Journal of Power Sources 301 (2016) 143–150

Contents lists available at ScienceDirect

Journal of Power Sources

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

Enhanced electrochemical performance and carbon anti-coking ability of solid oxide fuel cells with silver modified nickel-yttrium stabilized zirconia anode by electroless plating

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HIGHLIGHTS

- Conventional Ni/YSZ anode was decorated with silver particles by electroless plating.
- The electrochemical performance of decorated cells in H_2, CH_4 and C_2H_6 are all increased.
- The anti-coking ability of the modified anode is greatly improved.
- The decorated cell was run 24 h in C_2H_6 at 0.33 A/cm^2 with 1023 K.

ARTICLE INFO

Article history:
Received 2 April 2015
Received in revised form
1 October 2015
Accepted 3 October 2015

Keywords:
Solid oxide fuel cells
Ni/YSZ anode
Electroless silver plating
Hydrocarbon
Ethane
Carbon deposition

ABSTRACT

In this paper, silver (Ag) particles are introduced into the conventional Ni/YSZ anode by utilizing electroless plating method to improve its carbon anti-coking ability in hydrocarbons. The experimental results show that electrochemical performances of the decorated cells in H_2, CH_4 and C_2H_6 are all increased as compared to the cell with unmodified Ni/YSZ anode, which are verified by impedance spectrums as well. The durability experiment is carried out for as long as 24 h at the current density of 0.33 A/cm^2 where the modified anode is subjected to dry C_2H_6 indicating the anti-coking ability of the anode is greatly improved. Scanning electron microscope shows that the slight decreasing in the cell terminal voltage can be attributed to the minimized carbon deposition which maybe resulted from the aggregation of silver particles at high temperature. Energy-dispersive X-ray spectroscopy line scanning results after long-term stability operation of the anode suggest that the carbon deposition can be depressed effectively both inside the anode and on the surface of the anode. Therefore, the results show that silver is a promising candidate material for modifying the Ni/YSZ anode with regard to improving electrochemical performance and suppressing the carbon deposition when taking the hydrocarbons as fuels.

1. Introduction

Solid oxide fuel cell (SOFC) has attracted many attentions because of the inherent merits such as high energy conversion efficiency, environmental acceptability and great fuel flexibility. It possesses the ability of converting the chemical energy of the fuel directly into electrical energy without the limitation of the Carnot cycle under high temperature (873–1273 K) [1,2]. Electrical efficiencies of SOFC ranging from 40% (simple and small systems) to 50% (hybrid systems) have been demonstrated, and the theoretical efficiency is projected to be up to 60% [3,4]. SOFC with robust anodes can be fed with various fuels, such as syngas, biogas, gasified reformates from hydrocarbons and even with hydrocarbon apart from H_2 [5]. However, robust anodes immune to carbon coking are a prerequisite for direct hydrocarbon SOFC.

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http://dx.doi.org/10.1016/j.jpowsour.2015.10.006
0378-7753/

Conventional Ni/YSZ anode has been widely applied to the SOFC owing to its high electrochemical performance using H_2 as fuel and mature-technology manufacture. However, when carbonaceous fuel is directly fed into the cells, Ni/YSZ anode will suffer from the carbon deposition during the operation which can lead to the rapid deterioration in cell performance over the operation range [6]. For those reasons, great attentions have been paid to improve carbon deposition resistance of the Ni/YSZ anode. In general, two kinds of strategies arouse considerable interests to overcome the carbon deposition on the Ni/YSZ anode. One strategy is to utilize high temperature steam to reform the fuel gas or gasify the carbon deposition. However, high water-carbon ratio (S/C) reduces the electrical efficiency of SOFCs and increases energy consumption as well as equipment costs [7]. The other strategy is to advance anode with other elements by decorating, such as forming new alloy with Ni or rebuilding a new anode [8,9]. So far, the decoration of the Ni/YSZ anode with inert metals has the high proportion among all methods. These inert metals included copper (Cu), silver (Ag), gold (Au), platinum (Pt), ruthenium (Ru), rhodium (Rh), and palladium (Pd), *etc*..

Ag as one of the inert metals is not pursued for the SOFCs owing to its volatility at elevated temperature (1073–1273 K) [10]. However, the tendence of the SOFC operating temperature is nowadays reduced to 773–1073 K which is favorable to cell design and make the adoption of Ag into anode feasible [11,12]. For example, the silver adhesive and silver paste were frequently used as the sealing material [13] or current collector [14] because of its excellent ductility and high electric conductivity [15]. It is worth noting that a modification electrode with Ag-doped Ni/YSZ electrocatalyst by '*in-situ* combustion synthesis' had a good performance to suppress the carbon deposition during CH_4 steam reforming [16]. Ag as an alternative to Ni in direct hydrocarbon or direct carbon SOFC anode was also reported [17,18]. Evidently, Ag can be potentially applied as a SOFC material when operating the cell under temperatures ranging from 773 to 1073 K. However, there are still scarce concerned reports available in the literature with regard to the decoration of the Ni/YSZ anode supported SOFC with Ag. Given Ag is low catalytic activity for C–H dissociation and C–C formation [19]; it is considerable and feasible taking it as one of the very promising candidates for anode material to relieve the carbon deposition.

In this study, micro-size Ag particles decorated anodes were prepared by electroless silver plating (ESP) on porous Ni/YSZ, which is also known as silver mirror reaction. ESP, as one of electroless plating method, is well known for preparing mirrors and silver cans and identifying the presence of aldehyde groups [20]. Generally, electroless plating, known as chemical or auto-catalytic plating, is a non-galvanic plating method that involves several simultaneous reactions in an aqueous solution, which takes place without the use of external electrical power. It has been used to deposit Ni particles on YSZ powder [21] and Cu film for Ni/SDC anode [22]. The possibility of easy application for the SOFC anode makes it very attractive. Herein, the electrochemical performance and carbon deposition of thus formed Ag/Ni–YSZ anode were investigated when operated in H_2, CH_4 and C_2H_6 feeds at 1023 K. The maximal power density and long-term stability of the cell were improved greatly. The results of SEM, XRD and EDS indicated the modification of Ni-YSZ anode with Ag is a feasible and promising method to improve the performance of SOFC with the conventional Ni-YSZ anode when fed with carbon containing fuels.

2. Materials and methods

2.1. Single cell fabrication

In this study, the Ni/YSZ anode-supported cell was utilized in which both electrolyte and anode were fabricated by co-tape casting technique. Commercial NiO (mean diameter 0.67 μm, Qingdao, China) and YSZ (mean diameter 40 nm, E-type, TOSOH, Japan) powders were used for the cell fabrication. The electrolyte slurry was composed of YSZ, solvent (ethanol) and dispersant (glycerol trioleate). The anode slurry was consisted of NiO and YSZ with a weight ratio of 3:2 and starch (10–15 wt% in terms of the total weight of those two oxides) was added as the pore former. The slurries were ball-milled for 24 h. Diethyl-o-phthalate (PHT) was invoked as the plasticizers and the amount of PVB (binder) was 5 wt % with respect to the total weight of the electrode materials. The slurries were subsequently ball-milled for another 24 h. After co-tape casting, raw half cells were sintered (mean diameter, 15 mm) at 1673 K for 5 h, and a diameter of 12 mm of substrate was achieved. A screen-printed porous cathode layer (LSM/YSZ, Fuel cell materials, USA) with a 4 mm square was obtained after sintering at 1473 K for 2 h. The cross-sectional views of a single cell were (1) a 776 ± 1 μm Ni/YSZ anode, (2) a 32 ± 1 μm YSZ electrolyte, and (3) a 19 ± 1 μm LSM/YSZ cathode. The porosity of the anode before and after H_2 reduction by the Archimedes method was 36.5% and 53.8%, respectively. More details about the slurry, the cell geometry and the microstructure are referred to our previous paper [23].

As shown in Fig. 1, the ESP method was adopted to introduce Ag into the anodes [24]. The deposition process of Ag particles complies with the following reaction:

$$C_6H_{12}O_6 + 2Ag(NH_3)_2OH \rightarrow C_5H_{11}O_5COONH_4 + 3NH_3\uparrow + 2Ag\downarrow + H_2O \quad (1)$$

The preparation of Tollen reagent ($Ag(NH_3)_2OH$) in the reaction (1) was followed these steps, which was accorded to the silver–mirror reaction. The concentration of Ag^+ in this plating bath was 0.018 mol/L. 1 wt% solution (2 mL) of $AgNO_3$ was added into a 10 mL cuvette. Two drops of 10 wt% solution of NaOH were added and then shook up the cuvette until lots of grey brown precipitate produced in the mixed solution. Then some drops of 2 wt% aqueous ammonia were added until the precipitate was completely dissolved. Vacuum grease was used to protect the cathode and electrolyte surface from the plating reaction. The cells were dipped into the bottom of the cuvette with the anode kept upward free from sensitization and activation through soaking them in acidified $SnCl_2$ and $PdCl_2$ hydrosols, respectively. The 5 wt% solution (4 mL) of glucose was then added. The cuvette was shook up and then put

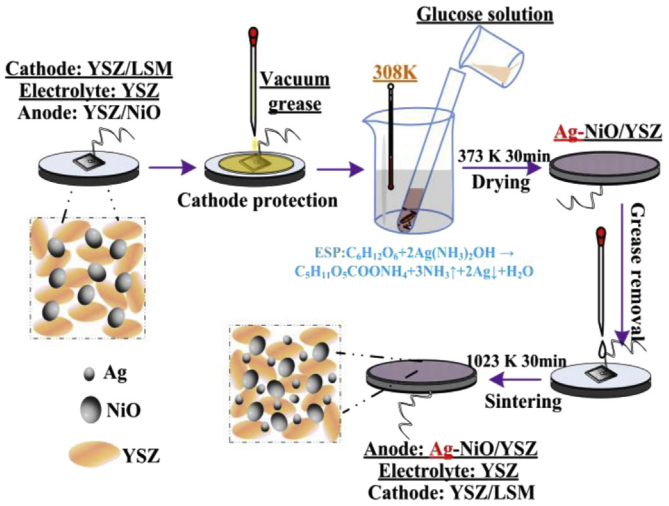

Fig. 1. Schematic diagram for the anode decorated with Ag by electroless plating method.