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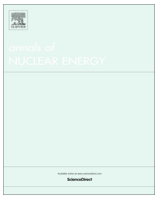

Electrolysis of carbon dioxide for carbon monoxide production in a tubular solid oxide electrolysis cell

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ABSTRACT

An active carbon recycling energy system (ACRES) based on carbon recycling has been proposed as a new energy transformation system. This energy transformation system reduces the carbon dioxide (CO_2) emissions in the atmosphere during the iron-making process. An experimental study for electrochemical CO production by CO_2 electrolysis based on the ACRES concept was carried out using a tubular solid oxide electrolysis cell. Experimental results show that the CO and oxygen (O_2) production rates at 800, 850, and 900 °C were almost proportional to the current passing through the cell. Both ionic conductivity and the chemical kinetics of CO_2 decomposition increased with increasing temperature. The highest current density and CO production rate at 900 °C were 2.97 mA/cm^2 and 0.78 μmol/(min cm^2), respectively. On the basis of the electrolytic characteristics of the cell, the scale of the combined ACRES CO_2 electrolysis/iron-making system was estimated.

1. Introduction

The excessive use of carbon in fossil fuels as the primary energy source for economic growth has resulted in a significant increase in the concentration of carbon dioxide (CO_2) in the atmosphere. Excess CO_2 in the atmosphere has caused global warming and climate change. To solve this problem, a new carbon recycling energy system, namely, active carbon recycling energy system (ACRES) has been proposed and developed to reduce the CO_2 emissions in the atmosphere during industrial processes. In this system, carbon is reused cyclically consuming non-CO_2-emitting primary energy sources, thus reducing CO_2 emissions in the atmosphere (Dipu et al., 2013; Kato, 2010, 2012, 2011).

The structure of the ACRES has been described by Kato (2010). The use of non-carbon primary energy sources is an essential requirement for the practical application of the ACRES. A high-temperature gas reactor (HTGR) is the most suitable energy source for the ACRES because of its high-temperature output of up to 950 °C with no carbon emissions and the availability of a sufficient amount of nuclear fuel to meet national demand (Kunitomi et al., 2004). A proposed application of the ACRES to an iron-making process has been described elsewhere (Dipu et al., 2013). The system was assumed to be an ideal iron-making process powered by electricity and thermal energy generated from an HTGR. The regenerated carbon monoxide (CO) is recycled and used to reduce iron oxide to pure iron. The resulting CO_2 is reduced to CO by using energy from the HTGR. One promising aspect of electrochemical CO production using the ACRES is that the CO_2 electrolysis using a solid oxide electrolysis cell (SOEC) occurs at high temperatures. Japan's original gas turbine high-temperature reactor 300 (GTHTR300) is the most suitable energy source for the practical application of the ACRES to an iron-making process because of its high-temperature output (Yan et al., 2011).

Recently, SOECs have attracted great interest because of their high efficiency in producing hydrogen (H_2) and other synthetic fuels via high-temperature steam electrolysis or steam-CO_2 co-electrolysis (Brisse et al., 2008; Ebbesen and Mogensen, 2009; Jensen et al., 2010; Wang et al., 2013; Yang et al., 2010; Yue and Irvine, 2012; Zhan and Zhao, 2010). In addition, several studies have been reported on the use of CO_2 electrolysis to produce propellants and life-support consumables for space missions using SOECs with Pt-based electrodes (Sridhar and Vaniman, 1997; Tao et al., 2004a,b). However, the use of noble metals such as Pt as the electrode material has been of concern because of their high cost. Recently, Ni-based cermet has been used as an alternative cathode material and perovskite as the anode material, resulting in long-term stability (Jensen et al., 2010).

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In this study, Ni was mixed with yttria-stabilized zirconia (YSZ) to form a Ni-YSZ cermet. The cermet and $La_{0.8}Sr_{0.2}MnO_3$ (LSM)-YSZ were attached to a tubular YSZ electrolyte as the cathode and the anode respectively. We then investigated the performance of the CO_2 electrolysis using a tubular SOEC. Based on the results of the SOEC experiments, we evaluated the performance of the ACRES for the iron-making process.

2. Experimental

An SOEC test apparatus was constructed to evaluate the performance of high-temperature electrolysis of CO_2 (Fig. 1). This test apparatus allowed the use of the gases, CO_2, CO, H_2, or Ar on the cathode side, while O_2 or nitrogen (N_2) could be used on the anode side.

In this study, the Ni-YSZ cermet and LSM-YSZ were attached to a tubular YSZ electrolyte as the cathode and the anode. A nickel oxide (NiO)-YSZ paste was prepared by ball milling 12.0 g of NiO (Wako Pure Chemicals Co., Ltd., Japan) and 8.0 g of YSZ powder (TZ-8Y, Tosoh Corp., Japan) using a planetary ball mill (Pulverisette 7, Fritsch, Germany). The resulting powders were then mixed with a binder, distilled water, and a dispersant. The components were thoroughly mixed, and the resulting paste was coated onto the outer surface of the YSZ electrolyte as the cathode by dip-coating. The LSM-YSZ paste was prepared by ball milling 10.0 g of LSM and 10.0 g of YSZ powder. The resulting powders were then mixed using a binder, distilled water, and a dispersant. The components were thoroughly mixed, and the resulting paste was coated onto the inner surface of the YSZ electrolyte as the anode by dip-coating. The effective surface area of the cathode electrode was 25.1 cm^2. The cell was sintered at 1100 °C under inert conditions using Ar at a flow rate of 25 mL/min for 4 h. Fig. 2 shows a representative cross-sectional scanning electron microscopy (SEM) micrograph of the Ni-YSZ|YSZ|LSM-YSZ cell as the cathode|electrolyte|anode.

A Pt mesh (Nilaco Corp., Japan) was used as the current collector, and a Pt wire was used as the current conductor. Electric current was supplied to the cell using a galvanostat (HAL 3001; Hokuto Denko, Japan). The CO and O_2 production rates were analyzed using a gas chromatograph (GC-8A, Shimadzu Corp., Japan) equipped with a thermal conductivity detector (TCD). He was used as the GC carrier gas and was set at a flow rate of 40 mL/min. The structure of the cathode|electrolyte samples were analyzed by X-ray diffraction (XRD) (D8 DISCOVER, Bruker AXS, USA). A scanning electron microscope (S-4800, Hitachi, Japan) was used to observe the microstructure of the cell after the electrolysis measurement.

Prior to the electrolysis experiments, the NiO-YSZ cathode was pretreated by H_2 reduction at 900 °C for ~2 h to prevent Ni oxidation and maintain the final form of the Ni-YSZ cathode. During the electrolysis, pure CO_2 and Ar (both at a flow rate of 25 mL/min) were supplied to the cathode, while N_2 at a flow rate of 25 mL/min was supplied to the anode.

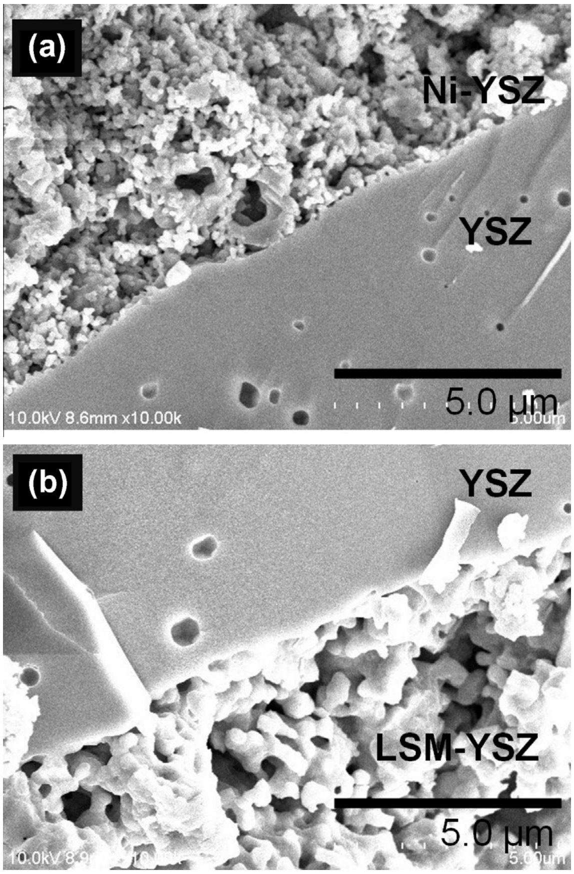

Fig. 2. SEM micrograph of the cross-sectional section of the Ni-YSZ|YSZ|LSM-YSZ cell. (a) Ni-YSZ|YSZ as the cathode|electrolyte and (b) YSZ|LSM-YSZ as the electrolyte|anode.

3. Results and discussion

3.1. Cell performance evaluation

The relationship between the applied cell voltage and current density at 800, 850, and 900 °C is shown in Fig. 3. The current densities at the same levels of applied cell voltage were strongly affected by the operating temperature. Higher operating temperature reduced the resistance of the cell, which in turn resulted in higher current densities. Furthermore, the YSZ electrolyte

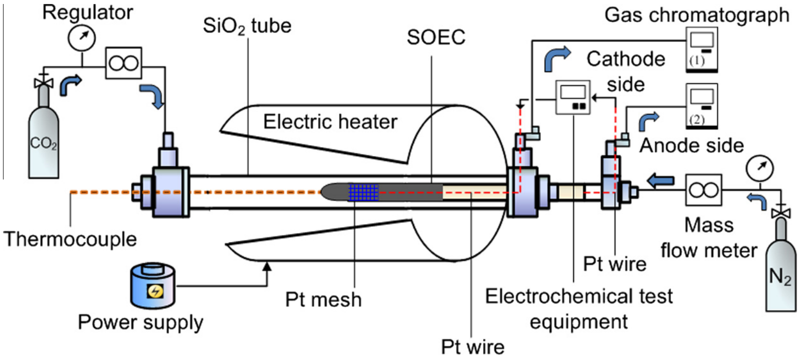

Fig. 1. Schematic drawing of experimental SOEC apparatus for CO_2 electrolysis.

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