



Development of lanthanum-doped praseodymium cuprates as cathode materials for intermediate-temperature solid oxide fuel cells

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ARTICLE INFO

Keywords:

Praseodymium cuprate
Composite cathode
Impedance spectroscopy
Electrochemical properties
SOFC

ABSTRACT

Electrochemical properties of the $\text{Pr}_{2-x}\text{La}_x\text{CuO}_4$ ($x = 0.05; 0.1; 0.3$) (PLCO) oxides in oxygen reduction reaction (ORR) were examined towards their applicability as cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFCs). $\text{Pr}_{1.95}\text{La}_{0.05}\text{CuO}_4$ (PLCO0.05) was defined as a favorable basis for the composite cathode material due to its conducting, thermomechanical and electrocatalytic properties. The optimization of the annealing temperature of the PLCO0.05-xGDC composite electrode deposited on GDC solid electrolyte surface had shown that the lowest area specific resistance (ASR) was achieved at 850 °C. The highest electrochemical activity in ORR was achieved for the composition containing 40 wt% GDC in the temperature range of 600–750 °C. The application of PLCO0.05-40GDC composite cathode instead of pure PLCO0.05 made it possible to reduce ASR up to 10 times at 700 °C in air (from 0.87 $\Omega\text{-cm}^2$ ($x = 0$ wt%) to 0.08 $\Omega\text{-cm}^2$ ($x = 40$ wt%)). According to the data obtained, PLCO0.05-40GDC can be considered as a promising cathode material for IT-SOFCs.

1. Introduction

Nowadays, alkali-earth-free (Sr or/and Ba) and Co-free mixed electron-ionic conductors provoke the research interest as alternative cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFCs) with an operating temperature range of 500–800 °C [1,2]. The rejection of the Sr and Ba content can allow improving the cathode tolerance towards CO_2 and by this way results in enhancing its long-term stability. Along with that Co-free cathode materials may provide a sustainable SOFC operation under heating-cooling cycling due to improved compatibility in thermal expansion between a cathode and a solid electrolyte.

Among the rare-earth (RE) cuprates Ln_2CuO_4 , where $\text{Ln} = \text{RE}$, praseodymium cuprate Pr_2CuO_4 (PCO) attracts much practical research interest as a cathode material from the viewpoint of SOFC application [3–7]. One of the promising ways to improve the functionality of the material is the partial substitution of praseodymium for lanthanum. The investigation of thermal expansion behavior and conductive properties of the $\text{Pr}_{2-x}\text{La}_x\text{CuO}_4$ (PLCO) cuprates showed that these compounds are of interest for further study as SOFC cathodes [8]. The materials possess a high electrical conductivity (~ 100 S/cm at 800 °C) and have a thermal expansion coefficient (TEC) of $(11.7\text{--}12.1) \times 10^{-6} \text{K}^{-1}$ [8]. The last one ensures its good thermo-mechanical compatibility with ceria solid electrolyte (TEC = $12.4 \times 10^{-6} \text{K}^{-1}$ for $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$

(GDC) [9]). Unfortunately, there are no electrochemical studies of PLCO electrodes are available to our knowledge. Therefore the presented work is aimed in evaluation of La-doped Pr_2CuO_4 as potential SOFC cathode materials.

2. Experimental

Single-phase $\text{Pr}_{2-x}\text{La}_x\text{CuO}_4$ ($x = 0; 0.05; 0.1; 0.3$) powders were prepared by a conventional solid-state route from pre-fired La_2O_3 , Pr_6O_{11} and CuO according to Ref. [8]. Appropriate amount of these initial reagents with 99.9% purity were mixed by ball-milling under heptane. After drying during the 12 h samples were pressed into pellet and annealed on Al_2O_3 crucibles at 1000 °C for 50 h in air. Phase purity of the samples was checked by X-ray powder diffraction (XRPD) recorded on Huber G670 Guinier diffractometer ($\text{CuK}\alpha_1$ radiation, image foil detector, $20^\circ \leq 2\theta \leq 70^\circ$).

Electrochemical properties of the PLCO electrode materials in oxygen reduction reaction (ORR) were studied using symmetrical electrochemical cells of the electrode/electrolyte/electrode configuration fabricated by electrode inks screen-printing on dense GDC electrolyte pellets. The GDC pellets (relative density $\sim 95\%$) were prepared from $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powder (Sigma Aldrich®) by uniaxial pressing followed by sintering at 1400 °C for 4 h in air. Before the preparation of the electrode inks the PLCO powders was preliminary grinded in a ball

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mill for 15 min under ethanol. The particle size distribution analysis carried out on laser particle sizer Fritsch Analysette 22 showed that the grinded powder particles predominantly had a size in the range of 1 to 3 μm . The outcome powders were then mixed with an organic binder (Heraeus V006) in the 1:1 ratio, and the obtained electrode inks were screen printed on a polished surface of GDC pellets using of VS-Monoprint PES HT PW 77/55 (Verseidag-Techfab GmbH) woven mesh to create working and counter electrodes on opposite sides of the pellet. This procedure was repeated 3 times. The pellets with electrode layers were dried at 130 °C for 1 h in air after each screen printing procedure. After then the pellets were annealed at 900 °C for 4 h in air. The area of single electrode was $\sim 0.25 \text{ cm}^2$. Pt-paste placed on the face site of GDC pellet and then annealed at 900 °C for 4 h in air was used as a reference electrode.

PLCO-xGDC composite electrodes based on the most promising PLCO composition and GDC solid electrolyte were prepared by mixing of the PLCO powder with an appropriate amount of GDC (x showed GDC content, which varied from 20 to 50 wt%) followed by their homogenization in a ball mill for 30 min under heptane. Thereafter the resulting mixtures were dried in air to remove the heptane. The preparation of electrode inks based on the PLCO-xGDC composites and their deposition technique were similar to that described above for the PLCO electrodes.

Microstructure of electrode/electrolyte interfaces was characterized by scanning electron microscopy (LEO Supra 50VP). Cross-section (cleavage) of the samples was analyzed.

Electrochemical characterization of the electrode/electrolyte interface was carried out by AC impedance spectroscopy. Impedance spectra were recorded using a P-5X impedance spectrometer (Elins Ltd., Russia) over the frequency range of 500 kHz–0.1 Hz. Measurements were performed using a three-electrode technique at the OCV conditions as a function of temperature (600–750 °C) in air. Signal amplitude of 30 mV was used to measurements of the $\text{Pr}_{2-x}\text{La}_x\text{CuO}_4$ electrodes. Study of the PLCO-xGDC composite electrodes was performed at the imposed signal amplitude of 10 mV. Impedance spectra fitting were carried out by Zview software (Scribner Associates, Inc.). The sample temperature was controlled by Pt-Pt/Rh thermocouple placed near the sample.

To test the electrode performance under DC loading condition, a current loading of 300 mA/cm^2 was supplied between the working and the reference electrode for 30 h. The DC experiment was performed by the P-20X potentiostat/galvanostat (Elins Ltd., Russia) at 710 °C in air. The electrode polarization resistance was measured by impedance spectroscopy before and after DC loading. The measurement after constant current operation for 30 h was performed 1 h after DC tuning off. The cathode overpotential (η_c) was calculated according to the following equation:

$$\eta_c = \Delta U_{WE} - iR_s \quad (1)$$

where ΔU_{WR} – the monitored potential difference between the working and the reference electrode, i – the supplied current, R_s – the series resistance, which mainly originates from the electrolyte, was given by the high-frequency intercept with the real axis on the spectra from the impedance measurements carried out between the working and the reference electrode.

3. Results and discussion

Since a chemical reaction at the electrode/electrolyte interface may provoke a degradation of the electrochemical performance at operation condition, the chemical stability between PLCO and GDC at a high temperature was studied. For this purpose a mixture of PLCO0.1 and GDC powders taken in a weight ratio of 1:1 was annealed at 900 °C and 1000 °C for 25 h in air. Fig. 1 shows XRPD patterns of the PLCO0.1-GDC mixtures after heat treatment. Neither additional reflections at XRPD pattern nor detectable changes of the unit cell parameters both for PLCO0.1 and GDC are observed after annealing at 900 °C. However, the

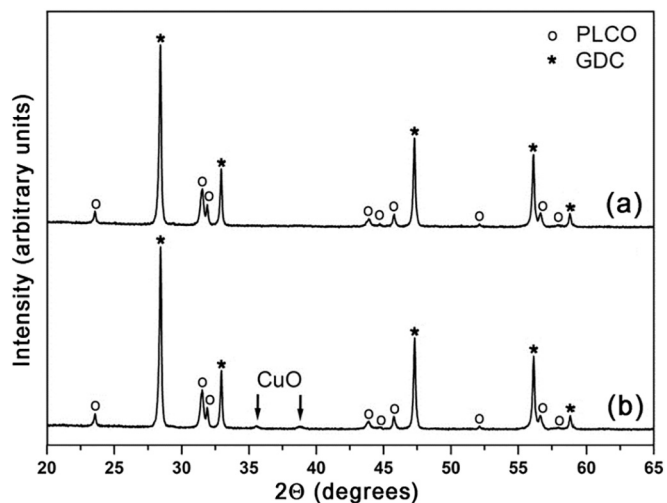


Fig. 1. XRPD patterns of the PLCO0.1-GDC powders annealed at 900 °C (a) and 1000 °C (b) for 25 h in air.

increase of the annealing temperature up to 1000 °C leads to the appearance of additional reflections corresponding to the position of the most intensive peaks of CuO (relative intensity did not exceed 2%). The reason for their appearance may be associated with the formation of solid solutions with the fluorite structure based on ceria and praseodymium oxide [10]. However, it can be assumed that annealing of the PLCO0.1-GDC mixture at 1000 °C leads to a slight decay of the cuprate phase due to the incorporation of RE-cations into the fluorite structure of the solid electrolyte, resulting in the formation of a new solid solution based on ceria [10,11]. Thus, the obtained results indicate that the PLCO electrodes can be used together with GDC at temperatures below 900 °C.

In order to determine the preferable electrode composition among the $\text{Pr}_{2-x}\text{La}_x\text{CuO}_4$ ($x = 0; 0.05; 0.1; 0.3$) cuprates, the electrochemical properties of the compounds were studied by impedance spectroscopy. Fig. 2(a) presents typical impedance spectra of the $\text{Pr}_{2-x}\text{La}_x\text{CuO}_4$ electrodes recorded nearby 660 °C in air. The high-frequency intercept value of the impedance arc with the real axis attributes to the ohmic resistance of an electrolyte and lead wires. To simplify comparison of the impedance responses of different electrode materials, the experimental impedance spectra were normalized by high-frequency intercept value to zero. Overall area specific resistance (ASR) of an electrode was calculated as a difference between low- and high-frequency intercepts of an impedance spectrum on the real axis of resistance after correction by the electrode surface area. Fig. 2(b) shows the temperature dependences of ASR for the $\text{Pr}_{2-x}\text{La}_x\text{CuO}_4$ electrodes in air. The dependences exhibit thermoactivated behavior over the whole studied temperature range. As one can see the PLCO0.05 composition possesses the highest electrochemical performance in the ORR. The possible reason of such behavior may be caused by the highest electrical conductivity of this compound ($\sim 120 \text{ S}/\text{cm}$ at 800 °C) in comparison with other cuprates of the $\text{Pr}_{2-x}\text{La}_x\text{CuO}_4$ family, and thermal expansion behavior similar to GDC [8].

One of the key parameters that determine the electrochemical performance of a SOFC cathode material, ceteris paribus, is the annealing temperature of an electrode layer to a solid electrolyte surface. It has an effect on the microstructure of the electrode and the electrode/electrolyte interface as well as and the reactivity between electrode and electrolyte, therefore, it affects the electrocatalytic active sites with respect to the oxygen reduction process. To determine the optimal annealing temperature for the PLCO-xGDC composite electrode, a series of identical symmetrical electrochemical cells with a composite electrode contained an average grade of GDC in the composite (PLCO0.05–30GDC) was prepared. Annealing of the cells was

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