

Effect of Pd-impregnation on the electrochemical performance of $\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3\text{-Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ composite anodes for solid oxide fuel cells

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In order to improve the catalytic activity of $\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3$ (SLT)- $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) composite anodes, Pd was impregnated as a co-catalyst using a glycine mediated impregnation method. When glycine was added into the Pd precursor solution, nano-sized Pd particles with the average particle size being approximately 20 nm were homogeneously distributed onto the SLT-GDC backbone. The polarization resistance (R_p) was significantly reduced by the impregnation of Pd due to the enlargement of the triple phase boundary (TPB) length, which promotes ionic exchange reactions at the anode/electrolyte interface, as well as the dissociation of H_2 molecules. The maximum power density of the single cell also increased significantly as the amount of Pd increased. Moreover, the single cell with a Pd-impregnated SLT-GDC15 anode showed a comparable performance using both CH_4 and H_2 fuel, which indicates that the Pd-impregnated SLT-GDC composite anode can be used for hydrocarbon-fueled SOFC as well.

Key words: Solid oxide fuel cells, Composite anode, Oxide anode, Impregnation, Co-catalyst.

Introduction

Solid oxide fuel cells (SOFCs) are energy conversion devices that directly convert chemical energy into electrical energy. A Ni-based composite is most commonly used as an anode material for SOFCs [1,2], and although Ni-based composite anodes show excellent catalytic activity for H_2 fuel, they suffer from carbon deposition and sulfur poisoning when hydrocarbon fuels are used [3, 4]. Additionally, Ni-based composite anodes show poor redox stability and agglomeration after long-term operation [5]. As a result, the development of Ni-free materials for anodes has attracted significant attention recently. Cu-ceria, doped SrTiO_3 , $(\text{La,Sr})(\text{Cr,Mn})\text{O}_3$, and $\text{Sr}_2\text{MgMoO}_{6-\delta}$ are potential candidates for alternative anodes [6-9]. SrTiO_3 with a perovskite structure is known as a mixed ionic and electronic conductor (MIEC). Replacement of Sr with La in the A-site of SrTiO_3 results in a charge-compensating transition from Ti^{4+} to Ti^{3+} in the reducing atmosphere, which leads to an increase in the amount of charge carriers [10-12]. Despite the high electrical conductivity and excellent sulfur tolerance, La doped SrTiO_3 does not exhibit a high enough catalytic activity for H_2 oxidation. The addition of precious metals such as Pt, Pd, and Ru to porous electrodes is known to improve electro-catalytic activity and performance [13]. In this regard, a small amount of Pd was incorporated

into the $\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3$ (SLT)- $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) composite anode in order to enhance the catalytic activity. The effect of Pd impregnation on the electrochemical performance is investigated in this study.

Experimental Procedure

$\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3$ (SLT) powders were synthesized using a solid state reaction method. Calculated amounts of La_2O_3 (Alfa Aesar, 99.9%), SrCO_3 (Alfa Aesar, 99.9%), and TiO_2 (Alfa Aesar, 99.9%) were mixed and calcined at 1100 °C for 3 hrs in air. SLT-GDC composite with 15 vol% of GDC (SLT-GDC15) was fabricated by mixing with a commercial GDC powder (CGO90/10 UHSA, Grand C&M Co. Ltd.). In order to impregnate the Pd particles, a Pd precursor solution was prepared with sodium tetrachloropalladate (Na_2PdCl_4), DI water, and glycine. Pd precursor solutions at 0.05 M and 0.1 M Pd were impregnated into both SLT-GDC composite anodes. The impregnated samples were dried in vacuum oven at 100 °C for 20 min. This process was repeated twice and followed by calcination at 800 °C for 30 min.

Microstructural characterizations of the prepared samples were carried out with a scanning electron microscope (SEM, SN-300 Hitachi, Japan). Electrochemical performance tests were carried out using AC impedance spectroscopy analysis and a single cell test with electrolyte supported-type single cells. Commercial GDC powder (CGO90/10 UHSA, Grand C&M Co., Ltd.) was compressed by cold iso-static pressing (CIP) and was then fired at 1450 °C for 4 hrs to fabricate a 0.5-mm-thick GDC electrolyte pellet. Electrode paste was prepared with SLT-GDC15 powder,

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polymer binder, and PMMA (SUNPMMA-S100, Sunjin Chemical) as pore formers. An SLT-GDC15 anode layer was screen-printed onto the GDC pellets and was then fired at 1300 °C for 2 hrs. Similarly, the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ - $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (BSCF-GDC) cathode layer was screen-printed onto the other side of the GDC pellets in a symmetric position followed by firing at 1050 °C for 2 hrs. The geometrical electrode area was 0.25 cm².

AC impedance analysis was performed using a universal potentiostat with a frequency response analyzer (SP150/VMP3, Biologic SAS, France) under humidified H₂ at 700–800 °C. The applied frequency was in the range of 50 mHz to 500 kHz with a voltage amplitude of 25 mV. Current-voltage (I-V) measurements of the single cells were also performed with the same configuration as the AC impedance analysis. A Pt mesh placed on the electrode with a spring-loaded alumina tube was used as the current corrector. A seal between the single cell and alumina tube was achieved using a Pyrex® glass ring. Humidified H₂ (with 3% H₂O at 30 °C) and air were supplied as a fuel and oxidant, respectively, at a rate of 100 cm³/min. Humidified CH₄ was also used as a fuel for the verification of hydrocarbon fuel use.

Results and Discussion

Fig. 1 shows the microstructure of a Pd-impregnated SLT-GDC15 composite anode. In order to obtain enough porosity, PMMA was used as a pore former. In the sample with 75 wt% PMMA, the final microstructure after

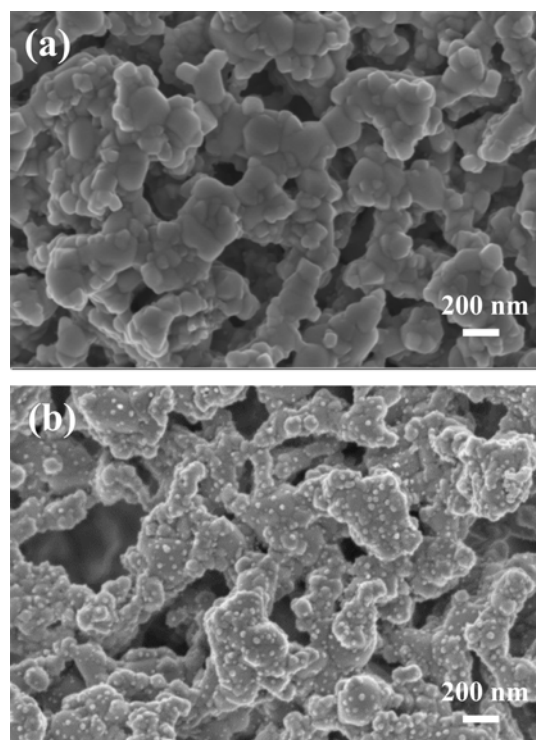


Fig. 1. FE-SEM images of the SLT-GDC15 composite anode (a) before and (b) after Pd-impregnation, fired at 800 °C for 30 min in air.

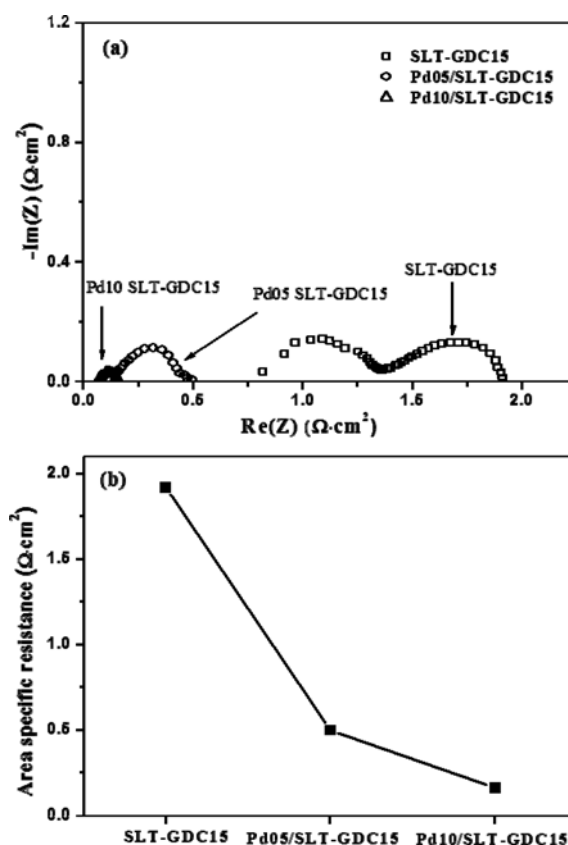


Fig. 2. (a) Typical AC impedance spectra (b) variation of R_p values of the Pd-impregnated SLT-GDC15 composite anode in H₂ at 800 °C.

sintering was collapsed due to the lack of connectivity. On the other hand, the sample with 50 wt% PMMA held the porous microstructure after sintering, as shown in Fig. 1(a). A highly porous network can be derived with the aid of a PMMA pore former. We believe this microstructure is appropriate for the discrete, deep level impregnation of co-catalysts. Meanwhile, when glycine was added into the Pd precursor solution, nano-sized Pd particles were homogeneously distributed onto the SLT-GDC15 backbone, with the average Pd particle size being approximately 20 nm.

Fig. 2 shows AC impedance spectra and the calculated anode area specific resistance (ASR) of a single cell with a Pd-impregnated SLT-GDC15 anode at 800 °C. An equivalent circuit consisting of an inductor (L), a resistor (R_o), and two RQ elements (R_1Q_1 and R_2Q_2) was employed to fit the impedance data. The left intercept with the impedance arc on the Z (real) axis at high frequencies corresponds to the ohmic resistance R_o , and the right intercept on the Z axis indicates the total resistance, R_{tot} . The polarization resistance R_p is the overall size of the arcs ($R_{tot}-R_o$). The impedance plot clearly shows that R_p was significantly reduced by the impregnation of Pd. The evaluated area specific resistances ($ASR = R_p \times \text{electrode area}/2$) for the bare SLT-GDC15, Pd5/SLT-GDC15, and Pd10/SLT-GDC15

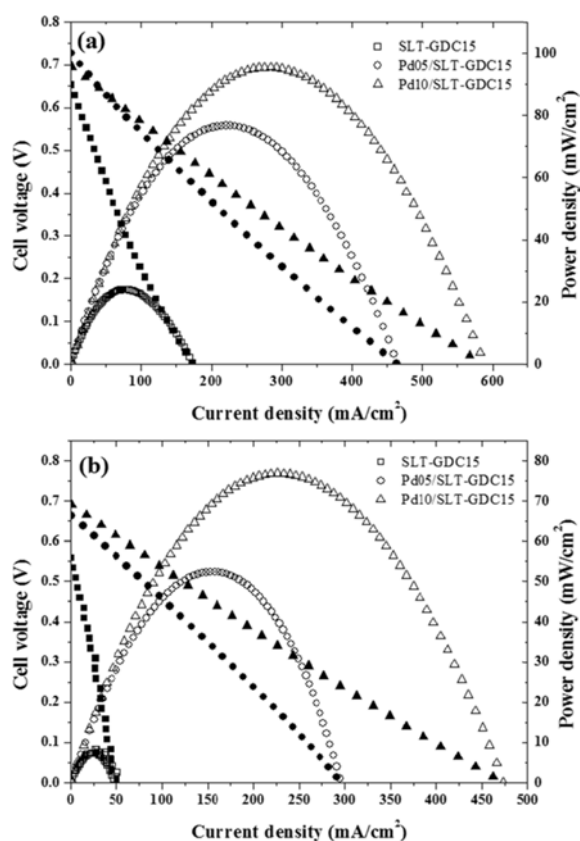


Fig. 3. Comparison of the I-V curves and power density of the Pd-impregnated SLT-GDC15 composite anodes in (a) H_2 and (b) CH_4 fuel at 800 °C.

electrodes were 1.92, 0.50, and 0.16 Ωcm^2 , respectively, at 800 °C under humidified H_2 . The decrease in R_p is mostly due to the enlargement of the triple phase boundary (TPB) length. The surface modification initiated by impregnation of a co-catalyst can increase the number of reaction sites, which improves the catalytic reaction. Moreover, it is well-known that the hydrogen binding energy, which is an important factor that influences the catalytic activity of hydrogen oxidation reactions, decreases in the metallic bonds of Pd more significantly than in Ni and other ceramics. Meanwhile, the high-frequency arc (R_1) presumably related to the activation process and the low-frequency arc (R_2) are likely related to the electrochemical kinetics of the electrode material, such as adsorption and/or diffusion processes of the reactant and/or the product to/from the interface [14]. The R_1 value for the Pd impregnated SLT-GDC 15 anode decreased significantly when the amount of Pd was increased. This indicates that Pd promotes ionic exchange reactions at the anode/electrolyte interface, as well as the dissociation of H_2 molecules.

Variations of the cell voltage and power density of a single cell with various SLT-GDC anodes at 800 °C using H_2 and CH_4 fuels are shown in Fig. 3. The open circuit voltages at 800 °C were about 0.7 V due to the reduction of GDC electrolyte in the reducing atmosphere. The

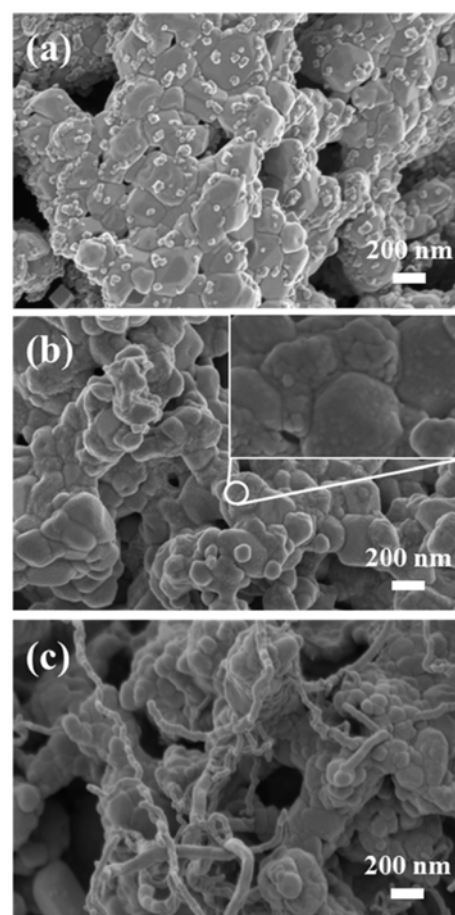


Fig. 4. (a) Cross-sectional FE-SEM images of the Pd-impregnated SLT-GDC15 composite anodes (a) before and (b) after the SOFC single cell test with H_2 and (c) with CH_4 fuel at 800 °C.

maximum power density of the single cell increased significantly with an increasing amount of Pd. The single cell with a Pd10/SLT-GDC15 anode exhibited the highest maximum power density of 95 mW/cm^2 , which is 400% higher than the single cell with a bare SLT-GDC15 anode. This trend is in accordance with AC impedance data shown in Fig. 2. Moreover, the single cell with a Pd-impregnated SLT-GDC15 anode showed a comparable maximum power density of 77 mW/cm^2 for the CH_4 fuel. This indicates that the Pd-impregnated SLT-GDC composite anode can be used for hydrocarbon-fueled SOFC.

Fig. 4 shows the microstructure of the Pd-impregnated SLT-GDC composite anode before and after a single cell test. After a 24 hrs operation with H_2 fuel, the Pd coarsening phenomenon occurred, which can lead to performance degradation. Moreover, carbon fibers cracked due to CH_4 and were deposited onto the surface of Pd during operation with CH_4 .

Conclusions

The effect of Pd impregnation on $\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3$ (SLT)- $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) composite anode performance has

been investigated. The addition of Pd metals to porous electrodes was carried out using a glycine mediated impregnation process. When glycine was added in the Pd precursor solution, nano-sized Pd particles were well dispersed on the surface of the SLT-GDC. The anode ASR value decreased significantly with Pd impregnation, because Pd has a high catalytic activity with regards to H₂ oxidation. This indicates that Pd promotes ionic exchange reactions at the anode/electrolyte interface, as well as the dissociation of H₂ molecules. The maximum power density of the single cell increased significantly with an increasing amount of Pd. The maximum power density of the single with the Pd10/SLT-GDC15 anode was approximately 95 mW/cm² at 800 °C in H₂. In addition, based on the AC impedance analysis and cell performance test for CH₄ fuel, the Pd-impregnated SLT-GDC15 anode

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (grant number: 2014R1A1A2056043). This work was also supported by the Korea Institute of

Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20164030201070).

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