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Mechanism for reversible CO/CO_2 electrochemical conversion on a patterned nickel electrode

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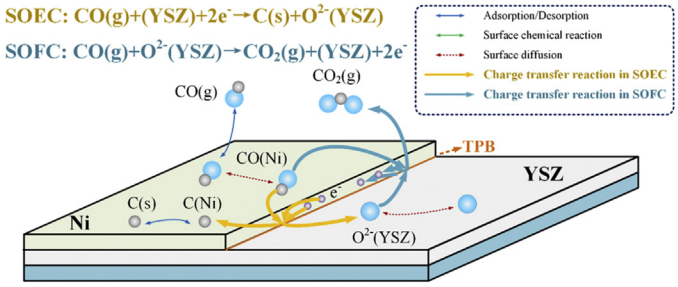
HIGHLIGHTS

- SOEC/SOFC modes Patterned Ni electrodes in CO-CO_2.
- Analytical model for rate determining step identification.
- Non-negligible carbon monoxide electrochemical reduction.

GRAPHICAL ABSTRACT



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ABSTRACT

The patterned Ni negative electrode on single-crystal YSZ in CO-CO2 atmosphere is investigated in both the solid oxide fuel cell (SOFC) and solid oxide electrolysis cell (SOEC) modes. The effects of the temperature T, partial pressure of CO and CO_2 (pCO and pCO_2) on the electrochemical performance are measured to obtain the intrinsic kinetic parameters by natural logarithm linear fitting. The strong dependency of surface diffusion resistance on pCO implies that surface diffusion could be related to CO(Ni). The electrochemical performance had an obviously positive correlation with T and pCO. The limitation of CO_2 adsorption leads to a weak dependency of polarization on pCO_2. The electrochemical performance of SOEC mode in the atmosphere without CO is 1.21 times higher than that in the atmosphere without CO_2, which implies that CO electrochemical reduction could be more significant than CO_2 electrochemical reduction in the patterned Ni electrode. An analytical calculation is performed for the speculation of rate-limiting steps. In the SOFC mode, CO oxidation into CO_2 is speculated to be rate-determining, besides, adsorbed carbon oxidation into CO could be also non-ignorable. In the SOEC mode, CO reduction into carbon could be more probably the major electrochemical reaction on the pure Ni surface.

1. Introduction

Reversible solid oxide cells (RSOC) can effectively utilize intermittent renewable power into gaseous fuels like hydrogen, syngas even methane (Power-to-gas, PtG) in the Solid oxide electrolysis cell (SOEC) modes, and convert gaseous fuel into stable electrical power in the Solid oxide fuel cell (SOFC). The oxygen-conducting

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electrolyte and high temperature operation (600–1000 °C) enables RSOC to directly convert CO/CO_2 to synchronously achieve seasonal energy storage, CO_2 emission reduction, and fast reaction kinetics. Not a few studies on the CO electrochemical conversion by SOFC can be found in the existing literature [1–7], while those on SOEC [8–10] has just arisen recently for energy storage of renewable energy and nuclear energy [11]. The porous Ni-YSZ (yttria stabilized zirconia) is currently main negative electrode material for the studies on the electrochemical conversion in CO-CO_2 atmosphere [1,2,8–10,12]. Nevertheless, the complexity of structure and interference of bulk diffusion in the porous Ni-YSZ electrode make it hard to understand the complicated elementary kinetic steps of the negative electrode in the SOC. Patterned Ni electrode is regarded as an ideal tool to simplify electrode structure in order to accurately define the length of triple phase boundary (TPB) and Ni area, as well as exclude the interference of microstructure [13,14].

In CO-CO_2 atmosphere, the overall reaction in the negative electrode is generally expressed as:

$$CO(g) + O^{2-}(YSZ) \underset{SOEC}{\overset{SOFC}{\rightleftharpoons}} CO_2(g) + 2e^- \quad (1)$$

Besides, carbon-related electrochemical process was also proposed based on the experimental evidence of the patterned Ni electrode [13]:

$$C(s) + O^{2-}(YSZ) \underset{SOEC}{\overset{SOFC}{\rightleftharpoons}} CO(g) + 2e^- \quad (2)$$

In spite of similar YSZ-based materials and reversible operation between SOEC and SOFC modes, there is still no direct evidence proving that the same reaction mechanism and rate-determining steps are available for both the SOEC mode and SOFC mode. In addition, the previous study in our group has found the difference in electrochemical performance between SOEC and SOFC modes [14]. Therefore, the rate-determining steps between SOEC and SOFC modes still need to be investigated.

Currently, the existing studies on the reaction mechanism in CO-CO_2 atmosphere were focused mainly on the SOFC mode. The oxygen spillover mechanism is the mostly used mechanism to describe the charge transfer reaction in CO-CO_2 atmosphere [2,4–7,14–18]:

$$O^{2-}(YSZ) + (Ni) \leftrightarrow O(Ni) + (YSZ) + 2e^- \quad (3)$$

Matsuzaki et al. [19] tested the porous Ni-YSZ electrodes in the SOFC and speculated that the electrochemical reaction rate could be limited by CO surface diffusion at below 750 °C, and co-limited by surface diffusion and charge transfer reaction at ~1000 °C. Lauvstad et al. [15,16] carried out analytical model simulation to analyze four CO/CO_2 reaction mechanisms in the SOFC. The analytical model indicates that adsorbed CO on the Ni surface and adsorbed O on the YSZ surface could be the key intermediate that is related to the rate-limiting steps. Sukeshini et al. [20] tested the patterned Ni electrodes with the stripe width of 10–100 μm and the stripe thickness of only 100–150 nm in the SOFC. Their experiments in the CO-CO_2 atmosphere showed the Ni electrode with a width of 20 μm had an optimal electrochemical performance, and 100 μm-in-width Ni electrode had higher electrochemical performance than 10 μm-in-width one. They speculated that CO adsorption and surface diffusion of CO could be non-ignorable. But the break-up of the Ni pattern shown by the SEM photo may greatly affect the accuracy of the experiments. Utz et al. [21] tested the patterned Ni electrode in the SOFC and found the positive dependency of polarization resistance on pCO, $p$$CO_2$ and T in CO-CO_2 atmosphere. Yurkiv et al. [17] further considered surface diffusion, surface elementary reactions and three charge transfer reactions to build an SOFC mechanism model based on the validation of Utz's experimental data. The modelling results indicate O^-(YSZ)+(Ni)→ O(Ni)+(YSZ)+e^- could be rate-limiting, and surface diffusion of adsorbed O on the YSZ surface as well as the other two charge transfer reactions occurring on the YSZ surface could be co-limiting at low molar ratio of CO/CO_2.

The previous studies [13,14] in our group have tested the relation between the polarization resistance and operating condition parameters (T, pCO and $p$$CO_2$) in the patterned Ni electrode in CO-CO_2 atmosphere in both the SOEC mode and SOFC mode. The dependency of electrochemical performance on pCO and T was found to be negative, but little effect of $p$$CO_2$ was found in both the SOEC mode and SOFC mode. Besides, carbon was found to be electrochemically generated in the SOEC mode and consumed in the SOFC mode mainly in crystal graphitic carbon structure. However, the stripe width of 100 μm of our previously tested patterned electrode could be too wide so that surface diffusion resistance was over twice as large as activation polarization resistance [14].

In this paper, the patterned Ni electrode with the stripe width of 10 μm was fabricated to alleviate the effect of surface diffusion and increase the TPB density. The dependency of polarization on operating parameters (T, pCO and $p$$CO_2$) will be investigated in both the SOEC mode and SOFC mode in CO-CO_2 atmosphere. The experimental data is compared with that from 100 μm-in-width patterned Ni electrode to estimate the effect of surface diffusion. Then, the analytical calculation based on oxygen spillover mechanism is compared with the experimental data to speculate the possible rate-determining steps in both SOFC and SOEC modes.

2. Experiment

Previously, we have tested the patterned Ni electrode with the stripe width of 100 μm and interval width of 200 μm in CO-CO_2 atmosphere [13,14]. In this study, the patterned Ni electrode with the stripe width of 10 μm and interval width of 90 μm was fabricated on the same single crystal electrolytes of 13 mol% Y_2O_3 stabilized ZrO_2 (YSZ) as before. The YSZ electrolyte has the diameter of 25 mm, the thickness of 0.5 mm, the crystal orientation of (100) as well as the roughness of 0.69 nm on one side and 540 nm on the other side (Shanghai Institute of optics and fine mechanics, Chinese Academy of Sciences). Before fabrication, the YSZ electrolyte was cleaned by radio frequency bias voltage. The patterned Ni electrode was fabricated by the same processes as Ref. [13,14]: including magnetron sputtering, photolithography and inductively coupled plasma (ICP) etching. The parameters for the fabrication of the patterned Ni electrode are summarized in Table 1. The Ni with the purity of 99.999% and the thickness of 800 nm was fabricated on the smoother surface of the single crystal electrolyte by magnetron sputtering (Denton Vaccum Discovery 365, USA), photolithography (SUSS MA6, Germany) and inductively coupled plasma etching (Sentech SI500, Germany), successively. The patterned Ni was a 5 mm × 10 mm region, including 101 10 μm-in-width parallel stripes with the length of 4.98 mm and the interval of 90 μm as well as two 10 μm-in-width current-collecting stripes with the length of 10 mm, as Fig. 1(a and b) shows. A 300 μm-in-width stripe conducts the electrons to the Ni bulk with the area of 3 mm × 6 mm, and the electronic current can be further collected by a platinum mesh. On the rougher surface of the YSZ electrolyte, the positive electrode was prepared by silk-screen printing of the platinum paste (MC-Pt100, Grikin Advanced Materials, China) to cover the 5 mm × 10 mm Ni pattern on the other surface but exclude the collector bulk. The patterned Ni electrode button cell was heated to 700 °C for over 10 h and kept at 700 °C for over 2 h for Pt sintering in Ar atmosphere before the test. The length of TPB l_{TPB} is