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The stability of molten carbonate fuel cell electrodes: A review of recent improvements

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ABSTRACT

The electrode stability is a key issue for the development of conventional hydrogen fuelled and direct internal reforming (DIR) molten carbonate fuel cells (MCFCs). While for conventional MCFC anodes the stability problem has been addressed by the addition of Al or Cr to Ni, the problems of the dissolution of the NiO cathode and of the deactivation of DIR-MCFC anodes have not been fully resolved too. This review reports recent improvements in the chemical and physicochemical stability of cathode and anode materials in MCFCs and DIR-MCFCs, respectively.

Contents

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1. Introduction

Molten carbonate fuel cells (MCFCs) are high-temperature fuel cells that use as an electrolyte a molten carbonate salt mixture suspended in a porous, chemically inert ceramic matrix of beta-alumina. The state-of-the-art MCFC consists of a porous nickel (containing dispersed aluminum or chromium to provide strength and sintering resistance) anode (fuel electrode), a porous, lithium-doped, nickel oxide cathode (oxidant electrode), and a lithium aluminate matrix filled with lithium and potassium carbonates (62–70 mol% Li_2CO_3) as the electrolyte. The cell is operated at a temperature of about 650 °C and at a pressure of 1–10 atm; the fuel gas is a humidified mixture of H_2 and CO, and the oxidant is a mixture of O_2 and CO_2 which may contain water vapor [1–3].

Because of the high operation temperature and the presence of corrosive molten alkaline carbonate degradation of the components can easily occur. The increase of cell life is one of the most important targets for MCFC to be brought into actual application. A key point in the development of electrode materials for MCFCs is the improvement in their chemical and physicochemical stability. Regarding the durability of a MCFC on commercial level, it is required a lifetime of 40,000 h and a voltage decay rate of less than 10% after this period. The voltage degradation of a MCFC is generally agreed to be divided into two phases as shown in Fig. 1 from Ref. [4]. The first phase shows a gradual degradation caused by the increase of ohmic resistance (*i.e.* internal resistance) and the electrode polarization due to the carbonate electrolyte loss. The second phase shows a rapid degradation, which may be caused by Ni short circuit or the gas cross leakage between the electrodes due to the cumulative electrolyte loss over the long period. The transfer from the first phase to the second phase determines the period of operating of a MCFC power unit.

The state-of-the-art cathode is usually formed by the *in situ* oxidation and subsequent lithiation of presintered porous nickel plaques [1]. In molten carbonate fuel cells the conductivity of NiO cathodes is enhanced by doping *in situ* with Li provided by the Li_2CO_3 component of the molten carbonate electrolyte, according to the following equation [5,6]:

$$(1-x)\mathrm{NiO} + x\mathrm{Li}^+ + x\mathrm{CO}_3^{2-} \rightarrow \mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O} + x\mathrm{CO}_2 + x\mathrm{e}^- \quad (1)$$

It was found that lithiation takes place at a potential around −0.4 V *vs.* (1:2) O_2:CO_2 reference electrode according to the parabolic rate law, involving the oxidation of Ni^{2+} to Ni^{3+} and the diffusion of Li^+ into the solid phase. The dissolution of NiO in the carbonate melt during operation of the cell, nevertheless, is one of the major factors restricting the cell life. The dissolved nickel ion diffuses from the cathode towards the anode by concentration gradient and, is reduced to metallic nickel deposits by dissolved hydrogen from the anode side. The accumulative nickel deposits eventually forms an electronic conductive chain in the matrix and causes short-circuit between cathode and anode. In addition to Ni short circuit, the change of the cathode structure by NiO dissolution could be responsible for the second phase shown in Fig. 1. Indeed, according to the results of the 650 °C–33,000 h long-term operation test, Morita et al. [4] inferred the transfer from the first to the second phase of Fig. 1 at 26,500 h is not caused by the Ni short circuit but by the cumulative increase of cathode polarization, caused by to the change of the cathode structure. In order to resolve these problems, the solutions is to reduce the dissolution of nickel oxide, by modifying the characteristic of the catalyst or by change the characteristics of the electrolyte.

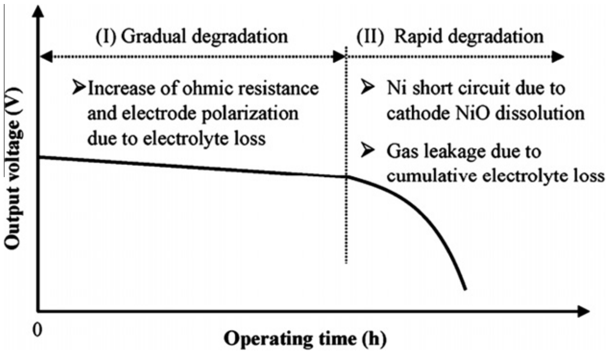

Fig. 1. Schematic diagram of MCFC degradation according to operating time (at a constant current). Reprinted from Ref. [4], copyright 2010, with permission from Elsevier.

The state-of-the-art anode catalysts for MCFC fuelled with H_2 or H_2/CO (Ni–10 wt.% Cr [7,8] or Ni–5 wt.% Al [9,10] systems) possess a satisfactory creep resistance and stability of its catalytic activity during fuel cell operation. Creep resistance can be defined as a the ability of a material to resist any kind of distortion under the influence of stresses over an extended period of time. For optimum performance and maximum lifetime, materials which are subjected to long-term stresses, should have a high creep resistance.

Generally the Ni–Al anode shows higher creep resistance than the Ni–Cr anode. Besides, Cr in the Ni–Cr anode is easily lithiated by the electrolyte to produce $LiCrO_2$ during cell operation. The production of $LiCrO_2$ usually accompanies creation of micropores and leads eventually to cell performance decay. This type of problem is not present in the Ni–Al anode. When properly sintered, the Ni–5 wt.% Al anode shows the morphology of a network structure of Ni–Al solid solution with small Al_2O_3 particles finely dispersed on its surface [9,10]. It is generally admitted that the high creep resistance of this anode is due to dispersion strengthening by the particles as well as solid solution strengthening.

Conversely, in the case of direct internal reforming molten carbonate fuel cells (DIR-MCFCs), where for the reforming of natural gas to produce hydrogen, nickel catalysts supported on silica, alumina, and magnesia are currently used [11], anode catalyst deactivation occurs, mainly due to vapor-phase pollution, caused by alkali poisoning originating from the molten carbonate electrolyte. Therefore, it is necessary to develop highly active and alkali-resistant catalysts, with the purpose is to obtain materials with low loss of catalytic activity during fuel cell operation.

This review reports recent improvements in the chemical and physicochemical stability of cathode and anode materials in MCFCs and DIR-MCFCs, respectively.

2. Cathode

The instability of NiO during cell operation is considered one of the major technical difficulties regarding MCFC development. Nickel oxide has a small degree of solubility in the carbonate electrolyte in the fuel cell cathode environment (about 10–15 ppm), which depends on CO_2 partial pressure and on the amount of Li present in the NiO lattice [12]. However, the dissolved nickel ions diffuse, under a concentration gradient, from the cathode toward the anode. At some location between the two electrodes and under the influence of reducing conditions caused by the anode gas, the dissolved nickel precipitates as nickel metal. The precipitation of nickel creates a sink for the nickel ions, which facilitates further NiO dissolution. Thus, the dissolution of NiO can be a major life-limiting factor for the MCFC [1]. Most testing to date has shown that the common failure mode is cell shorting due to nickel metal precipitation. To overcome/reduce the problem of NiO solubility, the stabilization of NiO by the control of the basicity of the electrolyte, the development of new stable cathode materials and the protection of the Ni-based cathode by an electrochemically active