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A New Sodium-ion-conducting Layered Perovskite Oxide as Highly Active and Sulfur Tolerant Electrocatalyst for Solid Oxide Fuel Cells

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Abstract

In this paper, a layered perovskite oxide NaLaTiO₄ with sodium-ion conductivity is proposed as a highly active, sulfur tolerant and stable anode for solid oxide fuel cells (SOFCs). The cell with NaLaTiO₄-infiltrated samaria-doped ceria (SDC) anode shows high power outputs and favorable stability over 200-hour operation with 1000 ppm H₂S-H₂ as fuel at 800 °C. The excellent sulfur tolerance of NaLaTiO₄ is attributed to its polarity, high surface basicity, oxygen vacancy concentrations and water storage capability. These results may open up new avenues for the design of high-performance, sulfur-tolerant anodes for SOFCs.

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Keywords: anode; layered perovskite oxide; sodium-ion conductor; solid oxide fuel cells; sulfur tolerance

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical energy conversion devices which can produce electric power directly from chemical energy. One distinct advantage of SOFCs is that in principle they can operate on any fuels at

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the anode as long as they are combustible. Although state-of-the-art Ni-based cermet anodes show high electrocatalytic activity for fuel oxidation reactions in the anode chamber [1], they can be poisoned by the sulfur impurity in hydrocarbon fuels even at an extremely low concentration (10 ppm). To overcome the sulfur poisoning challenge, developing novel anode materials is critical for the successful operation of SOFCs with fossil fuels.

Recently, we constructed a SOFC single cell with lithium-ion conductive $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ (LLTO) anode, which stably operated at 800 °C for 70 hours in H_2S -containing fuels without noticeable performance degradation and structural deterioration [2]. Another advantage of LLTO as an anode component is that any surface lithium that is lost due to evaporation/sintering can be recovered or compensated by the bulk diffusion because of the high Li^+ conductivity of LLTO, which accounts for the high stability of the LLTO-based anode material in SOFC operation at elevated temperatures. However, this LLTO perovskite anode suffered from relatively low electrocatalytic activity, the lack of lithium resources as well as the high cost of lithium, which presents a great challenge for commercial purposes and is in urgent need to be improved.

Herein, for the first time, we report a sodium-ion-conducting layered-structured NaLaTiO_4 (NLTO) perovskite oxide as a highly active and sulfur-resistant electrocatalyst for SOFCs. A composite anode with infiltrated NLTO into SDC scaffold was prepared and used as the anode for operating on H_2S -containing H_2 fuel with H_2S concentration up to 1000 ppm. High electrochemical activity, robust stability for H_2 oxidation, and excellent sulfur tolerance toward sulfur-containing fuels at intermediate temperatures was demonstrated for this novel anode. Such outstanding performance was associated with the high basicity, good polarity, favorable water storage capability and superior sodium-ion conductivity of the NLTO perovskite. These characteristics highlight the great potential of NLTO as an alternative sulfur tolerant anode for SOFCs that can boost the sustainable generation of clean energy.

2. Experimental

2.1. Powder synthesis and fabrication of the single cell

The $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) cathodes and SDC electrolyte used in this study were synthesized by an ethylenediaminetetraacetic acid (EDTA)-citrate complexing method [3]. The SDC electrolyte single-layer pellets were sintered at 1400 °C for 5 h and then polished to about 300 μm . The SDC scaffold with a porosity of ~50% was prepared by spraying deposition onto one side of the electrolyte followed by a subsequent calcination at 1250 °C for 5 h [2]. The cathode layer was also fabricated by a spraying deposition method on the other side of SDC single layer with an active area of 0.45 cm^2 , which was sintered at 1000 °C in static air for 2 h.

A solid state reaction approach was used to fabricate NLTO perovskite oxide. Stoichiometric amounts of Na_2CO_3 , La_2O_3 and TiO_2 were ball milled at 400 rpm for 30 min to obtain a homogeneously-dispersed mixture, followed by heating at 850 °C for 2 h to get the NLTO phase. NLTO precursor solution to be used in the infiltration process was prepared using NaNO_3 , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$. The detailed infiltration process is described elsewhere [4]. When the final loading reached ~30 wt.% of the scaffold, the infiltrated anode was sintered at 850 °C for 2 h in air. 10 wt.% Ni was added to the NLTO infiltrated anode to further enhance the electrocatalytic activity of the anode for H_2 electro-oxidation.

2.2. Characterization techniques

The crystal structures were studied by X-ray diffraction (XRD, Rigaku SmartLab) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$). The electrical conductivity of the anodes was tested by a four-probe DC method under a dry 10 vol. % H_2 -Ar atmosphere with temperatures ranging from 800 to 600 °C [2]. The sodium chemical diffusion coefficient of NLTO was calculated by an electrochemical impedance spectroscopy (EIS) method [5]. The I - V and I - P curves of the fuel cells were obtained by a Keithley 2420 source meter at 650-800 °C in the four-probe mode. During the cell

performance test, the cathode was exposed in the ambient air and the flow rates of H_2 or H_2S -containing fuels at the anode side were set to be 80 mL min^{-1} [STP].

3. Results and discussions

The microstructures of the infiltrated anodes were studied by SEM with the results given in Fig. 1. It can be observed that the blank SDC scaffold was well distributed with smooth particles and highly porous with a porosity of about 50%. Fig. 1b shows the SEM image of the NLTO-infiltrated SDC anode after calcination at 850°C and a subsequent reduction process in 3%- H_2O humidified H_2 at 800°C . Many NLTO nanoparticles with an average size of around 100 nm were heavily decorated on the inner wall of the SDC scaffold. To support the successful formation of NLTO in the infiltrated anode as well as the stability of NLTO in H_2 atmosphere, particles from infiltrated anode after reduction treatment were collected for high resolution TEM (HR-TEM) analysis. In Fig. 1c, a lattice spacing of 0.284 nm is observed at the near-surface region of the anode material, corresponding to the (103) plane of the NLTO phase. For a typical reduced NLTO-infiltrated SDC anode, the bulk of the particle can be recognized as the SDC-rich region whereas the outer layer can be regarded as the NLTO-rich region, which is evidenced by elemental distribution from EDX result shown in Fig. 1d. It was also found that the Na, La and Ti elements were uniformly distributed on the outer layer.

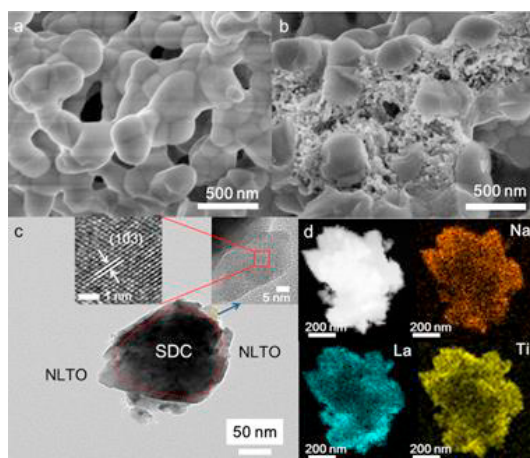


Fig. 1 SEM images of (a) blank SDC scaffold (b) reduced NLTO-infiltrated SDC anode, (c) TEM, HR-TEM images and (d) STEM-EDX mapping profiles of particles scraped from the reduced NLTO-infiltrated anode.

XRD patterns of above-mentioned infiltrated anodes were shown in Fig. 2a. It can be clearly seen that there were only two phases (SDC and NLTO) in the NLTO-infiltrated anode, suggesting no phase reaction between NLTO and SDC during the infiltration and reduction process. NaLnTiO_4 is a layered perovskite-type ceramic oxide in the Ruddlesden-Popper family with a general formula of $\text{A}_2[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]$, where A is an alkali, alkaline earth and/or rare earth metal; B is a transition metal; and m can be 1, 2, or 3 [6-8]. For $\text{Ln}=\text{La}$, Pr and Nd, the NaLnTiO_4 family show a tetragonal structure with the space group of $P4/nmm$. One feature of these layered compounds is that Na^+ and Ln^{3+} cations are ordered occupying sites between corners shared Ti-O octahedral layers while Ln^{3+} cations form a two-dimensional distorted square lattice [7, 8]. Similar to the sandwich structure, single layers of TiO_6 octahedra are separated in alternate layers by Na^+ and Ln^{3+} ions perpendicular to the c axis. The charge imbalance between Na^+ and Ln^{3+} ions both located at the interlayer is compensated by a displacement of the $\text{Ti}^{3+/4+}$ from the position of the regular octahedral center toward the Na^+ . There are many relatively free Na^+ in the NaLnTiO_4 structure, enabling high mobility of Na^+ in NaLnTiO_4 and high surface basicity. As a result, high sodium ion conductivity of NaLnTiO_4 can be achieved, the sodium chemical diffusion coefficient was calculated to be $4.66 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ using the reported method [5], which is among the highest values in the literature [9, 10], the possible sodium evaporation/loss on the NLTO surface can be compensated by sodium diffusion from the bulk. On the other hand, NLTO showed a good water storage capability due to the layered structure and exposed Na. As shown in Fig. 2b, the conductivity of the NLTO-infiltrated anode increased with the increasing temperature, peaking at about 0.26 S cm^{-1} at the

temperature of 800 °C. While this value is relatively low, it surpasses that of LLTO at the same temperature, indicating that NLTO may have a better electrochemical performance than LLTO.

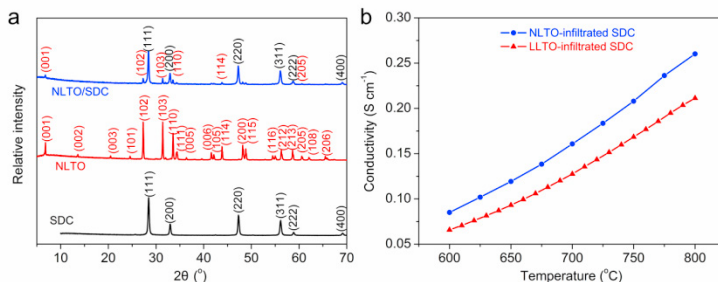


Fig. 2 (a) XRD patterns of SDC, NLTO and the NLTO-infiltrated SDC anode, (b) the electrical conductivity of the NLTO and LLTO-infiltrated SDC anodes in 10 vol.% H₂-Ar atmosphere.

To test the electrochemical performance, an SDC electrolyte-supported SOFC with a BSCF cathode was used. When operating on pure hydrogen, the cell with the NLTO-infiltrated anode exhibited a peak power density (PPD) of 277 mW cm⁻² at 800 °C (Fig. 3a). Surprisingly, when the fuel was switched to H₂S-containing hydrogen (i.e., 1000 ppm H₂S-H₂), the PPD experienced an enhancement by 12.6%, rising to 312 mW cm⁻² at the same temperature (Fig. 3b). This can be elucidated by the fact that H₂S promotes the catalytic oxidation of H₂ and increases the conductivity of Ti-based materials [11]. The fuel cell with the Ni-NLTO co-infiltrated anode generated a PPD of 446 mW cm⁻² at 800 °C when operating on H₂ fuel, this value appears very attractive considering the thick electrolyte used in this work. As depicted in Fig. 3c, with the addition of 1000 ppm H₂S to H₂, the area specific polarization resistance (R_p) of the cell decreased from 0.088 Ω cm² to 0.043 Ω cm² and the ohmic resistance decreased from 0.446 Ω cm² to 0.420 Ω cm². So NLTO-infiltrated fuel cell showed small R_p in H₂ and the value became even smaller with the addition of 1000 ppm H₂S, suggesting that the good activity of NLTO can be further promoted by H₂S [12]. Above results were in good agreement with the improvement of the PPD. The decline in R_p is attributed to the n-type semiconductor nature of NLTO, whose electronic conductivity was enhanced by H₂S. The lower ohmic resistance of the cell in H₂S-containing fuel can be ascribed to the formation of Ce-O-S in the SDC electrolyte, leading to the improvement of the conductivity of the SDC electrolyte [13].

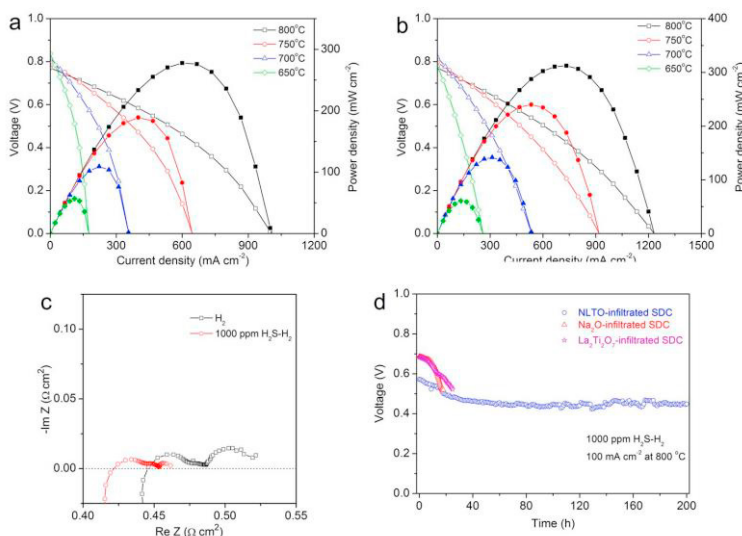


Fig. 3 *I-V* and *I-P* polarization curves of the SOFC single cell with NLTO-infiltrated anode operating on (a) H₂ and (b) 1000 ppm H₂S-H₂ fuels, (c) EIS spectra of SOFC single cell with NLTO-infiltrated anode operating on H₂ and 1000 ppm H₂S-H₂ fuels at 800 °C, (d) Stability test of the cell with NLTO-infiltrated, Na₂O-infiltrated and La₂Ti₂O₇-infiltrated anodes with 1000 ppm H₂S-H₂ as fuel at 800 °C.

To further demonstrate the high sulfur tolerance of the NLTO-infiltrated anode, the operational stability of the cells with SSC cathode operating on 1000 ppm H₂S-H₂ fuel was tested at 800 °C. As shown in Fig. 3d, a rapid decrease of the voltage was observed during the initial 40-hour operation with a decay rate of 0.0027 V h⁻¹, after which the cell voltage was found to be very stable at 0.45-0.46 V. The initial rapid decrease of the voltage may be caused by slightly poisoning and gradually reached equilibrium which was also reported in the literature [12]. Remarkably, there was not any obvious change of the voltage in the following 160-hour operation, giving a total decay rate of 0.00071 V h⁻¹ in the 200-hour operation. These results suggest that the NLTO-infiltrated SDC anode could afford stable operation under H₂S-containing conditions. For comparison, the operational stability tests were also conducted on the Na₂O and layered La₂Ti₂O₇ infiltrated SDC anodes. As shown in Fig. 3d, the cells with Na₂O or La₂Ti₂O₇ infiltrated SDC anodes were not stable in 1000 ppm H₂S-H₂ fuel. The quick decrease of the voltage may be due to lack of Na ions mobility and oxygen vacancy [14]. These results indicate that the use of a sodium-ion conductor as the SOFC anode is critical to achieve high sulfur tolerance.

Following the above analysis, the superior performance of the layered NLTO perovskite oxide as a sulfur-tolerant anode for SOFCs can be explained based on the mechanism as shown in Fig. 4. Firstly, the H₂ molecule in the fuel is oxidized by the O²⁻ from the cathode on the triple phase boundary (TPB) with the generation of water (Eq. 1); Secondly, water is adsorbed on the exposed Na sites in NLTO (Eq. 2) [15], at the same time, the water incorporation or storage into the perovskite oxide with the formation of the (OH)_o[•] species also occurs (Eq. 3); Then, the formed (OH)_o[•] or surface adsorbed water reacts with H₂S to generate SO₂ and H₂. Finally, SO₂ is removed from the Ni surface (Eq. 4 and Eq. 5), while H₂ is oxidized by O²⁻ to form H₂O. Furthermore, the high polarity of NLTO also allows the preferential adsorption of sulfur species on the [LaO]⁺ layer, thus promoting the oxidation of H₂S to SO₂.

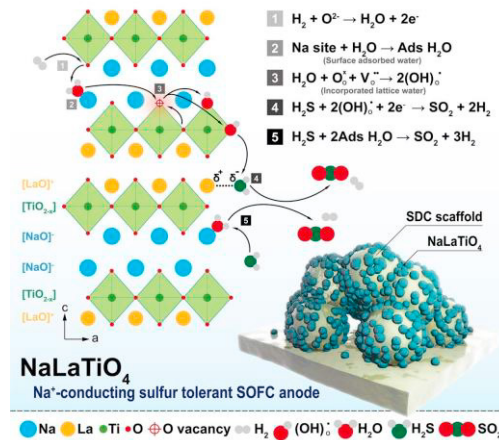
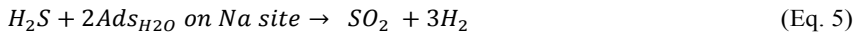
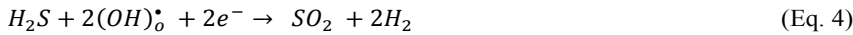
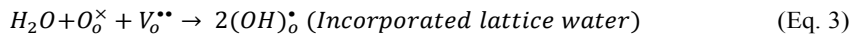
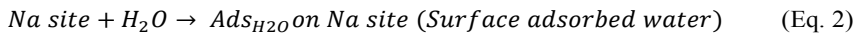


Fig. 4 Proposed mechanism for sulfur elimination process on the NLTO-infiltrated SDC anode.

4. Conclusions

In conclusion, a layered perovskite-type NLTO with a Ruddlesden-Popper structure was successfully synthesized into a porous SDC scaffold by an infiltration method to perform as a novel anode material for SOFCs, it exhibited a

favourable electrochemical stability over a 200-hour test using 1000 ppm H₂S-H₂ fuel at 800 °C. The excellent sulfur tolerance of NLTO was assigned to its polar structure, high surface basicity, rich oxygen vacancies and superior water storage capability, which promoted the elimination of adsorbed/deposited sulfur on the anode surface. The results in this work suggest that NLTO can be used as an efficient anode material to address the sulfur poisoning issue of SOFCs working on sulfur-containing fuels, which may propel the commercialization of the SOFC technology.

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