COBALTITES WITH VARIABLE DIMENSIONALITY AS CATHODE MATERIALS FOR SOFCs

N. Preux[1], K. Nagasawa[2], G. Ehora[1], A. Rolle[1], H. Nakatsugawa[2], S. Daviero-Minaud[1], O. Mentré[1]

[1] UCCS - Unité de Catalyse et de Chimie du Solide - UMR CNRS 8181, ENSCL / UST Lille1, Bâtiment C7a - BP 90 108, 59 652 Villeneuve d'Ascq Cedex, France

[2] Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501- Japan

nicolas.preux@gmail.com

Keywords: new cathode materials, SOFC, cobaltite, dimensionality

Introduction

Ceramic oxide with 3D-perovskite structure is considered as an ideal cathode material for intermediate temperature solid oxide fuel cell (IT-SOFC). Its versatile structure enables the adaptation of both cationic and anionic vacancies and a wide range of chemical dopants, responsible for a mixed electro-anionic conductivity, e.g. see the promising $Ln_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ cobaltites [1]., The $Co^{n+} \rightarrow Co^{(n-1)+}$ reduction plays in favour of good electrocatalytic activity for oxygen reduction through the creation of oxygen vacancies. However, major obstacles to their application such as their high thermal expansion coefficients are to be considered. An alternative approach would consist on the investigation of various structural types assorted with particular structural dimensionalities. In that frame, we have investigated several 1D/2D/3D Co-based oxides without *"a priori"* about their widely studied electronic/magnetic particularities intensively studied in solid state physics, e.g. $Ba_2Co_9O_{14}$, $Ca_3Co_2O_6$, $Ca_3Co_4O_9$, $YBaCo_2O_5$, $YBaCo_4O_7$.

Experimental

A systematic experimental procedure [2] has been selected with the aim to rationalize our results. It involves several stages including : the investigation of i) the electrolyte/electrode reactivity, ii) the thermal behavior iii) the bulk conductivity measurements iv) the preparation and the characterization of symmetrical cells. Even though several systems are currently under investigations, attractive performances have already been obtained.

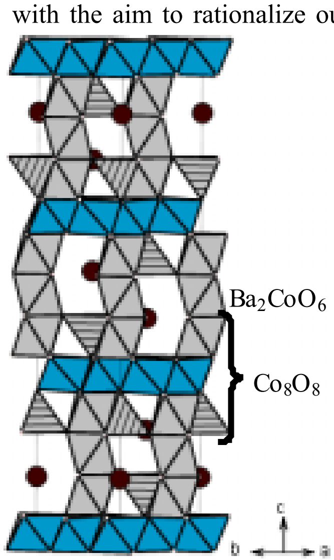

Fig. 1. $Ba_2Co_9O_{14}$ structure

They are detailed in this abstract for the recently evidenced $Ba_2Co^{2/3+}{}_9O_{14}$ oxide [3,4] while our presentation will be extended to a number of extra-cobaltites. $Ba_2Co_9O_{14}$ is the first term of the 3D-new series with general formula $Ba_{n+1}Co_nO_{3n+1}(Co_8O_8)$ [3] (Fig. 1). Its conductivity is 200 $S.cm^{-1}$ at 650°C. We observed a reversible partial reducibility on heating (T> 400°C), reminiscent of possible interesting concentration of vacancies, characteristics of perovskite. YSZ and CGO has been selected as the electrolyte materials while electrode/electrolyte composites have been adjusted for a good adhesion of the electrode.

Results and Discussion

For this oxide we obtained ASR value as low as 4 $\Omega.cm^2$ at 770°C, while the Rp(T) shows an Arrhenius behavior with Ea~1eV (Fig. 2). The electrochemical great time-stability is noteworthy, reinforced by the checking that the electrode resists after 2 months under high temperature testing and various atmosphere cycling. Our measurements versus pO_2 enable to distinguish complementary phenomena at the electrode reaction. It also highlights the limitation of the reaction by charge transfer at the TPB for this oxide.

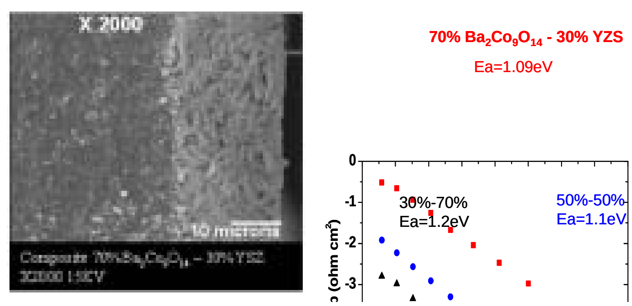

Fig. 2. a) SEM picture of the electrode layer b) ASR vs T for different YSZ/$Ba_2Co_9O_{14}$ ratios

Conclusions

The possibility to prepare efficient electrode/electrolyte systems, using original anisotropic cobaltites (from the structural point of view) opens a wide field of research, currently under investigation on a number of structural archetypes. Here, it is worth announcing the excellent performances just measured on the 2D- misfit $Ca_3Co_4O_9$.

References

[1] Shuyan L. Et al. , Solid State Ionics 178 (2008) 1853-1858

[2] Ehora G. et al., Chemistry of materials 20 (2008) 7425-7433

[3] Junliang S.et al.. *Inorg Mater*. 45 (2006) 9151

[4] Ehora G.,et al., *Chem. Mater*. 19 (2007) 2180.