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Electrochemical properties of ceramic membranes based on $\text{SrTi}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ in reduced atmosphere

A. Murashkina^a, V. Maragou^b, D. Medvedev^a, V. Sergeeva^a, A.K. Demin^{a,**},
P. Tsiakaras^{b,*}

^a Institute of High Temperature Electrochemistry, Laboratory of Solid Oxide Fuel Cells, 22 S. Kovalevskoy, 620990 Yekaterinburg, Russia

^b Dept. of Mechanical Engineering, School of Engineering, University of Thessaly, Pedion Areos, 383 34 Volos, Greece

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ABSTRACT

The present work aims at the investigation of the electrochemical properties of $\text{SrTi}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ as a membrane material for hydrogen production via electrochemical reforming. The dependence of the electrical conductivity on the oxygen partial pressure, as well as the oxygen permeability in the range of $10^{-20} \text{ atm} \leq p_{\text{O}_2} \leq 10^{-14} \text{ atm}$ is examined. The oxygen permeability is measured by an electrochemical method. The dependences of ion current as a function of the electromotive force (EMF) at various temperatures, oxygen partial pressures and the membrane surface conditions (rough and activated by PrO_x) are studied. Finally, the values of hydrogen flux at different temperatures are calculated and a long term investigation during 600 h at $p_{\text{O}_2} = 10^{-19} \text{ atm}$, $T = 1173 \text{ K}$ is carried out. According to the present results, the permeation current increases with the increase of temperature, oxygen partial pressure gradient and activation by PrO_x . The long term investigation shows that the electrical resistance of the $\text{SrTi}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ ceramic membrane increases by 10%, possibly due to the formation of micro-domains into the material's volume and the decrease in the grain boundary conductivity, because of the segregation of dopant-rich layers near the grain boundaries.

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1. Introduction

Perovskite-like oxides that present mixed oxygen ion–electron conductivity (MIEC) are considered as promising materials for oxygen permeable membranes. This kind of membranes are used for the electrochemical production of oxygen from gas mixtures, the production of hydrogen through the electrochemical reforming of water, as well as the production of synthesis gas ($\text{CO} + \text{H}_2$) through the partial oxidation of methane [1].

A schematic diagram of the transport process that takes place in a membrane with mixed ionic–electronic

conductivity is shown in Fig. 1. For the occurrence of oxygen flux through the membrane, a chemical potential gradient of oxygen (μ_{O_2}) on opposite sides of the membrane must be created. This moving force of the process can be defined using the various oxygen-containing buffer mixtures ($\text{CO} + \text{CO}_2$, $\text{H}_2\text{O} + \text{H}_2$) and atmospheres based on them ($\text{CH}_4 + \text{H}_2\text{O}$, $\text{CO} + \text{H}_2$). From the side with the high oxygen partial pressure, the process of oxygen reduction occurs, which is accompanied with the oxygen introduction to an anion sublattice of the perovskite. From the side with low oxygen partial pressure the reverse process takes place. The opposite electrochemical process results in the directed motion of ions and electrons

* Corresponding author. Tel.: +30 24210 74065; fax: +30 24210 74050.

** Corresponding author. Tel.: +7 343 3745431; fax: +7 343 3745992.

E-mail addresses: A.Demin@ihte.uran.ru (A.K. Demin), tsiak@mie.uth.gr (P. Tsiakaras).

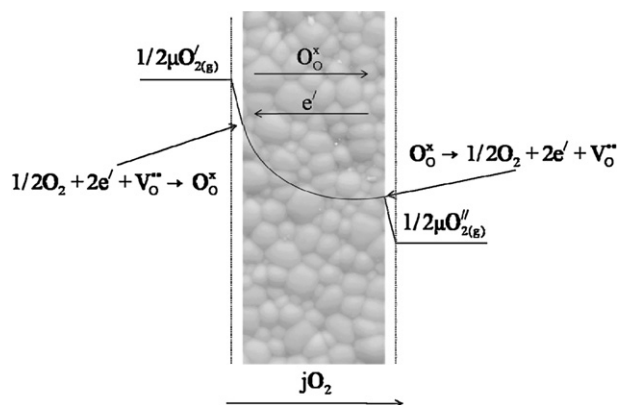


Fig. 1 – Schematic diagram of the transport process that takes place in a membrane with mixed ionic–electronic conductivity.

through the membrane. Since the ion current in the membrane is compensated by the electron current, it is necessary that the electronic conductivity of the membrane is comparable to or greater than the ionic one. The materials based on strontium titanates satisfy this requirement.

In general, strontium titanates are stable in a wide range of temperatures and oxygen partial pressures [2]. Moreover, the specific materials are more stable among other perovskite-related oxides against CO_2 -containing atmosphere [3]. The electrical properties of SrTiO_3 can be modified by doping with donors or acceptors in the A-site and B-site positions of the ABO_3 perovskite, providing high values of ionic and electronic conductivity [4–8].

The electrical properties of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$ ($x = 0-0.8$) have been studied in a wide range of oxygen partial pressures and temperatures [9]. The high level of mixed ionic–electronic conductivity that was observed constitutes them as promising membranes for oxygen extraction. The transport properties of Fe-doped strontium titanates have been also studied [9–11]; however, the reported differences, suggest further investigation.

In the present work, the $\text{SrTi}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ solid solution, which according to our previous work possesses high values of ionic and electronic conductivity [12,13], was synthesized, in order to investigate in detail its electrical and transport properties, and its suitability for application as membrane material for hydrogen production through electrochemical reforming.

2. Experimental

The $\text{SrTi}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ sample was calcined according to the conventional solid state reaction method, using SrCO_3 , Fe_2O_3 and TiO_2 of high purity as the initial materials. The main component content in the materials used for synthesis was no less than 99.99%. The synthesis of the sample was carried out at 1523 K for 5 h in air. Then the samples were stirred in ethanol, pressed at 250 MPa into 1×20 mm pellets and fired at 1723 K for 2 h. The activation of the pellets was performed by a brushing 5% solution of $\text{Pr}(\text{NO}_3)_3$ on the surface, with

following decomposition of nitrate to Pr_6O_{11} at 673 K. The density of the sintered ceramic sample determined by the hydrostatic weighing method was no less than 96% of the density calculated from the X-ray Diffraction (XRD) data.

The XRD analysis was carried out by using a DMAX-2500 RIGAKU diffractometer with CuK_α radiation in the range of $20^\circ \leq 2\theta \leq 80^\circ$. The morphology and the structure of the ceramic membrane's surface were determined by the aid of scanning electron microscopy (JSM-5500 LV JEOL microscope).

The electrical conductivity of the $\text{SrTi}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ material was measured in gas mixtures of $\text{H}_2/\text{H}_2\text{O}$ and $\text{H}_2\text{O}/\text{O}_2$ with the application of a Zirconia equipment [14] by employing the four-point dc technique at 1173 K. The cell with the sample under investigation was heated to the required temperature and the inside part of the cell was purged by pure oxygen. Thereafter, oxygen was passed through the evaporator. The evaporator was designed as a glass vessel of the original design and was filled by 2/3 with quartz sand in the lower part. The sand provides uniform heating and large surface evaporation. The evaporator was gradually heated from room temperature (partial pressure of water corresponds to 0.02–0.03 atm) to 373 K ($p_{\text{H}_2\text{O}} = 1$ atm). Afterward, the gates of the cell were blocked and further changes in the composition of the atmosphere inside the cell were carried out by an electrochemical oxygen pump.

At the beginning of the experiment the atmosphere inside the cell corresponded to pure oxygen ($p_{\text{O}_2} = 1$ atm). When the evaporator was heated, oxygen was slowly saturated by water vapor (with fulfilling condition $p_{\text{O}_2} + p_{\text{H}_2\text{O}} = 1$ atm), and after heating the evaporator to 373 K, the atmosphere in the interior of the cells corresponded to water vapor containing traces of oxygen. Thereafter, the cell's valves were blocked and the further changes in the composition of the atmosphere inside the cells were performed by pumping initially the residual oxygen, and then – bound oxygen (with fulfilling condition $p_{\text{H}_2\text{O}} + p_{\text{H}_2} = 1$ atm).

The oxygen permeability of the membrane and the hydrogen flux were measured by the electrochemical method using a specific device (Fig. 2) described in detail in a previous publication [13]. In order to study potential hydrogen production by high-temperature electrochemical conversion using the given material, a research cell was designed. Two

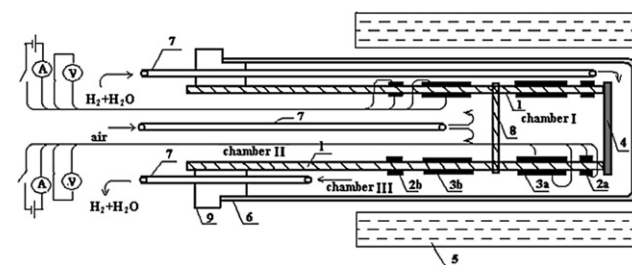


Fig. 2 – The electrochemical cell: 1 – $\text{ZrO}_2\text{-Y}_2\text{O}_3$ tube, 2a and 2b – Pt electrodes of an electrochemical sensor for oxygen partial pressure measurements, 3a and 3b – Pt electrodes of an electrochemical oxygen pump, 4 – solid state membrane, 5 – high temperature furnace, 6 – quartz tube, 7 – gas fed tube, 8 – gastight YSZ disk, 9 – teflon tap [13].

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