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New families of M^{n+} -doped $SrCo_{1-x}M_xO_{3-\delta}$ perovskites performing as cathodes in solid-oxide fuel cells

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ABSTRACT

We have investigated the effect of $M = Ti^{4+}$ and V^{5+} doping on the crystal structure and on the thermal, electrical, and electrochemical properties of $SrCo_{1-x}M_xO_{3-\delta}$ ($x = 0.03$ and 0.05) perovskite oxides performing as cathodes in solid oxide fuel cells (SOFC). The characterization of these materials included x-ray (XRD) and neutron powder diffraction (NPD) measurements. The introduction of Ti^{4+} and V^{5+} replacing Co in $SrCoO_{3-\delta}$ leads to the stabilization of a tetragonal perovskite superstructure at room temperature with $a = a_0$, $c = 2a_0$ ($a_0 \approx 3.9 \text{ \AA}$) defined in the $P4/mmm$ space group, containing two inequivalent Co positions. Flattened and elongated $(Co,M)O_6$ octahedra alternate along the c axis sharing corners in a three-dimensional array (3C-like structure). The thermal expansion coefficients of $SrCo_{0.95}Ti_{0.05}O_{3-\delta}$ and $SrCo_{0.97}V_{0.03}O_{3-\delta}$ have been measured between 25 and 850 °C. The electrical conductivity at the SOFCs working temperatures (650–850 °C) seems to be sufficient to yield a good performance in IT-SOFC; the polarization resistance in symmetrical cells is as low as $0.016 \Omega \text{ cm}^2$ at 850 °C for $M = Ti$. In single test cells these materials generated a maximum power of 824 mW/cm^2 at 850 °C with pure H_2 as a fuel. This good performance make these systems promising candidates as cathode materials in SOFC.

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Introduction

Solid oxide fuel cells (SOFCs) directly convert the chemical energy of a fuel into electricity; they are constituted by metal oxides as electrodes and electrolyte. Besides hydrogen they can utilize a wide variety of hydro-carbon fuels, which makes them tremendously attractive as a promising technology for off-grid generation of electrical energy [1]. The traditional SOFCs are operated above 1000 °C, but this high temperature

can cause complex materials problems, such an electrode sintering and interfacial reaction between electrolyte and electrodes materials [2]. It is thus desirable to operate SOFCs at an intermediate-temperature range between 550 and 850 °C. The cathode, catalyzing the reduction of O_2 to oxide ions, is responsible for a significant drop in the cell potential at intermediate temperatures, thus one of the major improvements required for the commercialization of IT-SOFC is the development of new mixed ionic-electronic conductors

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(MECs [3]) with better performance (lower resistance) at these temperatures.

The high-temperature cubic phase of $\text{SrCoO}_{3-\delta}$ is a promising material due to its high electrical conductivity and oxygen permeation flux [4,5]. However, this phase is not stable below 900 °C where a 3C-cubic to 2H-hexagonal phase transition takes place when the sample is slowly cooled down [5]. In order to avoid this transition, several substitutions have been performed in either the Sr (Y, Ho) or in the Co (Mo, Sn, Ti) positions [6–10]. In a previous work, we have stabilized a 3C perovskite phase by doping the $\text{SrCoO}_{3-\delta}$ system with $\text{M}^{n+} = \text{Sb}^{5+}$ or Nb^{5+} in $\text{SrCo}_{1-x}\text{M}_x\text{O}_{3-\delta}$ ($x = 0.05$) [11,12]. The introduction of even 5% doping atoms at Co positions totally avoids the stabilization of the competitive hexagonal 2H phase. In the present work we describe the effect of $\text{M} = \text{Ti}^{4+}$ and V^{5+} doping on the properties of the $\text{SrCo}_{1-x}\text{M}_x\text{O}_{3-\delta}$ system for low Ti and V substitution levels ($x = 0.05$ and 0.03 , respectively). We have studied its relationship between the crystal structure and the physical properties and we have shown that these oxides can be successfully used as cathodes in SOFCs with H_2 as a fuel.

Experimental

The reactive precursors for $\text{SrCo}_{0.95}\text{Ti}_{0.05}\text{O}_{3-\delta}$ (SCTO) and $\text{SrCo}_{0.97}\text{V}_{0.03}\text{O}_{3-\delta}$ (SCVO) have been obtained by wet-chemistry techniques. A mixture of $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_{10}\text{H}_{14}\text{O}_5\text{Ti}$ or NH_4VO_3 were dissolved in a citric acid aqueous solution with some droplets of HNO_3 ; the solution was slowly evaporated and the resulting resin was decomposed at temperatures up to 600 °C. A subsequent treatment in air at 900 °C for 12 h followed by a treatment at 1000 °C ($\text{M} = \text{Ti}$) or 1100 °C ($\text{M} = \text{V}$) for 24 h was carried out.

The initial characterization of the products was carried out by laboratory X-ray diffraction (XRD) using a Bruker D8 diffractometer (40 kV, 30 mA), controlled by a DIFFRACT^{PLUS} software, in Bragg-Brentano reflection geometry with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a PSD (Position Sensitive Detector). The data were obtained between 10° and 64° in steps of 0.05°. Neutron powder diffraction (NPD) diagrams of SCTO and SCVO were collected at RT and 1.3 K at the HRPT diffractometer of the SINQ spallation source (PSI, Switzerland), with $\lambda = 1.494 \text{ \AA}$ within the 2 θ range from 10 to 165°. About 2 g of sample was contained in a vanadium can; in all cases a time of 2 h was required to collect a full diffraction pattern. The refinement of the crystal structure was performed by the Rietveld method [13], using the FULLPROF refinement program [14]. A Cox-Thompson-Hastings function was chosen to generate the line shape of the diffraction peaks. The following parameters were refined in the final run of the fit: scale factor, background coefficients, zero-point error, unit-cell parameters, pseudo-Voigt corrected for asymmetry parameters and positional coordinates. The coherent scattering lengths of Sr, Co, Ti, V and O were 7.02, 2.49, –3.438, –0.382 and 5.803 fm, respectively.

Thermal analysis was carried out in a Mettler TA3000 system equipped with a TC10 processor unit. Thermogravimetric (TG) curves were obtained in a TG50 unit, working

either in air or in $\text{H}_2(5\%)/\text{N}_2(95\%)$ flow at a heating rate of 10 °C min^{-1} using about 50 mg of sample in each experiment.

Measurements of the thermal expansion coefficient and electrical conductivity required the use of sintered samples. Densification was performed by uniaxial pressing of pellets that were subsequently calcined at 1000 °C ($\text{M} = \text{Ti}$) or 1100 °C ($\text{M} = \text{V}$) for 12 h. Thermal expansion was performed in a dilatometer Linseis L75HX1000, between 25 and 850 °C in air atmosphere. The conductivity was measured between 25 and 850 °C in air by the four-point method in bar-shaped pellets under DC currents between 0.1 and 0.5 A. The currents were applied and collected with a Potentiostat-Galvanostat AUTOLAB PGSTAT 302 from ECO CHEMIE.

Ac impedance spectroscopy measurements were carried out in air conditions on symmetrical cells with $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ (LSGM) as electrolyte, in configurations SCTO/LSGM/SCTO and SCVO/LSGM/SCVO. For this purpose inks of the cathode materials and a binder (V-006 from Heraeus) were prepared and symmetrically painted onto both surfaces of the sintered disks obtaining symmetrical electrodes. The cells were calcined at 1000 °C for 4 h to obtain a good adherence between the cathodes and the electrolytes. Subsequently, two Pt electrodes were painted onto the cathode surfaces and calcined at 950 °C for 1 h to ensure equipotential conditions. The symmetrical cells were placed into a ceramic support and two Pt gauzes were used to supply the current and record the voltage drop through the system. Impedance measurements were performed from 550 °C to 850 °C in air, using an AUTOLAB FRA system (PGSTAT30 and FRA2 module) from Eco Chemie B.V. The measurements were carried out in potentiostatic mode from 1 KHz to 10 mHz in open circuit conditions with a signal amplitude of 50 mV.

Single cell tests were carried out using LSGM pellets as electrolyte, $\text{SrCo}_{1-x}\text{M}_x\text{O}_{3-\delta}$ (SCMO) ($\text{M}^{n+} = \text{Ti}^{4+}$, V^{5+}) as cathode material, and $\text{SrMo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SMFO) as anode material, recently developed in our group [15]. $\text{La}_{0.4}\text{Ce}_{0.6}\text{O}_{2-\delta}$ (LDC) was used as a buffer layer between the anode and the electrolyte in order to prevent the interdiffusion of ionic species. Inks of LDC, SMFO and SCMO were prepared with a binder (V-006 from Heraeus). LDC ink was screen-printed onto one side of the LSGM disk followed by a thermal treatment at 1300 °C in air for 1 h. SMFO was subsequently screen printed onto the LDC layer and fired at 1100 °C in air for 1 h. SCMO was finally screen printed onto the other side of the disk and fired at 1000 °C in air for 1 h. The working electrode area of the cell was 0.25 cm^2 (0.5 × 0.5 cm). Pt gauze with a small amount of Pt paste was used as current collector at both the anodic and the cathodic sides for ensuring electrical contact. The cells were tested in a vertical tubular furnace at 800 and 850 °C; the anode side was fed with pure dry H_2 , whereas the cathode worked in an air flow. The fuel-cell tests were performed with an AUTOLAB 302N Potentiostat/Galvanostat by changing the voltage of the cell from the OCV (“Open current voltage”) to 0.1 V, with steps of 0.010 V, holding 10 s at each step. Current density was calculated by the recorded current flux through the effective area of the cell (0.25 cm^2).

Scanning electron microscopy (SEM) images were carried out with a table-top Hitachi TM-1000 microscope.

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