The Electrochemical and thermal performances of $Ca_3Co_4O_{9-\delta}$ as a cathode material for IT-SOFCs

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The decreasing of the working temperature for intermediate temperature solid oxide fuel cells (IT-SOFC's) is such that the cathode has turned out to provide the major source of electrical loss. Recently, layered double perovskites with ordering of oxygen vacancies such as $LBaCo_2O_{5+\delta}$ (L=lanthanide) [1] have been presented as promising cathode materials, highlighting the important role of their 2D-characteristics in the electrochemical process.

Here, we present recent results on the 2D-$Ca_3Co_4O_{9-\delta}$ (Ca349) for cathode application for IT-SOFCs. This misfit-compound is most known for its thermoelectric properties [2] while, to our knowledge no solid-electrochemical properties been investigated so far. Ca349 is built up from sandwiching $[CdI_2]$-type and rock-salt slabs according to the formula $[CoO_2][Ca_2CoO_{3-\delta}]_{0.62}$, the rock-salt layers being oxygen deficient and potentially mixed conductors. Here, Ca349 could be considered as a natural intergrowth between electronic and potential O^{2-} conducting units. It makes of this compound and excellent candidate for SOFC cathode.

Both the thermal expansion coefficient ($9\text{-}10\times10^{-6}$ K^{-1}) and chemical stability tests (no reaction between palletized mixed phases after 100h at 1023 K) show an excellent compatibility between the title compound and CGO electrolyte, while YSZ was immediately discarded due to the formation of $CaZrO_3$. The preliminary electrochemical tests have been performed on symmetrical-electrode/CGO/electrode cells with electrode = pure Ca349 and composite 30 %CGO-70%$Ca_3Co_4O_9$ (30CGO). Thin electrode layers were deposited on dense CGO by ink painting and firing at 700°C.

Impedance spectroscopy measurements versus temperature and oxygen partial pressure were performed, leading to promising results. The total polarization resistance (ASR) obeys to an Arrhenius behavior with activation energy Ea = 1.55 and 1.23 eV, on air, for Ca349 and 30CGO respectively. It is assorted with ASR values around $3\Omega.cm^2$ at 700°C for Ca349 but it is remarkable that, at this point, no particular effort has been provided to optimize the microstructure and porosity of the electrode, nor to reduce its thickness (typically 30μm). However, for 30CGO, the ASR value becomes $0.75\Omega cm^2$ (Fig. 1) at 700°C with an improvement of the ionic diffusion process, evidenced as a function of the working pO_2.

To conclude, it was understood that both TEC and preliminary electrochemical measurements indicate the misfit 2D-$Ca_3Co_4O_{9-\delta}$ as promising original cathode material for IT-SOFCs.

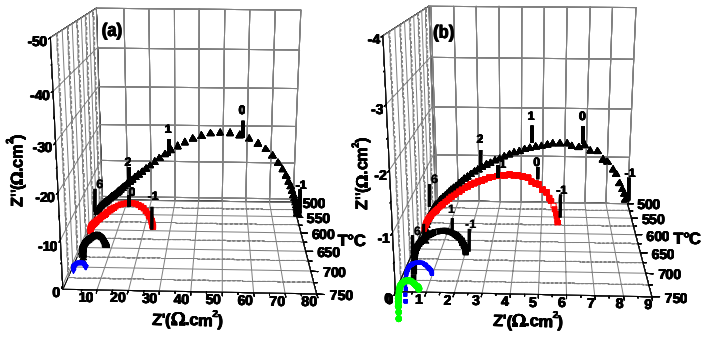

Fig. 1. Temperature dependence of impedance spectra of pure $Ca_3Co_4O_9$ (a) and 30CGO (b)

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[2] Siwen Li, Ryoji Funahashi, Ichiro Matsubara, Kazuo Ueno and Hiroyuki Yamada, *J. Mater. Chem.*, 9, (1999) p. 1659.