Chemical, electrical, and thermal properties of strontium doped lanthanum vanadate

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Abstract

Strontium doped lanthanum vanadates, $La_{1-x}Sr_xVO_3$ (denoted LSV with $x=0$, 0.3, 0.5, 0.7 and 1.0), were synthesized using a solid-state reaction method. The oxidation and reduction behaviors of LSV were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The chemical stability of LSV in a reducing atmosphere containing H_2S up to 10 vol.% at 950 °C was investigated and their electrical conductivity at 500–1000 °C in reducing atmospheres measured with a 4-electrode technique. The coefficient of thermal expansion (CTE) was determined by dilatometry. The electrochemical catalytic activity of LSV as anodes in solid oxide fuel cells (SOFCs) was characterized using impedance spectroscopy. It was found that the $La_{1-x}Sr_xVO_3$ materials with x in the range of 0.3–0.7 exhibit good resistance to H_2S, high electrical conductivity and acceptable catalytic activity at elevated temperatures in reducing atmosphere. However, the volume change associated with oxidation/reduction cycle may limit their tolerance to re-oxidation when used as anode materials for SOFCs.
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1. Introduction

It is well known that the Ni/YSZ composite anodes of solid oxide fuel cells (SOFCs) have very poor tolerance to H_2S contaminants in the fuel [1–3]. Although the mechanism of H_2S poisoning is yet to be determined [4], it is certain that exposure to fuels containing more than 100 ppm of H_2S causes great loss to the performance of SOFCs with Ni/YSZ anode [1,3]. The removal of H_2S in the fuel incurs additional complexity and cost. Recently, it was reported that a strontium doped lanthanum vanadate with a nominal composition of $La_{0.7}Sr_{0.3}VO_3$ was used as the anode material for SOFC operating on fuels containing high concentration (up to 10 vol.%) of H_2S [5,6]. The cell performances were among the best reported in the literature for SOFCs using H_2S-containing fuels [3,5–10]. In addition, it was found that $La_{0.7}Sr_{0.3}VO_3$ exhibited selective

oxidation of H_2S and its catalytic activity increased with increasing H_2S concentration [5,6].

Earlier investigations on the lanthanum strontium vanadates (LSV for $La_{1-x}Sr_xVO_3$) were focused on the crystal structure and the related electrical and magnetic properties at temperatures below $\sim$500 °C [11–16]. $LaVO_3$ is a semiconductor while $SrVO_3$ displays a metallic behavior with conductivity as high as 1000 S cm^{-1} [11,12,15–17] at 800 °C in reducing atmosphere. Previous researches showed that LSV exhibits a transition from antiferromagnetic insulator to paramagnetic metal with increasing Sr content near $x=0.2$ [13,15]. To the best of our knowledge, however, none of previous studies were directed towards the understanding of the chemical stability of LSV at high temperatures under various atmospheres, especially in sulfur containing fuels. Neither are there any reports on electrical conductivity nor coefficient of thermal expansion (CTE) of LSV at high temperatures ($>$500 °C) over a wide range of Sr contents. In this paper, we report our recent studies of the chemical stability, electrical conductivity, CTE and electrochemical

activity of LSV under conditions relevant to SOFCs powered by H_2S-containing fuels. Advantages and limitations of $La_{1-x}Sr_xVO_3$ as possible anode materials for SOFCs using H_2S-containing fuels are also discussed.

2. Experimental

2.1. Preparation of samples

$La_{1-x}Sr_xVO_3$ powders with $x=0$, 0.3, 0.5, 0.7 and 1.0 were prepared using a solid-state reaction method. The precursors were La_2O_3 (Aldrich, 99.9%), $SrCO_3$ (Aldrich, 99.9%) and V_2O_5 (Aldrich, 99.6%). La_2O_3 and $SrCO_3$ were calcined in air for 2 h at 800 and 300 °C, respectively, to remove the adsorbed moisture. The powders were mixed, ground for 1 h and pressed into pellets at 70 MPa. The pellets were calcined at 1450 °C for 5 h in the 4% H_2/96% Ar gas mixture followed by repeated grinding and calcination until complete reaction and uniform composition were achieved. The phases were identified using powder X-ray diffraction (XRD, PW1800 X-ray diffractometer, Philips Analytical). The radiation source was $Cu-K_\alpha$ lines.

2.2. Oxidation/reduction behaviors

The oxidation/reduction behaviors of the LSV materials were studied using a simultaneous thermal analyzer (STA, STA1500, Rheometric Scientific), which combines thermogravimetric analysis (TGA) with differential scanning calorimetry (DSC). The amount of sample used for experiment in the STA was ~15 mg. The heating rate was 5 °C/min up to 900 °C. The atmospheres used were air and the 4% H_2/96% Ar mixture for the oxidation and reduction experiment, respectively. In addition, oxidation and reduction of LSV were also carried out in a tube furnace at 900–1550 °C in air or a gas mixture containing 4% H_2 and 96% Ar. The weight change of the sample before and after reaction was measured and the reaction products were analyzed by XRD.

2.3. Evaluation of the chemical stability

Pellets of LSV were put in alumina boats placed in a tube furnace under H_2S-containing atmosphere to evaluate the chemical stability. The furnace was heated up to 950 °C and held for 5 days in a fuel mixture with a nominal composition of 10% H_2S/3% H_2O/87% H_2 (by volume). The chemical compatibility of LSV with yttrium stabilized zirconia (YSZ) was examined by heat-treating a pellet containing 50 wt.% $La_{0.7}Sr_{0.3}VO_3$ and 50 wt.% YSZ (TZ-8Y, Tosoh) at 1300 °C for 2 h in a gas mixture containing 4% H_2 and 96% Ar.

2.4. Measurement of electrical conductivity

The electrical conductivity of the $La_{1-x}Sr_xVO_3$ materials was measured using a four-electrode technique. Pellets of

LSV were sintered at 1450–1575 °C for 5 h in a gas mixture containing 4% H_2 and 96% Ar. Rectangular bars with approximate dimensions of 15 mm × 1.5 mm × 1.5 mm were cut from the sintered pellets using a precision diamond saw (Isocut® 4000, Buehler). Four pieces of Pt wires (0.1 mm diameter, annealed at 800 °C in air) were wrapped around the bar; the distance between the two inner electrodes was ~8 mm and the distance between the two outer electrodes was ~14 mm. The bar with the wires was mounted on a piece of alumina substrate by cement (Autostic™ FC6, Flexbar). Pt paste was applied to the contact regions between the bar and the Pt electrodes. The mounted sample was fired at 1050 °C for 2 h in a gas mixture containing 4% H_2 and 96% Ar to obtain a firm bonding and good electrical contact between the Pt wires and the sample. The conductivity was measured at 500–1000 °C in gas mixtures of 3% H_2O/97% H_2 and/or 10% H_2S/3% H_2O/87% H_2. A potentiostat/galvanostat (273A, Princeton Applied Research) was used to draw a constant DC current (I_i) between the two outer electrodes and a multimeter (MY-65, Mastech) to measure the voltage drop between the two inner electrodes (ΔV_i). Typically, five points of (ΔV_i, I_i) were collected at each temperature. Linear mean square regression analysis was performed from the data (ΔV_i, I_i) to obtain the resistance. The bulk conductivity σ was calculated using the following equation [18]:

$$\sigma = \frac{\sigma_m(2 + \varepsilon)}{2(1 - \varepsilon)} \quad (1)$$

in which σ_m is the measured conductivity and ε is the sample porosity. The values for the porosity of the used $La_{1-x}Sr_xVO_3$ samples are $\varepsilon=0.33$ for $x=0$, $\varepsilon=0.12$ for $x=0.3$, $\varepsilon=0.36$ for $x=0.5$, $\varepsilon=0.22$ for $x=0.7$ and $\varepsilon=0.23$ for $x=1.0$.

2.5. Measurement of the coefficient of thermal expansion (CTE)

The coefficient of thermal expansion for $La_{0.7}Sr_{0.3}VO_3$ in a reducing atmosphere was measured by a homemade non-contact dilatometer. The sample used for the CTE measurement was sintered at 1550 °C for 5 h in a gas mixture containing 4% H_2 and 96% Ar to achieve a relative density of 97%.

2.6. Characterization of the electrochemical activity

The electrochemical activity of $La_{1-x}Sr_xVO_3$ with $x=0.3$ and 1.0 was characterized using two-electrode impedance spectroscopy for cells with LSV anode and $La_{0.85}Sr_{0.15}MnO_3$ (LSM) cathode. The electrolyte was 250 μm thick YSZ and the active electrode area was ~0.25 cm^2. Paste of LSM cathode was brush painted on the YSZ substrate followed by firing at 1100 °C in air for 2 h. The anode paste was painted onto the other side of the YSZ substrate and fired in-situ at 1000 °C for 2 h before testing. The impedance spectra were measured under open circuit conditions using a

potentiostat/galvanostat (273A, Princeton Applied Research) and a 5210 lock-in amplifier (Princeton Applied Research) interfaced with a computer.

3. Results and discussion

3.1. Structure of LSV materials

Fig. 1 shows the XRD patterns of $La_{1-x}Sr_xVO_3$ with $x=0$, 0.3, 0.5, 0.7 and 1.0. $LaVO_3$ ($x=0$) has a tetragonal (distorted perovskite) structure (JCPDS card No. 11-0024) while $SrVO_3$ ($x=1.0$) has a cubic perovskite structure (JCPDS card No. 42-0039). For the other compositions investigated (i.e., $x=0.3$, 0.5 and 0.7), the XRD patterns match that of a cubic perovskite structure (see JCPDS card No. 33-1343), but the diffraction peaks for those samples are very broad. One explanation of the broadened diffraction peaks is that the A-sites in the ABO_3 perovskite structure are randomly occupied by the Sr and La atoms in these materials. As a result, there may be a broad distribution of the lattice constants throughout the reaction product, resulting in significant broadening of the diffraction peaks in the XRD patterns.

3.2. Redox behavior of LSV materials

Shown in Fig. 2 are the TGA curves for the oxidation of LSV in air with a heating rate of 5 °C/min. The oxidation behavior for $La_{1-x}Sr_xVO_3$ with $x=0$, 0.3, 0.5 and 0.7 is very similar. Significant oxidation of these materials started at ~400 °C and completed at ~600 °C. There was only a single stage of weight gain at around 500 °C, suggesting that there might be only one type of reactions going on during the entire oxidation processes of these materials. In contrast, the TGA curve for the oxidation of $SrVO_3$ shows several stages of weight gain. The multiple-step oxidation of $SrVO_3$ is illustrated more clearly in Fig. 3, which combines both the TGA and the DSC curves.
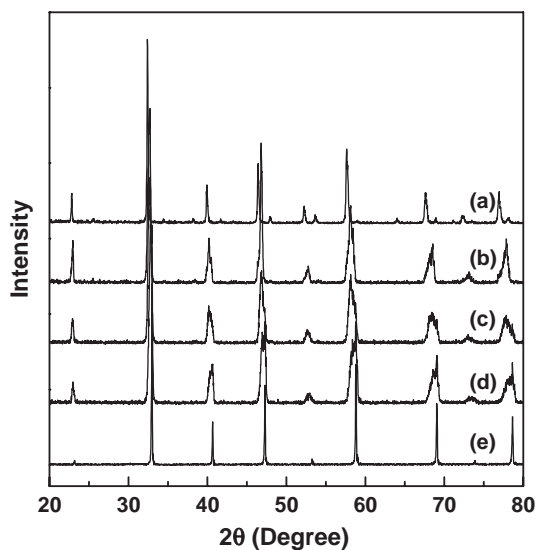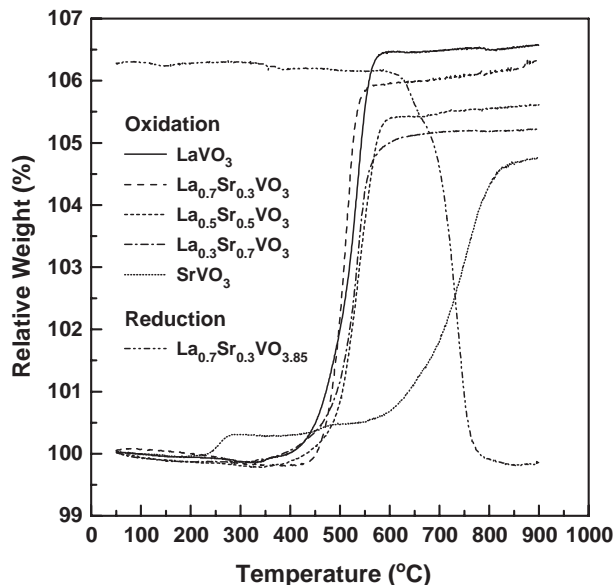

Fig. 2. TGA curves for the oxidation of $La_{1-x}Sr_xVO_3$ with $x=0$, 0.3, 0.5, 0.7 and 1.0 and the reduction of $La_{0.7}Sr_{0.3}VO_{3.85}$. Note that, for the reduction of $La_{0.7}Sr_{0.3}VO_{3.85}$, the weight of the reduction product, presumably $La_{0.7}Sr_{0.3}VO_3$, is taken as unit.

There are three exothermic peaks corresponding to three steps of weight gain. The first step was at around 220–280 °C with a weight gain of ~0.3%. The second step was in the 450–500 °C range with a weight gain even smaller (<0.1%). The third step of weight gain was gradual and occurred over a wide range of temperatures from ~600 to ~900 °C. The oxidation temperature of $La_{1-x}Sr_xVO_3$ material is comparable to that of fine nickel powders, which was reported to be oxidized in air at temperature as low as ~400 °C [19]. The oxidation of the $La_{1-x}Sr_xVO_3$ ($0 \leq x \leq 1$) materials is expected because the vanadium ions in them are believed to have a mixed valence of +3 and +4 [11,17]. Upon heat treatment in air, the valence of vanadium increased from +3 and/or +4 to +5. However, it is interesting to observe from the TGA curves that the oxidation

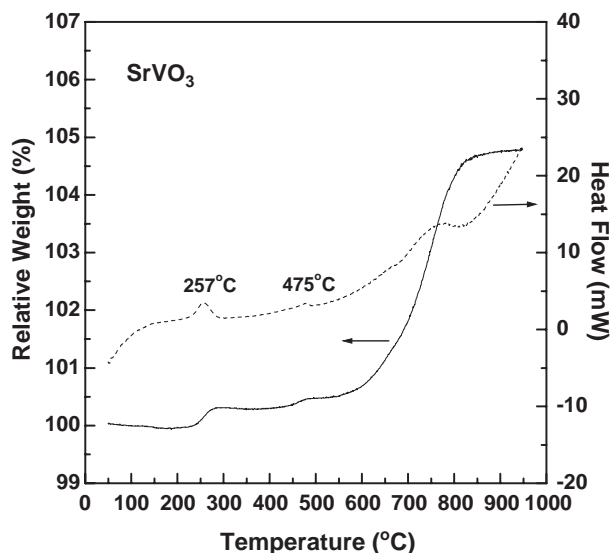Fig. 1. XRD patterns for the as-synthesized $La_{1-x}Sr_xVO_3$ materials: (a) $LaVO_3$, (b) $La_{0.7}Sr_{0.3}VO_3$, (c) $La_{0.5}Sr_{0.5}VO_3$, (d) $La_{0.3}Sr_{0.7}VO_3$ and (e) $SrVO_3$.

Fig. 3. TGA and DSC curves for the oxidation of $SrVO_3$ in air.

of SrVO$_3$ showed multiple steps while the oxidation of other LSV materials appeared to be a single-step process. Since it was reported that SrVO$_3$ could be non-stoichiometric [12,16,17,20], it is possible that the first step of weight gain during the oxidation of SrVO$_3$ was related to the combination of oxygen with oxygen vacancy in the SrVO$_3$ material, i.e., the transformation from SrVO$_{3-\delta}$ to SrVO$_3$. As stated, the weight gain in the first step (~220–280 °C) for the oxidation of SrVO$_3$ was 0.3%; this corresponds to a δ value of 0.03 (i.e., the material before oxidation was SrVO$_{2.97}$). Such explanation is consistent with the observation of a plateau in the sample weight when SrVO$_{3-\delta}$ was exposed to the 0.1% O$_2$/He mixture at 350 °C [20]. The second step for the oxidation of SrVO$_3$ may be related to the oxidation of V^{3+} to V^{5+} because the temperature for the second step (~450–500 °C) was close to that at which all other materials in the LSV family (containing much more V^{3+}) were oxidized. For SrVO$_3$, this step ceased very quickly because the amount of V^{3+} ions in SrVO$_3$ should be extremely limited. Further weight gain in air at elevated temperature (i.e., the third step) is expected to correspond to the transformation from V^{4+} to V^{5+}, leading to the complete disruption of the original perovskite structure. In comparison to SrVO$_3$, there are significant concentrations of V^{3+} ions in other La$_{1-x}$Sr$_x$VO$_3$ materials ($x=0$, 0.3, 0.5 and 0.7) [11]. When V^{3+} started to oxidize to V^{5+} at ~500 °C, the resulted structural change may be so large that the structure collapsed and the entire oxidation process (including the oxidation of V^{4+} to V^{5+}) happened within a short period of time. As a result, the oxidation appeared to be a single step process. Nonstoichiometry may also exist in these materials (i.e., $0 \le x(Sr) \le 0.7$); however, the effect during the oxidation process may be less obvious compared with SrVO$_3$.

Accompanied by the weight change, the structure of La$_{1-x}$Sr$_x$VO$_3$ materials changed dramatically during the oxidation. Fig. 4 shows the XRD patterns of the oxidation products of La$_{1-x}$Sr$_x$VO$_3$ with $x=0$, 0.3 and 1.0. For LaVO$_3$ and La$_{0.7}$Sr$_{0.3}$VO$_3$, the XRD patterns of the oxidation products match that of the monoclinic LaVO$_4$ (JCPDS card No. 25-0427). The change from the original (distorted) perovskite structure to the monoclinic structure results in a significant change in the unit cell volume. As an example, the oxidation of LaVO$_3$ is accompanied by a 40% increase in the unit cell volume (calculated from the lattice parameters given in the JCPDS cards). The volume change during the oxidation of La$_{1-x}$Sr$_x$VO$_3$ with $x=0$ and 0.3 was verified by the observation that sintered blocks of those materials became loose powders after complete oxidation. The structural change during the oxidation of SrVO$_3$ is different from that observed for LaVO$_3$ and La$_{0.7}$Sr$_{0.3}$VO$_3$. The XRD pattern of the oxidation product (Fig. 4(c)) matches that of Sr$_2$V$_2$O$_7$ (JCPDS card No. 32-1268) with a tetragonal structural. (There is some disagreement about the exact structure of Sr$_2$V$_2$O$_7$: both Fotiev and Makarov [21] and Solacolu et al. [22] suggested that it is monoclinic). Interestingly, the volume expansion from SrVO$_3$ to 1/2 Sr$_2$V$_2$O$_7$ is also ~40% if the tetragonal structure is assumed. It should be noted that Sr$_2$V$_2$O$_7$ is stable in air only up to ~1010–1120 °C: it decomposes into Sr$_3$V$_2$O$_8$ and V$_2$O$_5$ in that temperature range [21,22]. Therefore, heat treatment of SrVO$_3$ at higher temperature (>~1010 °C) in air may cause the majority of the final oxidation product to be Sr$_3$V$_2$O$_8$ since liquid V$_2$O$_5$ could be lost significantly. The oxidation of La$_{0.5}$Sr$_{0.5}$VO$_3$ and La$_{0.3}$Sr$_{0.7}$VO$_3$ at around 900 °C does not form single-phase products: their XRD patterns indicate

Fig. 4. XRD patterns for (a) LaVO$_4$, (b) La$_{0.7}$Sr$_{0.3}$VO$_{3.85}$ and (c) Sr$_2$V$_2$O$_7$, which are oxidation products of LaVO$_3$, La$_{0.7}$V$_{0.3}$VO$_3$ and SrVO$_3$, respectively.

that they are a mixture of Sr$_2$V$_2$O$_7$ and La$_{1-x}$Sr$_x$VO$_{4-x/2}$ type phase.

The oxidation of stoichiometric La$_{1-x}$Sr$_x$VO$_3$ at around 900 °C could be represented by:

$$\text{La}_{1-x}\text{Sr}_x\text{VO}_3 + \left(\frac{2-x}{4}\right)\text{O}_2 \rightarrow \text{La}_{1-x}\text{Sr}_x\text{VO}_{4-x/2} \quad (2a)$$

for $x=0$ and 0.3, or

$$2\text{SrVO}_3 + 0.5\text{O}_2 \rightarrow \text{Sr}_2\text{V}_2\text{O}_7 \quad (2b)$$

for $x=1.0$. The number of oxygen in the oxidation product in Eq. (2a) is $4-x/2$ instead of 4 because the charge balance requires the total number of oxygen to be $[3(1-x)+2x+5]/2=4-x/2$ when vanadium is in its fully oxidized state (V^{5+}). Table 1 compares the oxidation yields (by weight) calculated from Eqs. (2a) and (2b) and the yields measured in the experiments. Reasonable agreements are found between calculated and observed values for La$_{1-x}$Sr$_x$VO$_3$ with $x=0$ and 0.3. The largest difference is seen for SrVO$_3$. As it is pointed out before, the starting material might have a composition of SrVO$_{2.97}$ instead of SrVO$_3$. The weight change from SrVO$_{2.97}$ to SrVO$_3$ (i.e., the first step of oxidation) was 0.3% and the weight change for the entire oxidation process was 4.8%. Hence, the combined yield for the second and third step of the oxidation reaction (presumably from SrVO$_3$ to Sr$_2$V$_2$O$_7$) would be $(1+4.8\%)/(1+0.3\%)=104.5\%$, which matches the value calculated from reaction (2b) when $x=1.0$.

In addition to the oxidation of the LSV materials, the reduction of the oxidation products was also studied. The TGA curve for the reduction of La$_{0.7}$Sr$_{0.3}$VO$_{3.85}$ to La$_{0.7}$Sr$_{0.3}$VO$_3$ is shown in Fig. 2. The reduction process finished at around 800 °C. Heat treatments also confirmed that the reduction from La$_{1-x}$Sr$_x$VO$_{4-x/2}$ to La$_{1-x}$Sr$_x$VO$_3$ for $x=0$ and 0.3 could be achieved at around 1000 °C in 2 h. The reduction of other members in the LSV family (e.g., from Sr$_2$V$_2$O$_7$ to SrVO$_3$) did not seem to complete unless higher temperature or longer time

Table 1
Comparison of the calculated and measured yields for the oxidation reactions of $La_{1-x}Sr_xVO_3$ and the reverse reduction reactions
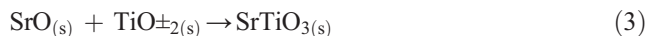
$La_{1-x}Sr_xVO_3$	Oxidation product	Yields of oxidation (%)		Yields of reduction (%)	
		Calculated	Measured	Calculated	Measured
$LaVO_3$	$LaVO_4$	106.7	106.5	93.7	93.4
$La_{0.7}Sr_{0.3}VO_3$	$La_{0.7}Sr_{0.3}VO_{3.85}$	106.1	106.0	94.3	93.7
$La_{0.5}Sr_{0.5}VO_3$	$La_{1-x}Sr_xVO_{4-x/2}+Sr_2V_2O_7$	105.7	105.4	94.6	94.1
$La_{0.3}Sr_{0.7}VO_3$	$La_{1-x}Sr_xVO_{4-x/2}+Sr_2V_2O_7$	105.1	105.2	95.1	94.3
$SrVO_3$	$Sr_2V_2O_7$	104.3	104.8	95.9	NA

was used. Similar phenomena for the reduction of $LaVO_4$ and $Sr_2V_2O_7$ were reported before [23,24]. The XRD patterns of the reduction products from $La_{1-x}Sr_xVO_{4-x/2}$ and/or $Sr_2V_2O_7$ match those for the original $La_{1-x}Sr_xVO_3$ materials. The measured yield values (by weight) for the reduction reactions are also listed in Table 1 and they agree with the values calculated from the chemical formula. All these data indicate that the oxidation/ reduction process is reversible in terms of crystal structure. However, the recrystallization during this process suggests that $La_{1-x}Sr_xVO_3$ may not be used alone as anode support for SOFC because of the large volume change involved in the reactions.

3.3. Chemical stability of LSV materials in H_2S-containing atmosphere

Shown in Fig. 5 are the XRD patterns of the $La_{1-x}Sr_xVO_3$ materials ($x=0$, 0.3, 0.5, 0.7 and 1.0) after exposure to a 10% H_2S/3% H_2O/87% H_2 mixture at 950 °C for 5 days. There were almost no changes in the XRD pattern for $La_{1-x}Sr_xVO_3$ materials with $x=0.3$, 0.5 and 0.7. For $LaVO_3$, a partial transformation from the tetragonal distorted perovskite structure (JCPDS card No. 11-0024) to an orthorhombic distorted perovskite structure (JCPDS card No. 36-0141) was observed. For $SrVO_3$, the majority of the material transformed into SrS (JCPDS card No. 08-0489).
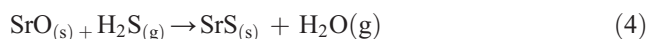
It is interesting to note that the stability of $La_{1-x}Sr_xVO_3$ materials in H_2S-containing atmosphere varies greatly with the Sr content. Since the thermochemical data for complex oxides like $La_{1-x}Sr_xVO_3$ are not available, direct analysis of the stability of those materials is not possible. However, because ABO_3 perovskites could be viewed, in some sense, as an ordered solid solution of the simple oxides of the A-site and B-site cations, the stability of these simple oxides may help to understand the stability of the perovskites. It is known that the Gibbs free energy change from the A-site and B-site simple oxides (e.g., AO and BO_2) to the complex oxides (e.g., ABO_3) would usually be negative [25,26]. For example, the reaction between SrO and TiO_2 to form $SiTiO_3$:

$$SrO_{(s)} + TiO\pm_{2(s)} \rightarrow SrTiO_{3(s)} \qquad (3)$$

is accompanied by a Gibbs free energy change of −138 kJ/mol (see Table 2) at 950 °C [25,26]. If the combined free energy change from SrO and TiO_2 to some other phase(s) is more negative than that for the reaction (3) (−138 kJ/mol), thermodynamics predicts that the transformation from $SrTiO_3$ to these other phase(s) will be energetically favorable.

Similarly, for the $La_{1-x}Sr_xVO_3$ compounds, $LaVO_3$ can be viewed as ($1/2$ La_2O_3+ $1/2$ V_2O_3) while $SrVO_3$ can be viewed as

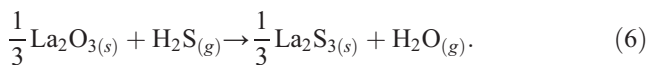(SrO+ $1/2$ V_2O_4). Table 2 lists the standard Gibbs formation energy values for some oxides (per mole of O_2), sulfides (per mole of S_2) and gases (per mole of H_2) discussed in this paper [25,26]. For simple oxides of the A-site ions, the reaction between SrO and H_2S is:

$$SrO_{(s)} + H_2S_{(g)} \rightarrow SrS_{(s)} + H_2O(g) \qquad (4)$$

and the change in Gibbs free energy at 950 °C is given by:

$$\Delta G = -92469 + 8.314 \cdot 1223 \cdot \ln\frac{P_{H_2O}}{P_{H_2S}} \text{ J/mol} \qquad (5)$$

The reaction between La_2O_3 and H_2S is given by:

$$\frac{1}{3}La_2O_{3(s)} + H_2S_{(g)} \rightarrow \frac{1}{3}La_2S_{3(s)} + H_2O_{(g)}. \qquad (6)$$

The change in free energy at 950 °C for the reaction (6) is given by:

$$\Delta G = -24561 + 8.314 \cdot 1223 \cdot \ln\frac{P_{H_2O}}{P_{H_2S}} \text{ J/mol}. \qquad (7)$$

The relative partial pressures of H_2S and H_2O under the stability test conditions were 0.1 and 0.03, respectively. Therefore, the change in Gibbs free energy at 950 °C for reactions (4) and (6)
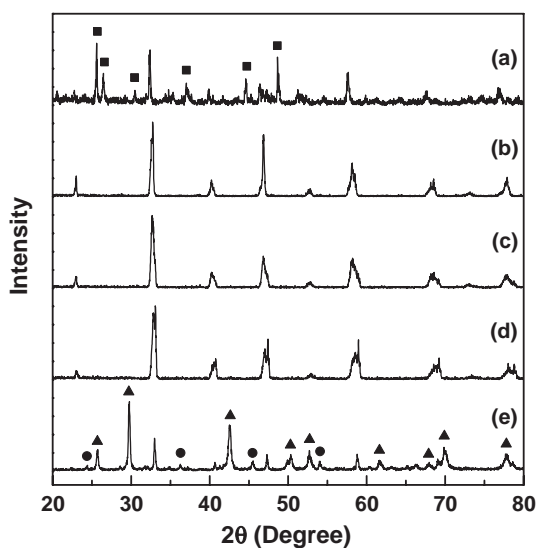

Fig. 5. XRD patterns for the LSV materials after exposure to 10%H_2S at 950°C for 5 days: (a) $LaVO_3$, (b) $La_{0.7}Sr_{0.3}VO_3$, (c) $La_{0.5}Sr_{0.5}VO_3$, (d) $La_{0.3}Sr_{0.7}VO_3$ and (e) $SrVO_3$. The symbols in the plot represent the impurity phases formed after the exposure: ■ orthorhombic distorted $LaVO_3$, ▲ SrS, ● V_2O_3.
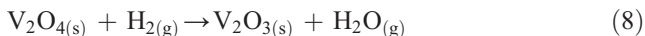
Table 2
Standard Gibbs formation energies, ΔG_f^0, for some oxides, sulfides (both in crystal state) and gases (in ideal gas state) at 950 °C (1223K) [25,26]

Material	ΔG_f^0 at 1223 K (kJ/mol)	Material	ΔG_f^0 at 1223 K (kJ/mol)
2/3 La$_2$O$_3$ (crystal)	−963.984	H$_2$ (ideal gas)	0.000
2SrO (crystal)	−938.636	H$_2$S (ideal gas)	−29.991
2/3 SrTiO$_3$ (crystal)	−886.682	H$_2$O (ideal gas)	−180.125
TiO$_2$ (crystal)	−723.126	2/3 La$_2$S$_3$ (crystal)	−712.836
2/3 V$_2$O$_3$ (crystal)	−605.723	2SrS (crystal)	−823.303
1/2 V$_2$O$_4$ (crystal)	−511.936		

(The standard Gibbs formation energy values were obtained by linear interpolation of the data at 1200 and 1300 K.).

is −105 and −37 kJ/mol, respectively, meaning that the sulfidation of both SrO and La$_2$O$_3$ are energetically favorable. For simple oxides of the B-site ions, i.e., V$_2$O$_4$ in SrVO$_3$ and V$_2$O$_3$ in LaVO$_3$, thermodynamics predicts that V$_2$O$_3$ is more stable than V$_2$O$_4$ in highly reducing atmosphere at elevated temperatures [17]. In fact, the Gibbs free energy change for the reaction:

$$V_2O_{4(s)} + H_{2(g)} \rightarrow V_2O_{3(s)} + H_2O_{(g)} \qquad (8)$$

at 950 °C is:
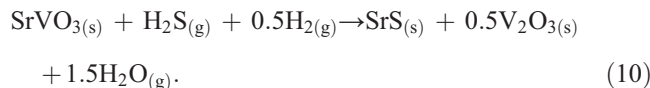
$$\Delta G = -64838 + 8.314 \cdot 1223 \cdot \ln \frac{P_{H_2O}}{P_{H_2}} \text{ J/mol.} \qquad (9)$$

Under the condition for the stability test (10% H$_2$S/3% H$_2$O/87% H$_2$ mixture), the free energy change for the reaction (8) would be −99 kJ/mol.

Therefore, for SrVO$_3$, the simple oxide of the A-site Sr^{2+} ion, SrO, tends to combine with H$_2$S and form SrS while the oxide of the B-site V^{4+} ion, V$_2$O$_4$, tends to be reduced to V$_2$O$_3$ in the environment of the stability test. Both processes are energetically favorable and the combined Gibbs free energy change (i.e., −105+(−99)/2=−154 kJ/mol) may turn out to be more negative than the free energy change when SrO and 1/2 V$_2$O$_4$ react to form SrVO$_3$. (The exact free energy change is not available in the literature, but it is expected to be close to that for the reaction (3) due to the similarity between SrTiO$_3$ and SrVO$_3$.) This makes the transformation from SrVO$_3$ to a mixture of SrS and V$_2$O$_3$ energetically favorable. In comparison, for LaVO$_3$, only the oxide of the A-site La^{3+} ion (La$_2$O$_3$) tends to combine with H$_2$S, and the free energy change (−37 kJ/mol) may be more positive than the free energy change when 1/3 La$_2$O$_3$ and 1/3 V$_2$O$_3$ react to form 2/3 LaVO$_3$. (The exact free energy change is also unavailable in the literature.) This makes the transformation from LaVO$_3$ to other phases (e.g., La$_2$S$_3$) energetically forbidden. For other La$_{1-x}$Sr$_x$VO$_3$ materials containing both Sr^{2+} and La^{3+} at the A-sites and both V^{3+} and V^{4+} at the B-sites, it is expected that the La^{3+} (also V^{3+}) rich materials would be similar to LaVO$_3$ and be resistant to H$_2$S while the Sr^{2+} (also V^{4+}) rich materials would be like SrVO$_3$ and react with high concentration of H$_2$S. However, the exact boundary has not been established.

The above explanations were supported by the presence of diffraction lines corresponding to V$_2$O$_3$ ((JCPDS card No. 34-0187)) in the XRD pattern of the SrVO$_3$ material after exposure to H$_2$S (Fig. 5(e)). It is also consistent with the weight change of the SrVO$_3$ sample after exposure to H$_2$S. If it is assumed that only the transformation of Sr^{2+} to SrS and the reduction of V^{4+} to

V^{3+} were happening when SrVO$_3$ was exposed to H$_2$S, the reaction could be written as:

$$SrVO_{3(s)} + H_2S_{(g)} + 0.5H_{2(g)} \rightarrow SrS_{(s)} + 0.5V_2O_{3(s)}$$
$$+ 1.5H_2O_{(g)}. \qquad (10)$$

The expected yield (defined by the ratio of total weight of products to reactants) for the reaction (10) is 104.3%, agreeing well with the measured value of 104.8%. (It should be pointed out that the presence of some minor unidentified diffraction lines in Fig. 5(e) indicates what was actually happening when SrVO$_3$ was exposed to H$_2$S/H$_2$O/H$_2$ gas mixture could be more complex than the reaction (10) and there may be other reactions proceeding simultaneously.

3.4. Chemical compatibility of LSV with the YSZ electrolyte

Fig. 6 shows the XRD pattern of the pellet of the La$_{0.7}$Sr$_{0.3}$VO$_3$/YSZ mixture after heat treatment at 1300 °C for 2 h in the 4% H$_2$/96% Ar mixture. Only La$_{0.7}$Sr$_{0.3}$VO$_3$ and YSZ phases could be identified from the pattern, indicating that the La$_{0.7}$Sr$_{0.3}$VO$_3$ material is chemically compatible with the YSZ at temperatures up to 1300 °C in a reducing atmosphere.

3.5. Electrical conductivity of LSV materials

Shown in Fig. 7 are the electrical conductivities of La$_{1-x}$Sr$_x$VO$_3$ (x=0, 0.3, 0.5, 0.7 and 1.0) materials in the 3% H$_2$O/97% H$_2$ mixture at various temperatures. The conductivity of LaVO$_3$ increased slowly with temperature, which is consistent with the trend observed in previous investigations at much lower temperatures [11,13,15]. For La$_{0.7}$Sr$_{0.3}$VO$_3$, typical metallic behavior was observed; the conductivity at 800 °C (149 S cm^{-1}) was more than one order of magnitude higher than that for LaVO$_3$ (5.7 S cm^{-1}) and was consistent with the literature [17]. As stated earlier, La$_{1-x}$Sr$_x$VO$_3$ is believed to undergo an insulator–metal (I–M) transformation with increasing Sr content when x is near 0.2 [13,15]. As the Sr content increases further, so does the high temperature electrical conductivity. The measured conductivity of La$_{0.3}$Sr$_{0.7}$VO$_3$ in humidified H$_2$ at 800 °C was around 800 S cm^{-1}. It is not very clear why the electrical conductivity of La$_{0.3}$Sr$_{0.7}$VO$_3$ is so close to that of SrVO$_3$. When the fuel was switched from humidified H$_2$ to humidified H$_2$S balanced by H$_2$, no significant difference in electrical conductivity was observed for La$_{1-x}$Sr$_x$VO$_3$ with x=0, 0.3, 0.5 and 0.7. This is expected because these materials are chemically stable in the presence of H$_2$S.

3.6. Coefficient of thermal expansion

Fig. 8 shows the linear expansion of a La$_{0.7}$Sr$_{0.3}$VO$_3$ sample in the temperature range of 200–1000 °C in reducing atmosphere. There was a region in the 450–550 °C range where the thermal expansion shows a sharp bend, indicating a phase transformation in this temperature range. The coefficients of thermal expansion are 9.6×10^{-6} and 11.5×10^{-6}/K in the temperature ranges of 200–450 °C and 550–950 °C, respectively, which are close to that of YSZ electrolyte [4].

3.7. Electrochemical activity

Previous studies [5,6] suggested that La$_{0.7}$Sr$_{0.3}$VO$_3$ has potential as sulfur-tolerant anode material for SOFCs. In this
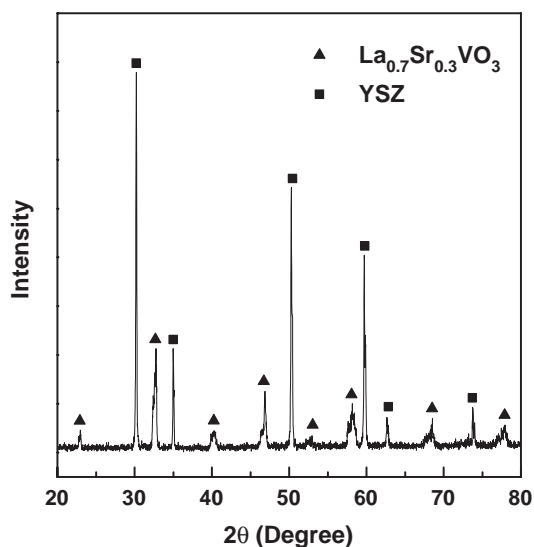
Fig. 6. XRD pattern of the pellet containing 50 wt.% $La_{0.7}Sr_{0.3}VO_3$ and 50 wt.% YSZ after heat treatment at 1300 °C for 2 h in a 4% H_2/96% Ar gas mixture.

Fig. 8. Linear thermal expansion of $La_{0.7}Sr_{0.3}VO_3$ at temperatures in the 200–1000 °C range in reducing atmosphere. The ramp rate was 2 °C/min.

study, the electrochemical activities of LSV with Sr content of 0.3 and 1.0 were studied using impedance spectroscopy in H_2 with or without H_2S. Shown in Fig. 9 are impedance spectra (after subtraction of the bulk resistance) of the button fuel cells with $La_{0.7}Sr_{0.3}VO_3$ or $SrVO_3$ anodes at 1000 °C. For $La_{0.7}Sr_{0.3}VO_3$, the total interfacial resistances (anode plus cathode) were 2.3 and 1.0 Ω cm^2 in the 3% H_2O/97% H_2 and 10% H_2S/3% H_2O/87% H_2 mixtures, respectively. This is consistent with previous investigations [5,6] and demonstrates the good activity of $La_{0.7}Sr_{0.3}VO_3$ towards H_2S oxidation. The $SrVO_3$ anode also shows decent activity towards H_2: the total

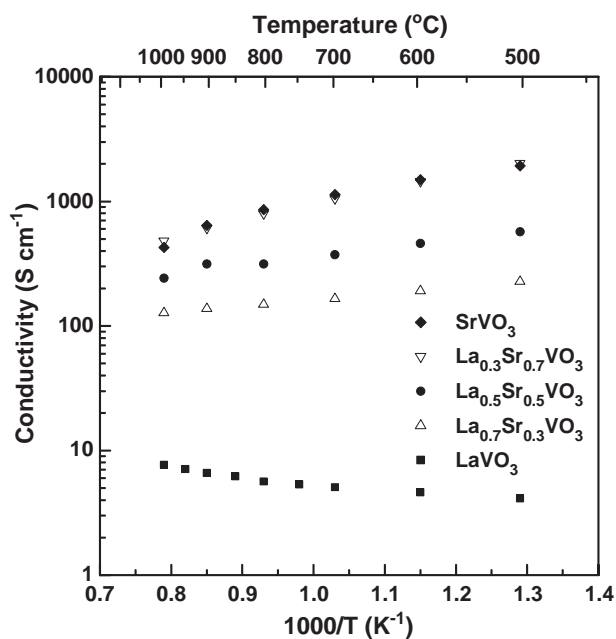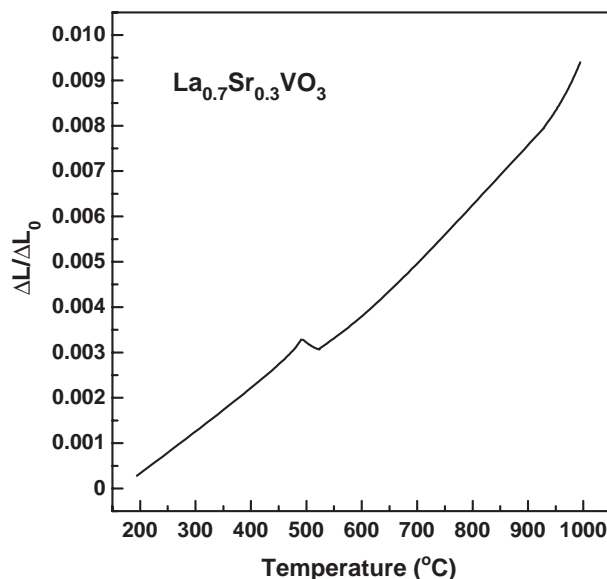interfacial resistance was as low as 1.2 Ω cm^2 in the 3% H_2O/97% H_2 gas mixture.

4. Conclusions

Some of the chemical and physical properties of $La_{1-x}Sr_xVO_3$ ($x=0$, 0.3, 0.5, 0.7 and 1.0) were investigated. The oxidation/reduction of the $La_{1-x}Sr_xVO_3$ materials involve recrystallization processes. When $La_{1-x}Sr_xVO_3$ were exposed to high concentration of H_2S at elevated temperatures, $SrVO_3$ reacted readily with H_2S while other compositions (i.e., $x=0$, 0.3, 0.5 and 0.7) showed resistance to H_2S. For $x=0.3$, the LSV material displayed good chemical and thermal compatibility with YSZ. The electrical conductivity of $La_{1-x}Sr_xVO_3$ in humidified H_2 at 800 °C increased from ~5.7 S cm^{-1} for $x=0$ to ~800–900 S cm^{-1} for $x=0.7–1.0$. LSV materials show decent activity towards the electrochemical oxidation of H_2 and/or H_2S. The results

Fig. 7. Electrical conductivities of $La_{1-x}Sr_xVO_3$ with $x=0$, 0.3, 0.5, 0.7 and 1.0 in the 3% H_2O/97% H_2 gas mixture at elevated temperatures.
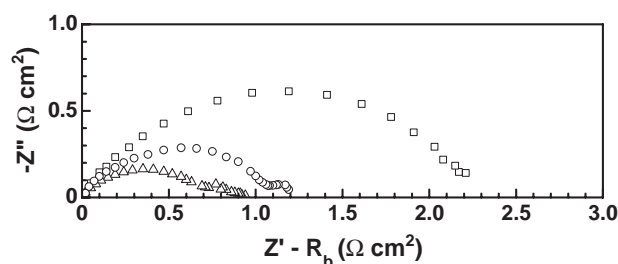

Fig. 9. Impedance spectra for three different cells operating at 1000 °C: □ stands for the cell with $La_{0.7}Sr_{0.3}VO_3$ anode operating in the 3% H_2O/97% H_2 gas mixture; ρ stands for the cell with $La_{0.7}Sr_{0.3}VO_3$ anode operating in the 10% H_2S/3% H_2O/87% H_2 gas mixture; △ stands for the cell with $SrVO_3$ anode operating in the 3%H_2O/97%H_2 gas mixture.

obtained in this study suggest that $La_{1-x}Sr_xVO_3$ with $0.3 \leq x \leq 0.7$ may be used as anode catalyst for SOFC running on fuels containing high concentration of H_2S. However, the volume change associated with the oxidation/ reduction cycle implies that these materials may have limited tolerance to re-oxidation when used as anode materials for SOFC.

Acknowledgements

References

[1] D.W. Dees, U. Balachandran, S.E. Dorris, J.J. Heiberger, C.C. McPheeters, J.J. Picciolo, Proceedings of the First International Symposium on Solid Oxide Fuel Cells, The Electrochemical Society Proceedings Series, vol. 89–11, The Electrochemical Society, Pennington, NJ, 1989, p. 317.

[2] Y. Matsuzaki, I. Yasuda, Solid State Ionics 132 (2000) 261.

[3] R. Mukundan, E.L. Brosha, F.H. Garzon, Electrochemical and Solid-State Letters 7 (2004) A5.

[4] N.Q. Minh, T. Takahashi. Science and Technology of Ceramic Fuel Cells, Elsevier Science, Netherlands, 1995, p.87, p. 157 and p. 209.

[5] L. Aguilar, S. Zha, S. Li, J. Winnick, M. Liu, Electrochemical and Solid-State Letters 7 (2004) A324.

[6] L. Aguilar, S. Zha, Z. Cheng, J. Winnick, M. Liu, Journal of Power Sources 135 (2004) 17.

[7] N.U. Pujare, K.W. Semkow, A.F. Sammells, Journal of the Electrochemical Society 134 (1987) 2639.

[8] D.R. Peterson, J. Winnick, Journal of the Electrochemical Society 145 (1998) 1449.

[9] C. Yates, J. Winnick, Journal of the Electrochemical Society 146 (1999) 2841.

[10] M. Liu, G. Wei, J. Luo, A.R. Ranger, K.T. Chuang, Journal of the Electrochemical Society 150 (2003) A1025.

[11] P. Dougier, A. Casalot, Journal of Solid State Chemistry 2 (1970) 396.

[12] P. Dougier, J.C.C. Fan, J.B. Goodenough, Journal of Solid State Chemistry 14 (1975) 247.

[13] P. Dougier, P. Hagenmuller, Journal of Solid State Chemistry 15 (1975) 158.

[14] A. Nozaki, H. Yoshikawa, T. Wada, H. Yamauchi, S. Tanaka, Physical Review B 43 (1991) 181.

[15] A.V. Mahajan, D.C. Johnston, D.R. Torgeson, F. Borsa, Physical Review B 46 (1992) 10973.

[16] V. Giannakopoulou, P. Odier, J.M. Bassat, J.P. Loup, Solid State Communications 93 (1995) 579.

[17] S. Hui, A. Petric, Solid State Ionics 143 (2001) 275.

[18] H.J. Juretchke, R. Landauer, J.A. Swanson, Journal of Applied Physics 27 (1956) 838.

[19] M.S. Hegde', D. Larcher, L. DuPont, B. Beaudoin, K. Tekaia-Elhsissen, J.-M. Tarascon, Solid State Ionics 93 (1997) 33.

[20] M.R. Rey, P.H. Dehaudt, J.C. Joubert, B. Lambert-Andron, M. Cyrot, F. Cyrot-Lackmann, Journal of Solid State Chemistry 86 (1990) 101.

[21] A.A. Fotiev, V.A. Makarov, Soviet Physics. Crystallography 14 (1970) 621.

[22] S. Solacolu, R. Dinescu, M. Zaharescu, Revue Roumaine de Chimie 17 (1972) 311.

[23] T. Palanisamy, J. Gopalakarshnan, M.V.C. Sastri, Zeitschrift fur Anorganische und Allgemeine Chemie 415 (1975) 275.

[24] H.-Zh. Li, L.-M. Liu, K.P. Reis, A.J. Jacobson, Journal of Alloys and Compounds 203 (1994) 181.

[25] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, JANAF Thermochemical Tables, Third edition, American Chemical Society, Washington D.C, 1985.

[26] M. Binnewies, E. Milke, Thermochemical Data of Elements and Compounds, Wiley-VCH, Weinheim, NY, 1999.