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Accurate in-operando study of molten carbonate fuel cell degradation processes -part I: Physiochemical processes individuation

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ABSTRACT

This work has the difficult task to deeply study the electrochemical processes that occur inside a 100 cm^2 of Molten Carbonate Fuel Cells (MCFC) impedance spectra using the high resolution of Distribution of Relaxation Time (DRT) method. Using this method, it is possible to shed light on the different physicochemical processes occurring within these cells, identifying the characteristic relaxation times by means of an appropriate experimental campaign where temperature and gas compositions in anode and cathode were varied one at a time. The quality of the recorded spectra was verified by Kramers-Kronig relation before applying DRT calculations. In this work, five distinct and separated peaks with different time constants ranging from 0.01 to 500 Hz were identified and associated with physiochemical processes of the cell. Three peaks at high frequency represent the charge transfer processes in anode and cathode active sites. The other two, located at low frequency, are associated with the gas diffusion in the electrodes and to the gas conversion process. This study represents the first application of the DRT approach to this technology allowing to understand the physicochemical origin of the individual polarization processes controlling the cell performance and the degradation. The analysis of degradation processes using the DRT method and the physiochemical processes identification presented in this paper will be shown in part II of this work.

1. Introduction

Molten carbonate fuel cells (MCFCs) are promising power generation devices enabling high-efficiency co-generation of electricity and heat with minimal environmental impact [1]. The main advantage in the development and the use of MCFC technology on a large scale is the exploitation of its operational flexibility. In fact, the high operating temperature (approximately 923 K) allows MCFCs to use CO (which is a contaminant for low temperature fuel cells) and low weight hydrocarbons as fuels. These fuels can be converted into hydrogen via water gas shift (WGS) and steam reforming (SR) reactions respectively, and this can take place directly in the cells (internal reforming) or in a separate reformer (external reforming) using the heat generated by the operating stack(s) [2,3].

In addition, this technology can be exploited as CO_2 concentrator thanks to its intrinsic operating mechanism. In fact, the electrochemical reactions taking place within the MCFC involve the migration of carbonate ions from the cathode to the anode, that corresponds to a depletion of CO_2 in the oxidant fed gas and the subsequent enrichment of CO_2 in the anode exhaust gas. During this process, the MCFC has the unique ability to operate as an integrated CO_2 concentrator and power generation unit, allowing to integrate it with conventional power generation in combination with carbon capture and storage (CCS) technology for the removal of the CO_2 from combustion flue gas [4,5].

These practical advantages explain the power generation market interest in MCFCs, but being a commercially embryonic technology compared to the conventional power generation systems, the resources needed to bring this technology into a commercial breakthrough necessary for a fast market penetration are still significant. Primarily, from an economic point of view, the costs of fuel cells per kW is still considerably higher than conventional power

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plants.

In addition, an important requirement for commercial applications is the long-term stability. In fact, for stationary applications, agreed target lifespan is generally more than 40,000 h.

The two main causes of performance degradation throughout cell lifetime are the loss of electrolyte and dissolution of the NiO in the cathode. Initially, the electrolyte is consumed by corrosion reactions with metal hardware in the fuel cell. Over a longer time, and at a more constant rate, the electrolyte is primarily lost by vaporization into the fuel gas. Although a careful electrolyte management with improved pore structure to maintain electrolyte within the electrodes has reduced the electrolyte loss due to vaporization, this mechanism remains the main cause of performance degradation in atmospheric systems [6].

The cathode is made of NiO, which is slightly soluble in the electrolyte (Eq. (1)). Dissolved nickel ions diffuse into the electrolyte, and precipitate as metallic nickel forming electronically conducting pathways between the anode and cathode.

$$NiO + CO_2 \rightarrow Ni^{2+} + CO_3^{2-} \quad [1]$$

The solubility of NiO is managed by a combination of electrolyte composition, gas composition, pressure and operating temperature in the electrolyte. It was early identified as a major obstacle to an increased lifetime of the fuel cell, as it threatens the integrity of the fuel cell by causing short-circuiting [7–10].

The identification of these degradation mechanisms is possible with a post-mortem analysis, underlining the difficulty to recognize them in-operando.

Although many studies have been conducted to reduce the degradation mechanisms that lead to cell failure [11–14], progress for a further performance improvement is partly constrained by an incomplete understanding of the physicochemical origin of the individual polarization processes controlling the cell performance.

Attending to these considerations, the scientific and industrial communities should work hand-in-hand to enhance the production of a high-performing, and robust products, developing advanced analysis tools and techniques to fully understand the degradation phenomena.

In this scenario, Electrochemical Impedance Spectroscopy (EIS) is proposed as a powerful tool to assess the MCFC performance [15]. EIS can be recorded without altering the working conditions of the fuel cell and can thus be used to determine the impact of different parameters (e.g. reactants stoichiometry, current density, temperature) during cell operation.

In literature, many works exploit this task, from the pioneering works of Selman et al. [16] or Nishina et al. [17] until to the recent works of C. -G. Lee [18,19], demonstrating the validity of this technique as an in-situ method for characterizing rate-limiting processes in MCFCs porous electrodes. Even though EIS is a very sensitive technique, it can hardly distinguish two processes that differ in their characteristic frequency by less than two decades, thus resulting deeply convoluted in the EIS spectrum and consequently in a not clear image of the real electrochemical processes that occurring the cell.

Impedance spectra can be interpreted using an equivalent circuit model (ECM) [20]. In this approach, physical phenomena, taking place in the fuel cell during operation, are represented by equivalent electrical elements. The value of such elements is obtained by the fitting of the measured impedance data by means of mathematical algorithms. An appropriate use of ECM to fit impedance data relies on a priori knowledge about the system since it requires a suitable model structure that represents the physical processes occurring in the cell. Conversely, if there is a little, or no a priori knowledge about the system, the choice of an appropriate model structure can become a difficult task, leading often to a severe ambiguity of the adopted model [15]. In order to overcome this issue, an alternative approach for analysing impedance spectra is the Distribution of Relaxation Times (DRT) method.

Originally introduced for the impedance analysis of solid oxide fuel cells [21–23] and lithium-ion batteries [24], DRT can be used for process identification in complex electrochemical systems, where resistive-capacitive (R//C) features are dominant [22]. The individual processes are separated on the basis of their typical time constants, derived from the associated (R//C) elements, allowing to bypass ambiguous EC modelling and to analyse spectra without pre-assumptions.

Moreover, DRT analysis is a useful instrument to investigate the degradation phenomena during a long-term test. In fact, as demonstrated in different studies on SOFCs [25,26], the use of DRT analysis combined with a valid ECM gives the possibility to observe qualitatively and quantitatively the behaviour of individual polarization processes *in operando*. In this field, accelerated lifetime tests can become a powerful tool to reduce significantly the experimental efforts for long-term tests [27]. A direct application of the existing monitoring methodologies is unfeasible as the lifetime and degradation rate of a fuel cell are governed by several concurring processes.

A deconvolution of the different degradation mechanisms by EIS coupled with DRT can provide the required information about the different ageing phenomena in the cell.

The global aim of this work is to analyse the degradation phenomena in 100 cm^2 class MCFCs, during an endurance test. The chosen tools are the EIS coupled with DRT method allowing to monitor the individual polarization processes controlling the cell performance *in operando*, and microstructural characterization techniques used for *pre-* and *post-mortem* analysis.

Since no other study is present in the literature about DRT applied to MCFCs, an identification of the single processes was necessary. For this reason, in this paper is reported the first part of the work, regarding the first findings on the deconvolution of MCFC impedance spectra and the identification of t the individual polarization processes using an appropriate experimental campaign where temperature and gas compositions in anode and cathode were varied one at a time. Whereas the results obtained from the endurance tests will be discussed in the second part.

2. Experimental

2.1. Equipment setup

The experimental data produced to support this activity were carried out at the Fuel Cell Research Center laboratories of KIST in Seoul, South Korea, using planar MCFC single cells with an active area of 100 cm^2.

The characteristics of the single cell components used are summarized in Table 1.

The electrolyte layers are alternated with the matrix layers and then assembled between the anode and cathode. The obtained fuel cell is sandwiched between the two current collectors and included in the anodic and cathodic frames (see Fig. 1a), where fuel and oxidant stream were in concurrent flow.

The cell was held in a heating block under a mechanic load of 2 $kgcm^{-2}$, obtained with a hydraulic piston as shown in Fig. 1b.

The anode and cathode gas compositions, fed to the cells, were measured and controlled by Brooks 5850E Digital Mass Flow Controllers and a thermo-controlled bubbler is used to adjust the required water content in the fuel.

The temperature of the anodic inlet pipeline is controlled through heating tapes from the water injection point up to the