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## YBa(Fe,Co,Cu)<sub>2</sub>O<sub>5+δ</sub> CATHODE MATERIALS FOR SOLID OXIDE FUEL CELLS

A.I. Klyndyuk<sup>1\*</sup>, M. Mosialek<sup>2</sup>, D.S. Kharitonov<sup>1,2</sup>, E.A. Chizhova<sup>1</sup>,  
M. Zimowska<sup>2</sup>, R.P. Socha<sup>2,3</sup>, A. Komenda<sup>2,3</sup>

<sup>1</sup>Belarusian State Technological University, Minsk, Belarus

<sup>2</sup>Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,  
Krakow, Poland

<sup>3</sup>Research and Development Center of Technology for Industry, Warsaw, Poland

\*e-mail: klyndyuk@belstu.by

Solid oxide fuel cells (SOFCs) are energy conversion devices, which directly convert stored chemical energy into usable electrical energy. Nowadays, SOFCs are widely introduced into commercial usage due to their high conversion efficiency, fuel flexibility, and low ecological impact. Traditional SOFCs are operating at high temperatures of 800–1000 °C, resulting in numerous drawbacks, such as high exploitation costs, chemical incompatibility, the difference in thermal expansion coefficients of constituents, and performance degradation [1].

A practical approach to overcome these problems is to lower the operating temperatures to an intermediate-temperature (IT) range of 600–800 °C. However, the large reduction of temperature leads to a dramatic increase in the electrode polarization resistance. The main voltage losses occur at the cathode, so the improvement of the cathode material performance in the IT range is necessary [2].

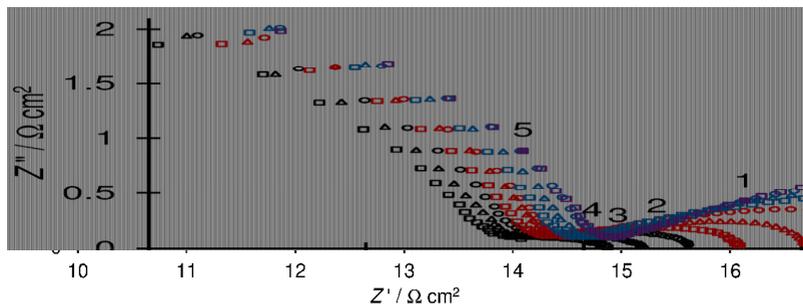
The key to the above-mentioned improvement is to develop new cathode materials with a high catalytic activity in the IT range. Perovskite-type oxides are widely examined materials for SOFC applications as they provide a mixed ionic and electronic conductivity, which is desirable in cathodes. Among them, layered oxides LnBaCo<sub>2</sub>O<sub>5+δ</sub> (Ln = Pr, Sm, Y, and Gd) can be of particular interest due to their sufficient oxygen ionic transport and high electric conductivity [3]. A B-site doping of Co with transition metals, such as Fe and Cu, can decrease the thermal expansion coefficient (TEC) and cost of these materials with simultaneous improvement in the structural stability. In this work, new types of YBa(Fe,Co,Cu)<sub>2</sub>O<sub>5+δ</sub> layered oxides have been synthesized and their crystal structure and electrochemical performance were examined.

Layered oxides YBaCuCoO<sub>5+δ</sub> (YBCC), YBaFeCoO<sub>5+δ</sub> (YBFC), YBaCuFe<sub>0.2</sub>Co<sub>0.8</sub>O<sub>5+δ</sub> (YBFCC1), and YBaCuFe<sub>0.6</sub>Co<sub>0.4</sub>O<sub>5+δ</sub> (YBFCC2) were prepared by conventional ceramic processing techniques using Y<sub>2</sub>O<sub>3</sub>, BaCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, and CuO as precursors. Appropriate mixtures were reacted in the air within 900–1000°C for 42–50 h [4, 5]. X-ray diffraction data revealed

that all synthesized materials were single-phase and had a tetragonal structure with lattice constants  $a = 3.868\text{--}3.872$ ,  $c = 7.549\text{--}7.611$  Å. The measured TEC values were  $14.3 \times 10^{-6}$ ,  $12.2 \times 10^{-6}$  ( $17.3 \times 10^{-6}$ ) at  $T < 520$  K ( $T > 520$  K),  $14.9 \times 10^{-6}$ , and  $13.9 \times 10^{-6}$  K<sup>-1</sup> for YBCC, YBFC, YBFCC1, and YBFCC2, respectively.

For electrochemical tests, obtained powders were mixed with ink vehicle (Nexceris) and then applied in the form of two identical circle-shaped working and reference electrodes on the Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> electrolyte pellet. The counter electrode was prepared by screen printing La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> ink on the opposite side of the pellet. The as-prepared electrodes were dried and then sintered at 1000 °C for 2h. The electrochemical properties of electrodes were tested by electrochemical impedance spectroscopy (EIS) in mixtures of argon and oxygen in assumed volume ratios.

The EIS spectra of examined cathodes recorded at 750 °C or lower temperatures consist of up to four semicircles. In most cases well separated high frequency (HF) and overlapped medium frequency (MF) and low frequency (LF) ones appear. The equivalent electrical circuit (EEC) used for fitting spectra consists of resistors and constant phase elements (CPEs):  $R_0(R_{HF}, CPE_{HF})(R_{MF}, CPE_{MF})(R_{LF}, CPE_{LF})$  in circuit description code notation [6]. The examples of spectra and results of fitting are presented in Figs. 1 and 2, respectively.

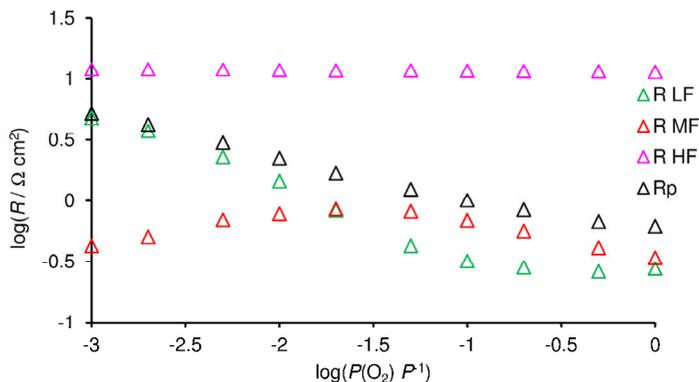


**Figure 1.** Examples of EIS spectra in Nyquist representation of YBCC electrode at 700 °C and open circuit potential (OCP) in oxygen and mixtures of oxygen and argon, oxygen concentration ( $P(O_2) P^{-1}$ ) are given in the legend. The numbers above filled experimental points denote the logarithm of the frequency.

The oxygen reduction reaction (ORR) mechanism can be described using  $m$  coefficient defined in the equation  $\log(R_i) = -m \log(P(O_2) P^{-1})$ .  $R_{HF}$  does not depend on  $P(O_2)$  practically ( $m = -0.0064$ ) and  $C_{HF}$  are of order 0.1 μF cm<sup>2</sup>, so HF should be ascribed to the grain boundary electrolyte resistance [7].  $R_{MF}$  slightly increases and then decreases ( $-0.31 < m < 0.31$ ) with the decreasing  $P(O_2)$ , this semicircle can be ascribed to the charge transfer resistance [8]. The  $R_{LF}$  is negligibly small at high  $P(O_2)$ , whereas at lower  $P(O_2)$  increasing



fast with decreasing oxygen concentration ( $m = 0.62$ ), this semicircle can be ascribed to the oxygen diffusion in the gas phase [9]. Polarization resistance does not depend on oxygen concentration if it is higher than 10%, whereas at lower oxygen concentration gas phase diffusion also limits the electrode performance.



**Figure 2.** Fitting results of resistances ascribed to each semicircle and polarization resistance of YBa cathode versus oxygen partial pressure at OCP at 700 °C.

Summarizing,  $\text{YBa(Fe,Co,Cu)}_2\text{O}_{5+\delta}$  double perovskites were successfully synthesized by conventional ceramic processing techniques and investigated as potential cathode materials for application in SOFCs. All obtained materials were single-phase and had a tetragonal structure. The Fe or/and Cu doping at the Co-site showed high effectiveness towards improvement in the thermal expansion coefficient and polarization resistance, offering further reduction in cathode polarization. From the present analysis, the synthesized materials can be recommended as potential cathode materials for intermediate-temperature SOFCs.

### References

1. Li R., Jin F., Zhang Y., Niu B. et al. // Int. J. Hydrogen Energy. 2019. V. 44. P. 8467–8478.
2. Dudek M., Lis B., Lach R., Daugela S. et al. // Electrochim. Acta. 2019. V. 304. P. 70–79.
3. Kim J.-H., Manthiram A. // J. Electrochem. Soc. 2008. V. 155. P. B385–B390.
4. Chizhova E.A., Klyndyuk A.I., Bashkirov L.A. et al. // Russ. J. Appl. Chem. 2005. V. 78. No. 5. P. 702–706.
5. Klyndyuk A.I. // Rus J. Inorg. Chem. 2009. V. 54. No. 7. P. 1014–1017.
6. Boukamp, B.A. // Solid State Ionics. 1986. V. 20. P. 31–44.



7. *Mosialek M., Michna A., Dziubaniuk M. et al.* // *Electrochim. Acta.* 2018. V. 282. P. 427–436.
8. *Liu B., Zhang Y., Zhang L.* // *Int. J. Hydrogen Energy.* 2009. V. 34. P. 1008–1014.
9. *Adler S.B., Lane J.A., Steele B.C.H.* // *J. Electrochem. Soc.* 1996. V. 143 P. 3554–3564.