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Application of symmetric solid oxide fuel cell in fuel containing sulfur: I. Effect of electrodes

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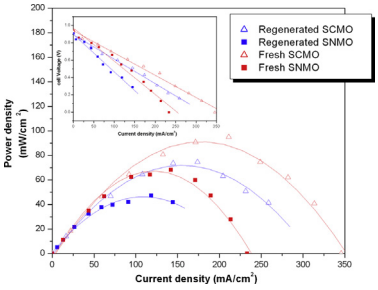
HIGHLIGHTS

- Symmetric SOFC with electrode Sr_2XMoO_6 was applied in fuel containing sulfur for the first time.
- Evaluations on catalytic activities and degree of sulfur poisoning of symmetric electrode.
- Sr_2CoMoO_6 is a good candidate for symmetric electrodes.
- Sulfur tolerance can be realized at lower temperature for Sr_2XMoO_6.
- Sr_2CoMoO_6 can be regenerated ex-situ in hot air.

GRAPHICAL ABSTRACT



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ABSTRACT

Symmetric solid oxide fuel cells (SFCs) with double perovskite materials serving as symmetric electrodes are applied for the first time in fuel containing sulfur, aiming to explore solution to sulfur poison. Temperature-programmed techniques, including H_2-TPR, O_2-TPD, were used to evaluate catalytic activities of electrodes in different atmosphere, while stabilities of electrode materials in sulfur containing fuel gas were characterized in terms of phase structures, conductivity, and microstructures by SEM, four-probe method and XRD as a function of temperature and operating time. It is evidenced that Sr_2CoMoO_6 (denoted as SCMO) possesses better hydrogen reducibility, oxygen desorption and stability in sulfur containing fuel gas. In configuration of Sr_2XMoO_6 (X = Co, Ni)|$Ce_{0.85}Sm_{0.15}O_{2-\delta}$ (SDC)|Sr_2XMoO_6, the maximum power density P_{max} reaches 95 mW cm^{-2} for SCMO and 68 mW cm^{-2} for SNMO with H_2-0.1% H_2S at 750 °C. Lower polarization resistance of SCMO (about 2.7 Ω cm^2 at 750 °C) is achieved. It is interestingly noted that SFC performance composed of ex-situ regenerated symmetric electrodes SCMO falls only by 21%, as compared to that of fresh electrodes. The combinations of thermal analysis (TG-DTA) and surface analysis (XPS) convince that an ex-situ regeneration of symmetric electrode can be realized.

1. Introduction

One of major challenges posed for the SOFC commercialization is how to operate SOFC in crude fuel gas besides pure hydrogen, because of severe material demands for crude fuel gas containing sulfur, phosphorus etc. Electrodes deactivated by these impurities cause the rapid decline of SOFC performance [1]. Thus, electrode

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materials with both electro-catalytically active and tolerant to crude fuel gas become a crucial issue.

Fortunately, some materials with perovskite structure are proved to resist sulfur well and applied as anodes in SOFC. For example, Tao et al. [2] verified that anode $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$(LSCMn) had good redox stability and performed well compared to traditional Ni–YSZ. Double perovskite Sr_2MMoO_6 (M = Mg, Fe, Co, Ni) has also been regarded as a promising MIEC with an excellent tolerance to sulfur since Goodenough et al. used $Sr_2Mg_{1-x}Mn_xMoO_{6-\delta}$ as anode during direct electrochemical oxidation of dry methane at 800 °C [3]. Most important of all, because of their redox stability both in reduced and oxidized atmosphere, these materials can be applied both as anode and cathode. In 2006, Chen [4] and Ruiz-Morales [5] proposed the concept of symmetric SOFC. The innovation on symmetric configuration of SOFC reduces costs greatly and meanwhile introduces new understanding about sulfur tolerance.

At present, more attention is paid to the redox stability and symmetric SOFC (SFC) performance of electrodes materials fueled by H_2 or/and CH_4 without introduction of H_2S [4–8]. Ruiz-Morales found that LSCMn-based SFCs with YSZ as electrolyte offered performances of 0.5 and 0.3 W cm^{-2} at 950 °C using H_2 and CH_4, respectively [6]. At lower temperature, single cell with configuration LSCrM|LSGM|LSCrM (M = Mn, Fe and Al) reached the best performance about 54 mW cm^{-2} at 800 °C in wet 5% H_2/Ar as fuel [7]. $La_{0.8}Sr_{0.2}Sc_{0.8}Mn_{0.2}O_3$(LSSM) [8] as well as (La,Sr)(TiFe)O_3(LSTF) [9] were successively tested in SFCs with H_2 or/and CH_4 as fuel gas. Other than ABO_3 oxygen-deficient perovskites, ordered double-perovskites $A_2BB'O_6$ are alternative for SFCs. So far, the highest power output reported in wet H_2 or CH_4 are 835 and 230 mW cm^{-2} at 900 °C, respectively, for SFC with double perovskite electrodes $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM)|LSGM|$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) [4].

Although Goodenough and Ruiz-Morales et al. claimed that SFC was one of solutions to sulfur tolerance for SOFC, few literature deal with the symmetric electrodes against sulfur operating in SOFC mode to our best knowledge. In this paper, Co and Ni were respectively doped into B site of double-perovskites Sr_2MoO_6 to fabricate SFCs with $Ce_{0.85}Sm_{0.15}O_{2-\delta}$ (SDC) serving as intermediate temperature electrolytes. The SOFC performances were presented when H_2 with 0.1% H_2S was used as fuel. The catalytic activities of symmetric electrodes in reduced and oxidized atmosphere were evaluated by means of H_2-TPR and O_2-TPD respectively. Their degree of sulfur poison and regeneration were explored by thermogravimetry analysis and XPS. For comparison, SFC performance composed of an ex-situ regenerated electrode was measured as well.

2. Experimental

2.1. Fabrications of symmetric SOFC

Sol–gel method was adopted to synthesize powders of Sr_2CoMoO_6 (SCMO) and Sr_2NiMoO_6 (SNMO). Detailed procedure was referred in Ref. [10]. The stoichiometric raw materials, $Sr(NO_3)_3$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $Co(NO_3)_2$ or $Ni(NO_3)_2$ were solved into a mixture of solution. EDTA as complexing agent was added and the pH value was adjusted to 9–10 by adding aqueous ammonia dropwise. After heating above solution on a hot plate, the gel obtained was then sintered at 400 °C for 6 h and 1300 °C for 24 h.

About 0.5 mm dense SDC electrolytes (15 mm in diameter) were prepared by dry pressing process and then sintered at 1300 °C for 8 h. Homemade electrode gel was prepared by mixing electrode powders (including fresh and regenerated powders) with turpentine and then was painted on both sides of electrolytes as symmetric electrodes with thickness about 40 um. Single cells in the configuration of Sr_2XMoO_6|SDC|Sr_2XMoO_6 (X = Co, Ni) were tested in H_2 with 0.1% H_2S as fuel and ambient air as oxidant respectively. Copper mesh was used to collect current, and the single cell performances were determined by *I–V* or *I–P* measurements at 650–750 °C. All performance data were collected by fuel cell tests instrument (SM-102 L43 Inc, Tianjin, China) after about 30 min when the potential/current data were stable. Impedance measurements were conducted under OCV condition with Versa STAT-4 (Princeton Applied Research, USA) analyzer from 0.1 Hz to 1 MHz with amplitude of 10 mV.

Three kinds of symmetric electrode powders used were labeled respectively as fresh, spent and regenerated samples. The so-called spent samples referred to those powders scraped from the anode side of single cell, which were beforehand exposed in fuel gas containing H_2S until SFC performance degraded (i.e., current closed to zero). The period lasted for about 3 h. These powders were applied for thermal analysis and XPS identification for sulfur species.

An ex-situ regenerated experiment was processed as follows and the obtained sample was called regenerated sample throughout the text. Hydrogen stream containing 0.1% H_2S was kept passing through fresh sample at 800 °C for 5 h, which was enough for SFC performance degradation. After cooling down to room temperature in 0.1% H_2S atmosphere, the stream was switched from 0.1% H_2S to air. The sample was then heated to 800 °C in air at a ramped temperature of 15 °C for purpose of regeneration.

2.2. Characterizations of symmetric electrodes

Stability experiments were performed on samples after exposure to 0.1% H_2S-containing atmosphere.

The symmetric electrode powders were identified by X-ray diffraction (XRD, Bruker D8 ADVANCE, Germany) using Cu$K\alpha$ radiation (λ = 0.15406 nm) at room temperature. And the diffraction patterns were registered over a 2θ range between 10° and 80°.

H_2 oxidation and O_2 desorption for symmetric electrodes materials were determined by programmed temperature measurements, i.e., H_2-TPR and O_2-TPD. The device is Micro-AutoChem II 2920 (Micromeritics, US) using 10% O_2/He as oxidative stream and 10% H_2/Ar as reductive stream, respectively. About 90 mg sample was first treated at 800 °C in O_2 for 1 h and cooled down to room temperature in the same atmosphere. In O_2-TPD experiments, the sample was heated to 800 °C at a rate of 10 °C min^{-1} in helium (12 mL min^{-1}) to record the spectra. In H_2-TPR experiments, the sample was heated to 800 °C at a rate of 10 °C min^{-1} in 10% H_2/Ar (60 mL min^{-1}) to record the spectra. The amount of H_2 consumed was calculated from the integrated peak area using Al_2O_3 as a standard, after peak integration/deconvolution was performed.

Scanning electron microscopy (SEM) analyses of the fresh and spent electrode materials were conducted using a Hitachi S4800 microscope scanning electron microscope.

Electrical conductivities of electrode materials were determined by DC four-probe method. A bar with dimensions of 2 mm × 5 mm × 12 mm was made and then sintered at 1200 °C for 2 h in air. Two silver wires were respectively attached at end of bar with silver paste to pass current. Meanwhile, the bar was bound by other two silver wires with good contact to detect voltage. Current data as well as voltage data were recorded at intervals of 50 °C over the range of 450–800 °C in H_2, 0.1 % H_2S–H_2 and air atmospheres. Electrical conductivity was calculated by $\sigma = L/RS$, where *L*, *S* and *R* were the length between two silver wires, section area of the bar and the resistance, respectively.