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A high-performance ammonia-fueled solid oxide fuel cell

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Abstract

Solid oxide fuel cells (SOFCs) with the construction of Ni-$BaCe_{0.8}Gd_{0.2}O_{2.9}$ (BCGO)/BCGO/$La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSCO)–BCGO are reported. With commercial liquefied ammonia directly used as the fuel, the performance of a single cell was tested from 600 to 750 °C. The OCV was 1.102 and 0.985 V at 600 and 700 °C, respectively, which is fairly consistent with the theoretical values calculated on the assumption of ammonia completely decomposing. Also a useful power density was achieved; the maximum power density was 355 mW cm^{-2} at 700 °C. For comparison, cells were also tested with hydrogen as the fuel and CO_2-free air as the oxidant at 700 °C, where the power density was about 371 or 324 mW cm^{-2}. The performance of the cells tested under various conditions implied that ammonia might be a good fuel for a SOFC.

Keywords: Solid oxide fuel cell; Ammonia; Doped barium cerate; Thin film electrolyte

1. Introduction

Solid oxide fuel cells (SOFCs) have increasingly attracted interest as an advanced power generation device with high energy conversion efficiency, low environment impact and good fuel flexibility. Portable applications of SOFCs are hardly practical because of the high price and low volumetric energy density of hydrogen, although it has been widely employed as the fuel for SOFC. Hydrocarbons, such like alcohols and liquefied petroleum gas, are easy to transport and have low cost, and hence are good candidates for fuels for SOFCs. But a severe coking problem has occurred with the traditional Ni anode, which has reduced the performance and long-term stability of SOFCs. Replacements for Ni have been explored to solve the coking by many researchers, but little progress has been made. Exploring possible alternative fuels may be a way to commercialize SOFCs.

Ammonia is a good hydrogen carrier, and might be a fine substitute for hydrogen and hydrocarbons for the following reasons. Firstly, the price of ammonia is as competitive as hydrocarbons. Secondly, ammonia can be easily liquefied under about 10 atm at ambient temperatures or at −33 °C under atmosphere pressure, and the volumetric energy density of liquefied ammonia is about 9×10^6 kJ m^{-3}, higher than that of liquid hydrogen, which is useful in transport and storage [1]. Thirdly, ammonia is less flammable compared with the other fuels and the leakage of ammonia can be easily detected by the human nose under 1 ppm. Fourthly, and most importantly, there are no concerns about anode coking, since all the by-products of the electrode reaction will be gaseous. All of the above imply that ammonia could be a candidate for a liquid fuel for SOFCs, at least at the present stage when the coking problem of hydrocarbon fuels has not yet been resolved.

Until now, little attention has been devoted to an ammonia-fueled SOFC. Wojcika et al. [2] made the first attempt to fuel an yttrium-stabled zirconia (YSZ) based SOFC with ammonia, and obtained a maximum power density of about 50 mW cm^{-2} at 800 °C. But in the SOFCs based on a oxygen-ion conducting electrolyte, such as YSZ, oxygen ions transport from the cathode to the anode and toxic NO may be produced:

$$2NH_3 + 5O^{2-} = 2NO + 3H_2O + 10e^-$$

Applying proton conductors (such as doped $BaCeO_3$) to the electrolyte is a proper way to avoid NO production. With the proton transferring from the anode to the cathode, H_2O is produced at the cathode while N_2 is produced at the anode. Maffei et al. [3] sketchily investigated the performance of the ammonia-fueled SOFCs based on a doped $BaCeO_3$ electrolyte. But due to the

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inappropriate cell configuration, the maximum power density was less than 40 mW cm^{-2} (700 °C).

In the present work, SOFCs based on a Gd-doped $BaCeO_3$ thin layer were prepared. And the cell performance with commercial liquefied ammonia as the fuel and oxygen as the oxidant was examined. To better explore the feasibility of ammonia as a fuel for SOFCs, the characteristics of a cell fueled by H_2 and a cell with CO_2-free air as the oxidant were also studied.

2. Experimental

$BaCe_{0.8}Gd_{0.2}O_{2.9}$ (BCGO) powders with active sinterability were synthesized by a modified glycine-nitrate process with stoichiometric precursors of $Ba(CH_3COO)_2$, $Ce(NO_3)_3$ and $Gd(NO_3)_3$, as detailed in the foregoing literature [4].

Composite anode powders were made by blending BCGO with NiO in the weight ratio of 35–65. Layers of composite anode substrate and BCGO electrolyte film were fabricated by the dry-pressing method, in which the thickness was controlled at 650 and 50 μm after co-firing at 1400 °C for 5 h, respectively.

A graded cathode was prepared on the electrolyte surface by screen-printing with a slurry made of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSCO) and BCGO powders. Adjacent to the electrolyte surface, the weight ratio of BCGO to LSCO was appointed at 6:4, and then was changed to 4:6. Single cells were achieved after calcinations at 1050 °C for 3 h. Ag paste was applied onto both electrodes as the current collectors.

Cells were tested from 600 to 750 °C in a home-developed cell-testing system. Commercial liquefied industrial ammonia and humid oxygen (~3% H_2O) was designated as the fuel and oxidant, respectively. Digital multi-meters (GDM-8145) were used to collect voltage and current data of the cells. A scanning electron microscope (SEM, JSM-6700F) was employed to observe the microstructure of the cells after test.

To better explore their characteristics, the cells were also operated with hydrogen as fuel and oxygen as oxidant, or ammonia as the fuel and CO_2-free air (produced by filtrating from NaOH solution, with ~3% H_2O) as the oxidant, respectively.

3. Results and discussion

In this work, commercial liquefied ammonia was directly imported into the anode apartment, where it decomposed into nitrogen and hydrogen, not only as fuel but also as the reduction agent for NiO:

$$2NH_3(g) + 3NiO(s) = N_2(g) + 3Ni(s) + 3H_2O(g)$$

Cells were operated at various temperatures with oxygen as the oxidant, and the corresponding electrode reactions are:

$$\text{Anode}: 2NH_3 + 6O_O^{x} = N_2 + 6OH_O^{\bullet} + 6e^-$$

$$\text{Cathode}: 4OH_O^{\bullet} + O_2 + 4e^- = 2H_2O + 4O_O^{x}$$

Fig. 1 presents open circuit voltages (OCVs) of the cell at different temperatures, after NiO was completely reduced. The broken lines indicate the theoretical values calculated from the Nernst equation, with the assumption that ammonia is completely decomposed into nitrogen and hydrogen. The OCV reached was 1.102 V at 600 °C, close to the theoretical value (about 1.173 V), indicating the compaction of the BCGO film (no porosity), the efficient decomposing ratio of ammonia and the pure ion conduction at the testing temperature. But the differences between the tested OCVs and the theoretical ones grow with increase of temperature. At 750 °C, the OCV was 0.963 V, about 0.2 V lower than the theoretical value. Noticing that there should be no density change for the BCSO thin film (Fig. 3), and that the ammonia-cracking reaction is positive at the elevated temperature, this implies that the change of hydrogen partial pressure should not be a factor to reduce the OCV at relative high temperatures, and that the decrease of the OCV was most probably due to the increase of electron conduction, which is also consistent with the literature [5–7].

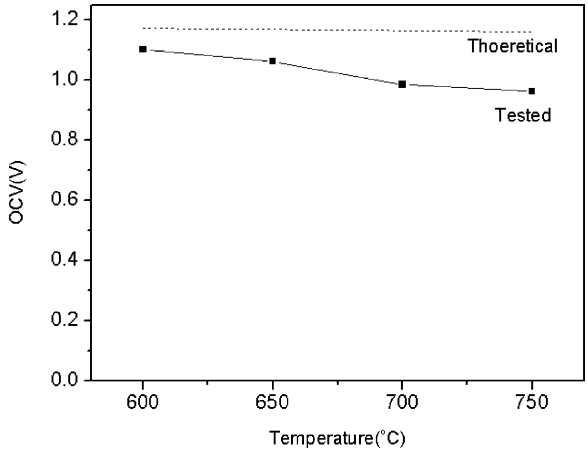

Fig. 1. OCVs of the cell with ammonia as fuel and oxygen as oxidant at different temperatures.

The performance of the cell is shown in Fig. 2. The maximum power densities stepped steadily from 600 to 700 °C, about 96, 184 and 355 mW cm^{-2} at 600, 650 and 700 °C, respectively. But the maximum power density at 750 °C was 384 mW cm^{-2}, and no marked enhancement was observed. The reasons for this

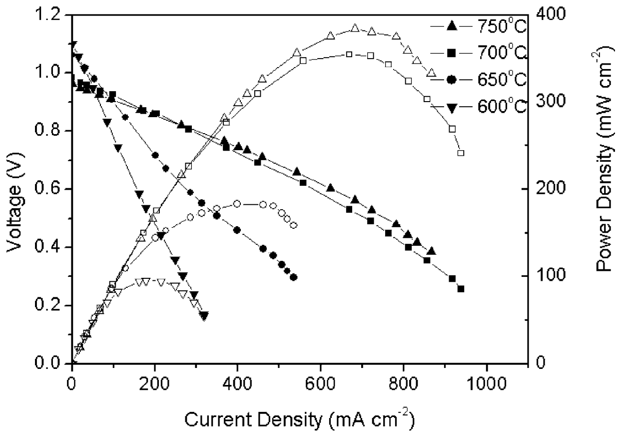

Fig. 2. Cell voltage (solid) and power density (hollow) as a function of current density for the cells, with ammonia as the fuel and oxygen as the oxidant at different temperatures.

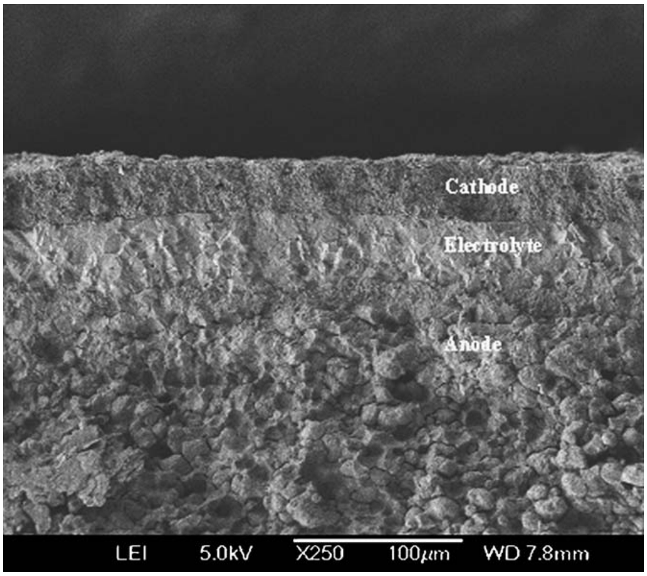

Fig. 3. Cross-sectional image of the tested cell with LSCO–BCGO, BCGO and Ni-BCGO from top to bottom.

phenomenon might be complicated, but the competition between a decrease of internal resistance and an increase in the electron conduction with the increasing temperature might be important.

Fig. 3 shows a cross-sectional view of a tested cell with the structure: Ni-BCGO/BCGO/LSCO–BCGO. The BCGO film was about 50 μm thick, quite dense, uniform and adhered very well to the Ni-BCGO anode substrate and the LSCO–BCGO cathode. Further improvement in cell performance could be expected with the optimization of the electrode microstructure.

To better explore the feasibility of ammonia as a substitute fuel for SOFC, cells were also tested with hydrogen as the fuel at 700 °C, and the results are shown in Fig. 4. With oxygen as the oxidant, the OCV was 0.996 V, about 0.01 V higher than that with ammonia as the fuel. The trivial improvement of OCV might come from the higher hydrogen pressure since no N_2 was produced on the anode in this case. It should be noted that the two *I–V* curves in Fig. 4 possess a similar slope, and similar power densities were also achieved, indicating the decomposing of ammonia was not a rate-determining step for the whole cell reaction. The close performance of cells fueled by ammonia and hydrogen suggest that ammonia has a potential as the substitute fuel for H_2. The maximum power density was 371 mW cm^{-2} with H_2 as fuel.

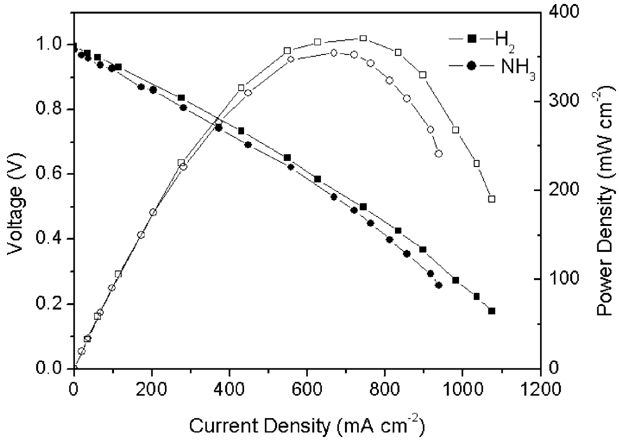

Fig. 4. *I–V* (solid) and *I–P* (hollow) curves of the cell fueled by ammonia (●) and hydrogen (■) at 700 °C with oxygen as the oxidant.

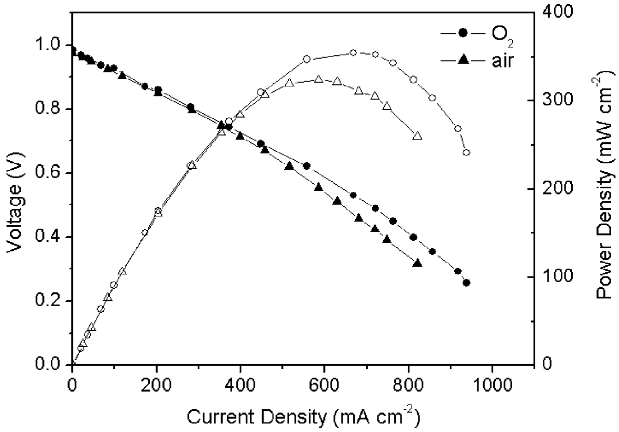

Fig. 5. At 700 °C, *I–V* (solid) and *I–P* (hollow) curves of the cell fueled by ammonia with oxygen (●) and CO_2-free air (▲) as the oxidant, respectively, with ammonia as the fuel.

Air, not oxygen, is of more practical application. Yet the CO_2 in the atmosphere might be harmful to the BCGO electrolyte due to the formation of poorly conductive $BaCO_3$ [8]. In this work, CO_2-free air was adopted as the oxidant, and the cells were tested at 700 °C with ammonia as the fuel, as illustrated in Fig. 5. The OCV was 0.975 V, about 0.01 V lower than that with oxygen as the oxidant due to the lower oxygen partial pressure. The maximum power density of the cell was 324 mW cm^{-2}. The high performance of the cell with industrial ammonia as the fuel and air free of CO_2 as the oxidant gives light to the actual utility of SOFC with a liquid fuel. The long-term performance of cells with a direct air oxidant will be investigated in our later work.

4. Conclusions

A $BaCe_{0.8}Gd_{0.2}O_{2.9}$ thin film based single cell with the structure:Ni-BCGO/BCGO/LSCO–BCGO was prepared and tested with commercial liquefied ammonia as the fuel and oxygen as the oxidant. The decomposition of ammonia was both sufficient and fast in the anode chamber, and the OCV and maximum power density were 0.985 V and 355 mW cm^{-2} at 700 °C, respectively, indicating practical usefulness. Comparisons of cells with hydrogen as the fuel or CO_2-free air as the oxidant both showed similar performance, indicating good feasibility for ammonia as the fuel for SOFCs.

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