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Short communication

Porous $Sr_2MgMo_{1-x}V_xO_{6-d}$ ceramics as anode materials for SOFCs using biogas fuel

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ABSTRACT

$Sr_2MgMo_{1-x}V_xO_{6-d}$ ($x = 0$–0.2) materials with double perovskite structure were synthesized by sol–gel method, and studied for the possibility of being the anode of solid oxide fuel cells (SOFCs) with biogas as the direct fuel. The sample of $Sr_2MgMo_{0.95}V_{0.05}O_{6-d}$ synthesized in 5%H_2/Ar showed a conductivity higher than the samples with $x > 0.05$, but close to the sample without V. Besides, it showed better catalytic activity, stability, and H_2S tolerance (up to 1% of H_2S in the feed gas) for biogas combustion than the sample without V. This sample is promising for the anode of SOFCs using biogas fuel.

1. Introduction

Biogas is an excellent renewable energy containing 40–70% CH_4, 25–50%CO_2, 0.005–1% H_2S [1], and some other impurities. Presently, biogas has been utilized as the fuels for cooking, thermal power generating, transportation, and so on. Unfortunately, these utilizations are relatively inefficient and pollutive.

Theoretically, biogas can be used to generate power high efficiently (60–90%) and cleanly by means of solid oxide fuel cells (SOFCs) [2]. But, presently, the direct use of biogas as the fuel for SOFCs is still limited due to the H_2S contamination on the anode [3–12]. Researches on various Ni based anodes [5–8] revealed that these anodes tolerated H_2S less than 100 ppm in H_2, and had the problems of H_2S poisoning and carbon deposition for direct biogas SOFCs.

Gorte et al. [9] found that at 1073 K Cu–CeO_2–YSZ anode could tolerate H_2S up to 450 ppm in H_2, and had no carbon deposition for methane fuel. Fuerte et al. [10] found that at 1023 K Cu–Co–CeO_2 anode could tolerate H_2S up to 1000 ppm in H_2, and also had no carbon deposition for methane fuel. Although Cu–Co–CeO_2 anode is better than others in H_2S tolerance and anti-carbon deposition, it does not yet meet the requirements for the biogas SOFCs because its H_2S tolerance is not yet up to the maximum level in biogas (about 1%) [1], besides, the single cell with this anode and CSO electrolyte (0.22 mm) could only produce a very low power density (0.1 W/cm^2) [10].

Many researchers studied metal oxide anodes [11,12]. Huang et al. [12] synthesized an anode material of Sr_2MgMoO_{6-d}(SMM) with double perovskite structure. They found that the single cell with this anode and LSGM electrolyte (0.3 mm) could produce the maximum power density at 1073 K of 0.838 W cm^{-2} for H_2 and 0.44 W cm^{-2} for CH_4, much higher than the single cell with the Cu–Co–CeO_2 anode [10]. Besides, no carbon deposition was observed for methane fuel. Unfortunately, this anode could only tolerate H_2S up to 50 ppm in H_2. If this anode can be further improved to tolerate H_2S up to the maximum level in biogas (about 1%), it should be an excellent anode for direct biogas SOFCs.

Considering that V^{5+} is close to Mo^{6+} in size, and V_2O_5 is an excellent sulfur-tolerating catalyst for oxidation reactions, partially replacing Mo^{6+} in SMM with V^{5+} is not only possible, but also has the possibility to improve the H_2S tolerance, the catalytic activity for biogas combustion, and even the electric conductivity. However, to the best of our knowledge, there is no study, so far, reported on this possibility.

In this study, $Sr_2MgMo_{1-x}V_xO_{6-d}$ ($x = 0$–0.2) materials were synthesized. The effect of V content was investigated on the structure, the conductivity, the catalytic activity and stability for biogas combustion, and the H_2S tolerance. A sample was found quite promising for the anode of biogas SOFCs.

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2. Experimental

2.1. Sample synthesis

$Sr_2MgMo_{1-x}V_xO_{6-d}$ (x = 0–0.2) samples were synthesized by the sol–gel method with citric acid as the chelating agent and $Sr(NO_3)_2$, $Mg(NO_3)_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and NH_4VO_3 as the starting materials. A mixed aqueous solution was prepared by dissolving the starting materials and citric acid into distilled water, and then evaporated at 353 K until the gel was formed. The gel was decomposed at 873 K in air for 4 h and then calcined at 1073 K for 10 h. The obtained powder was ground, pelletized, and fired in air three times each at different temperatures (1473 K, 1573 K and 1673 K) for 10 h, or fired in 5% H_2/Ar two times each at 1373 K for 24 h. The synthesized $Sr_2MgMo_{1-x}V_xO_{6-d}$ (x = 0–0.2) samples were denoted as SMMVx. The sample with x = 0 was denoted as SMM.

2.2. Sample characterization

The samples were characterized by XRD (Rigaku D/max-IIB), electro-chemical working-station (LK-2005), and ICP-AES (SPS8000) respectively for crystal structures, electrical conductivities, and chemical compositions.

2.3. Catalytic activity test

The catalytic activity of the samples for biogas combustion was tested on a fixbed reactor (8 mm i.d.) at 573–973 K and under atmospheric pressure with reactant mixtures of 6%CH_4, 6%O_2, 4%CO_2, 0 or 1%H_2S, and 84 or 83%N_2 at a total flow rate of 100 ml min^{-1}. The sample (60–80 mesh, 0.5 g) was loaded into a tubular quartz reactor (8 mm i.d.) and kept in the isothermal center part of the reactor. The measurements were performed under static isothermal conditions and the reaction temperature was increased step-by-step until the methane conversion reached the maximum under the reaction conditions. After the stabilization at each temperature for 30 min, the reaction products were analyzed.

The method provided in ref. [13] was used to analyze the reactants and products with a gas chromatograph (Shimadzu GC-9A) equipped with a TCD detector and three columns (propak Q, soda lime, and 5A molecular sieve) in series. Concentrations of the monitored gas components were calculated by the calibration of the standard gas mixture in the known quantities. The methane conversion was calculated according to the concentrations of methane at the inlet and outlet of the reactor.

3. Results and discussions

We found that the analyzed chemical compositions of the synthesized samples were all consistent with the designed compositions.

3.1. Structures of SMMVx samples

We firstly investigated the synthesis of SMM sample, and found that the best firing conditions were firing three times in air each at different temperatures (1473 K, 1573 K, 1673 K) for 10 h or firing two times in 5%H_2/Ar each at 1373 K for 24 h. Under the best firing conditions, the main phase of Sr_2MgMoO_6 in the synthesized SMM sample reached the maximum, while the impurity phases reached the minimum. Therefore, the best firing conditions were used to synthesize SMMVx samples.

Fig. 1 shows the XRD patterns of SMMVx (x = 0–0.2) synthesized in air. In addition to some tiny peaks at 24–31°, all the other peaks can be attributed to the $Sr_2MgMo_{1-x}V_xO_{6-d}$ phase of double perovskite structure [12]. The sample with x = 0 might have impurity phase of $SrMoO_4$ (27.7°), but the samples with x > 0 might have impurity phase of $Sr_3(VO_4)_2$ (28.7°).

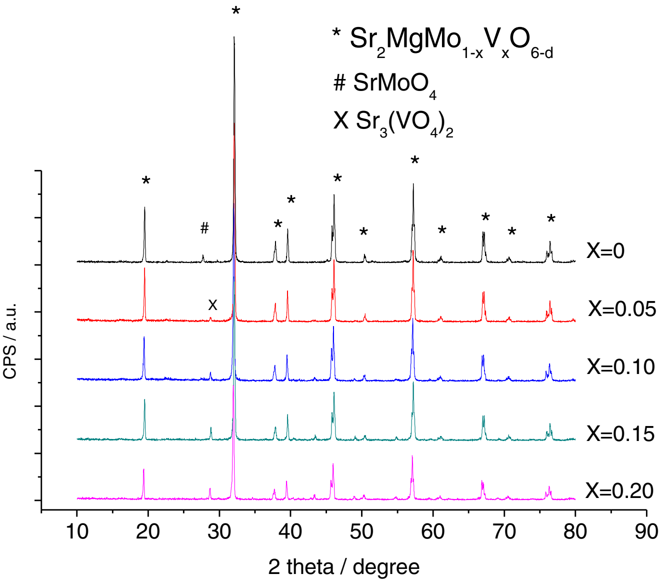

Fig. 1. XRD patterns of SMMVx (x = 0–0.2) synthesized in air.

Fig. 2 shows the XRD patterns of SMMVx (x = 0–0.2) synthesized in 5% H_2/Ar. In addition to a few tiny peaks at 24–31°, the other peaks are all attributed to $Sr_2MgMo_{1-x}V_xO_{6-d}$ phase of double perovskite structure [12]. The sample with x = 0 might have two impurity phases of $SrMoO_4$ (27.7°) and Sr_3MoO_6 (30.8°), but the V-containing samples might have impurity phases of SrV_2O_6 (29.6°) and Sr_3MoO_6 (30.8°).

The results in Figs. 1 and 2 demonstrate that $Sr_2MgMo_{1-x}V_xO_{6-d}$ materials of double perovskite structure with trace of impurities can be synthesized either in air or in 5% H_2/Ar. Chattopadhyay et al. [14] had successfully synthesized $Sr_2FeMo_{1-x}V_xO_{6-d}$ materials of double perovskite structure, suggesting that the Mo^{6+} in Sr_2MgMoO_6 lattice could be partially replaced by V^{5+}.

3.2. Conductivities of SMMVx samples

The conductivities (σ) of the SMMVx samples (x = 0–0.2) synthesized in air or 5%H_2/Ar were measured in air or H_2, and were presented in the curve of ln(σT) vs 1000/T.

For the samples synthesized in air, the atmosphere for conductivity measurement did not affect the conductivities of the samples

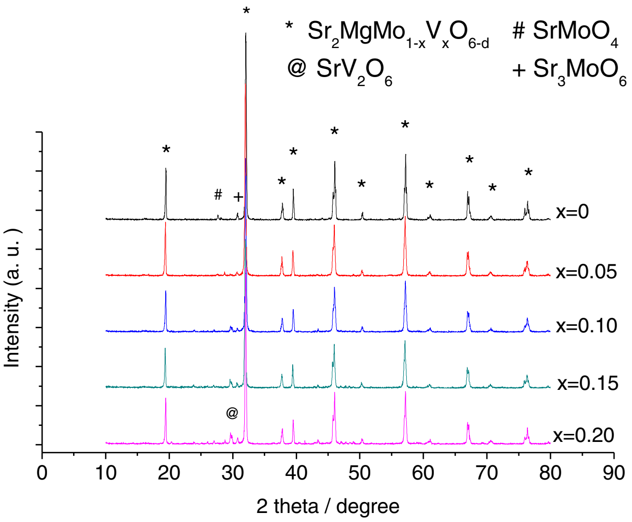

Fig. 2. XRD patterns of SMMVx (x = 0–0.2) synthesized in 5% H_2/Ar.