



High performance Bi-layered electrolytes via atomic layer deposition for solid oxide fuel cells



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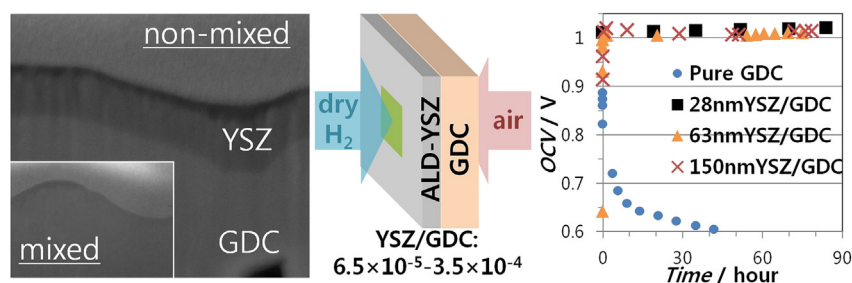
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HIGHLIGHTS

- Feasibility of ultra-thin protective layer for a stable and high-performing SOFC.
- Validates a theoretical guideline for bi-layered electrolytes prepared by ALD.
- Chemical and structural stability of bi-layered electrolytes in various environments.
- Useful design/operational guidelines for IT-SOFCs using bi-layered electrolyte scheme.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the functionality of bi-layered electrolytes in intermediate temperature solid oxide fuel cells. A thin yttria-stabilized zirconia (YSZ) layer is expected to protect the underlying gadolinia doped ceria (GDC) electrolyte from being chemically reduced and significantly improve cell stability and durability. Although a thinner YSZ layer is preferable to minimize ohmic loss, there are limitations as to how thin the YSZ film can be and still serves as a valid protection layer. The limitation is partially attributed to the inter-diffusion and significant morphological changes during the high temperature sintering processes. In this study, a stable operation was demonstrated for extended duration (>80 h) with only a 28 nm YSZ layer (corresponding to a YSZ/GDC thickness ratio of 6.5×10^{-5}) when limitations in both fabrication (<~800 °C) and operating conditions (<~600 °C, dry H₂) were imposed. Furthermore, the functionality of a protection layer with a given thickness was found to strongly depend on the method of depositing the protective layer. Protective layers deposited by atomic layer deposition (ALD) can be much thinner than those prepared by physical vapor deposition; the YSZ/GDC thickness ratio for a stable operation approached close to a theoretical value when the ALD was used.

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1. Introduction

Intermediate temperature (600–800 °C) solid oxide fuel cells (IT-SOFCs) have been actively studied due to many advantages over conventional SOFCs in terms of availability of sealants and metal interconnectors, cost effectiveness, degradation rate, packaging

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volume, start-up time and device applicability [1]. However, a decrease in operating temperature causes a significant sacrifice of ionic conductivity, which motivated researchers to seek electrolytes with much higher conductivity than yttria-stabilized zirconia (YSZ). Doped ceria such as gadolinia doped ceria (GDC) can be a good electrolyte candidate for IT-SOFCs because they are ~ 5 times more conductive than YSZ at 600 °C [2–4]. However, doped ceria is vulnerable to chemical instability in a low oxygen partial pressure environment. Ceria reduction gives rise to electronic conductivity, and thus lowers the open circuit voltage (OCV) and power density of the cell [5]. It can also cause internal stress owing to the resulting volumetric expansion, which will negatively affect the gas tightness and the structural reliability of cells [6,7].

Significant efforts to improve chemical stability while maintaining high ionic conductivity have resulted in various types of bi-layered electrolyte configurations [8–12]. The YSZ/GDC bi-layered electrolyte has been arguably one of the most popular approaches among the bi-layer schemes [13–18]. A thin YSZ film of the YSZ/GDC system serves as a protective layer against chemical degradation of ceria in a reducing gas environment.

An important issue of zirconia/ceria based bi-layered structure is inter-diffusion between the two layers. Tsoga et al. reported that YSZ and GDC layers were mixed and a resulting secondary phase ($\text{Ce}_{0.37}\text{Zr}_{0.38}\text{Gd}_{0.18}\text{Y}_{0.07}\text{O}_{1.87}$) has a lower ionic conductivity than YSZ by two orders of magnitude at 800 °C [19]. In another study, Zhou et al. showed that the diffusion of Ce into YSZ causes an increase in electronic conductivity and a decrease in ionic conductivity [20]. This is a critical issue for a nano-thin YSZ-based bi-layered electrolyte since a slight intermixing can disrupt the functionality of YSZ as a protection layer. Another issue was micro-cracks generated in the GDC layer during volumetric expansion under reducing conditions. This needs to be minimized because even a small morphological change on the surface of GDC can affect the adhesion and gas tightness of the neighboring YSZ layer. The volume expansion is caused by the replacement of Ce^{4+} ions (with an ionic radius of 0.97 nm) with larger Ce^{3+} ions (with an ionic radius of 1.14 nm) during the reduction process [21]. With these issues in mind, we examined the compositional and morphological changes of the bi-layered electrolytes with multi-thickness YSZ layers on GDC substrates under various temperatures and gas environments.

There are several requirements to obtain a high-performance protective layer. We need to be able to fine-control the optimal YSZ thickness to avoid redundant ohmic loss. A pinhole-free and dense layer is also needed to prevent the direct access of fuel gas to the underlying ceria layer. High film uniformity would suppress the formation of “hot spots” where electrical current is concentrated and/or ceria reduction is facilitated due to a thinner protection layer. In order to meet all these requirements, we employed atomic layer deposition (ALD) technique, which is known to provide pinhole free and dense layers with high uniformity, superior step coverage and accurate thickness control capabilities [22]. In this report, we also compare the functionality of YSZ protective layer prepared by the ALD with those by physical vapor deposition (PVD) techniques.

2. Experimental

We operated and characterized mixed-electrolyte cells exposed to a high temperature fabrication condition. Then we performed compositional and morphological stability tests in various environments for bi-layered samples without electrodes fabricated via ALD. Obeying the restrictions for operation and fabrication processes, we tested non-mixed bi-layered electrolyte cells and compared these results to the reported data from other deposition methods.

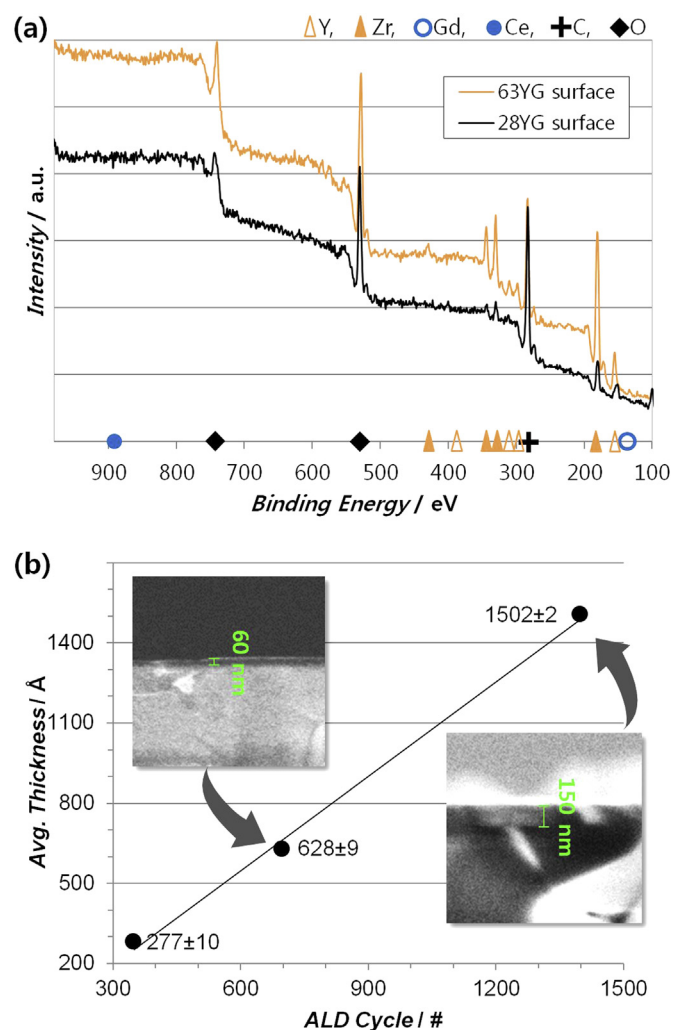


Fig. 1. Characterization results from as-deposited YSZ/GDC electrolytes. (a) XPS profiles for the 28YG and 63YG samples; no Gd or Ce peak found on their surfaces, and (b) ellipsometry thickness with the ALD pulsing cycles of 350, 700 and 1400 (corresponding to 28YG, 63YG and 150YG, respectively) and cross-sectional SEM images of 63YG and 150YG.

2.1. Bi-layered cell preparation

In order to fabricate GDC samples, 10% GDC powder ($(\text{Ce}_{0.9}\text{Gd}_{0.1})\text{O}_{1.95}$, GDC10-HP; NexTech Materials Ltd., USA) was pressed at 2000 bar in a cold isostatic press (CIP) followed by a sintering process at 1450 °C. The resulting GDC was grounded to a thickness of ~ 500 μm and the sliced pieces were thinned down to 430 μm with a mechanical polisher. Then, a firing process was performed at 600 °C for 2 h to eliminate polishing agents. The resulting average roughness was 134 nm. We applied the ALD technique to deposit a YSZ layer on the GDC. Tetrakis(dimethylamido)zirconium ($[(\text{CH}_3)_2\text{N}]_4\text{Zr}$, Sigma–Aldrich®, USA) and tris(methylcyclopentadienyl)yttrium ($(\text{CH}_3\text{C}_5\text{H}_4)_3\text{Y}$, Strem Chemicals, Inc., USA) were used as the precursors of the zirconia and yttria, where the ratio of pulsing numbers between zirconia and yttria was 7:1 [23]. The reaction chamber was controlled at 230 °C, while distilled water was used as the oxidant. The cycle numbers for the YSZ deposition were fourfold: 0, 350, 700 and 1400 cycles. The mole fraction of yttria in the YSZ is found to be $\sim 7\%$ from the X-ray photoelectron spectroscopy (XPS) analysis shown in Fig. 1(a).

For the cells exposed to high sintering temperatures, GDC–NiO cermet (50:50) and GDC–lanthanum strontium cobalt ferrite

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