

Characterisation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ - $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ composite as cathode for solid oxide fuel cells

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Mixture of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, was investigated as promising cathode for intermediate temperature solid oxide fuel cells (IT-SOFCs). The two perovskites possess high catalytic activity for the oxygen reduction (ORR), although some problems related to their chemical and structural stability have still to be overcome in view of improving durability of the cell performance. The achievement of a stable and high-performing composite material is the aim of this study. In principle, chemical equilibrium at the LSCF-BSCF interface may be reached through ions interdiffusion during the sintering process, resulting in the chemical stabilization of the material. The composite-cathode deposited on $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ electrolyte was then investigated by Electrochemical Impedance Spectroscopy (EIS) as a function of temperature, overpotential and time. The results exhibited an interesting electrochemical behavior of the electrode toward oxygen reduction reaction. XRD analysis was performed to detect structural modification during thermal or operation stages and it was found that after the sintering the two starting perovskites were no longer present; a new phase with a rhombohedral $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$ -type structure (LSF) is formed. An improvement in composite cathode durability has been detected under the considered operating conditions (200 mAcm⁻², 700 °C) in comparison with the pure BSCF electrode. The results confirmed this new electrode as promising system for further investigation as IT-SOFC cathode.

Keywords: SOFC cathode, long-term stability, LSCF-BSCF.

INTRODUCTION

One of the main goals for solid oxide fuel cells is the reduction of operating temperature below 800 °C to improve long-term stability and reduce costs. On the other hand the lowering of operating temperature causes a reduction in performance, mainly due to the high activation energy required for oxygen reduction reaction at the cathode [1,2].

Different efforts have been made to investigate new kind of materials and microstructure with the aim to understand which phenomena are responsible of the cathode performance changes as a function of time, thermal cycling, operating conditions and others factors [1,3–5].

One class of materials widely investigated are perovskite, with a general formula ABO_3 ; the A-site is occupied by lanthanides or alkaline earth metals, B-site contains cations of transition metal as Fe and Co. In particular the attention has been focused on the materials that shown a large ionic and electronic conductivity with a good electrocatalytic reduction of oxygen [6].

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) are two perovskites evaluated as promising cathode materials by several studies [7,8]. Excellent properties of BSCF were presented by Shao et al. [9] at the beginning of 2000.

This material showed a very high performance for temperature lower than 600 °C.

LSCF has been considered a possible electrode material thank to its electronic conductivity, over 300 S·cm⁻¹ and oxygen conductivity near to 0.1 S·cm⁻¹ at 800 °C, with consequent good results [10,11].

Nevertheless these two materials are affected by two main problems: stability and durability. LSCF suffers of La and Sr interdiffusion pointed as the reason of degradation; in fact the cation interdiffusion to electrode/electrolyte interface leads to the formation of an insulating phases as $\text{La}_2\text{Zr}_2\text{O}_7$ (LZO) or SrZrO_3 (SZO) when yttrium stabilised zirconia (YSZ) is used as electrolyte [12,13]. The presence of these phases has a negative effect on ionic conductivity, reducing the global cell performance. A possible solution, to avoid the formation of the insulating layer, is the application of an interlayer made by $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{3-\delta}$ (GDC) or $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{3-\delta}$ (SDC) between cathode and electrolyte or as directly as electrode [13,14].

A further solution to block the Sr segregation is the modification of surface chemistry through the infiltration technique. In this case LSCF cathode backbone was infiltrated by a stable compound rich

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43. J. Fleig, A. Schmid, G.M. Rupp, C. Slouka, E. Navickas, L. Andrejs, H. Hutter, L. Volgger, A. Nennung, *ActaChim. Slov.* **63**, 1 (2016).
A. Esquirol, N.P. Brandon, J.A. Kilner, M. Mogensen, *J. Electrochem. Soc.*, **151**, A1847 (2004).
44. S.B. Adler, J.A. Lane, B.C.H. Steele, *J. Electrochem. Soc.* **143**, 3554 (1996).
45. T. Kawada, J. Suzuki, M. Sase, A. Kaimai, K. Yashiro, Y. Nigara, J. Mizusaki, K. Kawamura, H. Yugami, *J. Electrochem. Soc.*, **149**, E252 (2002).
46. B. Hirschorn, M.E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, *Electrochim. Acta.* **55**, 6218 (2010).
47. C.R. Kreller, T.J. McDonald, S.B. Adler, E.J. Crumlin, E. Mutoro, S.J. Ahn, G.J. la O', Y. Shao-Horn, M.D. Biegalski, H.M. Christen, R.R. Chater, J. A. Kilner, *J. Electrochem. Soc.*, **160**, F931 (2013).
48. J. Jamnik, J. Maier, S. Pejovnik, *Electrochim. Acta.*, **44**, 4139 (1999).
49. M. Sogaard, P. VangHendriksen, M. Mogensen, *J. Solid State Chem.*, **180**, 1489 (2007).
50. M. Kuhn, Y. Fukuda, S. Hashimoto, K. Sato, K. Yashiro, J. Mizusaki, *J. Electrochem. Soc.* **160**, 34 (2013).
51. D.N. Mueller, M.L. Machala, H. Bluhm, W.C. Chueh, *Nat. Commun.* **6**, 6097 (2015).
52. W.G. Wang, M. Mogensen, *Solid State Ionics.* **176**, 457 (2005).
53. K. Park, S. Yu, J. Bae, H. Kim, Y. Ko, *Int. J. Hydrogen Energy*, **35**, 8670 (2010).
54. C. Endler, A. Leonide, A. Weber, F. Tietz, E. Ivers-Tiffée, *ECS Trans.* **25**, 2381 (2009).
55. J. Kim, S. Choi, A. Jun, H.Y. Jeong, J. Shin, G. Kim, *ChemSusChem*, **7**, 1669 (2014).
56. S. Baumann, F. Schulze-Küppers, S. Roitsch, M. Betz, M. Zwick, E.M. Pfaff, W.A. Meulenber, J. Mayer, D. Stöver, *J. Memb. Sci.*, **359**, 102 (2010).

ОХАРАКТЕРИЗИРАНЕ НА $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ - $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ КОМПОЗИТ КАТО КАТОДЕН МАТЕРИАЛ ЗА SOFC

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(Резюме)

Смес от $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ е изследвана като перспективен катоден материал за горивни клетки с твърдооксидни форивни клетки, работещи при междинна температура (IT-SOFCs). Двата перовскита притежават висока каталитична активност за редукция на кислорода (ORR), въпреки че някои проблеми, свързани с тяхната химическа и структурна стабилност, все още трябва да бъдат преодолен с оглед подобряване на стабилността на характеристиките на клетката. Постигането на стабилен и високоефективен композитен материал е целта на това изследване. По принцип химическото равновесие при интерфейса LSCF-BSCF може да бъде постигнато чрез интердифузия на йони по време на процеса на синтероване, което води до химическа стабилизация на материала. Композитният катод, отложен върху $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ електролит, след това беше изследван чрез електрохимична импедансна спектроскопия (EIS) като функция на температурата, свръхпотенциала и времето. Резултатите показаха интересно електрохимично поведение на електрода по отношение на кислородната редукция. XRD анализът е извършен за откриване на структурна модификация по време работа и е установено, че след синтероване двата изходни перовскити вече не присъстват; формира се нова фаза с ромбодрична структура $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$ (LSF). Подобрената устойчивост на композитния катод е открита при разглежданите работни условия (200 mAcm^{-2} , 700°C) в сравнение с чистия BSCF електрод. Резултатите потвърдиха този нов електрод като перспективна система за по-нататъшно изследване като IT-SOFC катод.

Ключови думи: SOFC катод, дългосрочна стабилност, LSCF-BSCF