Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Performance and stability in H_2S of $SrFe_{0.75}Mo_{0.25}O_{3-\delta}$ as electrode in proton ceramic fuel cells

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ARTICLE INFO

Keywords:
Proton ceramic fuel cells (PCFC)
Sulfur tolerance
H_2S
Strontium ferrite
Barium zirconate

ABSTRACT

The H_2S-tolerance of $SrFe_{0.75}Mo_{0.25}O_{3-\delta}$ (SFM) electrodes has been investigated in symmetric proton ceramic fuel cells (PCFC) with $BaZr_{0.8}Ce_{0.1}Y_{0.1}O_{3-\delta}$ (BZCY81) electrolyte. The ionic conductivity of the electrolyte under wet reducing conditions was found to be insignificantly affected in the presence of up to 5000 ppm H_2S. The fuel cell exhibited an OCV of about 0.9 V at 700 °C, which dropped to about 0.6 V and 0.4 V upon exposure to 500 and 5000 ppm H_2S, respectively, on the fuel side. Post characterization of the fuel cell revealed significant degradation of the anode in terms of microstructure and chemical composition due to formation of sulfides such as SrS, MoS_2 and Fe_3S_4. Nevertheless, the fuel cell was still functional due to the sufficient electronic conductivity of some of these sulfides.

1. Introduction

Fuel cells represent a clean and efficient technology of converting chemical to electrical energy in which H_2 fuel is electrochemically converted with air to H_2O, electricity and heat [1]. Apart from hydrogen, these electrochemical devices can utilize various hydrogen containing fuels [2,3], of which biogas is of particular interest [4]. The exact composition of the biogas is important for its further application and this highly depends on the production process and type of organic matter [5]. Biogas typically consists of 35–75 vol.% of methane and 25–40 vol.% of carbon dioxide with small amounts of other components such as water vapour and H_2S [5,6]. The H_2S concentration in biogas is typically in the range of tens to thousands ppm, and can reach up to 2 vol.% in extreme cases [5–8]. The presence of H_2S in the biogas is considered to be especially troublesome due to its corrosive nature and threat to health and environment, and it can form even more toxic and environmentally hazardous compounds such as SO_2, SO_3, and H_2SO_4 [6,9,10]. In fuel cells, H_2S can poison or lead to decomposition of fuel side electrodes [11–14], and it is particularly detrimental to the performance of Ni, a common anode component [12–14]. While gas purification processes such as chemical absorption, scrubbing, or biological purification can be applied to remove H_2S, these processes can be limited by scalability, low sustainability or high investment and/or running costs [6–8,10,15,16]. Furthermore, single-step purification processes cannot easily offer sufficient gas purity for fuel cell technologies, which typically requires H_2S concentrations lower than 1 ppm [10,15]. The prospect of H_2S tolerant anode materials is therefore particularly attractive.

Biogas can be converted into hydrogen via dry or steam reforming. Both processes require temperatures in the range of 600–800 °C in order to achieve high conversion and prevent carbon deposition [17–22]. Fuel cells operating in this temperature range therefore open the possibility for direct reforming of biogas. Moreover, it has been shown that formation of sulfides is restrained at temperatures above 500 °C [14], which makes high temperature devices promising in terms of H_2S tolerance.

Solid electrolyte fuel cells operating at high temperatures comprise the solid oxide fuel cell (SOFC) and proton ceramic fuel cell (PCFC). The former utilizes an oxide ion conducting electrolyte in which oxide ions migrate from the cathode to the anode. At the anode, the oxide ions may react with H_2S to form SO_2 and H_2O. In PCFCs on the other hand, protons migrate from the anode to the cathode, where they react with oxygen and form water vapour. Since there are no oxide ions transported to the anode, sulfur dioxide formation is suppressed [23–26]. In combination with the rather high operation temperature (typically 350–800 °C [27]), PCFCs are hence particularly interesting for the application of alternative fuels in which the presence of low H_2S concentrations cannot be avoided. The prospect of sulfur containing proton

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http://dx.doi.org/10.1016/j.jeurceramsoc.2017.08.020
Received 8 June 2017; Received in revised form 14 August 2017; Accepted 14 August 2017

Please cite this article as: Wachowski, S., Journal of the European Ceramic Society (2017), http://dx.doi.org/10.1016/j.jeurceramsoc.2017.08.020

conducting electrolytes which may be stable under H_2S-rich conditions has recently been investigated by first-principle calculations [28].

Strontium ferrite partially substituted with molybdenum is known for its mixed electronic-ionic conductivity and stability over a wide range of oxygen partial pressures [29–33]. Reported conductivity values for $SrFe_{0.75}Mo_{0.25}O_{3\text{-}\delta}$ (SFM) lie in the order of 0.1 S/cm at 400–800 °C in both oxidising (air) and reducing (dry 5% H_2) conditions [31]. The electronic conductivity in strontium ferrites is dominated by a small polaron hopping [30,34]. Under oxidising conditions, the material is predominantly a p-type conductor where hole polarons jump between Fe^{3+} and Fe^{4+} ions, whereas electrons jump between Fe^{2+} and Fe^{3+} in the n-type regime at low oxygen partial pressures. In both cases, the ionic conductivity is about two orders of magnitude lower than the electronic [30]. These properties make SFM an interesting candidate for electrode materials in SOFCs [31,33,35]. Zheng et al. [33,35] recently investigated an SOFC with symmetric SFM electrodes and a $Ce_{0.8}Gd_{0.2}O_{1.9}$ electrolyte and obtained a peak power density of about 15 mW/cm^2 at 800 °C. The effects of various biogas components, including CO, CH_4 [33,35] and H_2S [35], were studied and Mo-doped strontium ferrites were found to be coke resistant. SFM electrodes were exposed to 800 ppm H_2S for 12 h under steam reforming conditions and characterized by thermogravimetry (TG) and X-ray photoelectron spectroscopy (XPS): sulfur-containing compounds were formed on the surface, but the overall microstructure of the material remained quite intact. Considering the high concentration of H_2S in those experiments (800 ppm), SFM may be a promising H_2S tolerant electrode material.

The influence of H_2S on the performance of the SFM anode in a fuel cell has, however, not yet been investigated. Here, we present studies of symmetric PCFCs with SFM electrodes and $BaZr_{0.8}Ce_{0.1}Y_{0.1}O_{3\text{-}\delta}$ electrolyte. The stability and performance of the button cell were investigated in the presence of 500 and 5000 ppm H_2S in the fuel.

2. Experimental

2.1. $SrFe_{0.75}Mo_{0.25}O_{3\text{-}\delta}$ materials synthesis

$SrFe_{0.75}Mo_{0.25}O_{3\text{-}\delta}$ (SFM) powders were synthesized according to a solid state reaction method. First, stoichiometric amounts of $SrCO_3$ (Aldrich, 99.9%), Fe_2O_3 (Alfa Aesar, 99.5%) and MoO_3 (Alfa Aesar, 99.5%) were weighed and milled in isopropanol for 2 h at 300 rpm in a planetary ball mill using agate balls and container. The obtained slurry was dried at 100 °C overnight in a heating cabinet. The resulting powders were ground in a mortar and uniaxially pressed into pellets and calcined in air at 1100 °C for 30 h. The pellets obtained from the calcination were crushed, milled and dried in a process analogous to that before the calcination. The phase purity of the synthesized powder was characterized by X-ray diffraction (XRD) using a Bruker D8 Discover with a Cu Kα radiation source in a 2Θ range of 10–90° and a scan step of 0.05°.

2.2. Cell fabrication

The electrolytes used in this study were $BaZr_{0.8}Ce_{0.1}Y_{0.1}O_{3\text{-}\delta}$ (BZCY81) pellets fabricated by CoorsTek (USA) according to a solid state reactive sintering method with NiO as a sintering aid. The sintering was followed by NiO leaching process resulting in a virtually Ni-free electrolyte with a relative density higher than 95% [36]. The thickness of the pellets was about 1.2 mm.

The chemical compatibility between SFM and $BaZr_{0.85}Y_{0.15}O_{3\text{-}\delta}$ (BZY) was investigated by firing 1:1 wt.% powder mixtures at different temperatures. BZY powder from CerPoTech (Norway) and SFM powder were mixed and milled in isopropanol at 350 rpm for 30 min using the same ball mill. The slurry obtained from milling was then dried overnight at 120 °C. The dried powders were fired at 1200 and 1400 °C for 2 h and XRD measurements were performed after each firing.

For the electrodes, inks were prepared as a suspension of electrode powder in an organic ink vehicle, VEH (NexTech Materials). A BZY-SFM interlayer between the electrolyte and the electrodes was introduced in order to compensate for the thermal mismatch between the SFM and BZCY81, which otherwise would lead to delamination of the electrode in fuel cells if the SFM layer was deposited directly on the electrolyte. The thermal expansion coefficient (TEC) of SFM is reported to be $15.8 \times 10^{-6}\,K^{-1}$ in the temperature range of 25–800 °C [35], whereas $BaZrO_3$-related compounds typically exhibit TEC values of 7–9 $10^{-6}\,K^{-1}$ in the same temperature range [37–39]. Accordingly, two types of inks were made for application on the electrolyte pellet: the first layer from an ink consisting of 1:1 wt.% SFM and BZY, and the second layer of an ink with pure SFM.

An optimized fuel cell preparation procedure was realized via a two-step electrode deposition. In the first step, a layer of SFM–BZY ink was painted on each side of the electrolyte pellet and fired at 1200 °C for 5 h. In the second step, a layer of SFM ink was painted on the SFM-BZY layers and fired under the same conditions. This fabrication process thereby resulted in a symmetric SFM|SFM-BZY|BZCY81|SFM-BZY|SFM cell, with an electrode area of 0.5 cm^2. The estimated thicknesses of the SFM and SMF-BZY layers were 40 and 10 μm, respectively.

2.3. Materials and fuel cell performance characterization

The conductivity of the electrolyte was measured in order to determine the influence of H_2S on its electrical properties. A BZCY81 sample of 1.2 mm thickness was measured from 800 to 500 °C using a ProboStat sample holder (NorECs, Norway) in a standard two-electrode four-wire setup with Au paint and mesh as electrodes ($\varnothing$ = 8 mm) using a HIOKI IM 3533-01 LCR METER (10 kHz).

The gas compositions were controlled by a two-stage gas mixing system. First, a mixture of H_2 and Ar was passed through a saturated aqueous KBr solution, yielding gas mixtures with approx. 2.5% H_2O (80% relative humidity at room temperature). The wetted gas was subsequently mixed with a dry premixed gas of 1% H_2S in Ar in ratios yielding final H_2S contents of 500 and 5000 ppm. Due to this second mixing stage, the final concentration of H_2O was lowered to approx. 1.3% in the 5000 ppm H_2S mixture, while it was essentially unchanged at approximately 2.5% in the 500 ppm H_2S mixture.

The microstructures of the SFM electrodes before and after fuel cell tests were studied by means of scanning electron microscopy (SEM) supported by energy dispersive X-ray spectroscopy (EDS) using a FEI Quanta FEG 200 microscope in high vacuum mode.

The fuel cells were studied by measuring the open circuit voltage (OCV), I-V curves, and the electrochemical impedance. All of these measurements were performed with different modules of a Gamry Reference 3000 Potentiostat. The I–V curves were measured by varying the voltage applied across the button cells (fuel cell mode) in the range from 0 to 0.9 V with a 2 mV step while the current was recorded. Impedance spectroscopy was performed under open-circuit conditions in the 0.01 Hz − 1 MHz range with 25 mV rms amplitude. The impedance data were deconvoluted using the Equivalent Circuit for Windows software [40]. Model circuits used for fitting were typically a series of inductance (L) and ohmic resistance (R_{Ohm}) elements followed by a series of (RQ) elements. An (RQ) element is a parallel connection of a resistor, R, and a capacitive constant phase element, Q. The total electrode polarization resistance of the fuel cell, R_{pol}, containing contributions from both anode and cathode, was determined as the sum of all resistances from the (RQ) elements. The ohmic and polarization resistances were then normalized by the electrode surface area to obtain area specific resistances (ASR).

3. Results

Fig. 1 presents AC conductivity of the BZCY81 electrolyte as a function of temperature under wet reducing conditions and with 500 and 5000 ppm H_2S. Overall, it is clear that H_2S does not have a