Journal of Alloys and Compounds 708 (2017) 451–455

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

The electrochemical behavior of the promising $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ + $Ce_{0.8}Sm_{0.2}O_{1.9-\delta}$ anode for the intermediate temperature solid oxide fuel cells

D.A. Osinkin [a, b, *], N.I. Lobachevskaya [c], A. Yu. Suntsov [c]

[a] Institute of High-Temperature Electrochemistry, 20 Academicheskaya St., 620137, Yekaterinburg, Russia
[b] Ural Federal University, 19 Mira St., 620002, Yekaterinburg, Russia
[c] Institute of Solid State Chemistry, 91 Pervomayskaya St., 620990, Yekaterinburg, Russia

ARTICLE INFO

Article history:
Received 30 January 2017
Received in revised form
28 February 2017
Accepted 6 March 2017
Available online 7 March 2017

Keywords:
IT-SOFC
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$
SFM
Anode
Polarization resistance
DRT

ABSTRACT

A promising $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ + $Ce_{0.8}Sm_{0.2}O_{1.9-\delta}$ IT-SOFC anode material in contact with the lanthanum gallate based electrolyte in H_2+H_2O + Ar gas mixtures was studied. The anode has the polarization resistance nearly 0.3 Ω cm^2 at 700 °C that is considered as the acceptable value for the practical application in IT-SOFC. The distribution of relaxation time curves showed that the electrode reaction was limited by two rate-determining steps within the frequencies range 10–0.01 Hz. The opposite behavior of the polarization resistance vs. water and hydrogen partial pressure was founded. This behavior was explained by the low electrochemical activity of the anode to the water dehydrogenation. The additive of nickel into the anode resulted in the reduction of the polarization resistance and increase the rate of the water dehydrogenation. A long-term test carried out during 500 h at 700°C in a humid hydrogen demonstrated the exponential behavior of the polarization resistance. The weight decrease of about 4.5% for $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ powder in Ar + 5%H_2 at 700 °C within the 300 h the exposure was observed.

1. Introduction

Solid oxide fuel cells (SOFCs) are promising energy conversion systems. The most distinctive feature of SOFCs is the possibility to convert various kinds of fuel: hydrogen, simple and complex hydrocarbons, syngas, alcohols etc. However, materials used for SOFCs components production have some shortcomings, for example: the low conductivity of the doped zirconium oxide based electrolytes (YSZ) at medium temperatures [1], the interaction of lanthanum manganite based cathodes with YSZ at high temperatures [2,3], the degradation of nickel-cermet anode [4,5] etc. The high operation temperature of conventional SOFCs (near 900°C) also have a negative influence on the stability of their components. Therefore, the development of new materials for intermediate temperature SOFCs is of great current interest.

To date, the most studied alternative anode materials are doped titanium, chromium and manganese oxides. However, they do not have practical application in SOFCs due to their low conductivity and electrochemical activity, chromium evaporation and secondary phase formation on the electrolyte/electrode boundary etc. [6–9].

A new promising direction is the development of the anode materials based on strontium molybdate. The interest to these oxides is caused by the high value of electric conductivity of the basic $SrMoO_{3-\delta}$ oxide, about 10 kS/cm at room temperature for polycrystalline and more than 100 kS/cm for monocrystalline sample [10]. In the reduction environment the doped strontium molybdate may demonstrate the high electric conductivity due to the reduction of molybdenum ions [11]. The following compositions of doped strontium molybdates should be noted: $Sr_2VMoO_{6-\delta}$ due to the high electric conductivity (more than 10 kS/cm) after sintering in reducing atmosphere [12]; $Sr_2MgMoO_{6-\delta}$ due to the high chemical stability [13]; $Sr_2FeMoO_{6-\delta}$ due to the sufficient level of electric conductivity after the reduction sintering and the ability to operate in carbon containing atmospheres [14]. The necessity of reduction sintering of strontium ferrite-molybdate may be eliminated if the ratio Mo/Fe is changed from 1/1 to 0.5/1.5 [15]. The disadvantage of the molybdenum-containing electrodes materials is interaction with the zirconium oxide based electrolytes. However, they are chemically inert to the lanthanum gallate and cerium

* Corresponding author. Institute of High-Temperature Electrochemistry, 20 Academicheskaya St., 620137, Yekaterinburg, Russia.
E-mail address: OsinkinDA@mail.ru (D.A. Osinkin).

http://dx.doi.org/10.1016/j.jallcom.2017.03.057
0925-8388/

oxide based materials.

It is well known that the production of the composite material is an effective approach to improve the most important functional properties of the electrode [16]. In Ref. [17] it was reported that the addition of 10 wt.% of $Ce_{0.8}Sm_{0.2}O_{1.9-\delta}$ to $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ leads to the anode polarization resistance decrease. The further increase of $Ce_{0.8}Sm_{0.2}O_{1.9-\delta}$ concentration (up to 40 wt. %) in the anode leads to no significant changes of the anode electrochemical activity. Notwithstanding the relevance of the composite $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ - based anodes, they are not well investigated. The present work aims to the study the anode kinetics, concentration dependencies and stability of 90 wt.% $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ + 10 wt.%$Ce_{0.8}Sm_{0.2}O_{1.9-\delta}$ composite anode.

2. Experimental

The citrate method and combustion synthesis for obtaining of $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) and $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) respectively, were used. After the synthesis SFM powder was sintered at 1100°C for 5 h and SDC at 700 and 1100°C for 8 h. The composite 90 wt.% SFM + 10 wt.% SDC (SFM + SDC) powder was prepared by mixing the powders in the required mass proportions in the ethylene alcohol media for two hours in a Retsch PM 100 ball mill.

The electrode slurry was prepared by mixing SFM + SDC powder with polyvinylbutyrol and isopropyl alcohol. The slurry was applied onto the both sides $La_{0.85}Sr_{0.15}Ga_{0.85}Mg_{0.15}O_3$ (LSGM) electrolyte tablet [18]. After sintering at 1200°C for two hours in air, the electrode area and thickness were about 0.3 cm^2 and 25 μm, respectively.

At the last stage of the sample preparations the certain samples were impregnated by a saturated solution of nickel nitrate. Then the samples were annealed at 600 °C in a humid hydrogen atmosphere for 1 h. Weighing the samples before and after the impregnation showed that the specific mass of the introduced nickel was approximately 0.9 mg/cm^2. No additional current layers were put on SFM + SDC.

The powder phase compositions were determined using a Rigaku D/MAX-2200VIPC X-ray diffractometer. The specific surface area of the powders was measured by the method of low temperature nitrogen absorption using a SORBI N4.1 device. The microphotographs and maps of the element distribution were taken by a TESCAN MIRA 3 LMU scanning electron microscope. Thermogravimetric measurements were carried out with a Setaram Setsys Evolution thermoanalyzer with the accuracy better than 0.01 mg. The electrochemical studies were performed by means of the impedance spectroscopy in the frequency range of 10^4–10^{-2} Hz using a FRA-1260 and EI-1287 electrochemical interface. A Pt mesh and wires were used as current collectors. In the present work a program code, developed by the authors of [19], based on Tikhonov's regularization was applied for distribution of relaxation time (DRT) analysis.

The high-temperature studies were performed in water-hydrogen-argon mixtures at the atmospheric pressure. For the preparation of gaseous mixtures Ar and H_2 of the purity of 99.99 vol.% were used. The water partial pressure was set by the humidifier temperature, through which the hydrogen and argon flow passed. A sketch of the experiment setup is described in Ref. [4].

3. Results and discussions

3.1. Materials characterization

The XRD patterns of SFM, SDC and SFM + SDC are shown in Fig. 1. In order to obtain the reliable data of unit cell parameters the structure analysis was performed based on a Rietveld refinement using the FULLPROF software [20]. The structure of mixed oxides $Sr_2Fe_xMo_{2-x}O_6$ with x close to 1.0 presents a cubic perovskite with doubled unit cell parameter a_p = 7.845 Å and is commonly described with the use of *Fm*-3*m* space group [21,22]. In case of x deviates from 1.0 the ordering degree gradually decreases on increasing Fe content leading to transformation of the space group into *Pm*-3*m* [15]. Since the present study is devoted to compound with x = 1.5 the disordered type of structure was considered. As a result, the spectrum of SFM was successfully refined in the *Pm*-3*m* space group with the unit cell parameter a_p = 3.92719 Å. The SDC reflexes have a low intensity, is related with the small amount (10 wt. %) of SDC in SFM + SDC composite.

The microphotographs of SFM and SDC powders are presented in Fig. 2. As can be seen, SFM phase has a larger particle size of several microns, while SDC powder consists of the fine particle agglomerates. The measurement of the powder specific surfaces showed that they were about 1.35 and 12.2 m^2/g for SFM and SDC, respectively. Such a difference occurs due to the different powder preparation methods.

3.2. Electrochemical measurements

The SFM + SDC/LSGM cell impedance spectra at different temperatures in humid (3% H_2O) hydrogen and DRT curves are presented in Fig. 3. For a better perception, the cell serial resistance was subtracted from the spectra. The DRT curves demonstrate the presence of two peaks in the frequency ranges of 10–1 and 1–0.1 Hz, which corresponds two rate-determining steps of the electrode reaction. In Ref. [17] it was noted that SFM + SDC anode reaction was limited by low frequency steps. Taking into account the low frequency range, the surface diffusion and/or adsorption of species may be suggested as the rate-determining. However, it should be noted, that at the temperature increase the low frequency resistance decreases, which is represented by the peaks

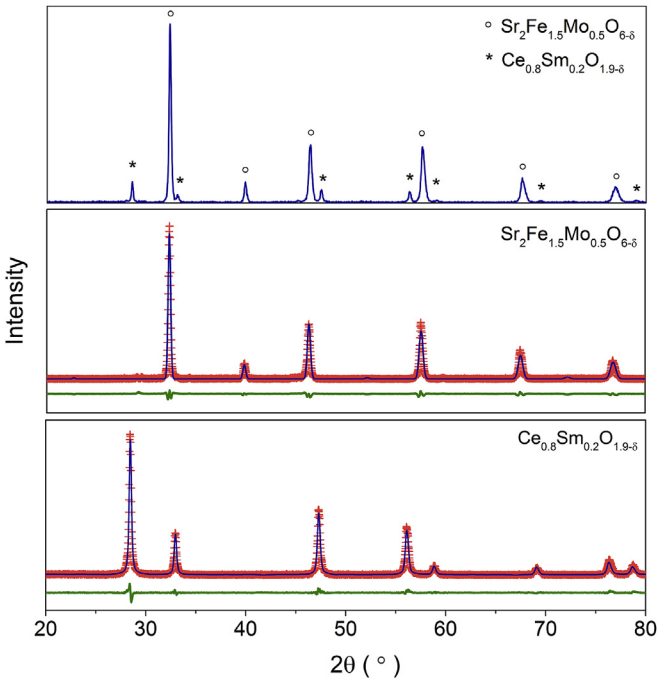

Fig. 1. XRD spectrums of 90 wt.% $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ + 10 wt.% $Ce_{0.8}Sm_{0.2}O_{1.9-\delta}$ composite (top) and refinement results for $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ and $Ce_{0.8}Sm_{0.2}O_{1.9-\delta}$ (middle and below).