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Redox transitions in strontium vanadates: Electrical conductivity and dimensional changes

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ABSTRACT

The reversibility of redox-induced phase transformations and accompanying electrical conductivity and dimensional changes in perovskite-type $SrVO_{3-\delta}$, a parent material for a family of potential solid oxide fuel cell anode materials, were evaluated employing X-ray diffraction, thermal analysis, dilatometry and electrical measurements. At 873–1273 K, the electrical conductivity of $SrVO_{3-\delta}$ is metallic-like and 6–8 orders of magnitude higher compared to semiconducting V^{5+}-based strontium pyrovanadate $Sr_2V_2O_7$ and strontium orthovanadate $Sr_3V_2O_8$ existing under oxidizing conditions. $SrVO_{3-\delta}$ is easily oxidized to a pyrovanadate phase at atmospheric oxygen pressure. Inverse reduction in 10%H_2–90%N_2 atmosphere occurs in two steps through ($5Sr_3V_2O_8 + SrV_6O_{11}$) intermediate. As $Sr_3V_2O_8$ is relatively stable even under reducing conditions, the perovskite phase and its high level of electrical conductivity cannot be recovered completely in a reasonable time span at temperatures $\leqslant$1273 K. Dilatometric studies confirmed that $SrVO_3 \leftrightarrow Sr_2V_2O_7$ redox transformation is accompanied with significant dimensional changes. Their extent depends on the degree of phase conversion and, apparently, on microstructural features.

1. Introduction

Ni-based cermet fuel electrodes show good electrochemical performance in hydrogen-based fuels and have been used in solid oxide fuel cell (SOFC) and solid oxide electrolysis cell (SOEC) prototypes for decades. A major limitation of these fuel electrodes is the limited redox tolerance in redox cycles and consequent microstructural and functional degradation, including delamination or fracture of cell components [1,2]. Other drawbacks are sulfur poisoning and coking in hydrocarbon-fueled SOFCs or CO_2 electrolyzers, leading to blocking of porous anodes and loss of performance [3,4]. Significant efforts are focused therefore on the development of alternative electrode components capable to ensure efficient long-term anode operation, preferably in different fuels. A number of perovskite-like oxide ceramic materials with electronic or mixed ionic-electronic conductivity are considered as potential candidates for individual fuel electrode layers or as replacement for nickel in cermet electrodes. Due to stability requirements, the choice of parent systems is essentially limited to chromites, titanates, molybdates and vanadates [4–6].

Perovskite-type strontium vanadate and its derivatives attracted attention in the last decade as prospective components of SOFC anodes [4,7–14]. Undoped $SrVO_3$ is known to exhibit high electronic conductivity under anode operation conditions (~1000 S/cm at 1073 K and $p(O_2) \sim 10^{-20}$ atm) [15–18]. Fairly good electrochemical performance was reported for cermet anodes made of (Sr,La)VO_3 with YSZ (yttria-stbilized zirconia) or GDC (gadolinia-doped ceria) in both hydrogen and wet CH_4 fuels, with no carbon deposition observed in the latter case [11–14]. Another advantage of $SrVO_3$-based anodes relates to a high tolerance with respect to the presence of H_2S in the fuels, even at concentrations as high as 5–10% [8–10].

The major drawback of $SrVO_3$ as potential SOFC anode component is instability of perovskite lattice in oxidizing atmospheres; the upper $p(O_2)$ stability boundary was reported to correspond to approximately 10^{-17} atm at 1073 K [15]. Under oxidizing conditions, the perovskite phase undergoes transformation to insulating strontium pyrovanadate [15,16]. In addition, the lattice parameters differences suggest that this should be accompanied with large volume changes [15]. The reversibility of this transformation under fuel cell operation conditions is under question since different literature reports are somewhat contradictory on that matter. While some reports claim that $SrVO_3$ can be obtained by reduction of $Sr_2V_2O_7$ in hydrogen flow at 1273 K [19–21], others indicate that perovskite phase cannot be fully recovered after oxidation even upon exposure to forming gas for 48 h at 1573 K [16]. Different intermediate phases or phase mixtures containing $Sr_3V_2O_8$ were

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reported for calcinations in H_2-containing atmospheres at temperatures $\leqslant$1273 K [22–25].

The present work was focused on the assessment of reversibility of redox transformations between V^{4+}-based $SrVO_{3-\delta}$ perovskite and V^{5+}-based strontium pyrovanadate $Sr_2V_2O_7$ and orthovanadate $Sr_3V_2O_8$ (or $Sr_3(VO_4)_2$), and accompanying dimensional changes and electrical properties variations. Electrical conductivity and thermal expansion of individual phases were characterized under appropriate conditions. Some preliminary results on $SrVO_{3-\delta}$ were reported in our previous work [7]; this work was focused mainly on the effect of yttrium and aluminum substitutions on the stability and thermal expansion of perovskite-type vanadate, and was performed using the samples with higher porosity.

2. Experimental

The powders of $SrVO_{3-\delta}$, $Sr_2V_2O_7$ and $Sr_3V_2O_8$ were prepared by solid state synthesis route starting from $SrCO_3$ ($\geqslant$99.9%, Sigma Aldrich) and V_2O_5 ($\geqslant$99%, Fluka). Weighed and mixed components were pre-reacted in air at 773 K and 873 K for 5 h at each temperature with intermediate regrinding. Strontium pyrovanadate and orthovanadate precursor powders were additionally calcined at 973 K for 5 h in air. After ball-milling (Retsch centrifugal mill S1) with ethanol and uniaxial compaction, ceramic samples of $Sr_2V_2O_7$ and $Sr_3V_2O_8$ were sintered in air for 5 h at 1373 K and 1723 K, respectively. The powder of $SrVO_{3-\delta}$ was calcined at 1173 K (3×5 h with intermediate regrinding) in flowing 10%H_2–N_2 atmosphere, and then subjected to high-energy milling (Retsch PM 100 planetary ball mill, 650 rpm, 3 h). Uniaxially compacted disk-shaped $SrVO_{3-\delta}$ ceramic samples were sintered in 10%H_2–N_2 atmosphere at 1773 K for 10 h. In all cases, the milling procedures were performed using nylon containers and Tosoh YTZ (yttria-doped tetragonal zirconia) grinding media. Sintering of the ceramic samples was performed using alumina plates as supports with interlayer of vanadate powder of the same composition to avoid possible interactions with alumina. The sintering temperatures were selected taking into account the latest available phase diagrams of SrO–V_2O_5 system [26,27] and operational limits of available equipment for sintering under reducing conditions (in case of $SrVO_3$). The absence of liquid phase formation under selected conditions was verified in the course of preliminary sintering tests.

Sintered ceramic samples were cut into rectangular bars and polished for the dilatometric and electrical measurements. The experimental density was calculated from the mass and geometric dimension of the samples. Powdered samples for X-ray diffraction (XRD) and thermal analysis were prepared by grinding sintered ceramics in a mortar.

Room-temperature XRD patterns were recorded using Rigaku D/Max-B (Cu Kα) and PANalytical X'Pert PRO (Cu Kα) diffractometers. The latter equipment was also used for high-temperature XRD studies. Unit cell parameters were calculated using Fullprof software (profile match method). Microstructural characterization was performed by scanning electron microscopy (SEM, Hitachi S-4100 instrument). The dilatometric measurements (vertical Linseis L70/2001 instrument) and thermogravimetric analysis (TGA, Setaram SetSys 16/18 instrument, sensitivity 0.4 μg, initial sample weight ~0.5 g) were carried out in flowing air or 10%H_2–N_2 mixture at 298–1273 K with constant heating/cooling rate 2–3 K/min or isothermally as function of time. Differential scanning calorimetry (DSC) was performed in air at 5 K/min using Netzsch STA 449 F3 instrument. Electrical conductivity was studied as function of temperature and oxygen partial pressure using 4-probe DC technique under reducing conditions (H_2–H_2O–N_2 mixtures) and impedance spectroscopy (Agilent 4284A precision LCR meter) under oxidizing conditions. Isothermal conductivity measurements in redox cycles were performed using impedance spectroscopy with automated data acquisition. In all cases (ceramic processing and measurements), oxygen partial pressure in gas mixtures was monitored by YSZ (yttria-stabilized zirconia) oxygen sensor. Representative values of $p(O_2)$ corresponded to $\sim 10^{-19}$ atm in 10%H_2–N_2 mixture at 1173 K and $\sim 5 \times 10^{-5}$ atm in argon atmosphere.

3. Results and discussion

3.1. Crystal structure and microstructure of as-prepared materials

As-prepared $SrVO_{3-\delta}$ ceramics were single-phase with cubic perovskite structure (Fig. 1A). The unit cell parameter (Table 1) was found to be close to previously reported values which vary in the range 3.840–3.856 Å [17–20,23]. Inspection of literature data suggests that the lattice parameter of $SrVO_{3-\delta}$ tends to increase with increasing oxygen nonstoichiometry (e.g. Refs. [18,19]). In this work, the room-temperature oxygen nonstoichiometry ($3-\delta$) in $SrVO_{3-\delta}$ ceramics equilibrated with gas atmosphere (10%H_2–N_2) was found equal to 2.932 ± 0.001, as calculated from the TGA results on oxidation. Sintered $SrVO_{3-\delta}$ ceramics were relatively porous with density ~80% of theoretical (Table 2) and grain size in the range 3–10 μm (Fig. 2A). Thus, even with the high-energy mechanical pre-treatment of the powder, preparation of dense $SrVO_3$ ceramics requires sintering under reducing condition at temperatures higher than 1773 K, which is the upper limit of the experimental apparatus available for this work.

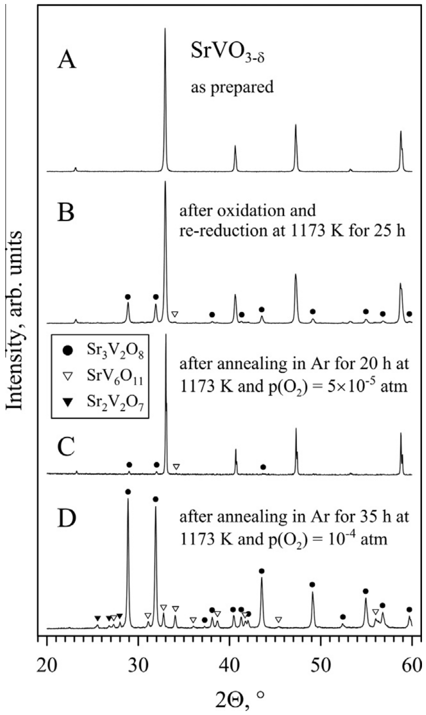

Fig. 1. XRD patterns of $SrVO_{3-\delta}$ samples: (A) as-prepared; (B) after oxidation in air for 25 h at 1173 K and subsequent reduction in 10%H_2 flow at 1173 K for 25 h; (C) after annealing in flowing Ar atmosphere with $p(O_2) = 5 \times 10^{-5}$ atm at 1173 K for 20 h; (D) after annealing in flowing Ar atmosphere with $p(O_2) = 10^{-4}$ atm at 1173 K for 35 h. Marked reflections are indexed according to JCPDS PDF # 81–1844 ($Sr_3V_2O_8$), 79–8160 (SrV_6O_{11}) and 81–0837 ($Sr_2V_2O_7$).

XRD analysis of as-prepared strontium orthovanadate ($Sr_3V_2O_8$) samples showed formation of single-phase ceramics with rhombohedral lattice (space group $R\bar{3}m$) (Fig. 3A), in agreement with literature reports [28,29]. This compound is isostructural with orthophosphate $Sr_3(PO_4)_2$ and palmierite $PbK_2(SO_4)_2$ [28], and the calculated lattice parameters are listed in Table 1. The density of prepared ceramics was above 90% of theoretical (Table 2). Sintering at elevated temperature promoted however excessive grain growth (Fig. 2B); these ceramic samples were quite brittle.

All reflection in the XRD pattern of as-prepared strontium pyrovanadate ceramics (Fig. 3C) can be indexed on the basis of triclinic cell (space group $P\bar{1}$) reported for α-$Sr_2V_2O_7$ single crystals [30,31]. The unit cell parameters (Table 1) were refined based on literature information, and allowed one to evaluate the relative density of pyrovanadate sintered ceramic (Table 2); this was ~89% of theoretical and grain size was in the range 8–55 μm (Fig. 2C).

Though α-$Sr_2V_2O_7$ is often referred to as a high-temperature polymorph [31], a "low-temperature" β-$Sr_2V_2O_7$ modification with tetragonal (space group $P4_1$) structure was reported however only in one work [32] for single crystals prepared by a slow cooling of $Sr_2V_2O_7$–$NaVO_3$ mixture (7:50 weight ratio) from 1323 K. Huang and Sleight [31] mentioned also that $\alpha \leftrightarrow \beta$ phase transition occurs at ~918 K, although no structural characterization of β phase has