



Short communication

Pd-impregnated SYT/LDC composite as sulfur-tolerant anode for solid oxide fuel cells

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ABSTRACT

An $\text{Sr}_{0.88}\text{Y}_{0.08}\text{TiO}_{3-\delta}$ (SYT)/ $\text{La}_{0.4}\text{Ce}_{0.6}\text{O}_{1.8}$ (LDC) composite impregnated with Pd was evaluated as a sulfur-tolerant anode for the $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ (LSGM)-supported cells. The impregnation of Pd into the porous SYT/LDC anode was found to significantly enhance the anode performance. With the addition of 1.5 wt.% Pd into the anode, the anodic overpotential was reduced to about half of the original value. The single cell with the Pd-impregnated SYT/LDC anode showed a maximum power density of 1006 and 577 mW cm^{-2} at 850 and 800 °C in dry H_2 , respectively, which was more than twice of that prior to impregnation. The Pd-impregnated composite anode exhibited good tolerance to sulfur, with essentially no decay in performance in H_2 containing up to 50 ppm H_2S .

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1. Introduction

Solid oxide fuel cells (SOFCs) have been widely studied as an energy conversion and power generation system due to their high fuel efficiency, low greenhouse emission, multiple fuel choice, and good tolerance to impurities in the fuel. In particular, the possibility of direct utilization of fossil fuels may significantly reduce the cost of SOFC technologies. Unfortunately, all fossil fuels contain certain amounts of contaminants, such as sulfur compounds, which are converted to gaseous hydrogen sulfide (H_2S) in reforming. Therefore, the design of anode materials that can operate on sulfur-containing fuels is essential for the commercialization of SOFCs.

While the conventional Ni–YSZ composite anode gives adequate performance in pure H_2 , Ni tends to catalyze the formation of carbon in hydrocarbon fuels. The Ni–YSZ composite is also significantly affected by sulfur in fuels containing H_2S [1], probably due to the sulfur adsorption on the Ni surfaces which blocks the active sites and therefore leads to a fast and dramatic degradation in anode performance [1–4]. Therefore, development of Ni-free materials as alternative anodes has attracted significant attention recently. Cu-ceria [5,6], doped SrTiO_3 [7,8], (La,Sr)(Cr,Mn) O_3 [9,10], $\text{Sr}_2\text{MgMoO}_{6-\delta}$ [11,12], and LaMoO [13] could be potential candidates for alternative anodes. In this paper, a composite of doped SrTiO_3 and doped ceria is chosen for evaluation as a sulfur-tolerant anode for a cell with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ (LSGM) as the elec-

trolyte. Y_2O_3 -doped SrTiO_3 is selected as one of the components in the composite due to its good chemical stability and relatively high electrical conductivity in the anodic atmosphere [7,8]. The perovskite phase SrTiO_3 is known as a mixed ionic/electronic conductor (MIEC). Replacement of Sr with La or Y in the A-site of SrTiO_3 results in a charge-compensating transition of Ti^{4+} to Ti^{3+} in the reducing atmosphere, which introduces the n-type conduction [14–16]. It was reported that the electrical conductivity of Y-doped SrTiO_3 (SYT) reached 20–100 S cm^{-1} at 800 °C in a reducing environment [7]. Doped SrTiO_3 also showed superior tolerance to sulfur [17,18]. The $\text{Sr}_{0.65}\text{La}_{0.35}\text{TiO}_3/\text{La}_{0.5}\text{Ce}_{0.5}\text{O}_{1.75}$ composite anode showed quite stable performance over 100 h in H_2 containing 280 ppm H_2S at 850 °C [17]. Despite the high electrical conductivity and excellent sulfur tolerance, doped SrTiO_3 does not show comparable catalytic ability towards H_2 oxidation as the Ni-based anodes. The electrocatalytic ability of doped SrTiO_3 might be improved by further doping with high-level of Mn [19] or low-level of Mn and Ga on the B-site [20]. La_2O_3 -doped CeO_2 (LDC) is selected as the second component in the composite anode, considering it as an MIEC with excellent tolerance to sulfur contaminants in the fuel. Since LDC has substantial catalytic activity for fuel oxidation, it is expected to improve the anode performance. The addition of metal catalysts such as Ni, Pt, Pd, Ru, Ir and Rh to porous electrodes is another approach to boost the electrocatalytic activity of the ceramic anodes [10,21,22]. These catalysts are usually incorporated into the porous electrodes via a wet impregnation method. Significant improvement in the cell performance was observed with Pd impregnation into the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) + Cu anode in our previous study [10].

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In this paper, the SYT/LDC composite was evaluated as a sulfur-tolerant anode. A small amount of Pd was incorporated into the anode to enhance the catalytic activity. The effects of Pd impregnation on the anode performance and the sulfur tolerance of the anode were investigated.

2. Experimental

2.1. Sample preparation

Both $\text{Sr}_{0.88}\text{Y}_{0.08}\text{Ti}_3\text{O}_{3-\delta}$ (SYT) and $\text{La}_{0.4}\text{Ce}_{0.6}\text{O}_{1.8}$ (LDC) were synthesized by the Pechini method [23]. To prepare the SYT powder, titanium isopropoxide (99.9%, Alfa Aesar) and citric acid (99.5%, Alfa Aesar) were dissolved into ethylene glycol (99.9%, Alfa Aesar) with a mole ratio of 1:3:8. The solution was mixed with a stirrer on a hot plate to dissolve the citric acid powders. Appropriate amounts of $\text{Sr}(\text{NO}_3)_2$ (99.9%, Alfa Aesar) and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Alfa Aesar) were then introduced into the solution and the mixture was further stirred on the hot plate at 300°C to form a gel. The gel was hand-ground and decomposed at 600°C in order to remove possible carbon residues. The LDC powders were synthesized in a similar way, starting with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.5%, Alfa Aesar) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Aldrich). The mole ratio between anion, citric acid and ethylene glycol is 1:1:1. The thus-obtained SYT and LDC powders were reground, pelletized, and fired at 1400°C in air, respectively. Finally, the pellets were ground and ball-milled to reduce the particle size. The powders consisting of 50 wt.% SYT and 50 wt.% LDC were thoroughly mixed as the anode material. To assess the chemical reactivity between SYT and LDC, the mixed powders were fired at 1400°C for 5 h and the XRD pattern of the resulting powders was carefully analyzed.

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ (LSGM) was chosen as the electrolyte material, which was synthesized by the solid-state reaction technique. The details regarding the preparation procedure were given in our previous papers [10,24,25]. Commercial $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) powder was used as the cathode material.

2.2. Single-cell fabrication

For all the single cells, a $300\text{-}\mu\text{m}$ -thick LSGM electrolyte was employed as support. LDC was used as a buffer layer between the anode and electrolyte. Single cells were fabricated as follows. A thin layer of LDC was first deposited on one side of the LSGM electrolyte via screen-printing. To make a porous anode, 10 wt.% carbon was added to the SYT/LDC powder mixture. The anode ink was then screen-printed on top of the LDC interlayer. The double layers were annealed at 1300°C for 0.5 h. The SSC cathode slurry was subsequently screen-printed on the opposite side of the electrolyte with a similar procedure and was fired at 950°C for 2 h. The effective working electrode area was 0.24 cm^2 . Reference electrodes consisting of the same materials as the working electrodes were deposited on the LSGM disc about 2.5 mm away from the working electrodes to monitor the overpotentials of the anode and cathode. About 1.5 wt.% of Pd was loaded into the porous SYT/LDC composite anode via a wet impregnation method using an aqueous solution of $(\text{NH}_3)_4\text{PdCl}_2 \cdot \text{H}_2\text{O}$ (0.2 M), as described previously [10].

2.3. Cell testing and evaluation

Electrical contacts to the electrodes were established using an Au mesh and Au paste at the anode and a Pt mesh and cathode paste at the cathode. The single cell was attached to an alumina tube with a glass sealant [10]. The assembled cell was then placed in the hot zone of a vertical furnace. Dry H_2 or $\text{H}_2/\text{H}_2\text{S}$ was fed to the anode surface at a fixed rate of 40 ml min^{-1} , and stationary

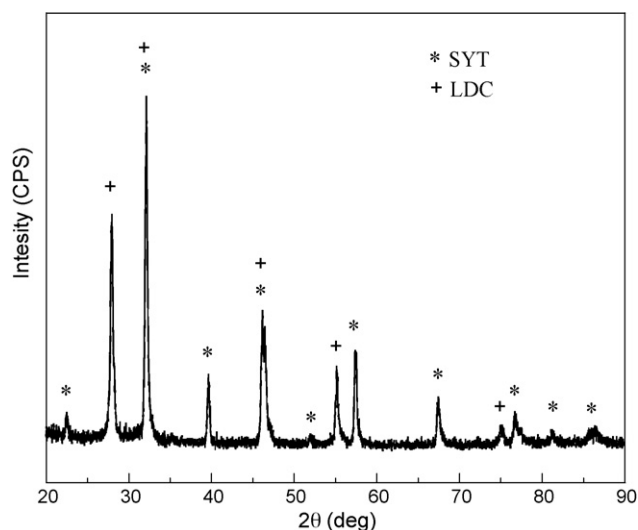


Fig. 1. XRD pattern of the mixture consisting of SYT and LDC after firing at 1400°C for 5 h in air.

air was used as oxidant at the cathode side, as described before [13]. The single cell tests were carried out using an electrochemical interface (Solartron 1287) with a LabView program at 800 and 850°C .

3. Results and discussion

Fig. 1 shows the XRD pattern of the SYT and LDC mixture (1:1 wt.%) after firing at 1400°C for 5 h. No peaks other than those expected for SYT and LDC were observed in the pattern, as seen in Fig. 1, indicating that no significant chemical reaction had occurred between the two components. Therefore, SYT and LDC were chemically compatible with each other.

Fig. 2 gives the overall cross-sectional view of a fractured cell near the anode side after cell testing. The LDC buffer layer was uniform and relatively dense with a thickness of around $10\text{ }\mu\text{m}$, which might block the possible interdiffusion across the anode/electrolyte according to our previous study [25]. The $30\text{-}\mu\text{m}$ -thick SYT/LDC anode layer was quite porous, which resulted from the addition of the pore former. The SYT and LDC particles were well interconnected in the composite anode, as seen from Fig. 2.

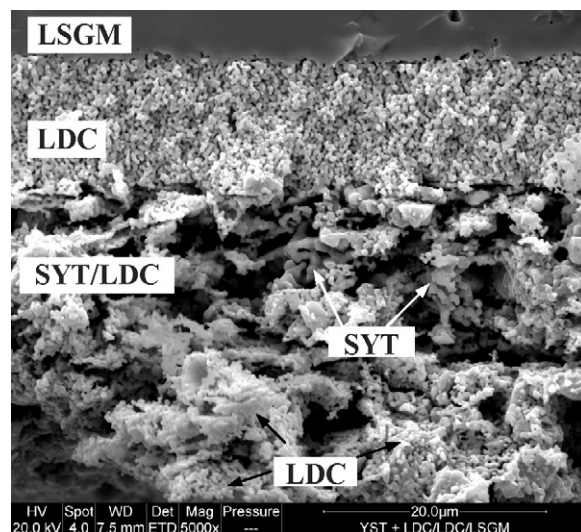


Fig. 2. SEM image of the cross-section of the tested cell near the anode side.

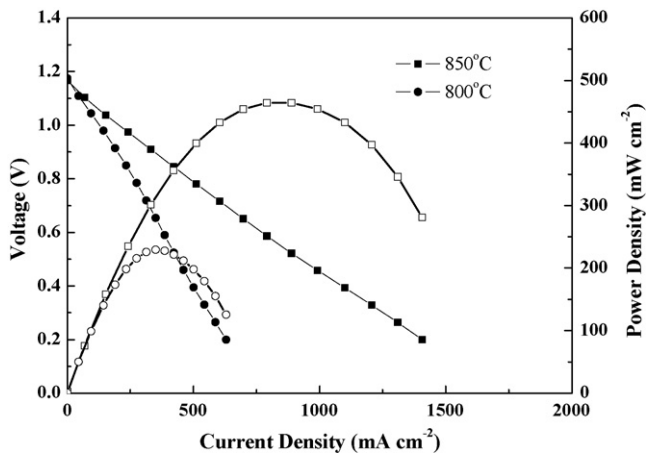


Fig. 3. Voltage and power density for a single cell with the SYT/LDC composite anode at different temperatures in dry H₂.

The performance of the composite anode prior to Pd impregnation was first evaluated. Fig. 3 shows the performance of a single cell with the SYT/LDC anode in dry H₂. As illustrated in Fig. 3, the cell only exhibited a maximum power density of 464 and 229 mW m⁻² at 850 and 800 °C in dry H₂, respectively. Compared to the LDC + Ni [25] or amorphous LaMoO [13] anodes, the SYT/LDC composite anode exhibited inferior performance with the same electrolyte and similar cathode. It was likely due to the relatively low electrical con-

ductivity and poor electrocatalytic activity of the anode towards H₂ oxidation. The electrical conductivity of SYT strongly depends on the sample preparation/processing procedures, e.g. sintering temperature and atmosphere [26]. Without a sintering treatment at high temperature (>1100 °C) in a reducing atmosphere, SYT does not show high electrical conductivity (>20 S cm⁻¹) under typical anode atmospheres, which is similar to that of La-doped SrTiO₃ [8]. This behavior might be related to the reduction/oxidation kinetics of transition of donor-substituted SrTiO₃ between a reduced state (high electronic conductor) and an oxidized state (poor electronic conductor) upon the variation of the oxygen partial pressure [15]. Considering that both the synthesis of anode powders and the fabrication of anode ceramic structure were conducted in air in the present study, it is reasonable to assume that the electrical conductivity of the SYT/LDC anode was much lower than that of the anodes containing a significant amount of metals such as the LDC + Ni anode. Furthermore, the catalytically active LDC particles in the composite had a relatively large size, due to the high sintering temperature of the anode, which would reduce the electrocatalytic activity of the SYT/LDC composite anode.

To improve the electrochemical properties of the SYT/LDC anode, a small amount of Pd (i.e. 1.5 wt.%) was incorporated into the porous structure. Fig. 4a compares the electrode overpotential of two cells using the SYT/LDC composite anodes with and without the Pd

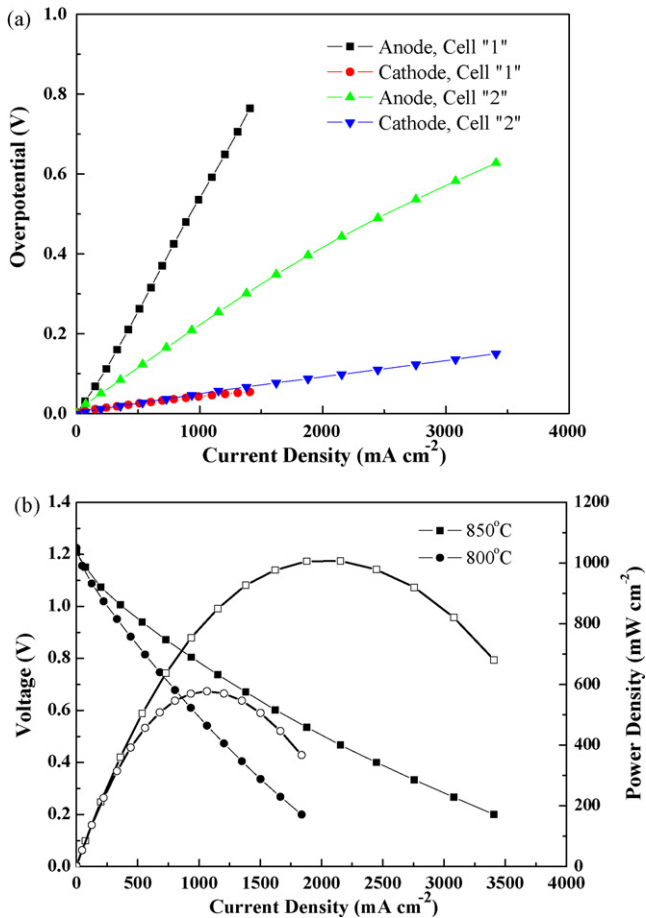


Fig. 4. (a) Comparison in electrode overpotential of two cells at 850 °C in dry H₂ (Cell "1": anode without Pd-impregnation; Cell "2": anode with Pd-impregnation); (b) voltage and power density of Cell "2" at different temperatures.

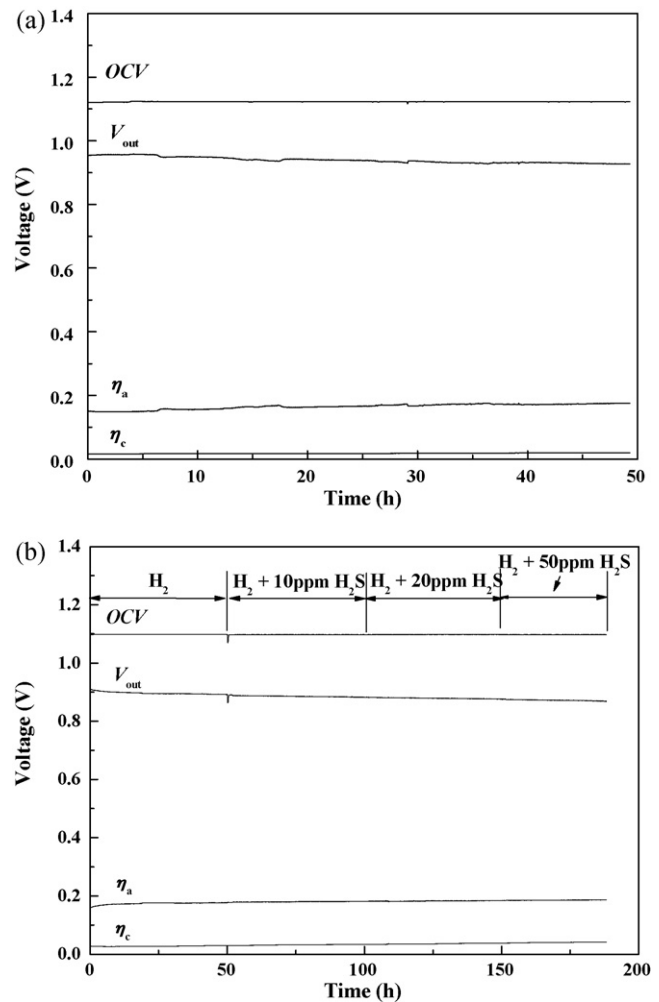


Fig. 5. The variation in OCV, output voltage, anodic and cathodic overpotential of single cells at 800 °C: (a) with the SYT/LDC anode in H₂ + 50 ppm H₂S fuels under a fixed current density of 208 mA cm⁻²; (b) with the Pd-impregnated SYT/LDC anode in H₂ and H₂/H₂S fuels under a fixed current density of 417 mA cm⁻² (V_{out} , output voltage; η_a , anodic overpotential; η_c , cathodic overpotential).

impregnation in dry H₂ at 850 °C. The cathodic overpotential was quite similar for the two cells, which is reasonable considering that the cathodes were identically prepared and the cathode performance should not be affected by the anode modification. With 1.5 wt.% of Pd infiltrated into the anode, the anodic overpotential in H₂ was reduced by half, as shown in Fig. 4a. Fig. 4b gives the voltage and power density of the cell with the Pd-impregnated SYT/LDC anode. The maximum power density of the cell was as high as 1006 and 577 mW cm⁻² at 850 and 800 °C in dry H₂, respectively, which was more than twice of that prior to impregnation. Clearly, the addition of a small amount of Pd into the SYT/LDC composite significantly enhanced the catalytic activity towards H₂ oxidation and therefore improved the anode and cell performance. Despite the excellent catalytic property, the relatively high cost of Pd may hinder its application in commercial SOFC anodes. Replacing Pd with some less expensive metals or alloys that could offer similar catalytic performance might be one of the choices.

The sulfur resistance of the SYT/LDC anode without Pd-impregnation was first evaluated and essentially no decay in anode overpotential was observed for about 50 h at 800 °C in H₂ + 50 ppm H₂S (Fig. 5a), which was consistent with the literature [17,27]. To investigate the sulfur tolerance of the Pd-impregnated anode, a single cell with the anode was run under a constant current density of 417 mA cm⁻² at 800 °C in H₂ containing various amounts of H₂S. As shown in Fig. 5b, the cell output voltage decreased slightly in the first few hours, which was followed by a stable performance in a 50 h operation in pure H₂. Upon switching the fuel to H₂/H₂S, the cell was operated for certain periods of time in H₂ containing 10, 20, and 50 ppm H₂S sequentially. As shown in Fig. 5b, during the exposure to various H₂/H₂S mixtures, the anodic overpotential showed essentially no decay and the slight degradation in cell performance was clearly due to the performance decrease of the cathode. Therefore, good sulfur-poisoning resistance was demonstrated for this anode. Compared to our recently reported amorphous LaMoO anode, which exhibited significant degradation in performance after exposure to H₂ + 50 ppm H₂S [13], the Pd-impregnated SYT/LDC composite clearly exhibited better tolerance to sulfur. In addition, the Pd-impregnated SYT/LDC composite might also have the potential for direct utilization of methane fuel. The performance of the anode in CH₄ and CH₄ + H₂S fuels will be investigated in the future.

4. Conclusions

Pd-impregnated SYT/LDC composite anode has been demonstrated as a sulfur-tolerant anode for SOFC application. Impregnation of a small amount of Pd into the SYT/LDC anode significantly enhanced the catalytic activity towards H₂ oxidation and therefore improved the anode performance. The single cell with the

Pd-impregnated SYT/LDC anode showed a maximum power density of 1006 and 577 mW cm⁻² at 850 and 800 °C in dry H₂, respectively. The single cell exhibited essentially no decay in anodic performance after exposure to H₂ containing up to 50 ppm H₂S.

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