Available online at www.sciencedirect.com
ScienceDirect
Journal of Power Sources 164 (2007) 86–89
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

A high-performance ammonia-fueled SOFC based on a YSZ thin-film electrolyte

Qianli Ma, Jianjun Ma, Sa Zhou, Ruiqiang Yan, Jianfeng Gao, Guangyao Meng*

Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China

Received 9 August 2006; received in revised form 4 September 2006; accepted 15 September 2006
Available online 28 November 2006

Abstract

Ammonia is a possible candidate as the fuel for solid oxide fuel cells (SOFCs). In this work, an anode-supported SOFC based on yttrium-stabled zircite (YSZ) thin-film electrolyte was fabricated by a simple dry-pressing process. Directly fueled by commercial liquefied ammonia, the single cell was tested at temperatures from 650 to 850 °C. The maximum power densities were 299 and 526 mW cm^{-2} at 750 and 850 °C, respectively, only slightly lower than that fueled by hydrogen. Analysis of open current voltages (OCVs) of the cell indicated the oxidation of ammonia within a SOFC is a two-stage process. Impedance spectra showed the cell fueled by ammonia had the same electrolyte resistances as that fueled by hydrogen, but a little larger interfacial polarization resistances. Further, the performances of the cell were essentially determined by the interfacial resistances under 750 °C.

Keywords: Solid oxide fuel cells; Ammonia; YSZ; Dry-pressing; AC impedance

1. Introduction

In association with the hydrogen economy, fuel-cell technology has been strongly promoted by governments of most of the world's leading industrialized nations. Of the various fuel cell types, solid oxide fuel cells (SOFCs) combine the benefits of high energy efficiency with fuel flexibility and have a very promising future.

For widespread commercialization of SOFCs, fuels should be properly selected. An eligible fuel for SOFCs is supposed to be cheap, safe, pollution-free, have no electrode contamination and be easy to store and transport. A typically used performance criteria for fuels are gravimetric and volumetric densities of hydrogen storage [1]. Table 1 shows relative values along with storage conditions of various fuels. Clearly, pound for pound, hydrogen is the best choice. Unfortunately, it also has the lowest volumetric density, and it has to be stored under the pressures of above 250 atm, which greatly increases the cost of storage and transportation. Also, the requirement of storage for liquid hydrogen is too severe, and the gravimetric density of metal hydride is too small. So comparatively, hydrocarbons in a liquid state are the better choice, especially in consideration of storage and transportation. However, the conventional Ni anode of SOFCs will cause them a severe coking problem, although recently more and more works were devoted to new anode research and many achievements were made [2,3], there still exist problems like insufficient catalysis activity, high cost, etc.

Ammonia may be a suitable choice. Of all the listed fuels, ammonia has the best volumetric density and a rather good gravimetric density of H_2 storage; the gentle requirements for liquefaction (10 atm or −33 °C) present a cheap and convenient way for storage and transportation, therefore ammonia is particularly suitable for small-scale portable systems. Moreover, the conventional Ni anode of SOFCs happens to be an excellent catalyst for ammonia decomposition, the by-products of cell reaction are merely nitrogen and water, no greenhouse gases are emitted as with hydrocarbons and there are no concerns about anode coking. Although ammonia is toxic, the leakage of which is easily sensed by the human nose below a concentration of 1 ppm, so there are no severe safety concerns.

As an indirect fuel for fuel cells operated at low temperatures, ammonia has been extensively researched [4–9], but there are significant barriers to be overcome for successful commer-

---

* Corresponding author. Tel.: +86 551 3603234; fax: +86 551 3607627.
E-mail address: mgym@ustc.edu.cn (G. Meng).

0378-7753/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2006.09.093

Table 1
Comparative properties of SOFCs fuels

Fuel	Storage conditions	Volumetric densities (mol l^{-1} H_2)	Gravimetric densities (wt% H)
Ammonia (NH_3)	1 atm at −33 °C or 10 atm at 20 °C	60	17.6
Gaseous hydrogen (H_2)	250 atm	10	100
Liquid hydrogen (H_2)	−253 °C	35	100
Metal hydride (Mg_2NiH_x)	Normal temperature and pressure	39	3.6
Methanol (CH_3OH)	Normal temperature and pressure	49	12.5
Nature gas (CH_4)	250 atm	21	25
Gasoline (C_8H_{18})	Normal temperature and pressure	55	15.8

cial implementation. Direct utilization of ammonia in SOFCs should be more seriously considered, but there are only a few reports in this area. Wojcika et al. [10] first tried to directly fuel yttrium-stabled zircite (YSZ) based SOFCs with ammonia. With Pt as the electrodes, a maximum power density of 50 mW cm^{-2} was obtained at 800 °C. Staniforth and Ormerod [11] indicated that ammonia completely decomposed at the Ni-YSZ anode at 600 °C, and no nitrogen oxide was produced at the anode when oxygen-ions transferred from cathode to anode. Some proton-conducting SOFCs also have been investigated [12,13], but as a more mature commercialized system, YSZ based SOFCs still deserve further investigations.

Dry-pressing is a simple, reproducible, and cost-effective method for thin film fabrication, in which the thickness of the thin film can be easily controlled by adopting suitable amount of the powders. In this paper, in order to raise the cell performance to a practical-using level, YSZ thin film was prepared on Ni anode by dry-pressing method, with ammonia and hydrogen as fuels, the electric properties of a single cell are reported.

2. Experimental

Optimized anode powders consisted of 40 wt% nanosized commercial YSZ (Y_2O_3 8 mol%, with a crystallite size of about 50 nm, Jiaozuo China) and 60 wt% NiO decomposed by analytical-grade $Ni(HCO_3)_2$ at 400 °C were used in this work. Powders of electrolyte were also the nanosized commercial YSZ mentioned above. NiO and YSZ powders were blended and pressed under 100 MPa as a green substrate with 15 mm in diameter and 0.5 mm in thickness. Proper amount of YSZ powders and the substrate were then co-pressed at 250 MPa to form a green bilayer and subsequently co-fired at 1400 °C in air for 4 h to densify the YSZ film. The thickness of the electrolyte was controlled at 30 μm. Cathode was prepared on the electrolyte with a screen-printing technique using slurry made of equal amount of $La_{0.5}Sr_{0.5}MnO_3$ (LSM) and YSZ powders. Single cells were achieved after calcinations at 1100 °C for 2 h. Ag paste was applied onto both electrodes as current collectors. Shown in Fig. 1 is the typical microstructure of the cell, as reviewed using a scanning electron microscope (SEM, Hitachi X-650).

Single cells were tested from 650 to 850 °C in a home-developed-cell-testing system with humidified hydrogen or commercial liquefied ammonia (∼3% H_2O) as fuels and air as oxidant, respectively. Fuel-cell performances were measured with digital multimeters (GDM-8145). AC impedance spectroscopy (Chi604a, Shanghai Chenhua) was performed on the cell under open-current conditions from 600 to 850 °C.

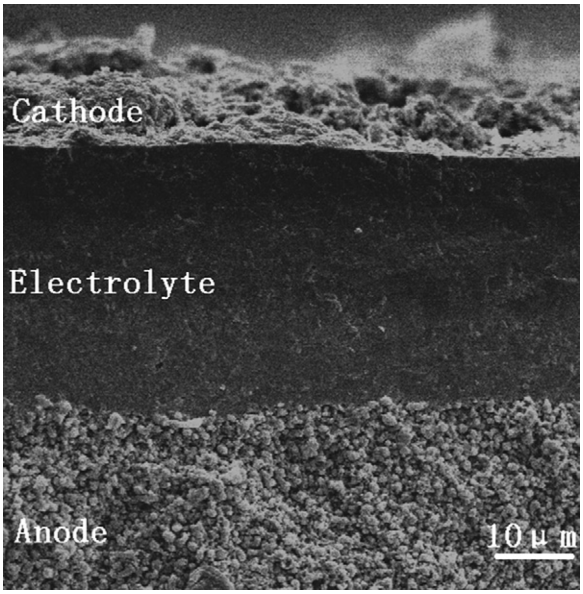

Fig. 1. Cross-sectional image of the tested cell with LSM-YSZ, YSZ and Ni-YSZ from top to bottom.

3. Result and discussion

It was believed that ammonia could completely decompose at 600 °C on Ni anode [11], but in this work, ammonia could not be directly used as the fuel at 600 °C without H_2 pre-reducing because the reduction process of NiO in ammonia was too slow. Only at the temperature over 750 °C, could ammonia be directly imported into the anode apartment, not only as fuel but also as reduction agent for NiO:

$$2NH_3(g) + 3NiO(s) = N_2(g) + 3Ni(s) + 3H_2O(g) \qquad (1)$$

No hydrogen pre-treatment was needed, which is a benefit for practical applications.

Shown in Fig. 2 are the *I–P* and *I–V* curves for a single cell fueled with ammonia or hydrogen at different temperatures. Open current voltages (OCVs) were 1.08, 1.07 and 1.02 V for

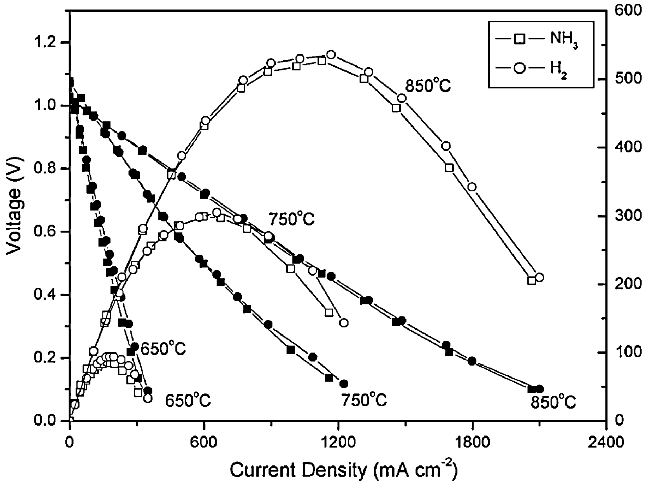

Fig. 2. Comparison of cell voltage (solid) and power density (hollow) as a function of current density between ammonia (■) and hydrogen (●) fueled single cell consisted of a Ni-YSZ anode, a YSZ electrolyte, and a LSM-YSZ cathode, tested at different temperatures with air as oxidant.

hydrogen, 1.08, 1.07 and 1.03 V for ammonia at 650, 750 and 850 °C, respectively; high OCVs indicate the hydrogen permeation through the electrolyte is negligible. The OCVs for ammonia decreased with increasing temperature, just as for hydrogen, which means that the oxidation of ammonia within an SOFC is not a one-stage process described in reaction (2):

$$4NH_3(g) + 3O_2(g) = 6H_2O(g) + 2N_2(g) \qquad (2)$$

Because the absolute value of ΔG° for reaction (2) is positive with increasing temperature, which means OCVs of SOFC fueled with ammonia should increase with operating temperature, but actually it is on the contrary. This suggests that the oxidation of ammonia within an SOFC may be a two-stage process, with decomposition of ammonia to nitrogen and hydrogen (3) occurring initially, followed by oxidation of hydrogen to water (4).

$$2NH_3(g) = N_2(g) + 3H_2(g) \qquad (3)$$

$$H_2(g) + O^{2-} = H_2O(g) + 2e^- \qquad (4)$$

Only reaction (4) is effective for the cell performance, so the change of OCVs is consistent with the thermodynamics of hydrogen oxidation. This result is also accordant with the former literature [11]. The OCV values for ammonia and hydrogen as fuels are almost the same at each different temperature, although the hydrogen partial pressure should be higher for hydrogen as the fuel since no N_2 is produced on anode simultaneously, the reason needs further research.

Maximum power densities were 86 and 94 mW cm^{-2} at 650 °C, 299 and 305 mW cm^{-2} at 750 °C, and 526 and 530 mW cm^{-2} at 850 °C, with ammonia and hydrogen as fuels, respectively. The cell performances for ammonia and hydrogen as the fuel are quite close at all tested temperatures, which suggests that ammonia is a good substitute for H_2, and the high power density of over 500 mW cm^{-2} is the best performance of all the reported ammonia-fueled fuel cells, which has a potential to be used in practice.

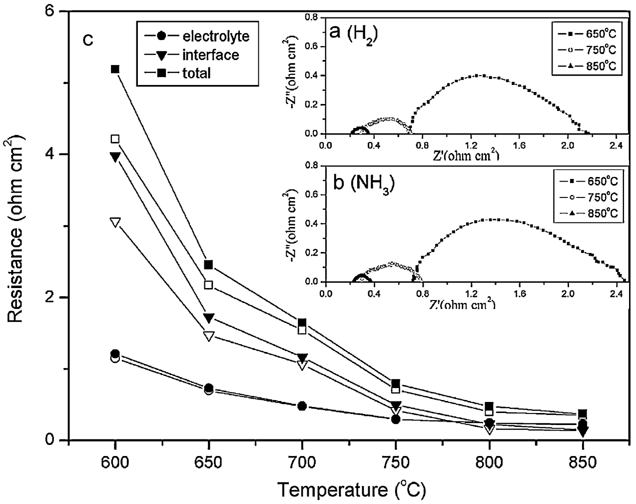

Fig. 3. Comparisons of impedance spectra between the cell fueled by hydrogen (a) or ammonia (b) under open-current conditions at different temperatures, and comparisons of the interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra between the cell fueled by hydrogen (hollow) or ammonia (solid) (c).

Shown in Fig. 3 are comparisons of impedance spectra between the cell fueled by hydrogen or ammonia under open-current conditions at different temperatures, the left intercept with the real axis of each depressed semicircle represents the electrolyte resistance, and the diameter of the depressed semicircle corresponds to the interfacial polarization resistance. The interfacial polarization resistances, electrolyte resistances, and total resistances of the cell are also compared with each other as determined from the impedance spectra. The differences of electrolyte resistances between hydrogen and ammonia as the fuel were almost negligible, which means the conductivity of YSZ remains to be same in the two fuels. But the interfacial polarization resistances had slight differences, especially at lower temperatures. This may be because ammonia-cracking process is slower at lower temperatures, which raises the electrode polarization. The trivial decrease of cell performance with ammonia as the fuel compared with hydrogen may also come from ammonia decompositions (see Fig. 2). Further, Fig. 3 shows that the cell performance is influenced by the interfacial resistances, especially at temperatures below 750 °C, where the cell performance is essentially determined by the interfacial resistances. It is believed improvement in cell performance can be expected when the electrode microstructure is further optimized.

4. Conclusions

A YSZ thin film based single cell consisting of Ni-YSZ/YSZ (30 μm)/LSM-YSZ was prepared by a dry-pressing process. Directly fueled by ammonia, the OCV and maximum power density of 1.03 V and 526 mW cm^{-2}, respectively, were obtained at 850 °C, only slightly lower than those of hydrogen, showing significant practicality. The oxidation of ammonia within an SOFC is a two-stage process: ammonia cracking and oxidation of the hydrogen to water. The cell fueled by ammonia had the same electrolyte resistance but a little larger interfacial polarization resistance as that fueled by hydrogen, and the performances of the cell were essentially determined by the interfacial resistances under 750 °C.

Acknowledgement

The authors wish to acknowledge funding for this project from Specialized research fund for the doctoral program of higher education (20040358025) and National Natural Science Foundation of China (50572099).

References

[1] S. Hynek, W. Fuller, J. Bentley, Int. J. Hydrogen Energy 22 (1997) 601.
[2] S.W. Tao, J.T.S. Irine, J. Electrochem. Soc. 151 (2004) 252.
[3] Z.P. Shao, S.M. Haile, Nature 143 (2004) 170.
[4] L.X. Li, J.A. Hurley, Int. J. Hydrogen Energy, in press.
[5] R.Z. Sørensen, L.J.E. Nielsen, S. Jensen, O. Hansen, T. Johannessen, U. Quaade, C.H. Christensen, Catal. Commun. 6 (2005) 229.
[6] S.F. Yin, B.Q. Xu, X.P. Zhou, C.T. Au, Appl. Catal. A 277 (2004) 1.
[7] N. Sifer, K. Gardner, J. Power Sources 132 (2004) 135.
[8] T.V. Choudhary, C. Sivadinarayana, D.W. Goodman, Chem. Eng. J. 93 (2003) 69.
[9] A.S. Chellappa, C.M. Fischer, W.J. Thomson, Appl. Catal. A 227 (2002) 231.
[10] A. Wojcika, H. Middletona, I. Damopoulosa, J.V. Herleb, J. Power Sources 118 (2003) 342.
[11] J. Staniforth, R.M. Ormerod, Green Chem. 5 (2003) 606.
[12] Q.L. Ma, R.R. Peng, Y.J. Lin, J.F. Gao, G.Y. Meng, J. Power Sources 161 (2006) 95.
[13] N. Maffei, L. Pelletier, J.P. Charland, A. McFarlan, J. Power Sources 140 (2005) 264.