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Correlation between internal chemical potential and durabilty of yttria-doped barium cerate (bcy)-based protonic ceramic fuel cells

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ABSTRACT

The correlation between internal chemical potential, and durability of anode-supported BCY ($BaCe_{0.85}Y_{0.15}O_{3-\delta}$) electrolyte cells, was investigated as a function of electrolyte thickness. Internal hydrogen and oxygen chemical potentials were measured on thin (~10 μm) and thick (~50 μm) BCY electrolyte using an embedded Pt probe. As the electrolyte thickness decreased, the internal chemical potential became dominated by the gases surrounding the cathode, indicating that the thin BCY cell may be vulnerable to water vapor produced at the cathode during operation. Constant-current tests were conducted on a thin (~10 μm) BCY electrolyte cell with a BCY + LSCF ($(La,Sr)(Co,Fe)O_{3-\delta}$) cathode, and a thick (~35 μm) BCY electrolyte cell with a BZY ($BaZr_{0.85}Y_{0.15}O_{3-\delta}$) + LSCF cathode, under positive and negative voltage conditions. Consistent with the results of the internal chemical-potential measurements, the former showed a significant rate of degradation due to changes in BCY composition in the electrolyte and cathode, while the latter showed much better durability, regardless of the sign of cell voltage. Thus, the present work shows the effect of BCY electrolyte thickness and selection of cathode material, on the durability of BCY based cells, in terms of their internal chemical potential.

1. Introduction

Protonic ceramic fuel cells (PCFCs) that operate at low temperature (<600 °C) have attracted much interest in recent years [1–6]. Perovskite type oxides, in particular, have been extensively studied for application as electrolytes. These include yttria-doped barium cerates (BCY), of interest for their superior ionic conductivity, and barium zirconate (BZY), of interest for its high chemical stability [4–6]. Barium cerates exhibit the highest proton conduction among perovskite type oxides; however, they are chemically unstable in contact with water vapor and carbon dioxide, limiting the application of this kind of materials as electrolyte in fuel cells [7–13]. The corresponding reactions of BCY with carbon dioxide (CO_2) and water vapor (H_2O) can be written as

$$BaCeO_3 + CO_2 \rightarrow BaCO_3 + CeO_2 \tag{1}$$

$$BaCeO_3 + H_2O \rightarrow Ba(OH)_2 + CeO_2 \tag{2}$$

The chemical stability of BCY has been investigated mainly using BCY powders or sintered specimens in H_2O/CO_2 rich atmosphere [14–16]. It was also found that the stability of BCY is related to the dopants used and their specific composition [17–25]. On the other hand, few studies on BCY electrolyte stability under actual operating conditions are reported [26–29]. Moreover, the results varied among the research groups. For example, a pure-BCY single-layer cell showed good stability (degradation rate ~ 0%) for 1000 h of long-term operation under the conditions of a very small current density (0.04–0.06 A cm^{-2}), an unconventional cathode (Nd_2NiO_{4+d}), and operation at 600 °C [7]. Under different operating conditions (higher current density at a constant voltage output of 0.5 V at 700 °C) and different cathode material, significant degradation was observed [29]. This implies that the stability of BCY-based cells depends on various complex factors related to cell components and operating conditions (e.g., current density, temperature). Therefore, more concrete studies of the usefulness of BCY as fuel-cell electrolyte should be carried out under actual operating conditions.

Our previous degradation study focused on a BCY-based cell under various operating conditions, including negative cell voltage (due to cell imbalance) [30]. Cell imbalance (cell-to-cell performance variation) in a series-connected fuel stack is one of the critical degradation mechanisms. A 'bad' cell with high resistance in a stack

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can be operated under a negative voltage operation, resulting in physical damage (electrode delamination) to the whole stack, as well as to the bad cell [31]. The results indicated that the degradation rate of BCY-based cells became more significant as the current density increased (from positive to negative cell voltage), and the rate of airflow decreased. The composition and phase in the electrolyte and cathode functional layer were obviously changed after the tests. From these results, it can be deduced that the stability of BCY cells strongly depends on the rate of water vapor formation (also important is the amount of water vapor remaining) at the cathode, and on the influence of water vapor on the BCY electrolyte and cathode functional layer during operation. It was also found that the sign of cell voltage (positive or negative) is not the main factor determining cell stability (unlike for pure YSZ (yttria stabilized zirconia)-based cells) because of sufficient electron/hole conduction in BCY electrolyte near the electrode/electrolyte interfaces [32,33]. This prevents internal partial pressure from increasing (and eventual electrode delamination). With this in mind, we might expect the durability of BCY-based cells to be improved by optimizing the operating conditions (e.g., current density, fuel/air flow rate, temperature) and the cell-design parameters (e.g., electrolyte thickness, electrolyte protection layer, selection of cathode material). This approach is supported by reports from other research groups: ~0% degradation rate was achieved with a novel cathode (no BCY) under mild operating conditions (low current densities) [7]. The present work was focused on the effect of electrolyte thickness and cathode-material selection on the durability of BCY-based cells, in terms of internal chemical potential, and under severe operating conditions.

The internal chemical potential profile (including oxygen, hydrogen and water vapor) through fuel-cell electrolyte depends on the electrolyte thickness. This should be taken into account for accurate investigation of the chemical stability of solid electrolyte. The procedures for calculating internal chemical potential using embedded voltage probes have been described elsewhere [32,34,35]. Because embedded Pt probes can exchange only electrons inside the electrolyte, the measured voltages from the internal probes correspond to negative reduced of electrochemical potential ($\phi = -\frac{\tilde{\mu}_e}{e}$ where $\tilde{\mu}_e$ and e are electrochemical potential of electrons and elementary charge) inside the electrolyte. Assuming that local equilibrium exists everywhere in the solid electrolyte (via conduction of protons and oxygen ions), a gradient of internal hydrogen and oxygen chemical potential (partial pressure) can be written in terms of a gradient of electrochemical potential [32–35].

$$\nabla\mu_{H_2} = 2(\nabla\tilde{\mu}_{H^+} + \nabla\tilde{\mu}_e) = 2(\nabla\tilde{\mu}_{H^+} - e\nabla\phi) \qquad (3)$$

$$\nabla\mu_{O_2} = 2(\nabla\tilde{\mu}_{O^{2-}} - 2\nabla\tilde{\mu}_e) = 2(\nabla\tilde{\mu}_{O^{2-}} + 2e\nabla\phi) \qquad (4)$$

where μ_{H_2} and μ_{O_2} are the chemical potentials of hydrogen and oxygen, respectively; while $\tilde{\mu}_{H^+}$ and $\tilde{\mu}_{O^{2-}}$ are the electrochemical potential of protons and oxygen ions, respectively. As mentioned above, the gradient of ϕ can be experimentally measured using embedded Pt probes, and the gradient of $\tilde{\mu}_{H^+}$ and $\tilde{\mu}_{O^{2-}}$ can be determined using transport equations:

$$\nabla\tilde{\mu}_{H^+} = -\frac{I_{H^+}e}{\sigma_{H^+}} \qquad (5)$$

$$\nabla\tilde{\mu}_{O^{2-}} = \frac{2I_{O^{2-}}e}{\sigma_{O^{2-}}} \qquad (6)$$

where I_{H^+} and $I_{O^{2-}}$ are protonic and oxygen ionic current densities, respectively; and σ_{H^+} and $\sigma_{O^{2-}}$ are conductivity due to protons and oxygen ions, respectively. Thus, internal chemical potentials can be estimated using the method of embedding Pt probes in the solid electrolyte.

In the present work, we investigated the correlation between internal chemical potential and durability as a function of electrolyte thickness. Internal hydrogen and oxygen chemical potentials (partial pressures) were measured on thin (~10 µm) and thick (~50 µm) BCY-electrolyte–anode-supported cells using an embedded Pt probe. The values were compared with regard to their durability under fuel-cell operating conditions. In addition, constant-current (CC) tests were conducted on BCY-based cells of different electrolyte thickness (~10 vs. ~35 µm) and with different cathode composite material (BCY vs. BZY), under severe operating conditions (from positive to negative cell voltage). Their performance (power density and impedance spectra) and galvanostatic profiles (voltage drop rates) were measured and compared. Post-test material analyses were also carried out to determine if any changes in microstructure and composition had occurred in the BCY electrolyte or cathode.

2. Experimental procedure

Anode supported cells were fabricated with BCY ($BaCe_{0.85}Y_{0.15}O_{2.925}$, 8.5 $m^2 g^{-1}$, Kceracell) electrolyte; Ni + BCY anode support; Ni + BCY anode functional layer; LSFC ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$, FCM, 4–8 $m^2 g^{-1}$) + BCY (or BZY ($BaZr_{0.85}Y_{0.15}O_{2.925}$)) cathode functional layer; and LSCF current collector. A detailed description of the fabrication of the anode support, anode functional layer and BCY electrolyte can be found elsewhere [32]. For the measurement of internal chemical potential, a Pt probe was embedded in thin (~10 µm) and thick (~50 µm) BCY electrolyte. The corresponding schematic is shown in Fig. 1. The electrolyte parts close to the cathode and the anode side were named "Region 1" and "Region 2", respectively. Note that the exposed part of the embedded probe was completely glass-sealed so that exchange of oxygen between the embedded probes and air

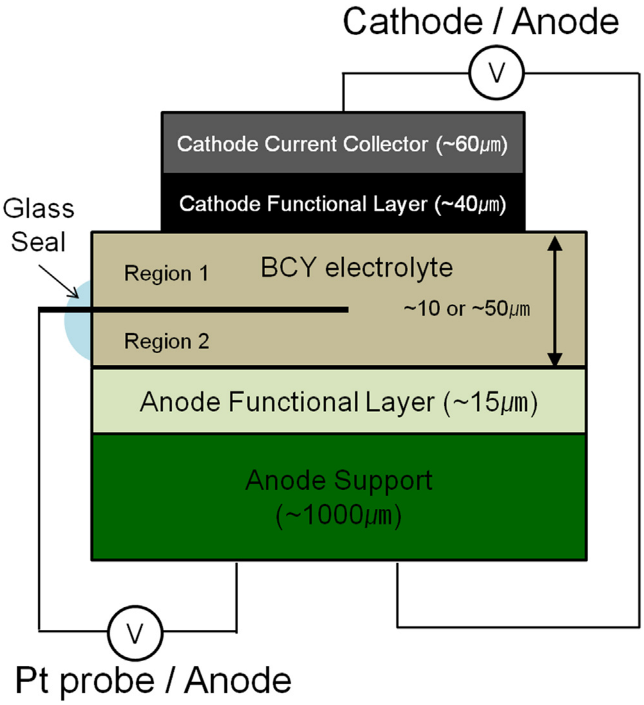

Fig. 1. Schematic of anode-supported BCY-based cell with an embedded Pt probe.