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Short communication

A rapid preparation of acicular Ni impregnated anode with enhanced conductivity and operational stability

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HIGHLIGHTS

- A novel method is proposed to prepare Ni impregnated YSZ anode.
- A novel needle-shaped Ni is presented after a drying and heating process.
- The preparation efficiency for Ni impregnated YSZ anode is improved by 3 times.
- The specific surface area of anode is improved by 1.14 times.
- The conductivity and operational stability of the anode are improved substantially.

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ABSTRACT

A novel method for fabricating $Ni(NO_3)_2$ solution impregnated YSZ (YSZ: Yttria Stabilized Zirconia) anodes for solid oxide fuel cells (SOFCs) is presented. In order to reduce the impregnation cycles and increase the reliability of the YSZ membrane, a YSZ support with a porosity of ~60% is soaked in a saturated $Ni(NO_3)_2$ solution with an increased temperature of 80 °C. The impregnated anode is dried in a vacuum drying device without heating, resulting in a flower-like $Ni(NO_3)_2 \cdot 6H_2O$ crystal. The formed porous structure is likely to facilitate the impregnating process and considered to be the key to success of the impregnation process with saturated solution. After heating at 700 °C, a novel needle-shaped NiO is presented, which exhibits some advantages including fast preparation, high connectivity, large specific surface area and high operational stability (i.e. high aggregation resistance). For the purpose of comparison, $Ni(NO_3)_2$ solution impregnated YSZ anodes prepared through the conventional impregnation process are also characterized under the same conditions.

1. Introduction

The solid oxide fuel cell (SOFC) is an electrochemical device that converts the energy of a chemical reaction directly into electrical energy [1–3]. It is considered to be a promising candidate of power generation technology in the 21st century due to its many advantages over conventional power-generating systems in terms of efficiency (40–60% unassisted, up to 70% in a pressurized hybrid system), reliability, modularity, fuel flexibility, and environmental friendliness [4,5]. The state-of-the-art material for SOFC anodes is Ni–YSZ (YSZ: Yttria Stabilized Zirconia) cermet that is an excellent catalyst for H_2 oxidation [6]. In addition, Ni acts as an electron conductor in the composite. Therefore, contiguous Ni–Ni chains have to be established within the anode to reduce the ohmic resistance and to achieve the percolation threshold, which requires a sufficient amount of Ni be present. However, one of the challenges related to the Ni-based SOFC is the problem of Ni-sintering at high temperatures, leading to Ni particle growth that will result in performance degradation through loss of electrical conductivity of the anode [7]. To the best of our knowledge, there are many researchers focusing on the study of operating stability of the Ni–YSZ anode or the redox stability of the Ni–NiO [8–11]. According to them, the Ni grain growth can take place through different mechanisms: evaporation–condensation, surface diffusion, grain boundary or volume (bulk) diffusion [12–14]. The sintering mechanisms have been found to depend on many process factors, such as, sintering temperature, sintering time, surface energy and interfacial adhesion [15,16]. Some efforts are underway to develop alternative new anode materials for SOFCs to overcome the inevitable Ni sintering [12,17,18]. Despite all this, the Ni–YSZ cermets are still widely used fuel electrodes.

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So far, there are many solutions that have been proposed to improve the operational stability of Ni-based anodes. The first one is to reduce the preparing and operating temperatures in order to avoid the Ni sintering process at elevated temperatures. J.Y. Yoo et al. proposed that Ni–YSZ cermets can be prepared by high frequency induction heated sintering, producing a uniformly porous microstructure without abnormal grain growth found in the conventional sintering method [19]. It is because of this that all sintering processes commence below 1150 °C and finish within 2 min, effectively avoiding the sintering process of Ni at high temperatures. The second one is to optimize the electrode structure (such as functionally graded structure), cermet microstructure (such as grain connectivity, grain size, pore size and pore size distribution), composition and the operating conditions (temperature and humidity) [9,20–23]. Besides temperature, the humidity also boosts Ni growth through increased surface diffusivity of the Ni_2–OH complex formed under humid conditions [24]. Finer conductive particles tend to be percolated through the composite material at lower concentrations and lower sintering temperatures, thus resulting in higher freedom in tailoring the Ni–YSZ composition. The third solution proposes to adopt novel but more labor consuming manufacturing techniques like impregnation [25,26]. The purpose of this work at first is to curb the Ni sintering by the introduction of inhibitors, such as, MgO, Al_2O_3, TiO_2, CeO_2, Gd- or Sm-doped CeO_2 (GDC or SDC), into the separation of Ni particles. Unfortunately, TiO_2 and Al_2O_3, and particularly MgO, are indicated to react with Ni and other elements, forming higher resistive phases and decreasing the overall conductivity.

Recently, Ni directly impregnated YSZ anodes were proposed and prepared with expected high catalytic activity owing to its fine particles and long three phase boundary (TPB) [25]. An advantage of the impregnated Ni–YSZ anode is the lower Ni content required to obtain electronic percolation. For this structure, percolation is obtained already around 9 vol% Ni, whereas 30 vol% Ni is required for percolation with the conventional powder based method with 1 μm sized Ni powder [27–29]. Wet impregnation is an alternative and effective technique in the development of the electrode structure which achieves high performance and an advantageous microstructure. However, the disadvantage of wet impregnation is a long preparation time, impregnation cycles >30 and production cycle >1 week [30–32]. Multiple impregnation steps are necessary to achieve sufficient electron conduction (conductive network). Such a repeated impregnation process is time-consuming and hinders the practical application of the impregnation approach [33,34]. Moreover, the repeated cooling and heating cycles are detrimental to the electrolyte membrane, and make it prone to cracking.

So, in this work, we attempt to establish a novel method of fast-preparing $Ni(NO_3)_2$ solution impregnated YSZ anode. The novel anode presents us with a new microstructure resulting in enhanced electrical conductivity and operational stability.

2. Experimental

2.1. Porous anode-support and cell preparation

Micro-scaled Yttria Stabilized Zirconia powder (YSZ, China) and tapioca (Singapore) were mixed thoroughly at a weight ratio of 5:3, which was then uniaxially pressed into wafers (button cells) with a diameter of 13 mm under a pressure of ~300 MPa, and sintered at 1000 °C for 2 h to guarantee the mechanical strength of green bodies. A dense YSZ electrolyte layer was then attached onto one surface of the pre-sintered wafers through a spin-coating technique and sintered at 1400 °C for 4 h [35]. The Archimedes principle was employed to measure the open porosity of the porous layer after sintering at 1400 °C for 4 h, which is ~60%. A cathode slurry of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) was coated onto the electrolyte membrane surface, and the three-layer was finally co-sintered at 1100 °C for 2 h in air to produce a full cell with a configuration of porous-YSZ|YSZ-membrane|LSM.

2.2. Ni impregnated YSZ anode preparation

In this study, there were two different ways to carry out the impregnation process.

2.2.1. The first way (Way_1, traditional method)

A $Ni(NO_3)_2$ solution (2 mol·L^{-1}) was dipped onto the surface of the YSZ anode support at room temperature, and which was infiltrated into the pores of the porous YSZ layer under capillary action, dried and heated at 300 °C. This impregnation process was repeated until a desired loading (38 wt%) of NiO was achieved.

2.2.2. The second way (Way_2, novel method)

Identical YSZ anode supports were soaked in $Ni(NO_3)_2$ saturated solution at a temperature of 80 °C. Here, the cathode was covered and protected with a silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins) that has been solidified at 300 °C. The impregnated pellets were all dried under a home-made vacuum drying device (as shown in Fig. 1) at room temperature. After that, they were all heated at 300 °C. This impregnation process was repeated until a desired loading (38 wt%) of NiO was achieved.

Please note that the concentration of the solution in the first way was controlled to lower than 2 mol L^{-1} in order to avoid the graded distribution of NiO in the thickness direction of the support, which has been demonstrated in our previous work [36]. The impregnated YSZ supports above were all finally fired at 700 °C for 1 h.

2.3. Characterization

The specific surface areas of impregnated anodes through different ways were tested using BET method based on an N_2 absorption apparatus (JW-BK112, China). The conductivities of different Ni–YSZ anodes were characterized by a four-probe

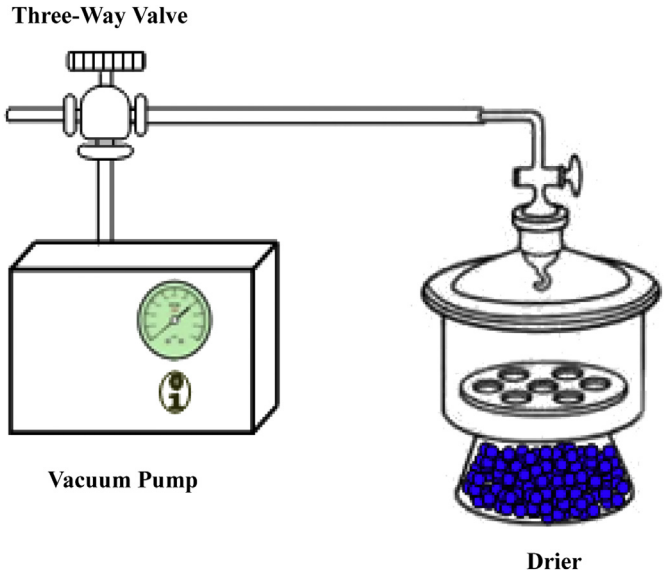

Fig. 1. A home-made drying device used for drying impregnated YSZ anode in the second way.