Solid State Ionics 181 (2010) 754–759

Contents lists available at ScienceDirect

Solid State Ionics

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

Isovalent and aliovalent substitution effects on redox chemistry of $Sr_2MgMoO_{6-\delta}$ SOFC-anode material

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ARTICLE INFO

Article history:
Received 10 November 2009
Received in revised form 13 March 2010
Accepted 29 March 2010

Keywords:
Double-perovskite oxide
Cation substitution
Degree of *B*-site cation order
Oxygen non-stoichiometry
Redox chemistry
XANES spectroscopy
Solid oxide fuel cell

ABSTRACT

An SOFC-anode material, $Sr_2MgMoO_{6-\delta}$, is investigated for both isovalent and aliovalent substitution effects at its redox-active cation site. Isovalent W^{VI}-for-Mo^{VI} substitution has little effect on crystal and redox chemistry of the phase, whereas aliovalent Nb^{V}-for-Mo^{VI} substitution lowers the degree of cation order and, rather importantly, creates oxygen vacancies in the lattice. The increased oxygen-vacancy concentration should be a positive factor regarding the SOFC-anode performance, but a disadvantage is that electrical conductivity is slightly depressed in $Sr_2Mg(Mo,Nb)O_{6-\delta}$ with increasing Nb content. The two systems, $Sr_2Mg(Mo,W)O_{6-\delta}$ and $Sr_2Mg(Mo,Nb)O_{6-\delta}$, are found stable (up to 1000 °C or higher) in both reductive (5% H_2/Ar) and oxidative (air) atmospheres, the range of oxygen-content variation upon such redox-cycling getting narrower with increasing substitution level. XANES data at the *L* edges of Mo, W and Nb reveal that in $Sr_2Mg(Mo,W)O_{6-\delta}$ both Mo and W show variable oxidation states whereas in $Sr_2Mg(Mo,Nb)O_{6-\delta}$ Nb is more redox-active than Mo.

1. Introduction

Solid oxide fuel cells (SOFCs) are promising devices for directly converting the chemical energy of fuels to electrical energy in applications ranging from large-scale power plants to small vehicle auxiliary power units [1–4]. The state-of-the-art SOFC with a Ni-based anode is highly efficient when hydrogen is used as a fuel [5], but tends to have some fatal problems with hydrocarbon fuels unless the fuel is reformed before use [1–4]. Ceramic mixed ionic-electronic conductor (MIEC) materials can overcome many of the most severe problems of the Ni-based anodes, such as poor redox stability, carbon build-up (coking) and sulphur poisoning [2–4]. The $Sr_2MgMoO_{6-\delta}$ oxide is one of the most promising new anode materials. It has been found to yield high power densities when using methane as a fuel, and to have good tolerance to sulphur [6,7]. In addition, partial substitution of Sr^{II} by La^{III} was reported to enhance the SOFC-anode performance of $(Sr,La)_2MgMoO_{6-\delta}$ for hydrocarbon fuels [8], but with the cost of lower stability under oxidizing conditions [9].

The $Sr_2MgMoO_{6-\delta}$ oxide has a *B*-site ordered $A_2B'B''O_6$ double-perovskite structure, derived from that of the simple perovskite, ABO_3, by having the *B*-cation site occupied by two different cation species, B' and B'', of equal amounts. In $Sr_2MgMoO_{6-\delta}$, the ordering between the two *B*-site cations, Mg^{II} and Mo^{VI}, is nearly perfect as the two cations differ enough from each other both in charge and size. It is, however, believed that a certain relation exists between ordering and concentration of oxygen vacancies in the material such that with increasing oxygen-vacancy concentration the degree of *B*-site ordering is lowered [10]. The oxygen-deficiency parameter, δ, of $Sr_2MgMoO_{6-\delta}$ is indeed important from the view point of SOFC-anode performance: oxygen vacancies both facilitate efficient oxide-ion conductivity and control the degree of mixed valency of molybdenum and thereby the electrical conductivity [6,7].

In this work we substitute the redox-active element Mo in $Sr_2MgMoO_{6-\delta}$ by its two periodic-table neighbours, W and Nb. Hexavalent tungsten is similar in both charge and size to Mo^{VI} and the structural/chemical changes due to the substitution are expected to be minimal, whereas replacing Mo^{VI} by the lower-valent Nb^{V} is expected to affect the redox chemistry of the system. We systematically characterize the samples for their crystal structure, oxygen stoichiometry, reducibility and electrical conductivity to show that indeed the replacement of Mo by W offers no apparent advantages regarding the material's possible use as a SOFC anode, whereas Nb-for-Mo (partial) substitution seems promising.

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doi:10.1016/j.ssi.2010.03.037

2. Experimental

Two sample series, $Sr_2Mg(Mo_{1-x}W_x)O_{6-\delta}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) and $Sr_2Mg(Mo_{1-x}Nb_x)O_{6-\delta}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8$ and 1.0), were prepared through solid-state reaction from stoichiometric mixtures of $SrCO_3$, MgO, MoO_3, Nb_2O_5 and W powders. Each powder mixture was first calcined in air at 900 °C for 12 h, and then after regrinding pressed into pellets (13 mm in diameter and 1–2 mm in thickness) and sintered in air. Pristine $Sr_2MgMoO_{6-\delta}$ and W-substituted $Sr_2Mg(Mo_{1-x}W_x)O_{6-\delta}$ samples were sintered at 1200 °C for 36 h and Nb-substituted $Sr_2Mg(Mo_{1-x}Nb_x)O_{6-\delta}$ samples at 1500 °C for 48 h. Typically one-time sintering was enough, but for $Sr_2MgWO_{6-\delta}$ second grinding and sintering for 36 h was needed.

Phase purity and crystal-structure details of the samples were examined by X-ray powder diffraction (XRD; Philips MPD 1880) using Cu K_α radiation. The XRD patterns were analyzed with a Rietveld refinement program FULLPROF [11] using triclinic space group *I*-1 (which can be thought of as a different setting of the *P*-1 space group). This space group was successfully utilized for $Sr_2MgMoO_{6-\delta}$ by Bernuy-Lopez et al. [10], who found that while the structure of $Sr_2MgMoO_{6-\delta}$ is metrically tetragonal, the triclinic space group is required to properly describe the structure due to distortions of the MO_6 octahedra. The degree of *B*-site ordering was determined by refining the portion of Mg atoms at the (Mo,W/Nb) site and *vice versa*. The degree of order, *S*, was calculated as $S = 2(g_{Mg} - 0.5)$ (where g_{Mg} is the occupancy of Mg at its right site) such that for $S = 1$ the structure is completely ordered and for $S = 0$ completely disordered. Note that for the sake of simplicity, it was assumed that the distribution between the two *B*-cation sites remained the same for Mo and W (or Nb).

The redox behaviour of the samples, *i.e.* the chemical stability and the change in oxygen content under reduction or oxidation, was studied by thermogravimetric (TG) measurements (Perkin Elmer Pyris 1 TGA) carried out both in flowing air and in 5% H_2/Ar gas flow. A powder specimen of 50–80 mg was heated up to 1000 °C at a rate of 2 °C/min and then cooled down to room temperature with the same rate. During a TG run, the sample does not necessarily reach the very thermodynamic equilibrium state even when the run is made with a slow heating/cooling rate. Therefore, several specimens of each sample were reduced in a tube furnace in flowing 5% H_2/Ar gas at 1000 °C for a period of 2 to 48 h in order to determine the minimum oxygen content of the sample under these conditions. In each case the specimen reduced for 48 h was found to have exactly the same oxygen content (within the estimated error limits) as that reduced for only two hours, indicating that a two-hour reduction was enough to reduce the samples completely.

The precise oxygen content, $6 - \delta$, was determined for each sample employing a wet-chemical redox analysis method with which the total amount of reduced (lower-valent) species of Mo, W and/or Nb is determined using Fe^{III} as the oxidant and then back-oxidating the resultant Fe^{II} species through coulometric titration [12–14]. For the analysis, an accurately weighted powder specimen of 30–60 mg was dissolved in 200 ml of 3 M HCl containing an excess of Fe^{III} ions [14]. The HCl solution was bubbled with N_2 *prior* to use in order to remove any dissolved oxygen, and the titration was performed under N_2 atmosphere. The electrochemical oxidation of Fe^{II} was performed using constant current of 1 mA until the potential against an Ag/AgCl electrode reached 820 mV. The analysis was typically repeated three times, with the standard deviation of oxygen-deficiency value δ being ± 0.002.

In order to determine which of the redox-active B''-site elements, Mo, W and/or Nb, in the $Sr_2Mg(Mo,W/Nb)O_{6-\delta}$ samples are reduced, X-ray absorption measurements were carried out at BL16A1 and BL17C1 beamlines at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Both beamlines employed a double Si(111)-crystal monochromator for energy selection with a resolution $E/\Delta E$ better than 6000. For Mo and Nb, the L_2- and L_3-edge spectra were collected, but for W, only the L_3-edge spectrum. The absorption spectra at Mo $L_{2,3}$- and Nb $L_{2,3}$-edges were recorded in the fluorescence mode using a Lytle detector, whereas the W L_3-edge spectra were measured in the transmission mode using gas-filled ionization chambers. Photon energies were calibrated using the *L* edges of Nb, W, and Mo foils, respectively.

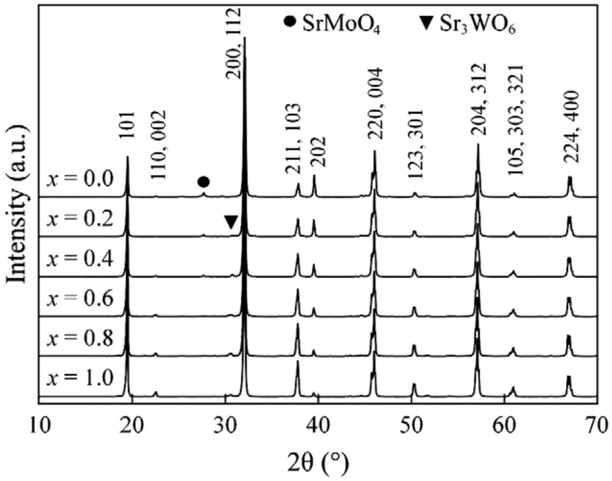

Fig. 1. X-ray diffraction patterns of the as-air-synthesized $Sr_2Mg(Mo_{1-x}W_x)O_{6-\delta}$ samples. The *hkl* indices are for the space group *I*-1.

Electrical conductivity for some of the samples was measured in 5% H_2/Ar using a conventional four-probe dc method. The sample powder was pressed into pellets and sintered in air at 1500 °C for 5 h. The pellets were then shaped into rectangular bars with the dimensions of $10 \times 4 \times 1.5$ mm^3. Electrical contacts were made using Pt wire and Pt paste. Resistance of the sample specimen was measured using a multimeter (Agilent 34401A). Before the conductivity measurement the sample was first annealed in 5% H_2/Ar at 850 °C for 12 h. Temperature was then lowered to 500 °C and the measurement was started. The measurement was made at temperatures from 500 to 850 °C with an interval of 35–40 °C. The temperature was raised at a rate of 2 °C/min, but before each measurement heating was stopped such that the sample resistance got stabilized.

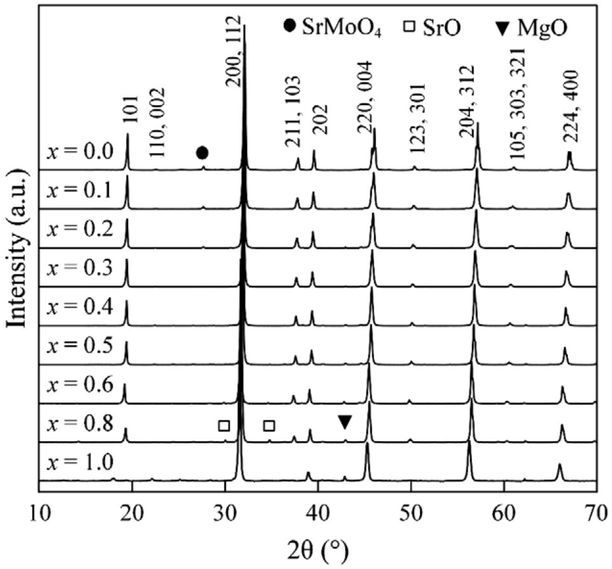

Fig. 2. X-ray diffraction patterns of the as-air-synthesized $Sr_2Mg(Mo_{1-x}Nb_x)O_{6-\delta}$ samples. The *hkl* indices are for the space group *I*-1.