Isovalent and aliovalent substitution effects on redox chemistry of Sr$_2$MgMoO$_6$ — SOFC-anode material

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ABSTRACT

An SOFC-anode material, Sr$_2$MgMoO$_6$ — $\delta$, 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$_2$Mg(Mo$_x$Nb$_{1-x}$)O$_6$ — $\delta$ with increasing Nb content. The two systems, Sr$_2$Mg(Mo,W)$_{1-x}$O$_6$ — $\delta$ and Sr$_2$MgMo(Nb)$_{1-x}$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$_2$ edges of Mo, W and Nb reveal that in Sr$_2$Mg(Mo,W)$_{1-x}$O$_6$ — $\delta$ both Mo and W show variable oxidation states whereas in Sr$_2$Mg(Mo,Nb)$_{1-x}$O$_6$ — $\delta$ Nb is more redox-active than Mo.

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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 — most severe problems of the Ni-based anodes, such as poor redox stability, carbon build-up (coking) and sulphur poisoning [2–4]. The Sr$_2$MgMoO$_6$ — $\delta$ 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 (SrLa)$_2$MgMoO$_6$ — $\delta$ for hydrocarbon fuels [8], but with the cost of lower stability under oxidizing conditions [9].

The Sr$_2$MgMoO$_6$ — $\delta$ oxide has a B-site ordered $A_2B_2B'O_6$ 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$_2$MgMoO$_6$ — $\delta$, 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, $\delta$, of Sr$_2$MgMoO$_6$ — $\delta$ is indeed important from the viewpoint of SOFC-anode performance: oxygen vacancies both facilitate efficient oxidation 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$_2$MgMoO$_6$ — $\delta$ 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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2. Experimental

Two sample series, Sr$_2$Mg(Mo$_{1-x}$W$_x$)O$_{6-\delta}$ ($x=0, 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) and Sr$_2$Mg(Mo$_{1-x}$Nb$_x$)O$_{6-\delta}$ ($x=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$, 0.8 and 1.0), were prepared through solid-state reaction from stoichiometric mixtures of SrCO$_3$, MgO, MoO$_3$, Nb$_2$O$_5$, and W powders. Each powder mixture was first calcined in air at 900 °C for 12 h, and then after regrouping pressed into pellets (13 mm in diameter and 1–2 mm in thickness) and sintered in air. Pristine Sr$_2$MgMoO$_{6-\delta}$ and W-substituted Sr$_2$Mg(Mo$_{1-x}$W$_x$)O$_{6-\delta}$ samples were sintered at 1200 °C for 36 h and Nb-substituted Sr$_2$Mg(Mo$_{1-x}$Nb$_x$)O$_{6-\delta}$ samples at 1500 °C for 48 h. Typically one-time sintering was enough, but for Sr$_2$MgWO$_{6-\delta}$ 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$_\alpha$ 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$_2$MgMoO$_{6-\delta}$ by Bernuy-Lopez et al. [10], who found that while the structure of Sr$_2$MgMoO$_6$ 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$_x$W$\_x$) 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 constant current of 1 mA until the potential against an Ag/AgCl electrode dissipated ionization chambers. Photon energies were calibrated using the $L$ edges of Nb, W, and Mo foils, respectively.

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 × 4 × 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.

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$^{II}$ as the oxidant and then back-oxidating the resultant Fe$^{III}$ 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$^{II}$ 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 $\delta$ being ±0.002.

In order to determine which of the redox-active $B$-site elements, Mo, W and/or Nb, in the Sr$_2$Mg(Mo$_x$W$_x$/Nb$_x$)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 $\Delta E/\Delta E$ 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$_2$Mg(Mo$_{1-x}$W$_x$)O$_{6-\delta}$ samples. The $hkl$ indices are for the space group $I$-1.](Image 1)

![Fig. 2. X-ray diffraction patterns of the as-air-synthesized Sr$_2$Mg(Mo$_{1-x}$Nb$_x$)O$_{6-\delta}$ samples. The $hkl$ indices are for the space group $I$-1.](Image 2)
3. Results and discussion

Figs. 1 and 2 show X-ray diffraction patterns for as-air-synthesized Sr$_2$Mg(Mo$_{1-x}$W$_x$)$_6$O$_{16-δ}$ and Sr$_2$Mg(Mo$_{1-x}$Nb$_x$)$_6$O$_{16-δ}$ samples, respectively. The samples were found to be essentially phase-pure, though a trace of SrMoO$_4$ (JCPDS 42-1222), a common impurity in such materials when sintered in air [15], was detected in some of the samples. In the W-substituted samples, traces of Sr$_3$WO$_6$ (JCPDS 28-1193) were also found. In each case, however, Rietveld refinement of these samples confirmed that the fractions of the SrMoO$_4$ and Sr$_3$WO$_6$ impurities were less than 2%. Some tiny unidentified reflections were also there, but they were very weak and not easily identified. In the Sr$_2$Mg(Mo$_{1-x}$Nb$_x$)$_6$O$_{16-δ}$ series for x = 0.5, increasing amounts of impurities such as MgO (JCPDS 4-0829) and SrO (JCPDS 6-0520) started to appear, and for this reason these samples were not further analyzed.

Colours of the samples are worth noticing. Non-substituted Sr$_2$MgMoO$_6$ sintered in air was almost white, with a slight yellowish or greenish tint. When sintered in reducing atmosphere or in Nb atoms in the W-substituted samples and in Tables 3 and 4 for the Nb-substituted samples. It has been suggested that A$_2$B'MoO$_6$-type double-perovskite oxides are prone to Mo deficiency due to the fact that MoO$_3$ has a relatively low melting temperature (ca. 795 °C) and may thus volatilize during the high-temperature synthesis [15]. In this work, no indication of Mo deficiency was found on the bases of Rietveld refinement for any of the samples. However, it is difficult to simultaneously determine the degree of B-site ordering and the possible Mo deficiency, and therefore possibility for small cation non-stoichiometry cannot be erased out.

In Fig. 3 we plot the unit-cell volume for the Sr$_2$Mg(Mo$_{1-x}$W$_x$)$_6$O$_{16-δ}$ and the Sr$_2$Mg(Mo$_{1-x}$Nb$_x$)$_6$O$_{16-δ}$ systems as a function of the W/Nb content. x. Substitution of Mo by W increases the unit-cell volume slightly, which is consistent with the fact that the ionic radius [16] of W$^6+$ (0.60 Å) is slightly larger than that of Mo$^6+$ (0.59 Å). Compared to the W substitution, substitution by Nb increases the unit-cell volume even more. This is mostly due to the fact that Nb$^5+$ with ionic radius of 0.64 Å is larger than W$^6+$. Moreover, substituting Mo$^6+$ by Nb$^5+$ creates oxygen vacancies in the lattice (see the coulometric titration data below). Loss of oxide anions causes more cation–cation repulsive interactions, which could also partially explain the cell-volume increase.

Table 2

<table>
<thead>
<tr>
<th>x</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
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<td>0.977</td>
<td>0.982</td>
<td>0.986</td>
<td>0.989</td>
<td>0.992</td>
<td>0.988</td>
</tr>
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<td>O1</td>
<td>0.010(2)</td>
<td>0.007(2)</td>
<td>0.006(1)</td>
<td>0.004(2)</td>
<td>0.021(1)</td>
<td>0.010(1)</td>
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<tr>
<td>O2</td>
<td>0.0192(9)</td>
<td>0.019(2)</td>
<td>0.019(1)</td>
<td>0.019(1)</td>
<td>0.019(1)</td>
<td>0.019(1)</td>
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<tr>
<td>O2b</td>
<td>0.021(1)</td>
<td>0.021(1)</td>
<td>0.021(1)</td>
<td>0.021(1)</td>
<td>0.021(1)</td>
<td>0.021(1)</td>
</tr>
<tr>
<td>y</td>
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<td>0.268(2)</td>
<td>0.268(2)</td>
<td>0.268(2)</td>
<td>0.268(2)</td>
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<tr>
<td>z</td>
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<td>0.010(2)</td>
<td>0.010(2)</td>
<td>0.010(2)</td>
<td>0.010(2)</td>
<td>0.010(2)</td>
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</tbody>
</table>

Note that Mo and Nb are at site 2(a) (0, 0, 0) and Mg at site 2(b) (0.5, 0.5, 0.5).
enhances the ordering even higher. In the Sr$_2$Mg(Mo$_{1-x}$Nb$_x$)O$_{6-\delta}$ sample series, on the other hand, the B-site ordering decreases notably as the Nb-for-Mo substitution proceeds. This could be primarily caused by the fact that the charge difference between Mg$^{II}$ and Nb$^V$ is smaller than that between Mg$^{II}$ and Mo$^{VI}$ [17,18]. In addition, the size difference between Nb$^V$ (0.64 Å) and Mg$^{II}$ (0.72 Å) is smaller than that between Mo$^{VI}$ (0.59 Å) and Mg$^{II}$. On the other hand, the increased disordering could be due to the increased concentration of oxygen vacancies created by the Nb$^V$ substitution. It is believed that divalent magnesium strongly dislikes five-coordination in a perovskite structure [10]. Hence, as the overall oxygen-vacancy concentration increases through the Nb substitution, it is enhanced such that the oxygen vacancies need not be located next to Mg$^{II}$ cations but rather between two (Mo,Nb) species.

Coulometric titration was used to determine precise oxygen contents of the samples. Titration results showed that the as-air-synthesized Sr$_2$Mg(Mo$_{1-x}$W$_x$)O$_{6-\delta}$ samples were all oxygen stoichiometric with the non-stoichiometry parameter $\delta$ determined at 0.000 within the estimated error limits of ±0.002. In the case of the Sr$_2$Mg(Mo$_{1-x}$Nb$_x$)O$_{6-\delta}$ series, the divalent Nb$^V$-for-Mo$^{VI}$ substitution was found to increase the concentration of oxygen vacancies exactly with the theoretical rate of $\delta = x/2$, see Fig. 5.

Table 3

<table>
<thead>
<tr>
<th>$x$</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
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<td>I-1</td>
<td>I-1</td>
<td>I-1</td>
<td>I-1</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>5.5814(2)</td>
<td>5.5908(8)</td>
<td>5.5961(2)</td>
<td>5.6077(2)</td>
<td>5.6150(4)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>5.5813(2)</td>
<td>5.5804(8)</td>
<td>5.6028(2)</td>
<td>5.6077(3)</td>
<td>5.6160(4)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>7.9330(2)</td>
<td>7.9483(2)</td>
<td>7.9434(1)</td>
<td>7.9482(1)</td>
<td>7.9587(2)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>89.859(2)</td>
<td>89.922(1)</td>
<td>89.902(3)</td>
<td>89.941(1)</td>
<td>89.907(5)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>90.108(2)</td>
<td>90.091(1)</td>
<td>90.099(4)</td>
<td>90.059(1)</td>
<td>90.041(6)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>89.078(5)</td>
<td>90.028(4)</td>
<td>90.062(6)</td>
<td>90.045(6)</td>
<td>90.050(8)</td>
</tr>
<tr>
<td>$V$(Å$^3$)</td>
<td>247.31(1)</td>
<td>248.05(5)</td>
<td>249.07(1)</td>
<td>249.94(5)</td>
<td>250.99(2)</td>
</tr>
</tbody>
</table>

\[ R_{Bragg} \] 2.95 3.20 3.10 3.91 4.54

The redox stability of as-synthesized samples was studied by reductive and oxidative annealings carried out in a thermobalances in 5% H$_2$/Ar gas flow and in air. It was found that all the samples were reduced and re-oxidized without decomposition at temperatures of up to 1000 °C and no signs of any additional phases due to decomposition were found in the XRD patterns (not shown here). In addition, the mass changes were reversible during consecutive redox cycles. Bernuy-Lopez et al. [10] noticed in their experiments that the Sr$_2$MgMoO$_{6-\delta}$ sample would partially decompose under reductive conditions at temperatures above 900 °C. However, Marro-Lozs et al. [15] came to somewhat different conclusion, as their sample showed only small amounts of secondary phases when reduced at 1000 °C. They proposed that different synthesis methods could explain these differences. In addition, the exact oxygen partial pressure in the experiments may vary between different groups, due to gas impurities or small furnace leaks, which could also explain these different results.

As it was found that the samples did not decompose during the TG-reduction cycles, they were put in a tube furnace with a reducing atmosphere of 5% H$_2$/Ar at 1000 °C for 2 h. The resultant change in oxygen stoichiometry, $\Delta \delta$, was determined by analyzing the precise oxygen contents of each sample before and after the reduction by means of coulometric titrations. The results are shown in Fig. 6. It is clear that replacing Mo by either Nb or W decreases reducibility, i.e. the $\Delta \delta$ value. In the case of Sr$_2$Mg(Mo$_{1-x}$X$_x$)O$_{6-\delta}$ with $x \geq 0.4$, the changes in oxygen stoichiometry due to the reduction were extremely tiny. However, the colour of the samples changed to a slight blue hue after the reduction, confirming that the samples had indeed reduced.

In order to investigate which of the cations Mo$^{VI}$, W$^{VI}$ and Nb$^V$ are reduced upon the reductive annealing, XANES spectroscopy measurements were carried out for several representative members of the two series, Sr$_2$Mg(Mo$_{1-x}$W$_x$)O$_{6-\delta}$ and Sr$_2$Mg(Mo$_{1-x}$Nb$_x$)O$_{6-\delta}$. The changes in oxygen stoichiometry due to the reduction were extrememly small. However, the colour of the samples changed to a slight blue hue after the reduction, confirming that the samples had indeed reduced.

In order to investigate which of the cations Mo$^{VI}$, W$^{VI}$ and Nb$^V$ are reduced upon the reductive annealing, XANES spectroscopy measurements were carried out for several representative members of the two series, Sr$_2$Mg(Mo$_{1-x}$W$_x$)O$_{6-\delta}$ and Sr$_2$Mg(Mo$_{1-x}$Nb$_x$)O$_{6-\delta}$. For Mo and Nb, $L_2$- and $L_3$-edge absorption spectra, corresponding respectively to the 2$p_{1/2} \rightarrow 4d$ and 2$p_{3/2} \rightarrow 4d$ transitions, were measured. The results are shown in Fig. 7.


→ 4d transitions [19], were measured, whereas for W, only the $L_{2,3}$-edge spectrum, corresponding to the $2p_{3/2} \rightarrow 5d$ transition, was measured. Fig. 7(a) shows the $L_2$- and $L_3$-edge spectra for the as-air-synthesized and reduced $\text{Sr}_2\text{MgMoO}_6$ samples. In both the spectral areas the spectrum consists of two distinct peaks. The lower-energy peak corresponds to the excitation to the $t_{2g}$ states and the higher-energy peak to transitions to the $e_g$ states. In their air-synthesized forms the $\text{Sr}_2\text{Mg}(\text{Mo}_{1-x}\text{W}_x)\text{O}_6 - \delta$ and $\text{Sr}_2\text{Mg}(\text{Mo}_{1-x}\text{Nb}_x)\text{O}_6 - \delta$ materials contain (based on our coulometric titration data) only $\text{Mo}^{VI}$, $\text{W}^{VI}$ and $\text{Nb}^{V}$ cations, which all have both the $t_{2g}$ and $e_g$ states completely empty. When these samples are reduced, electrons are introduced to the $t_{2g}$ states. This means that in the reduced samples fewer electrons can be excited to the $t_{2g}$ states than in the pristine ones, and accordingly the intensity of the corresponding absorption peak should be reduced [20]. As is seen from Fig. 7(a), in both the $L_2$- and $L_3$-edge areas intensity of the peak corresponding to transitions to the $t_{2g}$ states is smaller for the reduced $\text{Sr}_2\text{MgMoO}_6$ sample than for the as-air-synthesized one. This indicates that, indeed, Mo$^{VI}$ is partially reduced to Mo$^{V}$ in $\text{Sr}_2\text{MgMoO}_6 - \delta$ when the as-air-synthesized sample is reduced in 5% H$_2$/Ar.

Fig. 7(b) shows the Mo $L_2$- and $L_3$-absorption spectra for the as-air-synthesized and reduced samples of $\text{Sr}_2\text{Mg}(\text{Mo}_{0.6}\text{W}_{0.4})\text{O}_6 - \delta$. It is clearly seen that Mo is reduced in this sample too upon reductive annealing. Fig. 8 shows the W $L_3$-edge spectra for the same $\text{Sr}_2\text{Mg}(\text{Mo}_{0.6}\text{W}_{0.4})\text{O}_6 - \delta$ samples. The shape of the W $L_3$-edge spectrum is somewhat different from that at the Mo-$L_3$ edge, but the “two-peak” feature is still present. The two spectra shown in Fig. 8 indicate that upon reduction not only Mo but also W is reduced in $\text{Sr}_2\text{Mg}(\text{Mo}_{0.6}\text{W}_{0.4})\text{O}_6 - \delta$. Similar results were obtained for the $x = 0.2$ and 0.8 samples as well. Thus, it can be concluded that in the $\text{Sr}_2\text{Mg}(\text{Mo}_{1-x}\text{W}_x)\text{O}_6 - \delta$ system, both Mo and W are simultaneously reduced.

Similar study was carried out for the $\text{Sr}_2\text{Mg}(\text{Mo}_{1-x}\text{Nb}_x)\text{O}_6 - \delta$ series. Fig. 7(c) shows the Mo $L_2$- and $L_3$-absorption spectra for the as-air-synthesized and reduced $\text{Sr}_2\text{Mg}(\text{Mo}_{0.8}\text{Nb}_{0.2})\text{O}_6 - \delta$ samples. The two spectra are practically identical indicating that in $\text{Sr}_2\text{Mg}(\text{Mo}_{0.8}\text{Nb}_{0.2})\text{O}_6 - \delta$ Mo is not reduced. Fig. 9 displays the Nb
Finally we note that niobium is known to show excellent catalytic activity [21]. Most interestingly, niobium is not only catalytic itself, but can also function as a promoter when used together with other catalytic materials, such as molybdenum. Therefore, small substitution levels of Nb in Sr$_2$MgMoO$_{6-\delta}$ could enhance the materials electrocatalytic oxidation activity.

4. Conclusions

We have systematically studied the Sr$_2$MgMoO$_{6-\delta}$ double-perovskite oxide for both isovalent and aliovalent substitution effects at its redox-active cation site having the eye on its potential usability as SOFC-anode material. The study was accomplished by synthesizing high-quality samples of two series, Sr$_2$Mg(Mo,W)O$_{6-\delta}$ and Sr$_2$Mg(Mo,Nb)O$_{6-\delta}$ in wide substitution ranges and thoroughly examining the samples not only for electrical conductivity but also for crystal- and redox-chemistry properties using the XRD, XANES, TG and coulometric titration techniques.

Isovalent W$^{IV}$-for-Mo$^{IV}$ substitution had little effect on crystal and redox chemistry of Sr$_2$MgMoO$_{6-\delta}$ but considerably depressed the electrical conductivity. The isovalent Nb$^{V}$-for-Mo$^{V}$ substitution for Sr$_2$MgMoO$_{6-\delta}$ turned out to be potentially useful for enhancing its SOFC-anode performance, as oxygen vacancies are yielded in the lattice to enhance its ionic conductivity. An optimum substitution level needs to be determined as the Nb$^{V}$-for-Mo$^{V}$ substitution has not only positive but also negative consequences such as electrical conductivity depression, presumably due to the increased amount of oxygen vacancies and/or the fact that in Sr$_2$Mg(Mo,Nb)O$_{6-\delta}$, it is only Nb (and not Mo) that shows mixed valency. We conclude that a small amount of Nb of the order of few percents most likely would be useful considering the materials use as an SOFC anode. Proper fuel-cell tests are naturally needed to prove this.

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References


