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High-efficiency intermediate temperature solid oxide electrolyzer cells for the conversion of carbon dioxide to fuels

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HIGHLIGHTS

- Cell area specific resistance was current-dependent during high temperature CO_2 reduction.
- Ni—YSZ electrode showed higher resistance in SOEC mode than SOFC mode.
- The temperature drop at thermal minimum voltage created the condition for coking on Ni—YSZ.
- Higher temperature and higher CO_2 partial pressure could help minimize coking on Ni—YSZ.

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ABSTRACT

Electrochemical reduction of carbon dioxide in the intermediate temperature region was investigated by utilizing a reversible solid oxide electrolysis cell (SOEC). The current—potential (i—V) curve exhibited a nonlinear characteristic at low current density. Differentiation of i—V curves revealed that the cell area specific resistance (ASR) was current-dependent and had its maximum in electrolysis mode and minimum in fuel cell mode. Impedance measurements were performed under different current densities and gas compositions, and the results were analyzed by calculating the distribution of relaxation times. The ASR variation resulted from the difference in electrochemical reactions occurring on the Ni—YSZ electrode, i.e., Ni—YSZ is a better electrode for CO oxidation than for CO_2 reduction. Coke formation on Ni—YSZ played a crucial role in affecting its electrolysis performance in the intermediate temperature region. The ASR apex was associated with a decrease in cell temperature during electrolysis due to the endothermic nature of CO_2 reduction reaction. It was postulated that such a decrease in temperature and rise in CO concentration led to coke formation. As a consequence, higher temperature (>700 °C), higher CO_2 concentration (>50%), and the presence of hydrogen or steam are recommended for efficient CO_2 reduction in solid oxide electrochemical cells.

1. Introduction

The conversion of renewable electrical energy to fuels using common substrates (e.g. CO_2 and water) provides an opportunity to remove the temporal variation in the energy supply from solar and wind energy sources. As a consequence, electrolysis has gained substantial attention to convert water and/or carbon dioxide to fuels. In comparison with room temperature electrolysis techniques, the essence of solid oxide electrolyzer cells (SOECs) lies at its elevated operation temperatures (>650 °C), which result in (1) a higher electrolysis efficiency because of a lower Nernst potential — a thermodynamic potential required to split CO_2 — at higher operation temperatures, and (2) the use of inexpensive oxide-based electrodes as the catalysts for a cost-effective electrolysis, instead of the precious metals (e.g. Pt) used in solution-based electrolysis cells [1]. An additional advantage of conversion of CO_2 to CO in SOECs is their capability of generating oxygen where water is not available, for instance during the exploration of the Planet Mars [2,3]. Furthermore, the high temperature CO_2 electrolysis can be

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integrated with carbon fixation and syngas production, whereas syngas can undergo Fischer–Tropsch process to yield hydrocarbon fuels, thus facilitating a carbon-neutral cycle [4–8].

The primary challenge in developing SOECs is their degradation at elevated temperatures when LSM/YSZ was used as the air electrode, largely due to the delamination of air electrode [9–11] and the formation of pores at YSZ grain boundary [12]. $La_{1−x}Sr_xCo_{1−y}Fe_yO_{3−\delta}$ (LSCF), on the other hand, was found to be capable of suppressing the delamination problem [13]. Tietz et al. [14] recently reported a degradation rate of 3.8% per 1000 h over 9000 h at 778 °C for steam electrolysis with LSCF as the oxygen electrode. Since most works on high temperature electrolysis were carried out at approximately 800 °C or higher, the aim of the present research was to study the electrochemical reduction of CO_2 over the intermediate temperature regime (650–750 °C). LSCF was used as the air electrode, which can provide sufficient activity and less degradation in this temperature region. The results were analyzed by the differentiation of $i−V$ curve [15] for DC measurements and the distribution of relaxation times (DRT) [16–20] for impedance measurements.

2. Experimental

A bilayer comprised of Ni–YSZ and YSZ electrolyte was prepared by tape casting. The thickness and diameter of the bilayers were approximately 1 mm and 25 mm, respectively, and the dense electrolyte membrane was ~8 μm thick. A $Gd_{0.20}Ce_{0.80}O_{1.90}$ (GDC, Fuel cell materials, OH) layer was spin-coated on YSZ and co-sintered with anode current collector (Ni mesh embedded in NiO paste) at 1150 °C for 2 h. Micrometer carbon powders were added as a pore former for $(La_{0.60}Sr_{0.40})_{0.995}(Co_{0.20}Fe_{0.80})O_{3−x}$ (LSCF, Fuel cell materials, OH) and $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3−x}$ (LSM20, NexTech Materials, OH) inks. A layer of LSCF with 10 wt.% carbon was screen-printed on the GDC layer; then another layer of LSCF containing 20 wt.% carbon was added on the first layer. After sintering the LSCF at 900 °C for 2 h, LSM20 containing 50 wt.% carbon was screen-printed as the current collecting layer, and a piece of gold mesh was pressed into the wet LSM20 ink before heating up. The active cathode area was 2 cm^2 for calculating current density and area specific resistance (ASR). Fig. 1 shows a schematic illustration and a cross-sectional image of the cell structure.

Each cell was electrically connected to the test fixture with Pt wires, and then sealed on a tubular alumina stand with a glass paste. A perforated alumina cap was laid on top of the gold mesh and spring-loaded to provide sufficient mechanical contact to the LSCF electrode. The fuel to the Ni–YSZ electrode was 25% CO–75% CO_2 or 50% CO–50% CO_2 at a flow rate of 200 sccm, and the LSCF electrode was supplied with 400 sccm air. Solartron 1470E Multistat and 1255B Frequency Response Analyzer (Solartron Analytical, TN) were used for $i−V$ sweep and impedance measurement. The AC amplitude was either 5 mV at OCV or 5% of the applied direct current (from 0 up to ±0.4 A $cm^{−2}$) for impedance measurements ranging from 0.01 to 100 kHz. Cells were tested at 650, 700 and 750 °C.

3. Results and discussion

The $i−V$ curves and impedance spectra are illustrated in Figs. 2 and 3, respectively. Open circuit voltages were very close to the theoretical Nernst potentials, indicating the presence of a hermetic seal. All $i−V$ curves evolve smoothly from SOFC to SOEC mode in a nonlinear manner within the sweep range. Hence, the cell ASR, defined as dE_i/di, varies with current density. Impedance spectra in Fig. 3 show that the polarization resistance (R_p) decreased monotonously in proportion to the current density when the cell

was operated in fuel cell mode (e.g. under positive current). With the presence of negative current, *i.e.* electrolysis mode, R_p pattern was more complex. At 650 °C, R_p is found to decrease with increasing current density; while at 700 and 750 °C, R_p first increases at lower current density and then decreases at higher current density. It is also noticed that the ohmic resistance (R_Ω) increases in SOEC mode and decreases in SOFC mode with increasing current density. The deviated R_Ω could recover when the DC bias was removed, suggesting that it is a temporal effect under polarization. Such minor change of R_Ω with DC bias was observed in other studies [21,22], and its reason will be discussed further. Since the R_Ω variation was minor compared to R_p, the change of R_p dominated the change of ASR of the cell. The differentiation of the $i−V$ curve yields the total ASR of the cell. In our previous study [15] the ASR values derived from the differentiation of $i−V$ curve were compared to results from impedance measurements, and showed good agreement, thus analysis of impedance spectra can provide more details on the electrochemical processes occurring in SOECs.

Fig. 4 shows the total ASR of the cell measured by $i−V$ sweep. The $ASR_{t,dc}$ exhibited a maximum in SOEC mode and a minimum in SOFC mode. Moreover, the fuel rich in CO resulted in larger resistance. Such a phenomenon became more prominent at lower temperatures due to its thermally activated conversion process, which will be discussed further. Ebbesen and Mogensen [23] also observed the similar phenomenon on a LSM–YSZ based cell, with an ASR of 0.30 Ω cm^2 and 0.36 Ω cm^2 for SOFC and SOEC, respectively (850 °C, CO_2/CO = 50/50, ±0.25 A $cm^{−2}$). The change in gas composition influenced the ASR of SOEC more than that of SOFC. For instance, the difference in ASR between the fuels consisting of 25% CO and 50% CO was negligible at 700 °C when the current density increased from 0 to 0.4 A $cm^{−2}$; however in SOEC mode, the ASR between the two fuels differed as much as 0.2 Ω cm^2. Such an ASR change in SOEC mode was even more pronounced at 650 °C. In all experiments, switching fuel gas from 25% CO–75% CO_2 to 50% CO–50% CO_2 resulted in a higher ASR, suggesting that certain electrochemical processes on Ni–YSZ are responsible for the increase of ASR in SOEC mode. The analysis of DC measurement alone, however, cannot provide sufficient information on the origin of this phenomenon. The deconvolution of impedance spectra by analyzing the distribution of relaxation times (DRT) [17] becomes necessary, because this approach is capable of resolving overlapping arcs up to half a decade.

Fig. 5 illustrates DRT spectra derived from the imaginary part of the impedance data measured at 700 °C. The area under the curve represents the total polarization resistance, and each peak represents a process that contributes to the R_p. In the current case (700 °C and CO 50%–CO_2 50%), five peaks at 4073 Hz, 581 Hz, 38.9 Hz, 2.4 Hz and 0.1 Hz were observed and designated as P1 to P5, respectively. Such relaxation times distribution pattern is typical for a solid oxide cell with Ni–YSZ and LSCF electrodes. Leonide and Ivers-Tiffee [24] attributed the peaks at 2.3 kHz, 581 Hz, and 4.1 Hz to ionic transport, charge transfer, and gas diffusion in the anode, respectively. The peak at 16.2 Hz represents oxygen surface exchange and bulk diffusion in the cathode. Cathode gas diffusion is represented by the peak at 0.1 Hz. The aforementioned peak attribution serves as a framework for our analysis. P1, P2 and P3 shown in Fig. 5 dominate the spectrum measured under OCV. When the cell was operated with a positive current (SOFC mode), P2 and P3 were reduced by about 60%. A negative current (SOEC mode), however, resulted in a significant decrease in P3 while an increase in P2. The response of P2 to various operation modes appears interesting as it corresponds to electrochemical catalytic characteristics of the cell, *i.e.* whether it favors CO oxidation or CO_2 reduction. In order to identify the origin of this peak,