

Cathode Materials $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ for Low Temperature Solid Oxide Fuel Cells

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ABSTRACT

New cathode materials $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ (typically $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$) were synthesized using a co-precipitation method. The structure and morphology of the powders were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The composite material [$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2.8}$ (SDC) and carbonate ($\text{Na}_2\text{CO}_3, \text{Li}_2\text{CO}_3$)], NiO and $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ were used as the electrolyte, anode and cathode, respectively. The electrochemical performance of La-Ni-Cu-O perovskite oxide at low temperatures (400~550°C) was studied. The results showed that $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ precursor powder prepared through a co-precipitation method and calcined at 860°C for 2 h formed uniform grains with diameters in the range of 400~500 nm. The maximum power density and the short circuit current density of the single cell unit at 550°C were found to be 390 mW/cm² and 968 mA/cm², respectively.

Key words : Cathode materials, La-Ni-Cu-O compound, SOFC, Electrochemical performances

1. Introduction

Considerable research effort has been expended of late regarding the development of intermediate (600~800°C) and low (400~600°C) temperature solid oxide fuel cells (IT/LTSOFCs) for stationary applications and others, e.g., vehicles and portable applications.¹⁻⁴ Reducing the operating temperature of solid oxide fuel cells (SOFCs) can mitigate sealing and corrosion problems and improve the long-term stability of these cells. In addition, cheaper materials can be used for interconnects and manifolds, resulting in significantly lower fuel cell stack and system costs.

Regarding smaller SOFC stacks that are used in various combined heat and power (CHP) and auxiliary power unit (APU) applications, recent research has shown that the operating temperature should be as low as possible while nonetheless maintaining the electrode kinetics and internal resistance of the cell/stack. To maintain the desired power density at a relatively low operating temperature requires an improvement of the electrochemical performance of the fuel cell. This is especially true for highly functional electrolytes and cathodes.

Conventional electrolytes such as yttrium-stabilized zirconia (YSZ) and doped ceria (SDC, GDC) cannot function at low temperatures due to their low conductivities. Oxygen ionic conductivities of 5×10^{-3} – 10^{-2} Scm⁻¹ of SDC and less than 10^{-4} Scm⁻¹ of YSZ at 600°C are conditions that do not sufficiently ensure a high level of performance of SOFCs,

which require a range of 10^{-1} Scm⁻¹. Significant progress in this field has been made with the introduction of anode-supported thin film electrolyte technology and new types of electrolytes (i.e., doped ceria, doped LaGaO₃ and composite ceria).⁵⁻⁷ These ceria-salt-composites were developed as functional electrolytes for application to IT/LTSOFCs. These materials usually consist of two phases, the ceria, or host, phase and other phases, which usually involve carbonates, sulphates, halides or hydrates.³⁻⁶ Two-phase electrolytes have been shown to display a high ionic conductivity of 0.01–1 S cm⁻¹ in the IT/LT region.

Correspondingly, the exploration of an active and high-performance cathode material is another important subject for IT/LTSOFC R&D. A numbers of contributions concerning new cathode materials have been made for ITSOFCS⁸⁻¹²; however, similar contributions to LTSOFC cathodes are lacking. $\text{Ln}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ (LSCF) as cathodes is attractive in term of high conductivity and feasible catalytic activity. Furthermore, the thermal expansion coefficients (TECs) of LSCF decrease as the Fe content increases. Hence, it is a good candidate as a cathode material for ITSOFCS.^{13,14} Another candidate is the $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ ($x=0.4-0.8$) system (LNF). It has been reported that LNF has a high electronic conductivity and relatively low TEC as a cathode material for ITSOFCS.^{15,16} A series of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ ($x=0.4-0.8$) was synthesized by a coprecipitation method and LTSOFC was used as the cathode. These perovskite materials performed well in the temperature range of 400~600°C,^{17,18} implying that they are promising cathode materials for LTSOFCS. The Fe-rich region of the materials is favorable for use with SOFC cathode materials, as this region is more thermodynamically stable compared to a Ni-rich region. However, the conductivity values of LNF decrease sharply

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as the Fe content increases. It was reported that doped $\text{LaCuO}_{2.5}$ shows excellent electrical conductivity with a high oxygen vacancy concentration.¹⁰⁾ The partial substitution of Cu for Fe in La-Ni-Fe-O cathode materials to synthesize $\text{LaNi}_{0.2}\text{Fe}_{0.8-x}\text{Cu}_x\text{O}_3$ ($x=0.0-0.2$) improved the performance of these materials.¹⁹⁾ In the present study, new cathode materials $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ ($x=0.2-0.8$) (shorted as LNC) are synthesized with full substitution of Cu for Fe to evaluate the structures and fuel cell performance in the temperature range of 400~550°C.

2. Experimental

The $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ ($x=0.2-0.8$) materials were synthesized using the solution route with coprecipitation. A solution of nominal composition LNC was prepared from the regents $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ at various molar ratios. The solution was dropped into a sodium carbonate solution to ensure simultaneous precipitation. The precipitates were rinsed several times in deionized water and were then washed in ethanol three times to remove any water from the particle surfaces. The obtained precipitates were dried at 100°C overnight and were then calcined at 860°C for 4 h. $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) powder was also prepared for further preparation of the SDC-composite electrolyte for use in a fuel cell test. The syntheses of the SDC and SDC-carbonate composite electrolytes followed an established method from the literature.⁷⁾ A Rigaku X-ray diffractometer with $\text{Co K}\alpha$ radiation at a voltage of 35 kV and a current of 30 mA was used for the analysis of the powder structure. The morphologies of the powder and the cathode film of the cell were examined using a Philips330 scanning electron microscope (SEM).

The fuel cells were constructed using a composite anode-supported technique. The composite electrolyte and anode were prepared using a technique outlined in available literature⁷⁾ in which the anode material was a composite nickel oxide mixed with the electrolyte at a volume ratio 40:60. The electrolyte was a composite type consisting of SDC with 20 wt% carbonate ($\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$, $\text{Li}:\text{Na}=2:1$ in molar ratio). In addition, the composite cathode was formulated by mixing the LNC and the SDC-composite electrolyte in volume ratio of 50:50. The mixtures were suitably ground and were then heat-treated at 650°C for 0.5~1.0 h. They were directly taken from the furnace to cool to room temperature and were ground again thoroughly before use. The fuel cell was created by directly pressing the pure anode, the composite anode, the SDC-composite electrolyte, the composite cathode and the pure cathode. Using this construction method, the fuel cell assembly had an anode layer of approximately 1.0 mm, an electrolyte layer in the range of 0.2~0.3 mm and a cathode layer approximately 0.3 mm in thickness. The fuel cell assembly was heat-treated at 600°C for 0.5 h. Silver paste coated onto the electrode served as the current collector. Stainless steel was adopted as a fuel cell device holder. The cell size had an active gas area of

0.64 cm^2 with a diameter of 9 mm and a thickness of 1~1.5 mm. Hydrogen was used as the fuel, and air as the oxidant. The gas (fuel and air) flows were controlled in a range of 80~120 $\text{ml}\cdot\text{min}^{-1}$ at 1 atm of pressure. The measurements were carried out between 400°C and 550°C.

3. Results and Discussion

3.1. Structures and morphologies of the LNC materials

X-ray diffraction patterns of the $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ ($x=0.2-0.8$) powders calcined at 860°C for 4 h are shown in Fig. 1. Powdered $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ was found to have a hexagonal perovskite structure, which is identical to the crystal structure of LaNiO_3 . The $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ showed a second phase, as evidenced by additional peaks at the 2θ value (e.g. 28.2°, 36.2° and 38.6° etc.). The phase was not unambiguously identified but most closely matched the peaks of La_2CuO_4 . As the Cu content increased, the second phase diffraction peak increased and the main phase peak decreased. However, the crystal structure maintained its hexagonal perovskite structure. The lattice constants and the cell volume of the LNC increased slightly. The cell volume increased as the Cu content increased, as the radius of a Cu ion is larger than that of Ni. However, when $x \geq 0.70$, the second phase of $\text{La}_2\text{Cu}_2\text{O}_4$ appeared. This increased with the Cu content. This second phase of $\text{La}_2\text{Cu}_2\text{O}_4$ occurred because additional Cu atoms did not enter the lattice of LaNiO_3 . For the $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_4$ oxide, the lattice parameters of the main phase were found to be $a=0.5460$ nm and $c=0.6517$ nm with a hexagonal structure. The morphology of the $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ ($x=0.2-0.8$) powder was analyzed by SEM. The SEM images show that powders are mainly composed of nearly submicron-sized particles, although some agglomerates can be observed (see Fig. 2).

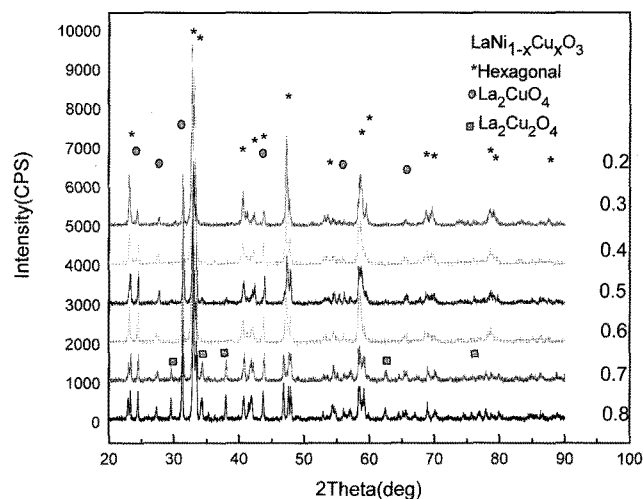


Fig. 1. XRD patterns of the $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ ($x=0.2-0.8$) powders.

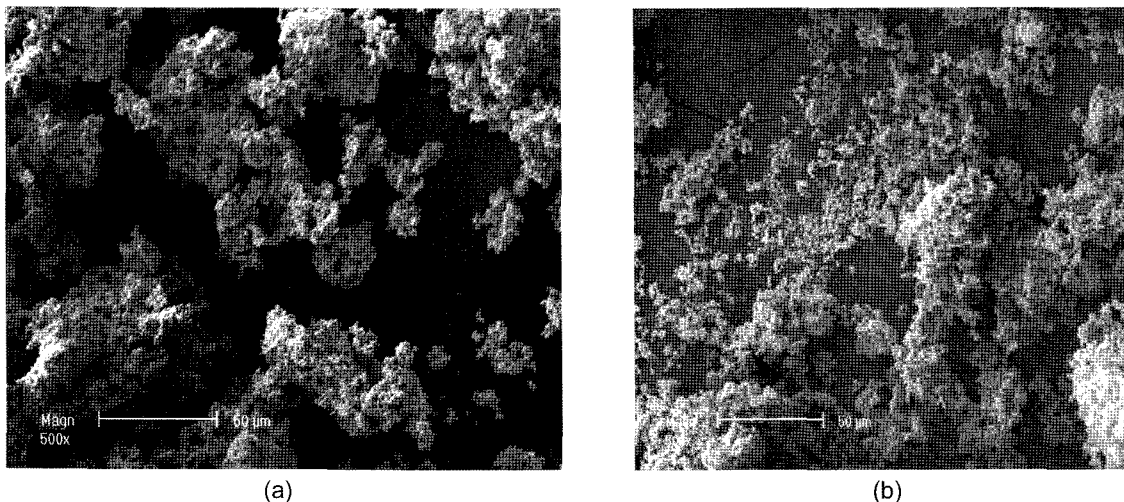


Fig. 2. SEM photograph of a $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ powder particle calcined at 860°C (a) $x=0.7$; (b) $x=0.2$.

3.2. Cathode and fuel cell performances of the LNC materials

Among the synthesized LNC materials, $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ ($x=0.8$) showed superior electrochemical performance at a low temperature ($T < 600^\circ\text{C}$). Fig. 3 shows a range of typical fuel cell performance values of the I - V and I - P characteristics using $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ as the cathode in a temperature range of $400 \sim 550^\circ\text{C}$. An open circuit voltage (OCV) of approximately 0.96 V was achieved at 400°C . The OCV changes slightly with the temperature. With pure SDC as the electrolyte, reduction of the Ce^{4+} in the SDC component to Ce^{3+} commenced when this component was exposed to a H_2 atmosphere at a high temperature. This resulted in a drop of the fuel cell voltage, an effect that may be more significant at higher temperatures. However, in the case of the SDC-carbonate composite electrolytes, the cell OCVs remained higher compared to those obtained using the pure SDC electrolyte. The SDC-carbonate composite electrolyte was stable in the fuel environment in terms of effectively

suppressing the electronic conductivity, due to the improved stability of the SDC-carbonate composite electrolytes relative to the pure SDC.⁷⁾ A maximum power density of $301\text{ mW}\cdot\text{cm}^{-2}$, $304\text{ mW}\cdot\text{cm}^{-2}$, $375\text{ mW}\cdot\text{cm}^{-2}$ and $390\text{ mW}\cdot\text{cm}^{-2}$ and short circuit currents of $844\text{ mA}\cdot\text{cm}^{-2}$, $875\text{ mA}\cdot\text{cm}^{-2}$, $953\text{ mA}\cdot\text{cm}^{-2}$ and $968\text{ mA}\cdot\text{cm}^{-2}$ were obtained at 400°C , 450°C , 500°C and 550°C , respectively. As the temperatures increased, the maximum power density of the fuel cell increased and the short circuit current increased. At temperatures of 400°C and 450°C , the maximum power densities were nearly identical.

It was interesting to find that a specific composition of $\text{LaNi}_{0.4}\text{Cu}_{0.6}\text{O}_3$ ($x=0.6$) led to lower cathode performance at low temperatures ($T \leq 500^\circ\text{C}$). Fig. 4 shows the I - V and I - P characteristics of a fuel cell using $\text{LaNi}_{0.4}\text{Cu}_{0.6}\text{O}_3$ as the cathode at temperatures of 400°C , 450°C and 500°C . The highest OCV is nearly 0.97 V at 400°C , and the OCV decreases as the temperature increases. However, all of the OCV values are higher than 0.93 V in this temperature range. This phenomenon suggests that the cathode possesses significant

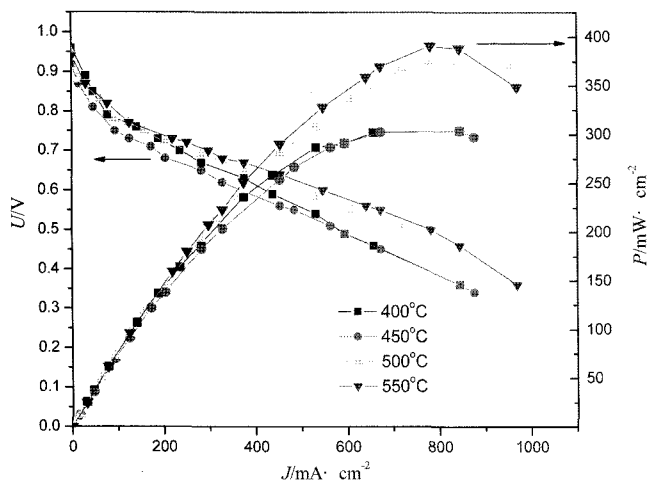


Fig. 3. I - V and I - P curves of a cell using $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ as the cathode at different temperatures of 400°C , 450°C , 500°C and 550°C .

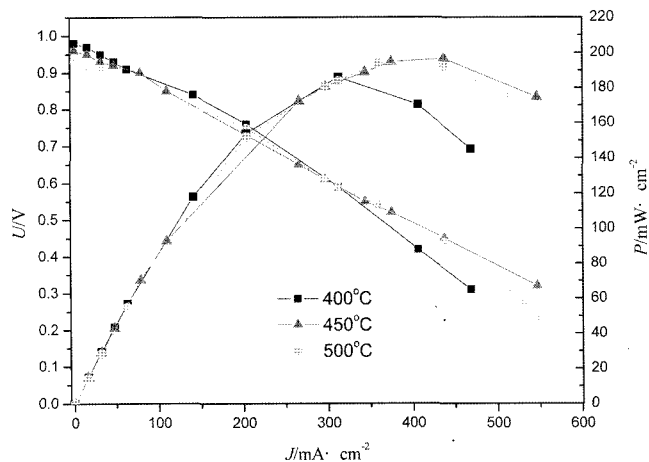


Fig. 4. I - V and I - P curves of a cell using $\text{LaNi}_{0.4}\text{Cu}_{0.6}\text{O}_3$ as the cathode at different temperatures of 400°C , 450°C , and 500°C .

catalytic characteristics at low temperatures. A maximum power density of $196 \text{ mW}\cdot\text{cm}^{-2}$ and a short circuit current density of $546 \text{ mA}\cdot\text{cm}^{-2}$ were achieved at 450°C . It was also noted that within a 100°C range between $400\sim 500^\circ\text{C}$, the fuel cell performance was mostly independent of the operating temperature, e.g., the maximum power densities were between 180 and $196 \text{ mW}\cdot\text{cm}^{-2}$. In terms of the electrolyte, on the one hand, many SDC composites possess a superionic conduction property²⁰⁾ and can create material conductivity nearly one order of magnitude higher than that of pure SDC, which benefits, of course, the LTSOFCs capable of high performance at lower temperatures. Moreover, with SDC-composite electrolytes in such a superionic conducting phase, the dependence of the conductivity on the temperature is very flat, resulting in very little change in the conductivity in a wide temperature range. This implies that sufficient electrolyte conductivity can support high performance over a wide temperature range in the present case. On the other hand, in terms of the cathode, the compositions of cathode materials greatly influence the fuel cell performances. Thus, this suggests that the $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ cathode functions very well over the tested temperature range, even at the aforementioned low temperatures. These considerations explain the aforementioned independence of the fuel cell performance on the temperature. According to the findings of this study, fuel cell performance can be increased considerably by reducing the current $0.2\sim 0.3 \text{ mm}$ thickness of the electrolyte.

It is well known that the cathode function is complex and that the cathode reaction processes and fuel cell performances are determined by many factors related to the cathodes, such as the conductivity (both e^- and O^{2-}), the catalyst function, the microstructure and the compatibility with the electrolyte. All of these factors can significantly affect the TPB and hence the cathode properties and fuel cell performance. For different compositions of $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ perovskite oxides, the electric conductivities are already at sufficiently high levels for fuel cell applications. Therefore, the catalyst, microstructure and stability of the cathode as well as its compatibility with the electrolyte may play a more important role in the cathode function. In $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$, the microstructure is mainly composed of the rhombohedral perovskite phase and a small amount of a La_2CuO_4 second phase. Additionally, in $\text{LaNi}_{0.4}\text{Cu}_{0.6}\text{O}_3$, much of the formed La_2CuO_4 second phase will reduce the cathode catalyst and degrade the stability. Therefore, compared with $\text{LaNi}_{0.4}\text{Cu}_{0.6}\text{O}_3$, $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ may have better stability in the presence of a SDC-composite electrolyte, resulting in better fuel cell performance.

4. Conclusions

$\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ ($x=0.2\sim 0.8$) materials were successfully synthesized via a co-precipitation route. A powder with a hexagonal structure was obtained after calcination at 860°C for 2 h, apart from an amount of La_2CuO_4 / $\text{La}_2\text{Cu}_2\text{O}_4$ of an

orthorhombic second phase. As the amount of Cu increases, the peaks of La_2CuO_4 increase. When $X>0.5$, the second phase of $\text{La}_2\text{Cu}_2\text{O}_4$ increases. In the synthesized $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ ($x=0.2\sim 0.8$), $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ shows the best cathode property and fuel cell performance with a maximum power density of $390 \text{ mW}/\text{cm}^2$ and a short-circuit current density of $968 \text{ mA}/\text{cm}^2$ in a temperature range of $450\sim 550^\circ\text{C}$. These results indicate that LNC-based materials, specifically LNC-82, are promising cathode materials for SOFCs operating at low temperatures below 600°C .

REFERENCES

- Weber A. and Tiffée E. I., "Materials and Concepts for Solid Oxide Fuel Cells (SOFCs) in Stationary and Mobile Applications," *J. Power Sources*, **127** 273 (2002).
- Fukui T., Ohara S., Murata K, et al., "Performance of Intermediate Temperature Solid Oxide Fuel Cells with La(Sr)Ga(Mg)O₃ Electrolyte Film," *J. Power Sources*, **106** 142 (2002).
- Xia C. R., Rauch W., Chen F. L., et al., "Sm_{0.8}Sr_{0.5}CoO₃ Cathodes for Low-Temperature SOFCs," *Solid State Ionics*, **149** [1-2] 11 (2002).
- Zhu B., "New Generation or Universal Fuel Cell System? R and D for Intermediate Temperature Solid Oxide Fuel Cells (ITSOFCs)," *J. New. Mater. Electrochem. Systems.*, **4** 239 (2001).
- T. Ishihara, M. Honda, T. Shibayama, et al., "Intermediate Temperature Solid Oxide Fuel Cells using a New LaGaO₃ Based Oxide Ion Conductor," *J. Electrochem. Soc.*, **145** 3177 (1998).
- Xia C. and Liu M., "Low-temperature SOFCs based on Gd_{0.1}Ce_{0.9}O_{1.95} Fabricated by Dry Pressing," *Solid State Ionics*, **144** [3-4] 249 (2001).
- Zhu B., "Functional Ceria-salt-composite Materials for Advanced ITSOFC Applications," *J. Power Sources*, **114** 1 (2003).
- T. Ishihara, S. Fukui, H. Nishiguchi, et al., *J. Electrochem. Soc.*, **149** A823 (2002).
- Ralph J. M., Rossignol C., and Kumar R., *J. Electrochem. Soc.*, **150** A1518 (2003).
- Yu H. C. and Fung K. Z., "La_{1-x}Sr_xCuO_{2.5-6} as new Cathode Materials for Intermediate Temperature Solid Oxide Fuel Cells," *Mater. Res. Bull.*, **38** [2] 231 (2003).
- Kharton V. V., Tsepis E. V., Yaremchenko A. A., et al., "Surface-limited Oxygen Transport and Electrode Properties of La₂Ni_{0.8}Cu_{0.2}O_{4+δ}," *Solid State Ionics*, **166** [3-4] 327 (2004).
- Coffey G., Hardy J., Marina O., et al., "Copper doped Lanthanum Strontium Ferrite for Reduced Temperature Solid Oxide Fuel Cells," *Solid State Ionics*, **175** 73 (2004).
- Wang S., Zheng R., Suzuki A., et al., "Preparation, Thermal Expansion and Electrical Conductivity of La_{0.6}Sr_{0.4}Co_{1-x}Ga_xO₃ ($x=0.0\sim 0.4$) as a New Cathode Material of SOFC," *Solid state Ionics*, **174** 157 (2004).
- Dyck C. R., Peterson R. C., Yu Z. B., et al., "Crystal Structure, Thermal Expansion and Electrical Conductivity of Dual-phase Gd_{0.8}Sr_{0.2}Co_{1-y}Fe_yO₃ (0-1.0)," *Solid State Ionics*,

- 176** [1-2] 103 (2005).
15. Chiba R., Yoshimura F., and Sakurai Y., "An Investigation of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ as a Cathode Material for Solid Oxide Fuel Cells," *Solid State Ionics*, **124** 281 (1999).
 16. Chiba R., Yoshimura F., and Sakurai Y., "Properties of $\text{La}_{1-y}\text{Sr}_y\text{Ni}_{1-x}\text{Fe}_x\text{O}_3$ as a Cathode Material for a Low-temperature Operating SOFC," *Solid State Ionics*, **152-153** 575 (2002).
 17. Li S., Sun J.C., Sun X.L., et al., "A High Functional Cathode Material $\text{LaNi}_{0.4}\text{Fe}_{0.6}\text{O}_3$ for Low-temperature Solid Oxide Fuel Cells," *Electrochemical and Solid-State Letters*, **9** [2] 86-7 (2006).
 18. Li S., Sun X.L., Wen Z.S., and Sun J.C., "A New Candidate as the Cathode Material for Intermediate and Low Temperature SOFCs," *Rare metals*, **25** 213-17 (2006).
 19. Li S. and Zhu B., "Electrochemical Performance of Nano-composite Solid Oxide Fuel Cells using Nano-size Material $\text{LaNi}_{0.2}\text{Fe}_{0.65}\text{Cu}_{0.15}\text{O}_3$ as cathode," *J. Nanosci and Nanotech*, in press (2008).
 20. Schober T., "Composites of Ceramic High-temperature Proton Conductors with Inorganic Compounds," *Electrochemical and Solid State Letters*, **8** [4] A199 (2005).