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# Composite fuel for direct carbon fuel cell

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ABSTRACT

The performance of the direct carbon solid oxide fuel cell (DC-SOFC) with various solid oxide electrolytes: 8 mol% $Y_2O_3$ in $ZrO_2$ (8YSZ), 9 mol% $Sc_2O_3$ in $ZrO_2$ (9ScSZ) and 10 mol% $Gd_2O_3$ in $CeO_2$ (20GDC) were examined in temperature range 600–880 °C. The highest current densities were obtained for DC-SOFC with 20GDC electrolyte. It was shown that the DC-SOFC performance improved when thickness of the electrolyte was reduced, which can be attributed to the decrease of ohmic polarisation. The performance of DC-SOFC was also improved for a composite fuel consisted of powdered carbon fuel and 8YSZ or 20GDC ionic oxide electrolyte in the amount of ca. 10 wt.%. Catalytic effects of Ag and Ni particles addition to the carbon fuel on the DC-SOFC operation were also investigated.

## 1. Introduction

Direct carbon fuel cell (DCFC) has a long and rich history as an applicable power source [1,2]. Recently, it again attracts a renewed interest, encompassing a variety of fuel cell configurations and approaches, which are actively investigated and developed. All these efforts are aimed at practical and economically feasible conversion of carbonaceous solids (coal, biomass, municipal solid waste, char, etc.) directly to electric power [3,4]. Various types of DCFC have been recently investigated. One of the most popular classification regards a kind of electrolyte used in the cell. So that, the carbon fuel can be oxidised in an environment of alkaline molten carbonate and solid oxide electrolytes. The latter system DC-SOFC, seems to be the most promising due to uncomplicated maintenance, although the current densities acquired from this fuel are very low as yet [5,6]. Low power of DC-SOFC results from a limited reaction zone in a solid state, restricted to a direct contacts between carbon fuel and solid oxide electrolyte. Further development and commercialisation of DCFC requires the efficiency of direct conversion of carbon fuels into electricity to be significantly improved. The hybrid direct carbon fuel cell (HDCFC), which is a combination of technological achievements of both, molten carbon fuel cell (MCFC) and solid oxide fuel cell (SOFC), is the most frequently proposed option to reach this aim. In HDCFC system, the coal particles are mixed with $Li_2CO_3$–$K_2CO_3$ molten eutectic and such prepared fuel is introduced into the anode chamber of SOFC cell. During the SOFC operation at temperatures 700–900 °C, carbon particles are dispersed in molten carbonate, which results in increase of zone of electrode reaction, because $CO_3^{2-}$ ions are directly involved in the reaction of carbon oxidation.

The HDCFC allows to obtain considerable higher power density in comparison to the DC-SOFC fed with pure solid carbon fuel [7,8]. The disadvantage of HDCFC system is severe corrosion of SOFC components in molten carbonate environment. The development of new catalysts, that enhance electrochemical reaction of carbon oxidation or elaboration of new solid composite carbon fuel that provides an extension of the anode reaction zone in DC-SOFC may also improve performance of this cell and be a competitive option to HDCFC [9].

In this work, the effect of different types of composite carbon fuels containing some additions of electrolyte or metallic particles was studied. The practical aim of these investigations was to obtain a carbon-based fuel, which could significantly increase the efficiency of DC-SOFC.

## 2. Experimental

Commercial carbon black (N-220) was used as a solid fuel for the DC-SOFC. Firstly, the carbon powder was attrition milled with zirconia grinding media in anhydrous alcohol. The hydrothermal treatment of co-precipitated ceria or zirconia gels under autogenous water pressure at 240 °C was applied for 6 h to synthesize 10 mol% $Gd_2O_3$ in $CeO_2$ (20GDC) or 8 mol% $Y_2O_3$ in $ZrO_2$ (8YSZ) nanopowders. The starting materials were $Ce(NO_3)_3{\cdot}6H_2O$, $Gd(NO_3)_3{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$ and $ZrO(NO_3)_2{\cdot}6H_2O$ (99.99% Aldrich). The reagents were mixed in distilled water in order to prepare zirconia–yttria or gadolinia–ceria solid solutions of stoichiometric composition $Zr_{0.84}Y_{0.16}O_2$ (8YSZ) or $Ce_{0.8}Gd_{0.2}O_2$

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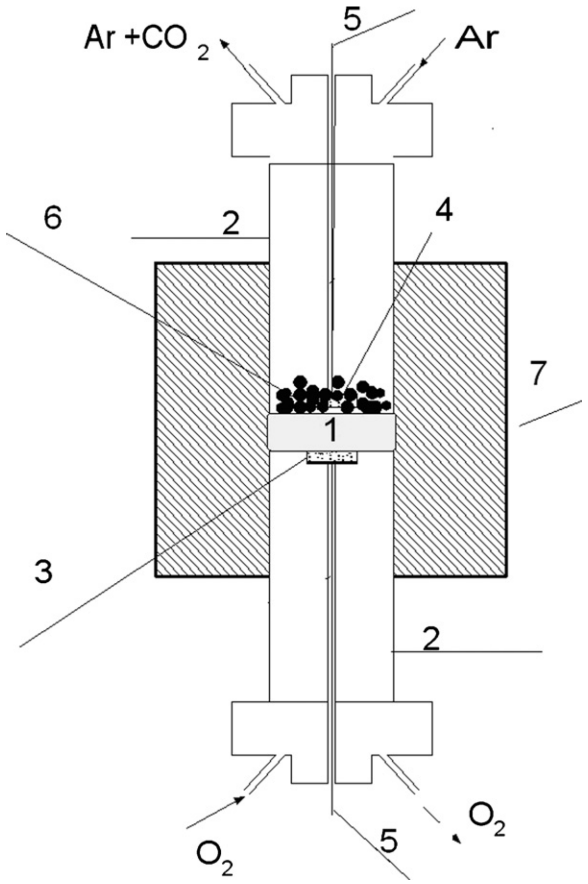

**Fig. 1.** The side view of the test direct carbon fuel cell (DC-SOFC): (1) solid oxide electrolyte; (2) $Al_2O_3$ tube; (3) air cathode; (4) current collector made from a platinum mesh; (5) Pt wire; (6) carbonaceous fuel; (7) electric resistance furnace.

(20GDC). Then the small doses of samples were introduced into a vigorously stirred $NH_3$ aqueous solution (1:1). The co-precipitated hydrogels were washed with distilled water by means of decantation and filtration. Finally they were hydrothermally treated for 4 h at 240 °C under an autogenous pressure of saturated water vapour. The details of applied procedure were described in previous papers [10,11].

The carbon black powder was physically mixed with oxide electrolyte nanopowder in order to prepare homogeneous mixtures containing up to 50 wt.% of 20 GDC or 8YSZ. The sample was homogenized in duration of 30 min with a rotary-vibratory mill. The samples with Ag or Ni particles added to carbon powder were obtained by a similar way. Homogenisation of the C–Ni or Ag–Ni system was achieved by rotary–vibratory milling with 5 mm TZP balls in ethyl alcohol for 30 min.

The phase composition of starting powders and sintered samples were identified by X-ray diffraction analysis (XRD). Specific surface area of powders was measured by $N_2$ adsorption using BET method. The morphology of carbon black powder was examined with a scanning electron microscopy.

The side view of the test DC-SOFC is shown in Fig. 1. The cell consisted of two chambers, separated by a 8YSZ, 9ScSZ or 20 GDC disk-shaped electrolyte (1), (20 mm in diameter and ca. 2 mm thick), which was stuck to $Al_2O_3$ tubes (2) from both sides. An air cathode (3) was made of platinum, which was serigraphically placed in form of paste layer (Heraus, Germany) on a side of the electrolyte, then desiccated and heated at 900 °C for 30 min. An anode current collector (4) was made from a platinum mesh welded to a platinum wire (5). It was dusted with 2 g of powdered coal or other carbonaceous fuel (6). The experimental setup was heated by a electrical resistance furnace (7). In duration of the experiment, argon was continuously supplied to the anodic chamber as a shielding gas. The geometric area of active surface of electrolyte was estimated to be 1.76 cm$^2$. Electrochemical measurements were performed using an electrochemical workstation AUTOLAB in the temperature range 600–900 °C.

**Table 1**
Basic characteristic of 8YSZ or 20GDC oxide electrolyte nanopowders.

| Powder | $d_{(\mathrm{BET})}$, nm | $d_{(hkl)}$, nm |
|---|---|---|
| 20GDC | 11.2 | 8.4 |
| 8YSZ | 9.6 | 6.8 |

## 3. Results and discussion

The basic characteristics of starting powders are listed in Table 1. The values of equivalent particle sizes $d_{\mathrm{BET}}$, are very close to their crystalline size of both $ZrO_2$ and $CeO_2$-based powders. This indicates that no extensive contacts occur between primary particles of the nanopowders and implicates existence at most weak agglomerates. Both, $ZrO_2$ and $CeO_2$ powders consisted of nanoparticles, which were isometric crystallines of size 6–12 nm. A typical SEM microphotograph of Carbon Black (N-220) is presented in Fig. 2. The distribution of isometric particles (0.7–40 μm) and some forms of agglomerates was observed.

Only pure cubic $MO_2$ phase, M = Zr, Ce was identified with XRD diffraction analysis for all the prepared composite solid fuels consisting of carbon and nanopowder of oxide ionic conductors. No other phase besides $Y_2O_3$ or $Gd_2O_3$ was detected to betoken possible product of decomposition of cubic ceria or zirconia ceria solid solutions after completing the experiments with the DC-SOFC. Only for the mixture of carbon and nickel powder with more than 10% weight a formation of $Ni_3C$ phase was observed as a product of reaction between carbon and nickel powders.

Firstly, the DC-SOFC with 8YSZ electrolyte was supplied with pure carbon powder. A typical family of dependencies between the overpotential and current density, measured for this cell at different temperatures is shown in Fig. 3a. Indeed, above 800 °C the DC-SOFC filled with pure carbon shows a good performance. Irwine et al. [7,8] suggested that the DC-SOFC does not work efficiently below 800 °C. Although improvement of DC-SOFC proceeds gradually, our

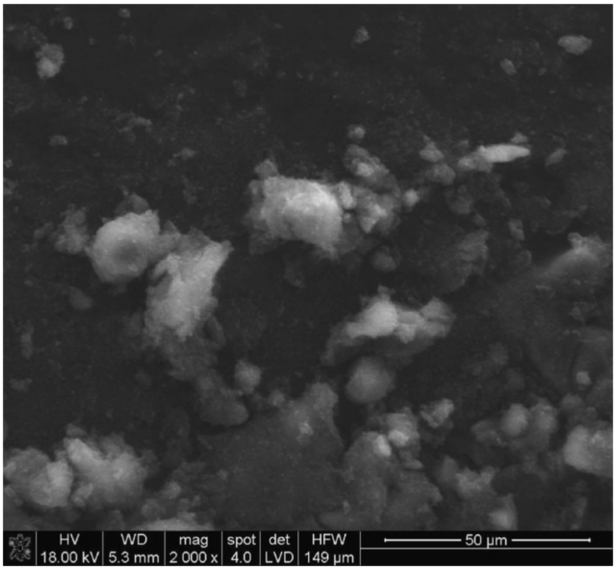

**Fig. 2.** The scanning electron microscopy image of carbon black (N-220) powder morphology.

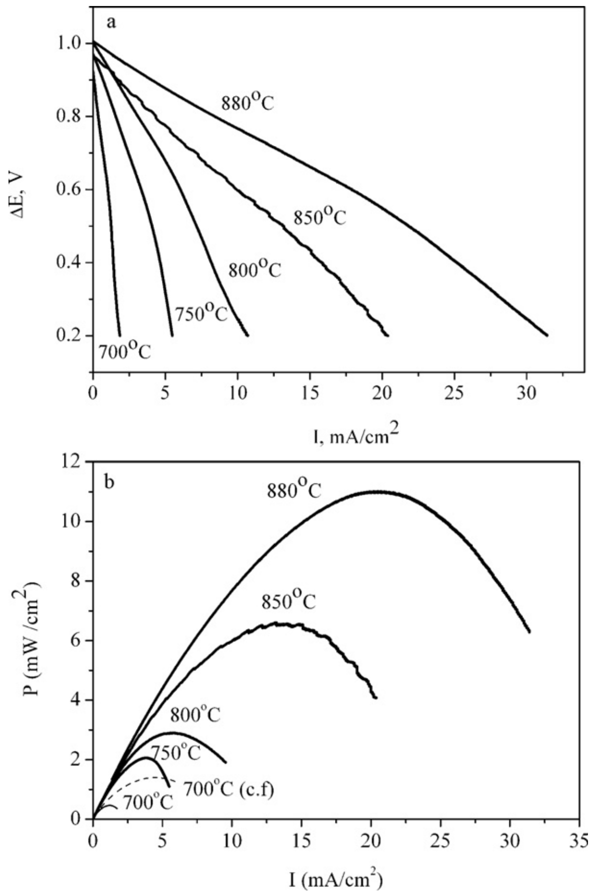

**Fig. 3.** (a) Family of curves $\Delta E$ vs. $I$ recorded for the DC-SOFC with 8YSZ electrolyte. (b) Family of curves $P$ vs. $I$ recorded for the DC-SOFC with 8YSZ electrolyte.

results qualitatively justified his observation. According to Irwin, the electro-oxidation of carbon in the DC-SOFC proceeds through oxidation of CO, that is formed during the reverse Boudoured reaction (1) [7,8,11]:

$$C + O_2 \rightarrow CO_2 \qquad (1)$$

Reaction (1) is shifted to left below 800 °C, hence at the lower temperatures, the observed current densities are very low, whereas at higher temperatures the performance and power of the fuel cell increases.

However, the quantitative comparison of the performance between the particular fuel cells on the basics of the $\Delta E$ vs. $I$ dependences is not straightforward. It can be done much easier, when the comparison is made in the coordinates: power density vs. current density ($P$ vs. $I$). These $P$ vs. $I$ dependencies, calculated for the data presented in Fig. 3a are show in Fig. 3b. Each curve in Fig. 3b has a characteristic maximum value, which corresponds to the maximum power density $P_{\max}$ produced by the fuel cell. These values will be used in the further part of this paper for comparison of operation parameters of DC-SOFCs. One of important factor, which influences $P_{\max}$ is the ohmic resistance of electrolyte as it is distinctly seen for the DC-SOFC with the YSZ electrolyte at temperatures below 800 °C. Reducing the thickness of YSZ electrolyte diminishes the contribution of ohmic polarisation and thus improves the efficiency of DC-SOFC. Another possible way to improve the DC-SOFC performance at the intermediate temperature range (600–800 °C) is to utilize an oxide electrolyte with higher ionic oxide conductivity than YSZ, for example 9 mol% $Sc_2O_3$ in $ZrO_2$ (9ScSZ) or 10 mol% $Gd_2O_3$ in $CeO_2$ (20GDC) solid solutions.

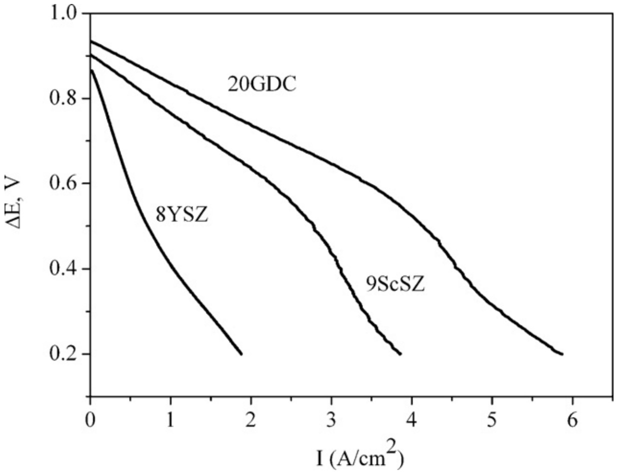

**Fig. 4.** Family of curves $\Delta E$ vs. $I$ recorded at 700 °C for the DC-SOFC with different oxide electrolytes: 8 mol% $Y_2O_3$ in $ZrO_2$ (8YSZ); 9 mol% $Sc_2O_3$ in $ZrO_2$ (9ScSZ); 10 mol% $Gd_2O_3$ in $CeO_2$ (20GDC).

The effect of ionic conductivity of oxide membranes on the DC-SOFC performance is presented in Fig. 4. As expected, the current densities of DC-SOFC increases for the solid oxide electrolytes with lower electrical resistance.

The incorporation of uniformly dispersed nanopowder of oxide electrolyte into carbon matrix allowed to extend the reaction zone. The idea of the proposed innovation is schematically presented in Fig. 5. In the case of the DC-SOFC supplied with pure carbon fuel, the electrochemical oxidation of carbon particles occurs exclusively at the surface of electrolyte (Fig. 5a). An oxide electrolyte inclusion into pulverized carbon expands zone of direct contacts between carbon particles and oxide ions to the whole volume of the fuel. The dispersed oxide electrolyte (nanometric particles) is additional source of $O^{2-}$ ions, which participate in carbon oxidation (Fig. 5b). To verify reliability of these arguments in the course of further experiments, carbon was mixed with a given amount of 8YSZ or 20GDC nanopowder and introduced to the anode chamber of DC-SOFC cell. Fig. 6a presents the selected $P$ vs. $I$ curves recorded for the DC-SOFC, which was filled with composite solid carbon fuel contained either 8YSZ or 20GDC. The resultant dependences of the peak

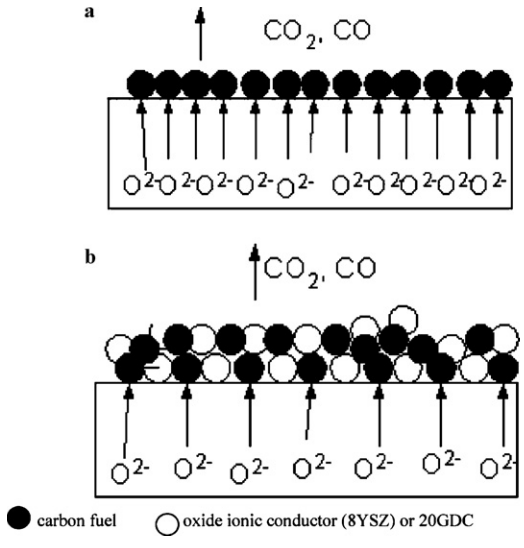

**Fig. 5.** The idea of proposed innovation: (a) electrochemical oxidation of carbon in DC-SOFC supplied with pure carbon and (b) electrochemical oxidation of carbon in DC-SOFC supplied with composite solid fuel consisted of carbon and nanopowder of oxide electrolyte.

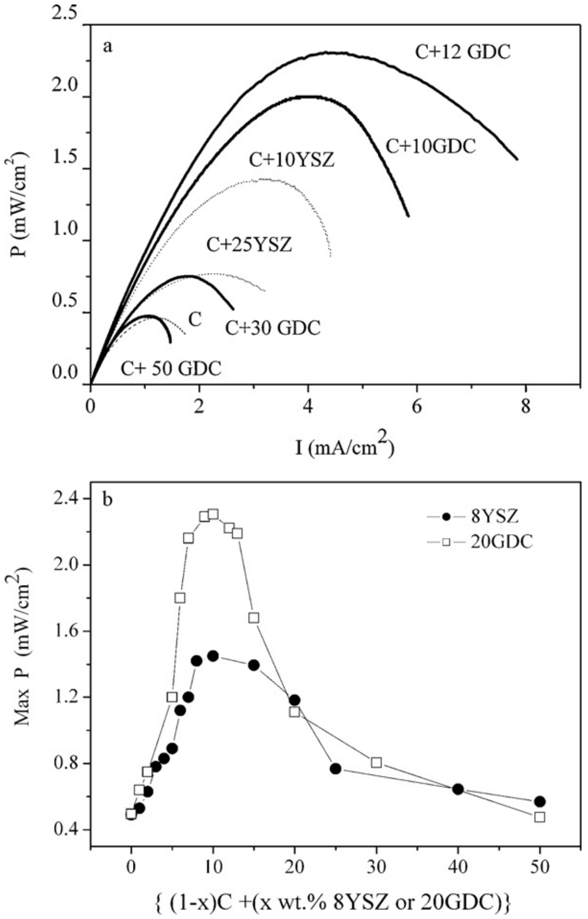

**Fig. 6.** The selected dependencies of the power density ($P$) on the current density ($I$) recorded for the DC-SOFC, filled with composite solid carbon fuel contained 8YSZ or 20GDC nanoparticles. (b) The resultant dependencies of the $P_{\max}$ on chemical composition of solid carbon composite fuel.

power density on the chemical composition of composite based fuel are presented in Fig. 6b.

Analysis of the experimental data shows that the introduction of 8YSZ or 20GDC nanoparticles into carbon matrix increases gradually the maximum output of power density of the cell up to 10 wt.% of electrolyte content in the composite fuel. Further addition of 8YSZ or 20GDC nanoparticles into the fuel causes that the power density of DC-SOFC decreases due to relative drop of the carbon content in the fuel mixture and resulted reduction in the number of contacts between carbon and electrolyte. The comparison between the maximum output power of DC-SOFC filled with composite fuel containing either 8YSZ or 20GDC shows that addition of 20GDC allows to obtain higher output power densities. The main advantage of 20GDC addition over 8YSZ is its lower ohmic resistance (higher oxide ionic mobility) at the investigated range temperatures. Another benefits from 20GDC addition into carbon matrix results from good catalytic properties of $CeO_2$-based materials. Ceria has been recognized as a key component of catalysts in car exhaust. One of the most important functions of ceria is acting as an oxygen buffer, releasing oxygen for CO and hydrocarbon oxidation. Ceria-based materials promote CO oxidation, which is probably an intermediate product of electrochemical oxidation of carbon [12–15].

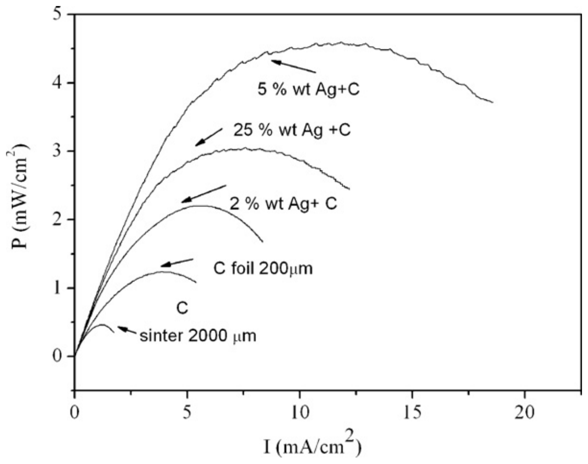

**Fig. 7.** The family of curves $P$ vs. $I$ obtained for DC-SOFC filled with either carbon or modified carbon fuel with Ag particles.

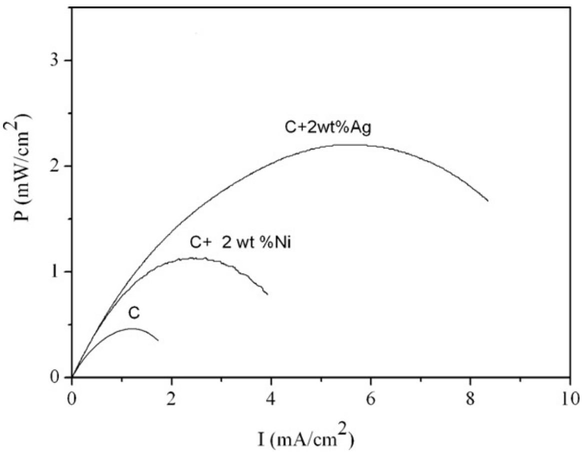

**Fig. 8.** The comparison of $P$ vs. $I$ curves recorded at 700 °C for the DC-SOFC filled with carbon (C), carbon contained addition of 2 wt.% Ni as a catalyst or carbon contained addition of 2 wt.% Ag as a catalyst.

Metallic Ag could be considered as a effective catalyst for carbon oxidation, although is inactive in CO decomposition [16,17]. Therefore, an addition of Ag particles into carbon matrix can also facilitate the anodic reaction in DC-SOFC. The family of curves $P$ vs. $I$ obtained for the DC-SOFC filled with either carbon or modified carbon fuel with Ag particles is presented in Fig. 7 As can be seen, the addition of Ag particles improve considerably the DC-SOFC performance. The effect of nickel catalyst was also investigated (Fig. 8). Ni shows distinctly lower performance in comparison with Ag particles probably due to formation of $Ni_3C$ as an undesirable product of chemical reaction between components of solid fuels.

## 4. Conclusion

The results presented in this paper shows that there are a couple of ways to improve performance of DC-SOFC with an oxide electrolyte. Of course, too thick electrolyte increases the ohmic polarisation and in consequence decreases the performance of fuel cell. An original option is use of composite fuel, which provides execution of the reaction zone to the whole volume of the fuel. Also an addition of metallic catalyst (Ag, Ni) to the carbon fuel leads to the improvement of operation parameters of DC-SOFC. Collective using of all these option for improvement of DC-SOFC efficiency needs further extensive investigations.

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