

Electrochemical Properties of Composite Cathode Materials $\text{Pr}_{1.95}\text{La}_{0.05}\text{CuO}_4\text{—Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ for Intermediate Temperature Solid Oxide Fuel Cells¹

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Abstract—The electrochemical properties are studied for composite electrodes $\text{Pr}_{1.95}\text{La}_{0.05}\text{CuO}_4(\text{PLCO})\text{—}x\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}(\text{GDC})$, where $x = 20, 30, 40$, and 50 wt % GDC with the aim of finding the composition with the best electrochemical efficiency in the oxygen reduction reaction. Varying the temperature of sintering of the PLCO— x GDC electrode layer to the surface of GDC solid electrolyte shows that the minimum polarization resistance (R_{η}) is reached at the temperature of 850°C . For the PLCO— x GDC composition containing 40 wt % GDC, in the temperature range of $600\text{—}750^{\circ}\text{C}$, the maximum electrochemical activity in oxygen reduction reaction is observed as indicated by 10 -fold decrease in R_{η} as compared with single-phase PLCO (from 0.87 ($x = 0$) to $0.08 \Omega \text{ cm}^2$ ($x = 40$) at 700°C in air). According to the data obtained, the PLCO— 40 GDC composite can be considered as a promising cathode material for intermediate temperature solid oxide fuel cells.

Keywords: praseodymium cuprate, composite cathode, electrode/electrolyte interface, impedance spectroscopy, SOFC

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INTRODUCTION

Among fuel cell types used today, the solid oxide fuel cells (SOFC) combine such qualities as the high energy efficiency and tolerance towards various kinds of fuel [1, 2]. At the same time, the high cost of the SOFC technology limits their prospects in the market of alternative power sources, being primarily associated with the high working temperature of such devices ($800\text{—}1000^{\circ}\text{C}$). To make SOFC more economically attractive as compared with traditional energy conversion technologies, their technology should be refined. The further development of the SOFC technology is first of all directed at lowering their working temperature range down to $500\text{—}800^{\circ}\text{C}$, which should decrease the degradation rate of materials and bring us closer to solving the problems associated with hermetical sealing of cells and also make it possible to use cheaper interconnectors. The latter factors will allow increasing device's service life, make it more economically attractive in the market of alter-

native power sources. However, as the temperature decreases, the electrochemical resistance of the main cell components increases, particularly, the resistance of the cathode material because of the relatively high activation energy required for the oxygen reduction reaction. Thus, the necessary condition for the development of commercially attractive SOFC is the creation of materials with the high electrocatalytic activity as regards oxygen reduction in the intermediate temperature region ($500\text{—}800^{\circ}\text{C}$).

Among cuprates of rare earth elements (REE) Ln_2CuO_4 , where $\text{Ln} = \text{REE}$, the praseodymium cuprate Pr_2CuO_4 (PCO) is of key interest as regards its use as the cathode in SOFC [3–5]. One of the ways to improve the functional characteristics of this material is to substitute lanthanum for a part of praseodymium. A study of thermomechanical and electroconduction properties of a group of $\text{Pr}_{2-x}\text{La}_x\text{CuO}_4$ cuprates has shown that the $\text{Pr}_{1.95}\text{La}_{0.05}\text{CuO}_4$ (PLCO) composition is the most interesting because exhibits the higher conduction characteristics as compared with PCO and demonstrates the much similar thermomechanical behavior [6]. This material has the high conductivity

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(~ 120 S/cm at 800°C [6]) and its thermal expansion coefficient (TEC) $11.9 \times 10^{-6} \text{ K}^{-1}$ [6] ensures its good thermomechanical compatibility (deviation by less than 5%) with the material of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) solid electrolyte (TEC = $12.4 \times 10^{-6} \text{ K}^{-1}$ [7]). In connection with this, the further investigation of properties of this material in its composites with the GDC solid electrolyte is of interest as regards the development of the efficient cathode for intermediate-temperature SOFC. Thus, the aim of this study was to consider the effect of the composition of complex electrodes PLCO–GDC on their electrocatalytic activity in the oxygen reduction reaction and assess whether it is expedient to use them as the cathode materials in SOFC.

EXPERIMENTAL

For studying the electrode characteristics of PLCO– x GDC composite cathode materials, we prepared symmetrical electrochemical cells with the configuration electrode/electrolyte/electrode. As the solid electrolyte, we used GDC pellets prepared from commercial reagent $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (Aldrich[®], powder particle size $0.1\text{--}0.5 \mu\text{m}$), which was sintered at 1400°C for 4 h. The relative density of the resulting GDC pellets was $\sim 94\%$. PLCO and GDC powders (Aldrich[®]) were used as the starting reagents for preparation of the PLCO– x GDC composite electrodes ($x = 20, 30, 40,$ and 50 wt % GDC). The PLCO powder was obtained by the ceramic method according to the procedure described earlier [6]. The phase composition of samples was identified by the X-ray diffraction (XRD) method by means of diffractometer Huber G670 ($\text{CuK}_{\alpha 1}$ radiation, 2θ interval $20^\circ\text{--}65^\circ$, Huber Diffraktionstechnik GmbH & Co. KG, Germany). For identifying the compound synthesized, we used the X-ray diffraction database ICDD PDF-2. Before the use, the synthesized PLCO powder was milled in a ball mill for 15 min in ethanol. The analysis of size distribution of powder particles carried out by the method of light scattering on a laser diffraction microanalyzer Analysette 22 “Fritsch” (Germany) has shown that the particle size was about $1\text{--}3 \mu\text{m}$. The electrode material PLCO– x GDC, where x varied from 20 to 50 wt % GDC, was prepared by mixing PLCO and GDC powders in the required ratio, which was followed by homogenization in a ball mill (agate mortar and agate balls were used) under a layer of heptane for 30 min. After this, the mixtures were dried in air until complete removal of heptane. Then, we prepared suspensions on the basis of the PLCO– x GDC mixture and an organic binder (Heraeus V006, Germany) in the 1 : 1 mass ratio. The suspensions were applied on the polished surface of sintered GDC pellets by the method of screen plating with the use of VS-Monoprint PES HT PW 77/55 woven mesh (Verseidag-Techfab, Germany). After application of electrode layers, the sam-

ples were dried at 130°C for 30 min. The deposition procedure was repeated three times on each side of the electrochemical cell. The surface area of an individual electrode was $\sim 0.25 \text{ cm}^2$.

The microstructure of the electrode/electrolyte interface was analyzed by scanning electron microscopy (SEM) (LEO Supra 50VP, Germany). The cross section (cleavage) of samples was analyzed.

The polarization resistance of the electrode/electrolyte interface was measured by the method of impedance spectroscopy for three-electrode circuit by means of impedance meter P-5X (Elins, Russia) in the frequency interval from 0.1 Hz to 500 kHz with the signal amplitude of 10 mV in the temperature range of $600\text{--}750^\circ\text{C}$ in air. The identical counter and working electrodes were screen printed on the surface of the solid electrolyte pellet. As the reference electrode, we used a Pt electrode, which was prepared by applying Pt paste on the side surface of the solid electrolyte pellet. The current connectors were platinum wires. As the current collecting contacts, we used Pt gauzes which were pressed closely to the counter and working electrodes. The sample temperature was measured by means of a Pt–Pt/Rh thermocouple placed near the sample. The polarization resistance (R_η) of the electrode was calculated based on the difference between the low and high-frequency intercepts on the real resistance axis, normalized to the electrode surface.

RESULTS AND DISCUSSION

One of the key parameters that determine the electrochemical efficiency of a SOFC cathode material all other conditions equal is the temperature at which the electrode layer is sintered to the solid electrolyte surface. It influences both the microstructure of electrode and the electrode/electrolyte interface and the reactivity between the electrode and electrolyte materials, acting on the electrocatalytic sites in which the oxygen reduction occurs. It should be noted that the choice of the sintering temperature is determined by the condition of absence of chemical reactions between the electrode and solid-electrolyte materials. For this purpose, we prepared a mixture of PLCO and GDC powders in the mass ratio 1 : 1, which was later annealed at 900°C and 1000°C for 25 h in air.

Figure 1 shows X-ray patterns for mixtures of PLCO and GDC powders after 25 h thermal treatment at 900 and 1000°C in air. According to XRD analysis data, the X-ray patterns of powder mixtures after annealing at 900°C show only the reflections belonging to the original phases. However, as the temperature of annealing of oxide mixtures was raised to 1000°C , the additional reflections appeared corresponding to the position of the most intense reflections of copper oxide CuO (the relative intensity did not exceed 2%). The reason for their appearance may be the possibility of formation of solid solutions with the fluorite struc-

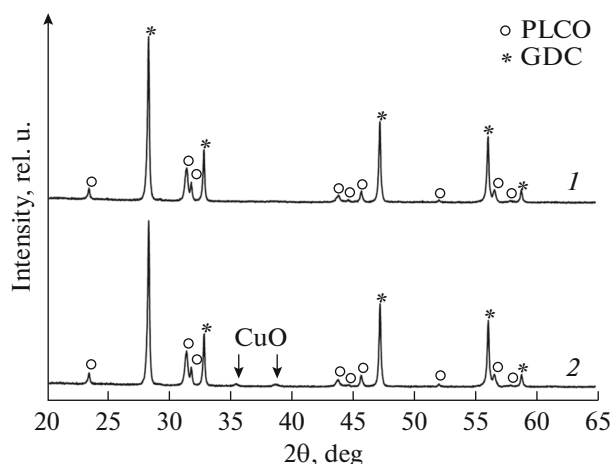


Fig. 1. X-ray diffraction patterns of mixed PLCO and GDC powders after thermal treatment at (1) 900°C and (2) 1000°C for 25 h in air.

ture based on ceria and praseodymia [8]. At the same time, we can assume that annealing of the mixture of PLCO and GDC powders at 1000°C may lead to insignificant decomposition of the PLCO cuprate phase due to incorporation of REE cations into the fluorite structure of solid electrolyte, which results in formation of a new solid solution based on ceria [8, 9]. Thus, these results suggest that the PLCO electrode material may be used together with the GDC electrolyte at temperatures below 900°C.

To determine the optimal temperature of sintering the PLCO electrode layer to the GDC surface, we prepared a series of symmetrical electrochemical cells with the composite electrode containing 30 wt % GDC (PLCO–30GDC). The resulting samples were annealed at 800, 850, or 900°C for 4 h in air.

Figure 2 shows temperature dependences of the polarization resistance for electrochemical cells PLCO–30GDC/GDC/PLCO–30GDC, prepared at different temperatures of electrode layer sintering. The closeness of polarization resistance values for the sintering temperatures of 800 and 850°C deserves mention. However, as seen from the above results, the highest electrochemical efficiency is obtained for the electrode layer sintered at 850°C. The minimum polarization resistance at 700°C amounted to $\sim 0.5 \Omega \text{ cm}^2$. The higher sintering temperature (850°C) should be preferred as providing the better contact between the electrode layer and the solid electrolyte surface. It should be noted that the dependences of R_{η} on the temperature are symbate, as confirmed by the close values of the effective activation energy (its average value is $1.11 \pm 0.03 \text{ eV}$) in the temperature interval of 600–750°C. To check the stability of the electrode/electrolyte interface under high-temperature conditions, we carried out an experiment in which the electrochemical cell

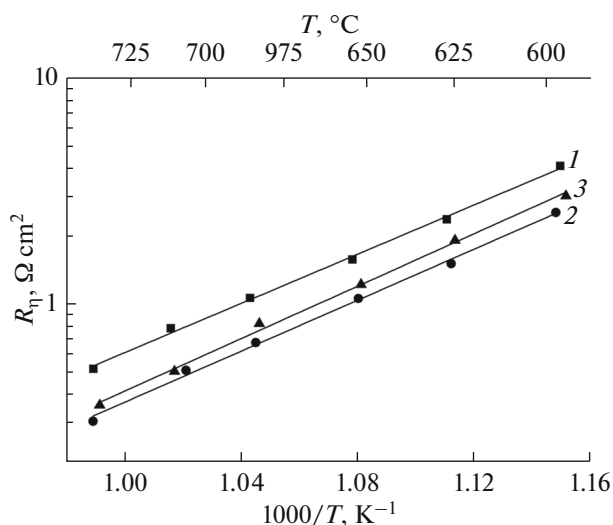


Fig. 2. Temperature dependence of the polarization resistance (R_{η}) for the composite PLCO–30GDC electrode applied on GDC solid electrolyte by screen printing at different temperatures of electrode layer sintering, °C: (1) 900; (2) 850; (3) 800.

with the PLCO–30GDC composite electrode sintered at 850°C was subjected to 5 heating-cooling cycles in the temperature range of 500–750°C in air. The results of electrochemical studies of the PLCO–30GDC composite electrode sintered at 850°C showed that the average value of R_{η} at $(685 \pm 2)^{\circ}\text{C}$ remained virtually unchanged with time, being equal to $0.68 \pm 0.03 \Omega \text{ cm}^2$, which pointed to the high stability of the electrode/electrolyte interface. The further search for the optimal composition of PLCO– x GDC electrodes was carried out on samples of symmetrical electrochemical cells electrode/electrolyte/electrode sintered at 850°C for 4 h in air.

Figure 3 shows SEM images of the microstructure for cross-sections of electrode/GDC-electrolyte interfaces. It is evident that the electrode layers of both single-phase PLCO and PLCO– x GDC composites ($x = 20$ –50 wt % GDC) have the porous structure, are uniform throughout their thickness, and display good adhesion with the solid electrolyte surface. All these samples demonstrated the close contact between the particles throughout the electrode layer and the uniform distribution of pores. The absence of any fundamental difference in the morphology of electrode layers with different composition deserves mention. The thickness of electrode layers was about 20 μm .

Figure 4 shows the dependence of the total polarization resistance R_{η} on the electrode composition at different temperatures. According to our results, the minimum polarization resistance is reached for the composition with 40 wt % GDC in the whole temperature interval (600–750°C). The increase in the content of the ion-conducting GDC phase in the

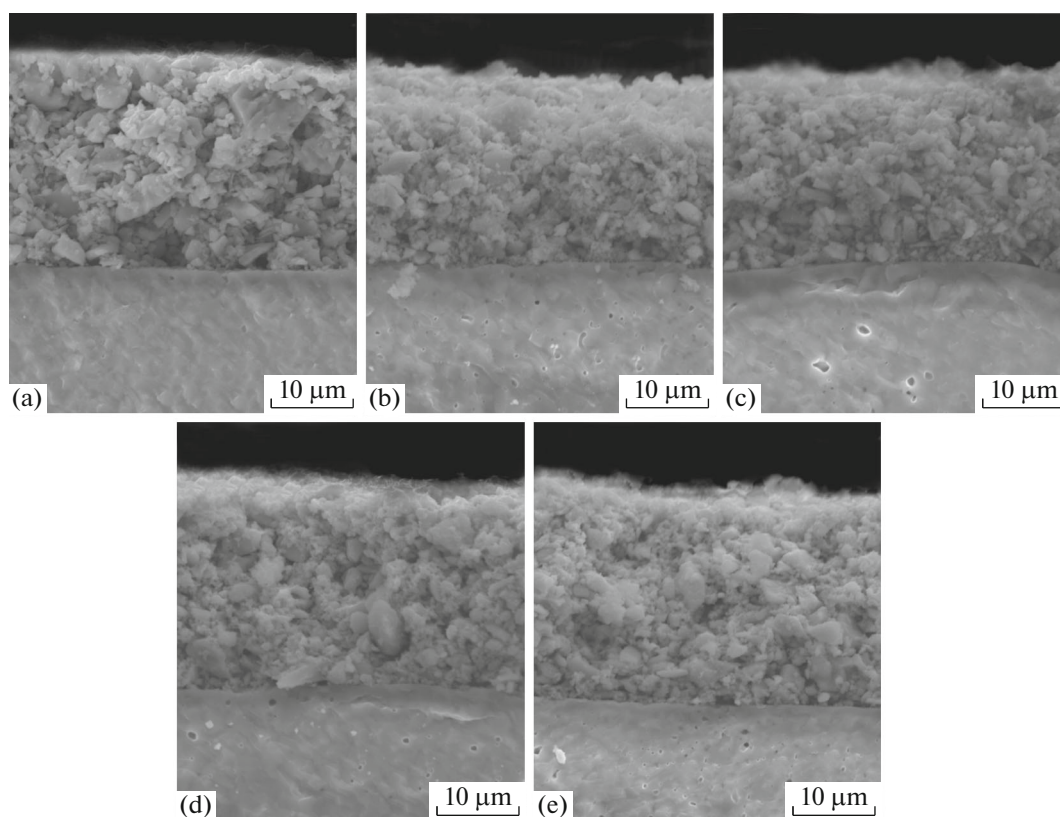


Fig. 3. SEM images of the microstructure of the electrode/GDC-electrolyte interface (cross section) on variation of the PLCO- x GDC composition (x is wt % GDC): (a) $x = 0$; (b) $x = 20$; (c) $x = 30$; (d) $x = 40$; (e) $x = 50$. The dense layer (in the bottom) is GDC, the porous layer (on the top) is the PLCO- x GDC electrode.

composite upon the transition from single-phase PLCO to the PLCO-based composite electrode favors a decrease in R_{η} , which is associated with the extension of the stable triple-phase boundary (TPB). This

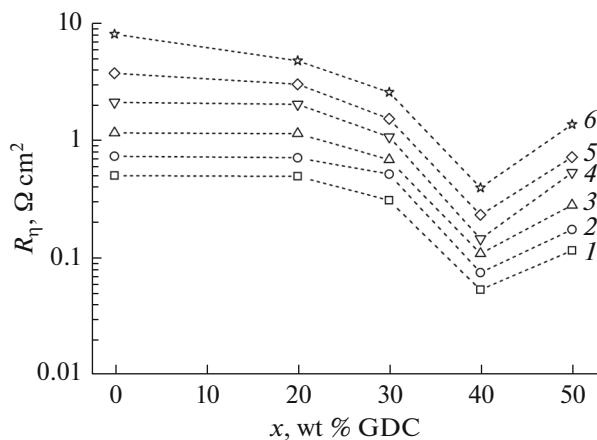


Fig. 4. Dependence of the total polarization resistance (R_{η}) of the composite electrode PLCO- x GDC on the GDC content at different temperatures in air, °C: (1) 740; (2) 705; (3) 685; (4) 650; (5) 625; (6) 600.

results in generation of additional electrocatalytic sites on the TPB for oxygen reduction and also to the development of additional routes for migration of oxygen ions, thus enhancing the electrocatalytic activity of the cathode material. As the GDC content increases from 40 to 50 wt %, the polarization resistance also increases somewhat. This may be associated with both the decrease in the concentration of electrocatalytically active sites on the TPB and a slight violation of electron migration routes as a result of partition of the continuous structure of the electron-conducting phase of the composite electrode. Thus, the transition from the single-phase cathode based on PLCO to the PLCO- x GDC composite provides a considerable decrease in R_{η} (at 700°C, ca. 10-fold: from 0.87 ($x = 0$) to 0.08 $\Omega \text{ cm}^2$ ($x = 40$)).

Figure 5 shows the temperature dependences of the total polarization resistance for PLCO- x GDC composite cathodes. These are thermoactivation dependences throughout the whole temperature interval studied. Table 1 shows the effective activation energy (E_a) calculated from the Arrhenius dependence of the reciprocal total polarization resistance in the temperature interval of 600–750°C in air. The introduction of the ion-conducting phase into the electrode composi-

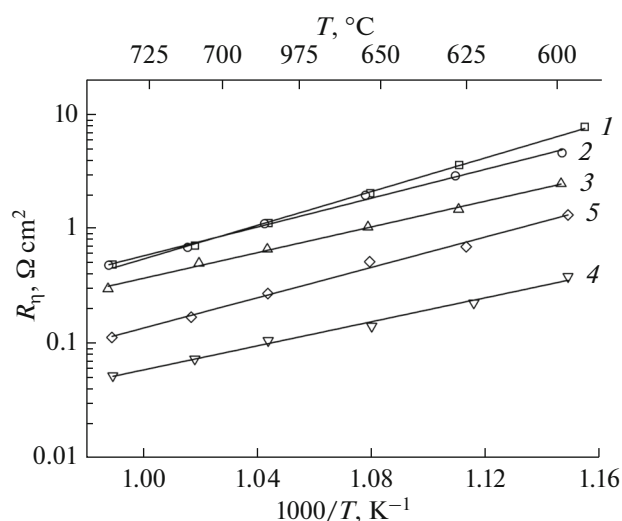


Fig. 5. Temperature dependence of the total polarization resistance (R_{η}) for electrodes based on (1) single-phase PLCO and (2) composites PLCO- x GDC (x is wt %) in air: (2) $x = 20$; (3) $x = 30$; (4) $x = 40$; (5) $x = 50$.

tion favors the decrease in E_a , which may be associated with the easier oxygen-ion transport across the electrode/electrolyte interface. As we pass to the composition with 40 wt % GDC characterized by the minimum polarization resistance, the activation energy also demonstrates a local minimum. Such behavior also counts in favor of our choice of this composite as regards making easier the oxygen-ion transport across the electrode/electrolyte interface. As the GDC content increases from 40 to 50 wt %, the activation barrier grows, which may be associated with violation of electron migration routes and leads to degeneration of electrochemical characteristics of this electrode. Moreover, the activation barrier observed for the PLCO-40GDC electrode with the optimal composition ($E_a = 1.04$ eV) proved to be lower as compared with composite cathodes based on

Table 1. Effective activation energies (E_a) of the reciprocal polarization resistance ($1/R_{\eta}$) of electrode materials based on PLCO- x GDC in air, calculated for the temperature range of 600–750°C

Electrode composition, x – wt % GDC	E_a , eV (± 0.03 eV)
0	1.46
20	1.25
30	1.11
40	1.04
50	1.32

$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM)/GDC ($E_a = 1.36$ eV) [10] and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF)/GDC ($E_a = 1.65$ eV) [11].

Comparing the polarization resistance of PLCO-40GDC ($0.08 \Omega \text{ cm}^2$) at 700°C with the literature data for composite cathode materials based on Pr_2CuO_4 [4, 5] and $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{CuO}_4$ [12] deposited on the GDC solid electrolyte demonstrated that we managed to achieve five and four-fold increase in the electrochemical efficiency of the electrode/electrolyte interface, respectively. As compared with the composite electrode based on traditional LSM, the polarization resistance is lowered by almost one order of magnitude [10]. Moreover, it deserves mention that as regards the R_{η} value, PLCO-40GDC is comparable by the order of magnitude with the composite electrode based on LSCF which is among the most promising cathode materials [10, 13]. However, the difference in TEC between the solid electrolyte ($12.4 \times 10^{-6} \text{ K}^{-1}$) [7] and PLCO ($11.9 \times 10^{-6} \text{ K}^{-1}$) [6] is much lower as compared with LSCF ($17.5 \times 10^{-6} \text{ K}^{-1}$) [14]. Thus, it can be assumed that SOFC employing PLCO-40GDC composite cathodes demonstrate the better thermomechanical stability in heating-cooling cycles.

CONCLUSIONS

Composite electrode materials PLCO- x GDC ($x = 20$ –50 wt %) are synthesized and their electrocatalytic properties in oxygen reduction reaction are studied. It is found that the maximum efficiency of PLCO- x GDC composite cathodes is realized when the electrode layer is sintered to the GDC solid electrolyte surface at the temperature of 850°C. Studying the electrochemical behavior of PLCO- x GDC electrodes has shown that the minimum polarization resistance is achieved for the composition containing 40 wt % GDC. At 700°C, the transition from the single-phase PLCO cathode to the PLCO-40GDC composite provides 10-fold decrease in the polarization resistance (from 0.87 ($x = 0$) to $0.08 \Omega \text{ cm}^2$ ($x = 40$)). The key parameters pointing to the considerable improvement of the electrocatalytic properties of the cathode material in oxygen reduction reaction are the high electrical conductivity of PLCO ($\sigma(\text{PLCO}) > 100 \text{ S/cm}$ at 600–900°C), the minimum TEC deviation between PLCO and GDC solid electrolyte (less than 5%), the optimal temperature at which the cathode layer was sintered to the surface of solid electrolyte as regards the absence of chemical interaction between PLCO and GDC, the formation of the extended TPB which is realized most efficiently for the composite electrode material with 40 wt % of the ion-conducting phase. Thus, the results obtained make it possible to consider the PLCO-40GDC composite as a promising cathode material for intermediate-temperature SOFC.

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