Plasma-Enhanced Atomic Layer Deposition of Zirconium Oxide Thin Films and Its Application to Solid Oxide Fuel Cells

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Abstract: Zirconium oxides were deposited using plasma-enhanced atomic layer deposition (PEALD) involving (2-(N-methylamino)1-MethylEthyleneCyclopentadienyl)Bis(DiMethylAmino)Zr (abbreviated as CMEN-Zr) and oxygen plasma as zirconium and oxygen sources. The zirconium oxide thin films demonstrate temperature-independent growth rates per cycle of 0.94 Å/cycle at 150–215 °C. The deposited ZrO₂ thin films were characterized using numerous analytical tools, i.e., X-ray photoelectron spectroscopy for chemical bonding state and composition, X-ray diffraction for crystallinity, atomic force microscopy for surface morphology, field-emission scanning electron microscopy for cross-sectional analysis, spectroscopic ellipsometry and UV–visible spectrophotometry for optical characterization, capacitance–voltage measurements for dielectric constants and atomic defects, and current–voltage characteristics for electrical information. The insulating features of the crystalline and stoichiometric ZrO₂ films were implemented in the anode composites to evaluate the influence of ALD-based nano-features on the electrochemical performance of solid oxide fuel cells, with the main emphasis on anode performance. The presence of nanomaterials on Ni/YSZ anode composites is analyzed to determine the negative effects on electrochemical performance and the degradation of cell performance of solid oxide fuel cells (SOFCs). The artificial design was proven to be effective in controlling the cell performance as long as proper material design was adopted in SOFC electrodes.

Keywords: PEALD; CMEN-Zr; surface chemistry; solid oxide fuel cells

1. Introduction

The advent of the hydrogen economy in association with the fourth industrial revolution has ignited extensive research into solid oxide fuel cells (SOFCs) due to their academic and industrial applications. SOFCs have become one of the powerful next generation energy resources due to their unique advantages such as high operation efficiency, contamination-free fuel flexibility, and minimized pollution [1–4]. SOFCs are typically constructed using a multitude of dissimilar materials with a variety of physical and chemical properties, including cathodes, electrolytes, and anodes, in addition to subsidiary sealing and interconnect materials. To maintain the highly efficient operation of SOFCs at intermediate temperatures ranging from 650 and 800 °C, electrodes should be improved dramatically by minimizing polarization loss and improving ionic conductivity. There have been a few attempts involving artificial controls on triple phase boundary reactions based on the charge transfer between electronic/ionic carries and fuels, depending largely on the microstructure of electrodes and interfacial geometries adjacent to the ionic electrolyte [5–7].

Atomic layer deposition (ALD) has been established as a unique thin film deposition technique originating from chemisorption between the reactants and underlying substrates. Starting with the pioneering report by Suntola [8], self-limiting atomic layer deposition
has been extended through low-temperature deposition, atomic scale thickness control, excellent step coverage characteristics of conformal coating, and conformal deposition of the materials under interest, all without limiting the electronic applications, including dynamic random access memory (DRAM), non-volatile random access memory, and metal-oxide-semiconductor field effect transistors (MOSFETs) [9–12]. Recently, ALD has been applied to non-electronic applications such as sensors, solar cells, water-splitting catalysts and materials, secondary batteries, and fuel cells due to its ability to deposit mainly metal and oxide materials to three-dimensional complex material structures [13–17]. In particular, ALD has been adapted to three-dimensional interconnected microstructures by adding the ALD-based penetration capability, unlike the conventional ceramic processing techniques. The conformal features of atomic layer deposition can be employed to control oxide-based cathodes and anodes of solid oxide fuel cells in terms of performance improvement or performance degradation. In order to verify the applicability of atomic layer deposition in the electrochemical performance in SOFCs, the current work chose metal oxide materials with a special emphasis on the degradation in SOFC cell performance. The roles of atomic layer deposition in SOFCs are discussed along with the processing designs with the aim of achieving optimized SOFC performance and stability.

To demonstrate the application of ALD-assisted surface modification concept, 2-(N-methylamino)1-MethylEthyleneCyclopentadienyl)Bis(Dimethylamino)Zr (abbreviated as CMEN-Zr) was combined with oxygen plasma to deposit ZrO₂ materials onto the Ni/YSZ anode composites of SOFCs. The current work focuses on the atomic layer deposition of ZrO₂ thin films involving a newly developed Zr precursor and its application to anode composites of SOFC materials, with the aim of controlling artificial cell performance by modifying the reactive sites present in porous electrodes. In addition, the potential of the atomic layer deposition of materials into solid oxide fuel cells is discussed in terms of the reliability and stability issues encountered in SOFCs.

2. Experimental

Zirconium oxide thin films were deposited using plasma-enhanced atomic layer deposition (PEALD) that employed CMEN-Zr (Hansol Chemical Co., Ltd., Seoul, Korea) as a zirconium precursor with oxygen plasma as an oxygen source. A PEALD system’s flow of reactants and products, controlled in shower head mode, was utilized. One basic PEALD cycle was performed based on the following sequence: (CMEN-Zr supply)–(Ar purge)–(O₂ plasma supply)–(Ar purge). The CMEN-Zr precursor was held at 70 °C to guarantee sufficient reactant molecules in the ALD reaction chamber, and the connecting lines were maintained at 110 °C. The oxygen source was supplied using oxygen plasma at a power of 100 W and frequency of 13.56 MHz. The substrate temperature varied between 90 °C and 215 °C for zirconium oxide thin films, and the total chamber pressure was controlled to 0.53 Torr. The Zr precursor was preheated to 70 °C and the line was maintained at 110 °C. The Si wafers were cleaned in the order of acetone (CH₃COCH₃ 99.5%, OCI Company, Seoul, Korea), methanol (CH₃OH 99.9%, OCI Company, Seoul, Korea), methanol (CH₃OH 99.9%, OCI Company, Seoul, Korea), and deionized water. Subsequently, the native oxide was removed using dilute hydrofluoric acid (HF: 48–51%, J.T. Baker, NJ, USA).

The chemical states of elements, compositions, and trace element amounts in the films were analyzed after the 34 s Ar bombardment sputtering using X-ray photoelectron spectroscopy (XPS, K-alpha model, Thermo Fisher Scientific, Waltham, MA, USA). X-ray diffraction (XRD) measurements were performed using a high-sensitivity diffractometer (D-2000, Rigaku, Tokyo, Japan). Surface morphologies were obtained using an atomic force microscope (AFM, XE150, PSIA, Suwon, Gyeonggi-do, Korea). Ultraviolet–visible spectrometers (UV-2450, Shimadzu, Kyoto, Japan) were employed to measure the transmission. Capacitance–voltage measurements (HP 4192A low-frequency impedance analyzer, Hewlett-Packard, Palo Alto, CA, USA) and dc-based current–voltage characteristics (4155C semiconductor parameter analyzer, Agilent, Santa Clara, CA, USA) were made to obtain the electrical/dielectric parameters of insulating zirconium oxide thin films, respectively.
The microstructure of the films was analyzed using high-resolution field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Tokyo, Japan). The optical thicknesses were measured using high-precision spectroscopic ellipsometers (UVISEL AGAX ER, HORIBA, Kyoto, Japan and MG-1000-UV, Nano-view, Ansan, Gyeonggi-do, Korea).

This work employed commercial SOFC cells (Kceracell Co., Ltd., Boksu-myeon, Korea) in order to understand the role of ALD-based ZrO\textsubscript{2} in the electrochemical performance. As shown in the schematic diagram of Figure 1, composite materials consisting of nickel oxide (NiO) and 3 mol\% yttria-stabilized zirconia (3YSZ) were used as anode layer materials with a thickness of 800–850 \(\mu\)m. Subsequently, the anode functional layer made up of NiO and (Yb\textsubscript{2}O\textsubscript{3})\textsubscript{0.06}(Sc\textsubscript{2}O\textsubscript{3})\textsubscript{0.04}(Zr\textsubscript{2}O\textsubscript{2})\textsubscript{0.9}(6Yb4ScSZ, 10–15 \(\mu\)m) and the electrolyte layer (6Yb4ScSZ, 10–15 \(\mu\)m) were coated using the screen-printing method and then laminated and co-sintered. On the electrolyte layer, a buffer layer (2–5 \(\mu\)m) was coated that consisted of Gd-Yb-Bi-Ce-O (GYBC), and heat treatment was performed. Afterward, a lanthanum strontium cobalt ferrite (LSCF)-Gd doped ceria (GDC) layer (5–10 \(\mu\)m) and LSCF layer (20–25 \(\mu\)m) were coated as a cathode functional layer and cathode layer, respectively. After heat-treatment, a low-temperature sintered cathode current collection (LTCCC) layer was coated (the detailed information on LTCCC is not available to the customers). The unit cell performance was quantified using a button cell with a size of 2 cm \(\times\) 2 cm. The fabricated SOFC cells were placed between platinum mesh and nickel foam materials as charge-collecting metals for cathode and anode composites. The whole cell assembly was heated to 800 °C, and a pressure of 15 kgf was applied to the SOFC assembly to guarantee perfect sealing between the SOFC cathode and anode compartments. At 800 °C, the mixture of N\textsubscript{2} and H\textsubscript{2} was controlled to the total flow rate of 200 sccm, and in order to reduce the NiO/YSZ anode composites to Ni/YSZ composites, which were initially 200 sccm N\textsubscript{2}, by progressively increasing the flow rate of H\textsubscript{2} and decreasing the flow rate of N\textsubscript{2} under the total flow rate of 200 sccm, and finally, they were 0 sccm N\textsubscript{2} and 200 sccm H\textsubscript{2}. After complete reduction, the air and hydrogen were supplied to both cathode and anode. On the reduced Ni/YSZ anode (the thickness of which was approximately 850 \(\mu\)m), ZrO\textsubscript{2} was deposited by PEALD with twice the pulse time and Ar purge time (CMEN-Zr (from 2.5 s to 5 s), O\textsubscript{2} plasma (from 9 s to 18 s), and Ar purge (from 60 s to 120 s)) because the reactants (i.e., zirconium and oxygen sources) needed to penetrate the porous reduced Ni/YSZ anode and the byproducts needed to be removed from the pore network. The deposition temperature was 150 °C, which is within the ALD window, and the deposition cycle was 200 cycles. Open cell voltages, current–voltage and impedance spectroscopy characteristics were measured to determine the electric characteristics in the temperature range of 650–800 °C using 4-point measurements (biologic electrochemical system).

**Figure 1.** Schematic description of solid oxide fuel cells employed in the application of atomic layer deposition to energy-based devices.

3. **Results and Discussion**

Initially, Zr-based halogen compounds were studied, such as ZrI\textsubscript{4} and ZrCl\textsubscript{4} [18,19]. However, strong corrosive byproducts such as HCl and HI unintentionally damaged the ZrO\textsubscript{2} thin films deposited. To solve the issue, alkoxide and alkylamide-based Zr pre-
cursors were developed, i.e., ZTB (Zirconium Tert-Butoxide; Zr[OC(CH3)3]4), TDMA-Zr (Tetrakis(DiMethylAmido)Zirconium (Zr[(CH3)2N]4), and TEMA-Zr (Tetrakis(EthylMethyl- Amido)Zirconium; Zr[N(CH3)2(C2H5)2]) [20–22]. The former alkoxide-based ZrO2 should be accompanied through the breakage of strong Zr-O, leading to a slower growth rate. Instead, alkylamide-based ZrO2 involved the weaker bond mediated between Zr and N, leading to a faster growth rate. However, alkyl-amide-based ZrO2 suffered from thermal instability. After improvement in thermal stability at relatively high temperatures, the cyclopentadienyl ring was attached to its preceding alkylamide-based precursor, producing alkylamido-cyclopentadiene compounds such as ZAC((Cyclopentadienyl)tris(dimethylAmino) Zirconium and CpZr[N(CH3)2]3) [23]. Continuously, CPNZr and CMEN-Zr were synthesized with the aim of increasing the corresponding thermal stability and crystallinity [24].

The current work employed a Zr-containing organometallic compound [2-(N-methy lamino)1-MethylEthyleneCyclopentadienyl]Bis(DiMethylAmino)Zr, which is an Alkylamido-cyclopentadiene compound, abbreviated as CMEN-Zr (η5:η1-CpCH(CH3)CH2NMe]Zr-(NMe2)2), where C is the Cp (cyclopentadienyl ring), M is the methyl group (-CH3), E is the ethylene bridge (-C2H2-), and N is the N-methylamino group (-NHCH3). The detailed molecular structure is demonstrated in Figure 2.

![Molecular structure of CMEN-Zr](image)

**Figure 2.** Molecular structure of CMEN-Zr employed in the plasma-enhanced atomic layer deposition of zirconium oxide thin films.

The pulse-time dependences for the CMEN-Zr precursor and oxygen plasma were performed at 150 °C, as shown in Figure 3a,b. The saturation conditions were 2.5 s and 9 s for CMEN-Zr precursor and oxygen plasma, respectively. The cycle dependence was investigated at 150 °C, taking into account the saturation states of CMEN-Zr and oxygen plasma sources, as shown in Figure 3c. The linear dependence of the deposited thickness on ALD cycle numbers allows empirical determination of the growth per cycle, 0.94 Å/Cycle. Finally, the pre-determined conditions of CMEN-Zr and oxygen plasma sources were monitored as a function of temperature, as shown in Figure 3d. The ALD windows were found to exist from 140 °C to 215 °C. Furthermore, there was a possibility of higher temperatures as an upper bound for the surface limiting ALD windows.

The chemical states and compositions of the CMEN-Zr-based ZrO2 were investigated using XPS analysis, which Figure 4a shows in the survey spectrum along with the core spectra of Zr 3d and O 1s displayed in Figure 4b,c. As shown in Figure 4b,c, the Zr 3d and O 1s peaks were found to be 182.8 and 530.7 eV, respectively, and their positions are in reasonable agreement with the reported literature [25–27]. From the XPS quantification of the Zr 3d and O 1s peaks, the Zr and O compositions were determined to be 36.02 and 59.61 atom percentiles, leading to an approximate stoichiometric ratio of one to two for the Zr versus O elements. No zirconium oxide thin films included significant amounts of carbon or nitrogen contamination, i.e., the contents were below the detection limit of XPS.
Figure 3. Empirical condition for atomic layer deposition involving CMEN-Zr and oxygen plasma for zirconium and oxygen sources, respectively. (a) Deposition temperature: 150 °C, O2 plasma pulse time: 12 s, (b) deposition temperature: 150 °C, CMEN-Zr pulse time: 4.5 s, (c) cycle dependence of CMEN-Zr-based ZrO2 deposition (CMEN-Zr pulse time: 2.5 s, O2 plasma pulse time: 9 s) and (d) temperature dependence of ALD deposition (temperature: 150 °C, O2 CMEN-Zr pulse time: 2.5 s, plasma pulse time: 9 s).

Figure 4. X-ray photoelectron spectrometry of ALD-based ZrO2 thin films: (a) survey spectrum, (b) core spectrum of Zr 3d, (c) core spectrum of O 1 s. Sample information: deposition temperature: 150 °C, CMEN-Zr pulse time: 2.5 s, O2 plasma pulse time: 9 s, substrate: P-type silicon.

X-ray diffraction was performed to evaluate the crystallinity of ZrO2-based thin films. As shown in Figure 5, the empirical X-ray diffraction information was compared in terms of the reported crystal structures, e.g., monoclinic and tetragonal structures whose JCDPS peaks were found in JCPDS No. 98-065-8755 and 98-065-5671, respectively.
The tetragonal peaks were indexed as (011), (110), (112), and (121), while the (11-1) peak of the monoclinic structure was located at 2θ = 28.182°. The current CMEN-Zr-based ZrO₂ thin films were present according to the characteristic of the structural composites composed of two different crystalline structures. The mixture of monoclinic and tetragonal ZrO₂ materials have mainly been reported at the semiconductor/dielectric interfaces, although a monoclinic structure was detected in the structural analyses [19,28,29].

The cross-sectional electron micrographs are shown in Figure 6a along with the crystalline features, indicating the non-flat features of the top thin film surface. From the AFM analysis results of Figure 7, the mixed crystalline phases seemed to produce a larger RMS compared to the Si bare specimen, where the ZrO₂ thin films and bare Si exhibited 0.27 nm and 0.113 nm, respectively. Taking into account the deposited thickness (of approximately 32.3 nm), the normalized RMS was less than 1%, which was superior to the preceding ZrO₂ results and could be considered as smooth in a relative manner, despite the X-ray diffraction analysis characteristic of the existence of crystalline phases. The surface roughnesses have been reported to range from 3.5% to 5.7% after the normalization based on the thickness of the ZrO₂ thin films under test, except for less than 1% in the ZrO₂ deposited using Zr amide precursors [21,23,24,30–32]. The current ZrO₂ thin films demonstrated a highly smooth surface morphology characteristic of the superior RMS value (which is equivalent to less than 1% in terms of ratios normalized based on thickness).

The optical UV–visible transmission was monitored to confirm the transparent features of the ALD-based ZrO₂ thin films between 300 and 800 nm and included the ultraviolet and visible light regimes. The optical transmittance increased monotonically with increasing photonic wavelength. The lowest transmittance of 76.6% was measured at a wavelength of 300 nm, and the highest transmittance of 95.5% was measured at 800 nm (see Figure 8). As shown in Figure 9, the as-deposited ZrO₂ thin films exhibited an order of 10⁻⁶ A/cm². However, the annealed ZrO₂ thin films showed an improved leakage current density of approximately 10⁻⁷ A/cm².
Figure 6. Cross-sectional electron microscopy analysis of (a) CMEN-Zr-based ZrO₂ thin films and (b) bare Si substrates. Deposition temperature: 150 °C, CMEN-Zr pulse time: 2.5 s, O₂ plasma pulse time: 9 s, PEALD cycle: 350 cycles (~30 nm), substrate: P-type silicon.

Figure 7. Atomic force microscopy analysis of CMEN-Zr-based ZrO₂ thin films. (a,b) ALD-deposited ZrO₂ thin films (deposition temperature: 150 °C, CMEN-Zr pulse time: 2.5 s, O₂ plasma pulse time: 9 s, PEALD cycle: 300 cycles (~27 nm)), (c,d) Si substrate: P-type silicon.

Figure 8. UV–visible spectrophotometric analysis of ALD-deposited ZrO₂ thin films (deposition temperature: 150 °C, CMEN-Zr pulse time: 2.5 s, O₂ plasma pulse time: 9 s, PEALD cycle: 350 cycles (~30 nm), substrate: borosilicate glass).
The improved electrical performance is attributed to the improvement in crystallinity, which is dependent on the thermal annealing and interfacial traps. The breakdown voltage was measured to approximately 4 MV/cm. The dielectric information was extracted from capacitance–voltage measurements on the as-deposited films and annealed at 500 °C and 600 °C, as shown in Figure 10. The dielectric constant of ZrO\textsubscript{2} thin films was calculated to be from 22.9 and 25.2. These empirical dielectric constants are in agreement with prior reports, even though they exhibited a higher constant than has been previously reported.

Furthermore, the flat band voltage hysteresis decreased from 5.6 V for the as-deposited ZrO\textsubscript{2} and 1.9 and 2.0 V for the annealed ZrO\textsubscript{2} thin films at 500 and 600 °C, respectively. Based on the capacitance–voltage measurement and current–voltage characteristics, the electrical and dielectric information can be extracted. Table 1 compares the electric and dielectric characteristics obtained from ALD-based ZrO\textsubscript{2} thin films. The current ZrO\textsubscript{2} thin films demonstrate that the CMENZr-based ZrO\textsubscript{2} thin films are classified as high-k dielectric materials featuring low leakage current density and high breakdown electric fields despite relatively large flat band voltage hysteresis compared to those of the ZrO\textsubscript{2} thin films reported previously [18,19,21,30–32].

**Figure 9.** Current–voltage characteristics of ALD-based ZrO\textsubscript{2} using CMEN-Zr and oxygen plasma as zirconium and oxygen sources, respectively: as-deposited, annealed at 500 °C, and annealed at 600 °C.

**Figure 10.** Capacitance–voltage measurements of ALD-based ZrO\textsubscript{2} using CMEN-Zr and oxygen plasma as zirconium and oxygen sources, respectively: (a) as-deposited, (b) annealed at 500 °C and (c) annealed at 600 °C.
Table 1. Summarized electrical and dielectric characteristics obtained from the current ZrO$_2$ and reported ZrO$_2$ thin films.

| ALD type  | ZrI$_4$ | ZTB     | Zr(MEA)$_2$ (guan-MEA)$_2$ | Cp$_2$Zr(CH$_3$)$_2$ | Zr-AMD | ZAC  | CMEN-Zr |
|-----------|---------|---------|-----------------------------|----------------------|--------|------|---------|
| Substrate | P-type Si | -       | (100) Si                    | (100) Si             | P-type Si | (100) Si | P-type Si |
| Thickness [nm] | 42       | 7       | 6–11                        | 3.3–19               | 4.3     | 5.9–6.5 | 31.2–33.1 |
| Annealing Condition | -       | 250 °C, Air (1 h) | -                           | -                    | 450 °C, N$_2$ + H$_2$ (30 min) | - | 600 °C, N$_2$ (2 h) |
| Leakage Current Density [A/cm$^2$] | ~107–108 (at 1 MV/cm) | 2 × 10$^{-1}$ (at –1.5 V) | 8 × 10$^{-3}$ (at 1 V) | 10$^{-6}$ (at 1 MV/cm) | 2 × 10$^{-3}$ (at –1 V) | 10$^{-7}$ (at 1 V) | 7.8 × 10$^{-8}$ (at –1 MV/cm) |
| Breakdown Electric Field [MV/cm] | 2–2.5 | -       | -                           | 1.9–9.5               | -       | -     | –3.9––4.7 |
| Dielectric Constant | 18–24 | 22       | 12–18                       | 12.5                 | 14      | 26–28 | 20–25   |
| $\Delta V_{FB}$ [V] | -       | 0.03 | -                           | 0.25                 | -       | -     | 0.6–2   |
| Reference | [18] | [19] | [23] | [30] | [31] | [32] | This work |

The ZrO$_2$ thin films were applied to the anode composites of SOFCs composed of Ni and YSZ composite. In order to probe the presence of ZrO$_2$ materials in the reduced Ni/YSZ composites, an XPS analysis was performed. The presence of the Zr element in the relatively higher concentration near the Ni/YSZ composite surface enabled one to differentiate the deposited ZrO$_2$ thin films deposited using CMEN-Zr and oxygen plasma. It is speculated that the ALD-based ZrO$_2$ can be deposited into the pore networks formed in the Ni/YSZ anode composites. To probe the effect of ALD-based ZrO$_2$ on the anode performance, three cases were tested, including ALD-based ZrO$_2$ thin films with 50 cycles and 200 cycles along with the reference anode without any presence of ZrO$_2$ thin films. Additionally, respective samples were tested to measure the cell performance, and then ZrO$_2$ thin films were applied to the reduced Ni/YSZ anodes, as described above.

The measured cell performances are shown in Figure 11 as a function of operating temperature and ZrO$_2$ cycles. The presence of 50-cycled ZrO$_2$ (4.7 nm) did not influence the SOFC performance. However, the 200-cycled ZrO$_2$ materials significantly deteriorated the cell performance in terms of open circuit voltages and maximum power. The extracted information is shown in Figure 12. At 800 °C, the maximum power decreased from 1284 to 1075 mW for the 200 cycled ZrO$_2$ films compared to the first cell test, which involved no coating of ZrO$_2$ nanomaterials, and so the maximum decreased from 1219 to 1133 mW for 50-cycled ZrO$_2$. In contrast, the standard reference cell showed powers of 1017 and 1039 mW for successive cell characterizations. In other words, the presence of ZrO$_2$ nanomaterials onto the cathode system degraded the cell performance of SOFC unit cells. The corresponding open cell voltages were also reduced by an approximately similar magnitude before and after coating of ZrO$_2$, as shown in Figure 12 between 1.10 V and 1.02 V. The presence of ZrO$_2$ materials does not affect the open cell voltage (OCV) due to the relative independence of OCV from the electrode responses. The presence of ZrO$_2$ materials can be depicted schematically, as in Figure 13. The presence of ZrO$_2$ nanomaterials can be deposited at triple phase boundaries on electronic conductors (i.e., metallic nickel), ionic conductor YSZ, and gaseous phase involving H$_2$ and H$_2$O. The following electrochemical reaction usually takes place:

$$2\text{H}_2 + 2\text{O}^{2−} \rightarrow 2\text{H}_2\text{O} + 4\text{e}^{−} \quad (1)$$
Figure 11. Open cell voltages and current–voltage characteristics: (a) no PEALD of ZrO$_2$, (b) PEALD ZrO$_2$ with 50 cycles, and (c) PEALD ZrO$_2$ with 200 cycles.

Figure 12. (a) Open cell voltages of reference cells and ZrO$_2$ ALD cells, (b) maximum power of reference cells and ZrO$_2$ ALD cells.

Figure 13. Schematic diagram describing the role of ALD-based ZrO$_2$ nanomaterials in the electrochemical performances of SOFC anodes.

The presence of ZrO$_2$ nanomaterials decreases the effective density of triple phase boundaries by reducing the resultant electrochemical performance.

Impedance spectroscopy analysis was performed in terms of equivalent circuits, incorporating the ohmic resistances and electrode-related responses composed of high-frequency, medium-frequency, and low-frequency regimes. The electrochemical impedance is mod-
eled using equivalent notation, which is described by $R_0$ ($R_{\text{high}}$CPE$_{\text{high}}$) ($R_{\text{med}}$CPE$_{\text{med}}$) ($R_{\text{low}}$CPE$_{\text{low}}$), where $R_0$ is the ohmic resistance, and $R_{\text{high}}$, $R_{\text{med}}$, $R_{\text{low}}$ and CPE$_{\text{high}}$, CPE$_{\text{med}}$, and CPE$_{\text{low}}$ are the resistances and constant phase elements, at high, medium, and low-frequency regimes, respectively. The ohmic resistances coexist with three parallel RC components, denoted by (R$_i$CPE$_i$) using parenthesis. In particular, this presence does not seem to influence the overall ohmic resistances and instead affects the electrode-related responses, especially high-frequency responses, compared to the remaining frequency responses. SOFCs have attracted academic and industrial interests as one of the powerful next generation energy resources due to their unique advantages such as high operation efficiency, contamination-free fuel flexibility, and minimized pollution. SOFCs are typically constructed using materials with dissimilar physical and chemical properties, including cathodes, electrolytes, and anodes, in addition to the subsidiary sealing and interconnect materials.

To achieve highly efficient operation of SOFCs at intermediate temperatures ranging from 650 and 800 °C, the electrodes, i.e., cathodes and anodes, should be improved dramatically by minimizing polarization loss of composite electrodes in addition to improving ionic conductivity in electrolytes. There has been a highly limited number of empirical attempts involving artificial controls on triple boundary reactions based on the charge transfer between electronic/ionic carries and fuels. This approach depends largely on the microstructure of electrodes and interfacial geometries adjacent to the ionic electrolyte in combination with triple phase boundaries and their contributions to electrochemical reactions at both the anodes and cathodes. Although the current work was applied to Ni/YSZ anode composites of SOFCs, the conformal feature of atomic layer deposition can be employed to control oxide-based cathodes and anodes as well in terms of performance improvement or performance degradation, depending on the beneficial and detrimental influences. The current study reports the success of atomic layer deposition combined with solid oxide fuel cells, with special emphasis on the triple phase boundaries. The current work chose metal oxide materials for controlling the SOFC anodes.

4. Conclusions

ZrO$_2$ thin films were successfully deposited through plasma-enhanced atomic layer deposition using (2-(N-methylamino)1-MethylEthyleneCyclopentadienyl)Bis(Dimethylamino)Zr (abbreviated as CMEN-Zr) as Zr sources and oxygen plasma as oxygen sources. The conformal deposition of insulating and the quasi-crystalline zirconium oxide nanomaterials were applied to the Ni/YSZ anode composites of solid oxide fuel cells. The atomic layer deposition of functional oxide materials can be in the structurally controlled manner deposited to the anode composites in the solid oxide fuel cells. The ALD-based ZrO$_2$ functions as an inhibitor for the electrode reactions at the triple phase boundaries (TPBs) of SOFCs, thus decreasing the maximum power. The understanding of the ALD-assisted ZrO$_2$ coating in association with the degraded electrochemical performance can be employed in searching for the synergistic materials (or catalytic materials). However, this approach should be tested for long-time stability issues in future studies.

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