



Efficient electrolysis of CO₂ in symmetrical solid oxide electrolysis cell with highly active La_{0.3}Sr_{0.7}Fe_{0.7}Ti_{0.3}O₃ electrode material



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ABSTRACT

Novel perovskite-type La_{0.3}Sr_{0.7}Fe_{0.7}Ti_{0.3}O₃ (LSFT) oxide is investigated as both anode and cathode materials in a symmetrical solid oxide electrolysis cell (SOEC) for direct electrolysis of pure CO₂ at 800 °C. The current density is 521 mA cm⁻² at an applied voltage of 2.0 V. The lowest polarization resistance *R*_p of this symmetrical SOEC is obtained at 2.0 V with a value of as low as 0.08 Ω cm², which is much lower than that of other perovskite and Ni-cermet cathode. LSFT cathode also shows excellent durability in pure CO₂ electrolysis, especially at high voltage of 2.0 V. Our results indicate that the LSFT is a promising alternative electrode material for CO₂ electrolysis.

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1. Introduction

In recent years, solid oxide electrolysis cells (SOECs) have attracted worldwide attention as a green and renewable energy conversion technology [1]. SOEC can convert electricity and thermal energy into chemical energy with high efficiency for H₂ generation through steam electrolysis [2]. Besides, SOECs are also capable of direct electrolyzing greenhouse gas CO₂ to CO in cathode chamber and oxygen at anode side.

The Ni-YSZ cermet, a conventional anode material of SOFC, is widely used as cathode in SOEC [3,4]. However, when it comes to CO₂ electrolysis, it has been found that the Ni can catalyze the coke formation reaction in high concentrations of CO or hydrocarbon atmospheres [5]. Furthermore, Ni-YSZ cermet requires a high H₂ concentration to prevent it from being oxidized to NiO. On the other hand, Ni can be oxidized in the pure and dry CO₂ electrolysis mode, leading to degradation of electrode performance [6]. In order to overcome the disadvantages of Ni-YSZ cermet, ceramic oxides have been considered as potential cathodes due to their high redox-stability and reasonable activity. To date, several perovskite oxides have been investigated as potential cathode materials for SOECs [7–12]. Direct electrolysis of CO₂ using redox-stable La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM) and La_{0.2}Sr_{0.8}TiO_{3-δ} (LSTO) composite cathodes are demonstrated without protective gas of H₂ or CO [11,12]. However, these perovskite materials show large

polarization resistances compared to the Ni-YSZ cermet cathode [3,4,8]. Moreover, a rapid performance degradation on LSCM cathode occurs when electrolyzing CO₂ at an applied voltage of 2.0 V [11]. Therefore, there is an urgent need to develop alternative cathode perovskite materials (such as Fe-based perovskite oxides) for more efficient and stable electrolysis of CO₂ [13–14]. Ni-Fe-La_{0.6}Sr_{0.4}Fe_{0.8}Mn_{0.2}O_{3-δ} has been studied for intermediate-temperature CO₂ electrolysis with reducing gas CO, which shows a high current density of 2320 mA cm⁻² at 1.6 V and 800 °C using a ca. 300 μm La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ electrolyte [14]. Raman spectra results confirm almost no coke formation on the cathode surface after electrolysis. In addition, the electrochemical performance of La_{0.3}Sr_{0.7}Fe_{0.7}Cr_{0.3}O_{3-δ} (LSFCr) has been studied as a cathode for electrolysis of CO₂ in reversible solid oxide cells. The LSFCr electrode is more active for CO₂ reduction than for CO oxidation [15–17]. Yao et al. have reported that the perovskite chromate doped with titanium (La_{0.75}Sr_{0.25}Cr_{0.5-x}Fe_{0.5}Ti_xO_{3-δ}, x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) can obviously improve the cathode activity for the CO₂ reduction in pure CO₂ electrolysis [18].

In our previous study [19], perovskite-type oxide La_{0.3}Sr_{0.7}Fe_{0.7}Ti_{0.3}O₃ (LSFT) has been investigated as both cathode and anode in symmetrical solid oxide fuel cell. In SOEC mode, it was reported that the oxygen vacancy defect in perovskite cathode plays a key role in the chemical adsorption of CO₂ [20–21]. In the case of LSFT cathode, the oxygen vacancy concentration increases with the increasing of temperature via partial reduction of Fe⁴⁺ to Fe³⁺ and Ti⁴⁺ to Ti³⁺ in reducing atmosphere at high temperature. Furthermore, the LSFT electrode exhibits a good phase stability under strong reducing atmosphere (humidified

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20% H₂/Ar at 800 °C, $P_{O_2} \sim 1.58 \times 10^{-20}$ atm, calculated by Nernst equation [19]. Actually, during a durability test of symmetrical SOEC for pure CO₂ electrolysis with an applied voltage of 2.0 V at 800 °C, CO/CO₂ ratio is no >10/90 ratio (corresponding to $P_{O_2} \sim 10^{-16.6}$). Consequently, the decomposition or phase separation of LSFT cathode is negligible during co-electrolysis and electrolysis CO₂.

In this work, LSFT material was employed as electrodes in a symmetrical SOEC for the direct electrolysis of CO₂ gas without protective gas (such as CO or H₂) during operation. The electrochemical performance of full SOEC with LSFT electrode material as well as the related behaviors during CO₂ electrolysis was presented. The related results for mechanism and kinetic of the LSFT cathode will be submitted by a separated paper.

2. Experimental

The La_{0.3}Sr_{0.7}Fe_{0.7}Ti_{0.3}O₃ (LSFT) powder was synthesized by a conventional solid-state reaction method. The detail of preparation process has been described elsewhere [19]. The effective areas of anode and cathode were 0.28 cm².

The electrochemical impedance spectra (EIS) and the relationship curves between current density and voltage (at the scan rate of 10 mV s⁻¹) were performed at 800 °C with an electrochemical workstation (Biologic VSP, France). EIS were tested with the static air on the anode side and pure CO₂ (purity > 99%) on the cathode side. The measurement was carried out at an AC amplitude of 20 mV and a frequency range of 400 kHz to 100 mHz. Pure CO₂ gas with a flow rate of 14.7 mL min⁻¹ was controlled by a mass flow controller during the test. The composition of outlet gas from the cathode side was analyzed by a mass spectrometer (Ametek LC-D100M, America).

3. Results and discussion

Fig. 1 shows the voltage recorded as a function of the current density of the symmetrical cell for the electrolysis of pure CO₂ with the applied voltages of 0–2 V at 800 °C. A constant current density of ca. 10 mA cm⁻² is observed in the voltage range of 0.4–0.8 V, which is related to a pumping process of oxygen gas that comes from the sealing leakage or CO₂ feeding. In order to further understand the change of electrochemical processes with voltage, the dV/dI–V curve is presented in the inset of Fig. 1. A distinct change in dV/dI–V curve is observed at approximately 0.8 V, which can be considered as the threshold voltage for electrolysis of pure CO₂. At the high voltage region (>0.8 V), the total cell resistance (dV/dI) is consistent with the data obtained from impedance spectra shown in Fig. 2(b). The current–voltage profile plots of the symmetrical SOEC at different flow rates of pure CO₂ are plotted in Fig. 1(b). The open circuit voltage (OCV) at the flow rates of 14.7, 29.4 and 58.9 mL min⁻¹ are 0.119, 0.134 and 0.157 V, respectively. It indicates that the oxygen partial pressure caused by oxygen leaking-in decreases with increasing CO₂ flow rate. The peak current density at ca. 0.25 V is obtained, which is probably ascribed to reduction of Fe⁴⁺ to Fe³⁺ [16].

To further investigate the electrochemical processes associated with different applied voltages, the AC impedance spectra of symmetrical SOEC for pure CO₂ electrolysis are presented in Fig. 2. At the OCV condition, the ohmic resistance R_s is approximately 1.91 Ω cm² which is consistent with the theoretical value calculated by the ionic conductivity of the electrolyte disc and SDC buffer layers. As shown in Fig. 2(a), the R_s increases with applied voltage from OCV to 0.8 V, which is due to the endothermic reaction of CO₂ electrolysis at low current density [3]. On the other hand, the significant decrease of R_s at the voltage over 1 V in Fig. 2(b) is attributed to Joule heat effect of the high current density. In addition, the polarization resistances (R_p) are obviously reduced with the voltage increase, demonstrating faster electrode kinetics at higher applied voltage [9,11]. Additionally, two arcs have been observed in the impedance spectra as Fig. 2(b) shown. The high frequency and low frequency arcs can be attributed to charge transfer process and

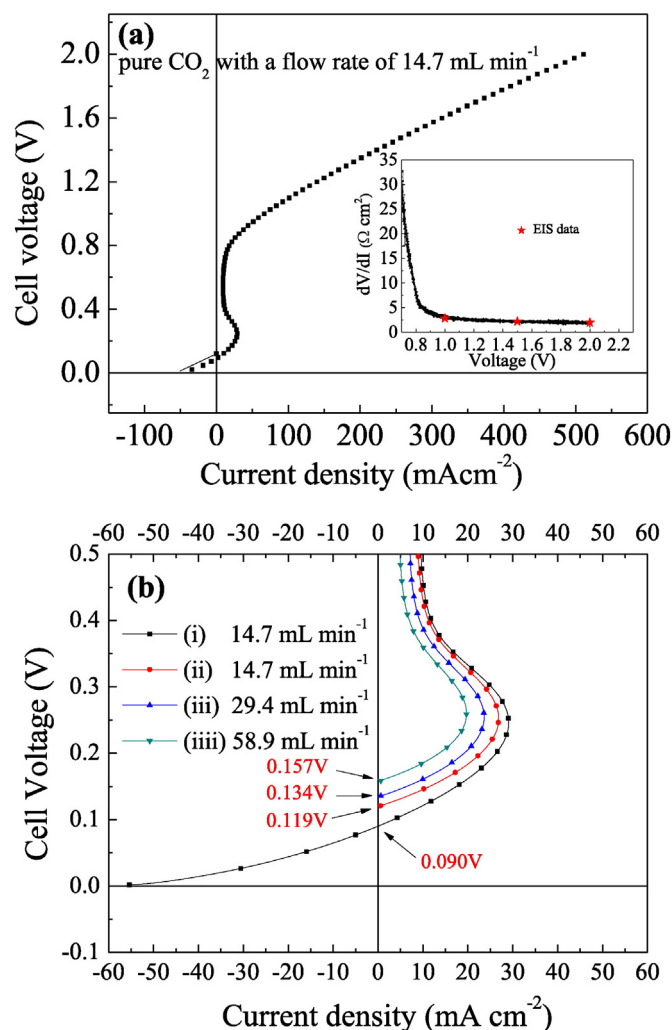


Fig. 1. The current density dependence of the voltage profile of the symmetric solid oxide electrolyzer cell for pure CO₂ direct electrolysis at 800 °C: (a) Full range current density–voltage profile with the applied voltages from 0 V to 2.0 V at the flow rate of 14.7 mL min⁻¹. The inset is the dV/dI–V curve of symmetrical SOEC. (b) The details of current density–voltage profiles at different flow rates of pure CO₂: (i) from 0 V to 2 V; (ii)–(iii) from open circuit voltage to 2.0 V.

dissociative adsorption/surface diffusion processes, respectively [4,20]. More importantly, the lowest polarization resistance R_p of symmetrical SOEC is obtained at 2.0 V and 800 °C with a value of approximately 0.08 Ω cm². For comparison, it is significantly lower than other perovskite materials such as La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (ca. 2.0 Ω cm² at 2.0 V and 800 °C) [11], La_{0.2}Sr_{0.8}Ti_{0.9}Mn_{0.1}O_{3-δ} (ca. 1.5 Ω cm² at 2.0 V and 800 °C) [20] and La_{0.65}Sr_{0.3}Ce_{0.05}Cr_{0.5}Fe_{0.5}O_{3-δ} (ca. 0.21 Ω cm² at 2.0 V and 850 °C) [21]. Furthermore, the polarization resistance of the whole cell (ca. 0.08 Ω cm²) is even much lower than the R_p of Ni-YSZ cathode (ca. 0.3 Ω cm²) at 900 °C and 1.5 V voltage [8], suggesting excellent electrocatalytic activity of LSFT cathode toward CO₂ reduction.

A short-term durability test of symmetrical SOEC for pure CO₂ electrolysis with an applied voltage of 1.5 V at 800 °C was conducted and the results are shown in Fig. 3(a). The current density of SOEC exhibits approximately 5% decrease during 24 h operation. The polarization resistance of the cell slightly increases from 0.21 to 0.23 Ω cm² after 24 h operation, likely due to the delamination behavior of LSFT oxygen electrode under anodic polarization [22]. The ohmic resistance increases from 2.05 to 2.14 Ω cm², which is likely attributed to the sintering of Ag current collector or increase of contact resistance between SDC and LSFT. The results show the performance of the symmetrical SOEC based on LSFT electrodes possesses good stability during 24 h test,

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