Development of a highly durable anode support for solid oxide fuel cells

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ABSTRACT

Solid oxide fuel cells are well known to be highly efficient and clean energy conversion devices for stationary and portable power generation. The ceramics based SOFC's operate at high temperatures (>700 °C) and the durability of SOFC is critical for the early commercialization of SOFC based systems. Anode support of the SOFC becomes vulnerable to severe degradation during the long-term operation due the thermal stresses, humid and reducing environment, and the threat of redox-cycling. The mechanical strength of the nickel-yttria-stabilized zirconia (Ni-YSZ) anode supports needs to be assessed and improved for a durable SOFC. In this study, we developed a highly durable Ni-3YSZ based anode support material for SOFC with higher mechanical strength and stability. The mechanical properties of Ni-3YSZ anode support were improved by the addition of dispersed nanoparticles of Al_2O_3. Different amounts of nano-Al_2O_3 were added and their effect on the long-term stability of the SOFC anode support was studied. The anode supports with 3wt. % nano-Al_2O_3 dispersed Ni-3YSZ showed only 18% degradation in the mechanical strength comparable to the strength of Ni-8YSZ after 1000h degradation test. Further analysis by SEM and XRD before and after the long-term degradation test showed that the tetragonal to monoclinic phase transformation in zirconia was reduced due to the addition of nano-Al_2O_3 in Ni-3YSZ cermet, resulting in an improved long-term stability and higher mechanical strength. The nano-oxide dispersed Ni-3YSZ anode support showed superior mechanical strength after 1000h long-term test and can be used to fabricate a durable SOFC promising structural integrity to fuel cell stack over the lifetime.

Keywords: solid oxide fuel cell, degradation, anode support, mechanical strength, Al_2O_3

1 INTRODUCTION

High-temperature solid oxide fuel cells (SOFCs) are a promising clean energy technology due to their high efficiency and fuel flexibility. The anode supported SOFC offers high current density, improved performance and low operation temperatures as compared to electrolyte supported configuration. For the anode supported SOFC, the anode support constitutes 85% of the material required to fabricate the complete fuel cell [1]. Also, high a structural integrity and strength of anode support material are required during long-term operation because the anode support undergoes severe thermal and mechanical stresses in SOFC stacks. Therefore, an anode support material having lower cost and higher mechanical strength is crucial for early commercialization of SOFCs for stationary and mobile power generation systems. Typically, nickel-8 mol % yttria-stabilised zirconia (Ni-8YSZ) is used as an anode support for SOFC. But, Ni-8YSZ based anode support has lower mechanical strength and high cost of manufacturing than the Nickel-3 mol % yttria-stabilised zirconia (Ni-3YSZ) [2]. So, Ni-3YSZ is a good candidate as an anode support for SOFC.

In literature, many researchers have focused on the changes in the strength of anode Ni-YSZ cermet due to the reduction of NiO to Ni, the effect of porosity and powder particle size etc. at anode operating conditions [3–6]. The presence of partially stabilized zirconia in Ni-3YSZ cermet also results in changes in the structural properties. In 3YSZ, the partially stabilized zirconia faces phase changes from tetragonal to monoclinic in the presence of high humidity at high temperatures. This causes the formation of micro cracks and induces weakness in structure and leads to decrease in strength [7,8]. Under long-term accelerated operating conditions, the phase change behavior of TZP present in Ni-3YSZ cermet and its effects on the mechanical strength needs to be studied.

The addition of metal oxides (Al_2O_3) helps to improve electrical and mechanical properties of Ni-YSZ cermet [9–11]. Introducing a second phase which has a thermal mismatch with the matrix, and hence, the induced internal stress field can deflector pin cracks [12]. Takeli [9] reported that the addition of Al_2O_3 helps to stabilize isothermal tetragonal-to-monoclinic phase transformation in a zirconia–yttria system. The purpose of this study was to investigate the degradation in the strength and structural properties of Ni-3YSZ anode support has been investigated on long-term operation of SOFC and to develop high stable anode support material for SOFC by the addition of nano-oxides (Al_2O_3) in Ni-3YSZ anode support.

2 EXPERIMENTAL

Anode support materials NiO-3YSZ (Nickle oxide - 3 mole % yttria-stabilized zirconia) and NiO-8YSZ (Nickle oxide - 3 mole % yttria-stabilized zirconia) were prepared by the solid-state method. Powders of NiO (J. T. Baker Co., USA), 3YSZ (TZ-3Y, Tosoh Co., Japan) and 8YSZ (TZ-8Y, Tosoh Co., Japan) were mixed (NiO:8YSZ = 60:40 by vol%) in appropriate amounts. Anode powders (NiO-3YSZ, NiO-8YSZ) and activated carbon as pore former were weighted and mixed in ethanol by ball milling with zirconia balls for 100 h. Aluminum oxide nanopowder (Al_2O_3 – Sigma-Aldrich) were added (1, 3, 5 wt.%) in NiO-3YSZ composite powders as stabilizing additives. Rectangular bar-type pellets (20 x 4 x 2 mm) of the Ni-YSZ composite powders were fabricated via uniaxial pressing and sintered in air at 1400 ℃. The pallets were reduced in hydrogen (H_2) for 8 h at 750 ^{o}C.

For the long-term degradation test, the reduced pellets were exposed to high humidity and hydrogen conditions at an elevated temperature for a prolonged time. The samples were withdrawn after 100, 500 and 1000 respectively and tested for strength and structural properties. The test was conducted at 900 ^{o}C and 30 % humidity. The hydrogen gas was supplied after passing through controlled humidifier. The temperature and humidity data inside the sample holder was monitored throughout the experiment. The flexural strengths of the composite materials were determined using the three-point flexural test method. The specimen was bent at a crosshead speed of 1 mm/min using a universal test machine (Instron 5544A; Instron Corp., USA). To improve the reliability of the strength results, at least 12 pallets were tested for each sample. Weibull statistical analysis was employed to determine the actual strength of composite materials. X-ray diffraction (XRD) patterns were measured using an automated Rigaku diffractometer (2500 D/MAX; Rigaku, Japan) with Cu–K α radiation. The microstructures of the sintered and degraded samples (polished cross section) were observed by using back-scattered SEM (FE-SEM, Hitachi S-4800).

3 RESULTS AND DISCUSSION

The mechanical strength of the as-reduced and the degraded samples was assessed by three-point bend tests where a stress is applied at a constant strain rate until failure occurred. The flexural strength data were collected and analyzed by using Weibull distribution method [13].

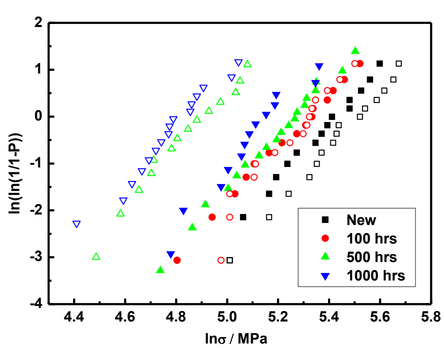

Figure 1: Weibull strength plots of probability of failure vs. maximum stress at which the fracture occurred. The open and closed symbols show data for Ni-3YSZ and Ni-8YSZ, respectively.

Figure 1 presents the Weibull plots for Ni-3YSZ and Ni-8YSZ composites before and after the degradation test. The figure shows that $ln[ln\{1/(1-P)\}]$ and $ln(\sigma)$ exhibit a linear relationship which is a key feature of the Weibull distributions. The changes in the flexural strength of Ni/YSZ composites are evident from Weibull plots. The flexural strength of Ni-3YSZ cermet is decreased significantly after the long-term test. Even in first 100 hours of operation, the Weibull strength decreased from 247.2 MPa to 204.3 MPa. Upon further degradation, the strength reached to 126.5 MPa after 1000 hrs. On the other hand, Ni-8YSZ cermet remained stable showing the Weibull strength of the as-reduced samples was 227.1 MPa and after 1000 hrs, the final strength value was 179.2 MPa. So, the Ni-3YSZ cermet resulted into 49% decrease in mechanical strength after 1000 hrs of exposure to SOFC anode operating conditions and the decrease in the strength of Ni-8YSZ cermet was only 21%.

Phase changes due to the long-term degradation of Ni-3YSZ and Ni-8YSZ anode support were assessed by XRD analysis. Figure 3(a) and 3(b) show the comparison of XRD patterns of Ni-8YSZ and Ni-3YSZ after 100, 500 and 1000 hours of degradation. Figure 3 (a) shows Ni-8YSZ remains completely stable in 1000 hours of degradation and no new phases are observed. JCPDS card (01-070-1849) indexed Ni phase and all other peaks correspond to 8YSZ cubic phases.

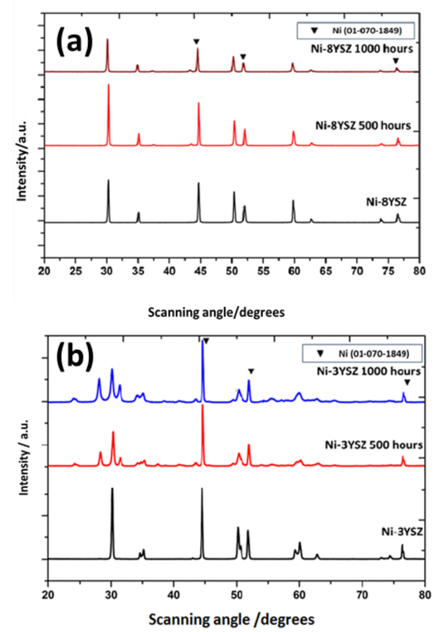

Figure 2: XRD plots showing phase changes in anode support cermet before and after long-term degradation test (a) Ni-8YSZ (b) Ni-3YSZ.

Figure 3(b) presents phase changes in Ni-3YSZ due to degradation. The XRD analysis Ni-3YSZ as-reduced sample showed tetragonal peaks but with as the degradation time passed, after 1000 hrs, Ni-3YSZ-1000 hours sample resulted in new monoclinic peaks. In the first 100 hours, new phases began to appear but more pronounced phase changes were seen afterward. Initially, Ni-3YSZ cermet possesses tetragonal phase structure. But due to exposure to high humidity in reducing environment as of SOFC anode, new monoclinic phases can be observed in Figure 3(b). It is evident from the comparison of Figure 3(a) and (b) that Ni-8YSZ cermet remains stable even after 1000 hours of exposure to high humidity anode conditions. But, Ni-3YSZ is less stable and shows significant structural degradation, which ultimately results in the loss of flexural strength.

The decrease in the flexural strength of Ni-3YSZ cermet after long-term exposure to anode operating conditions is originated from micro-cracks and micro-flaws that are generated by new phases inside the microstructure. The micro-flaws are aggravated due to the presence of reducing conditions, high temperature, and water. It is well established in the literature that Ni particles in Ni-YSZ cermet face coarsening and evaporation due to the reaction of water and hydrogen. This loss of nickel metal causes an added degradation effect in strength. In Ni-3YSZ composite, YSZ crystals face transformation due to the activity of water. The increase in the monoclinic phase and loss of Ni metal due to the presence of water causes major strength loss in Ni-3YSZ cermet.

The addition of metal oxides (Al_2O_3) helps to improve electrical and mechanical properties of Ni-YSZ cermet [11]. Introducing a second phase which has a thermal mismatch with the matrix, and hence, the induced internal stress field can deflect or pin cracks and improves the mechanical strength [12]. Tsubakino et al. reported that the addition of Al_2O_3 helps to stabilize isothermal tetragonal-to-monoclinic phase transformation in a zirconia–yttria system [8]. However, the long-term strength degradation of anode Ni-YSZ cermet with additives has not been reported yet.

Table 1: Weibull strength data for anode support materials before and after the long-term degradation test.

Sample Name	No of samples used	Weibull Strength (MPa)	Weibull Modulus
As reduced			
Ni-8YSZ	14	224.3	6.25
Ni-3YSZ	12	244.4	7.36
Ni-3YSZ+1% Al_2O_3	11	245.8	6.98
Ni-3YSZ+3% Al_2O_3	12	260.1	8.88
Ni-3YSZ+5% Al_2O_3	11	251.8	7.93
After long-term degradation			
Ni-8YSZ 1000 h	14	176.6	4.78
Ni-3YSZ 1000 h	14	113.4	6.26
Ni-3YSZ+1% Al_2O_3 1000 h	12	158.6	6.35
Ni-3YSZ+3% Al_2O_3 1000 h	15	185	5.84
Ni-3YSZ+5% Al_2O_3 1000 h	17	142.8	6.24

We added 1, 3 and 5wt% nano-Al_2O_3 in Ni-YSZ powder and studied its effects on the long-term stability of the anode support. Table 1 shows the Wiebull strength data of before and after 1000h degradation test. The strength data reveals that Ni-3YSZ addition in small amounts of Al_2O_3 increases the stability of composite under anode operating conditions. However, the 3% Al_2O_3 addition affects the stability of composite more than 1% Al_2O_3 addition. After 1000 hours, the flexural strength of Ni-3YSZ+1%Al_2O_3, Ni-3YSZ+3%Al_2O_3, Ni-3YSZ+5%Al_2O_3 is 158.6 MPa, 185.0 MPa and 142.8 MPa, respectively. While the strength of Ni-3YSZ without additives reached to 103.4 MPa after 1000 hours. This means that Al_2O_3 addition has a positive effect on strength and stability of Ni-3YSZ. The addition of alumina (Al_2O_3) not only increased the initial strength of anode support but also improved stability. The increased strength is attributed to enhanced ductile content addition along with Ni in the composite [12]. This improves sintering characteristics of composite and increases the flexural strength. But after long term exposure, Al_2O_3 helped to reduce degradation in mechanical properties. This may be due to the presence of new phases of Al_2O_3 which hindered phase changes in YSZ due to exposure to water.

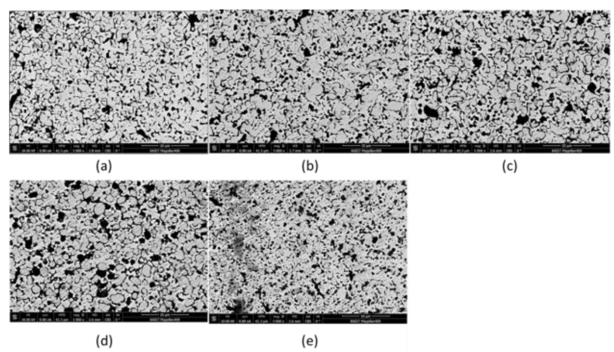

Figure 3: Backscattered SEM micrographs before degradation test for (a) Ni-8YSZ (b) Ni-3YSZ (c) Ni-3YSZ+1%Al_2O_3 (d) Ni-3YSZ+3%Al_2O_3 (e) Ni-3YSZ+5%Al_2O_3

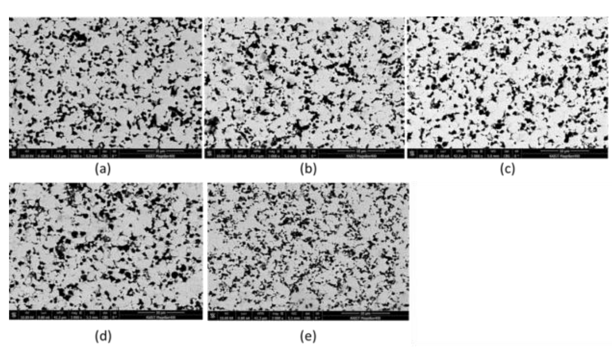

Figure 4: Backscattered SEM micrographs after degradation test for (a) Ni-8YSZ (b) Ni-3YSZ (c) Ni-3YSZ+1%Al_2O_3 (d) Ni-3YSZ+3%Al_2O_3 (e) Ni-3YSZ+5%Al_2O_3

Backscattered SEM images in Figure 3 and 4 show the microstructural changes in samples before and after 1000 hours of degradation, respectively. From these images, it is clear that addition of Al_2O_3 has improved sintering characteristics and reduced the grain growth during high-temperature long-term degradation test. Comparing Figure 3 and 4, we can see that the changes in particle size upon degradation were different in each sample. It was evident that the addition of Al_2O_3 into Ni-3YSZ helped to stabilize the particle and subsequently the strength of the cermet.

4 CONCLUSIONS

The degradation in the mechanical strength and structural properties of Ni-YSZ based anode support for SOFC was studied and the effect addition of small amount of Al_2O_3 was investigated to develop highly durable anode support for SOFC. The changes in the mechanical strength of Ni-YSZ were determined after long term degradation. The results showed the Ni-3YSZ strength decreased from 244.4 MPa to 103.4 MPa in 1000 hrs. XRD and SEM analysis also confirmed the formation of new phases in Ni-3YSZ cermet. On the other hand, Ni-8YSZ composite remained stable even after 1000 hours and a small decrease in mechanical strength was observed. The changes in the strength of Ni-3YSZ are attributed to partial stabilization of zirconia with yttria. Secondly, the effect of the addition of small amount (1, 3and 5wt %) of Al_2O_3 in Ni-3YSZ on long-term stability was studied. The addition of Al_2O_3 improved Ni-3YSZ stability and maximum strength after 1000 hours was observed by 3% Al_2O_3 sample. XRD and SEM analysis showed that Al_2O_3 addition helped in the suppression of formation of new phases in Ni-3YSZ and improved strength and structural characteristics. A phase transformation from tetragonal to monoclinic is observed in XRD analysis which results in a decrease in the mechanical strength. SOFC support based on Ni-3YSZ shows significant strength decreases after 1000 hours of degradation and addition of 3% Al_2O_3 helps to improve its strength and long-term stability.

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