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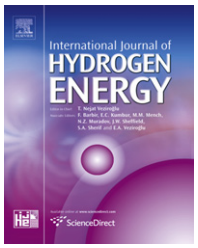

Quantifying multi-ionic conduction through doped ceria-carbonate composite electrolyte by a current-interruption technique and product analysis

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ABSTRACT

A composite electrolyte consisting of a samarium doped ceria and a binary eutectic carbonate phase is investigated in this work. It has been found that O^{2-}/H^{+} conductions take place when H_2 and O_2 used as the reactants. The presence of CO_2 in the cathode gas leads to the appearance of CO_3^{2-} conduction. The overall conductivity of the composite electrolyte is measured with a current-interruption technique and the ions transferred by $O^{2-}/H^{+}/CO_3^{2-}$ respectively are obtained by a quantitative measurement of the reaction products, i.e. H_2O and CO_2. The change of the carbonate content in the composite electrolyte presents a great influence on the conductivity of each ion. According to these experimental facts, the pathways for the individual ionic conductions are proposed.

1. Introduction

Solid oxide fuel cells (SOFCs) using conventional solid electrolyte, e.g. YSZ, work at a high temperature, often over 800 °C. The temperature has been a great challenge to the materials composing the fuel cell. Much effort has been made to explore novel ionic conductors working in the intermediate temperature (IT, 500–800 °C) range [1,2]. Recently, a doped ceria-carbonate (DCC) composite material presented a promising performance in IT-SOFC [3,4]. A similar ionic conductive oxide-carbonate composite material has been used by Lin and his coworkers [5,6] as the CO_2 separation membrane. The incorporation of a molten carbonate phase into a porous ionic conducting ceria-based oxide phase leads to a great increase of the ionic conductivity above the melting point of the carbonate [7,8]. A single cell using DCC as the electrolyte and hydrogen as the fuel gives a high power output, i.e. 1700 mW cm^{-2}, at 650 °C [9]. During the fuel cell operation, a large amount of water was detected in the gas outlets of both the electrode chambers. According to these experimental facts, a mechanism of binary ionic conduction was firstly proposed by Zhu [10]. When H_2 and O_2 are used as the reactants, H^{+}/O^{2-} binary ionic conduction takes place in the DCC leading to water generation in both anode and cathode as written in reactions (1)–(4).

For the O^{2-} conduction and reactions:

$$\text{Cathode: } 1/2O_2 + 2e \rightarrow O^{2-} \quad (1)$$

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$$\text{Anode: } H_2 + O^{2-} \rightarrow H_2O + 2e \quad (2)$$

For the H^+ conduction and reactions:

$$\text{Anode: } H_2 \rightarrow 2H^+ + 2e \quad (3)$$

$$\text{Cathode: } 1/2O_2 + 2H^+ + 2e \rightarrow H_2O \quad (4)$$

Recently, Xia et al. [9,11,12] found that the addition of CO_2 to the cathode gas effectively increased the total conductivity of the DCC and the power output of the composed single cell. In addition, the electrochemical enhancement of CO_2 permeation from the cathode to anode was observed by a gas chromatograph (GC) during the cell operation. This phenomenon indicates that the third ion conduction, i.e. CO_3^{2-} conduction, occurs when O_2/CO_2 mixed gas was used as the oxidant gas, i.e. reactions (5) and (6) taking place.

$$\text{Cathode: } 1/2O_2 + CO_2 + 2e \rightarrow CO_3^{2-} \quad (5)$$

$$\text{Anode: } H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e \quad (6)$$

Zhu and his coworkers [3,10] proposed that the interface of the two phases provides the paths of the multi-ionic conduction. They assume that the surface of the ceria be covered by various negatively charged oxygen adsorbents, which forms the conducting highways for oxygen ions [13]. Recently, a swing model pathway for proton conduction was also proposed by Zhu [14]. However, more quantitative experiments are needed to formulate a definite description.

To investigate the conductivity of each ion, σ_i, in DCC, a current-interruption and product analysis are carried out in this work to obtain the total conductivity, σ_{total}, and the transfer numbers, t_i, of each conducting ion, respectively. Thus, σ_i can be calculated as eq. (7).

$$\sigma_i = \sigma_{total} * t_i \quad (7)$$

The current-interruption technique has been widely used to get the Ohm drop excluding the influence of the electrode polarizations [15,16]. In addition, a quantitative measurement of the reaction products, i.e. H_2O and CO_2 in both anode and cathode outlet gas streams, allows to quantify the transfer numbers of the three conducting ions, i.e. H^+, O^{2-} and CO_3^{2-} under cell operating conditions. According to the observed experimental facts, the dominant ionic species and the pathways of the ionic conduction in the composite electrolyte are discussed.

2. Experimental

2.1. Preparation of the composite electrolyte

Samarium doped ceria ($Ce_{0.8}Sm_{0.2}O_{1.9}$, SDC) powder was prepared by an oxalate coprecipitation technique [11]. Li_2CO_3 and Na_2CO_3 were mixed with a mol ratio of 52:48, and heated at 600 °C in air for 1 h to form a binary eutectic salt. The eutectic salt and SDC powder were mixed thoroughly with various weight ratios as listed in Table 1, and then calcined at 650 °C in air for 1 h. The SDC-carbonate (SDCC) composite material was pressed at 300 MPa into a cylindrical pellet with a diameter of 13 mm and a thickness of 1 mm using a uniaxial die-pressing technique. The pellets were sintered at 650 °C for 1 h. Platinum paste was painted onto each side of the pellets as electrodes for the current-interrupt test.

2.2. Current-interrupt test

A galvanostatic step of 100 mA was applied on the pellet by an electrochemical workstation (VersaSTAT 3, Ametek) at 650 °C in the presence of H_2 in the anode and O_2/CO_2 (1:1 in vol.%) mixture or pure O_2 in the cathode. After steady state was reached, the current interruption leads to an abrupt drop of potential, ΔE_{IR}, within 10 μs which indicates the Ohm loss [17,18]. It is noted that the Ohm resistance of the Pt electrodes can be ignored compared to the electrolyte. Therefore, ΔE_{IR} is simplified as the potential drop through the SDCC electrolyte. According to eqs. (8) and (9), the resistance and the total conductivity of the electrolyte can be obtained:

$$R = \Delta E_{IR}/I_{app} \quad (8)$$

$$\sigma_{total} = L/(R^*S) \quad (9)$$

where R is the resistance of the electrolyte membrane (Ohm), I_{app} the applied current (A), σ_{total} the total conductivity (S cm^{-1}), L the thickness of the sample (cm), S the area of the sample (cm^2).

2.3. Products analysis of the cell reactions

The single cell was made by a co-pressing technique at 300 MPa. The anode material was a mixture of NiO (50 vol.%) and the composite electrolyte (50 vol.%). The cathode was made by mixing the composite electrolyte (50 vol.%) and the lithiated NiO powder (50 vol.%) prepared by solid-state reaction of LiOH and NiO at 700 °C for 3 h [19]. The thicknesses of the anode, electrolyte and cathode layers were 0.5 mm, 0.5 mm and 0.25 mm, respectively. The green pellet was sintered at 650 °C for 1 h, and silver paste was coated afterward on each side as the current collector. The single cells were

Table 1 – The composite electrolyte samples used in this work.

Composite name	Weight ratio SDC:$(Li_{0.52}Na_{0.48})_2CO_3$	Volume ratio SDC:$(Li_{0.52}Na_{0.48})_2CO_3$
SDC-10LN	90:10	71.5:28.5
SDC-20LN	80:20	52.7:47.3
SDC-30LN	70:30	39.4:60.6