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Ceramic proton conducting membranes for the electrochemical production of syngas

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ABSTRACT

A set of high quality ceramics membranes manufactured by tape casting was used to explore the performance of $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (BCZYZ) as an electrolyte in electrochemical cells. The material has very good proton conductivity (2.1 mS cm^{-1} at 600 °C), high transport proton number at T = 400–600 °C and can function well as the electrolyte in fuel cells or electrolysers using painted Pt as the electrodes. The co-electrolysis of CO_2 and H_2O to CO and H_2 has been shown to take place with Pt electrodes.

1. Introduction

The final aim of this work is to produce membranes that can co-electrolyse CO_2 and water to produce CO and H_2. Fig. 1 shows a ceramic proton conducting membrane in ideal operating conditions. In this work, we explore the properties of $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (labelled BCZYZ hereafter) as an electrolyte while subsequent papers will describe our work on the electrodes.

The co-electrolysis of CO_2 and steam has arisen some interest recently as it can provide a route to store the energy produced by intermittent sources of renewable energy (wind, solar) while using stranded sources of CO_2 and heat (e.g. from nuclear plants). Some work has been performed in the electrolysis of steam and CO_2 using oxygen ion conductors [1] However, studies of the same process using a proton conductor for an electrolyser are less frequent in the literature. The selected electrolyte material is based in $BaCeO_3$ a perovskite oxide where Y is added to promote oxygen vacancies/proton incorporation, with a chemical stability against CO_2 provided by Zr doping and with a reasonable sintering temperature when ZnO is incorporated. Our research group has determined the optimum composition for stability and proton conduction as BCZYZ [2]. We have also found that Ni is an excellent electrode in wet hydrogen [3] and we have also reported the direct production of methane using a proton conductor [4].

2. Experimental

2.1. Membrane manufacture

The material was prepared by precipitation of hydroxides with subsequent decomposition at high temperatures. The starting materials were $Ba(NO_3)_2$ (Alfa Aesar 99.95%), $Ce(NO_3)_36H_2O$ (Aldrich 99.5%), $Y(NO_3)_36H_2O$ (Aldrich 99.9%), $Zn(NO_3)_26H_2O$ (Aldrich 98%) and Zirconium acetyl-acetonate: $Zr(acac)_4$, (98% Aldrich). The nitrates were dissolved in de-ionised water under stirring and heating. $Zr(acac)_4$ was dissolved in a hot mixture of ethanol water (2:1). The solution of Zr is added to the nitrate solution followed by precipitation with concentrated ammonium hydroxide. The precipitate was then dehydrated overnight under constant stirring in a hot plate. Finally, the precipitate is heated to 350 °C to produce a spontaneous combustion. The remaining powder was calcined at 800 °C for 1 h.

Cells were fabricated by preparing a 3-layer BCZYZ wafer, consisting of two porous layers (100 μm thick each) separated by a dense electrolyte 200 μm thick as previously described [3]. Although the configuration of the porous scaffold is not yet exploited in this work, its purpose is to form a composite with the electrode material introduced by infiltration. This will be the subject of a forthcoming publication. The microstructure of the tapes was studied with a JEOL 5600 scanning electron microscope (SEM). XRD in the transmission mode using a STOE powder diffraction system was used to characterise the material.

2.2. Conductivity

Impedance spectroscopy was used to study the transport properties of the bulk and grain boundaries of dense samples using a frequency response analyzer (Solartron 1255) coupled with an electrochemical

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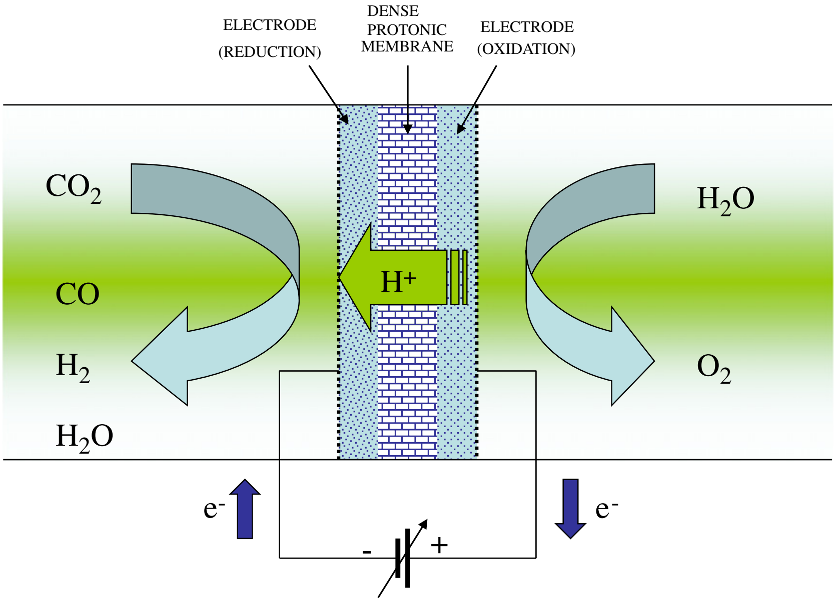

Fig. 1. Electrolysis cell with a proton conductor as the electrolyte.

interface (Solartron 1287) in the frequency range from 100 mHz to 1 MHz and amplitude of 50 mV. The temperature interval studied was from 550 °C to room temperatures with 2 h equilibration time for most temperatures. All measurements were performed during cooling. Concentrated sulfuric acid was used to dry the gases. Wet gases were bubbled in water at room temperature and are assumed to reach a 3% of water. A resistor and a constant phase element were used to fit the bulk data in the high frequency range; a similar arrangement was used to fit the grain boundary. In the temperature range where both bulk and grain boundary components were visible, these equivalent circuits were added in series. At high temperature only the grain boundary semicircle was visible. As usual in these cases, the bulk resistance was then taken as the intercept of the signal with the real impedance axis.

2.3. Electrochemical tests

The tests concentrated in the performance of the electrolyte and Pt was used as electrode. The samples studied were those of Fig. 2. Pt was painted on top of the porous scaffolds and annealed at 800 °C for 2 h before mounting the sample. Silver paint was used to contact the painted Pt with the silver wires used to connect to the impedance analyser.

The properties of the electrolyte in the BCZYZ membrane were studied using:

a) *EMF measurements.* The open circuit voltage or EMF was measured under different gas atmospheres to study the nature of the charge carrier in the temperature of interest. The OCV measurements were started at 650 °C kept for at least 2 h under the experimental conditions and then slowly cooled down overnight (0.3 deg/min) to 400 °C where they were left for 2 more hours.
b) *Fuel cell mode.* Different cells were mounted and set under operation in fuel cell conditions with Pt and wet 5% H_2 (argon balance) and air. The humidity level is assumed to be 3%.
c) *Electrolysis mode*. A constant current was passed through the BCZYZ membrane with H_2/H_2O feed at the cathode and pure CO_2 at the anode with Pt painted on the porous surface as electrodes. An on line mass spectrometer was used to identify the species formed.

3. Results and discussion

3.1. Microstructure

The discs used are mechanically stable, flat and olive green in colour. They were stable in air and when left in water (pH 3–12) for several months no sign of degradation was visible.

Fig. 2a shows a picture of some typical BCZYZ membranes while Fig. 2b and 2c show the micrograph of a cross section obtained by SEM. The clear circles are the porous BCZYZ on top of the dense electrolyte made of the same material. The thickness of the electrolytes was normally 200 microns and that of the porous scaffolds 100 microns on each side.

3.2. Conductivity

The conductivity studies in this section correspond only to a dense sample with no porous scaffold and with the painted silver electrodes. The conductivity of the BCZYZ discs is high and can even be measured at low temperatures. Fig. 3 shows an impedance plot at 108 °C.

Fig. 4a shows the Arrhenius plot of the bulk conductivity. The highest conductivity is observed for wet 5% hydrogen while the lowest is measured in dry argon although there are no large differences between the two. This suggests that protons dominate the conductivity even in dry conditions unless a high temperature treatment under vacuum is used to remove them completely [5]. The trend of the bulk conductivity observed in Fig. 4a shows a change in the activation energy around 400 °C. This is due either to a gradual de-protonation that decimates the conductivity or to a phase change with the corresponding variation in the activation energy.

Fig. 4b shows the Arrhenius plot of the grain boundary. Below 200 °C the conductivity seems to be purely protonic in wet and even dry conditions. Protons dominate the grain boundary in wet 5% H_2 at all temperatures. Above 300 °C other charge carriers may contribute to the conductivity as indicated by a higher activation energy.

The total conductivity at 600 °C is 2.1 mS cm^{-1} in wet 5% H_2 with very similar contributions from bulk and grain boundary. At 400 °C