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Investigation on the microstructures, mechanical and electrical properties of solid oxide fuel cells anodes fabricated by using chitosan and cold mounts powders as new pore formers

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ABSTRACT

The physical properties and microstructures of supporting anodes are extremely important for the performances of solid oxide fuel cells (SOFCs). In the present work, for the first time, two new pore formers, cold mount powder and chitosan as well as graphite, activated carbon and corn starch as three well-known pore formers were studied and used for fabrication of porous Ni-YSZ anodes of solid oxide fuel cells. Morphological features and size of the pore former particles were characterized by using scanning electron microscopy (SEM) and particle size analyzer (PSA) technique and their thermal decomposition/oxidation properties were determined by thermo gravimetric analysis (TGA). The performances of the fabricated porous Ni-YSZ anodes were evaluated in terms of the resultant microstructure, mechanical strength, and electrical conductivity measurements. The strengths were measured by ball-on-ring method. Weibull statistics were used to describe the distribution of the measured strengths. The results indicated that the microstructure, mechanical strength, and electrical conductivity of the fabricated porous Ni-YSZ anodes depend directly on the type of pore former used. The results also showed that the cold mount powder and chitosan, by creating porosities with irregular shapes, produce anodes with lower fracture strength and modest electrical conductivity with respect to the other used pore formers.

1. Introduction

Fuel cells have drawn considerable attention in recent years as an alternative energy technology with no pollutant emissions. Among different types of fuel cells, the solid oxide fuel cells (SOFCs) have advantages such as fuel flexibility, higher efficiency and are environmental friendly [1–5]. The conventional SOFC configuration consists of three major layers including an electrolyte, an anode and a cathode. Electrolyte layer is a dense ceramic material that only permits transfer of ions while anode and cathode layers are usually made of porous ceramic and cermet materials, to allow transfer of ions, gases and electrons. In order to increase the power density, the efficiencies of the electrodes need to be improved while the electrolyte and contact resistances should be decreased to lower the ohmic losses [6–8]. Many attempts have been made to decrease the thickness of the electrolyte in order to minimize its contribution to the ohmic polarization. Anode supported SOFC design with a thin layer of electrolyte has gained importance, and has been extensively investigated for their higher power density at relatively low operation temperatures, in comparison with electrolyte-supported SOFCs [6,9,10]. An anode layer is required to have (i) high electronic and ionic conductivity, (ii) uniform distribution and percolation of all phases, (iii) fine grain sizes with high surface area for enhanced catalytic activity and (iv) high permeability for the fuel gas and the reaction products [6,11]. Porous nickel–yttria-stabilized zirconia (Ni/YSZ) cermet is currently the most frequently used anode material for SOFC applications [9]. In this cermet, YSZ forms the porous ceramic network required to create an extended reaction zone and to adapt the thermo-mechanical properties of the anodes to the electrolytes. Nickel acts as a catalyst for the reduction of steam, which should be homogeneously distributed to form a well-extended three-dimensional structure to promote the catalytic activity of the anode [9,12]. Gas permeability, electrical conductivity and strength of SOFC anodes are strongly dependent on the anode microstructure, such as porosity content, pore shape and distribution. Therefore,

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reasonable control of the microstructure is crucial to the optimization of the electrochemical performance of the anode [9,13]. Various pore formers can be utilized to control the development of the porous electrodes. However, each pore former results in a different shrinkage profile due to its characteristic particle morphology, at the same time it requires controlled removal with a specific heating profile due to its particular thermal decomposition/oxidation behavior [13,14].

Pore forming materials are usually selected according to desired properties. The characteristics that are considered for the selection of pore formers include particle size and shape. This contributes to better understanding of the effect of the pore former morphology on the final pore structure, and decomposition/oxidation of pore formers with a minimum amount of remaining carbon and other trace impurities that can affect the sintering behavior and properties of the Ni/YSZ matrix [14].

Although several studies have reported the effects of pore formers on the properties of the supporting anodes for SOFC, in this research, for the first time, two new pore formers; chitosan and cold mount powder, as well as graphite, activated carbon and corn starch, were used for fabrication of porous Ni-YSZ anodes of solid oxide fuel cells. Chitosan is a linear polysaccharide copolymer of β-(1–4)-linked D-glucosamine (deacetylated unit) and *N*-acetyl-D-glucosamine (acetylated unit). It is obtained by deacetylation of its parent polymer chitin, a polysaccharide widely distributed in nature (e.g. in the bodies of crustaceans, insects and certain fungi) [15]. Cold mount powder is a resin with short curing time and negligible shrinkage. They consist of self-polymerizing components that harden with the addition of a catalyst. Therefore, the aim of the present work was to study the influence of the morphology of five different pore formers with distinct properties (shape, size, distribution and thermal decomposition/oxidation behavior) on microstructure, mechanical behavior and electrical conductivity of supporting anodes. Fracture behaviors of the fabricated anodes were characterized in terms of the stress to fracture of disk samples placed under diametrical compression loading (biaxial flexure test). Simple Weibull statistics were applied to the obtained results for characterizing the fracture behavior of the anode samples.

2. Experimental procedure

Investigations on the anode pore structures were performed on single anode layers. Various pore formers including flake graphite with plate-like particles, spheroidal activated carbon, cold mount powder with poly disperse spherical particles, corn starch and chitosan with random shapes and sizes were employed in this study to further analyze their effects on processing and performance of anode microstructures. The morphologies of the pore former particles were investigated using a scanning electron microscope (SEM). Pore former particles were dispersed in acetone and lightly coated on glass stubs prior to analyzing their morphologies. Pore formers particle size distribution analysis were carried out in a laser diffraction analyzer (W3325, Microtrac, USA). To carry out this experiment, all the pore former particles were dispersed in alcohol except chitosan. Chitosan was dispersed in acetic acid. Thermo gravimetric analysis (TGA) (STA 503, BAHR) of the pore formers was performed in order to analyze their decomposition behavior. A heating rate of 5 °C/min was used up to 600 °C for cold mount powder, corn starch and chitosan and up to 1200 °C for graphite and activated carbon with heating rate of 10 °C/min, all in air. Commercial powder of green nickel oxide (NiO, Acros Organics Co., USA) and yttria-stabilized zirconia (YSZ) (8 mol% Yttria Stabilized Zirconia, Inframat Advanced Materials Co., USA) were used to prepare NiO–YSZ powder mixture. The morphologies and particle size distribution of NiO and YSZ powders were investigated, by means of laser diffraction and an electron microscope. The starting powders were mixed at the ratio of NiO/YSZ at 60/40 wt % by attrition milling in ethanol for 4 h to ensure good dispersion. Then they were mixed with different amounts of the five above-mentioned pore formers in order to reach equal density (or equal amount of remained porosity; ~20 vol%) for each pore former after the firing process. In order to create the same porosity by using different pore formers, the change in the amount of the created porosities versus the amount of pore former, for each pore former, were measured and are reported in Fig. 1. By drawing a horizontal line starting at 20 vol% porosity (80% relative density) on vertical axes of Fig. 1, the amount of different pore formers for creating 20 vol% porosity were determined at the intersect of the drawn horizontal line with each pore former line shown in Fig. 1. Table 1 shows the amount of each type of pore former used in this study for creating 20 vol% porosity. Appropriate amount of pore former is mixed with the prepared NiO/YSZ mixture by attrition milling, for 4 h in ethanol using 5 mm zirconia balls as a grinding medium. The mass ratio of powder to zirconia balls was always 1:50. After milling process, the created slurries were dried at 90 °C for 2 h and passed through 60 mesh screen for producing granules. Then 1.5 g of the granules of NiO–YSZ mixtures (including pore former or without it) was uniaxially pressed into a 25 mm diameter plate by applying 200 MPa pressure. The anode layers containing pore formers were heated to 600 °C with a rate of 1.5 °C/min and kept there for 2 h to completely remove the pyrolyzable content. Then all the anode layers were heated up to the sintering temperature of 1450 °C for 2 h. Finally, the nickel oxide was reduced to nickel metal in a reduction stage by heating the samples at 750 °C in a 10% hydrogen/90% nitrogen reducing atmosphere for 2 h in a tube furnace. Considering the measured weight loss due to the reduction of nickel oxide to nickel metal and comparing it with the expected theoretical weight loss, confirmed that each composite sample was reduced more than 90%. The density of the anode substrates with pore former and without it, before and after the reduction were measured via Archimedes method and reported in Table 1. Final microstructures of the porous Ni–YSZ samples on the fractured cross-sections were examined by SEM. The biaxial flexure test (BFT) was used to evaluate mechanical properties of the sintered samples before and after the reduction. Since failure of ceramics is typically determined by defect distributions, it is appropriate to employ a two parameter Weibull distribution to

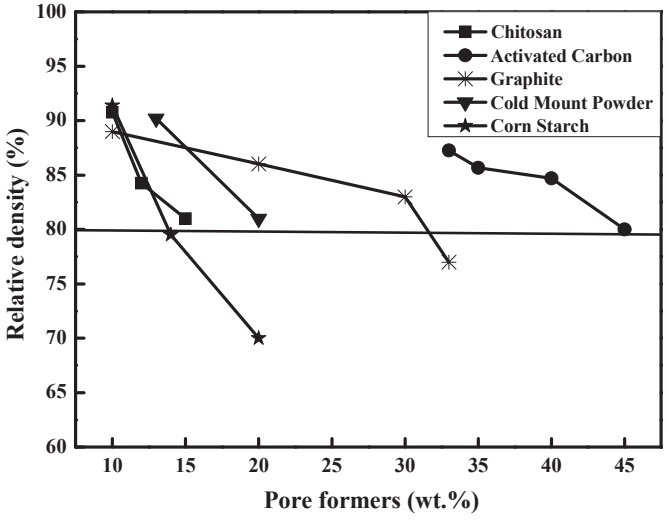

Fig. 1. Unreduced anode relative density versus the amount of pore former, for five different pore formers used.