ARTICLE IN PRESS

Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Effect of NiO/YSZ cathode support pore structure on CO_2 electrolysis *via* solid oxide electrolysis cells

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ARTICLE INFO

Keywords:
Solid oxide electrolysis cells
CO_2 electrolysis
Cathode support
Pore structure
Gas diffusion

ABSTRACT

Gas diffusion within supporting cathodes of solid oxide electrolysis cells (SOECs) plays an important role in CO_2 electrolysis process. This study has investigated the effect of cathode pore structure on gas diffusion during CO_2 electrolysis. The cathode pore structure was adjusted by applying the different amounts of pore former during cathode preparation. The more pore former added produced the higher porosity of cathode and the higher limiting current density. High limiting current densities are beneficial to diminish or even eliminate gas diffusion limitation in practical applications, where the electrolysis is expected to be operated at low CO_2 concentrations to increase CO_2 conversion. An advanced impedance spectroscopy study is performed to confirm the limiting current density measured according to current-voltage curves. It was revealed that CO_2 electrolysis performance is greatly affected by gas diffusion, which is determined by the employed cathode pore structure.

1. Introduction

With the rapid development of global industrialization, the amount of greenhouse gas CO_2 emission is increased rapidly, contributing to climate change [1]. CO_2 electrolysis is a promising technology to deal with the carbon emission since it electrochemically converts CO_2 into CO [2], which can be converted into liquid synthetic fuels or industrial raw materials and therefore reduce atmospheric CO_2 emissions [3–6]. Compared with low temperature electrolysis, high temperature electrolysis consumes less electrical energy, which has attracted extensive attention in recent years [7–10]. High temperature CO_2 electrolysis is conducted over solid oxide electrolysis cells (SOECs).

SOEC is a reversely operated solid oxide fuel cell (SOFC), being consisted of the same components [10,11]. Initially, electrolyte-supported configurations were developed, and the cells exhibited high ohmic resistances due to the thick employed electrolyte layer. In order to reduce resistance, electrode-supported SOFCs were developed with the need to co-sinter the supporting electrode and electrolyte layer at high temperatures to form the dense electrolyte film during preparation. However, high temperature sintering results in low electrode porosities and hence gas diffusion limitations within the supporting electrodes. Moreover, a short triple phase boundary is formed, limiting the active electrochemical zone where electrochemical reactions are taking place [12–15]. Therefore, the pore structure of supporting electrodes greatly affects cell performance.

Researchers have investigated the effect of supporting cathode pore structure on SOEC performance. For example, the effect of cathode porosity on steam electrolysis performance by modifying the sintering temperature was studied [16]. Concentration polarization resistance increased with the decrease of porosity. Using processed YSZ to vary anode pore structure, the cathode with a porosity of 33% negatively affected gas diffusion compared to cathode porosity of 46% [17]. An important limitation step during H_2O electrolysis operation is gas diffusion in cathode supports when steam concentration is below 70% [18]. Large straight open pores within the cathode support facilitate mass transport and thus minimize the concentration polarization during steam electrolysis [19].

Gas diffusion limitation was found under both SOEC and SOFC operation, which is more important in SOECs [20]. In SOFCs, small H_2 molecules are commonly used as fuel. However, in electrolysis cells, CO_2 or H_2O are much larger molecules than H_2, and electrolysis process is readily limited by the gas diffusion within the supporting cathodes [7,21,22]. There are several aspects making gas diffusion in SOECs more critical: SOECs are generally operated at high currents to achieve

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https://doi.org/10.1016/j.jeurceramsoc.2018.07.005
Received 15 May 2018; Received in revised form 4 July 2018; Accepted 5 July 2018

Please cite this article as: Wang, T., Journal of the European Ceramic Society (2018), https://doi.org/10.1016/j.jeurceramsoc.2018.07.005

high conversion rates/fuel yields, and mass transport limitations can readily occur at high currents; in order to improve CO_2 utilization, electrolysis should be able to be operated at low feed concentrations, which exacerbates the gas diffusion limitation [23]; during CO_2 electrolysis, carbon deposition can occur at the cathode/electrolyte interface at high CO concentrations, which is also influenced by gas diffusion. Therefore, the gas diffusion limitation would promote the carbon deposition [24,25].

Researchers have also studied the effect of electrode pore structure on SOFCs performance and water electrolysis in SOECs [21,26–28]. In the existing literature, there is a lack of information regarding the effect of the cathode pore structure on CO_2 electrolysis. This study aims to investigate the influence of supporting cathode pore structure on gas diffusion during CO_2 electrolysis. In this context, the cathode pore structure was tuned by the amount of pore former used during cathode preparation. An advanced impedance spectroscopy study combined with polarization measurements were used to examine how gas diffusion is affected by the cathode pore structure during CO_2 electrolysis.

2. Experimental procedure

2.1. Preparation of SOECs

The cathode supported cell consisted of a porous cathode support, a cathode functional layer, an electrolyte film and a porous anode layer. The powders of NiO (NiO-F, Fuel Cell Materials, Ohio, USA) and $(Y_2O_3)_{0.08}Zr_{0.92}O_2$ (YSZ-TC, Fuel Cell Materials, Ohio, USA) with a weight ratio of 60:40 were mixed in ethanol by ball-milling for 24 h. Starch was added as a pore former, and the weight ratios of starch in the mixture were 5%, 7%, 10% and 15%, respectively. Hereinafter, the prepared cathodes are referred to as cathode-1, cathode-2, cathode-3, and cathode-4. The mixtures were dried at 130 °C under magnetic stirring. The NiO/YSZ cathode substrates were prepared by dry pressing and subsequent pre-sintering in air at 1050 °C for 2 h.

To prepare the functional layer, a slurry was prepared by ball-milling YSZ (YSZ-U1, Fuel Cell Materials, Ohio, USA), NiO and Polyvinylpyrrolidone (PVP, MW = 40,000, Shanghai Dibo Chemical Technology Co. Ltd., Shanghai, China) in ethanol for 24 h. The weight ratio of NiO and YSZ is 60:40. PVP amount is 7 wt% of the ceramic powders, and the solid loading of the slurry is 10 wt%. The same slurry composition was used for preparing electrolyte and cathode slurry. The YSZ-U1 powder and $Gd_{0.1}Ce_{0.9}O_2$ (GDC-TC, Fuel Cell Materials, Ohio, USA) powder were used to prepare YSZ and GDC slurry for electrolyte preparation. The functional layer slurry was coated on the NiO/YSZ cathode substrate by dip-coating and subsequent sintering at 1050 °C for 2 h. Then, the NiO/YSZ cathode-supported functional layer was dipped into the YSZ slurry and GDC slurry subsequently to form the electrolyte film after co-sintering at 1400 °C for 5 h [29].

The anode slurry was prepared by mixing $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF-HP, Fuel Cell Materials, Ohio, USA) powder and GDC powder with the weight ratio of 70:30. The anode slurry was spray coated on the dense electrolyte film and sintered at 1050 °C for 2 h to form an anode layer [30]. The cells made with the cathode-1, cathode-2, cathode-3 and cathode-4 were referred to as cell-1, cell-2, cell-3 and cell-4, respectively.

2.2. Characterization and testing of the cells

The NiO/YSZ cathode green bodies were sintered in air at 1400 °C for 5 h and then reduced at 750 °C in H_2 for 2 h. The porosity and pore size distribution of the Ni/YSZ cathodes were measured by a mercury intrusion porosimetry (AutoPore IV 9500, Micrometrics), and gas permeability was tested at different nitrogen pressures. The microstructure of the Ni/YSZ cathodes and SOECs were examined by scanning electron microscopy (SEM, Phenom, ProX, Netherland).

The prepared electrolysis cell was sealed on a ceramic tube using ceramic adhesive (552-VFG, Aremco Products Inc., USA). Platinum paste was applied on anode surface as a current collector, and Ag wire was used to electrically connect the two electrodes to an electrochemical workstation (Solartron 1287/1260, USA). The electrolysis cells were tested at 800 °C and different CO_2/H_2 ratios in feeding gas. Current-voltage curves and impedance spectra were acquired with the electrochemical workstation. The active surface areas of anodes were about 0.6 cm^2 for all cells.

Table 1
Porosity, pore size of the Ni/YSZ cathodes made with different starch contents.

Starch content (%)	Porosity (%)	Pore size range (μm)	Average pore size (μm)
5	26.3	0.03-0.4	0.16
7	28.5	0.03-0.4	0.18
10	30.6	0.015-0.2; 0.2-1	0.31
15	34.6	0.015-0.2; 0.2-1	0.66

3. Results and discussion

3.1. Cathode support pore structure and sintering shrinkage

There are three ways to form pores in the cathode supports, such as particle packing, NiO reduction, starch removal. The porosity and pore size distribution of cathode supports prepared with different starch contents is shown in Table 1. The porosity was increased from 26.3% to 34.6% as starch content was increased from 5% to 15%. The pore sizes of the cathodes are in the range of 0.06 and 1.06 μm, and the average pore sizes of the cathode-1, cathode-2, cathode-3, and cathode-4 are 0.16, 0.18, 0.31 and 0.66 μm, respectively. Fig.1 shows the pore size distribution of the Ni/YSZ cathodes. Cathode-3 and cathode-4 have two pore size ranges since large pores (0.2–1 μm) were formed due to starch aggregation at high starch contents. Cathode-1 and cathode-2 with low starch contents show a single pore size range, which falls in between the two ranges exhibited for cathode-3 and cathode-4. The small pores (0.015-0.2 μm) within the cathode-3 and cathode-4 were formed by particle parking and NiO reduction. In cathode-1 and cathode-2, medium sized pores (0.03-0.4 μm) were formed by the synergistic effect of the aforementioned pore formation ways. The microstructure of Ni/YSZ cathodes is shown in Fig. 2. It is obvious that the number of large pores increases with starch content. Therefore, the large pores were formed by the aggregated starch particles.

Starch content also affected cathode sintering shrinkage. The total sintering shrinkages of cathode-1, cathode-2, cathode-3 and cathode-4

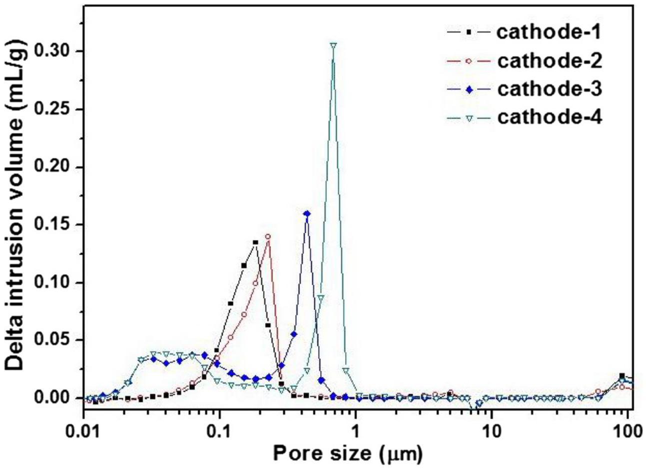

Fig. 1. The pore size distribution of the Ni/YSZ cathodes made with different starch contents.