Electrochimica Acta 274 (2018) 91–102

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Pd-impregnated $Sr_{1.9}VMoO_{6-\delta}$ double perovskite as an efficient and stable anode for solid-oxide fuel cells operating on sulfur-containing syngas

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A R T I C L E I N F O

Article history:
Received 19 November 2017
Received in revised form
8 April 2018
Accepted 9 April 2018
Available online 13 April 2018

Keywords:
Solid oxide fuel cell
Double perovskite anode
Hydrocarbon fuel
Stability
Electrochemical performance

A B S T R A C T

The development of carbon- and sulfur-tolerant anode materials is highly desirable for the commercial application of solid-oxide fuel cells (SOFCs). We report herein the performance of $Sr_{1.9}VMoO_{6-\delta}$ (SVMO) double perovskite as a potential anode material for SOFCs and the improvement of its electrochemical performance on hydrogen and H_2S-containing syngas operation. SVMO has a cubic structure and thermal expansion coefficient of $13.3 \times 10^{-6}\ K^{-1}$ between 30 and 1000 °C in 5% H_2/Ar. The electrical conductivities of SVMO in H_2 are considerably higher than those of existing double-perovskite anodes and traditional Ni–YSZ (40 vol% Ni) anode. The impregnation of Pd nanoparticles to form a composite anode (Pd–SVMO) or the addition of a $Ce_{0.8}Sm_{0.2}O_{1.9}$ buffer layer between anode and electrolyte significantly improves the electrochemical performance of SVMO for hydrogen oxidation, and the former is considerably more effective than the latter. The Pd–SVMO composite anode exhibits good stability and resistance to carbon deposition and sulfur poisoning for an SOFC operated on H_2S-containing syngas based on an 80 h test, suggesting the potential of this anode material for SOFCs running on hydrocarbon fuels. The mechanisms for improving the electrochemical performance of the anodes and the resistance to carbon deposition and sulfur poisoning are also discussed.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that can convert chemical energy of fuel directly into electricity. SOFCs offer many advantages, such as high energy conversion efficiency, low pollution, and direct utilization of a variety of different hydrocarbon fuels, attracting considerable attention as energy conversion in the future [1,2]. Ni-based cermet is this traditional anode material, which exhibits excellent electrocatalytic activity for H_2 oxidation reaction. However, this traditional method encounters many problems, such as Ni particle sintering and coarsening during cell fabrication and operation, poor redox stability, and carbon deposition and sulfur poisoning when hydrocarbon fuels are directly used, resulting in a significant degradation of cell performance [3–6]. Therefore, developing an alternative anode material having a good structural stability and high carbon and sulfur resistance operating on hydrocarbon fuels is highly desirable.

A desired anode material should have high electronic conductivity and appropriate ionic conductivity over a wide range of oxygen partial pressures, high electrocatalytic activity toward fuel oxidation, and good chemical stability and thermal compatibility with the electrolyte and interconnect materials under SOFC operating conditions [5,7]. Perovskite oxides, doped $LaCrO_3$, doped $SrTiO_3$, and doped $SrVO_3$, have been studied as alternative anode materials [1,7–12]. Doped $SrTiO_3$ is one of the most widely studied hydrocarbon-fed SOFC anodes because of its high electronic conductivity under reducing conditions and redox stability. However, the oxygen ionic conductivity and catalytic activity for the fuel oxidation of this material is relatively low [7,10,13]. Similarly, the doped $LaCrO_3$ as anodes displayed low catalytic activity for oxidation of hydrogen and hydrocarbon fuels [14,15]. In doped $SrVO_3$, the most obvious advantage is that the material was reported to have inherent oxygen deficiencies, which in turn reveals a certain degree

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https://doi.org/10.1016/j.electacta.2018.04.066
0013-4686/

of catalytic activity for the fuel oxidation in H_2 and wet CH_4 fuels [16]. Further studies showed that the Vanadates had good sulfur tolerance when H_2S-containing fuels are used [17–20]. However, the insufficient catalytic activity to fuel oxidation and limited stability of the perovskite lattice are the main disadvantages of the Vanadates [16,20,21].

The double perovskite $Sr_2MgMoO_{6-\delta}$ (SMMO) was proposed as an anode material for SOFC because of its superior mixed ionic–electronic conducting feature and good electrocatalytic activity to the fuel oxidation [22–24]. For example, the power densities of the single cell with SMMO anode reached 838, 829, and 438 mW cm^{-2} at 800 °C in H_2, H_2 containing 5 ppm H_2S, and CH_4 fuels, respectively. The stability of the cell with SMMO anode in the three fuels indicated that the performance loss was very limited after 50 cycles of operation and no carbon or sulfur species were detected, indicating high tolerance to carbon deposition and sulfur poisoning [22]. Afterwards, the related molybdenum-based double perovskites $Sr_2MMoO_{6-\delta}$ ($M = Mn$, Fe, Co, and Ni) and their derivatives have also been developed as potential hydrocarbon-fed SOFC anodes [25–37], which either improved the electrocatalytic properties for fuel oxidation, increased the electrical conductivity or the stability, or both, showing some positive effects. However, subsequent studies demonstrated that only the SMMO double perovskite was stable in a wide range of oxygen partial pressures, while the Mn- and Fe-containing materials were unstable in oxidizing conditions, and the Co- and Ni-containing materials were unstable in reducing conditions [38–41]. Furthermore, the double perovskite SMMO was reported to manifest low electrocatalytic activity for the oxidation of H_2 and CH_4 without Pt current collector [42]. Therefore, improvement of the chemical stability and electrocatalytic activity will significantly promote the practical applications of the molybdenum-based double perovskites as anodes for SOFCs.

Recently, Weisentein et al. [43] and Childs et al. [44] reported the synthesis and electrical properties of $Sr_{2-x}VMoO_{6-\delta}$ ($x = 0$, 0.1, 0.2) double perovskites. The $Sr_{2-x}VMoO_{6-\delta}$ showed excellent electrical conductivity in a reducing atmosphere (The electrical conductivity of the Sr_2VMoO_6 reached 12000 S cm^{-1} at room temperature in the He-cryostat [45]). The electrical conductivity values of the samples were 1250, 3610, and 2530 S cm^{-1} at 600 °C in a 2.9% H_2O/4.9% H_2/92.2% N_2 atmosphere for $x = 0$, 0.1, 0.2, respectively, which is significantly higher than that of the traditional SOFC anode Ni/YSZ (50 vol% Ni; 989 S cm^{-1} at 600 °C [46]), and easily surpasses the desirable target value of 100 S cm^{-1} for electronic conductivity in an anode material [1]. The $Sr_{2-x}VMoO_{6-\delta}$ exhibited the highest electrical conductivity in the existing double-perovskite anodes [44]. Particularly, the $x = 0.1$ sample showed the highest electrical conductivity in the $Sr_{2-x}VMoO_{6-\delta}$ materials. However, the stability, compatibility, and electrochemical performance of the material as SOFC anode have not been studied.

As mentioned above, the V- and Mo-based perovskites have been observed to have good tolerance to sulfur. Furthermore, previous studies have shown that Mo–V–O oxides as catalysts for oxidation reactions manifested lower reducibility and oxidative dehydrogenation rates [47–49], which can be advantageous for the anode material to improve the stability as well as carbon and sulfur tolerance.

Therefore, taking all these factors into consideration, $Sr_{1.9}VMoO_{6-\delta}$ (SVMO) was selected and its feasibility as a potential anode material for use in SOFC operated on directly using hydrogen and commercial sulfur-containing syngas as fuels was investigated; this study is an extension of our previous work on Mo-based double perovskite anodes operated on commercial city gas [35,36]. The electrocatalytic activity of SVMO anode was improved by wet impregnation of the Pd nanoparticles into a porous SVMO anode or addition of a $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) buffer layer. The performance and stability of single cell with SVMO and Pd-impregnated SVMO (Pd–SVMO) as anodes, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) as electrolyte, and $NdBaCo_{2/3}Fe_{2/3}Cu_{2/3}O_{5+\delta}$ (NBCFC) as cathode were assessed in various fuels.

2. Experimental

2.1. Sample preparation and cell fabrication

$Sr_{1.9}VMoO_{6-\delta}$ (SVMO) powders were synthesized by a conventional solid-state reaction. $SrCO_3$ (99%), V_2O_5 (99%), and MoO_3 (99.5%) were weighed as the raw materials based on the constituent of SVMO and well mixed in an agate mortar for 2 h. The mixture was then calcined at 900 °C in 5% H_2/Ar for 10 h. The calcined powders were pelletized and finally sintered at 1200 °C in 5% H_2/Ar for 10 h to achieve a highly pure phase. NBCFC was prepared by the EDTA–citrate complexing method as described in previous work [50]. LSGM and SDC were prepared by glycine nitrate process (GNP) and sintered at 1450 and 1400 °C for 10 h, respectively. The sintered LSGM pellets were thinned to a fixed thickness of 300 μm or 200 μm, depending on the needs through polishing on both faces of the substrate. The impregnation of Pd was applied by using an aqueous solution of 0.1 M $Pd(NO_3)_2$. The solution was impregnated into the porous SVMO backbone at room temperature by using a microsyringe followed by heating at 850 °C for 0.5 h in nitrogen to form Pd species and subsequent Pd–SVMO composite anode. For comparison, NiO–YSZ (YSZ: $Zr_{0.84}Y_{0.16}O_{1.92}$; 40 vol%Ni) composite anodes were prepared by the GNP and sintered at 1380 °C for 6 h in air. Ni–SDC/SDC/LSGM (300 μm thickness)/NBCFC and Ni–YSZ/YSZ/NBCFC cells were also prepared.

The electrochemical performances of the anodes were studied by electrochemical impedance spectroscopy (EIS) using symmetrical cell configuration. SVMO electrode powders were thoroughly blended with the ethyl cellulose (binder, 6%) and terpineol (solvent, 36.3%) to form slurry. The anode layers were screen printed symmetrically onto both sides of the LSGM electrolyte, and then calcined at 950 °C for 5 h in nitrogen. Electrolyte-supported single cells with the anode/SDC/LSGM/NBCFC configuration were prepared by screen-printing method, where a 200-μm-thick LSGM pellet was used as the electrolyte, SVMO/Pd–SVMO were used as the anodes, NBCFC was the cathode, and SDC was used as a buffer layer between the anode and the electrolyte. The thin SDC buffer (~8 μm thickness) was screen printed onto the LSGM electrolyte, followed by firing at 1300 °C for 1 h in air. SVMO was screen printed on one side of the LSGM electrolyte, and NBCFC was screen printed on the other side of the LSGM and co-fired at 950 °C for 5 h. The firing process of the anode and cathode was conducted in nitrogen atmosphere [35]. Ag grids were printed on the anode and cathode surfaces with silver paste as the contact layers for current collection. The single cells were sealed onto an alumina tube using silver paste as sealant. The single cell performances were monitored using an electrochemical workstation. Hydrogen- and commercial sulfur-containing syngas were used as fuels, and oxygen was used as oxidant in a flow rate of 100 mL min^{-1}.

2.2. Characterization

The crystal structure of the anode material and chemical compatibility with the electrolytes were determined by X–ray diffraction (XRD, Rigaku D/Max–2550) using Cu Kα radiation (λ = 1.5418 Å) at room temperature with a 0.02° step size. The full pattern Rietveld refinements were performed using the FULLPROF software package as described elsewhere [51]. Raman spectroscopy was used to monitor the formation of solid carbon and sulfide