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Proceedings of EFC2015
European Fuel Cell Technology & Applications Conference - Piero Lunghi Conference
December 16-18, 2015, Naples, Italy

EFC15185

EFFECT OF SYNTHETIC ROUTE ON PERFORMANCE OF $La_{0.8}Sr_{1.2}Fe_{0.9}Cu_{0.1}O_{4\pm\delta}$ ELECTRODES FOR SYMMETRIC SOLID OXIDES FUEL CELLS

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Abstract **- The solid oxide $La_{0.8}Sr_{1.2}Fe_{0.9}Cu_{0.1}O_{4\pm\delta}$ of interest as electrode for Symmetric Solid Oxide Fuel Cells (SSOFCs) has been prepared via three different synthetic methods: solid-state reaction (SSR), melt citrate route (MC) and co-precipitation (CoP). In order to determine advantages and drawbacks of each synthesis, the materials have been characterized by X-Ray Powder Diffraction (XRD) and Scanning Electron Microscopy (SEM) analysis. Phase purity, structural and morphological characteristics of the powders have been determined. Wet chemical methods (CIT and COP) have the advantage over SSR synthesis of yielding small-sized powders (~ 1μm); moreover, melt citrate route allows lowering the preparation temperature down to 1000 °C. Electrochemical characterization was performed by Electrochemical Impedance Spectroscopy (EIS) in air in an electrolyte supported symmetric cells configuration. Preliminary results allow to draw some conclusions on the relation between the structural and microstructural characteristics of the powders and the electrochemical performance.**

Index Terms **- K_2NiF_4-type electrodes, Synthetics Route, SSOFC, Impedance Spectroscopy.**

I. INTRODUCTION

In last years, the idea of Symmetric Solid Oxides Fuel Cells (SSOFC) structure proposed in literature has drawn researchers' attention [1, 2]. Using the same material as both anode and cathode in a SOFC allows overcoming some issues of SOFC technologies, like thermal mismatch among materials, carbon deposition in anode, Sulphur poisoning; moreover, this configuration can open the way to reversible operation as both SOFC and SOEC (Solid Oxide Electrolysis Cells) in a single device. However, the requirements of a SSOFC electrode are several and strict; primarily, the material of choice should be stable in both oxidizing and reducing environment, and should show good catalytic activity for fuel (H_2 or hydrocarbons) oxidation and O_2 reduction. Among the investigated materials, K_2NiF_4-type oxides are an interesting class, due to their electrical and physical properties. Among them, $La_xSr_{2-x}CuO_4$ and $La_xSr_{2-x}FeO_4$ [3, 4] show chemical stability and high oxygen diffusion coefficients in the intermediate temperature range. The compound $La_{0.8}Sr_{1.2}Fe_{0.9}Cu_{0.1}O_{4\pm\delta}$ was selected among other compositions as the most promising one [5]. In this study, three different synthetic methods are compared. The traditional solid state reaction (SSR) is compared with two wet chemical methods, namely Co-precipitation (CoP) [6] and Melt citrate route (MC) [7] to synthesize the electrode materials. Microstructural and Electrochemical methods are used to discuss the advantages and drawbacks of each route.

II. EXPERIMENTAL WORK

$La_{0.8}Sr_{1.2}Fe_{0.9}Cu_{0.1}O_{4\pm\delta}$ (LSFC) was prepared via SSR starting from La_2O_3 (99.5%, Sigma Aldrich), $SrCO_3$ (99%, Sigma Aldrich), Fe_2O_3 (99.8%, Sigma Aldrich) and Cu_2O (99%, Sigma Aldrich). The compounds were weighted according to the desired stoichiometry and ball-milled in ethanol for 12 h, before firing at 1000 and 1400 °C for 12 h. MC sample was prepared by the same precursors except for iron, which was added as $Fe(NO_3)_3 \cdot 9H_2O$ (99%, Sigma Aldrich). The precursors were dissolved in melt citric acid in a beaker under vigorous stirring; the obtained gel was heated in

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oven to 300°C for 24 h and after calcined at 500 and 1000 °C. The co-precipitation procedure is reported in details elsewhere [6]; the obtained powders were fired at 1000 and 1200 °C. All the produced powders were characterized by X-Ray Powder Diffraction (XRPD) and Scanning Electron Microscopy (SEM). The electrical conductivity and polarization resistance were determined as a function of temperature in electrolyte supported cells ($La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$, LSGM, Fuel cells Materials). The electrolyte pellets were realized by cold pressing at 10 MPa and the electrodes were brush painted on both sides of the electrolyte. An ink was used for the deposition, composed by a 60-40% mixture of electrode-binder (the binder is made by 76% terpineol, 20% propanol and 4% etilcellulose). A potentiostat/galvanostat (Amel 7050) equipped with a frequency response analyzer (510 V10, Materials and Mates) was used for the measurements.

III. RESULTS AND DISCUSSION

XRPD patterns of the fired samples are reported in Fig. 1. SSR sample (A) fired at 1400 °C still contains small amounts of a secondary phase identified as $Sr_3Fe_2O_7$, revealing that the reaction is not completed. CoP sample was multiphase at 1000°C (B) with many unreacted phases (La_2O_3, $SrCO_3$, $Sr(OH)_2$). On the contrary, sample prepared via MC route shows only the peaks belonging to the K_2NiF_4-type phase already after firing at 1000°C (C).

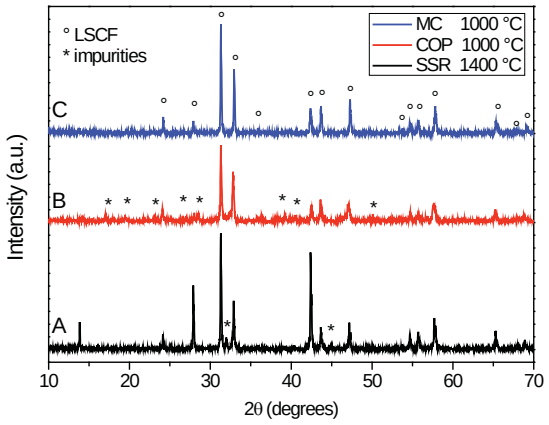

Fig. 1. XRPD pattern of SSR, CoP and MC samples.

SEM analysis (Fig.2) revealed that morphology and grain size of the powders is strongly dependent on the synthetic route and on the firing temperature. SSR sample shows large bulk grains with average size of 5-20 µm, due to the firing at 1400°C that promotes grain sintering. MC and CoP samples prepared via wet chemical routes get advantage of the dissolution of the reactants and retain small sized grains in the sub-micron range in MC sample and in the micron range in CoP material. These small-sized grains are arranged in large agglomerated particles in the 5-10 µm size in MC and even larger in CoP.

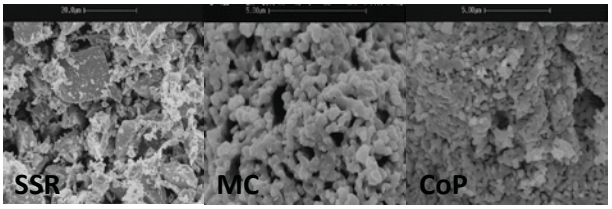

Fig. 2. SEM pictures of SSR, MC and CoP samples.

IV. CONCLUSION

K_2NiF_4-type electrodes for Symmetric solid oxide fuel cells were prepared via three different preparation routes. Sample prepared via solid state reaction requires high temperature (1400 °C) that leads to bulky grains (10-20 µm) and moreover, it retains a small amount of $Sr_3Fe_2O_7$ secondary phase. CoP sample developed a pure phase at 1200 °C with small grain size (5-10 µm). MC method allowed obtaining a pure phase already at 1000 °C with even smaller grain size (< 1 µm). Polarization resistance measurements in electrolyte supported button cells show that the wet chemical methods are advantageous for the preparation of electrode materials that showed improved activity when compared with those prepared by solid state reaction.

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