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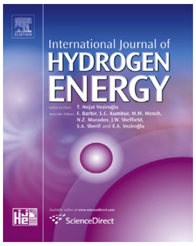

A high-performance ceramic composite anode for protonic ceramic fuel cells based on lanthanum strontium vanadate

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ABSTRACT

The composite electrodes for protonic ceramic fuel cells (PCFC) were fabricated by infiltration of $(La_{0.8}Sr_{0.2})FeO_{3-\delta}$ (LSF) cathode and $(La_{0.7}Sr_{0.3})V_{0.90}O_{3-\delta}$ (LSV) anode into a porous protonic ceramic, $Ba(Ce_{0.51}Zr_{0.30}Y_{0.15}Zn_{0.04})O_{3-\delta}$ (BCZY-Zn), respectively. Further, Pd-ceria catalysts were added into the composite anode. In the same method, the oxygen ion conducting fuel cells with the yttria-stabilized zirconia as an electrolyte (YSZ cell) were also fabricated. At 973 K, the non-ohmic area specific resistance (ASR) of PCFC (0.09 Ω cm^2) was much smaller than that of the YSZ cell (0.28 Ω cm^2) although the protonic conductivity of BCZY-Zn was slightly smaller than the oxygen ion conductivity of YSZ. According to the analysis of the symmetric cells with BCZY-Zn as an electrolyte, the LSV-composite anode showed better performance than the LSF-composite cathode at low temperatures.

Introduction

Proton conducting ceramics such as rare-earth-doped $BaCeO_3$ (RE-$BaCeO_3$) are promising electrolyte materials for intermediate temperature solid oxide fuel cells (IT-SOFC) because of their higher ionic conductivity in the intermediate temperature regime compared with oxygen-ion-conducting ceramics such as yttria-stabilized zirconia (YSZ) [1]. Recently, the poor sinterability of $BaZrO_3$ was improved through the use of sintering agents such as ZnO and CuO, while the chemical stability was enhanced by partially substituting Ce^{4+} in RE-$BaCeO_3$ with Zr^{4+} (RE-BCZ) [2–5]. As a result, several reports describing the performance of cells made using RE-BCZ-based protonic ceramics have been published [6–8].

Most of the electronically conductive ceramics used in the composite electrodes of SOFCs possess the perovskite structure, which is identical to that of RE-BCZ. Such similarity in the crystal structures facilitates the chemical reaction between these two materials (conductive ceramics and RE-BCZ) in the composite electrodes [9–12]. In addition, the nickel used in the cermet of an anode can react with the protonic ceramics based on either $BaCeO_3$ or $BaZrO_3$ at high temperatures [13,14].

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Therefore, a reduction in the fabrication temperature is needed.

The infiltration method can reduce the fabrication temperature of the composite electrode because the porous scaffold can be sintered separately at a high temperature before calcination of the infiltrated phases [15]. Recently, by infiltration of $(La_{0.7}Sr_{0.3})V_{0.90}O_{3-\delta}$ (LSV) into a porous YSZ scaffold, a ceramic composite anode was successfully fabricated at 973 K, which was a much lower temperature compared to both 1473 K for the $(La,Sr)(Cr_{0.5}Mn_{0.5})O_3$ (LSCM)-YSZ composite anode or 1773 K for the nickel-YSZ cermet anode [16,17]. In addition, the cell with LSV performed well after the addition of catalysts, such as CeO_2 and Pd, in small amounts to the anode. The V-deficiency in the LSV improved the redox stability of the catalysts on the LSV [17].

Apart from reduction of the fabrication temperature for making composite electrodes, another merit of the infiltration method is the fixed nature of the porous scaffold structures. In other words, identical pore structures can be prepared by using the same pore former, even if the material of the porous scaffold is changed. As a result, it is easier to compare the performances of the electrodes composed of different materials by disregarding the effect of the microstructure [18].

Therefore, in the present work, we applied the infiltration method to the fabrication of protonic ceramic fuel cells (PCFC) using $Ba(Ce_{0.51}Zr_{0.30}Y_{0.15}Zn_{0.04})O_{3-\delta}$ (BCZY-Zn) as an electrolyte. $(La_{0.8}Sr_{0.2})FeO_{3-\delta}$ (LSF) and LSV respectively infiltrated into the porous scaffold of BCZY-Zn to make the composite cathode and anode. Catalysts, such as CeO_2 (2.8 vol%) and Pd (0.5 vol%), were added in small amounts to the composite anode. Moreover, an oxygen-ion-conducting fuel cell with YSZ as an electrolyte (YSZ cell) was made analogously to the PCFC in order to obtain a similar microstructure in the composite electrodes. By comparing the electrode performances of PCFC and YSZ cells, we determined the effect of the proton conductor on the performance of the composite electrodes. By measuring the electrode performances of the symmetric cells with the BCZY-Zn electrolyte containing LSF or LSV, we tried to identify the performance-limiting electrode at the intermediate temperature range.

Experimental procedure

BCZY-Zn composed of $Ba(Ce_{0.51}Zr_{0.30}Y_{0.15}Zn_{0.04})O_{3-\delta}$ was prepared using a solid oxide reaction. Appropriate amounts of starting materials such as $BaCO_3$(99.8%, Alfa Acer, USA), CeO_2(99.9%, Alfa Acer, USA), ZrO_2(99.9%, Alfa Acer, USA), Y_2O_3(99.9%, Alfa Acer, USA), and ZnO(99.9%, Alfa Acer, USA) were weighed and mixed in a jar, using zirconia balls and ethanol, for 24 h. Then the mixture was calcined at 1473 K followed by wet-milling for 40 h.

The PCFC containing BCZY-Zn was fabricated analogously to previously reported procedures (tape casting and infiltration) for making the cells with YSZ electrolytes [16]. The tapes for the dense electrolyte as well as the porous electrode scaffold were fabricated using an organic slurry composed of BCZY-Zn powder, solvents, dispersants, binders, and plasticizers. To fabricate the tape for porous electrode scaffolds, synthetic graphite powder (300 mesh, Alfa Aesar) was added to the slurry as a pore former. The detailed composition of the organic slurry can be found elsewhere [19].

These two kinds of tapes for dense electrolytes and porous electrodes were laminated and sintered at 1573 K for 2 h to make a tri-layer BCZY-Zn wafer in which a 50 μm porous BCZY-Zn scaffold was placed on both sides of a 70 μm dense BCZY-Zn electrolyte. The tri-layer YSZ wafer was prepared similarly by sintering the laminated tape at 1773 K for 4 h in order to make a YSZ-cell with a 65 μm dense YSZ electrolyte and 50 μm thick porous YSZ scaffold composite electrodes.

The 40 wt% LSF and 35 wt% LSV were infiltrated into the cathode or anode side of the tri-layer wafer, respectively. The starting materials for making aqueous solutions of LSF and LSV were $La(NO_3)_3\cdot 6H_2O$ (99.9%, Alfa Aesar), $Sr(NO_3)_2$ (99%, Alfa Aesar), $Fe(NO_3)_3\cdot 9H_2O$ (98%, Alfa Aesar), NH_4VO_3 (99%, Alfa Aesar), and citric acid (99.5%, Alfa Aesar). The LSF and LSV in the porous scaffold were calcined at 1123 K and 973 K, respectively, after completing the infiltration. Finally, 2.8 vol% CeO_2 (1 M $Ce(NO_3)_3$, Alfa Aesar, 99.5%) and 0.5 vol% Pd (0.45 M tetraamminepalladium(II) nitrate solution, Alfa Aesar, 99.9%) were added to the anode composites as catalysts. A detailed description of the infiltration procedure is available elsewhere [17].

For the fuel cell tests, a silver paste was painted onto the composite electrodes as a current collector and the fabricated cell was mounted on an alumina tube using ceramic bonding. Humidified hydrogen (3% H_2O) and air were supplied to the anode and cathode at a rate of 50 sccm. *I*–*V* curves and impedance spectra were measured using a potentiostat (Gamry Instruments) in the temperature range 973–773 K. The impedance spectra were measured at −0.1 V bias voltage from the open circuit voltage (OCV) in the frequency range from 100 kHz to 0.01 Hz, with a 20-mV AC perturbation.

Further, in order to find the each contribution of the cathode or anode to the electrode polarizations, the symmetric cells with the BCZY-Zn electrolyte were also fabricated by infiltration of LSF or LSV into electrodes on both sides of the cells. In the case of the LSV symmetric cells, 2.8 vol% CeO_2 and 0.5 vol% Pd were also added into electrodes as catalysts. The impedance spectra of the symmetric cells with the LSF or LSV were measured at OCV under humidified air or hydrogen respectively.

The chemical reactions between the BCZY-Zn and the LSV or LSF were examined by performing X-ray diffraction (XRD) analyses on the mixed powder after heat-treatment at the fabrication temperature of the composite electrode, at 973 K in H_2 for the LSV/BCZY-Zn, and at 1123 K in air for the LSF/BCZY-Zn respectively. The microstructures of composite electrodes were also investigated using the scanning electron microscopy (SEM).

Results and discussion

Fig. 1 shows the XRD patterns of (a) BCZY-Zn sintered at 1573 K, (b) LSV reduced in H_2 at 973 K, (c) the mixture of LSV and BCZY-Zn treated at 973 K in H_2 for 2 h, (d) LSF calcined at 1123 K and (e) the mixture of LSF and BCZY-Zn treated at 1123 K in air for 2 h. As shown in Fig. 1(c) and (e), there was no unwanted phase in the mixed powder after the heat-