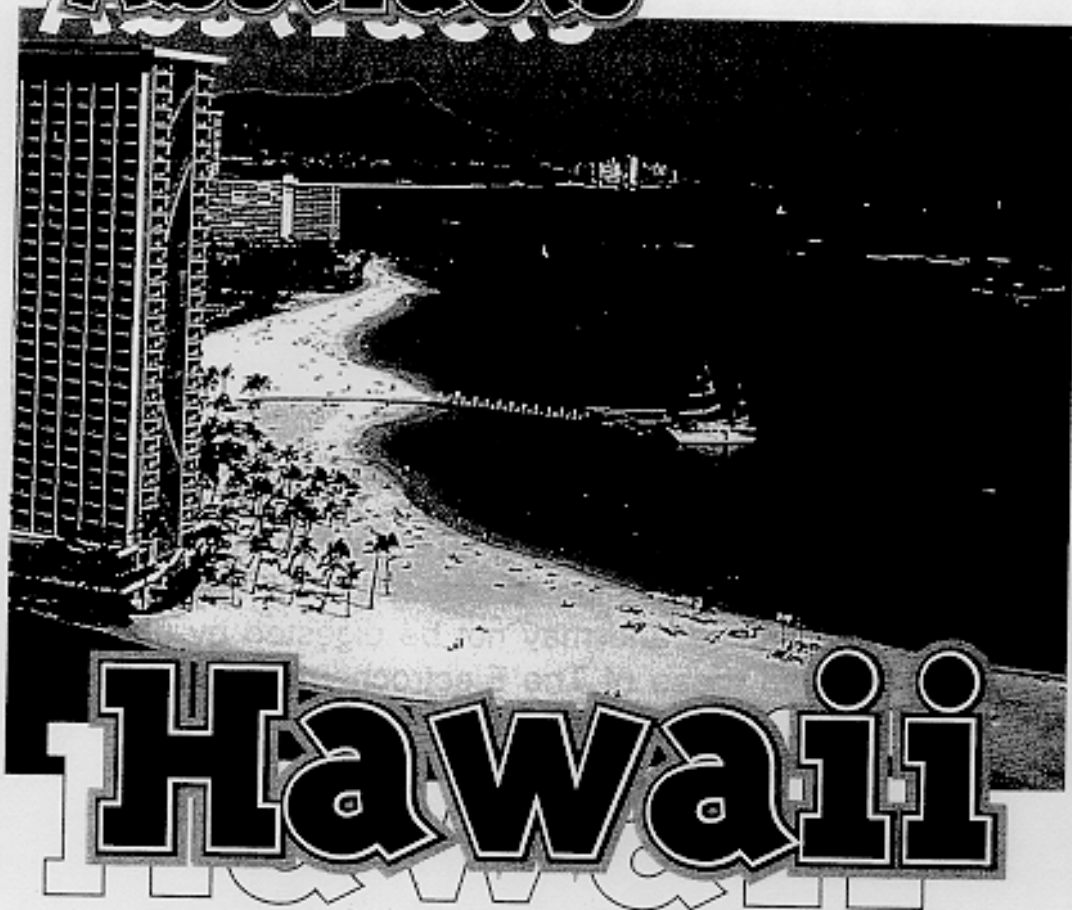


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Cathode Materials for Molten Carbonate Fuel Cells

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The Molten Carbonate Fuel Cells (MCFC) technology is developing in order to reach the target of a lifetime of 40,000 h, and the bottle neck is represented by cathode stability. In fact, the MCFC cathode is obtained by in-situ oxidation/lithiation of a presintered porous nickel tape. This material ($\text{NiLi}_2\text{O}_{1-x}$) offers good electrochemical activity [1], but it is subjected to a low and continuous dissolution process when it is in contact with the carbonates electrolyte. This problem is a heavy limitation for the cell lifetime, because also if the nickel equilibrium solubility is between 30 and 50 ppm, a pumping effect toward the anode side not allows the system to reach its equilibrium solubility and thus the dissolution process of the cathode structure becomes continuous. The dissolution of $\text{NiLi}_2\text{O}_{1-x}$ produces a loss of cathode mass with a reduction of the surface area available for electrochemical oxygen reduction; furthermore, the massive precipitation of metallic nickel particles in the matrix can generate short-circuit in the cell.

To understand and solve this problem, significant research have been carried out. Two different ways have been followed to limit the cathode dissolution. The first consists in the optimization of the operative conditions of the cell (electrolyte composition, gas reactants composition and temperature). The second way is based on the developing alternative cathode materials [2]. These material should provide performances close to $\text{NiLi}_2\text{O}_{1-x}$ and have a lower solubility in molten carbonates. For this purpose, several ceramic compounds (oxides) have been investigated. Attention has been focused on the following materials: lithium ferrite (LiFeO_2) [3,10], lanthanum-strontium-cobalt perovskite ($\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$) [4,5] and lithium cobaltite (LiCoO_2) [6,7,8,9].

LiFeO_2 is quite insoluble in molten carbonates, but the high cathode overvoltage greatly reduces the cell performance. The cell voltage difference, relatively to $\text{NiLi}_2\text{O}_{1-x}$, increases with current density (40% at 150 mA cm^{-2}). By means of EIS [10], the dissociation/reduction of molecular oxygen and the formation/reduction of peroxy carbonate are verified in detail. Furthermore, the diffusional control of oxygen and carbon dioxide on the cathode kinetic was determined. So the low LiFeO_2 performance can be attributed to its low electrical conductivity.

The $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ material present a very high electrical conductivity (100 S cm^{-1}) [4] and a reasonable mechanical strength [5]. The in-cell tests indicated the perovskite electrodes were comparable to NiO in mass transfer performance. Although the results of the cathodic reaction mechanism indicate a different path, the overall kinetic performance was comparable to that of $\text{NiLi}_2\text{O}_{1-x}$. EIS measurement in a symmetric cell have put in evidence for a long term instability of $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ in molten carbonates [4], due to the formation of a not conductive surface film, probably as a consequence of a

reaction between the perovskite and the $\gamma\text{-LiAlO}_2$ of the tile.

LiCoO_2 is the much promising material because it shows a cathodic performance close or higher than $\text{NiLi}_2\text{O}_{1-x}$, and a solubility an order of magnitude lower [6,8], also if in high pressure operation the superiority of LiCoO_2 becomes smaller [11]. The electrical conductivity of lithium cobaltite increases considerably with excess of lithium respect to the stoichiometric composition (1 S cm^{-1}). Moreover, the doping with magnesium ($\text{LiMg}_{0.05}\text{CoO}_2$) drastically increases the conductivity (5 S cm^{-1}), and also the electrochemical stability [7] and performance are increased exceeding the $\text{NiLi}_2\text{O}_{1-x}$ ones [12]. The polarization of LiCoO_2 is mainly related to the electrode morphology, rather than chemical behaviour [6]. Therefore the correct morphology can be obtained by using appropriate poreformers and heat treatment for the sintering [13]. In that way the performances are even higher than for $\text{NiLi}_2\text{O}_{1-x}$ [14].

The practical use of LiCoO_2 cathode in MCFC stacks is limited by the low mechanical strength and price of cobalt precursors. To overcome these problems, layers of LiCoO_2 have been deposited, by solution-gel technique, on the inner surface of porous Ni or NiO cathode [15,16]. The electrochemical performance are quite good and the nickel solubility is reduced by half.

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