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Degradation mechanism of Ni-based anode in low concentrations of dry methane

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ABSTRACT

Degradation mechanism of $Ni_{0.5}Cu_{0.5}$–$Gd_{0.2}Ce_{0.8}O_{1.9}$ (CGO) bimetallic anode in low concentrations of dry methane is studied with a $(La_{0.75}Sr_{0.25})_{0.95}MnO_{3-\delta}$–CGO cathode supported SOFC. Leakage tests suggested that as-prepared cells are well-sealed by glass ring at elevated temperatures. OCV of as-prepared cell in each concentration of CH_4 is over 1.2 V, indicating that the ScSZ electrolyte film prepared by a dual drying pressing method is dense enough. It is found that rapid degradation phenomenon easily occurred at relatively high current density in 7.4 and 14.8% of dry methane in the performance test. XRD and EIS analyses indicated that the degradation of the $Ni_{0.5}Cu_{0.5}$–CGO anode at high current density could be mainly attributed to the re-oxidation of Ni. GC results showed that the re-oxidation of Ni always occurred at a relatively high $p(H_2O)$, which always appeared at a relatively high current density. The degraded cell is successfully recovered by burning the anode with O_2 and re-reducing with H_2.

1. Introduction

Solid oxide fuel cell (SOFC) operated by directly using hydrocarbon fuels without external reforming is expected to be an important device for energy generation in future [1,2]. The generally used SOFC anode materials such as Ni/YSZ usually show a number of disadvantages including Ni coarsening [3], sulfur poisoning [4–6], carbon deposition [7–11] and redox instability [12–15]. In order to overcome these disadvantages, several alternative materials have been developed as potential anodes in recent years [16–18]. Gorte et al. [19–23] solved the problem of carbon deposition by using a Cu–CeO_2 anode. It is possible that Cu is a poor catalyst for making and breaking C–C bonds, and it could prevent graphite formation [24]. Kim et al. [25] also demonstrated that carbon formation was greatly suppressed when Cu–Ni alloys were used. Sin et al. [26] found that NiCu–CGO anode had a good long-term stability when running in dry methane at 750 °C. However, the output voltage as well as the corresponding power density of the cell with NiCu–CGO anode decreased rapidly when the current density increased to a higher value in dry methane. You et al. [27] reported a similar phenomenon even when the Ni–ScSZ anode was operated in low concentration of dry methane. In order to understand the degradation mechanism, many researchers [28–30] usually studied the structural and dimensional change of the Ni-based anode, which resulted in the damage of the cell, through reducing and oxidizing Ni in hydrogen and oxygen repeatedly. However, the degradation mechanism of Ni-based anode is still unclear when it is performed at high current density. In this study, the rapid degradation phenomenon was observed at high current density in low concentration of methane by gradual loading of current in the performance test, and a better understanding of the degradation mechanism was achieved.

Compared with SOFCs using pure methane as fuel, those cells using low-concentration methane can generate the similar amount of power density but lead to little carbon deposition. In this case, it is possible to investigate the reaction as well as the degradation mechanism via analysis of the outlet gas compositions on the anode side since the effect of carbon deposition can be ignored. In this study, in order to understand the degradation mechanism of the Ni-based anodes in low concentrations of dry methane, $Ni_{0.5}Cu_{0.5}$–CGO bimetallic anode was fabricated on a 11 mol% Sc_2O_3-doped ZrO_2 (ScSZ) electrolyte film with a $(La_{0.75}Sr_{0.25})_{0.95}MnO_{3-\delta}$ (LSM) + CGO cathode substrate, and its performance was investigated in 7.4 and 14.8% of dry methane environment, respectively.

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2. Experimental

2.1. Fabrication of unit-cells

$Ni_{0.5}Cu_{0.5}O$ powders were prepared by a glycine–nitrate combustion method as reported previously [31]. Commercial LSM (CAS, China), CGO (CAS, China) and starch powders in a weight ratio of 6:4:3.5 were first ball-milled in ethanol for 24 h and 5 wt% (relative to LSM + CGO) of polyvinyl butyral (PVB) was then added with ethanol. The obtained mixture was subsequently dried with agitation and ground with mortar and pestle, and the powder was then sieved through a 150 μm mesh sieve. The mixed powder was pressed under 30 MPa in a stainless-steel die in order to obtain the substrate. The ScSZ (Tosoh Corporation, Japan) powder with 5 wt% PVB (relative to ScSZ) was added onto the substrate and co-pressed at 200 MPa to form an assembly. In order to obtain a cell with better bending strength and a sufficiently dense electrolyte film, the assembly was subsequently sintered at 1300 °C for 8 h in air. The thickness of the electrolyte film was determined by the amount of ScSZ powder. The porosity of the cathode substrate was measured using a standard Archimedes method. $Ni_{0.5}Cu_{0.5}O$–CGO powders in a weight ratio of 6:4 were also ball-milled in ethanol for 24 h, and coated on the electrolyte as anode by a slurry coating method. Then, the as-prepared anode was sintered at 1000 °C in air for 3 h. For comparison, NiO–CGO anode in a weight ratio of 6:4 was prepared on the electrolyte and sintered at 1300 °C for 3 h. The effective area of the anode was $0.78\ cm^2$.

2.2. Measurement

As-prepared cells were tested in Norwegian Electro Ceramics AS (NorECs) SOFC performance testing rig, in which cell was sealed by a glass ring. It is found that the glass ring began to soften up, and the cell was able to be well sealed at a temperature above 750 °C. The performances of the cells with $Ni_{0.5}Cu_{0.5}O$–CGO anode were tested by changing the external current load in 7.4% and 14.8% of dry methane with Ar at different temperatures, respectively. The flow rate of different concentrations of methane with Ar was kept at $54\ ml\ min^{-1}$. The current collector was Pt mesh. The anode was reduced with hydrogen for 30 min prior to test. For comparison, a cell with NiO–CGO anode was tested in 10% of H_2 with Ar. The flow rate of O_2 for all tested cells was kept at $50\ ml\ min^{-1}$. The impedances were measured between 0.1 Hz and 1 MHz using a frequency response analyzer and a potentiostat (Solartron 1250B and 1286, respectively). The microstructure and morphology of the cell after testing were observed using scanning electron microscopy (SEM, Hitachi, S-800, Japan). To check the NiCu alloy phase after performance testing, X-ray diffraction (XRD, Shimadzu, Japan) with Cu Kα radiation was used. The anode outlet gases were analyzed online using the Agilent GC 7890A gas chromatography system. Each measurement was performed in 10 min as the current was changed. The current density in this study was calculated by current based on the anode area of $0.78\ cm^2$.

3. Results and discussion

Fig. 1 shows the performance testing results of the as-prepared cell with $Ni_{0.5}Cu_{0.5}$–CGO anode at 800 °C. Firstly, the anode was reduced in $100\ ml\ min^{-1}$ of H_2, while $100\ ml\ min^{-1}$ of O_2 flowed on the cathode side simultaneously. The open-circuit voltage (OCV) was 1.242 V in process I in a stable state, indicating that the cell was well-sealed and the ScSZ electrolyte film prepared by dual dry pressing method was sufficiently dense. Then the cell was tested in 7.4% of dry methane, and a value of 1.305 V for the OCV was obtained. As indicated in process II of Fig. 1, the output voltage of the cell in 7.4% of dry methane kept unchanged during the test period if the current density in the cell circuit was set to a value below $0.18\ A\ cm^{-2}$. However, the output voltage of the cell began to decline with the test time at $0.18\ A\ cm^{-2}$, and rapidly declined at $0.218\ A\ cm^{-2}$. The same phenomenon was also observed when the $Ni_{0.5}Cu_{0.5}$–CGO anode was operated in 14.8% of dry methane at 850 °C (as indicated in process I of Fig. 2) and when the Ni–CGO anode worked in 10% of H_2 at 800 °C (as indicated in process I of Fig. 3). As indicated in process I of Fig. 2, no obvious degradation was observed when the $Ni_{0.5}Cu_{0.5}$–CGO anode was tested at $0.218\ A\ cm^{-2}$ for 2 h in 14.8% of dry methane at 850 °C. However, the output voltage began to decline with the test time at $0.333\ A\ cm^{-2}$, and rapidly declined at $0.41\ A\ cm^{-2}$ in process I of Fig. 2. As shown in Fig. 4, after being tested in 14.8% of dry methane at 850 °C for 11 h, almost no degradation was observed in the $Ni_{0.5}Cu_{0.5}$–CGO

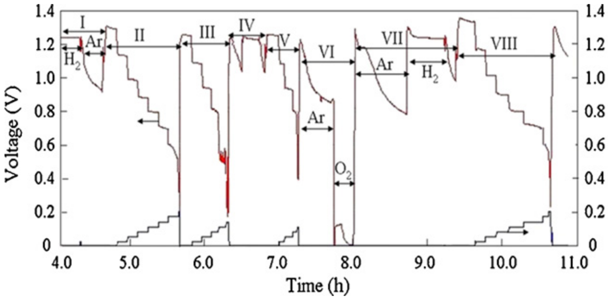

Fig. 1. Performance testing process of the cell with $Ni_{0.5}Cu_{0.5}$–CGO anode in 7.4% of dry methane at 800 °C (I. H_2 reduction and Ar purging; II. performance testing; III. performance testing after degradation; IV. second H_2 reduction and Ar purging; V. performance testing after second H_2 reduction; VI. Ar purging and O_2 burning; VII. Ar purging and H_2 reduction; VIII. performance testing after performance recovered).

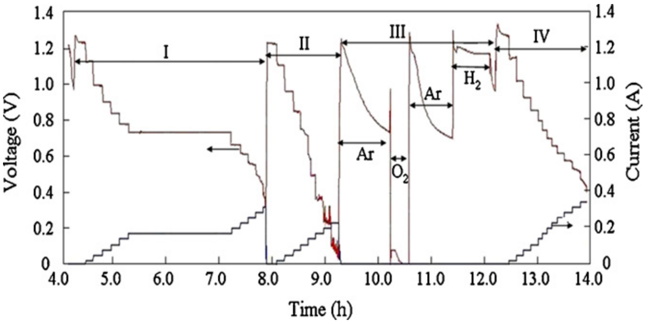

Fig. 2. Performance testing process of the cell with $Ni_{0.5}Cu_{0.5}$–CGO anode in 14.8% of dry methane at 850 °C (I. performance testing; II. performance testing after degradation; III. Ar purging, O_2 burning, Ar purging and H_2 reduction; IV. performance testing after performance recovered).

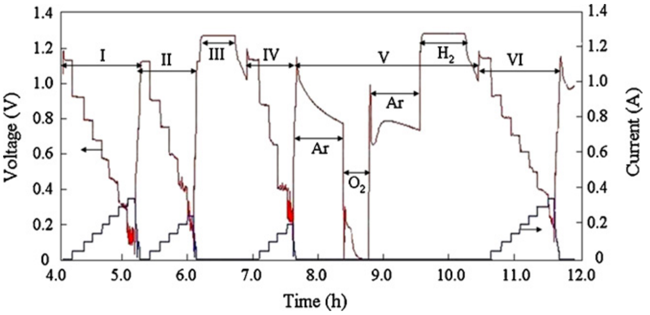

Fig. 3. Performance testing process of the cell with Ni–CGO anode in 10% of H_2 at 800 °C (I. performance testing; II. performance testing after degradation; III. second H_2 reduction; IV. performance testing after second H_2 reduction; V. Ar purging, O_2 burning, Ar purging and H_2 reduction; VI. performance testing after recovered).