Short communication

Comparative study on the performance of a SDC-based SOFC fueled by ammonia and hydrogen

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Abstract

A nickel-based anode-supported solid oxide fuel cell (SOFC) was assembled with a 10 μm thick $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) electrolyte and a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) cathode. The cell performance was investigated with hydrogen and ammonia gas evaporated from liquefied ammonia as fuel. Fueled by hydrogen the maximum power densities were 1872, 1357, and 748 mW cm^{-2} at 650, 600, and 550 °C, respectively. While with ammonia as fuel, the cell showed the maximum power densities of 1190, 434, and 167 mW cm^{-2}, correspondingly. The power densities lower than that predicted, particularly at the lower operating temperatures for ammonia fuel cell, compared to hydrogen fuel cell, could be attributed to actual lower temperature than thermocouple display due to endothermic reaction of ammonia decomposition as well as the rather larger inlet ammonia flow rate. The results demonstrated that the ammonia was a right convenient liquid fuel for SOFCs as long as it was keeping the decomposition completion of ammonia in the cell or before entering the cell.
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1. Introduction

Solid oxide fuel cells (SOFCs) have been extensively studied as advanced power generation devices because of their high-energy conversion efficiency, low environment impact, and good fuel flexibility [1]. The great progress in R&D of SOFCs has been made by developing new materials of high performance and proper techniques to fabricate thin electrolyte membrane on porous anode support in order to reduce operation temperatures to 500–750 °C (IT-SOFCs) to overcome or avoid the problems met in high-temperature (>950 °C) SOFCs. For instance, Liu et al. [2] recently reported a maximum power density of 1329 mW cm^{-2} at 600 °C for a cell with a thin (10 μm) of Gd-doped ceria (GDC) electrolyte on anode support and with H$_2$ as fuel. The development of practical devices, however, is being still hindered by some problems, including the coking on the well-developed nickel-based anode when using hydrocarbon fuels that severely degrade the cell performance. The obvious

route to avoid coking problem is to try using carbon-free fuels. Industrially available liquid ammonia is certainly a carbon-free SOFCs fuel with high content of H$_2$ and is favorable due to on-site hydrogen generation on the catalysis of nickel-based and Pt anode in the ordinary operation temperatures of 500–900 °C [3,4].

In 1980, Farr and Vayenas [5] first reported the application of ammonia fuel to YSZ electrolyte-based fuel and found NO was the primary production with Pt electrode. And then, much attention on ammonia fuel was diverted to proton conducting solid electrolyte-based fuel cell [6–8]. The investigations made by Wojcik et al. [9] showed that no nitric oxide was formed by incorporating iron-based catalysts into a silver anode, which gave new information on the application of ammonia fuel on SOFCs. Recently, our group successfully attempted to use liquid ammonia as fuel for IT-SOFCs with both proton conductive electrolytes, $BaCe_{0.8}Gd_{0.2}O_{2.9}$ [10] or oxide ion conductive $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) [11] and YSZ electrolyte [12]. Originally, we were worrying if NO$_x$ might be formed in the anode compartment of the SDC- or YSZ-based cells because of NH$_3$ containing nitrogen. Actually, no NO$_x$ was detected in the anode-off gas by gas chromatography during the cell operation [12]

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that is consistent with the theoretical prediction: the oxide ions (O^{2-}) coming from the cathode side through electrolyte are not as active as oxygen atoms and hardly oxidize the N_2 to form NO_x. The maximum power densities of the cell based on SDC [11], however, were only 271.2 and 252.8 mW cm^{-2} at 700 °C for hydrogen and ammonia fuel, respectively. The rather poor performance and the unexpected smaller difference in the power densities for H_2 and NH_3 fuels are apparent due to the poor cell structure, such as thick SDC electrolyte (50 μm) and the lower catalysis activity of the cathode materials.

In this study, a much improved cell with SDC electrolyte of only 10 μm thickness and using an efficient catalyst of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) cathode was assembled to investigate its performance, particularly to compare the behavior using hydrogen and ammonia fuel in order to further verify the applicability of liquid ammonia fuel for SOFCs.

2. Experimental

2.1. Preparation of the ceramic powders involved

All the powders required in this work were synthesized by a glycine-nitrate process. Sm_2O_3 and $Ce(NO_3)_3 \cdot 6H_2O$ were the starting materials for the synthesis of the electrolyte $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) powder. The glycine was added to the mixture of samarium and cerium nitrates maintaining total metal ions to glycine ratio at 1:1.5. The synthesis process was conducted on a hot plate. The precursor solution was heated until a highly viscous gel was formed. And then the gel swelled and ignited, resulting in a voluminous SDC powder. The resulting ash-like powders were subsequently calcined at 600 °C for 2 h. The synthesis process of the anode and cathode powders, NiO and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), was similar to that of SDC powder. To obtain pure-phase powders, the primary NiO and BSCF powders obtained after auto-ignition were calcined at 600 and 800 °C for 2 h, respectively.

2.2. Preparation and testing of the cells

The anode materials were prepared by mixing NiO and SDC powders in the 50 wt.%. A bi-layer of SDC electrolyte and anode support was co-pressed into disks of 15 mm in diameter and then co-fired at 1400 °C for 5 h. The subsequent layer of a BSCF cathode with an effective area of 0.25 cm^2 was screen printed onto the surface of the electrolyte and was then sintered at 950 °C for 2 h.

The performance of the cells was tested in a self-assembled setup as shown in Fig. 1. The cell was sealed on the top of an alumina tube, which was placed in a programmable furnace with a thermocouple near the cell and outside of the alumina tube to control and record the cell operation temperatures. The cell output voltage and current are measured and recorded using digital multi-meters (GDM-8145) at a temperature of 550–650 °C with hydrogen or ammonia as fuel and static air as the oxidant.

AC impedance spectra measurements were carried out on a cell using electrochemical impedance spectrum analyzer (CHI 600A, Chenhua Inc., Shanghai) in the frequency range of
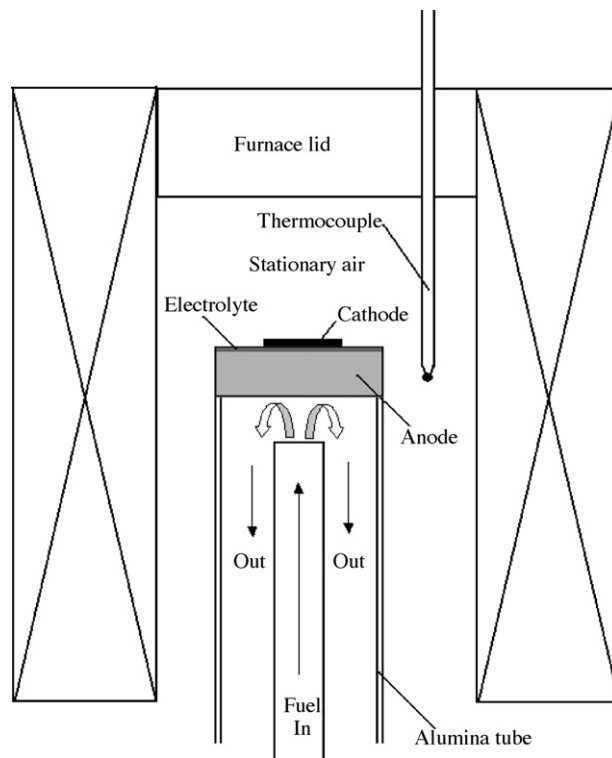

Fig. 1. Configuration for the cell performance measurement.

1.0–100 kHz with a signal amplitude of 5 mV under open-circuit conditions. Scanning electron microscopy (SEM, KYKY 1010B) was employed to observe the microstructure of a cell before and after testing.

3. Results and discussions

Fig. 2 shows the performance of a cell with hydrogen fuel. As can be seen, the cell with hydrogen fuel exhibited the open-circuit voltages (OCVs) of 0.747, 0.787, 0.816 V (Fig. 2), respectively, at 650, 600, and 550 °C, which are in good agreement with our last paper [13]. These OCV values showed a decrease in tendency with temperature increase,
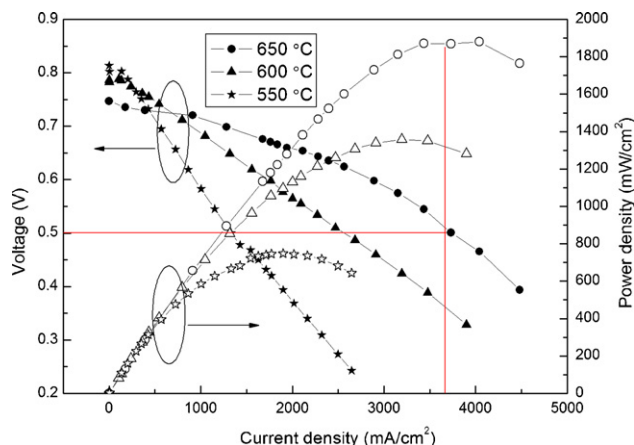

Fig. 2. Cell performance with hydrogen fuel at various temperatures. The solid symbols correspond to the cell voltage and open symbols to power density.

which is just the behavior predicted by electric moving force (EMF to which OCV is very close) expression of the cell, $EMF = E^0 + (\Delta S/nF)(T - T_0)$ (E^0 is the theoretical voltage under standard-state conditions, ΔS is the reaction entropy, n is the number of moles of electrons transferred, F is the Faraday's constant, T is the arbitrary temperature, and T_0 is 298.15 K) where $\Delta S > 0$ for the total cell reaction: $H_2 + (1/2)O_2 = H_2O$. The lower OCV values compared with that of the cell in previous work [4] might be due to the higher partial electronic conduction of SDC electrolyte with very thin thickness under the testing condition.

As can be seen from Fig. 2, the cell performance is fairly high. The maximum power densities of the cell reached $1872 \, mW \, cm^{-2}$ at 650 °C and $748 \, mW \, cm^{-2}$ at 550 °C. The power density at 600 °C is $1357 \, mW \, cm^{-2}$, which is as high as the highest record known to date ($1329 \, mW \, cm^{-2}$ at 600 °C) reported by Liu et al. [2] for a cell based on a GDC thin electrolyte.

The V–I curves for SOFCs reported in literature, particularly for YSZ-based cells, commonly show a rapid drop in voltage at low current densities, as seen in ref. [14]. This is called as activation polarization that has been usually attributed to the slow reaction of oxygen molecule reduction into ions and mass transfer at the triple phase boundary of the cathode and electrolyte interface. We can see from Fig. 2 that the cell voltage drops slowly with the increase in current at low current densities. This means the activation and cathode polarization is quite small, indicating the high catalysis activity and the better compatibility with electrolyte and the cathode materials, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF). The result is fairly consistent with that reported by Liu et al. [2]. The V–I curve at 650 °C, however, showed a slight bending down when current density is higher than $3000 \, mA \, cm^{-2}$, indicating a behavior of the concentration polarization which may be reasonably attributed to the insufficient mass transfer process through anode structure under such a high current density. In principle, the maximum power density would occur at the cell voltage of OCV/2 that should be around 0.38 V for this cell at 650 °C. But the voltage for peak power density here is around 0.5 V. Thus, it is expected that the maximum power density might reach an even much higher value if the mass transfer process at anode is improved further and then the voltage for peak power density may be close to OCV/2.

The cross-sectional micrograph of the cell in Fig. 3(a) shows that the SDC electrolyte layer of only about 10 μm in thickness is well adhered to both the porous Ni-SDC anode and the cathode, almost without any cracks and noticeable pores. The very dense and thin SDC electrolyte membrane certainly played an important role to lower electrolyte resistance hence to achieve a higher power output. BSCF is a well-known cathode material with the highest catalysis activity known to date. As seen in Fig. 3(a) its thickness is only 6–8 μm and well coherent to SDC electrolyte which exhibits high oxygen ionic conductivity and partial electronic conduction, which ensures not only a high cathode catalysis but also the good mass transfer process electrochemically at the BSCF and SDC layer interface. This can explain the cell behavior of having almost no activation polarization and it is another major factor to bestow high performance to the cell. The magnified anode microstructure shown in
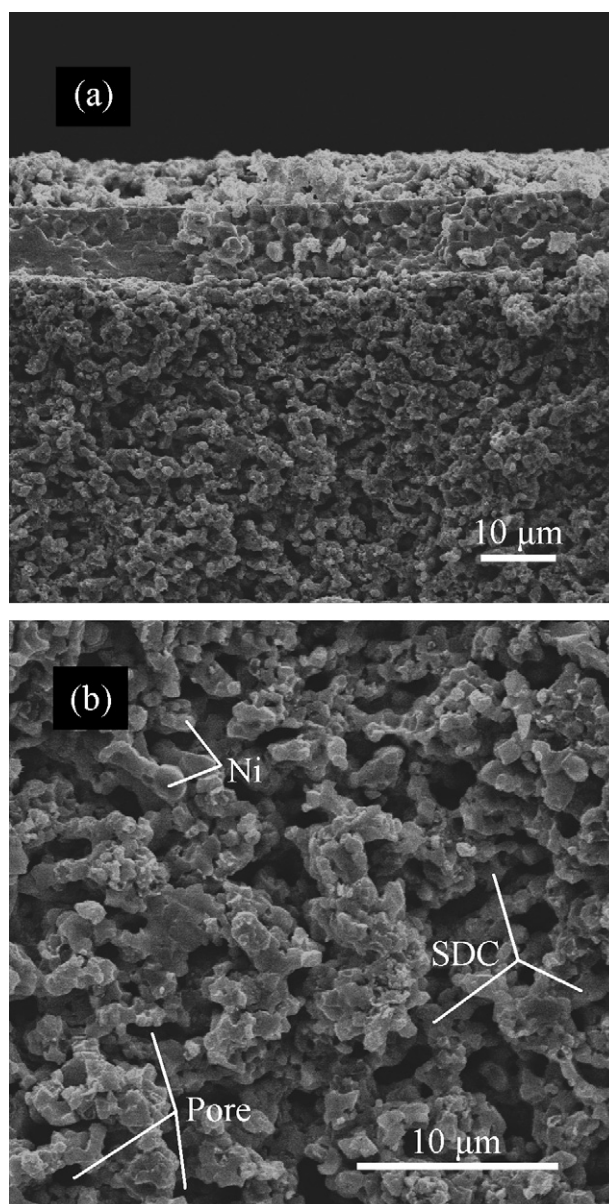

Fig. 3. (a) Cross-section micrograph of the cell after the cell testing and (b) the magnified anode microstructure of the anode.

Fig. 3(b) illustrates that the anode has sufficient porosity which was measured separately to be about 45%, and the SDC and Ni grains in sizes of 1–2 μm are of quite uniform distribution. This certainly also contributes to the high performance of the cell. As seen from the microstructure, however, the pores in the anode are around 1–3 μm which apparently is a little bigger than the optimized requirement (below 1 μm) and might imply that the gaseous mass transfer becomes dominant in anode process. This means that there is still a room to improve the anode microstructure and modify the active reaction sites, which would eliminate the anode concentration polarization and further increase the power density of the cells.

Fig. 4 presents the performance result for such a good cell fueled with ammonia instead of hydrogen. The OCV values at 650, 600, and 550 °C are, respectively, 0.768, 0.771, and 0.795 V,
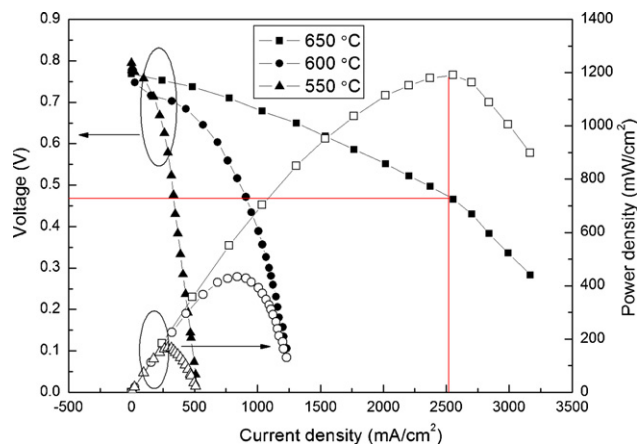
Fig. 4. Cell performance with ammonia as fuel at various temperatures. The solid symbols correspond to the cell voltage and open symbols to power density.

Fig. 5. Impedance spectra of the cell with H_2 fuel (star symbol) and NH_3 fuel (squares symbol) as fuel under open-circuit conditions.

which are close to but slightly lower than that from H_2 cell as mentioned above. This is also consistent with the theoretical prediction from the EMF expression of the cell with lower H_2 partial pressure in NH_3 feed anode compartment than that with pure H_2 as fuel. The *V–I* curve at 650 °C is quite normal but bends down at the current density of around 2500 mA cm^{-2} which is lower than 3000 mA cm^{-2} in the case of H_2 cell. This made the cell not reach the right cell voltage (about 0.39 V) for the maximum power density and the latter actually obtained was 1190 mW cm^{-2} which is 63.8% of the value for H_2 cell and obviously lower than the expected 75%, the H_2 partial pressure in ambient of completely decomposed NH_3. For the lower operation temperatures (600–550 °C) the *V–I* curves of the cell are even rather strange in that they fall down rapidly at quite small current densities and therefore the much lower peak power densities of 434 and 167 mW cm^{-2} far from the expected, respectively, at 600 and 550 °C are obtained. This phenomenon may be attributed to the incomplete decomposition of ammonia fuel in the anode compartment as well as the mass transfer behavior much different from the H_2-fueled cell.

The result reported in last paper [11,12] has already demonstrated that in ammonia-fueled SOFCs it is H_2 instead of NH_3 itself that enters the cell reaction. Thus, the most important step for NH_3 fuel cells is to completely decompose NH_3 into H_2 and N_2. The completeness of NH_3 converting into $H_2 + N_2$ is determined by a number of factors including NH_3 inlet flow rate, the temperature and catalysis surface area of the anode, etc. In the previous work it was found that at above 600 °C NH_3 could decompose completely (>99%) and its converting percent at 500 °C was only 79 and 95%, respectively, for the flow rates of 30 and 5 ml min^{-1} [4]. That is, the larger the inlet flow rate of NH_3 gas is, the less the decomposition percent of NH_3 is, as the process kinetically needs energy and time. In this work, the flow rate of inlet ammonia was about 40 ml min^{-1}, and NH_3 decomposition was probably not complete at 600 °C and even at 650 °C. And the power density of the cell at 650 °C lower than the expected value might be related to this point. In addition, during the time of the cell test, NH_3 gas evaporated from liquid ammonia was directly inlet into the cell with a rather large flow
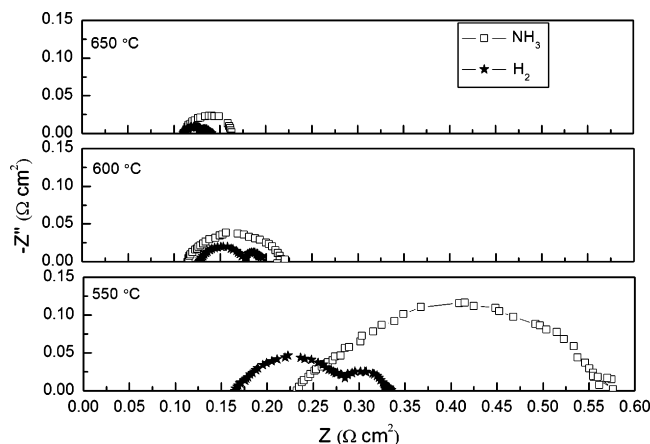
rate and decomposed into H_2 and N_2 in anode compartment. The process is certainly endothermic and therefore the temperature inside the cell was actually lower than outside where the thermocouple was placed (see Fig. 1). This means that the temperature recorded by thermocouple was higher than the real temperature in the cell anode compartment. And the difference may be much larger at a lower temperature. This might be the major factor for the lower cell performance of NH_3 fuel cell compared with H_2 fuel cell at below 650 °C mentioned above. The lower temperature and hence the adsorption of the undecomposed NH_3 molecules on the anode surface would severely block the mass transfer process to lead an abnormal behavior just like the concentration polarization that occurs at higher current densities. Based on the above result and analysis, the performance of the cells fueled with liquid ammonia may be readily improved by taking some measures such as lower NH_3 flow rate, pre-heating, larger anode compartment as well as relative higher cell temperature, to ensure the complete decomposition of the inlet NH_3 into H_2 and N_2.

Fig. 5 shows the impedance spectra of the cell with hydrogen and ammonia as fuel under open-circuit condition. It can be seen that the spectra for H_2 fuel cell consist of two semicircles, while for NH_3 cell the spectra reduced to a depressed single semicircle that is surely related to the anode process involving NH_3 that is different from the case in H_2-fueled cell. Ohmic electric resistance of the cell (R_e) and interfacial polarization resistance ($R_a + R_c$) can be obtained from the intercept with the real axis at high frequency range and the difference between low frequency and high frequency intercept with the real axis, respectively [15,16]. As listed in Table 1, the R_e and $R_a + R_c$ values of the cell with H_2 and NH_3 fuels at 650 and 600 °C are rather close to each other, while for the lower temperature (550 °C) the values for NH_3-fueled cell are twice than that of H_2-fueled cell. It is noted that the interfacial polarization resistance including anode/electrolyte (R_a) and cathode/electrolyte resistance (R_c) is greatly lower than ohmic resistance at 650 °C. While, with the temperature decrease, the interfacial polarization resistance increased only to a low 50% of total resistance ($R_T = R_e + R_a + R_c$) hence the cell performance was still fairly

Table 1
Ohmic resistance (R_e) and interfacial resistance ($R_a + R_c$) of the cell with hydrogen and ammonia as the fuel, obtained from AC impedance spectra

Cell (°C)	H$_2$		NH$_3$	
	R_e ($\Omega\,cm^2$)	$R_a + R_c$ ($\Omega\,cm^2$)	R_e ($\Omega\,cm^2$)	$R_a + R_c$ ($\Omega\,cm^2$)
650	0.111	0.03	0.111	0.05
600	0.128	0.07	0.116	0.10
550	0.166	0.17	0.232	0.33

high at 550 °C. This proved that BSCF is an efficient cathode material with high catalytic activity and good enough anode and cathode microstructure obtained in this work. In another paper, a cell consisting of SDC electrolyte and $Sm_{0.5}Sr_{0.5}Co_{3-\delta}$ (SSC) cathode exhibited a R_e of 0.089 and 0.095 $\Omega\,cm^2$ for $R_a + R_c$ at 650 °C [6]. The higher interfacial resistance than that in this work (0.03 $\Omega\,cm^2$) indicated the better cathode property of BSCF than SSC. Although the even thinner SDC electrolyte layer than that in this cell was deduced from its smaller R_e of 0.089 than 0.111 $\Omega\,cm^2$ the maximum power density of the cell was only 936 mW cm^{-2}.

The interfacial polarization resistances in NH$_3$ cell are higher than that in H$_2$ cell at all the operating temperatures, and the difference increased with the temperature decrease, which led to its lower cell performance compared to H$_2$-fueled cell. The much higher resistance to the motion of electrical carriers in NH$_3$-fueled cell is unlikely related to the existence of N$_2$ but probably due to the ammonia processing on the anode structure.

4. Conclusions

SOFC with a SDC electrolyte thin membrane of 10 μm on Ni + SDC anode support and a porous BSCF cathode of 6–8 μm in thickness was prepared and tested with liquid ammonia and H$_2$ as fuels. Though the OCV values of the cell were slightly lower than theoretical ones, the cell produced fairly high performance to get the maximum power densities of 1872 and 1190 mW cm^{-2} at 650 °C with hydrogen and ammonia fuel, respectively. The high performance can be attributed to the fairly optimized cell structure including the thin and dense electrolytes and highly uniform anode cermet as well as the highly efficient BSCF cathode layer. Both SEM observation and AC impedance spectra of the cell proved this point.

The relative lower power densities with NH$_3$ fuel at lower temperature (600 and 550 °C) were obtained compared with the cell with H$_2$ fuel. Based on the previous studies and the theoretical considerations, it has been attributed to the incomplete decomposition of NH$_3$ because of much lower anode temperature than the thermocouple display due to the endothermic effects from both decomposition of NH$_3$ with larger flow rate and the liquid ammonia evaporation. It is believed that the cell performance could be much improved by keeping the temperature, pre-treating ammonia or adjusting the NH$_3$ flow rate to fit the cell situation.

Acknowledgements

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