TOPICAL REVIEW

Review on process-microstructure-performance relationship in ALD-engineered SOFCs

Jeong Woo Shin¹, Dohyun Go¹, Seung Hyeon Kye, Sungje Lee and Jihwan An

Department of Manufacturing Systems and Design Engineering, Seoul National University of Science and Technology, Republic of Korea

¹ These authors contributed equally to this work.

E-mail: jihwanan@seoultech.ac.kr

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Abstract

Solid oxide fuel cells (SOFCs) are promising candidates for next-generation energy conversion devices, and much effort has been made to lower their operating temperature for wider applicability. Recently, atomic layer deposition (ALD), a novel variant of chemical vapor deposition, has demonstrated interesting research opportunities for SOFCs due to its unique features such as conformality and precise thickness/doping controllability. Individual components of SOFCs, namely the electrolyte, electrolyte–electrode interface, and electrode, can be effectively engineered by ALD nanostructures to yield higher performance and better stability. While the particulate or porous structures may benefit the electrode performance by maximizing the surface area, the dense film effectively blocks the chemical or physical shorting even at nanoscale thickness when applied to the electrolyte, which helps to increase the performance at low operating temperature. In this article, recent examples of the application of ALD-processed nanostructures to SOFCs are reviewed, and the quantitative relationship between ALD process, ALD nanostructure and the performance and stability of SOFCs is elucidated.

Abbreviations

AAO Anodized aluminum oxide
ALD Atomic layer deposition
Ar Aspect ratio
BOP Balance of plant
BSCF (Ba, Sr)(Co, Fe)O₃
BYZ BaZrO₃
CHP Combined heat and power
CVD Chemical vapor deposition
DFT Density functional theory
DRAMs Dynamic random access memories
DRIE Deep reactive ion etching
EIS Electrochemical impedance spectroscopy
GBs Grain boundaries
GDC Gadolinium-doped ceria
HOR Hydrogen oxidation reaction
LSC (La₅Sr₁₋ₓ)CoO₃
LSCF (La₅Sr₁₋ₓ)(Co₅Fe₁₋ₓ)O₃
LSF (La, Sr)FeO$_{x}$
LSM (La$_{x}$Sr$_{1-x}$)MnO$_{3}$
LSR Line-specific resistance
LT-SOFC Low-temperature solid oxide fuel cells
MEA Membrane-electrode assembly
MEMS Micro-electro-mechanical system
MOSFETs Metal–oxide–semiconductor field-effect transistors
MPD Maximum power density
NSL Nanosphere lithography
OCV Open circuit voltage
ORR Oxygen reduction reaction
PEALD Plasma-enhanced atomic layer deposition
PGMs Platinum group metals
PLD Pulsed laser deposition
PVD Physical vapor deposition
SDC Samarium-doped ceria
SOFCs Solid oxide fuel cells
TPB Triple phase boundary
YDC Yttrium-doped ceria
YSZ Yttrium-stabilized zirconia
ZDC Zirconium-doped ceria

1. Introduction

Fuel cells are energy conversion devices that convert chemical energy in fuel into electrical energy. Compared to the conventional heat-engine, fuel cells generally operate at higher efficiency, and emit much less or no global-warming or toxic pollutants (e.g., CO$_2$ or NO$_x$/SO$_x$) [1, 2]. Among various types of fuel cells, solid oxide fuel cells (SOFCs) adopt solid oxide materials as electrolytes. They are known to be promising candidates as next-generation energy conversion systems owing to several advantages over other types of fuel cell systems including (1) high-energy conversion efficiency, especially when used in combined heat and power (CHP) mode because of their high-quality waste heat, (2) flexibility in fuel utilization, ranging from hydrogen to simple hydrocarbons (e.g., methane, methanol) or even conventional fuels (e.g., diesel), and (3) the possibility of using inexpensive ceramic catalysts rather than precious metal catalysts. SOFCs can also be employed to compensate the discrepancy between demand and supply of energy in electrical grid systems, and intermittent power generation from renewable resources [1–8]. Many of SOFCs’ advantages are ascribed to their high operating temperature (>800 °C), which, however, can also lead to practical issues such as limited applications (generally in stationary systems for distributed power generation), higher cost of membrane-electrode assembly (MEA) and balance of plant (BOP), and faster thermal degradation.

Low-temperature SOFCs (LT-SOFCs) that operate at a relatively lower temperature range (600–650 °C) [1] have drawn attention from many research groups. LT-SOFCs may have various advantages compared to their high-temperature counterparts; for example, Cr volatilization that has been reported to induce thermal degradation may be reduced, and also the rate of other degradation mechanisms, e.g., cation transport or particle coarsening may slow down [9–12]. Furthermore, the utilization of less expensive insulation or interconnects as well as cost reduction in balance of plant (BOP) is possible for lower operating temperatures, resulting in reduced manufacturing costs. Rapid start-up and shut-down also contribute to the deployment of the LT-SOFC systems for portable applications.

Nevertheless, the performance of the cell at low operating temperature drops drastically due to the impediment in electrochemical reactions associated with the cell operation. The rates of the charge transport inside the electrolyte, as well as the kinetics at the electrodes, decrease exponentially as the operating temperature is lowered. Especially in the operation of LT-SOFCs, the kinetics at the cathode, i.e., oxygen reduction reaction (ORR), is the rate-determining step in the fuel cell operation due to higher activation energy than anode kinetics (hydrogen oxidation reaction (HOR)). Therefore, exploring designs and materials for high performance and durable cathodes in LT-SOFCs, e.g., the ORR catalyst, interlayers has been the main engineering target of many
researchers in this field [13–49]. Meanwhile, in LT-SOFCs directly operating on complex fuels such as hydrocarbon gases or liquid alcohols, the operation loss by anode kinetics may become dominant. The growing need for LT-SOFC systems as portable power sources poses a challenge for direct alcohol-fueled LT-SOFC, which is also discussed in a recent review [50].

To tackle the challenges faced to develop high-performance LT-SOFCs, various engineering efforts have been made so far, particularly, novel nano-materials and fabrication techniques have been studied and reported, some of which have not been extensively explored in conventional high temperature SOFCs. Nanoscale structures such as 0-dimensional (0D) nanoparticles, 1D nanowires/nanofibers, 2D thin films (<1 μm in thickness), and 3D nano-porous layer structures, have been explored. SOFCs with thin (~10 μm) yttria-stabilized zirconia (YSZ) electrolytes first developed in the 1990s allowed significant reduction in the operating temperature from ~850 °C to the intermediate temperature range, from 700 to 850 °C [1]. Recently, thinner (<1 μm) ion-conducting oxides are being studied as electrolytes for high-performance LT-SOFCs. Such thin film electrolytes maximize the electrical/chemical gradient between the two electrode sides facilitating the charge transport. Nanoparticles and/or nano-porous layers are being widely employed as electrodes because they can maximize the surface-to-volume ratio as well as the interfacial area between electrodes and the electrolyte, which can accelerate the charge transfer rates. Nevertheless, the intrinsic issue with mechanical/chemical stability of nanoscale structures may adversely affect the durability of the cells if they are employed in SOFC membrane-electrode-assemblies (MEAs). Atomic layer deposition (ALD), which is a variant of chemical vapor deposition (CVD) based on surface-limited film growth, has shown potential as a nanostructure fabrication technique for SOFCs. Unique features of ALD films, such as excellent conformality, ultra-thin (<100 nm) but pin-hole free morphology, and precise doping/thickness controllability, have enabled the fabrication of nanostructures equipped with two desired features—performance and stability.

Figure 1. Schematic illustrations of (a) the ALD process, (b) ALD nanostructures, and (c) SOFC components. (b) Reproduced with permission [19]. John Wiley & Sons. Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Reproduced with permission [30]. John Wiley & Sons. © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Reproduced with permission from [35]. Copyright (2013) American Chemical Society. Reproduced with permission from [52]. Copyright (2007) American Chemical Society. Reproduced with permission from [35]. Copyright (2013) American Chemical Society. Reproduced with permission from [52]. Copyright (2007) American Chemical Society.
In this review, recent reports on the application of ALD nanostructures in SOFCs will be reviewed and discussed in the aspect of the process-structure-performance relationship [13–77]. While ALD nanostructures have mostly been used in LT-SOFCs due to their reduced mechanical/chemical stabilities at elevated temperatures, several reports have shown their successful incorporation in SOFCs operating at intermediate- to high-temperature regimes [34, 35, 37–41]. Before reviewing the examples of applications in section 3, we will first revisit the fundamentals of SOFC and ALD in section 2. In section 3, we will present examples and discuss how the intrinsic and unique features of the ALD process, and the nanostructures fabricated by ALD, have contributed to enhance the performance and durability of SOFC components as the electrolyte (section 3.1), electrode-electrolyte interface (section 3.2), and electrode (section 3.3) (figure 1). Systematic and quantitative comparison in terms of the performance and durability of SOFC components by the application of ALD processes and structures will be presented (section 3.4). In section 4, we will summarize the review with the outlook on the application of ALD to fabricate components for SOFCs.

## 2. Fundamentals of SOFC and ALD

In this section, the fundamentals regarding the performance and losses of SOFC will be reviewed first. Principles of operation, and loss mechanisms of LT-SOFCs are similar to their high-temperature counterparts that are worth revisiting when nanoscale components are employed. In addition, the features of ALD processes and the nanostructures fabricated by ALD will be more extensively introduced to demonstrate their potential as effective tools for interface engineering of SOFCs.

### 2.1. Losses in SOFC with nanostructures

The cell voltage \( V \) of a SOFC can be described as a function of the open circuit voltage \( V_{oc} \) and losses including activation loss at the anode \( \eta_{act, anode} \) and cathode \( \eta_{act, cathode} \), ohmic loss \( \eta_{ohmic} \), and concentration loss \( \eta_{conc} \), as shown in the following equation [50, 78]:

\[
V = V_{oc} - \eta_{act, anode} - \eta_{act, cathode} - \eta_{ohmic} - \eta_{conc}.
\]

To acquire high cell voltage at a given current density, the OCV should be maximized while the losses are minimized. The OCV is ideally determined by the operating temperature, activities or pressures, and thermodynamic potentials of fuel and the oxidant as expressed in the so-called Nernst equation [78]. While lower temperature seems to be preferable in achieving high OCV, it always occurs at the expense of a drastic drop of reaction rates, which increases the loss terms and eventually lowers the cell performance.

The ohmic loss is governed by the thickness \( t \) and the ionic conductivity \( \sigma \) of the electrolyte when \( j \) is the current density:

\[
\eta_{ohmic} = j \times \left( \frac{t}{\sigma} \right).
\]

Because the ionic conductivity is usually lower than the electronic conductivity by several orders of magnitude, minimizing the thickness of the electrolyte is favorable [78], as per the equation above. However, reducing the electrolyte thickness, potentially down to nanoscale thickness, raises practical issues, and is limited by mechanical integrity, non-uniformity, shorting, or fuel crossover. The OCV (the voltage at zero current density) may decrease if the nanoscale solid electrolyte is not free of such limitations. For example, a mixture of conducting oxides, e.g., doped CeO\(_2\), as the electrolyte may be susceptible to a reduction of the electrolyte at the anode at elevated temperatures, leading to electronic conduction (shorting) through the electrolyte and a lowered OCV; this becomes even more dominant when the electrolyte becomes thinner [71]. In some cases, direct electrical path (i.e., pin-hole in electrolyte) between electrodes exist, and no OCV is observed [59, 60, 68, 70].

Cathode polarization loss, is usually the main operational loss in LT-SOFCs because of the high activation energy associated with ORR. Optimal cathode materials should possess high catalytic activity upon ORR, sufficient electronic conductivity, an adequate thermal expansion coefficient, and thermal stability [1]. While ORR is composed of several different steps, it usually includes (1) adsorption of molecular oxygen on catalyst surfaces, (2) dissociation of molecular oxygen into atomic species, (3) surface diffusion of atomic oxygen to the triple phase boundary (TPB), (4) charge (electron) transfer reaction, and (5) the incorporation of oxygen ions into electrolytes [26]. The typical rate-limiting steps are known to be oxygen surface exchange and bulk/surface diffusion [79–83].

Anode polarization loss is not dominant in SOFCs if hydrogen is used as fuel and the cell is operated in a low temperature regime. Regardless of the details of the HOR process, the hydrogen oxidation kinetics occur near TPB (i.e., Ni-YSZ-vapor interface in Ni-YSZ cermet anode), and are represented by polarization resistance per unit length of the TPB (i.e., line-specific resistance or LSR) [1]. If C-containing chemicals, are directly used as
fuel, the electrochemical oxidation at the anode becomes much more complex, some of which are not well understood yet [50, 84]. For example, the oxidation of methane is not expected to take place in a single step; some possible reaction paths include [85]:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{C} + 2\text{H}_2 \\
\text{C} + \text{O}^{2-} & \rightarrow \text{CO}, \text{CO}_2 \\
\text{H}_2 + \text{O}^{2-} & \rightarrow \text{H}_2\text{O} \\
\text{CH}_4 + \text{O}^{2-} & \rightarrow \text{CH}_3\text{OH} + 2e^- \\
\text{CH}_3\text{OH} + \text{O}^{2-} & \rightarrow \text{HCOOH} + \text{H}_2\text{O} + 4e^- \\
\text{HCOOH} + \text{O}^{2-} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2e^-.
\end{align*}
\]

An important thing to note regarding the effective cathode and anode structures is that the reactions are associated with the surface area and TPB. Therefore, high density of surface area as well as TPB are preferred at electrodes. Nanoporous structures of metals and ceramic, in combination with nanoparticles, are employed. However, the mechanical and chemical stability of electrode structures with high surface-to-volume ratio, especially nanostructures, may become a serious issue at elevated temperatures [27–33].

2.2. Characteristics of the ALD process

ALD is based on sequential self-limiting surface reaction between the precursor and oxidant. One ALD cycle is usually composed of two surface reactions, each of which comprises two steps (precursor pulse/purge or oxidant pulse/purge) (figure 1). In a binary oxide process, for example, two surface reactions alternately occur forming a binary compound film. Thicker film is deposited by repeating the cycles; one can also alternately repeat two or more binary oxide processes to synthesize more complex films with precise composition and doping control by cycle ratio.

ALD has originally emerged as a means to deposit thin films for displays and is recently being applied to semiconductor processes for metal–oxide–semiconductor field-effect transistors (MOSFETs) or dynamic random access memories (DRAMs) due to rapid miniaturization of the electronic devices at fully commercialized scale [86, 87]. Such shrinkage of the size of modern electronic devices has favored the features of ALD films, such as high conformality over very high aspect structures of DRAM capacitors, continuous and pinhole-free deposition even at several nanometers thickness for gate oxide in MOSFETs, or low gas permeability for diffusion barrier coatings. ALD nanostructures may be used in high-performance SOFC components. The morphologies of ALD nanostructures could be either particulate, porous-film, or dense-film structures depending on the film growth stage (as a function of ALD cycles) (figure 1), each of which may satisfy the optimal properties and morphology of different SOFC components (table 1). Our reviews hereafter will focus on how those different morphologies of ALD films and the following features of the ALD process have affected or contributed to the SOFC engineering:

(1) Conformal nature: the conformal and dense nature of ALD film is beneficial for the SOFC electrolyte, because limitations posed on thin-film electrolytes, such as mechanical integrity, non-uniformity, shorting, or fuel crossover can be resolved. Also conformal surface treatment or decoration of catalytically active and chemically stable materials on generally-porous electrodes by infiltration of gaseous precursors and/or oxidants into complex nanopore structures could be possible, which can tune the chemical activity as well as the stability of electrodes.

(2) Doping controllability: using ALD, one can easily alter material properties that are dependent on the doping level, e.g., ionic conductivity or surface exchange, which dominate the charge transport and the charge transfer reactions in SOFCs.

(3) Precise control of film thickness: ALD is a suitable technique to fabricate nanoscale thin-films that can minimize the losses associated with the film thickness (such as ohmic loss) when applied as interlayers or electrolytes. It enables the dense surface decoration of nanoparticles on porous electrode structures with ultra-low loading, which is crucial for noble metal catalyst materials.

Several techniques, e.g. sputtering, pulsed laser deposition (PLD), screen printing, tape-casting, etc., have been applied to fabricate nanostructures for SOFCs over the past decades. However, these techniques have encountered challenges such as poor surface coverage on three-dimensional (3D) structures, difficulties in precise doping level or thickness control, or limited scalability. ALD has shown to be more effective than other techniques for fabricating proper nanostructures to improve the performance of SOFCs in the above-mentioned aspects.
Table 1. Required properties and morphology of ALD nanostructures depending on the SOFC component (OO: strongly required, O: required, Δ: conditionally required, X: not required).

| Component          | Requirement | High ionic conductivity | High surface exchange | Coking tolerance | Optimal morphology (Reference) | References |
|--------------------|-------------|-------------------------|-----------------------|-----------------|--------------------------------|------------|
| 3.1 Electrolyte    | Δ (necessary if no interlayer is employed) | O                       | Δ                     | X               | Dense film needed (>tens of nms) | [52, 53, 57, 74] |
| 3.2.1 Cathodic interlayer | Δ           | O                       | Δ                     | X               | Dense film preferred (> ∼10 nm) | [13, 21, 23, 24, 26] |
| 3.2.2 Anodic interlayer | Δ           | O                       | Δ                     | X               | Dense film preferred (> ∼10 nm) | [60, 77] |
| 3.3.1 Cathode      | Δ           | O                       | Δ                     | X               | Particulate or porous structure needed (<10 nm) | [29, 33, 37, 39, 40] |
| 3.3.2 Anode        | Δ           | O                       | Δ                     | X               | Particulate or porous structure needed (<10 nm) | [135, 151, 153] |
3. Process-structure-performance relationship in ALD-engineered SOFCs

3.1. Effect on electrolyte performance
Ions transport through the electrolyte of the SOFC. There are a few essential properties of electrolytes, such as high ion selectivity (oxide ion conducting or proton conducting), physical separation between fuel and oxidant, and lack of electronic conductivity. As mentioned in section 2, the ohmic resistance in the electrolyte is influenced by the thickness of the electrolyte and ionic conductivity. By using ALD, the thickness of the electrolyte that satisfies the properties above can be adjusted down to even several nanometers in thickness, and the ionic conductivity of the film can be tuned; moreover, doping level can be controlled precisely by changing the sequence of the process.

Two groups of solid oxides have mainly been studied as SOFC electrolytes: oxide-ion conducting, e.g., doped ZrO_2 or CeO_2, and proton-conducting oxides, e.g., doped BaZrO_3, BaCeO_3, or Ba(Zr, Ce)O_3. The ion conduction mechanisms in these oxides differ from each other. In oxide-ion conducting electrolytes, oxide-ions conduct through electrolyte via hopping mechanism from one oxygen vacancy to another, which is extrinsically formed by doping [78, 88]. Whereas, in the family of proton-conducting perovskites, protons conduct through hydroxide defects that are produced by the incorporation of water molecules into oxide ion vacancies in the crystal lattice [74, 75].

3.1.1. Oxide-ion conducting electrolytes

3.1.1.1. Zirconia-based electrolytes
Fundamentals on ALD YSZ processes
Yttria-stabilized zirconia (YSZ) is the most popularly used oxide-ion conducting electrolyte due to its reasonably high ion conductivity and high chemical stability. While the several- to tens-of-micrometers thick YSZ electrolytes have been employed since the 1990s, the application of nanoscale thin film (<1 μm) oxide-conducting solid oxide electrolytes in SOFCs has been reported in the 2000s. Freestanding ultra-thin SOFC have been realized by this method. For instance, Huang et al reported the use of a sputtered (a type of physical vapor deposition) YSZ, oxide-ion conducting electrolyte, for Si-based thin film SOFCs [89–97]. They achieved high electrochemical performance from cells of 130 mW cm⁻² at 350 °C; nevertheless, the limitations, such as fuel permeation through the electrolyte and electrical leakage, have also been pointed out [89, 90, 93]. Later reports by Prinz et al have demonstrated that the ALD YSZ, when applied to the identical cell structure as the one reported by Huang et al can resolve the practical limitations of PVD-processed counterparts [51–76].

The base oxide processes, i.e., ZrO_2 and Y_2O_3, for ALD YSZ have been known for decades [98–109]. Later in 2002, the optimal ALD process for ZrO_2 with smooth, pure, conformal, highly stoichiometric properties and broad deposition temperature range (50–450 °C) was reported [105]. While the ALD process for Y_2O_3 was first developed in 1994 [106], it was not until 2001 when a wide deposition temperature range of 200–400 °C with the reasonable growth rate of ~0.1 nm/cycle was reported [107].

The fabrication of YSZ by mixing the two base oxides, i.e., ZrO_2 and Y_2O_3, using various combinations of Zr and Y precursors and cycle ratios, has been reported, including Goubin et al [108], Cassir et al [109], Putkonen et al [100], and Bernay et al [101]. The first possibility of using YSZ fabricated by ALD for SOFCs was reported in 2006 by Brahim et al [51]; they deposited a thin film (300–1000 nm) electrolyte on Lao.8Sr0.2MnO3 (LSM) cathodes at 300 °C, and electrochemically characterized it using impedance spectroscopy. They found out that the ion conductivity was ~3 times lower than that of bulk YSZ, whose microstructural origin was not clearly elucidated.

ALD YSZ for freestanding electrolyte
The actual application of YSZ thin films to a fully operating SOFC was first reported by Shim et al (figure 2(a)) [52]. They deposited an ultrathin 8 mol% doped YSZ using ALD, the resulting film had high ion conductivity and was used as a planar electrolyte for thin film SOFC MEA. Only 60 nm-thick ultrathin YSZ film (~60 nm) with polycrystalline structure (grains of tens of nanometers diameter) effectively blocked the electric and chemical shorts between electrodes, while achieving high OCVs in the range from 1.01 V to 1.02 V. In addition, between the temperature of 265 °C and 300 °C, it showed similar ionic conductivity to that of bulk YSZ, but a 4 times higher exchange current density at the electrode-electrolyte interface [110]. As a result, high power density of 270 mW cm⁻² at 350 °C was achieved on a freestanding Si-based structure. The physical thickness limit of YSZ thin film for application as an electrolyte has recently been studied by Su et al [53]. Using ALD, they fabricated a 10-nm thick YSZ freestanding electrolyte supported by perforated Si (figure 2(d)). To improve the mechanical strength of the YSZ film, they used a bi-layer structure combining two separate ALD processes (i.e., patching layer on structure layer), each of which deposits a few nanometer thick YSZ film. In spite of the 10-nm thick electrolyte, their cell showed stable OCV value (1.05 V) for 14 h at 350 °C, which demonstrates the advantage of ALD-processed thin film as a dense and mechanically stable freestanding electrolyte.
ALD YSZ for 3D structured electrolytes

Even though the ALD-fabricated YSZ thin film electrolyte was first applied to the planar structured MEA [52], another well-known unique feature of ALD, the excellent conformality, makes it more suitable for 3D structured electrolytes, whose aspect ratio (AR) ranges from 2 to 20. High AR and high surface area structures have been realized using micro-electro-mechanical system (MEMS) processes including conventional photolithography [54, 55], non-conventional patterning techniques (e.g., nanosphere lithography (NSL) [56, 57] or nanowire-templated patterning [58]). The first attempt to use ALD for the fabrication of 3D-structured YSZ electrolytes was reported by Su et al in 2008 [54]. They fabricated cup-shaped 3D-structured SOFCs using photolithography and deep reactive ion etching (DRIE), and a deposited YSZ electrolyte (~70 nm) using ALD process. This cup-shaped electrolyte–electrode interface has an active area that is 5 times higher than the planar electrolyte–electrode interface reported earlier [52]. Theoretically expected OCV was observed, which meant that the YSZ layer blocked fuel cross-over between the anode and cathode effectively in this 3D structure. The maximum power density of the cup-shaped 3D-structured SOFC was 861 mW cm^{-2} at 450 °C, which was ~1.5 times higher than that of the planar cell. They speculated that the limitation of the electrode deposition method (sputtering) on the vertical wall, and possible residues from an incomplete etching process could be responsible for this observation. Su’s group later reported similar 3D cup-shaped SOFCs with a YSZ electrolyte with improved mechanical and thermal stabilities [55]. Using an improved DRIE process, they additionally fabricated so-called edge reinforcement structures for their originally freestanding MEA, which demonstrated a stable OCV over 30 h at 350 °C.

As a means of less expensive but complex patterning, NSL also showed possibilities of forming templates for SOFCs with ALD thin film electrolytes. In their report in 2011, Chao et al fabricated a corrugated 3D-structured thin film SOFC membrane with ALD fabricated YSZ electrolytes (~80 nm) using an NSL-based template [56]. Although the NSL-based template had a smaller surface enhancement factor (~2) (i.e., surface area/projected area) than their photolithographic counterparts, it showed easy manufacturability and facile accommodation for PVD methods resulting in the maximum power density of 1340 mW cm^{-2} at 500 °C. Similarly, a corrugated NSL-based template was applied to an ALD-fabricated YSZ—pulsed-laser-deposited (PLD) YDC bilayer electrolyte (figure 2(b)) [57]. Only 50 nm-thick YSZ was used as the electrolyte to effectively block gas permeation and an electrical short-circuit. The combination of chemically stable and dense YSZ and highly surface-reactive YDC showed a positive synergetic effect resulting in maximum power density of 1300 mW cm^{-2} at 450 °C. Nanotubular SOFC using a nanowire-based template was also fabricated by Motoyama et al. The ALD process was applied to deposit the YSZ electrolyte in a high AR (~25) nanotubular
structure. Theoretically, the nanotubular structure resulted in a 20-fold increase of the electrolyte–electrode interface and the ALD fabricated YSZ film almost conformally coated the nanotubular template. However, the cell performance was very low (＜1 mW cm⁻² at 550 °C) due to physical defects induced by the chemical etching process leading to chemical shorting through the electrolyte.

**ALD YSZ electrolytes on a nanoporous substrate**

ALD thin films have also been widely employed as dense electrolytes for nanoporous substrates (e.g., anodized aluminum-oxide (AAO)-based MEA designs [59–71]). In 2011, ALD Al₂O₃, which is not an ionic conductor, was used to fabricate gas–tight electrolytes by physically filling pinholes and voids. Being deposited on PLD YSZ (300 nm), the ALD Al₂O₃ layer (∼20 nm) effectively increased the OCV from 0.77 to 1.02 V [59]. On the other hand, Ha et al. applied ALD YSZ, which is an ionic conductor, for reducing the size of pinholes stemming from AAO pores and fabricated a pinhole-free sputtered YSZ electrolyte. OCV increased (from 0.5 to 1.14 V) by blocking pinholes using ALD YSZ. In addition, the anode structure was stabilized [64]. Cha’s group reported the use of an ALD YSZ layer at the anode to impede reduction of doped CeO₂ (GDC or YDC) at elevated temperature [60, 61, 70, 71]. By adopting the ALD YSZ layer, the OCV increased from ∼0.3 V to ＞1.0 V. Hong et al. reported anodized aluminum oxide (AAO)-based SOFCs with a 180 nm layer of YSZ electrolyte fabricated by ALD [62]. In this study, pinholes could be avoided even with a much thinner electrolyte using ALD-fabricated YSZ as compared to sputtered YSZ-only electrolytes (0.5–1 μm) for a perfect gas permeation block with high OCV value of about 1.05 V. By optimizing the thickness of an ALD-fabricated YSZ-only electrolyte, they achieved 5.5 times higher performance than the cell with a 500 nm thick layer. The optimal thickness of the YSZ-only layer for perfect gas permeation blocking varied depending on the anode thicknesses [65] and density (porous or dense) [66]. Recently, the use of a 25 nm-thick ALD YSZ layer to prepare a sputtered SDC–ALD YSZ–sputtered SDC sandwich structured electrolyte (figure 2(e)) was reported. The OCV dramatically increased from ∼0.4 V without ALD YSZ to ∼1.1 V with ALD YSZ, and the maximum power density was 562 mW cm⁻² at 450 °C, the highest reported among AAO-based thin film SOFCs [68].

Additionally, using plasma-enhanced ALD (PEALD) instead of thermal ALD enabled the fabrication of denser and more crystalline thin-film YSZ. Ji et al. applied PEALD YSZ for fabricating AAO-based SOFCs, and reported that a 70 nm-thick PEALD YSZ electrolyte was sufficient (1.17 V of OCV), as compared to 180 nm required for ALD YSZ (figure 2(c)) [69]. Additionally, they found out that reduction of the grain size stemming from lower thickness accommodated high surface grain boundary density, which can reduce the activation resistance at the cathode-electrolyte interface. Recently, a similarly structured SOFC with PEALD YSZ was reported by Lee et al. They fabricated a Ni anode instead of Pt, and achieved comparable OCV and maximum power density [63]. PEALD YSZ was also applied as a protective layer for less dense YSZ electrolyte fabricated otherwise (using sputtering); it did not have pinholes, and therefore perfectly blocked the gas permeation [70]. PEALD YSZ was also adopted for protecting sputtered GDC that was used as a cathodic interfacial electrolyte [71]. The thickness of PEALD YSZ was controlled by changing the number of cycles to 0, 250, and 1000, and the OCV value increased with increasing film thickness, from 1.08 V to 1.19 V.

**3.1.2. Ceria-based electrolytes**

ALD CeO₂ or doped CeO₂ layers have also been reported and applied in SOFCs. Possibly due to practical issues regarding precursor development or process optimization, ALD CeO₂ processes have been reported by only few groups since 2000 [111–113]. The first application of doped CeO₂ (GDC) to SOFCs reported in 2003 showed that the doped CeO₂ electrolyte had higher ion conductivity than YSZ, and can operate at lower temperatures without increasing ohmic losses [72]. They used 1 μm-thick ALD GDC on Ni-YSZ anode, and observed that 1 μm-thick ALD GDC showed 30 times lower ion conductivity than the 5 μm-thick layer. Balle et al. reported ALD YDC films with varying Y contents in the range of 10 to 20 at%. A 16 at%-doped, 400 nm thick YDC film had the highest ionic conductivity, but showed 350 times lower ion conductivity than bulk YDC at 400 °C, the reason for which remains unexplained [73]. Most examples reported regarding the ALD doped CeO₂ were for the electrolyte–electrode or electrode–gas interfaces engineering, which will be more extensively reviewed in the following sections (sections 3.2 and 3.3).

**3.1.2. Proton-conducting electrolytes**

In the case of proton-conducting solid oxide electrolytes, the practical fabrication challenges, such as the refractory nature of doped barium zirconate/cerate and the evaporation of barium oxide during high temperature processing, have posed difficulties in sintering of high-density materials, and therefore the fabrication of their thin films [114]. Starting from 2008, proton-conducting solid thin films have been fabricated using limited thin film fabrication techniques, e.g., pulsed laser deposition (PLD) [115–120].

For the ALD fabrication of proton-conducting oxides, the deposition of another base oxide, BaO, is necessary. The ALD process for BaO has been rarely reported because of the tendency of Ba to form oligomeric structures which limited the volatility of Ba precursor, and high reactivity of Ba precursor with a surface –OH
group [121, 122]. ALD processes for yttrium-doped BaZrO$_3$ (BYZ), which has higher chemical stability towards acid gases and high proton conductivity in the intermediate temperatures of 300–500 °C, has been reported.

Shim et al reported the first employment of proton-conducting ALD thin film (ALD BYZ) in SOFCs [74]. For comparison, ALD BYZ and PLD BYZ were prepared containing Ba: Zr: Y = 1: 0.8: 0.2 with varying thicknesses of 110 nm and 130 nm. The ALD BYZ electrolyte showed better exchange current density (3–10 times higher) than PLD BYZ electrolyte because of smoother surface morphology and lower surface energy. Also, the 110 nm thick ALD BYZ electrolyte showed high OCV values in the range 1.08–1.10 V at 300–400 °C. The maximum power densities were measured 15, 53 and 136 mW cm$^{-2}$ at 300, 350 and 400 °C, respectively. Park et al synthesized ALD BYZ films by depositing Ba to Zr content ratios using ALD and studied the ionic conductivity of ALD BYZ films according to respective Ba to Zr ratios [75]. Three types of BYZ films were fabricated; barium-deficient (Ba$_{0.8}$Zr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$), nominal composition (Ba$_{0.8}$Zr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$), and barium-excessive (Ba$_{1.6}$Zr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$). The barium content significantly affected the structural defects and chemical stability, thereby changing the ionic conductivity of ALD BYZ. ALD BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ showed the highest ionic conductivity in the temperature range of 400–550 °C.

Interestingly, the possible proton conduction in ALD YSZ has also been reported.

Park et al studied and revealed proton transport in nanostructured ALD YSZ [76]. After annealing in wet environment (15 Torr of H$_2$O), significant hydroxyl ions (OH$^-$) were involved in ALD YSZ, which was 100 times more than the content in single-crystalline YSZ. They speculated that the high density of grain boundaries in ALD YSZ attributed to the facile proton conduction.

### 3.2. Effect on interlayer performance

Charge transfer reactions occur at the electrode–electrolyte interfaces of SOFCs. The reactivity at the interface between the electrode and electrolyte in solid oxide fuel cells is affected by various factors such as grain boundary density, intrinsic surface exchange coefficient and the length of triple phase boundary (where the gas, electrode, and electrolyte meet), which can be effectively modified by structural and material engineering by the ALD process.

Grain boundaries (GBs) at the electrolyte surface are known to significantly alter the reactions at the electrode–electrolyte interface, e.g., the oxygen ion incorporation at the cathode–electrolyte interface. While GBs are generally known to impede the ion conduction that occurs perpendicular to the GB plane due to local electrical potential build-up by defect segregation [123, 124], oxygen vacancy segregation near GBs has been reported to improve oxygen exchange and incorporation near GBs [25, 36, 124, 125]. Such phenomena have been recently substantiated by the latest micro-characterization techniques, e.g., aberration-corrected TEM or nano-SIMs, which are also supported by simulations at the molecular level [14, 25, 36, 124–126]. Therefore, ALD thin films with nano-crystalline granular structures and the high density of GBs may effectively improve the surface reaction of SOFCs.

In addition, inserting materials with intrinsically high surface exchange reactivity can also help to improve activation processes. The doping level of the materials can affect the surface exchange reactivity; for example, 14–19 mol% doped YSZ showed the highest surface exchange coefficient as compared to 8 mol% YSZ doping, which is widely adopted as the SOFC electrolyte due to optimal ionic conductivity [45, 46, 78]. Doped CeO$_2$/Bi$_2$O$_3$ materials are known to have higher surface exchange coefficient than doped ZrO$_2$ [110]. The existence of structural polymorphs of doped CeO$_2$/Bi$_2$O$_3$ is a unique characteristic in precious metal-oxide interaction, or the redox activity [127–130], while their chemical stabilities could be issues when practically applied to actual devices. ALD can fabricate such reactive materials surfaces with precise doping-level control, which, for instance, can be utilized to locally tune the surface properties on chemically more stable, but less surface reactive, electrolytes (e.g., YSZ).

Additionally, TPB is known to be the preferential site for incorporation of ions that are reduced from gaseous molecules. While the exact geometry of TPB has not been clearly elucidated, and also can be altered by operation conditions, recent experimental results indicate that the width of TPB is nanometric [123, 124, 131, 132]. Essentially, the potential of ALD to form highly dense nanoscale particulate or porous structures may greatly help maximize the TPB density.

#### 3.2.1. Cathodic interlayers

A comparison of activation resistances between differently processed YSZ layers including ALD has been reported by Benamira et al in 2009 [44]. They compared cathodic interlayers fabricated by ALD, dip-coating, and sputtering, and confirmed that the ALD layer effectively reduces the interfacial resistance by using EIS. An in-depth investigation about the source of the enhanced cathodic activation at the ALD YSZ surface is well-studied in the report by Park et al (figures 3(c), (d)) [13]. They studied the effects of GB on surface oxygen incorporation using quantum simulation and EIS measurements, and found that the activation energy for
incorporation into surface vacancy at a grain boundary was nearly zero, it was 0.26 eV in the absence of grain boundary. EIS results also showed 20 nm-thick ALD YSZ cathodic interlayer promoted oxygen incorporation, resulting in 3 times lower activation resistance as compared to the single-crystalline YSZ surface.

The dependence of surface reactivity of ALD layer on the local doping level was studied and reported by Chao et al [45, 46]. The doping level of YSZ was modified by a change sequence of ALD cycle between ZrO2 and Y2O3, and was deposited on cathode side of 8 mol% YSZ bulk electrolyte. Y2O3 molar percent was modified from 0 to 100%, and 14–19 mol% YSZ showed the highest surface exchange. As a result, the maximum power density of the cell with 14–19 mol%-doped ALD YSZ cathodic interface increased by 50% at 400 °C. In addition, it was confirmed that the overall conductance of 8 mol% YSZ electrolyte was not affected by ALD YSZ doping level and thickness (<10 nm). Brahim et al studied ALD ZrO2-In2O3, which improved surface exchange and reduced the polarization resistance [17]. The cell with 91.5 mol%-doped interlayer showed the lowest activation energy, about 44% lower than other samples at 300 °C.

Doping level optimization was also demonstrated for ALD-doped CeO2 cathodic interlayers; Fan et al studied the optimal doping level and thickness for ALD yttria-doped ceria (YDC) cathodic interlayers by changing the cycle ratio of the two base oxides, CeO2 and Y2O3. They found out that 12–17 mol% doped YDC shows the highest enhancement in performance at the temperature range of 300 to 500 °C. In terms of thickness, they confirmed that the enhancement in cathodic activation process is saturated at a thickness of 10 supercycles (1 supercycle = 6 CeO2 cycles + 1 Y2O3 cycle) of ALD YSZ (about 6–7 nm), which was similar to the results for the ALD YSZ cathodic interlayers studied by Chao et al (figures 3(a), (b)) [48, 49]. Recently, a new process for the fabrication of CeO2 via ALD with high growth-rate was reported using a newly developed Ce precursor with cyclopentadienyl(Cp-) ligands, and applied to SOFCs as interlayers [15, 16]. Yu et al showed that the ALD fabricated CeO2 contains a large content of Ce4+ even in undoped film, which could potentially lead to high ion conductivity and high surface reactivity [15]. By applying a 20 nm thick ALD CeO2 cathodic interlayer, they showed that the exchange current density increased by 75%. Using the same process, Yang et al investigated ALD

Figure 3. ALD nanostructures for cathodic interlayers; (a) schematic of YDC interlayered micro SOFC, (b) relationship between Ce: Y pulsing ratio and maximum power density enhancement ratio in the corresponding YDC interlayer, (c) DFT calculation of the activation energy for atomic oxygen incorporation at the grain boundary and grain center (no gb), and (d) Arrhenius plot of cathodic activation resistances at the bulk YSZ surface and ALD YSZ surface at a cell voltage of 0.8 V. (a) Reproduced from [49]. Copyright 2012, with permission from Elsevier. (b) Reproduced from [48] with permission of The Royal Society of Chemistry. (c), (d) Reproduced with permission from [13]. © Materials Research Society 2012.
YSZ was thicker than ZrO2-doped CeO2 (ZDC) cathodic interlayers with varying doping levels of 0, 20, and 60 mol% [16]. They revealed that the insertion of ZrO2 into CeO2 gives rise to structure defects with high oxygen vacancy content, which improved the cathodic surface kinetics. Additionally, the inclusion of ZrO2 and CeO2 enhanced the resistance towards nanoscale grain coarsening at elevated temperature (800 °C). A 20 mol%-doped ZDC interlayer showed the smallest activation resistance improving the maximum power density by ~60% as compared to the cell without any interlayers.

ALD-processed interlayers have been applied to thin film SOFCs with thin film oxide electrolytes; for example, Park et al applied the ALD YSZ cathodic interlayer for AAO-based thin film SOFC [47], and observed improved cathodic reactivity as compared to a sputtered YSZ surface by applying nano-granular ALD YSZ films to the electrolyte and cathode electrode interfaces of AAO-based thin film SOFCs, which corroborated well with the previous results by Chao et al and Park et al [13, 45, 46].

The ease of mixing various materials at nanoscale has also enabled the fabrication of an ultra-thin cermet layer; An et al applied ALD YSZ/Pt cermet as the cathodic interlayer to enhance the density of catalytic sites. Only a 2 nm thick ALD YSZ/Pt cermet interlayer enhanced the oxygen reduction kinetics by expanding TPB density, and exhibited improved exchange current density over the polycrystalline YSZ surface by a factor of 3 [18].

### 3.2.2. Anodic interlayers

Compared to cathodic interlayers, anodic interlayers have been rarely reported due to generally faster anodic kinetics (i.e., hydrogen oxidation reaction (HOR)) as compared to cathodic ones (i.e., ORR). While cathodic interlayers have been optimized to enhance the sluggish ORR, anodic interlayers were often fabricated as blocking layers to impede the reduction of a CeO2-based electrolyte by locating pinhole-free and chemically stable ALD YSZ at the anode side. This is because a significant reduction of CeO2 in low oxygen partial pressure environment near anode can increase the electronic conductivity, resulting in a decreased OCV. Additionally, during the reduction process, the difference of ionic radius between Ce4+(0.97 nm) and Ce3+(1.14 nm) may lead to volumetric expansion that raises problems in fuel/oxygen blocking and reliability. Kwon et al reported that the thickness ratio of the YSZ layer to the doped ceria layer should be ≥10$^{-4}$ at 800 °C to prevent reduction of ceria [133]. This implies that the required minimum thickness of the YSZ layer for electron blockage at 450 °C, if the thickness of the SDC layer is 1 μm, is only <1 nm as the minimum ratio further decreases as the temperature decreases. In the studies reporting the use of anodic interlayers, interlayer deposition by PLD [132] and ALD [77], the superiority of the ALD YSZ layer in hindering the reduction of doped CeO2 electrolyte was proved. The PLD YSZ layer could not maintain stable OCV even at much higher thickness ratio compared to an ALD YSZ layer that provided a stable OCV with a thickness very similar to the theoretically predicted ratio. When the ALD YSZ layer is inserted between the GDC electrolyte and Pt anode, the inter-diffusion of Ce into the ALD YSZ layer occurred only at a temperature of 1200 °C or higher, while no inter-diffusion was observed at below 1200 °C, and the morphology of the ALD YSZ layer was unchanged below 800 °C.

The use of an ALD YSZ protecting layer in AAO-based thin film SOFCs was reported; even though the ALD YSZ was thicker (40 nm) than the theoretical requirement due to porosities propagated from the substrate (AAO), it showed perfect blockage of the GDC reduction, with high OCV of 1.07 V, as compared to low OCV (0.3 V) of the reference (GDC electrolyte only) cell [60]. An ALD YSZ protecting layer with a similar structure, i.e., Pt(cathode)/sputtered YDC/ALD YSZ/Pt(anode), but fabricated by PEALD, was also reported. The cell with a sputtered YSZ layer at the anode side had low OCV of 0.88 V at 450 °C, while that with the PEALD YSZ protective layer had 1.0 V OCV, due to effective pore blockage [70].

### 3.3. Effect on electrode performance

The electrode of the SOFC is divided into the cathode where the ORR reaction takes place and the anode where the HOR reaction takes place. The main concern regarding the electrode is maximizing the catalytic activity; one can effectively tackle such a challenge by maximizing the surface area as well as the density of TPB that is the active site for electrochemical reactions. By controlling the film growth phases, i.e., (i) nucleation, (ii) coalescence, and (iii) continuous film formation of the ALD process, one can tune the morphology and therefore the surface area or TPB density of ALD-processed nanostructures.

Local use of catalytically more active material, e.g., precious metals or platinum group metals (PGMs), on the electrode surface could be an effective strategy to enhance overall electrode surface activity. However, the high price of precious metals is an obvious challenge. Here, the capability of ALD to fabricate an ultra-low loading PGM nanostructure can provide solutions.

PGMs, especially when they are porous at nanoscale, are usually thermally unstable due to their high surface energy, and suffer from coarsening at relatively low temperature regime for SOFC operation (<500 °C). Methods to improve the thermal stability are therefore explored, the coating of thermally stable oxide on the
The application of the ALD layer for perovskite oxide electrodes, which are widely used electrode materials in SOFCs, has been reported by several groups. The fabrication of an ALD-processed perovskite oxide electrode, e.g., (La,Sr)MnO$_x$ (LSM), as well as the coating of a thin ALD layer on perovskite oxide electrode surfaces to improve the surface activity and the thermal stability have been reported.

3.3.1. Cathode

ALD of precious metals

As previously mentioned, the cathodic activation loss stemming from sluggish ORR dominates in SOFC operation; therefore, ALD processes of the precious metal catalysts have been more widely applied to the cathode side of SOFCs. The application of the ALD layer for precious metal electrodes, which are widely used electrode materials in SOFCs, has been reported by several groups. The fabrication of an ALD-processed perovskite oxide electrode, e.g., (La,Sr)MnO$_x$ (LSM), as well as the coating of a thin ALD layer on perovskite oxide electrode surfaces to improve the surface activity and the thermal stability have been reported.

Figure 4. ALD precious metal nanostructures for SOFC electrodes; (a) plan-view TEM image and corresponding SAED image of 20-cycle ALD Pt, (b) summary of EIS result (ohmic and activation resistances) according to ALD Pt cycles, (c), (d) plan-view SEM image of a 10 nm-thick as-deposited ALD Pt film, and dependence of maximum power densities on the thickness of the Pt anode deposited by ALD and dc-sputtering techniques. (a) Reproduced with permission [19]. John Wiley & Sons. Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Reproduced from [21] with permission of The Royal Society of Chemistry. (c), (d) Reproduced with permission from [135]. Copyright (2008) American Chemical Society.

As previously mentioned, the cathodic activation loss stemming from sluggish ORR dominates in SOFC operation; therefore, ALD processes of the precious metal catalysts have been more widely applied to the cathode side of SOFCs. The application of the ALD process for precious metals has first been reported by Jiang et al where they applied a ALD Pt layer of 10–30 nm in thickness as the anode (figures 4(c), (d)) [135]. In a study by Chao et al, nano-particle ALD Pt was applied at the cathode side of the electrolyte below the sputtered Pt electrode (figure 4(a)). By doing so, the density of the TPB was increased in comparison to the sputtered Pt only. Resultantly, the exchange current density ($i_0$) with 20 cycles (10 nm thick) of ALD Pt increased by a factor of 3 as compared to that with the sputtered Pt-only cell (0.35 versus 0.13 mAcm$^{-2}$), and the maximum power density improved by about 90%. A thicker ALD Pt layer (100 cycles) in turn affected the TPB density and the performance [19]. Sole use of ALD Pt as the cathode (i.e., without additional layers) was reported by An et al. For the application of the ALD Pt layer in SOFCs, not only its TPB density but also the electrical conductivity, is to be considered; therefore, the Pt layer with nanoporous morphology and congruity is preferred. They prepared and tested 6, 8, 10 and 14 nm thick ALD Pt cathodes; the 10 nm thick ALD Pt cathode demonstrated high TPB density and low sheet resistivity, and performed similar to a 80 nm thick sputtered Pt cathode (figure 4(b)) [21].
In a later study by Ji et al., the insertion of a 25 nm thick ALD Pt layer between a sputtered Pd cathode and GDC electrolyte was also investigated, although the exact role of the ALD Pt layer was not elucidated [20].

ALD processes of precious metals were also applied to the surface tuning of metallic electrodes, because they can conformally decorate highly catalytically active nano-particulates on porous metal electrodes. The morphology of precious metal nano-particles fabricated by ALD may be largely dependent on parameters, such as substrate materials [23, 24] and thicknesses (or the number of cycles) [23], therefore, differences in performances are observed. Shim et al. fabricated ALD Pt-coated Ag, Pd, Ru, and Au cathodes; they found out that 3 nm thick ALD Pt-coated Ag, Pd, and Ru cathodes showed ORR activity similar to that of 80 nm thick sputtered bare Pt cathodes (figures 5(a),(b)) [23].

1. ALD oxide on metallic cathode

ALD oxide overlayers (or overcoatings, capping layers), e.g., MnOx [31], ZrO2 [28], SnO2 [29], doped ZrO2 [30, 32], CeO2 [33], on metal cathodes have been actively researched in recent years [28–32] because they can compensate for the low thermal stability of porous metal electrodes, and in some cases, can also improve the ORR activity. While oxide overlayers can be fabricated by using other techniques (sputtering [31–33], infiltration [139–141]), the conformal nature of the ALD process may further help to enhance the stability of metallic electrodes. The stabilization mechanism of metal nanoparticles by the oxide overlay may include: (1) anchoring of metallic nanoparticles to the substrate, (2) stabilization of unstable metal surface atoms, which may impede the physical merging, and (3) Ostwald ripening of metallic nanoparticles [136, 142–146]. More interestingly, when ion conducting oxides, such as doped ZrO2 or CeO2, were applied, clear enhancement in ORR at the metal surface was observed, whose mechanism was recently proposed by Lee et al. (figures 5(c), (d)) [26]. They investigated the mechanism of ORR enhancement by applying an ALD YSZ overcoating on the Pt cathode; among the individual steps of ORR on the Pt surface (i.e., O2 adsorption, dissociation into atomic oxygen, oxygen diffusion, charge transfer, and incorporation at the electrode–electrolyte interface), dissociation, diffusion as well as charge transfer steps were facilitated as well; this is proven by EIS analysis on the activation resistance dependence on oxygen partial pressure.

Liu et al. demonstrated that the ALD ZrO2 capping layer on a nano-porous Pt cathode surface can prevent thermal degradation of the electrode and enhance oxygen reduction reactivity at the cathode. The activation resistance after 10 cycles (1 nm thick) of a ZrO2 capped Pt cathode significantly dropped as compared to the uncapped cathode (50 Ω cm−2 → 5.3 Ω cm−2). They speculated that the improved cathode ORR may originate from the non-continuous ALD ZrO2 film attached on the Pt surface that promoted oxygen adsorption and dissociation. The degradation in the performance of the cell with a ZrO2 capped cathode dropped to about one third when compared to the cell with an uncapped cathode [28]. Another type of ALD oxide, SnO2, was demonstrated as an overlay for the Pt cathode; Chang et al. investigated ALD SnO2 coating on Pt for stabilizing

Figure 5. ALD nanostructures for the cathodic overlayer of SOFCs: (a), (b) schematic of ALD Pt particles on a sputtered porous metal cathode and comparison of maximum power density with that of a sputtered metal-ALD Pt (3 nm) cathode and a bare sputtered Pt cathode, (c), (d) schematics of ORR steps on a Pt cathode with/without an ALD YSZ cathode overlayer, and before/after (14 h) SEM images of the without (BP) and with (CP) an ALD YSZ overlayer on cathode, (e), (f) mechanisms of ALD ZrO2 overlayer effect on LSC cathode, TEM diffraction contrast image of nanoscale ALD ZrO2 overlayer (50 ALD cycles) on a LSC cathode, (g), (h) schematic of the ALD LSC overlayer effect on a LSCF cathode, and DFT-calculated relative position of the bulk oxygen p-band center to Fermi energy of crystalline LSCF, crystalline LSC, and amorphous LSC with their ASR value. (a), (b) Reproduced with permission from [23]. © 2010 ECS - The Electrochemical Society. (c), (d) Reproduced with permission from [26]. https://pubs.acs.org/doi/full/10.1021/acsomega.6b00433. Further permissions related to this material should be directed to the ACS. Copyright (2017) American Chemical Society. (e), (f) Reproduced with permission from [35]. Copyright (2013) American Chemical Society. (g), (h) Reproduced with permission [41]. John Wiley & Sons. © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
a porous metal-based nanostructure. They observed the improvement in thermal stability, but not in cathodic activity, at 300–500 °C [29].

Clear improvement in ORR activity is shown when an ALD oxide-ion conducting overlayer is applied. Chang et al demonstrated an ultra-thin ALD YSZ overcoating on a Pt cathode to stabilize its morphology under a prolonged operational condition. The thin ALD YSZ coating (5 nm) indeed not only preserved the overall Pt morphology, but also improved ORR. The improved ORR activity was ascribed to the formation of denser TPB due to the interconnected network of YSZ nanoparticles. The power density of a cell with a 5 nm thick YSZ coating on a Pt cathode was ~2.5 times higher than that of a cell without any coating [30]. Li et al demonstrated the Ag, which is thermally more unstable than Pt, cathode surface treatment by ALD YSZ nano-particulates in order to enhance the performance and stability of SOFCs. As a result, the maximum power density of a bare Ag cathode cell was 10.6 mW cm⁻² and Ag-7 cycles YSZ cell was 14.7 mW cm⁻² at 450 °C. EIS confirmed the enhanced performance was due to improved electrode kinetics, presumably the increase in TPB sites between the supporting Ag and the ALD YSZ particulates. Ag-ALD YSZ cathodes were thermally and chemically stable for a long period of time, 4 h in this test, while the bare silver cathodes degraded within 1 h [32]. Neoh et al applied ALD CeO₂ on a Ag cathode. The peak power density of the cell with a Ag cathode, with two cycles of ALD CeO₂ overlayer, was about 50% higher than that of a Pt-only cathode. The thermal stability improvement was also observed in the ALD CeO₂ overlayer [33].

(2) ALD oxide on perovskite electrodes

ALD oxides were also applied to the perovskite oxide cathodes, e.g., (La₅Sr₁₋ₓ)MnO₃ (LSM), (La₅Sr₁₋ₓ)CoO₂ (LSC), or (La₅Sr₁₋ₓ)(CoₓFe₁₋ₓ)O₃ (LSCF), of SOFCs. The sole use of the ALD perovskite cathode was first reported in 2007 by Holme et al. They fabricated an ALD LSM cathode by mixing LaO, SrO, and MnO₂ processes and tested it in the cell; nevertheless, its performance was very poor (~1 uW cm⁻² at 450 °C) [22].

ALD oxide overcoating, in many reports, has been shown to deactivate the perovskite cathode surfaces, leading to lower electrode performances. Kungas et al applied ALD Al₂O₃ on (La,Sr)FeOₓ (LSF) cathode surfaces, and examined the electrode performance depending on the O₂ partial pressure. As a result, after Al2O3 deposition, the electrode resistance increased from 0.8 ± 0.2 Ω cm² to 1.1, 2.5, 4.2, 6.0, 9.4, and 24.5 Ω cm² at 600 °C after 1, 2, 5, 10, 20, 50 cycles of ALD Al₂O₃, respectively. This can be explained by the fact that ALD Al₂O₃ limits the O₂ adsorption on the LSF surface [34]. Similarly, Kim et al applied ALD Al₂O₃ on a LSC cathode, in which the cell with an ALD Al₂O₃ overcoated LSC cathode showed lower performances with similar OCVs at 800 °C [37].

Gorte’s group systematically examined the effect of various ALD overcoating materials, e.g., ALD CeO₂/SrO/Al₂O₃/ZrO₂/La₂O₃/Fe₂O₃ on LSF-YSZ, LSC-YSZ, and (Ba,Sr)(Co,Fe)Ox (BSCF)-YSZ cathodes. ALD SrO and Al₂O₃ increase electrode resistance because they deactivate the cathode surface by forming an inert blocking layer. Moreover, ALD CeO₂ also increases electrode resistance because preferential interactions with oxygen vacancies on the electrode surface deactivate the ORR [38]. In addition, ALD ZrO₂ and Fe₂O₃ increase the activation resistance because of simple O₂ adsorption sites blocking, while ALD La₂O₃ (10 cycles) reduce activation resistance [43]. Choi et al examined the effect of the ALD CoOₓ overlayer on the LSC cathode, in which the maximum power density was found to decrease. The ALD CoOₓ overlayer was speculated to impede oxygen adsorption and dissociation reaction on the cathode surface [40]. In another study by Chen et al, the ALD CoOₓ overlayer interacted with the LSC/YSZ cathode and formed CoOₓ-MnO₂-xOₓ at the LSM grain surface, which created additional oxygen transport pathways and extended TPB length [42].

Meanwhile, other reports on the ALD overlayers for perovskite cathodes demonstrated the stabilization of electrodes by impeding the cathode surface segregation that can otherwise significantly degrade the electrode performance. The stabilization effect of perovskite cathodes by ALD ZrO₂ overcoating was clearly observed in a study by Gong et al (figure 5(e)). They showed that the ALD ZrO₂ overcoating on a LSC cathode can suppress agglomeration of nanoparticles, and retain oxygen reduction reaction (ORR) activity of the cathode (figure 5(f)). As a result, the cell with ZrO₂ overcoating shows 19 times better stability than a cell with a pristine cathode at 700 °C over 4000 h [35]. In another report, they also applied ALD ZrO₂ to a LSCF-GDC cathode. The multifunctionality of porosity, mixed ionic and electronic conductivity, and the inhibited Sr-enrichment enabled by the ALD ZrO₂ overlayer contributed to the retention of ORR activity of the LSCF-GDC cathode. As a result, the cell with an ALD ZrO₂ overlayer shows polarization and ohmic resistance 3 and 1.5 times lower than the cell without ALD ZrO₂ at 800 °C over 1100 h [39]. In a recent report by Choi et al. they, for the first time, deposited ALD LSC by mixing LaO₃, SrO, and CoOₓ processes on a LSCF cathode. (figure 5(g)) Impressively, the ALD LSC overlayer with the optimal thickness of 8 nm can enhance charge transfer kinetics at the surface of the cathode and also greatly improve the power density by 80%, which corroborated well with density functional theory (DFT) simulations (figure 5(h)) [41].
3.3.2. Anode

When hydrogen is used as a fuel for a SOFC, the hydrogen oxidation reaction (HOR) at the anode is even more active than the ORR at the cathode, so that the reaction loss at the anode is relatively small, or negligible. However, since the hydrocarbon oxidation reaction is much more complex than the hydrogen oxidation reaction, as discussed in section 2, the anode reaction of the SOFC using a hydrocarbon fuel, such as methane, methanol, or ethanol, significantly slows down. Additionally, carbon of the hydrocarbon fuel cause elemental carbon formation, or coking, at the anode surface, which causes a decrease in the catalytic reactivity and stability.

In case of hydrogen fueled SOFC, only a few studies on the application of ALD to anode have been reported. Jiang et al., for the first time, reported the application of an ALD Pt layer of 10–30 nm thickness as the sole anode. They reported that the 10 nm-thick ALD Pt anode was an optimal thickness due to its higher nanopore (5 nm in width) density leading to higher TPB density. Also, impressively, the ALD Pt anode with the optimal thickness of 10 nm showed similar power density as a 50 nm thick sputtered Pt anode [135]. Keuter et al. deposited a 100 nm-thick ALD ZrO2 layer on Ni-8 mol% YSZ anode for Ni oxidation resistance layer. The ALD ZrO2 layer protected the Ni against oxidation for 17 re-oxidation/re-reduction cycles [27].

Meanwhile, there are several reports on the application of ALD technique to the anodes of hydrocarbon fueled SOFCs. Jiang et al. applied the ALD co-deposited Pt-Ru (10 nm thick) catalyst to the anode for direct methanol oxidation at the cell level. ALD co-deposited Pt-Ru showed similar methanol oxidation catalytic reactivity as the sputtered Pt–Ru catalyst. Moreover, they demonstrated that the sub-nm ALD Pt skin layer (~0.5 nm thick) on a sputtered Ru anode, which has an extremely low Pt loading, can strongly enhance methanol oxidation, displaying superior catalytic activity over pure Pt [147]. Christensen et al. studied bimetallic Pt-Ru nanoparticles deposited by ALD (1.2 nm thick) on Al2O3 spheres, and measured methanol decomposition rate as a function of temperature. These nanoparticles showed different properties than the physical mixture of monometallic Pt and Ru catalysts. A bimetallic ALD Pt-Ru mixture showed better methanol decomposition rates than a monometallic Pt and Ru physical mixture [148]. Feng et al. deposited ALD Pd for methanol oxidation reaction, and investigated the effect of substrate and particle size on methanol oxidation. ALD Pd was deposited on Al2O3 and ZnO. ALD Pd nanoparticles of 1–2 nm in diameter were uniformly dispersed on both Al2O3 and ZnO substrates. Pd-AlOx catalysts showed exceptionally good methanol oxidation catalytic activity. On the other hand, Pd-ZnO catalysts showed limited catalytic activity and rapid catalytic degradation because of formation of the Pd-Zn bond. By the Pd-Zn bond, Pd was dissolved and eventually absorbed to the substrate. In a follow-up study from the same group, the effect of ALD Pd particle size was investigated, where small (<1 nm) and medium (1–2 nm) sized particles showed a higher (by a factor of 2) methanol decomposition rate than the large ones (>2 nm) [149, 150].

In recent papers reported by Jeong et al., the applicability of ALD Ru (<10 nm) on sputtered metal anodes (Pt and Ni) for improving methanol/ethanol oxidation reaction and carbon tolerance was investigated (figures 6(a), (c)). First, Pt anode with 4 nm-thick ALD Ru showed 10 times higher maximum power density than the Pt-only anode. In addition, carbon formation, which tends to form –CO or =CO bonds especially on Pt surfaces, had been reduced by the application of ALD Ru to sputtered Pt anodes. It can be explained by the superior ability of Ru to catalyze CO oxidation by dehydrogenation of water, and a subsequent release of CO2, decreasing carbon formation on a Pt anode surface (figure 6(b)) [151]. ALD Ru also reduced carbon formation on Ni surface of all carbon types such as C–C, C=O, and C=O (figure 6(d)) [152]. ALD Ru also encouraged ethanol oxidation with a more complex molecular structure than methanol. The power density of Pt with ALD Ru (2 nm) is ~6 times higher than that with only Pt anode. Additionally, ALD Ru suppressed carbon formation in an ethanol oxidation environment as well [153].

3.4. Quantitative comparison in performance enhancement

Table 2 summarizes the improvements in various performance metrics (ionic conductivity, exchange current density, OCV, ohmic/activation resistance, maximum power density (MPD)) depending on the components where the ALD technique is applied. We have also demonstrated a so-called enhancement factor that shows how much, in a quantitative manner, the performance has improved as compared to the cell without the ALD-processed component or with otherwise fabricated components (e.g., sputtering, PLD, etc.).

First, when the ALD oxide is employed as the electrolyte, the blocking effect of gas permeation as well as electronic conduction (when it is used with a doped CeO2 electrolyte) is clearly shown by high OCV [68], and therefore the use of much thinner electrolytes become possible [62] while the ionic conductivity is comparable to or slightly lower than that of the bulk counterpart (in YSZ case) [52, 57]; additionally, the high exchange current density due to the high surface GB density of ALD oxide leads to less activation loss, the combined effects of which improve the MPD of the thin-film SOFC by up to a few times [52, 61, 62, 68, 71, 74].

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When the ALD layers are used as cathodic interlayers, a few times enhancement in the exchange current density and activation resistance is clearly observed, and accordingly, the MPD increased by a factor of 1.6 (3 in previous reports [13, 15, 16, 47–49]). When applied to SOFC cathodes, ALD precious metal catalysts/electrodes of less than 10 nm thickness significantly improved the surface exchange by a factor of 2.7 and doubled the MPD [19]. Alternately, they demonstrated similar performances (alone [21] or in composite with less expensive/less catalytically active material (Ag) [23]) when they replaced a much thicker precious metal electrode, e.g., a 80 nm-thick sputtered Pt. In cases of ALD oxide overlayers on metallic cathodes, the improvement in a cathodic activation process is significant as an order of 1–4 [26, 28], which improves the MPD as well. Notably, they also enhance the thermal stability or impede the thermal degradation by a few times [28, 32] or even up to a couple of orders [26]. ALD oxide overlayers such as CoOx or LSC on perovskite cathodes also help to reduce the activation resistance (by a factor of 1.3–2.2), and enhance the MPD (by a factor of 1.6–1.8) [41, 42]. ALD precious metal overlayers (Ru) on SOFC anodes operating directly with alcohol fuels not only improve the activation process and enhance the MPD, but also significantly stabilize the anode, which seems to be partly due to better coking resistance [151–153].

4. Summary and outlook

In this paper, recent results on the application of nanostructures fabricated by the ALD technique for SOFCs have been reviewed. In particular, important interfaces of SOFCs that are closely relevant to their performance were discerned, and the contribution of nanostructures to reduce operation losses have been discussed. Unique features of the ALD-processed nanostructures, such as ultra-low thickness, dense and pinhole-free morphology, conformality, or nanocrystallinity (i.e., high grain-boundary density), are effective in minimizing the losses and improving the overall performance of SOFCs.

It should be noted that there is still room for further research on the application of ALD to SOFCs for designing novel nano-materials or structures. Less explored but interesting features of the ALD process, e.g., doping controllability, crystallinity control, etc., may present possibilities to accurately tune the properties of ALD films such as conductivity, catalytic activity, or chemical/mechanical stability. Furthermore, the development of new ALD processes that can enable novel combinations of various base materials is being explored, most of which is attributed to novel precursor development. Cost and productivity, which are the
| SOFC component | Cell structure and operating temperature | Performance Metric | Reference cell | ALD-engined cell | Enhancement factor | References |
|----------------|----------------------------------------|--------------------|----------------|------------------|-------------------|------------|
| Electrolyte   | Oxide-ion conducting                    | Ionic conductivity (S cm\(^{-1}\)) | 4.7 × 10\(^{-6}\) (bulk YSZ electrolyte) | 4.52 × 10\(^{-6}\) (ALD YSZ electrolyte) | ~10\(^{-1}\) | [51]      |
|               | Pt cathode/sputtered (50 nm) or ALD YSZ (~60 nm)/Pt anode at 350 °C | Ionic conductivity (S cm\(^{-1}\)) | ~ (bulk YSZ) | ~ (ALD YSZ) | ~1 | [52]      |
|               | Pt cathode/PLD YDC (10 nm)/ALD YSZ (50 nm)/Pt anode | Exchange current density (A cm\(^{-2}\)) | ~10\(^{-4}\) (sputtered YSZ electrolyte) | ~10\(^{-5}\) (ALD YSZ electrolyte) | ~10\(^{3}\) |           |
|               | Pt cathode (250 nm)/sputtered YSZ (220 nm) + ALD YSZ (30 nm) + sputtered GDC (110 nm) electrolyte/Pt anode (330 nm) at 500 °C | Ionic conductivity (S cm\(^{-1}\)) | 140 (sputtered YSZ electrolyte) | 270 (ALD YSZ electrolyte) | ~1.9 | [57]      |
|               | Pt cathode (80 nm)/sputtered (500 nm) or ALD YSZ electrolyte (180 nm)/Pt anode (80 nm) at 450 °C | Ionic conductivity (S cm\(^{-1}\)) | 146 (without ALD YSZ) | 172 (with ALD YSZ) | ~1.18 | [61]      |
|               | Pt cathode (80 nm)/sputtered SDC (180 nm) + ALD YSZ (25 nm) + sputtered SDC (180 nm) electrolyte/Pt anode (300 nm) at 450 °C | MPD (mW cm\(^{-2}\)) | 70 (sputtered YSZ electrolyte) | 380 (ALD YSZ electrolyte) | ~5.43 | [62]      |
|               | Pt cathode (230 nm)/sputtered YSZ (100 nm) + PEALD YSZ (120 nm) + sputtered GDC (100 nm) electrolyte/Pt anode (300 nm) at 500 °C | Activation resistance (Ω cm\(^{-2}\)) | 3.12 (without ALD YSZ) | 0.2 (with ALD YSZ) | ~15 |           |
|               | Pt cathode (80 nm)/sputtered YDC (100 nm) electrolyte/sputtered (150 nm) or PEALD YSZ (150 nm) interlayer/Pt anode (80 nm) at 450 °C | MPD (mW cm\(^{-2}\)) | 80 (without ALD YSZ) | 562 (with ALD YSZ) | ~7 |           |
|               | Pt cathode (80 nm)/PLD BYZ (110 nm) electrolyte/Pt anode (80 nm) at 400 °C | MPD (mW cm\(^{-2}\)) | 124 (without PEALD YSZ) | 214 (with PEALD YSZ) | ~1.7 | [71]      |
| Proton        |                                        | MPD (mW cm\(^{-2}\)) | 0.45 (sputtered YSZ) | 0.28 (PEALD YSZ) | ~1.6 | [70]      |
| Conducting    |                                        | Activation resistance (Ω cm\(^{-2}\)) | 0.28 (PEALD YSZ) | ~2.6 | [74]      |
| Interlayer    | Cathodic                               | Exchange current density (A cm\(^{-2}\)) | ~ (PLD BYZ) | ~ (ALD BYZ) | ~3–10 |           |
|               | Pt cathode (80 nm)/ALD YSZ (20 nm) interlayer/Bulk YSZ (300 μm)/Pt anode (80 nm) at 450 °C | MPD (mW cm\(^{-2}\)) | 49 (PLD BYZ) | 136 (ALD BYZ) | ~2.8 |           |
|               | Pt cathode/ALD YDC interlayer (15–18 nm)/bulk YSZ electrolyte (200 μm)/Pt anode at 350 °C | Activation resistance (Ω cm\(^{-2}\)) | ~ (with ALD YSZ) | ~3 | [13]      |
|               |                                        | MPD (mW cm\(^{-2}\)) | ~0.3 (without ALD YSZ) | ~0.6 (with ALD YSZ) | ~2 |           |
|               |                                        | MPD (mW cm\(^{-2}\)) | 0.325 (without ALD YDC) | ~1 (with ALD YDC) | ~3 | [48]      |
| SOFC component | Cell structure and operating temperature | Performance Metric | Reference cell | ALD-engineered cell | Enhancement factor | References |
|----------------|-----------------------------------------|-------------------|---------------|---------------------|-------------------|------------|
| Pt cathode (80 nm)/ALD YDC (6–7 nm) interlayer/ALD YSZ (100 nm) electrolyte/Pt anode (80 nm) at 450 °C | | MPD (mW cm⁻²) | 530 (without ALD YDC) | 710 (with ALD YDC) | ~1.3 | [49] |
| Pt cathode (80 nm)/ALD CeO₂ (~23 nm) interlayer/bulk YSZ (300 μm) electrolyte/Pt anode (80 nm) at 450 °C | | Exchange current density (mA cm⁻²) | 0.21 (without ALD CeO₂) | 0.37 (with ALD CeO₂) | ~1.8 | [15] |
| | | MPD (mW cm⁻²) | 2.66 (without ALD CeO₂) | 3.85 (with ALD CeO₂) | ~1.5 | |
| | | Stability | ~4%/hour (without ALD CeO₂) | ~1%/hour (with ALD CeO₂) | ~4 | |
| Pt cathode (80 nm)/ALD ZDC (~20 nm) interlayer/bulk YSZ (300 μm) electrolyte/Pt anode (80 nm) at 450 °C | | Activation resistance (Ω cm²) | 43 (without ALD ZDC) | 13 (with ALD ZDC) | ~3.3 | [16] |
| Pt cathode (150 nm)/ALD YSZ (~150 nm) interlayer/sputtered YSZ (~300 nm) electrolyte/Pt anode (300 nm) at 450 °C | | MPD (mW cm⁻²) | 3.0 (without ALD ZDC) | 4.7 (with ALD ZDC) | ~1.6 | |
| | | MPD (mW cm⁻²) | 66.2 (without ALD YSZ) | 139.1 (with ALD YSZ) | ~2.1 | [47] |
| Pt cathode (80 nm)/ALD YSZ-Pt (2 nm) + ALD YSZ (7 nm) interlayer/bulk YSZ (~300 μm) electrolyte/Pt anode (80 nm) at 450 °C | | Activation resistance (Ω cm²) | 2500 (without ALD YSZ-Pt) | 1500 (with ALD YSZ-Pt) | ~1.7 | [18] |
| Electrode | Cathode | ALD of precious metal | Pt cathode (80 nm)YSZ (100 nm) electrolyte/sputtered (10 nm) or ALD Pt (5–30 nm) anode at 350 °C | | | |
| Pt cathode (80 nm)/ALD Pt (~5 nm) layer/bulk YSZ (200 μm) electrolyte/Pt anode (80 nm) at 400 °C | | Exchange current density (mA cm⁻²) | 0.13 (without ALD Pt) | 0.35 (with ALD Pt) | ~2.7 | [19] |
| Sputtered (80 nm) or ALD Pt (~10 nm) cathode/bulk YSZ (300 μm) electrolyte/Pt anode (80 nm) at 450 °C | | | 1 (without ALD Pt) | 1.9 (with ALD Pt) | 2 | |
| Pt, Ag, Pd, Ru (80 nm) + ALD Pt (~3 nm) cathode/bulk YSZ (200 μm) electrolyte/Pt anode (80 nm) at 450 °C | | MPD (mW cm⁻²) | 3.3 (sputtered Pt 80 nm) | 3.4 (ALD Pt ~10 nm) | ~1 | [21] |
| Pt cathode (100 nm)/ALD ZrO₂ (1.6 nm) overlayer/bulk YSZ electrolyte/Pt anode at 450 °C | | Activation resistance (Ω cm²) | 50.3 (without ALD ZrO₂) | 5.3 (with ALD ZrO₂) | ~10 | [28] |
| ALD oxide on metallic cathode | | MPD (mW cm⁻²) | ~2 (without ALD ZrO₂) | ~2.5 (with ALD ZrO₂) | ~1.3 | |
| | | Thermal stability (performance degradation rate (%/hour)) | 1.4%/hour (without ALD ZrO₂) | 0.4%/hour (with ALD ZrO₂) | ~3 | |
| SOFC component | Cell structure and operating temperature | Performance Metric | Reference cell | ALD-engineered cell | Enhancement factor | References |
|----------------|-----------------------------------------|-------------------|---------------|---------------------|-------------------|------------|
| Pt cathode (200 nm) / ALD YSZ (~5 nm) overlayer / ALD YSZ (120 nm) + sputtered GDC (300 nm) + ALD YSZ (120 nm) electrolyte / Pt anode (300 nm) at 500 °C | MPD (mW cm⁻²) | 120 (without ALD YSZ) | 265 (with ALD YSZ) | ~2.2 | [30] |
| Ag cathode (150 nm) / ALD YSZ (~7 nm) overlayer / bulk GDC electrolyte (350 μm) / Pt anode (150 nm) at 450 °C | MPD (mW cm⁻²) | 10.6 (without ALD YSZ) | 14.7 (with ALD YSZ) | ~1.4 | [32] |
| Ag cathode (50 nm) / ALD CeO₂ (5 cycles) overlayer / bulk GDC electrolyte (350 μm) / Pt anode (150 nm) at 450 °C | MPD (mW cm⁻²) | ~0.1 (without ALD CeO₂) | 8.89 (with ALD CeO₂) | ~90 | [33] |
| Pt cathode (100 nm) / ALD YSZ (~3 nm) overlayer / bulk YSZ (~270 μm) electrolyte / Pt anode (100 nm) at 600 °C | Activation resistance (Ω cm⁻²) | ~10⁷ (without ALD YSZ) | ~10⁵ (with ALD YSZ) | ~10 | [26] |
| ALD oxide on perovskite cathode | LSC-GDC (~30 μm) cathode / ALD Al₂O₃ (0.6–2.4 m) overlayer screen-printing GDC (~10 μm) + screen-printing (AL,Sc doped ZrO₂ (~15 μm) / NiO-YSZ (~11 μm) anode at 800 °C | MPD (mW cm⁻²) | 1619 (without ALD Al₂O₃) | 1507 (with ALD Al₂O₃) | ~1 | [37] |
| LSCF cathode / ALD LSC (8 nm) layer PLD GDC + powder processed YSZ electrolyte / Ni-YSZ anode at 600 °C | Activation resistance (Ω cm⁻²) | 3.28 (without ALD LSC) | 1.48 (with ALD LSC) | ~2.2 | [41] |

MPD (mW cm⁻²)
| SOFC component | Cell structure and operating temperature | Performance Metric | Reference cell | ALD-engineered cell | Enhancement factor | References |
|----------------|------------------------------------------|--------------------|----------------|---------------------|-------------------|------------|
|                | LSM-YSZ (~15 μm) cathode/ALD CoOₓ (10 nm) overlayer/YSZ (~12 μm) electrolyte/Ni-YSZ (~15 μm) anode at 730 °C | Activation resistance (Ω cm²) | 0.641 (without ALD CoOₓ) | 0.492 (with ALD CoOₓ) | ~1.3 | [42] |
| Anode (hydro-carbon fuel) | Pt cathode (150 nm)/bulk GDC electrolyte (350 μm)/Pt anode (150 nm)/ALD Ru (4 nm) overlayer at 400 °C | MPD (mW cm⁻²) | 298 (without ALD CoOₓ) | 480 (with ALD CoOₓ) | ~1.6 | ~100 | [151] |
|                |                                            | Activation resistance (Ω cm²) | ~0.5 (without ALD Ru) | ~4.5 (with ALD Ru) | ~10 | ~10² | |
|                |                                            | Stability (performance degradation rate) | ~0.1 (without ALD Ru) | ~0.5 (with ALD Ru) | ~5 | ~2 | [153] |
|                |                                            | Exchange current density (mA cm⁻²) | 0.001 (without ALD Ru) | 0.073 (with ALD Ru) | ~70 | ~152 | |
|                |                                            | MPD (mW cm⁻²) | ~5 (without ALD Ru) | ~25 (with ALD Ru) | ~2 | ~3 | [155] |
|                |                                            | Activation resistance (Ω cm²) | ~3 (without ALD Ru) | ~13 (with ALD Ru) | ~4 | ~3 | |
|                |                                            | Stability (Polarization resistance increase rate (%/hr)) | ~5%/hr (without ALD Ru) | ~2%/hr (with ALD Ru) | ~2.5 | ~2.5 | |
most critical factors for widespread use of ALD processes in this field, must also be considered. The compatibility of ALD process with conventional bulk processes, including sintering, screen printing, etc., also requires addressing. Additionally, a successful industrial-level ALD system is required for applying ALD to SOFC fabrication with reasonable cost-effectiveness. Recently, various ALD strategies, such as batch ALD, roll-to-roll ALD, spatial ALD, and atmospheric pressure ALD, are being actively researched to improve throughput while retaining unique advantages of ALD process [86, 154]. Only after such considerations, investigations on the applicability of ALD to SOFCs could have useful practical consequences, advancing beyond the laboratory scale to the prototyping level.

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ORCID iDs

Jihwan An © https://orcid.org/0000-0002-7697-9935

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