Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 3463–3478

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Review paper

The stability of $LiAlO_2$ powders and electrolyte matrices in molten carbonate fuel cell environment

Ermete Antolini*

Scuola di Scienza dei Materiali, Via 25 aprile 22, 16016 Cogoleto, Genova, Italy

Received 24 September 2012; received in revised form 20 October 2012; accepted 20 October 2012
Available online 9 November 2012

Abstract

The stability of $LiAlO_2$ electrolyte matrix is a key issue for the development of molten carbonate fuel cells (MCFCs). The phase transformation and particle growth of $LiAlO_2$ particles, observed after a long period of cell operation, is a serious problem and must be overcome in order to attain more than 40,000 h of MCFC life. This process is accompanied by pore size increase of the matrix, leading to a loss of capillary retention for electrolyte in the matrix, causing redistribution of electrolyte and finally resulting in the cross-over of gas. Therefore, efforts have been addressed to obtain a stable matrix with an appropriate pore structure and mechanical strength to provide effective gas-sealing properties without cracks formation during MCFC operation. This review deals on the chemical stability of $LiAlO_2$ powders in molten carbonates and the structural stability of $LiAlO_2$ matrices in MCFCs.

Keywords: C. Strength; E. Fuel cells; $LiAlO_2$; Phase transition

Contents

---

*Tel.: +39 0 109 182 880.
E-mail address: ermantol@libero.it

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.10.236

1. Introduction

Fuel cells are electrochemical devices, which convert chemical energy of electrochemical reactions directly into electrical energy. Molten carbonate fuel cell (MCFC) demonstrations have been able to show the highest fuel-to-electricity conversion efficiencies (> 50%) of any stand-alone fuel cell type. MCFC technology is more fuel flexible than lower temperature fuel cell technologies and is well suited for on-site stationary combined heat and power applications as well as to marine, military, and traction applications [1]. MCFCs consists of a porous nickel anode, containing dispersed chromium to provide strength and sintering resistance (fuel electrode), a porous, lithium-doped, nickel oxide cathode (oxidant electrode), and a lithium aluminate matrix filled with lithium and potassium or sodium carbonates (50–70 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 [2–4]. It is generally assumed that a stack lifetime of atleast 40,000 h is required in order to achieve cost of electric targets, provided that the system is used for co-generation [4]. It is well known that the lifetime limiting issues for MCFC systems are mainly materials issues of the stack. Dissolution of NiO cathode material, corrosion of separator plates, electrolyte losses, electrolyte retention capacity, catalyst deactivation (in the case of internal reforming), matrix cracking, high temperature creep of porous components and contaminants are the main lifetime limiting constraints [5,6]. Therefore improvement in endurance of the MCFC stack and its components is an important issue in the worldwide research and development of MCFC.

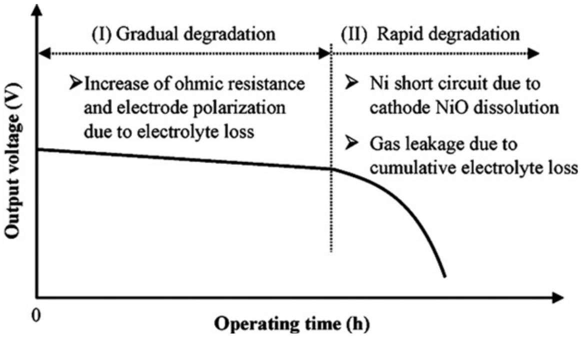

Fig. 1. Schematic diagram of MCFC degradation according to operating time (at a constant current). Reprinted from Ref. [7] copyright 2010, with permission from Elsevier.

The voltage degradation of a MCFC is generally divided into two phases as shown in Fig. 1 [7]. 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.

In a previous work, the stability of molten carbonate fuel cell electrodes has been reviewed [8]. Another key point affecting the durability of a MCFC is the amount of electrolyte in the cell. It is well known that one of the major causes of the deterioration of MCFCs is electrolyte depletion. Indeed, the cell performance depends greatly on the amount

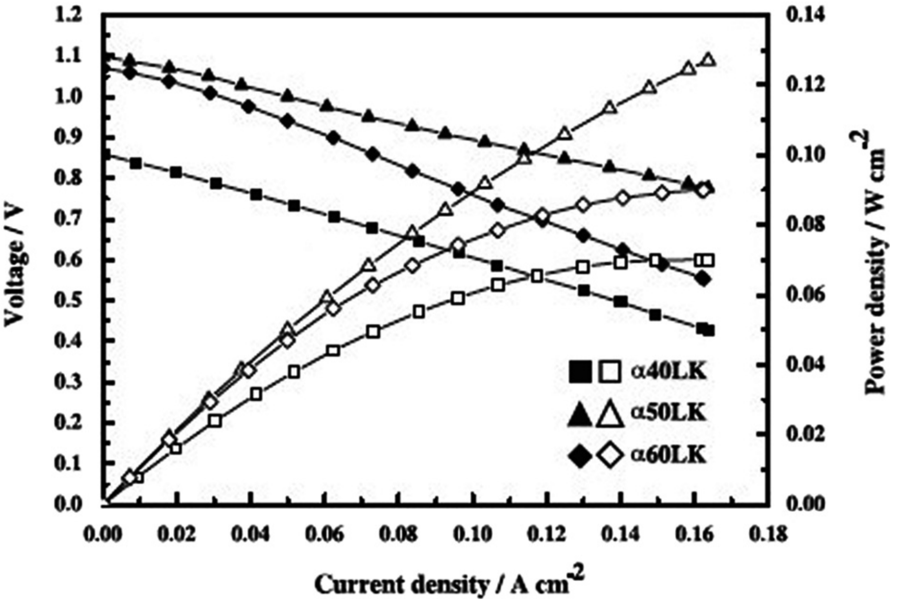

Fig. 2. Polarization and power density curves in single MCFC with different Li_2CO_3/K_2CO_3 (62/38 mol%) electrolyte content in α-$LiAlO_2$ matrices. Anode: Ni alloy. Cathode: in-situ lithiated NiO. Full symbols: polarization curves; open symbols: power density curves. Reprinted from Ref. [9] copyright 2011, with permission from Elsevier.