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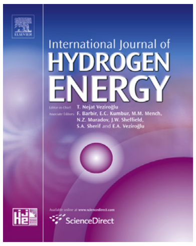

Electrochemical performance of reversible molten carbonate fuel cells

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ABSTRACT

The electrochemical performance of a state-of-the-art molten carbonate cell was investigated in both fuel cell (MCFC) and electrolysis cell (MCEC) modes by using polarization curves and electrochemical impedance spectroscopy (EIS). The results show that it is feasible to run a reversible molten carbonate fuel cell and that the cell actually exhibits lower polarization in the MCEC mode, at least for the short-term tests undertaken in this study. The Ni hydrogen electrode and the NiO oxygen electrode were also studied in fuel cell and electrolysis cell modes under different operating conditions, including temperatures and gas compositions. The polarization of the Ni hydrogen electrode turned out to be slightly higher in the electrolysis cell mode than in the fuel cell mode at all operating temperatures and water contents. This was probably due to the slightly larger mass-transfer polarization rather than to charge-transfer polarization according to the impedance results. The CO_2 content has an important effect on the Ni electrode in electrolysis cell mode. Increasing the CO_2 content the Ni electrode exhibits slightly lower polarization in the electrolysis cell mode. The NiO oxygen electrode shows lower polarization loss in the electrolysis cell mode than in the fuel cell mode in the temperature range of 600–675 °C. The impedance showed that both charge-transfer and mass-transfer polarization of the NiO electrode are lower in the electrolysis cell than in the fuel cell mode.

Introduction

Hydrogen and syngas ($H_2 + CO$) are today considered as important fuels in future energy systems. Hydrogen is a promising clean energy carrier for a future zero-carbon economy [1], and syngas is the raw material for synthetic hydrocarbon fuels produced by the Fischer-Tropsch synthesis technology [2]. However, these fuels are traditionally produced from fossil fuels and natural gas reforming [3]. Due to the limited fossil fuel sources, present high oil prices and environmental considerations, there is a growing interest in high-temperature electrolysis cell technology for producing hydrogen and syngas, such as the molten carbonate electrolysis cell (MCEC) and the solid oxide electrolysis cell (SOEC). An advantage of high-temperature electrolysis is the reduction of applied voltage due to favorable thermodynamic and kinetic conditions when compared to low-temperature electrolysis [4]. A further advantage is that a variety of renewable energy sources such as solar energy, wind power or nuclear power,

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and waste heat from high-temperature industrial processes can be used to supply the power and heat required for high-temperature electrolysis.

The MCEC typically operates at about 650 °C, which means that the MCEC will consume less heat to reach the operating temperature than the SOEC. When a MCEC is operated in reverse, it operates as a molten carbonate fuel cell (MCFC) to generate electricity. Today MCFC technology has reached a level of maturity enough for commercialization in various countries such as the USA, Japan, South Korea, Italy and Germany [5]. In terms of scale of installed power generation units, the MCFC is the leader among all fuel cell technologies, for example in total more than 100 MW has been installed in about 60 different places worldwide [6,7].Therefore, the so-called reversible molten carbonate fuel cell (RMCFC) can be regarded as a dual energy converter that operates as an electrolysis cell to produce fuel gases and as a fuel cell to produce electricity; this could improve the efficiency of the system and increase the economic benefits.

Studies on high-temperature water electrolysis for hydrogen production have been carried out since the early 1980s but have been limited to SOEC technology [8]. During these 30 years, water electrolysis by SOEC technology has achieved much progress, for example when regarding electrode and electrolyte materials, electrochemical performance and durability and modeling of SOEC and systems [9]. Lately researchers have focused not only on SOEC for hydrogen production, but also on co-electrolysis of H_2O and CO_2 to generate syngas ($H_2 + CO$). Mogensen et al. [10–12] reported that it is possible to electrolyze CO_2 and H_2O during co-electrolysis to produce a mixture of H_2 and CO at operating temperatures ranging from 750 to 850 °C. They also presented that the area specific resistances (ASR) of the solid oxide cells were higher in electrolysis cell than in fuel cell mode in this temperature range. When it comes to MCEC research, only a few studies are done until now. Kaplan et al. [13,14] reported the conversion of CO_2 to CO by using a cell with a molten electrolyte mixture of lithium carbonate and lithium oxide at 850–900 °C. The electrodes were graphite (anode) and titanium (cathode) and not conventional MCFC electrodes (Ni-based materials), and the working temperature was much higher than that of the MCFC system. So far the performance and durability of RMCFC is not clear and the effect on electrode materials of operating the cell both as an electrolyzer and a fuel cell is also unknown.

In this work, state-of-the-art MCFC components were used to operate the reversible molten carbonate fuel cell. The electrochemical performance of the cell was compared in MCFC and MCEC modes. The polarization loss and the impedance of the Ni hydrogen electrode and the NiO oxygen electrode were also investigated in both modes under varying operating conditions, including operating temperature and gas composition.

Experimental

Experimental data were obtained from the laboratory cell unit with a geometrical electrode area of 3 cm^2. The state-of-the-art components used in the study were provided by Ansaldo Fuel Cells, Italy. The hydrogen electrode consists of porous Ni–Cr alloy and the oxygen electrode consists of porous nickel, oxidized and lithiated in situ. The electrodes are separated by a porous $LiAlO_2$ matrix, which also supports the electrolyte, a eutectic mixture of 62/38 mol% Li_2CO_3/K_2CO_3. Two reference electrodes (Au wires with a 33/67% O_2/CO_2 gas mixture) are placed in separate chambers filled with the same electrolyte as in the cell. They are connected to the cell through a capillary with a gold plug. A schematic drawing of the laboratory cell is shown in Fig. 1 [15].

Standard gas mixtures consisting of 64/16/20% $H_2/CO_2/H_2O$ and 15/30/55% $O_2/CO_2/N_2$ were used for the Ni hydrogen electrode and the NiO oxygen electrode, respectively. In the experiments the H_2O content in the fuel gas was controlled by the temperature of the water in the humidifier. The flow rate of the dry H_2/CO_2 mixture was held at approximately 150 ml min^{-1}. The gas flow rate for the oxygen electrode was also about 150 ml min^{-1}, while the reference gases had a flow rate of 20 ml min^{-1}. All the gases used in the experiments were certified gas mixtures from AGA Gas AB, Sweden.

The electrochemical performances of the full cell and individual electrodes were measured by steady-state polarization curves and electrochemical impedance spectroscopy (EIS). The polarization curves were performed in potentiostatic steps by using a Solartron Interface SI1287 supported by CorrWare software. To separate the ohmic losses from other types of polarization, the current interrupt technique was used [16]. It was automatically controlled by Corrware and the shortest duration of a current interrupt was 27 μs. In all the polarization curves plotted below, the positive current density refers to fuel cell mode and the negative current density refers to electrolysis cell mode.

For the electrochemical impedance measurements Solartron frequency response analyzer 1255 and Solartron Interface SI1287 were used. The frequency spectra were recorded at three different operating conditions, including open circuit voltage (OCV), fuel cell and electrolysis cell modes. These measurements were run potentiostatically in the frequency range 10 mHz–10 kHz with an amplitude of 10 mV.

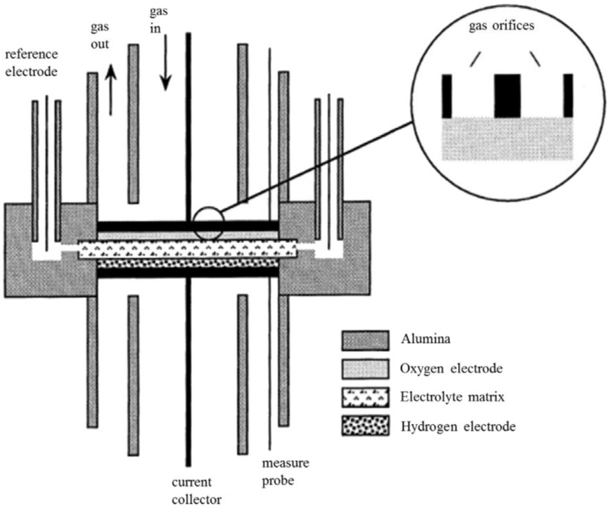

Fig. 1 – Schematic drawing of the laboratory cell unit [15].