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Doped yttrium chromite–ceria composite as a redox-stable and sulfur-tolerant anode for solid oxide fuel cells

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ABSTRACT

A new high performance ceramic solid oxide fuel cell (SOFC) anode, Ca- and Co-doped yttrium chromite (YCCC)–samaria-doped ceria (SDC) composite, that resists deactivation by sulfur and does not show degradation during multiple reduction–oxidation cycles is developed. The electrocatalytic activity of the YCCC–SDC anodes in yttria-stabilized zirconia (YSZ) electrolyte-supported cells toward hydrogen oxidation is comparable to that of the Ni/YSZ anode. YCCC–SDC exhibits superior sulfur tolerance showing less than 10% increase in electrode resistance, fully reversible, upon exposure to 20 ppm H_2S. The excellent redox tolerance is attributed to the dimensional and chemical stability of the YCCC exhibiting minimal isothermal "chemical" expansion.

1. Introduction

High temperature SOFCs are a promising option for the production of clean energy. SOFCs with all-ceramic anodes have been of considerable interest because they offer attractive and important features such as reduction–oxidation stability, tolerance to sulfur and resistance to coking [1–4]. Conventional Ni/YSZ cermet anodes may fail during redox cycles caused by intermittent air exposures because of significant volume changes during the nickel-to-nickel oxide phase transformations [5]. Nickel is very sensitive to the presence of sulfur in the fuel and is readily poisoned by even 0.1–1 ppm H_2S, although reversibly [6], and the anode recovery becomes sluggish after exposures to $\geq$5 ppm H_2S. Ni promotes coke deposition in the presence of hydrocarbons, especially when a steam-to-carbon ratio is low [7]. An anode material with improved redox, sulfur, and coking tolerance would substantially simplify the SOFC system operating on fuels derived from natural gas, coal and biomass, and hence reduce SOFC packaging and costs. Many different ceramics have been considered as the alternative SOFC anodes, either as single phase materials [2], or as composites with the YSZ or doped ceria [8,9]. Although some of these compositions exhibited reasonable electrical and mechanical properties, sulfur and carbon tolerance, only few showed electrochemical performance comparable to that of the Ni/YSZ anode. An acceptable all-ceramic anode has been elusive.

In this work, $Y_{0.8}Ca_{0.2}Cr_{0.8}Co_{0.2}O_3$ (YCCC)–$Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) composite anode was developed and tested in hydrogen with 3% H_2O and 10–20 ppm H_2S, realistic concentrations for practical SOFC fuels. Stability in oxidizing conditions was assessed in multiple redox cycles. Yttrium chromites offer many advantages over lanthanum chromite such as improved chemical [10] and dimensional [11] stability in SOFC operating conditions, and chemical compatibility with the YSZ electrolyte at high processing temperatures [10]. The electrical properties of yttrium chromite are substantially improved by B-site doping with transition metals [12].

2. Experimental procedure

The 60 mol% YCCC–40 mol% SDC composite powder was synthesized by the glycine nitrate method [13], a single combustion step followed by calcinations in air at 1150 °C for 2 hours. All nitrate precursors were standardized prior mixing. Pure YCCC and SDC powders were synthesized separately, as described elsewhere [14]. The phase purity was verified by X-ray diffraction (XRD) analysis (Philips 3100 XRG). Electrolyte-supported button cells were fabricated using 300 μm thick 8 mol% YSZ disks (Fuel Cell Materials, Ohio). A YCCC–SDC anode was screen-printed in a circular pattern with a 2.0 cm^2 active area on one side of the disk. A $(La_{0.8}Sr_{0.2})_{0.97}MnO_{3\pm\delta}$–8 mol% YSZ (50:50 wt%) cathode was screen printed symmetrically on the opposite side and co-fired at 1150 °C for 2 hours. Cells were sealed to an alumina test fixture with a barium aluminosilicate glass and tested at 700–800 °C. Humidified (3% H_2O) hydrogen and air were fed to the anode and the cathode, respectively, at the same flow rate, 200 cm^3min^{-1}. In sulfur sensitivity tests, H_2S balanced with helium was added to the fuel bypassing the humidifier via a calibrated electronic flow controller. The redox cycling was conducted at 800 °C by alternating the supply of hydrogen and bottled air to the anode. The cell voltage was monitored

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at a constant current of 0.2 A cm^{-2} when operated on fuel gas or without electrical load during oxidation. Electrochemical measurements were conducted using a Solartron 1260/1287 potentiostat/frequency response analyzer system. Post-test analyses were performed by scanning electron microscopy (SEM).

For dimensional stability assessment, rectangular specimens of dense (>95% theoretical density) YCCC were prepared by uniaxial pressing at 35 MPa and isostatic pressing at 200 MPa followed by sintering at 1450 °C for 12 hours. Isothermal "chemical" expansion was measured in a dilatometer at 800 °C in oxidizing, $p_{O2} = 0.001$–0.21 atm, and reducing, $p_{O2} = 4.5\times10^{-19}$–$10^{-11}$ atm, atmospheres.

3. Results and discussion

3.1. Phase characterization

XRD patterns of the YCCC, SDC, and YCCC–SDC composite powders are given in Fig. 1. YCCC consisted of a single phase orthorhombic perovskite structure, SDC contained a single phase cubic fluorite structure, and the YCCC–SDC composite was composed of both the YCCC perovskite and SDC fluorite structures. No indication of secondary phase formation or major peak shift was detected within sensitivity of the instrument. This result suggests that the composite of structurally different YCCC and SDC phases can be co-synthesized by a simple and cost-effective single step combustion process without undesired phases. No decomposition products were detected after reducing YCCC–SDC at $p_{O2} = 4\times10^{-22}$ atm for 24 hours at 800 °C.

The morphology of the sintered anode and the distribution of the YCCC and SDC phases were analyzed by SEM. Cross-sectional SEM images of the fractured anode (Fig. 1b) revealed highly porous structure with fine well-connected particles. The low angle backscattered electron imaging and energy dispersive spectroscopic analysis of the polished cross-sections discriminated two separate phases mixed homogeneously, Fig. 1c. The SDC particles were finer, 0.1–0.2 μm in diameter, and the YCCC particles appeared larger (0.3–0.4 μm) and formed the structural framework.

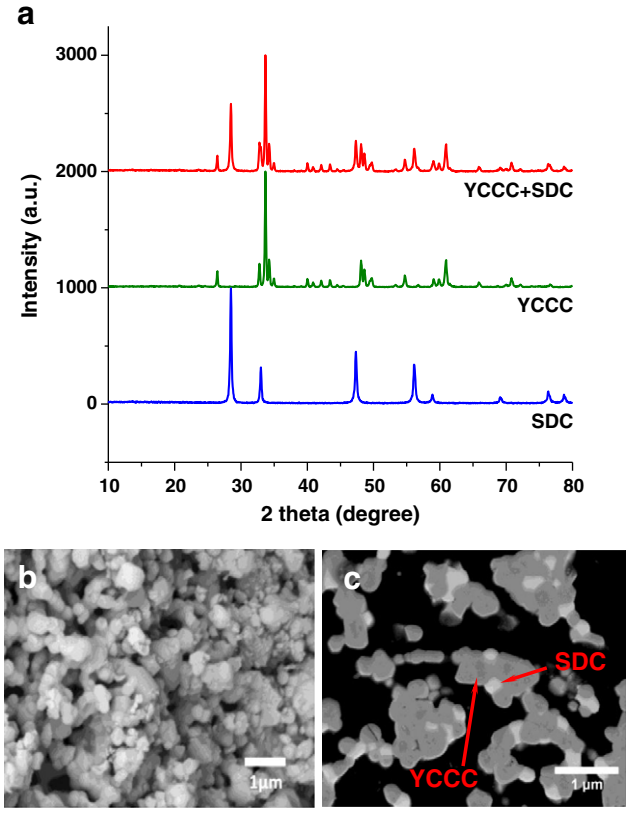

Fig. 1. (a) XRD patterns of SDC, YCCC, and YCCC–SDC composite powders, and SEM images of the (b) fractured and (c) polished surfaces of the sintered YCCC–SDC anode. YCCC is gray, SCD is white, and pores are black.

3.2. Cell performance in moist hydrogen

Fig. 2a illustrates voltage–current characteristics and the corresponding power densities of the electrolyte-supported cell with the YCCC–SDC anode at 700, 750, and 800 °C. The cell performance improved with increasing temperature. A maximum power density of 150 mW cm^{-2} was obtained at 800 °C. Impedance spectra are given in Fig. 2b. Cell ohmic losses (the high frequency intercept) dominate. The sum of anodic and cathodic resistances (the difference between the low and high frequency intercepts) is 0.31 Ω cm^2 at 800 °C. Such power density and electrode resistance values are comparable to those reported for the Ni/YSZ anode in electrolyte-supported cells under similar operating conditions (100–200 mW cm^{-2}, 0.3–1.0 Ω cm^2[15–17]), attesting to an excellent electrocatalytic activity of the YCCC–SDC composite anode towards hydrogen oxidation.

3.3. Effect of H_2S on anode performance

The effect of sulfur on the YCCC–SDC anode was investigated at 800 °C at a constant current density of 200 mA cm^{-2}. When 10 ppm of H_2S was added to the moist hydrogen, the cell potential slightly decreased by 0.8 % at ~0.7 V, remained stable over the next 72 hours of exposure and fully recovered after removing H_2S from the fuel, Fig. 3a. For comparison, a 12.7% current density decrease at 0.7 V

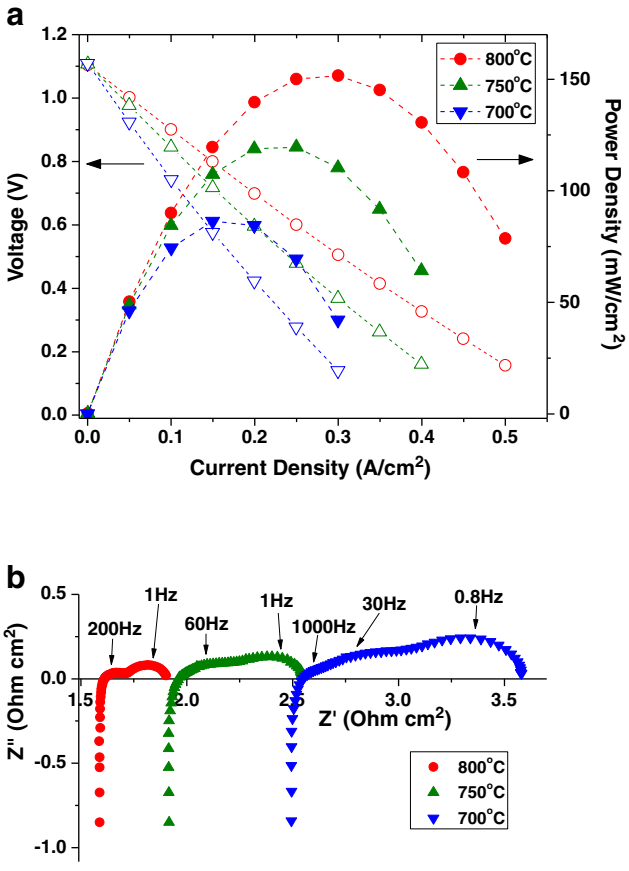

Fig. 2. (a) Current–voltage characteristics and the corresponding power densities, and (b) the complex electrochemical impedance spectra of an electrolyte-supported cell obtained at open-circuit conditions between 700 and 800 °C with hydrogen–3%H_2O as the fuel and air as the oxidant.