: Significantly Increased Catalytic Activity and Power Density Induced by ALD Coating

ALD coated cells demonstrated both the increased catalytic activity and the increased durability upon utilization of hydrocarbon fuel. Compared with the baseline cell hindered by the carbon formation upon fueling the hydrocarbon, the ALD coated cell showed increased power density and also higher carbon formation resistance.

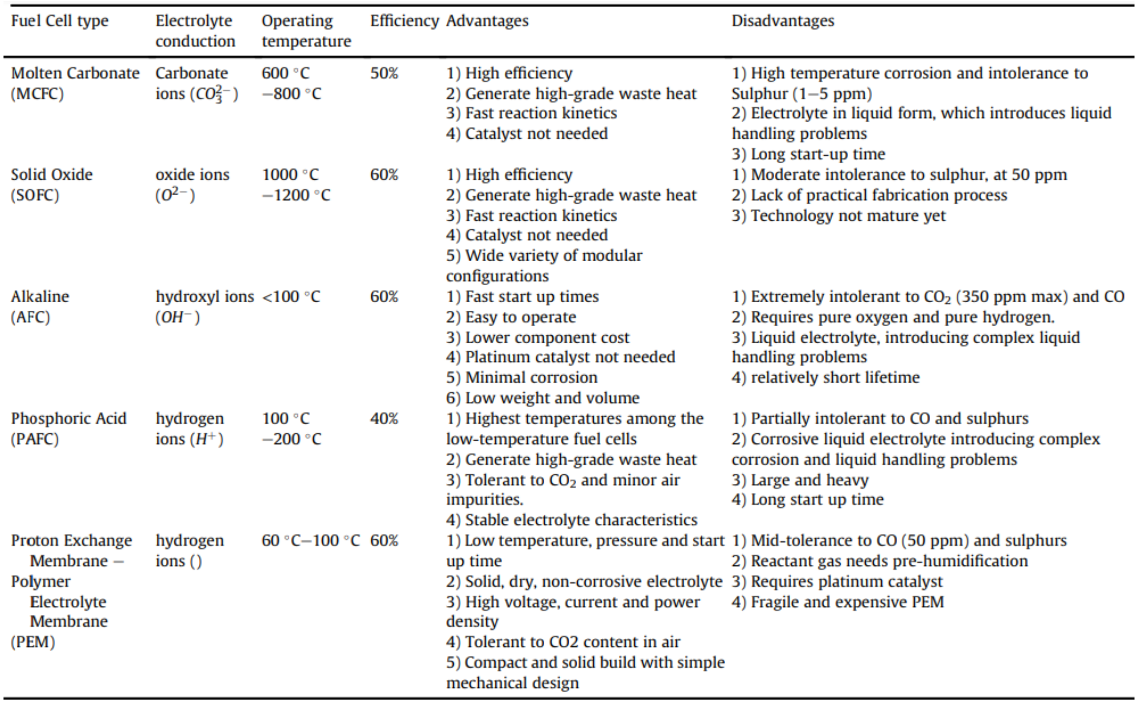
3.3 References cited

4 Internal Surface Modification of Ni/YSZ Electrode, ALD and Uniqueness of This Project

4.1 Ni/YSZ Fuel Electrode In SOFCs and Its Related Degradation

The world lacks safe, low-carbon, and cheap large-scale energy alternatives to fossil fuels. Until we scale up those alternatives, the world will continue to face the two energy problems of today. The energy problem that receives the most attention is the link between energy consumption and greenhouse gas emissions.[1] Alternative power generation systems are critical to meet the increasing demand for energy consumption. At the same time, those energy solutions need to tackle the complex challenges of climate change. The required power generation technologies not only need to focus on reducing byproduct contaminants but also need competitive performance over conventional technologies in order to be commercially accepted. Fuel Cells are one of the mainstream technologies that have been proposed as a critical part to achieve an efficient reversible conversion ecosystem to combat the increasing demand for energy and, at the same time, reduce the fossil fuel emissions from conventional energy conversion devices. 2

Table 1 Classification of most common fuel cells [4]



Fuel Cell type	Electrolyte conduction	Operating temperature	Efficiency	Advantages	Disadvantages
Molten Carbonate (MCFC)	Carbonate ions (CO_3^{2-})	600 °C –800 °C	50%	1) High efficiency 2) Generate high-grade waste heat 3) Fast reaction kinetics 4) Catalyst not needed	1) High temperature corrosion and intolerance to Sulphur (1–5 ppm) 2) Electrolyte in liquid form, which introduces liquid handling problems 3) Long start-up time
Solid Oxide (SOFC)	oxide ions (O^{2-})	1000 °C –1200 °C	60%	1) High efficiency 2) Generate high-grade waste heat 3) Fast reaction kinetics 4) Catalyst not needed 5) Wide variety of modular configurations	1) Moderate intolerance to sulphur, at 50 ppm 2) Lack of practical fabrication process 3) Technology not mature yet
Alkaline (AFC)	hydroxyl ions (OH^-)	<100 °C	60%	1) Fast start up times 2) Easy to operate 3) Lower component cost 4) Platinum catalyst not needed 5) Minimal corrosion 6) Low weight and volume	1) Extremely intolerant to CO_2 (350 ppm max) and CO 2) Requires pure oxygen and pure hydrogen. 3) Liquid electrolyte, introducing complex liquid handling problems 4) relatively short lifetime
Phosphoric Acid (PAFC)	hydrogen ions (H^+)	100 °C –200 °C	40%	1) Highest temperatures among the low-temperature fuel cells 2) Generate high-grade waste heat 3) Tolerant to CO_2 and minor air impurities. 4) Stable electrolyte characteristics	1) Partially intolerant to CO and sulphurs 2) Corrosive liquid electrolyte introducing complex corrosion and liquid handling problems 3) Large and heavy 4) Long start up time
Proton Exchange Membrane – Polymer Electrolyte Membrane (PEM)	hydrogen ions ()	60 °C–100 °C	60%	1) Low temperature, pressure and start up time 2) Solid, dry, non-corrosive electrolyte 3) High voltage, current and power density 4) Tolerant to CO2 content in air 5) Compact and solid build with simple mechanical design	1) Mid-tolerance to CO (50 ppm) and sulphurs 2) Reactant gas needs pre-humidification 3) Requires platinum catalyst 4) Fragile and expensive PEM

Fuel cells convert chemical energy directly to electrical energy with efficiencies as high as 70%.3 Commonly used fuel cells are listed in Table 1. 4 Solid Oxide Cells (SOCs) are one of the most promising fuel cells. SOCs can be used to store electricity as chemical fuels (electrolysis mode/SOEC mode) and convert fuels to electricity (fuel-cell mode/SOFC mode). [5,6,7] The SOC is composed of a dense electrolyte layer that is sandwiched between two porous electrodes (i.e., cathode and anode). [8] Figure 1 shows schematic representation and the main electrochemical reactions in the electrolyte, the fuel electrode, and the oxygen electrode for both the SOEC and SOFC modes.

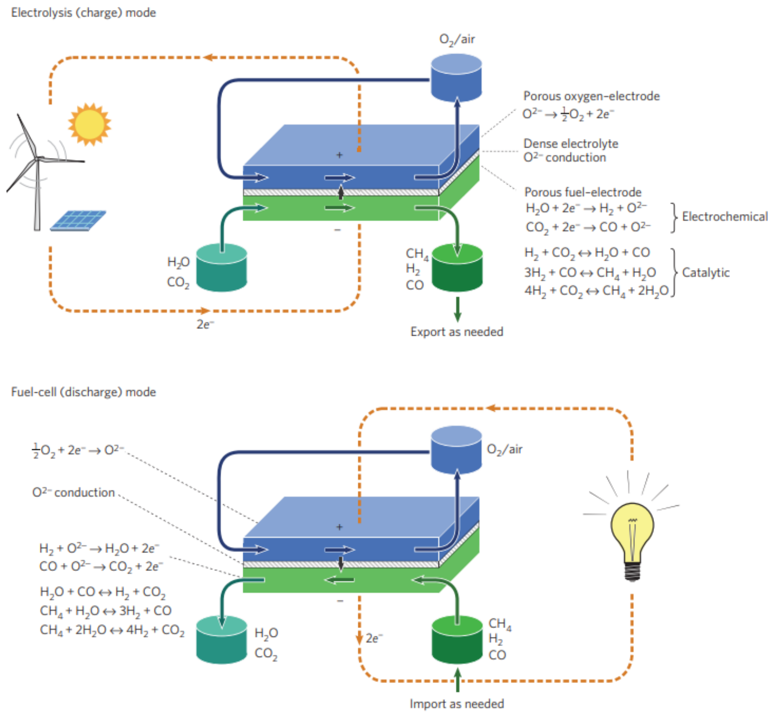


Figure 1 Schematic representation of SOFC and SOEC modes showing electrochemical reactions on electrolyte and electrodes. [7]

Successful SOCs devices are comprised of compatible cutting-edge materials for the electrolyte and electrodes. Notwithstanding, the material selection is complex and often leads to problems including electrode sintering, catalyst poisoning, interfacial diffusion between electrolyte and electrode materials, thermal instability, and mismatching coefficients of thermal expansion (CTE), limiting the development and use of SOCs. [9] The most common related issues for the anode, cathode, and electrolyte are presented in Figure 2.

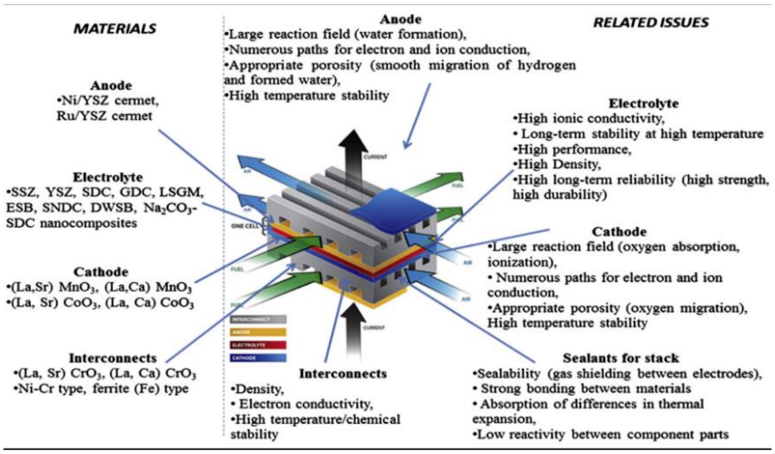
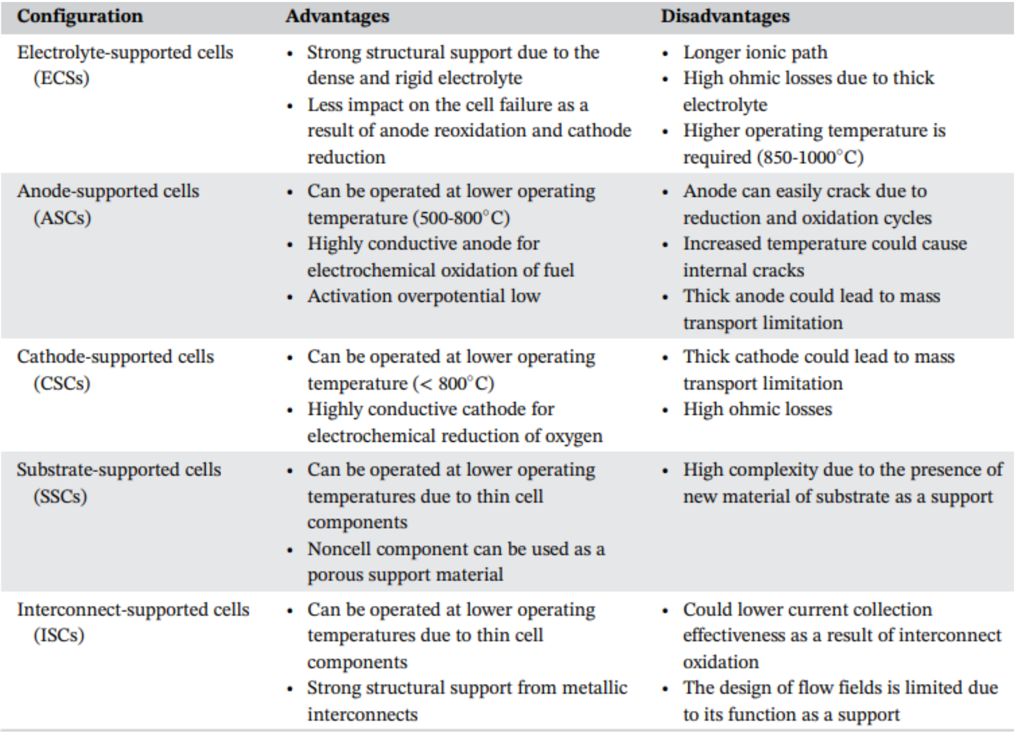


Figure 2 SOC material selection and related issues. [9]

Table 2 Commonly used SOC configuration advantages and disadvantages.[13]

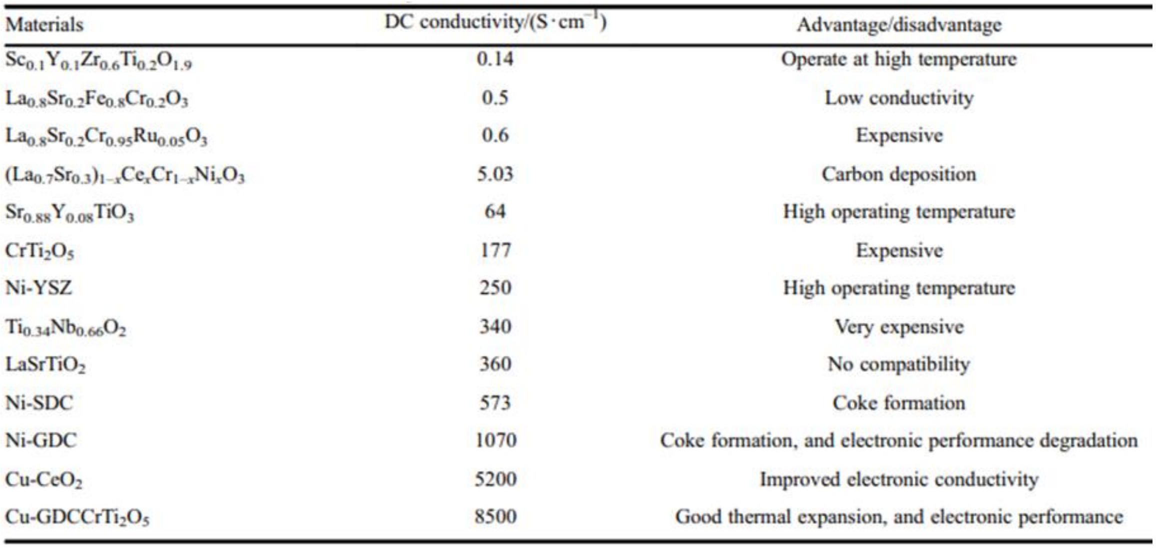


Configuration	Advantages	Disadvantages
Electrolyte-supported cells (ECSs)	• Strong structural support due to the dense and rigid electrolyte • Less impact on the cell failure as a result of anode reoxidation and cathode reduction	• Longer ionic path • High ohmic losses due to thick electrolyte • Higher operating temperature is required (850-1000°C)
Anode-supported cells (ASCs)	• Can be operated at lower operating temperature (500-800°C) • Highly conductive anode for electrochemical oxidation of fuel • Activation overpotential low	• Anode can easily crack due to reduction and oxidation cycles • Increased temperature could cause internal cracks • Thick anode could lead to mass transport limitation
Cathode-supported cells (CSCs)	• Can be operated at lower operating temperature (< 800°C) • Highly conductive cathode for electrochemical reduction of oxygen	• Thick cathode could lead to mass transport limitation • High ohmic losses
Substrate-supported cells (SSCs)	• Can be operated at lower operating temperatures due to thin cell components • Noncell component can be used as a porous support material	• High complexity due to the presence of new material of substrate as a support
Interconnect-supported cells (ISCs)	• Can be operated at lower operating temperatures due to thin cell components • Strong structural support from metallic interconnects	• Could lower current collection effectiveness as a result of interconnect oxidation • The design of flow fields is limited due to its function as a support

The fuel electrode is the component of SOFC where H_2 is oxidized in the presence of O_2- ions to produce H_2O. The characteristics necessary for the fuel electrode to perform adequately are related to the microstructure of the electrode (sufficient porosity to allow diffusion of gases), the stability of the material utilized in the electrode (chemical and mechanical stability), the electronic and ionic transport properties of the fuel electrode materials(high electronic and ionic conductivity), and the compatibility with the other components of the cell. [8]

The fuel electrode material is the main component utilized in the state-of-the-art SOCs anode-supported cells and accounts for nearly 95 % of the overall cell. [10] Therefore, the selection of the best anode material is important. The main characteristics that a fuel electrode material should possess are high electronic conductivity and sufficient electrocatalytic activity in order to minimize the polarization losses of the H2 oxidation reaction and achieve complete fuel oxidation. Another important material that SOCs systems require is that the fuel electrode material should be able to operate under different fuels (e.g., hydrogen, CO, natural gas) while tolerating carbon deposition, sulfur poisoning, and reoxidation. [11] Table 3 shows the conductivity of commonly used materials for fuel electrodes of SOCs, highlighting the advantages/disadvantages for each of them.

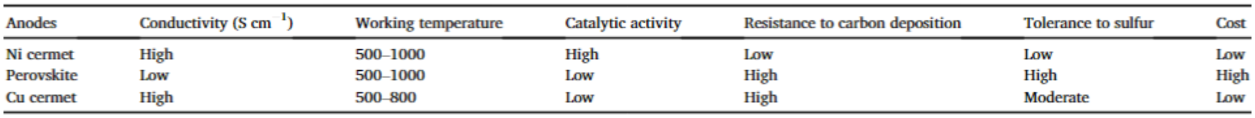
Table 3 Conductivities of commonly used fuel electrodes for SOCs. [10]



Materials	DC conductivity/($S \cdot cm^{-1}$)	Advantage/disadvantage
$Sc_{0.1}Y_{0.1}Zr_{0.6}Ti_{0.2}O_{1.9}$	0.14	Operate at high temperature
$La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$	0.5	Low conductivity
$La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O_3$	0.6	Expensive
$(La_{0.7}Sr_{0.3})_{1-x}Ce_xCr_{1-x}Ni_xO_3$	5.03	Carbon deposition
$Sr_{0.88}Y_{0.08}TiO_3$	64	High operating temperature
$CrTi_2O_5$	177	Expensive
Ni-YSZ	250	High operating temperature
$Ti_{0.34}Nb_{0.66}O_2$	340	Very expensive
$LaSrTiO_2$	360	No compatibility
Ni-SDC	573	Coke formation
Ni-GDC	1070	Coke formation, and electronic performance degradation
Cu-CeO_2	5200	Improved electronic conductivity
Cu-GDC$CrTi_2O_5$	8500	Good thermal expansion, and electronic performance

From the list of fuel electrode materials utilized in the SOC systems, Ni cermet material provides a better catalytic activity than the perovskite and Cu-cermet materials used as fuel electrodes, but one of the common characteristics of Ni-cermet electrodes is their low resistance for carbon deposition and a low tolerance for sulfur as depicted in Table 4. The best performance for the fuel electrode is usually achieved by optimizing the amount and size of Ni and YSZ particles (40 % Ni and 60 % YSZ composite have been found to have the lowest R_p among different compositions tested with a porosity value of 30–40 % to ensure insignificant concentration of polarization). [12] As is described in Table 2, the cell configuration of the most commonly used (anode-supported) cell can easily crack due to reduction and oxidation cycles. Therefore, the stability of anode for redox and thermal cycling is important for anode research. [13]

Table 4 Electrical and catalytic characteristics of fuel electrode materials for SOCs. [14]



Anodes	Conductivity (S cm ^{1})	Working temperature	Catalytic activity	Resistance to carbon deposition	Tolerance to sulfur	Cost
Ni cermet	High	500–1000	High	Low	Low	Low
Perovskite	Low	500–1000	Low	High	High	High
Cu cermet	High	500–800	Low	High	Moderate	Low

4.1.1 Degradation on Ni-Based anode due to Redox Instability

As it was previously discussed, the Ni/YSZ electrode degrades due to surface poisoning by contaminants in the utilized fuel, Ni coarsening, Ni migration (including Ni depletion close to active layer), destruction of Ni–YSZ interface, and formation of ZrO_2 on Ni surface due to redox cycling of YSZ. The main degradation challenges of the Ni-YSZ fuel electrode are associated with the Ni stability upon electrochemical operation. The Ni-YSZ electrode suffers from Ni grain growth, changes in its surface morphology, or its deactivation (from contaminants of hydrocarbon fuels), which results in a reduction of TPB density. The degradation mechanism encompasses three main issues. [15] The first degradation mechanism can be associated with the material transport properties where the Ni atoms, at higher temperatures, agglomerate by diffusion or by transport in the gas phase. Additionally, chemical gradients upon electrochemical operation can develop due to the presence of impurities or unsuitable material combinations, which will affect the transport of particles throughout the microstructure of the fuel electrode. The redox instability in the fuel electrode is of special importance because the redox cycling alters the microstructure of the anode and thereby degrades the performance of the anode and the associated electrical, electrochemical, and mechanical properties of the entire cell. [16] Figure 3 shows the microstructural changes during a redox process in ceramic-metallic anodes (such as Ni/YSZ). During long-term operation, the SOCs are expected to undergo multiple redox cycles. The main redox issues are presented when the fuel supply is interrupted. Since the oxygen ions continue passing through the electrolyte, the O_{2-} ions traveling to the anode will cause oxidation of Ni to NiO. The oxidation can also occur if the H_2O content in fuel and fuel utilization is high.

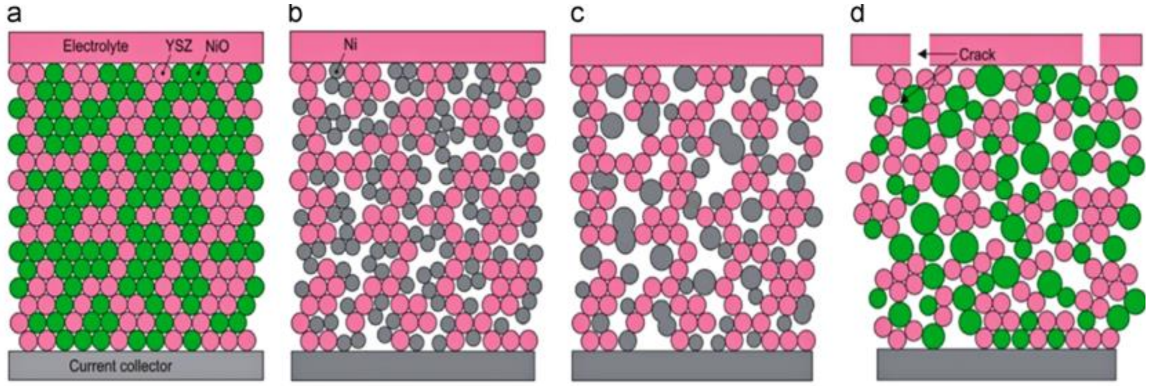


Figure 3 Microstructural changes during a redox process in cermet anodes. (a) As-sintered state, (b) Short-term reduced state, (c) Long-term reduced state, and (d) First re-oxidized state. [17]

Mitigation strategies for the redox stability of the fuel electrode include restricting the flow of extra air (from bad sealing components), reducing the Ni oxidation rate (coating the Ni surface with oxides such as Y, Zr, Ce to prevent Ni oxidation), increasing porosity (to reduce strain in the fuel electrode), and nanostructuring of the Ni-YSZ electrode. This mitigation strategy is intended to reduce the stresses that can cause additional porosity, network distortions, and eventually cracks in the electrolyte.

The degradation of the Ni-based fuel cell due to Ni coarsening and migration of Ni grains is significant because it changes the microstructure of the Ni/YSZ electrode (reducing the TPB density due to agglomeration of Ni particles) and results in some cases in the depletion of the active layer of the electrode (reduced/diminished TPB sites at the active layer). Ni coarsening/migration effect on the TPB density and depletion on the active layer is shown in Figure 4. It was reported that severe Ni depletion could increase total overpotential by up to 52.8 % compared to the initial state due to the reduction of the active reaction site.[19] The evolution of the morphology is a complex interaction of various microstructural parameters, such as particle size, porosity, volume fraction, and surface area. One of the correlated issues due to Ni coarsening/migration is the decreased TPB density, which increases anode R_p and decreases electrical conductivity due to loss of Ni–Ni contact (increase ohmic resistance). [18] There is also a direct relation of the smaller particle size (faster Ni coarsening) and the excessive volume fraction of Ni or YSZ (low percolation rate) to the overall TPB density in the fuel electrode.

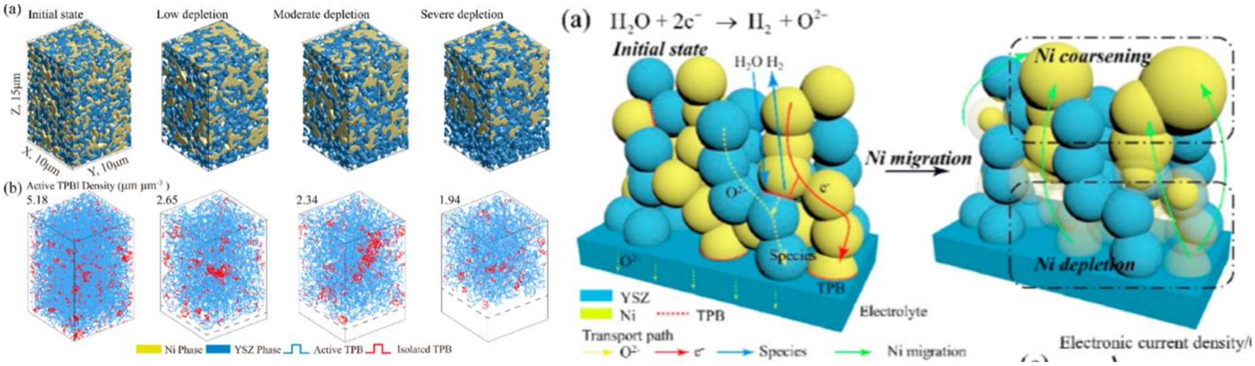


Figure 4 Effect of Ni depletion and schematic of Ni migration process in the fuel electrode. [19]

The two main mechanisms related to the microstructural change of Ni in the fuel electrode are related to diffusion and sintering of Ni particles (diffusion of vacancies, particles, and GBs) and to the Ni transport in the gas phase. According to reported data, during SOEC operation, the electrode/electrolyte interface presents a higher contact angle compared to the region in the gas channel, which leads to Ni migration from the active electrode towards the support layer. On the other hand, during SOFC operation, the contact angle at the electrode/electrolyte interface is lower than in the gas channel region, which leads to Ni migration from support enriching the active electrode area. [20] This suggests that Ni atoms diffuse from high chemical potential regions to low chemical potential (regions with lower contact angles present lower chemical potential), which explains the different Ni migration mechanisms for SOFC and SOEC operation. Nonetheless, there are some contradictive reports that show that SOFC operation can also lead to a reduction of Ni content, and its coarsening reduce TPB density in the functional layer, which will increase active polarization. [21] This effect is attributed to the formation of volatile $Ni(OH)_2$ that is supposedly formed when the critical humidity values are reached. (in Figure 5)

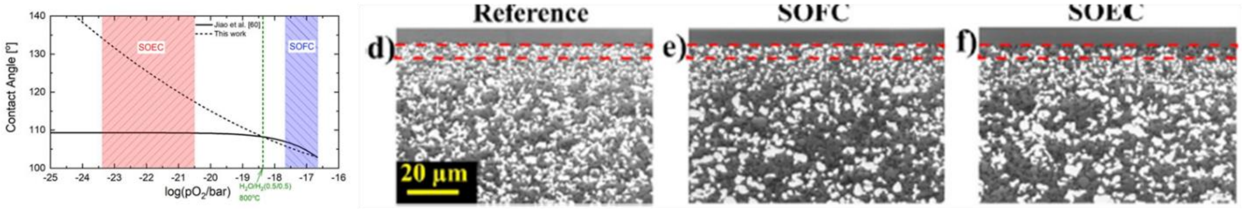
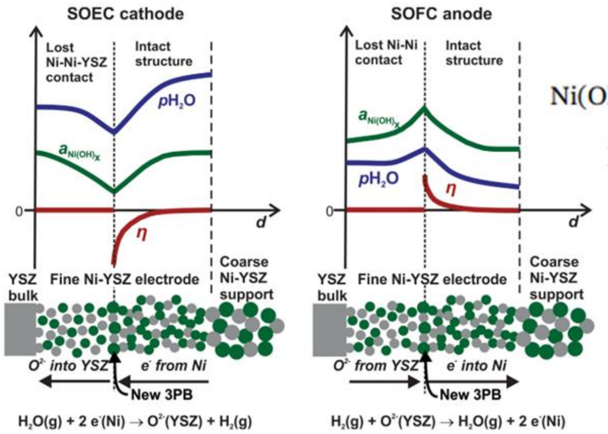


Figure 5 Contact angle relation to overpotential for SOFC and SOEC. SEM images showing the microstructural changes to the Ni/YSZ microstructure. [20]

Another approach to explain the overall mechanism of the microstructural changes in the Ni/YSZ electrode is that Ni migrates via surface diffusion of $Ni(OH)_x$ species below ca. 800 ºC and via Ni(OH)x species in the gas phase above ca. 900 ºC. [22] However, there are other reports that suggest that surface activity or partial pressure of $Ni(OH)_x$ are very low and will require exorbitant high diffusion rates in order to explain the observed migrations rates. [23] It is suggested that Ni migrates down the electrochemical and/or pO_2 potential gradients from relative positive local potential toward relative negative potential. The basic mechanism is associated with the Ni surface energy difference between small and large particles (Ni particles grow larger, and small ones get smaller). Authors suggest that NiOH species (lowest energy formation and diffusion) dominate transport in steam and H_2 atmospheres. Additionally, authors describe that the TPB active layer moves away from the electrolyte, and activity of Ni in a positive oxidation state will be lowest at most reducing condition (active TPB layer close to electrode/electrolyte interface), Ni diffuses until it precipitates to the new most active TPB region. [24] (in Figure 6)



$$Ni(OH)_x\,(g) + 2x\,e^-\,(Ni) \rightleftharpoons Ni\,(s) + x\,O^{2-}\,(YSZ) + \tfrac{1}{2}x\,H_2\,(g)$$

$$Ni(OH)_x\,(g) + \frac{1}{2}x\,H_2\,(g) \rightleftharpoons Ni\,(s) + x\,H_2O\,(g)$$

Figure 6 Qualitative variations of three critical parameters, η, the local overvoltage of Ni particles, p_{H2O}, steam partial pressure, and $aNi(OH)_x$, the activity of $Ni(OH)_x$ species versus distance from original electrolyte/electrode interface (d = 0) and their effect on Ni migration. Associated Ni migration mechanism related to the $Ni(OH)_x$.

There are diverse factors that aggravate or alleviate the Ni migration on the fuel electrode. During SOECs mode, the Ni depletion was more severe for higher fuel gas humidity (perhaps increased $Ni(OH)_x$ formation). Additionally, for higher current densities (larger overpotentials), Ni particles are more negatively polarized and stronger potential gradients emerge within the electrode, which leads to Ni depletion. The adverse effects are for humidity above 80 %, and temperatures above 800 °C. [29] Although some reports also described the Ni depletion effects under SOEC operation for Ni/YSZ electrodes,[25,26] some reports show no considerable impact of migration/depletion under either SOFC or SOEC modes in Ni/YSZ electrodes.[27] However, such results are still experiencing Ni coarsening due to temperature aging and decreasing electrochemically active sites per electrode volume from coarsening (higher degradation rates in SOEC mode). Other Ni-based electrodes show enhanced resistance for Ni migration, such as Ni/GDC that shows enhanced properties against severe Ni migration on the electrode due to improved ionic conductivity of GDC. [28] (in Figure 7)

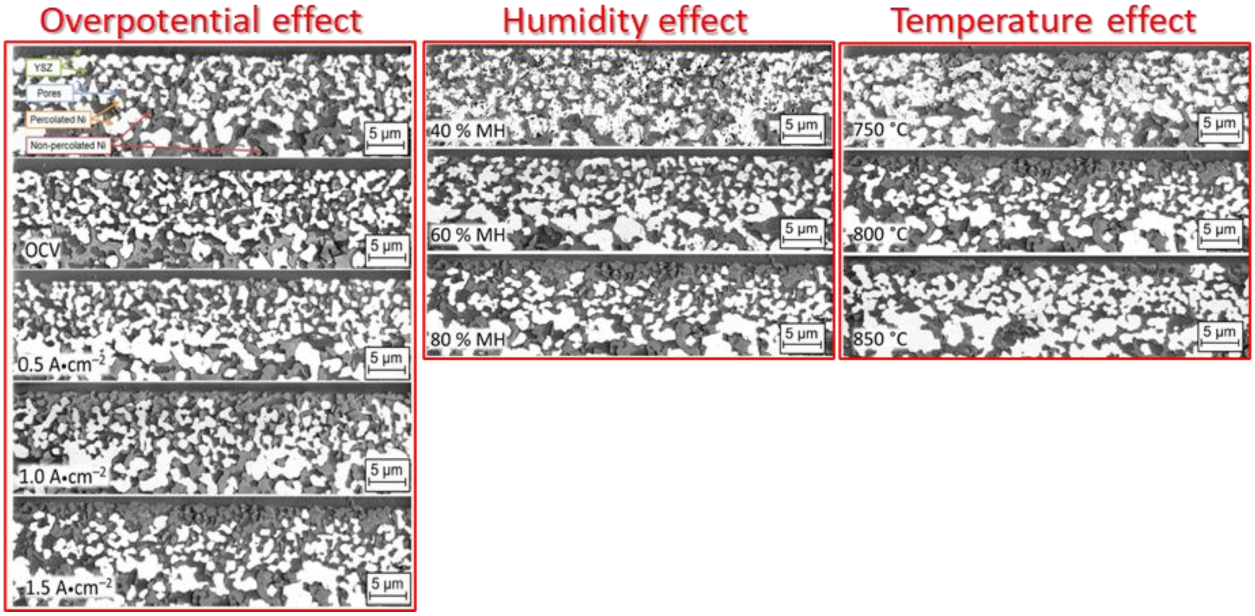


Figure 7 Effects of overpotential, humidity, and temperature on Ni depletion on the fuel electrode. [29]

Overall, the humidity concentration gradient would drive volatile Ni(OH)$_x$ outwards from the TPB region. [30] Since the diffusion mechanisms affecting the Ni-base electrode are associated with the surface diffusion and vaporization transport due to surface adsorbed species, one possible method to mitigate the Ni migration in the SOCs is the surface modification of the Ni/YSZ backbone. In the following section, the diverse modification strategies are discussed.

4.1.2 Degradation on Ni-Based anode due to Carbon Deposition

The second type of degradation is associated with the deactivation and passivation of the Ni active sites. For gradual internal methane reforming SOFCs, the attack on the Ni phase could be much more severe due to the presence of multi oxidants (e.g. H_2O, CO_2, and CO in Figure 8). Carbon deposition is one critical problem to be avoided because Ni is well-known for its propensity to promote hydrocarbon pyrolysis and the build-up of carbon. [31] Furthermore, Ni could be corroded by a combination of atom migration through surface carbon deposits as well as carbon intrusion and precipitation in the bulk metal in which is driven by the mechanism called thermochemical metal-dusting mechanism. [32,33]

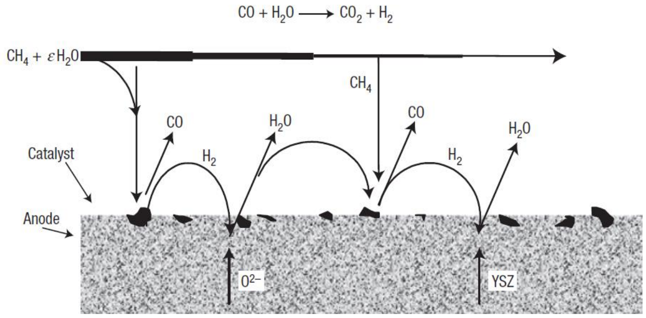


Figure 8 The series of processes that lead to the gradual internal methane reforming.

The active sites of the fuel electrode can be affected by impurities (mainly carbon and sulfur) which cause faster degradation of Ni–YSZ anode. Additionally, during carbon deposition(coking), carbon particles settle on Ni particles and inhibit the electrochemical reactions. Lastly, the sulfur content in fuel as H_2S reacts with O_2 to release H_2O and S. Sulfur atoms deposition on active sites can lead to the formation of Ni_3S_2 volatile compound, reducing Ni content on fuel electrode. The third degradation mechanism is associated with the thermo-mechanical cycling (also termed redox instability) in the SOC. The deterioration of the fuel electrode during redox cycles can produce residual stresses between interfaces at a small scale or due to stack parameters at a large scale which will lead to total failure of the cell. The degradation mechanisms for Ni-based electrodes are discussed in further detail in the following sections.

SOCs are capable of working in different kinds of fuels, including H_2, biofuels, hydrocarbons, diesel, natural gas, coal, etc. Nonetheless, carbon deposition (coking) occurs when hydrocarbon fuels are used, which blocks Ni active sites and decreases catalytic activity, deteriorating the cell performance. This limitation restricts the practical application of hydrocarbons in state-of-the-art Ni-based fuel electrode cells. Figure 9 shows the carbon deposition regions predicted on the carbon-rich side of the boundary lines for hydrocarbon utilized in SOCs. [34]

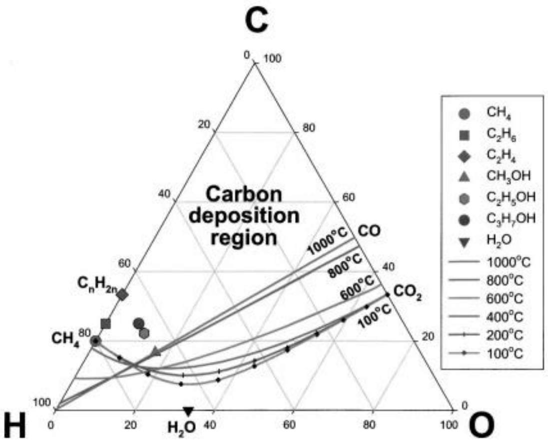


Figure 9 Boundaries of carbon deposition for hydrocarbon fuels.[34]

Strategies to use hydrocarbons in SOCs include feeding reformed hydrocarbon fuel to the SOFC (external reforming), adding additional material or layer that acts as reforming layer (internal reforming), and the direct hydrocarbon utilization strategies are depicted in Figure 10.35 The reforming strategies are intended to add oxygen content to the fuel to shift the equilibrium of fuel content away from the carbon forming region(eliminating the carbon deposition on the active sites of the Ni fuel electrode). Oxygen can be added from water (steam reforming, $CH_4+H_2O \rightleftharpoons CO+3H_2$), carbon dioxide/carbon (dry reforming, $CO_2+CH_4 \rightleftharpoons 2H_2+2CO$), or a small amount of oxidation (partial oxidation, $CH_4+ \frac{1}{2}O_2 \rightleftharpoons CO+2H_2$).

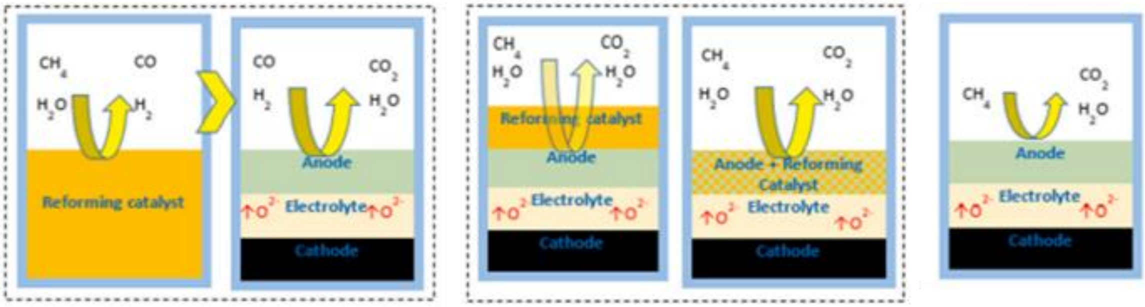
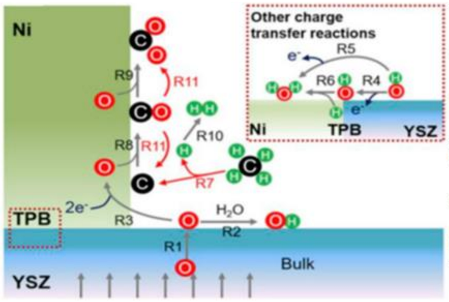


Figure 10 Left, External reforming. Middle, Internal reforming. Right, Direct hydrocarbon utilization. [35]

Reforming strategies can help to alleviate the carbon formation in the Ni electrode. Notwithstanding, understanding the mechanisms for carbon formation is important to determine the best strategies to reduce coking on the fuel electrode. One important hydrocarbon fuel considered as promised alternative to be utilized in SOC systems are methane-based fuels (the major component of natural gas). [36] Figure 11 shows the mechanism of cooking reaction on Ni electrode during SOFC operation in CH_4 fuel. The main degradation mechanism involves oxygen ion transport in the YSZ electrolyte (Reaction (1) and (2)), charge transfer and ion migration near the TPB (Reaction (3)–(5)), dehydrogenation of water, and adsorption of hydrocarbons on Ni surfaces (Reaction (6) and (7)), oxidation of hydrocarbon and carbon monoxide (Reaction (8)–(10)), and CO disproportionation reaction (Reaction (11)). The carbon formation is then attributed to the fact that the breaking of C–H bonds is fast, and the transmission of oxygen ions is hindered, leading to a large amount of carbon deposition reaction occurring at the Ni grains. Suppose the catalytic activity and transport of oxygen ions on fuel the electrode is improved to react at a faster rate. In that case, the carbon formation on the Ni electrode surface might be reversibly eliminated. Thus, improving ionic conductivity by adding a catalyst material (e.g., via infiltration or ALD) could be a mitigation strategy for carbon cooking on the Ni electrode. [37] Additionally, it was reported that some factors affecting the carbon deposition on Ni electrode include the temperature (degradation rate of Ni/YSZ electrode increased with operating temperature), the fuel consumption (adding more CO_2, O_2 or H_2O could inhibit carbon deposition due to greater oxygen to carbon ratio), and the size of catalyst (smaller Ni crystals have higher resistance to carbon formation). [37] The main mechanism of carbon affecting/blocking the active sites of the Ni-YSZ has been ascribed to the carbon deposition preferentially occurring on Ni particles and the area close to the Ni/YSZ interfaces (TPB), which could inhibit growth on Ni surfaces leading to the deposition of carbon encapsulating the Ni particles. [38]



YSZ surface:

$$O^{2-}(YSZ) + V_O^{\cdot\cdot}(YSZ) \Leftrightarrow O_O^{x}(YSZ) + (YSZ) \quad (1)$$

$$H_2O(YSZ) + O^{2-}(YSZ) \Leftrightarrow 2OH^-(YSZ) \quad (2)$$

TPB regions:

$$O^{2-}(YSZ) + [\ ](Ni) \Leftrightarrow O(Ni) + 2e^-(Ni) + (YSZ) \quad (3)$$

$$OH^-(YSZ) + [\ ](Ni) \Leftrightarrow OH(Ni) + e^-(Ni) + (YSZ) \quad (4)$$

$$H(Ni) + OH^-(YSZ) \Leftrightarrow H_2O(YSZ) + [\,](Ni) + e^-(Ni) \quad (5)$$

Ni surface:

$$OH(Ni) + H(Ni) \Leftrightarrow H_2O(Ni) + [\ ](Ni) \quad (6)$$

$$CH_4(g) + [\,](Ni) \Leftrightarrow CH_4(Ni) \Leftrightarrow CH_3(Ni) + H(Ni) \Leftrightarrow CH_2(Ni) + H(Ni) \Leftrightarrow CH(Ni) + H(Ni) \;\; CH(Ni) + [\,](Ni) \Leftrightarrow C(Ni) + H(Ni) \quad (7)$$

$$C(Ni) + O(Ni) \Leftrightarrow CO(Ni) + [\,](Ni) \Leftrightarrow CO(g) + [\,](Ni) \quad (8)$$

$$CO(Ni) + O(Ni) \Leftrightarrow CO_2(Ni) + [\,](Ni) \Leftrightarrow H_2(g) + [\,](Ni) \quad (9)$$

$$2H(Ni) \Leftrightarrow H_2(Ni) + [\,](Ni) \Leftrightarrow H_2(g) + [\,](Ni) \quad (10)$$

$$2CO(Ni) \Leftrightarrow CO_2(Ni) + C(Ni) \quad (11)$$

Figure 11 Schematic for the reaction mechanism of CH_4 oxidization on Ni/YSZ electrode.

It is important to address the carbon formation on the Ni electrode because the chemisorbed or physically adsorbed species could block the flow and reaction of fuel in the electrode, leading to carbon formation surrounding the particle and deactivating the active sites completely, ultimately inducing stress formation from the carbon filament formation cracking the Ni-YSZ electrode. In the following section, some approaches to mitigate carbon formation are presented.

4.1.3 Mitigation of Ni/YSZ Electrode Degradation and Carbon Deposition on Fuel Electrode

To further increase market competitiveness, the state-of-the-art SOFC technology requires further maturation in cost and durability. The present technical goal is the optimization of performance and durability in a stable operating range from 650 °C to 800 °C. SOFC stack operation at the lower end of the range would mitigate degradation, reduce sealing problems, enable the application of less expensive materials (e.g., ferritic stainless steels for interconnect), and improve response to rapid start-up and repeat thermal cycling from ambient to operating temperatures. However, electrochemical resistances of key cell components will increase with reduced operating temperatures. Many efforts have been put into developing the cathode in recent years due to the relatively high activation energy required for the oxygen reduction reaction. [39] On the other hand, lowering the operating temperature also causes an increase in the resistance of the anode. One essential problem with the reduction of the operating temperature is the significant reduction in the efficiency of their endothermic catalytic reactions for hydrogen dissociation and further fuel oxidation.

Recent findings by the US Energy Information Administration have shown the presence of over 280 million cubic feet of proven natural gas reserves and 850 trillion cubic feet of estimated recoverable resources in the US. [40] The direct electrochemical oxidation of dry hydrocarbon fuels to generate electrical power has the potential to accelerate the use of fuel cells in transportation and distributed-power applications substantially. [41] To support the DOE's mission of developing SOFC technology suitable for natural gas-fueled distributed generation applications and natural gas fuel cell, the current commercial Ni/YSZ anode face some critical challenges, and its structure and properties need to be further improved.

Aforementioned, a cermet consisting of Ni and YSZ has many of the properties required for efficient anode material. Ni provides excellent electronic conductivity, catalytic activity in H_2 oxidation, and good chemical compatibility with other SOCs components, which is the main reason Ni/YSZ are still a commonly used material in the fuel electrode. It has high electronic conductivity, reasonable ionic conductivity, and high catalytic activity for hydrogen oxidation. This cermet, however, also has faced multiple challenges. The following sections discuss the degradation challenges and mitigation strategies for the Ni/YSZ fuel electrode.

One important characteristic of solid oxide cells (SOCs) is their fuel flexibility, offering the potential for direct conversion to the electricity of hydrocarbons, coal gas, and other renewable fuels.[42] Nonetheless, the most important challenge using hydrocarbon fuels is the susceptibility of Ni-YSZ cermet fuel electrodes to coking(carbon deposition) and deactivation by other contaminants. [43] One of the possible alternatives to overcome these critical technical barriers for fuel flexibility is the use of electronically conducting ceramics, which provide better fuel flexibility, stability under redox cycling, and sulfur tolerance over the Ni/YSZ anodes. [44] However, it is common that such conductive oxide presents (i) lower electrical conductivity than Ni-cermet (reducing the anode performance), (ii) poor fuel oxidation, (iii) reduced catalytic activity and (iv) incompatibility with the adjacent cell components. [3] Other cermet composites such as Cu-CeO_2 are also resistant to carbon formation, but its catalytic activity for hydrogen oxidation is much lower than that of Ni-YSZ. [45] Therefore, Ni-based dual electrodes still represent the best option for SOCs because of the excellent catalytic activity for hydrogen oxidation, electrical conductivity for current collection, and compatibility with the electrolyte.[43]

Surface modification via infiltrated materials has been adopted as an efficient approach to enhance the structural stability of the Ni-based electrode. [46] The mitigation mechanism is associated with the type of material utilized. For inert metal modified anodes, the metal tends to be alloyed with Ni and occupies the Ni catalytic active sites, preventing the formation of the C-C bond. For basic oxide modified anode, the basic oxide helps to enhance the interaction between carbon and the produced H_2O or CO_2, decreasing the carbon deposit. While for doped ceria modified anodes, it functions as oxygen storage material to store and transfer O^{2-}, facilitating the carbon oxidization and promoting the methane reforming. [47]

A different approach was investigated to extend the potential lifetime of a SOC system where the infiltrated material was incorporated after 900 h of operation where the degradation of the fuel electrode was reduced by a factor of two over the course of 2300 h. [48] 8-cell stack of Ni/YSZ|YSZ|GDC|LSCF/GDC anode supported cells operated for ~3000 h in electrolysis mode with 95 % CO_2 as reactant gas and 5 % of either H_2 or CO to avoid Ni oxidation. ASR contribution of fuel electrode decreased by a factor of 5 from 80 mΩ cm^2 to 16 mΩ cm^2 for a CGO+Cu infiltrated fuel electrode. It is important to highlight that even after initial degradation and reactivation (polarization resistance is almost exactly identical to that before carbon deposition, i.e., 110 mΩ cm^2) the repaired cell fuel electrode resistance is 140 mΩ cm^2 after 2300 h, while the reference cell value is double that with 270 mΩ cm^2. Cu-CeO_2 impregnated in the Ni-YSZ support layer also promotes ethanol reformation and minimizes coking. [45] Authors showed that Cu reacts with Ni to form an alloy in the fuel electrode. Moreover, infiltration of SDC into Ni/YSZ electrode has also been reported to further improve the performance of the cell while serving as a catalyst reforming layer for hydrocarbon. [49] SDC modified Ni-YSZ anode show stable performance with the peak power density of 0.65 Wcm^{-2} at 800 ºC using methane as fuel. The infiltrated nano-sized SDC coat increases the TPB length in the fuel electrode while providing resistance against the formation of Ni carbide (onset of carbon deposition). [48]

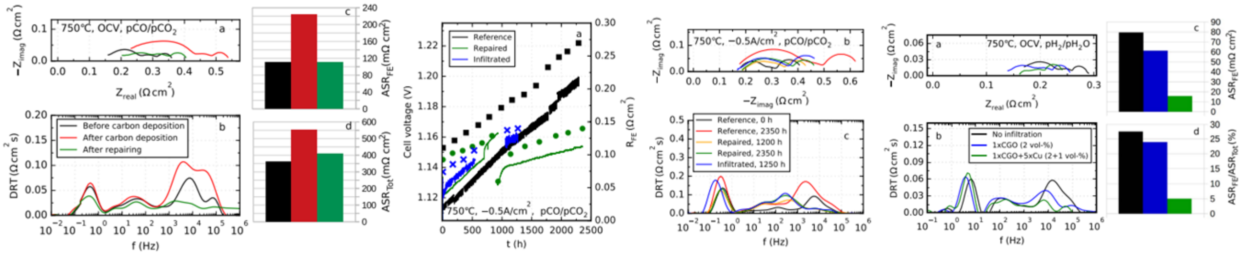


Figure 12 Polarization resistance and performance degradation over 2300h test. [48]

GDC and ($La_{0.8}Sr_{0.2}FeO_3$)LSF were infiltrated into a NiO/YSZ||YSZ||YSZ-LSF anode supported cell (in Figure 13). [50] For the infiltrated cell with GDC, the catalyst improves both the electrochemical performance and stability of the cell due to the GDC having high O^{2-} ionic conductivity, which extends the TPB length for performance improvement and facilitates the O^{2-} transfer for carbon resistance. Although LSF decreases the electrochemical performance of Ni/YSZ anode, it provides cell stability under methane fuel. LSF improved resistance for carbon deposition might arise from additional O^{2-} for C-O bond formation and also decreases the methane oxidation, which reduces the formation of C-C bonds; both factors contribute to eliminating the carbon on the surface. (in Figure 13)

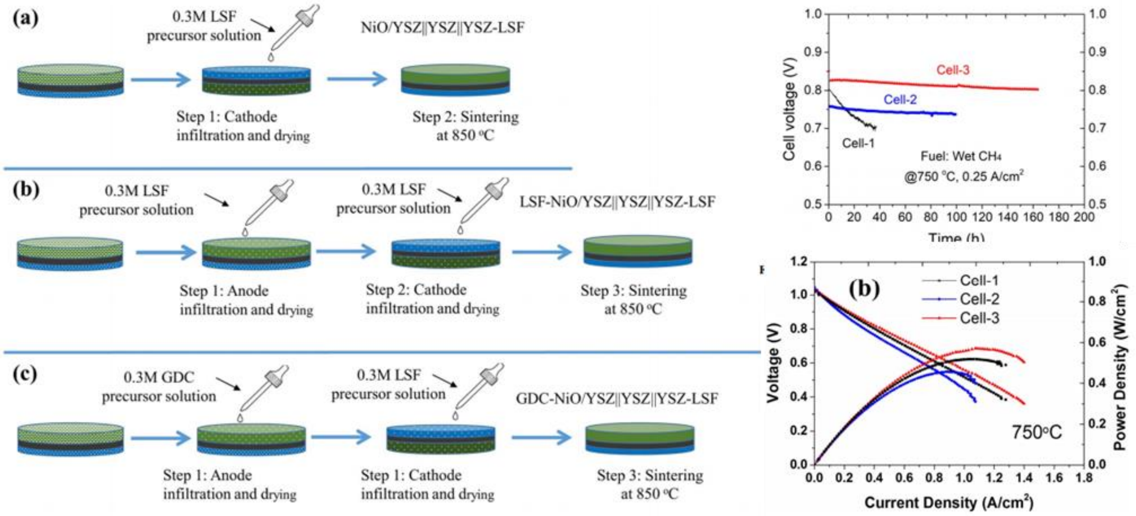


Figure 13 Infiltration steps for different cells and the performance under wet H_2 and wet methane. [50]

Alkaline earth metals-based-oxides (CaO, BaO, SrO, MgO) and La_2O_3 were investigated as basic additives in Ni–SDC to mitigate degradation of cells.[51] CaO infiltration in Ni–SDC anode displayed the highest methane conversion (83.1 %) and CO selectivity while also providing improved coking resistance (25 % improvement rate). MgO, SrO, and BaO have a negative effect on the Ni-SDC anode. The different infiltrated materials display peak power densities of 966, 1009, 742, 585, 281, and 56 mW cm^{-2} at 700 °C for Ni–SDC, Ni–SDC–Ca, Ni–SDC–Ba, Ni–SDC–La, Ni–SDC–Sr and Ni–SDC–Mg, respectively. Decay rates under humidified methane fuel are 710 and 6.5 mV per 10 h for Ni–SDC and Ni–SDC–Ca anodes. Additionally, BaO introduced via evaporation deposition method on Ni/YSZ|YSZ|LSCF/SDC anode supported cell was also reported as an effective mitigation strategy for carbon deposition. [52] Introduced BaO accelerates the COH dissociation to CO and H, which enhances coking tolerance. The BaO/Ni interfaces do not impede charge transfer while promoting a water-mediated carbon removal process and mitigating the Ni deactivation. Similarly, infiltrated $BaCO_3$ into Ni-YSZ has synergistic catalytic effects on H_2O/CO_2 reduction (conversion of H_2O/CO_2 to H_2/CO is a possible solution to transforming greenhouse gas into syngas). [53] The electrolysis current density for $BaCO_3$ infiltrated cell is 1.06 A cm^{-2} at 1.6 V, higher than the value of 0.66 A cm^{-2} for the unmodified cell. The R_p is reduced from 4.00 to 2.88 Ω cm^2 for H_2O electrolysis, from 7.52 to 5.49 Ω cm^2 for CO_2 electrolysis, and from 6.30 to 3.63 Ω cm^2 for H_2O-CO_2 co-electrolysis, showing the improved electrochemical activity in Ni-YSZ for electrolysis of H_2O, CO_2, and H_2O-CO for the modified cell. The improved performance was depicted in Figure 14 and Figure 15, respectively.

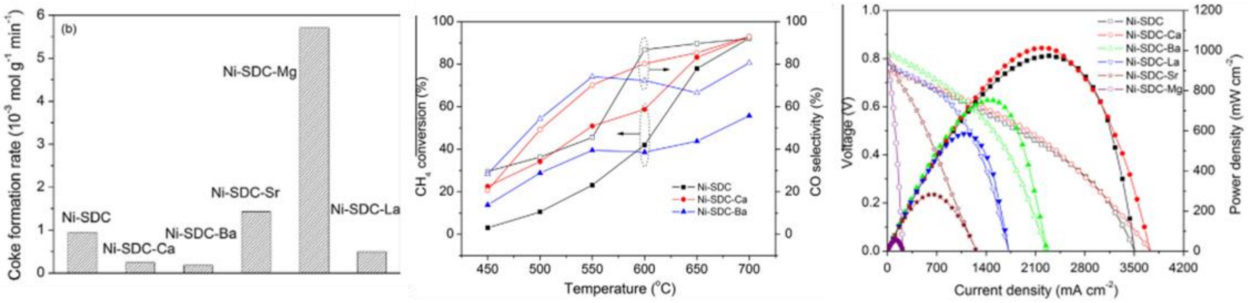


Figure 14 Carbon formation, CH4 conversion, CO selectivity, and performance of different infiltrated alkaline earth metals into Ni/SDC anode cell. [51]

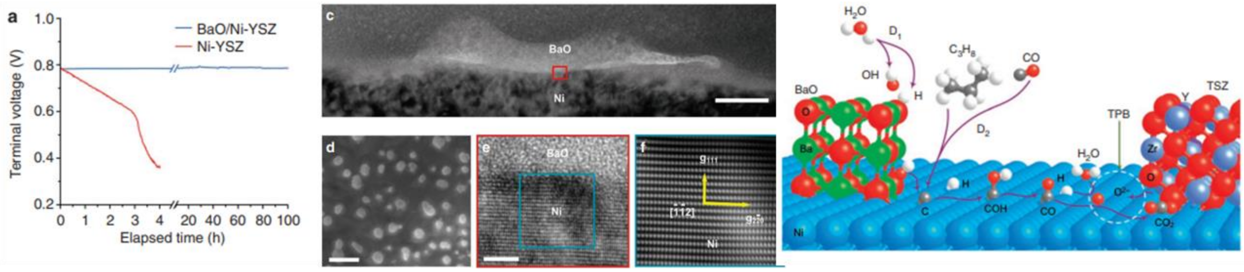


Figure 15 Fuel cell performance in Co and gasified carbon, BaO-Ni microstructure, and proposed mechanism of carbon removal.[52]

Biofuel such as pyrolysis oil can be generated from a wide range of biomass (important as energy sources because of its abundance, renewability, and easy storage). Pyrolysis oil contains up to 12% of acetic acid, representing a technological challenge to be used as a fuel in SOCs due to possible carbon deposition on Ni electrodes. 17 wt% Ni/MgO–Al_2O_3 was reported as an anode top catalyst layer for internal catalytic decomposition and steam reforming of acetic acid. [54] Catalyst layer on top of the Ni/YSZ|YSZ |SDC| ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$) BSCF/SDC anode supported cell to boost the peak power density to 1.32 W cm^{-2} at 750 C(cell temperature) without noticeable performance degradation, delamination of the catalyst layer, or carbon deposition for over 200 h. Ni/MgO–Al_2O_3 catalyst layer provides catalytic activity for decomposition of acetic acid to syngas (H_2+CO), (Figure 16).

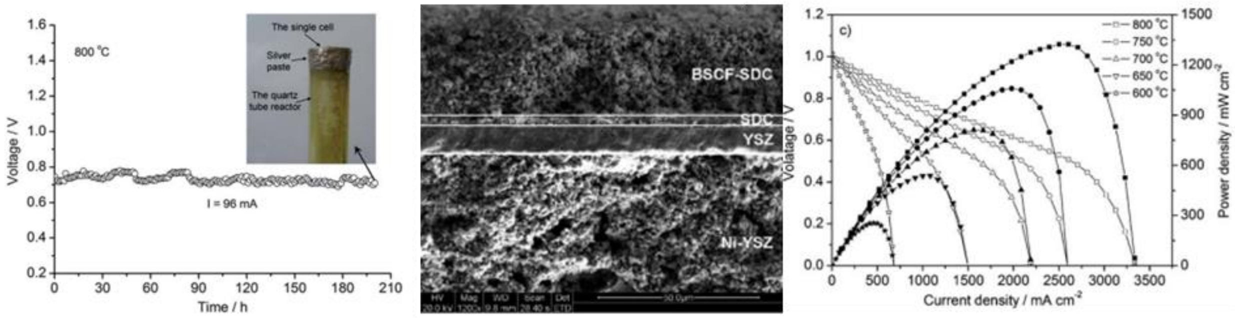


Figure 16 Cell voltage during durability test and performance under acetic acid–steam gas. [54]

Biogas (CH_4, CO_2, and traces of H_2S) is also an attractive alternative fuel for SOCs. However, Ni-YSZ anode is inclined to cause carbon formation as well as to form inert and non-conductive S-containing species in biogas. Infiltrated $PrBaMn_2O_5$ perovskite materials were proved as highly active, and coke/sulfur tolerant for hydrocarbon fueled SOFC. [55] The infiltrated Ni/YSZ|YSZ|GDC|LSCF/GDC anode supported cell achieves a power density of 1.35Wcm^{-2} in biogas at 800C. The power density of Ni-YSZ degraded from 0.57Wcm^{-2} to 0.49Wcm^{-2} in 24 h, while the infiltrated Ni-YSZ stabilized at around 0.80Wcm^{-2} under methane, CO_2, and H_2S environment. The infiltrated $PrBaMn_2O_5$ perovskite resists C formation and S adsorption and serves as CO^{2-} captor. Additionally, it works as a catalyst for O^{2-} diffusion to accelerate carbon removal and S desorption processes (in Figure 17).

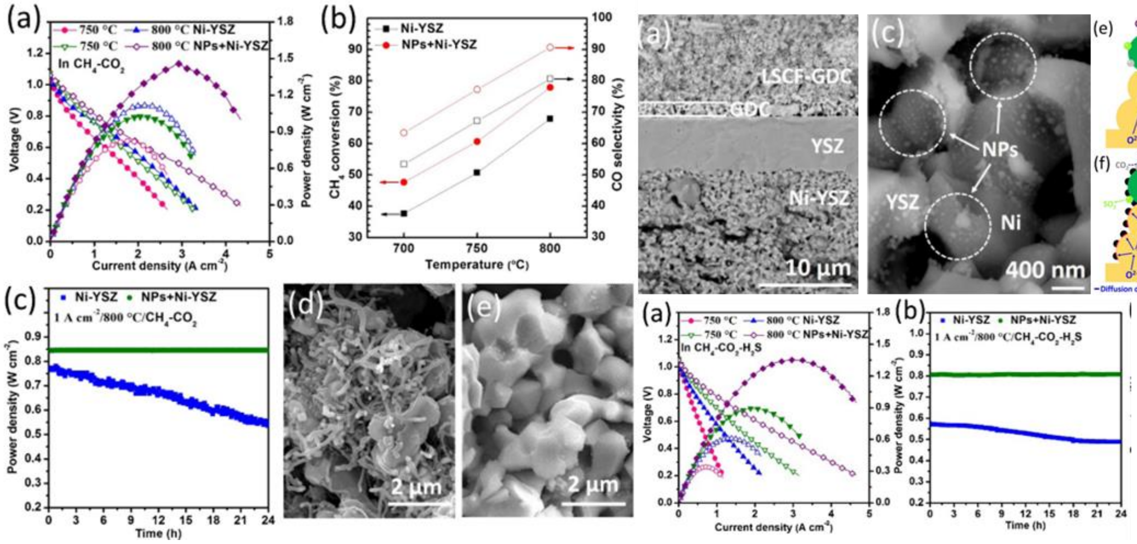


Figure 17 Performance and microstructural characteristics for the Ni-YSZ infiltrated with PrBaMn$_2$O$_5$ under CH$_4$, CO$_2$ and H$_2$S environment.[55]

4.2 ALD Coating of Ni/YSZ, its Advantages and Technical Challenges

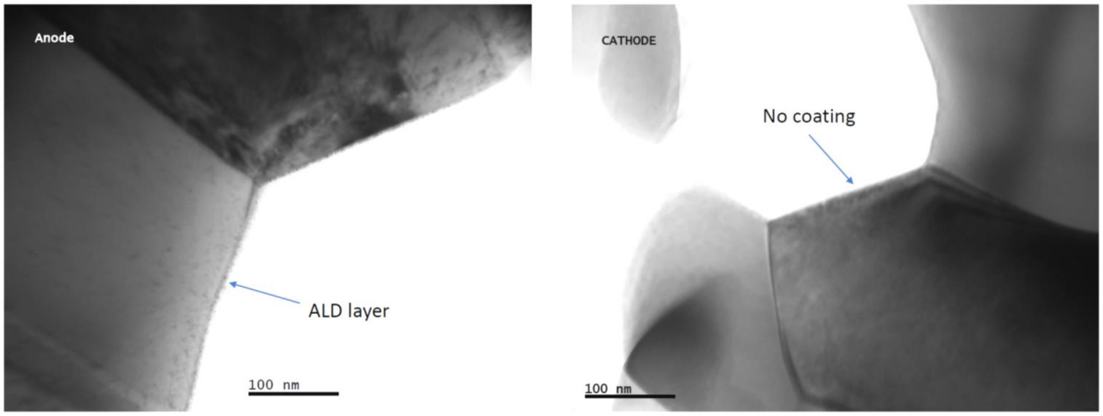
The uniqueness of ALD processing on SOFCs: ALD is a **chemical vapor deposition** technique that sequentially applies atomic monolayers to a substrate, typically alternating compounds, to produce a locally balanced atomic distribution of the target material. [56] ALD is uniquely suitable for depositing uniform and conformal films on complex three-dimensional topographies with a high aspect ratio. The indifference of ALD to substrate shape makes it particularly promising for applications to SOFCs, which presses porous active structure with complex three-dimensional topographies, and with electrode performance strictly depending on the surface properties. ALD processing is in a large batch and features easy scale-up and simplified handling precursors. Such capacity of ALD processing permits the simultaneous processing of hundreds of SOFCs. [57]

Technical challenges: Although ALD possesses significant promise as an SOFC processing technique, insufficient research has been completed to assure success of ALD coating in commercial applications. Recent work was reported for ALD coated symmetric cells [58,59] and some showed that the ALD coating symmetrical cells was detrimental to the electrode performance. [60,61] One of the major obstacles for processing of SOFC anode using ALD is to **identify a target**

compound and structure of the ALD layer that is compatible with the viable Ni/YSZ anode, active, stable, and promotes electrochemical SOFC reactions at high temperatures. Another concern is the **penetration of ALD precursor chemical vapor into the active layer** of the anode of the commercial cell. Depending on the fabrication methods, the commercial anode support cells usually have a dense anode. For example, the anode support button cells, which are fabricated by NexTech (fuelcellmaterials.com) and composed of NiO and YSZ, have an entire anode thickness of ~ 0.4 mm and porosity of ~35 %.

4.3 Uniqueness of ALD developed from this project: Ni/YSZ Anode Only and deep penetration

All of the ALD processing for Ni/YSZ anode is one-step ALD processing without heat-treatment before or after the ALD coatings. The coatings are entirely automatic and can be finished within a few hours. To avoid the ALD coating occurring on the cathode side during the processing of the anode side, we sealed the whole cathode area exposing only the portion of the anode, which is about 2.8 cm^2. To verify such overall cell performance enhancement was all caused by the ALD coating of the anode and no ALD layer was deposited on the cathode end, we have performed the TEM imaging of the ALD coated cell (without operation) and did the TEM imaging of the cathode and anode of the same cell. For the same cell that is with cathode sealed to avoid the ALD coating, the anode side is clearly with the ALD coating layer. By contrast, the cathode is free of ALD coating.



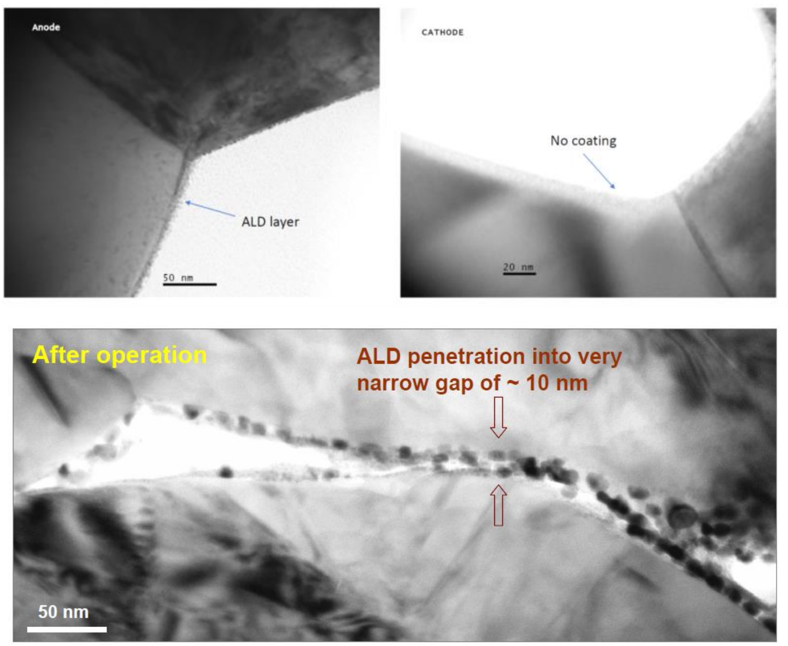


Figure 18 TEM images show the cathode of the cell is without an ALD layer, and the ALD coating is applied on the Ni/YSZ anode alone. Deep penetration of the ALD vapor into the narrow gap of the anode from the as-received cells and subsequent formation of the conformal and stable nanostructure on the internal surface of the anode upon cell operation.

In addition, the ALD processing was controlled to have deep penetration into the narrow gaps of the porous electrode. For example, the uniform and conformal ALD layer appear to be deeply covering the narrow gap of ~ 10 nm of the original porous electrode.

The ALD processing and **architectures of ALD layer into Ni/YSZ anode developed possess the following characteristics**: (1) Unlimited and uniform penetration into the active layer of the porous electrode using chemical vapor phase precursor; (2) Controllable ALD layer thickness and chemistry; (3) Designable nano-scale 3D scaffold of the ALD layer including monometallic catalyst, bimetallic catalytic alloys, and multifunctional nanocomposite consisting both the conductor oxide and catalyst metal. Overall, without materials set changes, significant enhancement of electrochemical performance and durability for the commercial cells can be achieved using cost-effective, time-efficient, and scale-up ready additive manufacturing ALD processing. Such ALD process promotes the SOFC applications using direct hydrocarbon and has an immediate impact on the industry commercialization.

4.4 References cited

1 https://ourworldindata.org/worlds-energy-problem

Singh, M., Zappa, D., & Comini, E. (2021). Solid oxide fuel cell: Decade of progress, future perspectives and challenges. International Journal of Hydrogen Energy, 46(54), 27643–27674. doi:10.1016/j.ijhydene.2021.06.020

3 Mahato, N., Banerjee, A., Gupta, A., Omar, S., & Balani, K. (2015). Progress in material selection for solid oxide fuel cell technology: A review. Progress in Materials Science, 72, 141–337. doi:10.1016/j.pmatsci.2015.01.001

4 Olabi, A. G., Wilberforce, T., & Abdelkareem, M. A. (2020). Fuel cell application in the automotive industry and future perspective. Energy, 118955. doi:10.1016/j.energy.2020.118955

5 Boldrin, P., & Brandon, N. P. (2019). Progress and outlook for solid oxide fuel cells for transportation applications. Nature Catalysis, 2(7), 571–577.

6 Shen, M., Ai, F., Ma, H., Xu, H., & Zhang, Y. (2021). Progress and prospects of reversible solid oxide fuel cell materials. iScience, 103464.

7 Graves, C., Ebbesen, S. D., Jensen, S. H., Simonsen, S. B., & Mogensen, M. B. (2014). Eliminating degradation in solid oxide electrochemical cells by reversible operation. Nature Materials, 14(2), 239–244. Doi:10.1038/nmat4165

8 Khan, M. S., Lee, S.-B., Song, R.-H., Lee, J.-W., Lim, T.-H., & Park, S.-J. (2016). Fundamental mechanisms involved in the degradation of nickel–yttria stabilized zirconia (Ni–YSZ) anode during solid oxide fuel cells operation: A review. Ceramics International, 42(1), 35–48. doi:10.1016/j.ceramint.2015.09.006

9 Mahato, N., Banerjee, A., Gupta, A., Omar, S., & Balani, K. (2015). Progress in Materials Science, 72, 141–337.

10 Abdalla, A. M., Hossain, S., Petra, P. M., Ghasemi, M., & Azad, A. K. (2018). Achievements and trends of solid oxide fuel cells in clean energy field: a perspective review. Frontiers in Energy. Doi:10.1007/s11708-018-0546^{-2}

11 Li, R., Zhang, C., Liu, J., Zhou, J., & Xu, L. (2019). A review on the electrical properties of doped SrTiO3 as anode materials for solid oxide fuel cells. Materials Research Express. doi:10.1088/2053-1591/ab4303

12 Jiang, S. P., & Chan, S. H. (2004). A review of anode materials development in solid oxide fuel cells. Journal of Materials Science, 39(14), 4405–4439. doi:10.1023/b:jmsc.0000034135.52164.6b

13 Hadi, N. H., Somalu, M. R., Samat, A. A., Muchtar, A., Baharuddin, N. A., & Anwar, M. (2021). A review on the preparation of anode materials and anode films for solid oxide fuel cell applications. International Journal of Energy Research, 45(10), 14357–14388. doi:10.1002/er.6763

14 Liu, Y., Shao, Z., & Mori, T. (2021). Development of nickel based cermet anode materials in solid oxide fuel cells–Now and future. Materials Reports: Energy, 1(1), 100003.

15 Khan, M. S., Lee, S.-B., Song, R.-H., Lee, J.-W., Lim, T.-H., & Park, S.-J. (2016). Fundamental mechanisms involved in the degradation of nickel–yttria stabilized zirconia (Ni–YSZ) anode during

solid oxide fuel cells operation: A review. Ceramics International, 42(1), 35–48. doi:10.1016/j.ceramint.2015.09.006

16 Shri Prakash, B., Senthil Kumar, S., & Aruna, S. T. (2014). Properties and development of Ni/YSZ as an anode material in solid oxide fuel cell: A review. Renewable and Sustainable Energy Reviews, 36, 149–179. doi:10.1016/j.rser.2014.04.043

17 Klemensoe T. Relationships between structure and performance of SOFC anodes. Topsoe fuel cell. Risø, Denmark: Technical University of Danemark, Risoe National Laboratory; 2005 (Ph.D. thesis)

18 Khan, M. S., Lee, S.-B., Song, R.-H., Lee, J.-W., Lim, T.-H., & Park, S.-J. (2016). Fundamental mechanisms involved in the degradation of nickel–yttria stabilized zirconia (Ni–YSZ) anode during solid oxide fuel cells operation: A review. Ceramics International, 42(1), 35–48. doi:10.1016/j.ceramint.2015.09.006

19 Wang, Y., Wu, C., Zu, B., Han, M., Du, Q., Ni, M., & Jiao, K. (2021). Ni migration of Ni-YSZ electrode in solid oxide electrolysis cell: An integrated model study. Journal of Power Sources, 516, 230660.

20 Trini, M., Hauch, A., De Angelis, S., Tong, X., Hendriksen, P. V., & Chen, M. (2020). Comparison of microstructural evolution of fuel electrodes in solid oxide fuel cells and electrolysis cells. Journal of Power Sources, 450, 227599.

21 Geng, J., Jiao, Z., Yan, D., Jia, L., Pu, J., & Li, J. (2021). Comparative study on solid oxide fuel cell anode microstructure evolution after long-term operation. Journal of Power Sources, 495, 229792.

22 Mogensen, M. B., Chen, M., Frandsen, H. L., Graves, C., Hauch, A., Hendriksen, P. V., … Sun, X. (2021). Ni migration in solid oxide cell electrodes: Review and revised hypothesis. Fuel Cells.

23 Mogensen, M. B., Chen, M., Frandsen, H. L., Graves, C., Hauch, A., Jacobsen, T., ... & Sun, X. (2019). Comprehensive Hypotheses for Degradation Mechanisms in Ni-Stabilized Zirconia Electrodes. ECS Transactions, 91(1), 613.

24 Mogensen, M. B., Hauch, A., Sun, X., Chen, M., Tao, Y., Ebbesen, S. D., … Hendriksen, P. V. (2017). Relation Between Ni Particle Shape Change and Ni Migration in Ni-YSZ Electrodes - a Hypothesis. Fuel Cells, 17(4), 434–441.

25 Rao, M., Jensen, S. H., Sun, X., & Hagen, A. (2019). Unwinding entangled degradation mechanisms in solid oxide electrolysis cells through electrode modifications and impedance analysis. Fuel Cells, 19(4), 445-457.

26 Sun, X., Hendriksen, P. V., Mogensen, M. B., & Chen, M. (2019). Degradation in solid oxide electrolysis cells during long term testing. Fuel Cells, 19(6), 740-747.

27 Hubert, M., Laurencin, J., Cloetens, P., Morel, B., Montinaro, D., & Lefebvre-Joud, F. (2018). Impact of Nickel agglomeration on Solid Oxide Cell operated in fuel cell and electrolysis modes. Journal of Power Sources, 397, 240^{-2}51.

28 Uchida, H., Brito, M. E., & Nishino, H. (2021). Depth-direction analysis of nickel depletion in a Ni–gadolinia-doped ceria hydrogen electrode after steam electrolysis operation. Journal of the Ceramic Society of Japan, 129(2), 111-117.

29 Hoerlein, M. P., Riegraf, M., Costa, R., Schiller, G., & Friedrich, K. A. (2018). A parameter study of solid oxide electrolysis cell degradation: Microstructural changes of the fuel electrode. Electrochimica

Acta, 276, 162-175.

30 Jiao, Z., Takagi, N., Shikazono, N., & Kasagi, N. (2011). Study on local morphological changes of nickel in solid oxide fuel cell anode using porous Ni pellet electrode. Journal of Power Sources, 196(3), 1019–1029.

31 C. Singhal, K. Kendall (Eds.), High Temperature Solid Oxide Fuel Cells, Fundamentals, Design and Application (first edition), Elsevier (2003

32 G. Hackett, K. Gerdes, Y. Chen, X. Song, and J. Zondlo, "Performance Impact Associated with Ni-Based SOFCs Fueled with Higher Hydrocarbon-Doped Coal Syngas," Metallurgical and Materials Transactions E 1-12 (2015).

33 C.M. Chun, G. Bhargava, and T.A. Ramanarayanan: J. Electrochem.Soc., 2007, vol. 154, pp. C231–40.

34 Sasaki, K., & Teraoka, Y. (2003). Equilibria in Fuel Cell Gases. Journal of The Electrochemical Society, 150(7), A885. doi:10.1149/1.1577338

35 Shabri, H. A., Othman, M. H. D., Mohamed, M. A., Kurniawan, T. A., & Jamil, S. M. (2021). Recent progress in metal-ceramic anode of solid oxide fuel cell for direct hydrocarbon fuel utilization: A review. Fuel Processing Technology, 212, 106626. doi:10.1016/j.fuproc.2020.106626

36 Chien, A. C., Lin, E. Y., & Lai, A. D. (2020). Aid of a metallic functional layer on Ni/YSZ anode for Direct Methane Fuel Cell. International Journal of Hydrogen Energy. doi:10.1016/j.ijhydene.2020.06.169

37 Pan, J., Ye, Y., Zhou, M., Sun, X., Ling, Y., Yashiro, K., & Chen, Y. (2021). Improving the activity and stability of Ni-based electrodes for solid oxide cells through surface engineering: Recent progress and future perspectives. Materials Reports: Energy, 1(2), 100025. doi:10.1016/j.matre.2021.100025

38 Watanabe, H., Okino, R., & Hanamura, K. (2019). Structural evolution of carbon deposition on a Ni/YSZ cermet of a SOFC analyzed by soft x-ray XANES spectroscopy. International Journal of Hydrogen Energy, 44(43), 24028–24035. doi:10.1016/j.ijhydene.2019.07.122

39 D. Ding, X. Li, S. Y. Lai, K. Gerdes, and M. Liu, "Enhancing SOFC cathode performance by surface modification through infiltration," Energy & Environmental Science, 7[2] 552-75 (2014).

40 D. Pakhare and J. Spivey, "A review of dry (CO2) reforming of methane over noble metal catalysts," Chem. Soc. Rev., 43[22] 7813-37 (2014).

41 B. C. H. Steele, "Fuel-cell technology - Running on natural gas," Nature, 400[6745] 619- (1999).

42 Shao, Z. et al. Electric power and synthesis gas co-generation from methane with zero waste gas emission. Angew. Chem. Int. Ed. 50, 1792–1797 (2011)

43 Liu, M., Lynch, M. E., Blinn, K., Alamgir, F. M., & Choi, Y. (2011). Rational SOFC material design: new advances and tools. Materials Today, 14(11), 534–546. doi:10.1016/s1369-7021(11)70279-6

44 Madsen, B. D., & Barnett, S. A. (2005). Effect of fuel composition on the performance of ceramic-based solid oxide fuel cell anodes. Solid State Ionics, 176(35-36), $2545^{-2}553$.

45 Armstrong, E. N., Park, J.-W., & Minh, N. Q. (2012). High-Performance Direct Ethanol Solid Oxide Fuel Cells. Electrochemical and Solid-State Letters, 15(5), B75. doi:10.1149/2.010206esl

46 Liu, Z., Liu, B., Ding, D., Liu, M., Chen, F., & Xia, C. (2013). Fabrication and modification of solid

oxide fuel cell anodes via wet impregnation/infiltration technique. Journal of Power Sources, 237, 243–259.

47 Zhang, Y., Xu, N., Fan, H., & Han, M. (2019). La0.6Sr0.4Co0.2Fe0.8O3-δ nanoparticles modified Ni-based anode for direct methane-fueled SOFCs. Energy Procedia, 158, 2250–2255. doi:10.1016/j.egypro.2019.01.179

48 Skafte, T. L., Hjelm, J., Blennow, P., & Graves, C. (2018). Reactivating the Ni-YSZ electrode in solid oxide cells and stacks by infiltration. Journal of Power Sources, 378, 685–690. doi:10.1016/j.jpowsour.2018.01.021

49 Chen, Y., Zhang, Y., Lin, Y., Yang, Z., Su, D., Han, M., & Chen, F. (2014). Direct-methane solid oxide fuel cells with hierarchically porous Ni-based anode deposited with nanocatalyst layer. Nano Energy, 10, 1–9. doi:10.1016/j.nanoen.2014.08.016

50 Zhang, Y., Fan, H., & Han, M. (2018). Stability of Ni-YSZ Anode for SOFCs in Methane Fuel: The Effects of Infiltrating La0.8Sr0.2FeO3-δand Gd-Doped CeO2 Materials. Journal of The Electrochemical Society, 165(10), F756–F763.

51 Qu, J., Wang, W., Chen, Y., Deng, X., & Shao, Z. (2016). Stable direct-methane solid oxide fuel cells with calcium-oxide-modified nickel-based anodes operating at reduced temperatures. Applied Energy, 164, 563–571. doi:10.1016/j.apenergy.2015.12.014

52 Yang, L., Choi, Y., Qin, W., Chen, H., Blinn, K., Liu, M., … Liu, M. (2011). Promotion of water-mediated carbon removal by nanostructured barium oxide/nickel interfaces in solid oxide fuel cells. Nature Communications, 2(1). doi:10.1038/ncomms1359

53 Zheng, M., Wang, S., Yang, Y., & Xia, C. (2018). Barium carbonate as a synergistic catalyst for the H2O/CO2 reduction reaction at Ni–yttria stabilized zirconia cathodes for solid oxide electrolysis cells. Journal of Materials Chemistry A, 6(6), 2721–2729. doi:10.1039/c7ta08249e

54 Su, C., Wang, W., Ran, R., Shao, Z., Tade, M. O., & Liu, S. (2013). Renewable acetic acid in combination with solid oxide fuel cells for sustainable clean electric power generation. Journal of Materials Chemistry A, 1(18), 5620. doi:10.1039/c3ta10538e

55 Hua, B., Li, M., Sun, Y.-F., Zhang, Y.-Q., Yan, N., Li, J., … Luo, J.-L. (2017). Grafting doped manganite into nickel anode enables efficient and durable energy conversions in biogas solid oxide fuel cells. Applied Catalysis B: Environmental, 200, 174–181. doi:10.1016/j.apcatb.2016.07.001

56 MIIKKULAINEN, V., LESKELA, M., RITALA, M. & PUURUNEN, R. L. 2013. Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends. Journal of Applied Physics, 113. 021301.

57 SKARP, J. I., SOININEN, P. J. & SOININEN, P. T. 1997. ALE-reactor for large area depositions. Applied Surface Science, 112, 251^{-2}54.

58 GONG, Y., PATEL, R. L., LIANG, X., PALACIO, D., SONG, X., GOODENOUGH, J. B. & HUANG, K. 2013. Atomic Layer Deposition Functionalized Composite SOFC Cathode La0.6Sr0.4Fe0.8Co0.2O3-δ - Gd0.2Ce0.8O1.9: Enhanced Long-Term Stability. Chemistry of Materials, 25, 4224- 4231.

59 GONG, Y., PALACIO, D., SONG, X., PATEL, R. L., LIANG, X., ZHAO, X., GOODENOUGH, J. B.

& HUANG, K. 2013. Stabilizing Nanostructured Solid Oxide Fuel Cell Cathode with Atomic Layer Deposition. Nano Letters, 13, 4340-4345.

60 KÜNGAS, R., YU, A. S., LEVINE, J., VOHS, J. M. & GORTE, R. J. 2013. An Investigation of Oxygen Reduction Kinetics in LSF Electrodes. Journal of The Electrochemical Society, 160, F205-F211.

61 YU, A. S., KÜNGAS, R., VOHS, J. M. & GORTE, R. J. 2013. Modification of SOFC Cathodes by Atomic Layer Deposition. Journal of The Electrochemical Society, 160, F1225-F1231.

9 Technical Effectiveness of ALD, Project Conclusion and Product

9.1 Target community of beneficiaries:

The following key aspects make the proposed work relevant to SECA industry teams and produce a significant impact to the DOE-SOFC program's technical development and objectives. (1). Modifying the internal surface of Ni/YSZ **from commercial cells for direct hydrocarbon utilization**. (2). **Highly repeatable and controllable (to atomic scale) manufacturing processing of ALD**. (3). **Cost-effective processing**. The surface architecture/scaffold possesses engineered nanostructure but features commonly used oxide conductors and electro-catalyst materials. The surface layer possesses a minimum thickness of ~2-40 nm and is solely designed to control the surface reforming reactions and increased catalytic activity. (4). **Simple one-step gas/vapor automatic infiltration and time-efficient**. ALD processing is fully automatic. For a 40 nm ALD single or multiple layers, one can finish deposition within several hours. (5). **Scale-up ready**. ALD systems for large-scale SOFC stack processing are commercially available. Overall, the proposed surface architectures added into the Ni/YSZ anode are expected to result in significant enhancement of electrochemical performance and durability for the commercial anodes, without materials set changes of the cells, and leading to the immediate impact on the industry commercialization.

Solid oxide fuel cells offer high energy conversion efficiency, minimize emissions compared to combustion-based electrical power generation methods, and features excellent fuel flexibility. The cells are modular and scalable. SOFCs are with broad applicability, including stationary power supply fueled by natural gas for residential use and portable power supplies in transportation applications. There are three primary segments of the market: stationary applications, transportation applications, and portable applications. The global solid oxide fuel cell market was estimated at approximately $175 million in 2017 and is expected to increase significantly to an estimated $1.4 billion by 2025. [1]

Growth in the market is expected to be driven by increased awareness about alternative energy applications, the global energy crisis. Most importantly, growth in the market is expected to be driven by the increased market competitiveness of SOFC technology in terms of cell power density, cell longevity, and cell/stack fabrication and maintenance cost.

9.2 State-Of-The-Art Solution Based Infiltration and its Technical Barrier

One of the most reliable and efficient ways to further improve the performance of the SOFC cathodes is to modify the surface of the state-of-the-art cathodes to achieve enhancement in activity and stability. Electrode fabrication and modification by infiltration [2,3,4,5,6] of active components into a porous scaffold can achieve outstanding electrochemical performance. Over the past several years, solution-based infiltration processes have been developed for deposition of both discontinuous (discrete particle) and continuous (dense) coatings of catalysts into the state-of-the-art cathodes to enhance the surface electrocatalytic activity and stability. [7,8]

Solution-based infiltration processes have been developed for deposition of metals and oxide into the Ni/YSZ anode to either increase the conductivity or the catalytic activity.[9] Among the different infiltration materials investigated, when a small amount of Pd, Pt, Rh, Ni and/or ceria was subsequently added as catalyst, the anodes exhibited much higher performance in H_2 and CH_4 fuels.[10,11,12,13,14] Solution based infiltration methods enable application of diverse materials, however key material criteria must be satisfied before commercialization. (1). The thick and dense anode support layer is very difficult for the solution to penetrate and adds cost with respect to both fabrication with repeated infiltration steps and materials. (2). The decrease of the original porosity for gas penetration and the reduction of the original active reaction sites could easily occur during solution infiltration and adversely affect the cell performance. (3). Most importantly, the **Ni/YSZ internal surface structure** modified by infiltration is **not controllable** through solution based infiltration processing.

9.3 Uniqueness of ALD and its Technical Challenge for SOFC Applications

Uniqueness of ALD processing on SOFCs: ALD is a **chemical vapor deposition** technique that sequentially applied atomic monolayers to a substrate, typically alternating compounds to produce a locally balanced atomic distribution of the target material. [15] ALD is uniquely suitable for depositing uniform and conformal films on complex three-dimensional topographies with a high aspect ratio. The indifference of ALD to substrate shape makes it particularly promising for applications to SOFCs, which presses porous active structure with complex three-dimensional topographies, and with electrode performance strictly depending on the surface properties. ALD processing is large batch and features easy scale-up and simplified handling precursors. Such capacity of ALD processing permits the simultaneous processing of hundreds of SOFCs.[16]

Technical challenges: Although ALD possesses significant promise as SOFC processing techniques, insufficient research has been completed to assure success in commercial applications. Recent work was reported for ALD-coated symmetric cells [17,18] and some showed that the ALD coating symmetrical cells was detrimental to the cathode performance. [19 , 20] Similar to conventional cathode infiltration, judicious selection of the ALD coating layer chemistry and crystal structure is a critical achievement of the high cell performance. Several ALD coated material has been demonstrated detrimental for the cell performance, including Al_2O_3.21

9.4 Technical Effectiveness and Economic Feasibility of ALD Developed Through This Project

Determination of efficacious materials and structures for application to commercial cells is imperative to support commercial cell modifications using ALD. The results from this project have shown that significantly enhanced performance can be achieved by the ALD infiltration of commercial Ni/YSZ anode.

The ALD processing developed through this project features the following (1) Simple and straightforward one-step processing and time-efficient. (2). Highly repeatable and controllable manufacturing processing. (3). Cost-effective. The surface architecture/scaffold possesses engineered nanostructure but features commonly used electrocatalyst materials. The developed surface layer possesses a minimum thickness of ~3-20 nm and is solely designed to maximize the TPB density. The fabrication methods offer precise structural control for maximum power density with minimum materials consumption. The ALD processing developed through this project thus bears immediate breakthrough on the SOFC technology since the applied ALD processing is scalable to both the single cells and SOFC stacks. Overall, the success of this project demonstrated the commercial scalability of the ALD processing with minimal impact on the cost structure of the cells and the stacks.

9.5 Project Conclusion and Product

The surface scaffold architecture developed through this project is multi-functional and nano-scaled, facilitated by multiple heterostructured interfaces that will significantly enhance the power density and cell durability. This objective has been 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); and (5) accelerating anode reactions thereby decreasing the over-potential, and (6) mitigating YSZ degradation.

ALD has been employed to generate stable anode surface architectures that are uniform, repeatable, and precisely controllable at the atomic scale. This project will enhance power density and increase reliability, robustness, and endurance of commercial SOFCs upon operation using various fuels, including natural gas (methane), over the operational temperature range of 650-800ºC. The technology process will be cost-effective and scale-up ready for mass manufacturing.

Actual Accomplishment: The choice of chemistry and crystal structure of the ALD layer is critical for their compatibilities with the backbones. Therefore, the PIs are using commercially-relevant proton conductors, electro-catalysts, and noble metal materials and develop special nanostructure on the surface of the commercial composite anodes:

To the best of our knowledge, this project and this report is the First Report on ALD of Ni/YSZ; Seven Sets ALD coating have been successfully developed from This Project. **Actual achievement of this Project include (1).** Successful demonstration of 7 types of ALD layers on Ni/YSZ anode, mono-catalysts and multi-functional nano-composite. (2). Demonstrated ALD coating increased both catalytic activity andand conductivity of Ni/YSZ. (3). ALD coating of Ni/YSZ anode increased the power density of entire cell by 300%. (4). ALD coating of nano-composite on Ni/YSZ anode has significantly increased cell durability upon.

9.6 References Cite

1 Solid Oxide Fuel Cell (SOFC) Market Analysis by Application, by Region, and Segment Forecasts, 2018 –2025, Grand View Research, September 2017.

2 VOHS, J. M. & GORTE, R. J. 2009. High-Performance SOFC Cathodes Prepared by Infiltration. Advanced Materials, 21, 943-956.

3 CRACIUN, R., PARK, S., GORTE, R. J., VOHS, J. M., WANG, C. & WORRELL, W. L. 1999. A Novel Method for Preparing Anode Cermets for Solid Oxide Fuel Cells. Journal of The Electrochemical Society, 146, 4019-4022.

4 KIM, H., LU, C., WORRELL, W. L., VOHS, J. M. & GORTE, R. J. 2002. Cu-Ni Cermet Anodes for Direct Oxidation of Methane in Solid-Oxide Fuel Cells. Journal of The Electrochemical Society, 149, A247-A250.

5 GORTE, R. J., PARK, S., VOHS, J. M. & WANG, C. H. 2000. Anodes for direct oxidation of dry hydrocarbons in a solid-oxide fuel cell. Advanced Materials, 12, 1465-1469.

6 HE, H. P., HUANG, Y. Y., REGAL, J., BOARO, M., VOHS, J. M. & GORTE, R. J. 2004. Low-temperature fabrication of oxide composites for solid-oxide fuel cells. Journal of the American Ceramic Society, 87, 331-336.

7 LEE, S., MILLER, N., STARUCH, M., GERDES, K., JAIN, M. & MANIVANNAN, A. 2011. Pr0.6Sr0.4CoO3-delta electrocatalyst for solid oxide fuel cell cathode introduced via infiltration. Electrochimica Acta, 56, 9904-9909.

8 LEE, S., MILLER, N. & GERDES, K. 2012. Long-Term Stability of SOFC Composite Cathode Activated by Electrocatalyst Infiltration. Journal of the Electrochemical Society, 159, F301-F308.

9 Liu, Z.; Liu, B.; Ding, D.; Liu, M.; Chen, F.; Xia, C., Fabrication and modification of solid oxide fuel cell anodes via wet impregnation/infiltration technique. *Journal of Power Sources* **2013,** *237,* 243-259.

10 Kim, G.; Corre, G.; Irvine, J. T. S.; Vohs, J. M.; Gorte, R. J., Engineering Composite Oxide SOFC Anodes for Efficient Oxidation of Methane. *Electrochemical and Solid-State Letters* **2008,** *11* (2), B16-B19.

11 Kim, G.; Lee, S.; Shin, J. Y.; Corre, G.; Irvine, J. T. S.; Vohs, J. M.; Gorte, R. J., Investigation of the Structural and Catalytic Requirements for High-Performance SOFC Anodes Formed by Infiltration of LSCM. *Electrochemical and Solid-State Letters* **2009,** *12* (3), B48-B52.

12 Kim, J.-S.; Nair, V. V.; Vohs, J. M.; Gorte, R. J., A study of the methane tolerance of LSCM–YSZ composite anodes with Pt, Ni, Pd and ceria catalysts. *Scripta Materialia* **2011,** *65* (2), 90-95.

13 Zhu, X.; Lü, Z.; Wei, B.; Huang, X.; Zhang, Y.; Su, W., A symmetrical solid oxide fuel cell prepared by dry-pressing and impregnating methods. *Journal of Power Sources* **2011,** *196* (2), 729-733.

14 Zhu, X.; Lü, Z.; Wei, B.; Chen, K.; Liu, M.; Huang, X.; Su, W., Fabrication and performance of membrane solid oxide fuel cells with La0.75Sr0.25Cr0.5Mn0.5O3−δ impregnated anodes. *Journal of Power Sources* **2010,** *195* (7), 1793-1798.

15 MIIKKULAINEN, V., LESKELA, M., RITALA, M. & PUURUNEN, R. L. 2013. Crystallinity of inorganic films grown by

atomic layer deposition: Overview and general trends. Journal of Applied Physics, 113. 021301.

16 SKARP, J. I., SOININEN, P. J. & SOININEN, P. T. 1997. ALE-reactor for large area depositions. Applied Surface Science, 112, 251-254.

17 GONG, Y., PATEL, R. L., LIANG, X., PALACIO, D., SONG, X., GOODENOUGH, J. B. & HUANG, K. 2013. Atomic Layer Deposition Functionalized Composite SOFC Cathode La0.6Sr0.4Fe0.8Co0.2O3-δ - Gd0.2Ce0.8O1.9: Enhanced Long-Term Stability. Chemistry of Materials, 25, 4224- 4231.

18 GONG, Y., PALACIO, D., SONG, X., PATEL, R. L., LIANG, X., ZHAO, X., GOODENOUGH, J. B. & HUANG, K. 2013. Stabilizing Nanostructured Solid Oxide Fuel Cell Cathode with Atomic Layer Deposition. Nano Letters, 13, 4340-4345.

19 KÜNGAS, R., YU, A. S., LEVINE, J., VOHS, J. M. & GORTE, R. J. 2013. An Investigation of Oxygen Reduction Kinetics in LSF Electrodes. Journal of The Electrochemical Society, 160, F205-F211.

20 YU, A. S., KÜNGAS, R., VOHS, J. M. & GORTE, R. J. 2013. Modification of SOFC Cathodes by Atomic Layer Deposition. Journal of The Electrochemical Society, 160, F1225-F1231.