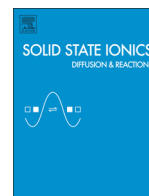




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Evaluation of W-containing $\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ ($x = 0, 0.5, 1$) anode materials for solid oxide fuel cells

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ABSTRACT

In this work, W-containing $\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ ($x = 0, 0.5, 1$) perovskite-related oxides have been for the first time evaluated in terms of their possible application as anode materials in solid oxide fuel cells. Crystal structure, thermal expansion coefficient, transport properties, oxygen content, chemical compatibility in relation to ceria-based electrolyte, and stability of the materials in reducing atmospheres have been studied. It was found that $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ and $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ oxides show simple perovskite-type structure with cubic $Pm\bar{3}m$ symmetry, while $\text{BaFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ exhibits hexagonal $P6_3/mmc$ structure. Small grains ($\sim 2 \mu\text{m}$) can be obtained for $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ compound with very simple, high-temperature synthesis process in air. Large oxygen nonstoichiometry changes of $\Delta\delta \approx 0.36$ were observed for $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ oxide upon heating in 5 vol.% H_2 in argon. Seebeck coefficient and electrical conductivity measurements revealed that $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ oxide exhibits p -type conductivity in air and n -type conductivity under reducing conditions. This oxide presents relatively good chemical compatibility in relation to $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolyte, and chemical stability in 5 vol.% H_2 in argon up to at least 800 °C. Electrochemical impedance spectroscopy studies for $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ -based cells conducted in pure hydrogen and CH_4 indicated the possibility of the application of $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ as the anode material in SOFCs.

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1. Introduction

Fuel flexibility of solid oxide fuel cells (SOFC), with the possibility of utilization of non-hydrogen fuels, can be an essential factor for the commercial adoption of SOFC technology in power generation, as the future of hydrogen economy is still to be realized, due to some of the major barriers related to costs, technological uncertainty, and infrastructure setup [1,2]. One of the main problems with SOFCs directly running on non-hydrogen fuels, such as natural gas, methane, or syngas, is carbon deposition on the anode, which can cause significant or even detrimental decrease of the cell's performance [1–3]. For the most commonly used Ni-YSZ cermet anode, the performance degradation due to the carbon deposition mainly arises from a decrease of the triple phase boundary length, which limits number of catalytic sites for fuel oxidation [1–3]. Moreover, the deposited carbon may destroy mechanical integrity of the electrode. Also, the considered non-hydrogen fuels usually contain sulfur (in a form of H_2S), which can irreversibly poison Ni-YSZ cermet anodes [1,2,4]. Therefore, the development of novel materials with improved tolerance towards carbon deposition and sulfur poisoning is essential for the construction of robust SOFCs with fuel versatility.

The application of mixed ionic–electronic conductors (MIEC) in the SOFC anode is considered to be highly beneficial, as it allows for the electrode reaction to occur on the whole surface on the electrode material, improving electrochemical properties [1,5]. Among the new anode material candidates, perovskite-type oxides from $\text{AMMoO}_{6-\delta}$ and $\text{AMWO}_{6-\delta}$ (A–Sr, Ba; M–Mg, Mn, Fe, Co, Ni) families, either B-site cation ordered or disordered, seem to be particularly attractive [4,6–9]. These materials show mixed ionic–electronic conduction in reducing conditions, moderate thermal expansion, and have already shown a great potential of application in SOFCs fueled with H_2 , CO, CH_4 or iso-octane [8,10,11]. Concerning electrical conductivity, particularly high values around $1000 \text{ S}\cdot\text{cm}^{-1}$ were reported for $\text{Sr}_2\text{FeMoO}_{6-\delta}$ in dry 5 vol.% H_2 in argon over a wide temperature range [9], almost $200 \text{ S}\cdot\text{cm}^{-1}$ at 850 °C for $\text{Ba}_2\text{FeMoO}_{6-\delta}$ in H_2 [12], as well as $550 \text{ S}\cdot\text{cm}^{-1}$ for $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ at 780 °C in air [13]. Interestingly, it was shown that modification of the chemical composition significantly affects stability of the materials, and while $\text{Sr}_2\text{FeMoO}_{6-\delta}$ compound was found to be stable only in reducing conditions [9], $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ was proved to be redox stable [13]. Nevertheless, chemical stability of these materials may be a limiting factor [9,14], especially in the case of Co- and Ni-containing compounds [15,16]. As a consequence, studies of the chemical stability of such compounds in reducing conditions, as well as chemical compatibility in relation to the electrolyte seem to be very important. While data concerning physico-chemical properties of Mo-containing materials are relatively complete, $\text{AMWO}_{6-\delta}$ -type compounds are generally less studied.

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In this work, the possibility of the application of novel W-containing anode materials with $\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ ($x = 0, 0.5, 1$) composition in electrolyte-supported SOFCs was evaluated. Previously it was reported that W-containing oxides, similarly to Mo-based ones, may possess carbon deposition and sulfur poisoning tolerance [17,18], and the idea of selection of the chemical composition (i.e., $\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$) is based on authors' previous work concerning properties of $\text{SrFe}_{0.75}\text{Mo}_{0.25}\text{O}_{3-\delta}$ [8]. Details about synthesis procedure, crystal structure, transport properties, and oxygen content together with chemical stability studies are presented. Electrochemical impedance spectroscopy (EIS) measurements of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolyte-supported button-type cells with electrodes based on the considered materials are given in pure hydrogen and in wet methane (3 mol.% H_2O). The obtained results indicate that physicochemical properties of $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ are attractive, considering its application in ceria-based SOFCs.

2. Experimental

$\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ ($x = 0, 0.5, 1$) samples were synthesized by a high-temperature solid-state reaction method with SrCO_3 , BaCO_3 , Fe_2O_3 , and WO_3 (all with $\geq 99.9\%$ purity) as the initial chemicals. After milling in a high efficiency Spex Sample-Prep 8000 M planetary ball mill (in zirconia vials), the powders were pressed into pellets and sintered for 24 h in air at 1300°C . X-ray diffraction studies (XRD) were performed on the materials in the 10° – 110° range, using Panalytical Empyrean diffractometer with $\text{Cu K}\alpha$ radiation. The diffraction data were refined with Rietveld refinement method using the GSAS/EXPGUI set of software [19,20]. Thermal expansion studies were performed for cathode materials in air up to 900°C on Linseis L75 Platinum Series dilatometer. The microstructure of the powders was studied using FEI Nova NanoSEM 200 apparatus.

Thermogravimetric analysis (TGA) was conducted on TA Q5000IR thermobalance up to 850°C in air, argon, and dry 5 vol.% H_2 in Ar (with H_2O content ≤ 3 ppm). For these measurements, about 20 mg of the powdered material, evenly placed on a Pt holder, was used. All data were corrected for buoyancy, which was established on a basis of runs performed with an empty Pt holder in the respective atmospheres.

Electrical conductivity (σ) and Seebeck coefficient (α) were measured simultaneously on dense ($\sim 90\%$) cuboid bars with dimensions of approximately $3 \times 3 \times 10$ mm. A four-probe DC method was applied for measurements of total conductivity. For the outer current electrodes Au plates were used, while the inner voltage probes, made from thin Pt wire, were wrapped around the central part of the bar sample. Absolute values of the electrical conductivity were obtained from Bruggeman's effective medium approximation, with the appropriate porosity-related parameter included for calculations [21]. The Seebeck coefficient was obtained from the dependence of thermoelectric voltage on temperature gradient (2 – 5°C) induced along length of the sample.

Chemical stability of $\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ ($x = 0, 0.5, 1$) under reducing conditions was evaluated by annealing of the anode materials under reducing atmosphere of 5 vol. % H_2/Ar at 800°C or 1000°C for 40 h, or at 600°C in pure H_2 for 4 h. After every annealing, consecutive XRD measurements were performed. Chemical compatibility between the considered materials and the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolyte was investigated by annealing of respective powder mixture (1:1 wt. ratio) in air at temperatures of 800°C for 100 h.

EIS measurements of lab-scale, button-type SOFCs were conducted on constructed cells, based on $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (CGO) electrolyte pellets, densely sintered at 1300°C in air (with approximately 0.6 mm thickness). In order to obtain good mechanical adhesion between electrodes and the electrolyte, as well as to minimize thermal expansion coefficient mismatch, composite electrodes of $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ anode material and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathode material with 40 wt.% $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolyte powder were fabricated, respectively. Symmetrical cell with two identical $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ -based composite electrodes was also constructed. Electrode pastes were prepared by

thoroughly mixing ground powders with a texanol-based binder. Sintering of the electrode layers was conducted at 1200°C , with a pre-ceding dwell step at 400°C for decomposition of the binder. The area of both electrodes was approximately 0.15 cm^2 with a thickness of about $50\text{ }\mu\text{m}$. EIS data were recorded using Solartron SI 1287 electrochemical interface and Solartron 1252A frequency response analyzer. Impedance spectroscopy was performed under open-circuit conditions in the 0.1 Hz – 300 kHz range with 25 mV amplitude. Ohmic resistance R_{ohm} and the total interfacial polarization resistance with anode and cathode contributions, $R_t = R_a + R_c$, were refined using an equivalent circuit consisting of L – R_{ohm} – $(RQ)_{\text{HF}}$ – $(RQ)_{\text{LF}}$, where L represents inductance, R resistance, Q capacitive constant phase element, and subscripts HF and LF, respectively, denote high and low-frequency contributions to the polarization resistance.

3. Results and discussion

3.1. Crystal structure, thermal expansion, and microstructure

Parameters of the crystal structural, obtained by Rietveld analysis of XRD data for all synthesized materials: $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$, $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ and $\text{BaFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$, are gathered in Table 1. Simple perovskite structure with $Pm\bar{3}m$ space group was observed for $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ and $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ samples, while in the case of $\text{BaFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$, 6H-type cation-ordered crystal structure with $P6_3/mmc$ symmetry was recorded (Fig. 1a). The same hexagonal symmetry was reported previously for the parent compound, $\text{Ba}_3\text{Fe}_2\text{WO}_9$ [22]. It can be therefore stated that despite modification of Fe:W ratio, from perfect 2:1 to 2.25:0.75, the material maintains its cation-ordered structure. Interestingly, $\text{Ba}_3\text{Fe}_2\text{WO}_9$ can be transformed to the oxygen-deficient, cation-ordered cubic perovskite-type structure ($Fm\bar{3}m$ space group) on annealing at 1350°C in low $p\text{O}_2$ atmosphere [22]. For materials with different Fe:W ratio, e.g., Ba_2FeWO_6 and Sr_2FeWO_6 , different crystal structure, tetragonal ($I4/m$), and monoclinic ($P2_1/n$) were reported, respectively [23]. In the case of the studied $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ and $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$, it seems that the introduced smaller Sr^{2+} cations prevent formation of the cation-ordered structure. All the above indicate that modification of either A-site, B-site or oxygen stoichiometry can significantly change the crystal structure of $\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{1-y}\text{W}_y\text{O}_{3-\delta}$. As can be observed in Table 1, due to different structure (and connectivity of FeO_6 and WO_6 octahedra), no linear relationship between normalized unit cell volume and average A-site radius of cations ($r_{\text{Sr}_{1-x}\text{Ba}_x}$) occurs. At the same time, with the increase of barium content, density of the materials increase, as expected, but also nonlinearly. Cubic, cation-disordered structure of $\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ and $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ seems to be more favourable from a point of view of application, as no phase transitions are expected to occur at the elevated temperatures and in reducing conditions. Dilatometry measurements were performed for the considered $\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ ($x = 0, 0.5, 1$) in air up to 900°C . The thermal expansion studies revealed that considered oxides show

Table 1
Structural parameters of $\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ ($x = 0, 0.5, 1$) oxides.

Composition	$\text{SrFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$	$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$	$\text{BaFe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$
Space group	$Pm\bar{3}m$	$Pm\bar{3}m$	$P6_3/mmc$
a [Å]	3.92229(1)	3.9781(1)	5.7469(1)
c [Å]			14.1210(1)
γ [°]			120
V [Å ³]	60.37(1)	62.95(1)	403.90(1) 67.32(1)*
$r_{\text{Sr}_{1-x}\text{Ba}_x}$ [Å]	1.44	1.53	1.61
d (g cm ⁻³)	6.147	6.550	7.002
χ^2	4.23	4.51	5.85
R_p [%]	1.67	2.18	2.93
R_{wp} [%]	2.55	3.51	4.58

* Normalized.

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