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Short communication

Nanostructured and functionally graded cathodes for intermediate temperature solid oxide fuel cells

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Abstract

Nanostructured composite cathodes graded in both composition and microstructure have been successfully fabricated for the first time using combustion CVD process. The functionally graded structures of these cathodes dramatically increase the rates of electrode reactions, enhance the transport of oxygen molecules to the active reaction sites, and significantly improve the compatibility between the electrodes and other cell components. As a result, extremely low interfacial polarization resistances and high power densities have been achieved at operating temperatures of 600–850 °C, suggesting that the CCVD process has great potential for cost-effective fabrication of nanostructured fuel cell electrodes.

Keywords: Solid oxide fuel cells; Combustion CVD; Nanostructured electrodes; Functionally graded materials

1. Introduction

Solid oxide fuel cells (SOFCs) will inevitably exert a great impact on the development of the next generation energy technology and the hydrogen economy as fossil fuels are running out. For conventional SOFCs, a high operating temperature (for example, 800–1000 °C) is required to ensure sufficiently high ionic conductivity and fast electrode kinetics. Reduction of the operating temperature of SOFCs is desirable to lower the materials cost and mitigate technical issues associated with elevated temperatures [1–6]. However, conductivities of cell component materials decrease exponentially as temperature drops, and interfacial polarization resistances increase significantly, dramatically diminishing the output power densities of these fuel cells. Previous researchers have reported fabrication of compositionally graded composite cathodes using various techniques to tailor the mismatch between the physical properties of electrode materials and the electrolyte. Traditional high-temperature SOFCs, which usually employ a yttria-stabilized zirconia (YSZ) electrolyte, a LSM cathode and a nickel-YSZ cermet anode, operate in the temperature range of 800–1000 °C. LSM perovskite is widely used as a cathode material due to its high electrochemical activity, good stability, and thermal expansion compatibility with YSZ at the cell operating temperature. Reducing the operating temperature down to 600–800 °C brings both dramatic technical and economic benefits. The cost of SOFC technology may be dramatically reduced since much less expensive materials can be used in cell construction and novel fabrication techniques can be applied to the stack and system integration. Further, as the operating temperature is reduced, system reliability and operational life increase as does the possibility of using SOFCs for a wide variety of applications, including residential and automotive applications. However, as the operating temperature is reduced, some critical issues arise, such as the exponential reduction in conductivity for LSM, and the dramatic increase of interfacial polarization resistances between the LSM cathode and YSZ electrolyte. It has been recognized that LSC offers a much higher electrical conductivity than LSM at all temperatures. Unfortunately, a higher thermal

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expansion coefficient and reactivity restrict its direct use with YSZ electrolyte.

Several strategies have been adopted to improve interfacial conditions and electrochemical performance of the LSM/YSZ system, including introduction of ionically conducting secondary phases to form composite electrodes, development of compositionally graded structures, and the employment of other fabrication approaches. It was found that the interfacial polarization resistance could be reduced to one-fourth of its original value by adding 50 wt.% YSZ into the LSM cathode [7,8]. It was later reported that 50 wt.% addition of gadolinia-doped ceria (GDC) instead YSZ reduces the value to 1.06 Ω cm^2 at 700 °C and 0.49 Ω cm^2 at 750 °C, which is two to three times lower than for LSM–YSZ composite cathodes on a YSZ electrolyte [9]. Jiang demonstrated that by using ion impregnation methods, the interfacial polarization resistances of the LSM–GDC/YSZ system can be further reduced down to 0.72 Ω cm^2 at 700 °C [10].

Functionally graded materials (FGM) have been employed to join dissimilar materials or to achieve unique properties. A compositional gradient is required in a large number of engineering applications, such as joining metallic materials with ceramics [11]. On the other hand, materials exhibiting graded porosity are attractive for other applications, including graded ceramic preforms [12], special heat insulation and/or thermal shock resistant structures [13], and medical implants [14,15]. Recently the concept of FGM was introduced to fabricate SOFC components. Single-phase cathode materials (such as LSM/LSC) and composite cathodes (such as LSM/LSC–YSZ/GDC) were prepared on a YSZ electrolyte by different methods, such as screen printing [16], slurry-spraying [17], spray-painting [18], and slurry coating [19]. Reduced interfacial polarization resistances and improved electrochemical performances have been reported (i.e. 0.47 Ω cm^2 [19] and 0.2 Ω cm^2 [18] at 750 °C). However, all the work reported in the literature only focused on cathodes with a compositional gradient. Ideally, the best structure for a functional SOFC should be the one with both compositional gradient and porosity gradient, consisting of fine grains (and high surface area) close to the electrode/electrolyte surface, and large grains (and thus large pore size) at air/oxygen side.

It has been demonstrated that nanostructured electrodes with significantly high surface area offer superior electrochemical properties as long as sufficiently large pore size and enough porosity are provided [20,21]. Our recent work showed that nanostructured electrodes dramatically reduce electrode/electrolyte interfacial polarization resistances and improve cell performance [22]. In this article, we report our work on fabrication of nanostructured and functionally graded composite cathodes, which are graded in microstructure as well as in composition, using combustion CVD process. A schematic diagram of the fabricated SOFC system is depicted in Fig. 1. The resulting SOFCs exhibited extremely low interfacial polarization resistances and high powder density at the operating temperature range of 600–800 °C.

2. Experimental methods

Detailed description of combustion CVD apparatus used for this study is available elsewhere [23]. Metal nitrates of Sr, Sm, Co, Ce, and Ni were obtained from Aldrich. A solution was prepared by dissolving stoichiometric amounts of precursors into an organic solvent and a magnetically stirring until completely dissolved. Methane was used as the fuel gas and oxygen served as the oxidant for the combustion flame.

Dense YSZ pellets of 14 mm diameter and 240 μm thickness were prepared by tape casting and sintered at 1400 °C for 5 h. Fig. 1 shows a schematic diagram of the SOFC design. Starting with a tape cast YSZ pellet of 14 mm diameter and 240 μm thickness, a 30 μm layer of porous 60 wt.% NiO–40 wt.% GDC was deposited onto one side of the pellet using combustion CVD at a temperature of 1250 °C. After deposition of one electrode, the precursor solution was switched, and substrates were turned over for deposition of the cathode materials. First a 10 μm thick fine grained 60 wt.% LSM–40 wt.% GDC was deposited on YSZ electrolyte. Following this, the composition of the precursor solution was changed to 30 wt.% LSM–30 wt.% LSC–40 wt.% GDC. Sequentially, a coarse layer of 60 wt.% LSC–40 wt.% GDC was deposited on top of the cathode.

The microscopic features of the prepared electrodes were characterized using a scanning electron microscope (SEM, Hitachi S-800) with an energy dispersive spectroscopy (EDS) attachment. Electrochemical performance of the cells was measured from 600 to 850 °C at 50 °C increment using humidified (3 vol.% water) hydrogen as fuel and stationary air as oxidant, both at ambient pressure. Cell impedance was measured in the frequency range from 0.01 Hz to 100 kHz with an EG&G Potentiostat/Galvanostat (Model 273A) and Lock-in Amplifier (5210).

3. Results and discussion

Shown in Fig. 2(a) is a cross-sectional view (as fractured) of a half-cell with the composite cathode supported by a 240 μm thick dense YSZ electrolyte. The cathode fabricated by combustion CVD consists of three porous layer structures and is graded in both microstructure and composition, with about 5 μm thick 60 wt.% LSM–40 wt.% GDC fine

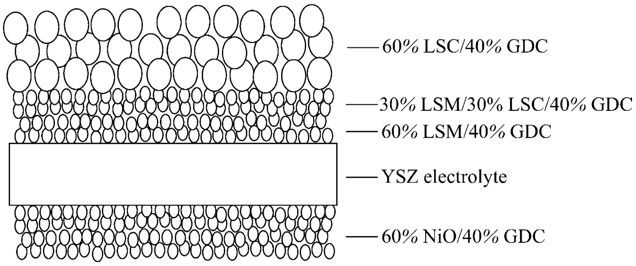

Fig. 1. A schematic diagram of the functionally graded SOFC configuration.

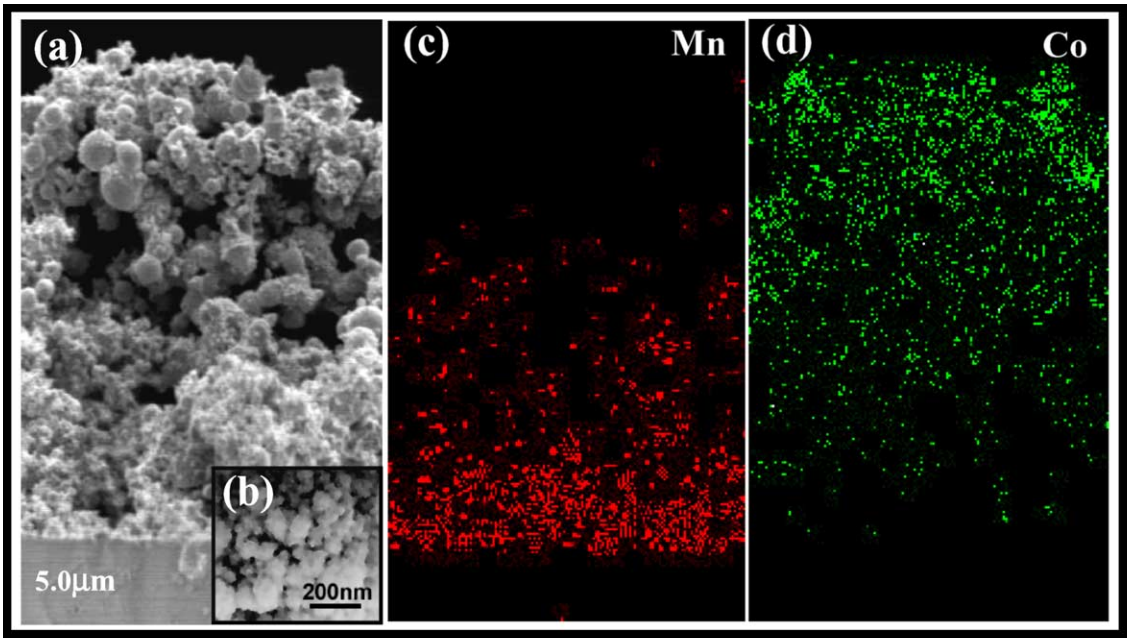

Fig. 2. (a) Cross-sectional fracture surface of the functionally graded cathode fabricated on an YSZ pellet using a combustion CVD process, (b) higher magnification image of the cathode showing the nanostructure, (c) EDS dot mapping showing Mn distribution on the cross-section surface, and (d) EDS dot mapping of Co distribution.

agglomerates (0.5 μm diameter) at the bottom (close to YSZ electrolyte), followed by 5 μm thick 30 wt.% LSM–30 wt.% LSC–40 wt.% GDC fine agglomerates (0.5 μm diameter), and 15 μm thick 60 wt.% LSC–40 wt.% GDC coarse agglomerates (2–3 μm diameter) on the top (air side). The two bottom layers are actually nanostructured as shown in Fig. 2(b), offering extremely high surface area for oxygen reduction. In addition, these Mn rich layers provide a fast electrochemical reaction rate, high stability and a satisfactory match in thermal expansion with the YSZ electrolyte. Meanwhile, the large interconnected pore channels within the coarse top layer facilitate oxygen mass transport. The Co rich top layer has a higher conductivity as well.

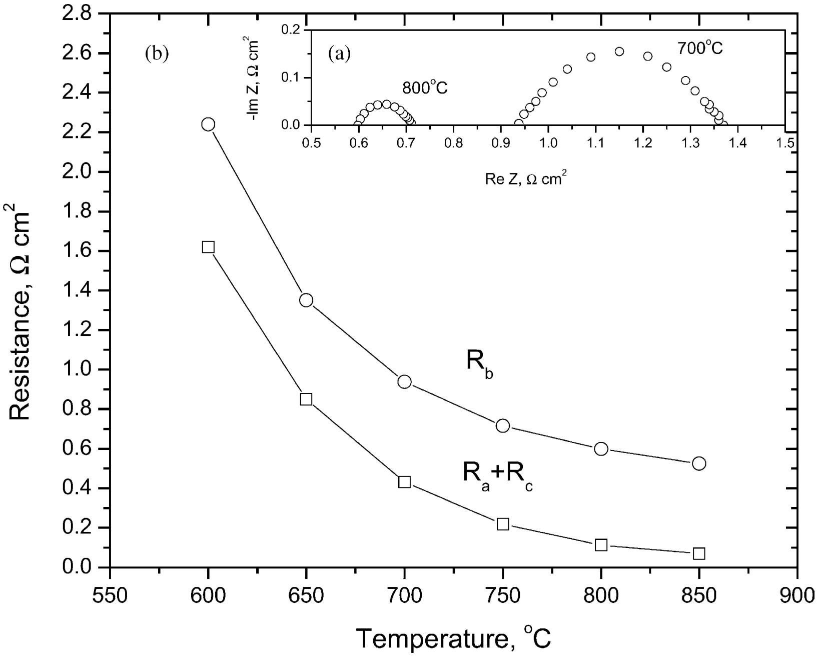

Fig. 3. (a) Impedance spectra of a single fuel cell as measured using a two-electrode configuration, and (b) bulk electrolyte resistance (R_b) and interfacial polarization resistances ($R_a + R_c$) determined from impedance spectra acquired at different temperatures.

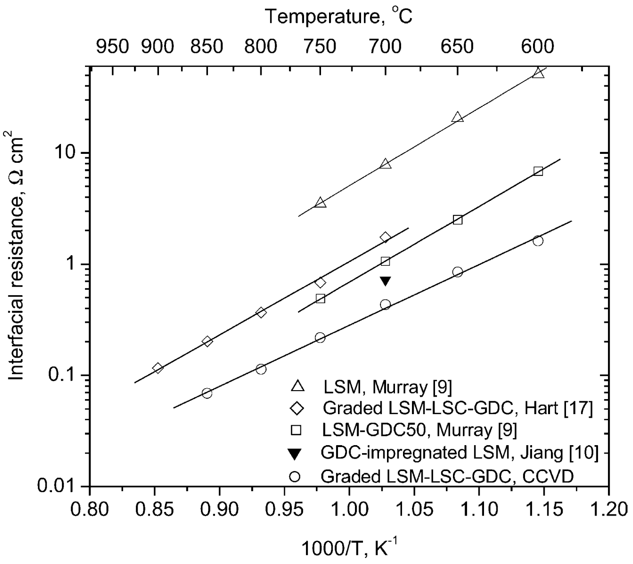

Fig. 4. Comparison of interfacial polarization resistances for YSZ electrolyte/LSM based electrodes fabricated using different techniques: spin-coating (symmetrical cell, tested in air) [9], slurry-spraying (symmetrical cell, tested in air) [17], ion impregnation (asymmetrical cell with Pt counter electrode on the other side of electrolyte, tested in air) [10], and combustion CVD (full cell, tested in air).

It is difficult to distinguish the bottom layers, 60 wt.% LSM–40 wt.% GDC and 30 wt.% LSM–30 wt.% LSC–40 wt.% GDC in the SEM micrographs, indicating that the porosity and microstructural features were similar. However, an EDS dot mapping technique revealed the compositional changes on the cross-sectional micrograph. As shown in Fig. 2(c), the Mn content gradually decreased from the YSZ/LSM–GDC interface to LSC–GDC airside, while the Co distribution exhibited the opposite trend as shown in Fig. 2(d). Unlike compositional layered structures fabricated by stacking or spray-painting [18], where the abrupt composition change was usually easily observed between adjacent layers, composition of the structures fabricated by combustion CVD changed gradually across the interface.

Shown in Fig. 3(a) are the impedance spectra of the fuel cell measured at 700 and 800 °C under open circuit conditions using a two-electrode configuration. The open circuit voltages (OCV) were 1.06, 1.03 and 1.0 V at testing temperatures of 600, 700 and 800 °C, respectively, indicating no gas crossover and negligible electronic conductivity of the YSZ electrolyte. The bulk resistance of the electrolyte (R_b) and the polarization resistances of the electrode–electrolyte interfaces ($R_a + R_c$) can thus be determined directly from the impedance data. Shown in Fig. 3(b) are the electrolyte resistances (R_b) and the total interfacial resistances ($R_a + R_c$) The electrode–electrolyte interfacial polarization resistance is estimated to be 1.62 Ω cm^2 at 600 °C, 0.43 Ω cm^2 at 700 °C, and 0.11 Ω cm^2 at 800 °C, respectively. At the same testing temperatures, the bulk resistances are 2.24, 0.94, and 0.60 cm^2, respectively.

Fig. 4 shows the polarization resistance of the cell with electrodes fabricated by combustion CVD, together with data reported in the literature for SOFCs with LSM based cathodes and YSZ electrolyte. While most polarization resistances reported in the literature were measured using a symmetrical cell configuration, they should be comparable to those obtained from fuel cells if the cathode–electrolyte interfacial polarization resistances are properly separated from the rest of the cell since partial shorting due to electronic conduction

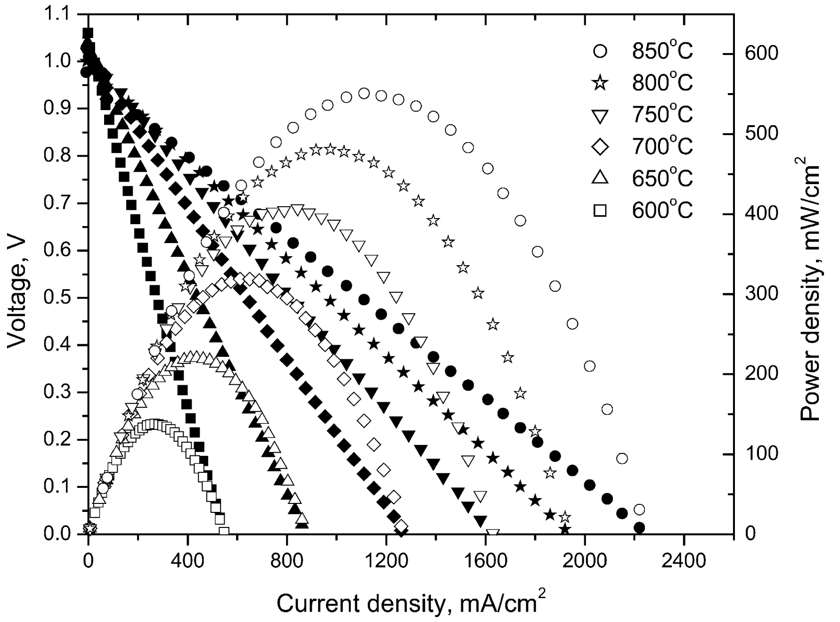

Fig. 5. Cell voltages and power densities as a function of current density for a fuel cell with functionally graded cathode and anode fabricated using combustion CVD on a YSZ electrolyte membrane of 240 μm thick (Testing conditions: hydrogen with 3 vol.% of water vapor as the fuel and stationary air as the oxidant, both at ambient pressure).

of YSZ is negligible under fuel cell conditions. Clearly, the fuel cell with electrodes fabricated by combustion CVD displayed lower interfacial polarization resistances than those prepared by other methods: spin-coating [9], slurry-spraying [17], and ion impregnation [10]. All electrodes were tested in stationary air using a symmetrical cell configuration except the electrodes prepared by ion impregnation, which were tested in an asymmetric cell with porous Pt as the counter electrode. In fact, the observed interfacial polarization resistances of the electrodes fabricated by combustion CVD represent the lowest ever reported for these cathode/electrolyte systems.

Fig. 5 shows the cell voltages and power densities as a function of current density for a single cell with both anode and functionally graded cathode fabricated by combustion CVD. The maximum power densities are 138, 319, and 481 mW/cm^2 at 600, 700, and 800 °C, respectively. At 850 °C, the highest power density of 551 W/cm^2 was recorded. These are impressive performance data for a fuel cell based on a 240-μm thick electrolyte. As revealed from impedance spectra shown in Fig. 3(a), electrolyte resistances were much higher than the electrode–electrolyte interfacial polarization resistance and, thus, the cell performance was mainly limited by the electrolyte resistance.

4. Conclusions

Nanostructured and functionally graded LSM–LSC–GDC composite cathodes have been successfully fabricated on 240 μm thick YSZ electrolyte supports using a combustion CVD method. The fabricated cathodes were graded in both composition and structure with higher strontium-doped lanthanum manganite (LSM) content and finer primary grain size at electrolyte side while higher strontium-doped lanthanum cobaltite (LSC) content and coarser primary grain size at air/oxygen side. Extremely low interfacial polarization resistances (i.e. 0.43 Ω cm^2 at 700 °C) and impressively high power densities (i.e. 481 mW/cm^2 at 800 °C) were generated at operating temperatures of 600–850 °C. This is the first instance in which the existing ideal SOFC model has been experimentally verified. The promising results suggest that high power density, intermediate operating temperature, and low cost SOFCs can be fabricated using combustion CVD method.

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