



Evaluation of $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{4+\delta}$ and $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{4+\delta}$ Ruddlesden-Popper-type layered oxides as cathode materials for solid oxide fuel cells



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ABSTRACT

$\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ and $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ Ruddlesden-Popper-type oxides were synthesized by a soft chemistry method and characterized in terms of their crystal structure as a function of temperature, thermal expansion coefficient, oxygen content, transport properties and chemical stability, as well as compatibility in relation to $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolyte. $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ crystallizes in $F4/mmm$ space group, while $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ possesses $Bmab$ symmetry. Oxygen nonstoichiometry was determined, showing oxygen excess at room temperature: $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{4.12}$ and $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{4.07}$, but with only small changes in air up to 850 °C. The obtained TECs are compatible to most commonly used electrolytes. $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ possesses relatively good electrical conductivity, exceeding 100 S cm^{-1} in 300–800 °C. A maximum on the electrical conductivity, present for both materials, correlates well with minimum, observed on Seebeck coefficient characteristics. For $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ -based SOFC, maximum power densities exceeding 0.13 W cm^{-2} at 800 °C were recorded. Despite good performance, stability issues arise from a partial decomposition of the materials at 1000 °C.

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1. Introduction

Lowering working temperature of Solid Oxide Fuel Cells (SOFC) to the intermediate range (600–800 °C) is considered highly beneficial, due to the expected improvement of corrosion resistance and enhanced stability of cell's components, but also because of availability of cheaper metallic interconnects [1–7]. Apart from typical $\text{Ln}_{1-x}(\text{Sr},\text{Ba})_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ simple perovskites [4–6] or $\text{Ln}_{2-x}(\text{Ba},\text{Sr})_x\text{Co}_{2-y}\text{M}_y\text{O}_{6-\delta}$ (Ln: lanthanides, M: 3d metals) double perovskites [2,8], which are considered as candidate cathode materials for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFC), Ruddlesden-Popper-type $\text{Ln}_2\text{MO}_{4\pm\delta}$ and $(\text{Ln}_{1-x}\text{Sr}_x)_2\text{MO}_{4\pm\delta}$ oxides are also studied, due to their good mixed ionic-electronic transport properties and moderate values of thermal expansion coefficient [9,10]. In these materials, especially if $\text{M}=\text{Ni}$, significant amount of interstitial oxygen is present in oxidizing atmospheres, diffusion of which may enhance oxygen reduction reaction occurring on the cathode in the intermediate temperature range [11–14]. In general, in Ln_2MO_4 -type oxides the interstitial oxygen can provide good ionic conductivity, which is

attractive for the application. For example, for $\text{La}_2\text{NiO}_{4+\delta}$ compound, the preferential site of the interstitial oxygen is the center of the pseudo-tetrahedron of lanthanum in the rock salt layer [15]. Fast ionic conduction path extends in parallelly to the rock salt layers. The anisotropic, two-dimensional oxygen diffusion was confirmed by theoretical calculations and experiments on a single crystal specimen [16,17].

The structural aristotype for $\text{Ln}_2\text{MO}_{4\pm\delta}$, realized in case of K_2NiF_4 , is characterized by tetragonal structure with $I4/mmm$ space group. It can be described as layered sequence of perovskite-like ABO_3 and NaCl-like AO units along c -axis, with M (Ni) cations having octahedral coordination. It can be also considered as $n=1$ example of Ruddlesden-Popper series $\text{A}_{n+1}\text{B}_n\text{X}_{3n+1}$, and is labelled as T-phase [18]. Assuming all possibilities of octahedra tilting, additional 32 distorted structures are possible, giving different crystal symmetries [19], and for instance, for Pr_2NiO_4 $Fmmm$ symmetry was reported [20]. Depending on M cation, for compounds with smaller Ln^{3+} cations T'-phase can be observed, which differs from T-phase mostly in displacement of oxygen anions along c -axis. In such structure coordination of M (for instance copper) is square planar. Exemplary compound having such the structure is Pr_2CuO_4 [21]. Intermediate T*-phase is also known, with 5-fold pyramidal coordination of M [18].

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There are literature reports showing good electrochemical properties of Ln_2NiO_4 nickelates, which were used as cathode materials in IT-SOFCs, especially Pr_2NiO_4 oxide [4,11,20]. However, due to the thermodynamic metastability of Pr_2NiO_4 at temperatures below 850°C in oxidizing atmospheres, decomposition of the material into the Ruddlesden-Popper type $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ and Pr_6O_{11} oxides was found to occur [20,22]. The $\text{Ln}_2\text{CuO}_{4\pm\delta}$ cuprates with good chemical stability were also considered as cathode materials for IT-SOFCs [21,23–25], but in general, cuprates are characterized by a lower content of the interstitial oxygen (δ can be also <0) and lower catalytic activity [26]. Materials with Ni and Cu cations present together at the M-site were also investigated [26–29], and it was shown that $\text{La}_2\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}_4$ has a high oxygen diffusivity with fast surface exchange rate, comparable to the undoped La_2NiO_4 oxide [30]. Very high values of oxygen diffusion coefficients and surface exchange coefficients were reported for the $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_4$ series, especially at temperatures in between 500°C and 700°C [26]. $\text{Pr}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_4$ [31] and $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_4$ [26–28,31,32] were also studied as cathode materials for SOFCs, showing promising results. Considering the above, further studies on Ruddlesden-Popper-type Ln_2MO_4 with Cu and Ni present at the M-site at the same time are of interest.

In this work, physicochemical properties regarding crystal structure, microstructure, thermal expansion properties, oxygen nonstoichiometry, electrical conductivity and Seebeck coefficient of $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ and $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ oxides were systematically investigated. Electrochemical properties of $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ and $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ -based laboratory-scale IT-SOFCs were also given. The results were supplemented by chemical stability data of the considered materials at high temperatures and reactivity in relation to $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$ electrolytes.

2. Experimental

Soft chemistry method was used in order to synthesize $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ and $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ oxides. Stoichiometric amounts of respective nitrates were dissolved in a small amount of deionized water. Then, ammonia salt of ethylenediaminetetraacetic acid (used as the complexing agent) was added into the solutions. The obtained homogeneous mixtures were heated in quartz containers up to around 400°C . During the heating, evaporation of water, decomposition of excessive ammonia nitrate and oxidation of residual carbon were observed. Final heat treatment of the materials was conducted at 1100°C for 30 h in air. Synthesis of $\text{Nd}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ compound was also attempted, however, a multiphase product was always obtained, with presence of Nd_2CuO_4 -like T'-type and Nd_2NiO_4 -like T-type phases, among others. This is crucial result, showing possible tendency of separation of $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ into Cu- and Ni-rich components at high temperatures. This effect is discussed below for the studied $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ and $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ oxides.

Structural studies at room temperature (RT) of the synthesized compounds were performed using Panalytical Empyrean diffractometer in 10 – 110 deg range with $\text{CuK}\alpha$ radiation. The X-ray data were refined using Rietveld method with GSAS/EXPGUI set of software [33,34]. High temperature XRD measurements were performed on Panalytical Empyrean apparatus equipped with Anton Paar HTK 1200N oven-chamber, and the results of the refinements allowed for calculation of thermal expansion coefficient (TEC). Thermal expansion studies were also performed for cathode materials in air up to 900°C on Linseis L75 Platinum Series dilatometer.

Additional Scanning Electron Microscopy (SEM) measurements were performed using FEI Nova NanoSEM 200 apparatus on powders obtained after crushing and grinding of “as synthesized” pellets.

Thermogravimetric (TG) measurements were performed on TA Instruments Q5000IR apparatus in RT – 850°C range in artificial air up to 850°C and in 5 vol.% H_2 in Ar atmosphere up to 600°C , with heating rate of 2°min^{-1} in air and 5°min^{-1} during reduction. Oxygen content in the materials at room temperature was evaluated on a basis of TG reduction experiments, during which the initial compounds were reduced to Ln_2O_3 respective oxides and metallic Cu and Ni, as confirmed by XRD studies. This allowed to calculate temperature dependence of δ in the compounds in air. For TG-based calculations the buoyancy effect was appropriately considered.

Transport properties of the synthesized materials were characterized by a four-probe DC method for evaluation of the electrical conductivity (σ) and dynamic (slope) method for Seebeck coefficient measurements (α). Studies were done on dense samples with cuboid shape (approx. $3 \times 4 \times 10$ mm). The effect of porosity of the sinters was taken into account, with an appropriate correction taken from Bruggeman's effective medium approximation [35].

Chemical stability of the oxides towards typical $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (CGO20) solid electrolyte was evaluated by analyzing XRD data gathered for respective cathode material and electrolyte powder mixtures (50:50 wt.%), which were heated at 1000°C in air for 100 h.

Button-type electrolyte-supported IT-SOFC cells were constructed based on the considered cathode materials. Commonly used 40 wt.% 8YSZ – 60 wt.% NiO paste was used for anode fabrication. The paste was painted on one side of the 0.5 mm gas tight CGO20 pellet and fired at 1200°C in air. Cathode paste was prepared by mixing of thoroughly grinded $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ or $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ powder with an appropriate amount of texanol-based binder. Initial attempt to sinter cathode was conducted at 1100°C , but the layer had insufficient adhesion to the electrolyte, however, successful firing was achieved at 1200°C . Symmetrical cells with identical $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ electrode material were also fabricated, and impedance data were collected in the conditions of artificial air. Area of both electrodes in the constructed cells was approx. 0.25 cm^2 with a thickness of about 0.3 mm. Cells were fueled with dry hydrogen with $20\text{ cm}^3\text{ min}^{-1}$ of the gas flow, and air flow on the cathode side.

Cell performance was studied using Solartron SI 1287 electrochemical interface and Solartron 1252A frequency response analyzer. The impedance spectroscopy measurements were performed under open-circuit conditions in 0.1 – 300 kHz range with 25 mV amplitude. The interpretation of data was conducted in accordance with the method presented in the work [36]: ohmic resistance R_{ohm} and the total interfacial polarization resistance ($R_a + R_c$), which consists of contributions from both electrodes, were refined using equivalent circuit consisting of L - R_{ohm} -(RQ) $_{\text{HF}}$ -(RQ) $_{\text{LF}}$, where L is an inductance, R – resistance, Q – constant phase element, HF and LF stand for high-frequency and low-frequency contribution.

3. Results and discussion

3.1. Crystal structure, microstructure and thermal expansion

XRD data collected at room temperature for the synthesized materials are shown in Fig. 1a, and refined structural parameters of $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ and $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ oxides are gathered in Table 1. Based on previous report, in the case of $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$, $F4/mmm$ space group was selected for Rietveld refinement [29]. However, the data could also be successfully refined choosing $Bmab$ space group, with similar residues. For $\text{Pr}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ material, structural refinement was performed in the mentioned $Bmab$ space group. In both cases, Ni and Cu cations are present in octahedral

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