

**Influence of oxidant gas composition on the behavior of molten carbonate fuel cell with  $\text{LiCoO}_2$  and  $\text{LiMg}_{0.05}\text{CoO}_2$  cathodes**

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In the last years the molten carbonate fuel cells (MCFCs) were subjected to several studies due to their capability to produce electrical power with high efficiency, heat co-generation and low pollution. The new materials for the cathode represent one of the main research areas. The conventional cathode material is the lithiated nickel oxide  $\text{Li}_x\text{NiO}$ , which presents a high solubility in the melted carbonates. As alternative to  $\text{Li}_x\text{NiO}$  several materials were proposed:  $\text{LiFeO}_2$ ,  $\text{Li}_2\text{MnO}_3$ ,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ , and  $\text{LiCoO}_2$  [1]. The more promising material seems to be the lithium cobaltite with solubility lower than  $\text{Li}_x\text{NiO}$  [2-6].

The present work had the aim to verify the electrochemical performances of different innovative cathode materials: iper-stoichiometric lithium cobaltite  $\text{Li}_{1.1}\text{CoO}_2$  (LICO) and Mg-doped lithium cobaltite  $\text{LiMg}_{0.06}\text{CoO}_2$  (LICOA).

The sintered cathodes, characterized by mercury porosimetry, had porosity between 55 and 60 %, 8  $\mu\text{m}$  medium pore diameter and thickness of 500  $\mu\text{m}$ . The anode was Ni-5Cr and the electrolyte was the eutectic Li/K=62/38 mol% at 650 °C.

The electrochemical behavior of lithium cobaltite cathodes (LICO and LICOA) was investigated in a single cell (up to 100  $\text{cm}^2$ ). The tests were carried out in various operating conditions (atmosphere, temperature), for a lifetime up to 1,000 hours.

During the experiments the cathode gas composition was changed to check the influence of oxygen and carbon dioxide partial pressure on the performance and to study the cathode kinetic. Moreover the influence of temperature on cathode kinetic was evaluated. The data for LICOA (after 550 and 890 h of cell life-time) confirm the marked dependence of  $p\text{O}_2$  on OCV, especially at low partial pressure. Instead, the influence of  $p\text{CO}_2$  is not so marked for all partial pressures.

The polarization characteristic plots both of LICO and LICOA were simulated by a semi-empirical equation [7], which take in account for different parameters: Tafel slope, exchange current density, ohmic resistance, polarization resistance related to mass transfer phenomena. The physico-chemical interpretation of of all parameters used in the equation is given.

The electrochemical performances increase as the oxygen and carbon dioxide partial pressure is increased, indicating a positive effect on the cathode kinetic.

It was pointed out a more complicated relationship between current density and  $p\text{O}_2$  than in the case of carbon dioxide. The oxygen reduction reaction mechanism is different with LICO and LICOA

LICOA cathode has a better performance compared to

LICO. The Mg-doped lithium cobaltite showed a very good performance compared to lithiated nickel oxide, if the optimal gas is chosen (LINIO). The best performance of LICOA were achieved by using an oxygen rich gas composition, while for LINIO it was necessary to use a less rich gas. That means that the electrochemical mechanism is very different for the two materials.

In conclusion the Mg-doped lithium cobaltite (LICOA) shows, whatever the cathode gas composition, best performances respect to iper-stoichiometric lithium cobaltite (LICO).

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