Electrochimica Acta 259 (2018) 143–150

Contents lists available at ScienceDirect

Electrochimica Acta

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

Evaluation of Sc_2O_3–CeO_2–ZrO_2 electrolyte-based tubular fuel cells using activated charcoal and hydrogen fuels

Daniel Fini [a, b], Sukhvinder P.S. Badwal [a, *], Sarbjit Giddey [a], Aniruddha P. Kulkarni [a], Sankar Bhattacharya [b]

[a] CSIRO Energy, Private Bag 10, Clayton South, Victoria 3169, Australia
[b] Department of Chemical Engineering, Monash University, Clayton, Australia

ARTICLE INFO

Article history:
Received 29 June 2017
Received in revised form
3 October 2017
Accepted 21 October 2017
Available online 26 October 2017

Keywords:
SOFC
DCFC
Solid oxide electrolyte
Zirconia
High-temperature fuel cell

ABSTRACT

Solid oxide fuel cells (SOFCs), as energy conversion devices, can use a variety of gaseous (hydrogen, methane, ammonia, carbon monoxide) and solid carbon fuels derived from coal and biomass. A critical component of SOFCs is the oxygen-ion conducting electrolyte material. Yttria-stabilised zirconia (YSZ) is a state-of-the-art electrolyte material often used in SOFCs; it has excellent stability in both reducing and oxidising atmospheres, good mechanical strength and compatibility with electrodes. However, YSZ electrolyte has low ionic conductivity, which leads to high voltage losses in electrolyte-supported SOFCs. Scandia-stabilised zirconia has much higher conductivity, but the phase assemblage is complex, with many phases having detrimental effect on the conductivity. Additions of a small quantity of dopants, such as ceria, appear to stabilise the cubic structure. In this work, we investigate the electrochemical performance of ceria-stabilised scandia–zirconia electrolyte supported tubular fuel cells using hydrogen fuel, and directly compare its electrochemical performance with YSZ-electrolyte supported cells using $Ce_{0.9}Gd_{0.1}O_2$–Ag composite electrodes for both types of cells. The electrolyte conductivity and phase assemblage of ceria stabilised scandia-zirconia have been investigated. We also analysed the electrochemical performance of a tubular cell using activated charcoal as a fuel, and nitrogen and carbon dioxide as purge gases. Electrochemical impedance spectroscopy was used to investigate rate-limiting processes and other factors affecting the fuel oxidation reaction.

1. Introduction

Solid oxide fuel cell (SOFC) technology has been under development for many decades, with commercial SOFCs now available that range in size from under 1 kW up to 250 kW [1–3]. SOFC fuel is typically H_2/CO produced from coal or natural gas. Carbon fuel cells (CFC) based on oxygen-ion conducting solid electrolyte are similar in operation to SOFC but use solid carbon as the fuel, in contrast to the gaseous fuels used by most other fuel cells. In a CFC, the solid fuel may oxidise directly at the anode/electrolyte interface, or be converted in-situ to CO on reaction with CO_2 [4–6]. The CO_2 can be generated electrochemically within the anode compartment, supplied externally or converted to gaseous form in thermally integrated gasifier and SOFC systems [4–6].

Most commercial SOFC systems operating in the 800–1000 °C range use Y_2O_3-stabilised zirconia (YSZ) as the electrolyte [7]. Doped ceria, which has an ionic conductivity almost twice that of 8 mol% Y_2O_3–ZrO_2 at 800 °C [7], is the preferred choice for lower-temperature operation in the vicinity of 600–650 °C. This is due to its tendency to develop appreciable electronic conductivity in reducing environments at higher temperatures, and its loss of microstructural stability in hydrogen [8,9]. Alternative strategies for higher-temperature SOFCs include the use of a thin layer of stabilised zirconia on the anode side of the doped ceria electrolyte. A similar choice of electrolyte materials exists for solid electrolyte-based CFCs.

In the quest to increase fuel-cell performance, several other electrolyte materials have been investigated. These include Sc_2O_3–ZrO_2 (ScSZ), doped Bi_2O_3, BIMEVOX (BI: bismuth, ME: dopant metal, V: vanadium, OX: oxygen) and $(La_{1-x}Sr_x)(Ga_{1-y}Mg_y)O_{3-\alpha}$ [7,10,11]. Of these, Sc_2O_3-stabilised zirconia is the toughest, has high ionic conductivity comparable to or better than that of doped ceria materials at 800 °C, and is stable over a wide range of oxygen

---

* Corresponding author.
E-mail address: Sukhvinder.Badwal@csiroalumni.org.au (S.P.S. Badwal).

https://doi.org/10.1016/j.electacta.2017.10.140
0013-4686/© 2017 Elsevier Ltd. All rights reserved.

partial pressures (both extreme oxidising and reducing conditions) [7]. However, considerable discrepancy is found in the phase diagram of this material, as explained below.

Both Sc^{3+} and Zr^{4+} have a similar ionic radius. A uniform mixing of cations during preparation of electrolyte powders is therefore critical; otherwise, undesired multi-component phase assemblages may occur. Furthermore, the ionic conductivity of Sc_2O_3-ZrO_2 compositions is reported to degrade over time at fuel-cell operating temperatures of 800–1000 °C [12]. The major cause of this is a metastable distorted cubic phase, also referred to as the t'-phase, in the 5–9 mol% Sc_2O_3–ZrO_2 compositions [13]. Note that high-resolution X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques are more beneficial to identify this phase. The t'-phase slowly decomposes over time, leading to the formation of low-conducting tetragonal zirconia precipitates and a Sc_2O_3-rich cubic phase. This results in significant conductivity degradation [12,14]. However, the t'-phase becomes increasingly unstable with increasing Sc_2O_3 composition and is undetectable at and above about 9 mol% Sc_2O_3–ZrO_2 composition (only cubic phase is detected at room temperature), with consequent low conductivity degradation. For example, at 1000 °C and over a period of 5000 min, a conductivity degradation of only 2% was reported for 9.3 mol% Sc_2O_3–ZrO_2, compared with >70% for 7.8 mol% Sc_2O_3–ZrO_2 [12]. These compositions have high ionic conductivity (~0.26–0.30 Scm^{-1}) at 1000 °C and show much lower conductivity degradation as a function of time at 800–1000 °C [12]. However, with increasing Sc_2O_3 content (10 mol% and above), an ordered rhombohedral phase, also known as β-phase ($Sc_2Zr_7O_{17}$), has been detected at room temperature [12]. The rhombohedral phase formed at lower temperatures (below about 600 °C) has a significantly lower conductivity than the cubic phase [12]. This phase transformation of the electrolyte during thermal cycling of any device would have a detrimental effect on the structural integrity of the device. However, the addition of a mere 0.5–1.0 mol% dopant with a larger ionic radius than Zr^{4+} and Sc^{3+} (e.g. Ce^{4+}, Hf^{4+}, Y^{3+}, Yb^{3+}) can suppress the formation of the rhombohedral β-phase for compositions with 10 mol% or higher Sc_2O_3 content [15–18]. The $(Sc_2O_3)_{0.10}(CeO_2)_{0.01}(ZrO_2)_{0.89}$ composition is of considerable interest as an electrolyte materials for use in SOFCs or steam-electrolysis cells [16–20]. The presence of small quantity of the β-phase has been reported by some authors in this composition, depending on the sintering temperature and time [21,22]. However, it is to be noted that homogenisation of all cations, material processing techniques and sintering conditions, and presence of impurities can all play a role in determining the final phase assemblage to some extent. Nevertheless, the electrolyte material of $(Sc_2O_3)_{0.10}(CeO_2)_{0.01}(ZrO_2)_{0.89}$ composition can be synthesised with a single cubic-phase structure with high ionic conductivity [16,17,19].

In this investigation, we have extensively studied material of $(Sc_2O_3)_{0.10}(CeO_2)_{0.01}(ZrO_2)_{0.89}$ nominal composition as a potential electrolyte for use in intermediate temperature (800 °C) SOFCs with hydrogen and solid carbon fuels. Conductivity and structural studies have been performed following sintering of the electrolyte material. We also constructed complete electrolyte-supported tubular fuel cells with this electrolyte composition, which were evaluated under a range of operating conditions and compared with similar fuel cells constructed using 8 mol% Y_2O_3–ZrO_2.

2. Experimental procedures

2.1. Materials

The electrolyte powder of $(Sc_2O_3)_{0.10}(CeO_2)_{0.01}(ZrO_2)_{0.89}$ nominal composition was obtained from Ningbo SOFCMAN Energy Technology, China. The material contained HfO_2 and many other impurities. Based on the certificate of analysis supplied by the manufacturer, the actual chemical composition of the electrolyte powder was $(Sc_2O_3)_{0.094}(CeO_2)_{0.011}(HfO_2)_{0.012}(ZrO_2)_{0.883}$ (referred to hereafter as 10Sc1Ce1Hf88Zr). Impurities present included 0.0277 wt% SiO_2, 0.022 wt% Fe_2O_3, 0.014 wt% Y_2O_3, 0.0117 wt% CaO, 0.01 wt% CuO and 0.009 wt% Al_2O_3. The particle size (D50) was 0.594 μm with a surface area of 8.05 m^2/g. For comparison of fuel-cell performance and conductivity, 8 mol% Y_2O_3–ZrO_2 (8YSZ) powder was purchased from Tosoh Corporation Japan.

The anode and cathode materials were prepared by milling $Ce_{0.9}Gd_{0.1}O_2$ (GDC) (Fuel Cell Materials) and Ag (Alfa Aesar) powders in the ratio of 50:50 (by volume) with ink vehicle (Fuel Cell Materials Inc, OH, USA). The particle size (D50) of GDC was 0.18 μm and surface area was 10.9 m^2/g. The silver powder surface area was 0.1–0.4 m^2/g.

For fuel-cell evaluation with carbon as the fuel, activated charcoal (Sigma-Aldrich) and iron oxide (Sigma-Aldrich) was used in the ratio of 95:5 (by weight). The powders were combined with ethanol in a mortar using a pestle to form a paste. The activated charcoal had a surface area of 600–800 m^2/g, while iron (III) oxide particle size was <5 μm.

2.2. Conductivity measurements

For conductivity measurements, bars of 10Sc1Ce1Hf88Zr and 8YSZ were pressed at 215 MPa and sintered at 1500 °C for 2 h in air. The sintered bars were 20 mm (length) x 3.5 mm × 4.2 mm. Voltage probes in the form of 0.25 mm Pt–Rh wire were wedged in a shallow groove, spaced about 4 mm from each end, and Pt paste electrodes were used at both ends of the bar for the current passage. The details of the measurement procedure are given in a previous publication [23]. In summary, specimens were heated in air and conductivity data were recorded between 400 and 850 °C using a four-probe DC technique. At 850 °C, the conductivity was continuously monitored in an atmosphere of air as a function of time for a period of 5000 min. The electrochemical impedance spectroscopy was performed on 2-mm-thick specimens with an area of 0.8 cm^2 using Pt paste electrodes in air in the 450-300 °C temperature range at 25 °C intervals with HP4192LF impedance analyser over the frequency range of 5 Hz to 10 MHz.

2.3. Fuel-cell fabrication

Electrolyte-supported, closed-end tubes for fuel-cell evaluation were fabricated via isostatic pressing of the 10Sc1Ce1Hf88Zr or 8YSZ powder at 170 MPa in a specially designed die followed by sintering at 1500 °C for 2 h in air. The final dimensions of the fuel-cell tube were: OD 10.3 mm, length 200 mm and electrolyte thickness 0.5 mm. The anode and cathode ink was prepared by milling $Ce_{0.9}Gd_{0.1}O_2$ and Ag powders in the ratio of 50:50 (by volume) with yttria tetragonal zirconia milling media. The anode ink was painted on the inside and cathode ink on the outside (in line with the anode) of the sintered electrolyte tubes, each with an active area of 3 cm^2. Both anode and cathode were given heat treatment at 825 °C for 2 h before cell assembly and evaluation. The final thickness of the cathode and anode was between 30 and 50 μm.

Current was collected from the anode using a 1-mm-thick silver wire spiral wound within the tube. Similarly, cathode current was collected using a 0.5-mm-thick silver wire wound around the outside of the tube. Silver paste was then used to fasten the silver wire to the cathode electrode interface.