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Investigation of carbon formation on Ni/YSZ anode of solid oxide fuel cell from CO disproportionation reaction

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ABSTRACT

A challenge in the operation of solid oxide fuel cells (SOFCs) with hydrocarbon fuels is carbon deposition on the nickel/yttria-stabilized zirconia (Ni/YSZ) anode. This paper investigated the carbon formation on Ni/YSZ anode of solid oxide fuel cell (SOFC) due to CO disproportionation reaction. The steady-state rates of carbon formation under different CO/CO_2 gas compositions were measured at temperature range from 600°C to 800°C. Experimental results showed that the steady-state rate of carbon formation caused by CO disproportionation reaction cannot solely be expressed with temperature or CO/CO_2 gas ratios. A kinetic model divides the CO disproportionation reaction into several stepwise reactions, among which one of the stepwise reactions, namely, the C-O bond cleavage reaction, is considered as the rate-limiting step of the overall reaction. This kinetic model fits very well with the experimental results. Based on the kinetic model and experimental data, a steady-state rate equation of carbon formation in the process of CO disproportionation reaction was derived at the temperature from 600°C to 800°C on Ni/YSZ anode of SOFCs.

1. Introduction

Energy supply security and environmental pollution have been attracted a growing number of concerns worldwide. New advanced technologies for energy conversation and emission reduction are becoming inevitable requests for a continuous economic development. Many countries in the world are focusing on sustainable development of new energy utilization technologies. Fuel cells are energy conversion devices that convert the chemical energy of fuels (i.e., hydrogen, hydrocarbon gases) directly into electricity through electrochemical reactions. It is considered as the fourth generation of power generator that may replace the internal combustion engine for its advantages of high efficiency and low emissions [1]. Of all different types of fuel cells, the solid oxide fuel cell (SOFC) is one of the most promising technologies owing to its high reliability, modularity and fuel adaptability [1,2]. A single cell of SOFC is a composition of anode, cathode and electrolyte, and Ni/YSZ is the most widely used material for SOFC anode. Typically, the operating temperature range of SOFCs is 600°C to 1000°C. At such high temperature, hydrocarbon fuels, including natural gas, biogas, and coal gas, etc., are able to be reformed directly in the SOFCs. However, such high operating temperatures also bring about cracking reaction of carbon-containing compounds. In the case of SOFCs fueled by natural gas, both methane cracking and CO disproportionation will lead to carbon deposition on Ni/YSZ anode of SOFCs, which, will result in performance degradation and even damage of SOFCs.

Due to these adverse impacts of carbon deposition on anode of SOFCs, many researchers at home and abroad have started to focus on it and have reported methodologies for inhibiting the carbon formation in SOFCs [3–17]. One of the popular approaches in the study of anode material of SOFCs was to develop new anti-carbon materials or metal-doped Ni/YSZ for SOFC anode [3–11]. Li et al. [3,4] calculated the adsorption properties of carbon on the surface of nickel and copper. Their results showed that small amount of copper can effectively inhibit the adsorption process of carbon atoms on nickel. Besides, carbon formation can be reduced by doping Ni-MnO into Ni/YSZ anode [4]. Gavrielatos [5,6] and Nikolaos [7] respectively demonstrated that Ag or Au doped Ni/YSZ anode could result in less carbon formation. Liu et al. [8–11] systematically studied carbon formation of Ni/YSZ anode through the tendency and the detection of carbon formation process as well as its mechanism. They proposed a method to reduce the carbon formation by plating new materials on Ni/YSZ surface. Meanwhile, methods of SERS and QGC are reported can be adopted to detect the carbon formation process and measure the quality of carbon [10,11]. On the other hand, some researchers have investigated the dependence of carbon formation on different operating parameters of SOFCs, such as fuel composition, operating temperature and pressure. Shao et al. [12,13] proceeded with fuel species and tried to find new hydrocarbons

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to replace methane with the purpose of decreasing carbon formation. Wang et al. [14,15] performed experiments on single SOFC cells with simulated syngas as fuels to explore the characteristics of carbon formation. They found that the cell performance degradation was closely related with the C-H-O ratio of simulated syngas, and an addition of small amount of H_2O and CO_2 can be helpful to decrease carbon deposition. Other researchers simulated the carbon formation process to study the performance degradation and destruction mechanism on SOFC anode caused by carbon formation. Wang et al. [16,17] established a SOFC model with the consideration of carbon formation, and simulated the effects of the carbon deposition on heat and mass transfer in porous media. Mishakov et al. [18] presented the influence of composition of reaction mixture of hydrocarbons on morphological feature and textural characteristics of carbon nanofibrous materials. Alstrup et al. [19,20] measured the carbon formation rate of different H_2/CH_4 gas mixtures under various temperatures, thus derived a carbon formation formula for Ni/SiO_2. Similarly, Fan et al. [21] established a carbon formation rate formula from methane cracking on Ni/YSZ anode through experiments. In particular, Snoeck et al. [22–24] tried to figure out the mechanism of methane cracking and CO disproportionation reaction. Vedyagin et al. [25] studied the peculiarities of the CO disproportionation reaction over iron-containing catalysts within temperature range of 120–600°C, and showed that preparative technique has significant effect on catalytic performance of iron-containing catalysis.

As the operating temperature range of typical intermediate temperature SOFCs is 600–800°C, carbon deposition on anode of SOFCs mainly originated from methane cracking and CO disproportionation reaction. This paper aims to develop the carbon formation model of CO disproportionation reaction for intermediate temperature of SOFCs. Temperature and CO/CO_2 ratio are two influential factors of carbon formation. The experiments were carried out in CO/CO_2 gas mixtures at the temperature range from 600°C to 800°C, every 50°C will be the temperature point for experiments, and the CO/CO_2 gas mixture were set at suitable ratios at different temperature points. A kinetic model will be adopted to divide CO disproportionation reaction into stepwise reactions, and C—O bond cleavage will be assumed as the rate-limiting reaction. A carbon formation rate was theoretically formulated and validated by experiments.

2. Experimental set

Carbon formation rate from CO disproportionation reaction were measured by the experimental set shown in Fig. 1.

Fig. 1 is a schematic of the experimental system of SOFC carbon formation test bed. It contains gases feeding section, gases mass flow controllers (MFCs), gases mixing chamber and chemical reaction section. Supplied from gas tanks, the flow rates of gases (N_2, H_2, CO_2, CO) are controlled by mass controllers (MFCs). The purity of all the gases used in the experiments is over 99.95%. A stainless steel mixing chamber makes gases well mixed at pre-set ratios before piped into the chemical reaction section. All the gas pipes used in the system, whose outer diameter is 6 mm, are made of stainless steel. A quartz tube and an electric heating furnace are used in the chemical reaction section. Sealed with stainless steel flange on both sides, the quartz tube, with an outer diameter of 10 cm and a length of 120 cm, is installed in the electric heating furnace. The working highest temperature of the furnace can be 1200°C. A thermocouple installed in the furnace is used to measure the reaction temperature, while a temperature indicator and a controller installed together with the thermocouple are applied to monitor and control the reaction temperature. The carbon deposition on Ni/YSZ anode samples is weighed by an electronic balance, of which the measurement accuracy can reach to 0.1 mg.

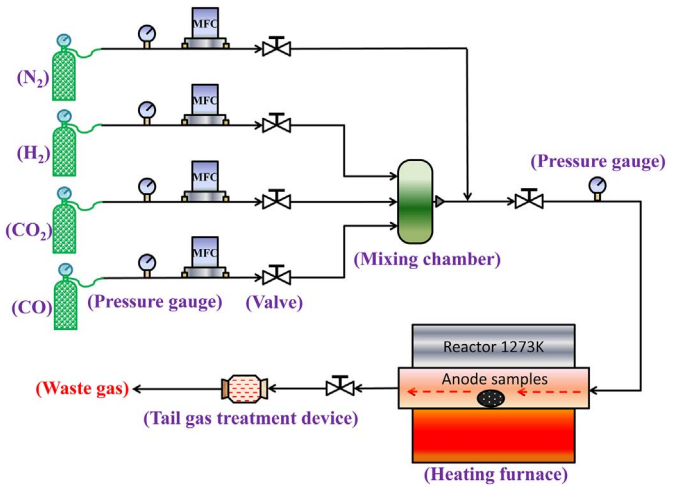

Fig. 1. Schematic of the flow system for CO disproportionation.

3. Anode samples fabrication procedure

The main materials used to make anode samples are NiO and YSZ powders which were purchased from Ningbo SOFCMAN Energy Technology Company. The NiO powder is single-phase with a particle size of 1–3 μm, and its purity is higher than 99.5%. The purity of YSZ powder is over 99.9% and is composed of $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ with a particle size of 0.5 μm. After being mixed NiO with YSZ, whose mass fraction were 60% and 40% respectively, the powder used for pressing anode samples was then pressed at a pressure of 30 MPa for 5 min and shaped into buttons with a diameter of 13 mm and a thickness of about 0.4 mm.

The pressed button anode samples were then processed in a reduction procedure with the following steps: first, put the anode samples into the electric heating furnace and heated from ambient temperature (~25°C) to about 800°C with a temperature rising rate of 5°C/min in nitrogen atmosphere. Next, expose the anode samples in hydrogen environment for 2 h at operating temperature of 800°C for reduction. Finally, remain the anode sample in hydrogen atmosphere when the operation temperature decreased to room temperature (~25°C) at a decreasing rate of 5°C/min. The anode samples composition for experiments should be Ni/YSZ, and to revert NiO in button anode sample to Ni would be the main object of the reduction procedure. Therefore, the mass loss of the button anode samples was the theoretical weight of oxygen in NiO/YSZ samples, of which the percentage was 12.87%. The weight loss of anode samples is shown in Fig. 2, and the average mass loss percentage of anode samples after deoxidization treatment is

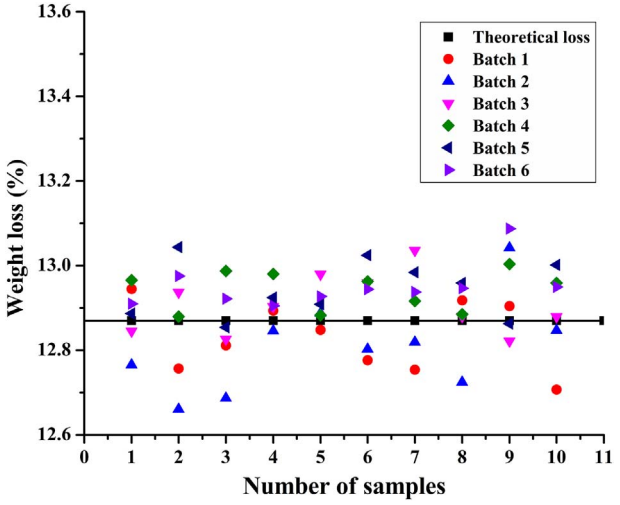

Fig. 2. Percentage of weight loss of anode samples.