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# Direct utilization of ammonia in intermediate-temperature solid oxide fuel cells

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#### Abstract

Ammonia is considered to be one of the most promising candidates as the fuel for solid oxide fuel cells (SOFCs). In this work, nitrogen oxide formation was thermodynamically determined as a function of ammonia conversion rate and temperature. The result showed that more NO was formed at higher temperature. Therefore, ammonia was experimentally investigated as the fuel for an intermediatetemperature SOFC (IT-SOFC) consisted of a Ni–Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> (SDC) anode, an SDC (50 µm) electrolyte, and an Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3- $\delta$ </sub> (SSC)–SDC cathode. The components of anode off-gas were analyzed both theoretically and experimentally, especially for the possibility of nitrogen oxide formation. Performances of the cells fueled with ammonia and hydrogen were quite similar at the same temperatures. Maximum power densities were 168.1 and 191.8 mW cm<sup>-2</sup> at 600 °C with ammonia and hydrogen as the fuels, respectively. The electrode polarization resistances and electrolyte resistances of cells fueled by ammonia and hydrogen were characterized by AC impedance spectroscopy. The long-term endurance of cells in ammonia was also tested. © 2006 Elsevier B.V. All rights reserved.

Keywords: Solid oxide fuel cell; Ammonia; Doped ceria; AC impedance; Nitrogen oxide

# 1. Introduction

Nowadays exploring proper fuels seems to be crucial for the commercialization of solid oxide fuel cells (SOFCs) since there are significant difficulties for pure hydrogen and hydrocarbons, the now-extensively used fuels for SOFCs. Pure hydrogen is both expensive and hard to store or transport; hydrocarbons will cause a severe coking for traditional Ni anode of SOFCs, and little progress has been made to find replacements for Ni. Ammonia, a less concerned feedstock for SOFCs, is probably a fine substitute for hydrogen and hydrocarbons. Ammonia is commercially manufactured with Haber–Bosch process at temperatures around 450 °C and pressures about 250 atm.

 $N_2(g)$ +3 $H_2(g)$  $\leftrightarrow$ 2 $NH_3(g)$ +92.4 kJ

Very coincidently, nickel, the traditional anode material for SOFCs, is an excellent catalyst for this reaction. With ammonia as the fuel for SOFCs, there are no concerns about anode coking since all the by-products of electrode reaction are gaseous, and no greenhouse gas like CO<sub>2</sub> is emitted during the operation of a fuel cell. In consideration of output and cost, ammonia is produced in massive quantities by chemical industry, and its price is as competitive as hydrocarbons. Moreover, ammonia is safer than other fuels since it does not burn in air under common conditions, and its leakage can be easily detected by human nose under 1 ppm though it is usually regard as a toxic [1]. Furthermore, pure ammonia can be easily liquefied under 10 atm at ambient temperatures or at -33 °C under atmosphere pressure, which presents a cheap and convenient way for storage and transportation, and therefore is particularly suitable for portable systems. As to the volume energy density, ammonia has been compared with liquid fuels such as methanol and gasoline [2,3], the results

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indicate that ammonia can be a good candidate as a liquid fuel for SOFCs.

Wojcika et al. [4] fueled ammonia to a SOFC based on an yttrium-stabled zirconia (YSZ) electrolyte and Pt electrodes, maximum power density of about 50 mW cm<sup>-2</sup> was obtained at 800 °C. However, toxic NO<sub>x</sub> was suggested to be produced at the anode because of an overage oxidation problem:

$$2NH_3 + 5O^{2-} = 2NO + 3H_2O + 10e^{-1}$$

But no specific theoretical or experimental validation was carried out. To avoid NO generation, ammonia was fueled to an SOFC with a proton-conducting electrolyte [5]. In the proton-conductor based fuel cell, oxygen was theoretically unavailable at the anode side, and therefore, no possibility existed for NO formation. But whether NO generates with oxygen-ion conducting electrolytes still needs to be investigated. In this paper, both theoretical analysis and experiment demonstration were carried to investigate the NO generation. And the performance of ammonia fueled SOFCs with oxygen-ion electrolyte was also investigated.

# 2. Theoretical analysis

When transferred to the anode side of a cell that is heated to elevated temperature, ammonia cracks to  $H_2$ and  $N_2$  over Ni catalyst. The  $H_2$  is then oxidized to  $H_2O$ by oxide ions. The decomposition and oxidation reactions can be shown by (1) and (2), respectively.

$$2NH_3 = N_2 + 3H_2$$
(1)

$$H_2 + O^{2-} = H_2 O + 2e^-$$
(2)

And Eq. (3) gives the overall reaction,

$$4NH_3 + 3O_2 = 6H_2O + 2N_2 \tag{3}$$

Suppose the conversion rate of  $NH_3$  is the ratio of hydrogen attending the cell reaction (2) to hydrogen produced by reaction (1), so the partial pressure of  $H_2O$  can be calculated by Eq. (3) as function of conversion rate of  $NH_3$ . NO might be also generated through oxidation of  $N_2$  with oxygen ions, shown as Eq. (4),

$$N_2 + 2O^{2-} = 2NO + 4e^{-}$$
 (4)

Due to the competition of  $N_2$  and  $H_2$  for  $O^{2-}$ , a metathesis reaction can be written as Eq. (5),

$$H_2 + NO = H_2O + N_2 \tag{5}$$

Suppose that ammonia ( $\sim 3\%$  H<sub>2</sub>O) cracks completely over Ni catalyst at the operating temperature of SOFCs, and that negligible NO is produced at the working conditions of SOFCs in which H<sub>2</sub>O is the major products, partial pressure of NO could be thermodynamically valued as a function of ammonia conversion rate according to Eqs. (1)–(5).

Fig. 1 presents the calculated partial pressure of NO as the function of ammonia conversion rate at various temperatures. It can be clearly seen that partial pressure of



Fig. 1. Logarithm of NO pressure as a function of conversion rate of ammonia at different temperatures.

NO increases with the conversion rate of ammonia. That is because high flux of oxygen ions get across the SDC electrolyte to the anode at high conversion rate of ammonia, leading to more oxidizing conditions at the anode, resulting in more NO generation. Partial pressure of NO also increases at elevated temperature, because reaction (5) is an exothermic reaction. The highest pressure is got at 800 °C with ammonia conversion rate of 0.99, but the value is only about  $10^{-12}$  atm, indicating that NO amount is actually negligible, and is consistent with the primary assumption. But the theoretical prediction still needs experimental verification.

# 3. Experimental

Since partial pressure of NO theoretically increases with increasing temperature, IT-SOFC is a better choice for ammonia fuel than high-temperature SOFC. Doped-ceria is regarded as one of the best electrolyte for IT-SOFC because of its high ionic conductivity at the lowered temperature [6–8], and therefore,  $Ce_{0.8}Sm_{0.2}O_{1.9}$  (SDC) is chosen as the electrolyte in this work.

 $Ce_{0.8}Sm_{0.2}O_{1.9}$  (SDC) powders were synthesized by modified glycine-nitrate process. Stoichiometric precursors of Sm(NO)<sub>3</sub>, and Ce(NO<sub>3</sub>)<sub>3</sub> were dissolved and glycine was then added with the glycine/metal mole ratio set at 1.5. The solution was heated under stirring, converted to a viscous gel and ignited to flame, resulting in the pale yellow ash. The ash was calcined at 600 °C for 2 h to remove any carbon residues.

Composite anode powders were made by blending SDC with NiO in the weight ratio of 35–65. Bi-layers of the anode substrate and SDC film were produced by dry-pressing method, and the thickness was controlled at 700  $\mu$ m and 50  $\mu$ m after co-firing at 1400 °C for 5 h, respectively. Cathode was prepared on the electrolyte with a screen-printing technique using slurry made of equal amount of Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3- $\delta$ </sub> (SSC) and SDC powders. Single cells were achieved after calcinations at 950 °C for 2 h. Ag paste

was applied onto both electrodes as current collectors. Shown in Fig. 2 is the typical microstructure of the cell, as reviewed using a scanning electron microscope (SEM, Hitachi X-650).

Fig. 2. Cross-sectional image of the tested cell with SSC-SDC, SDC and

Cells were pre-reduced at 600 °C in hydrogen for several hours, and then tested from 500 °C to 700 °C in a homedeveloped-cell-testing system with commercial liquefied industrial ammonia or hydrogen as the fuel, air as the oxidant. Digital multi-meters (GDM-8145) were used to collect voltage and current data of the cells. AC impedance spectroscopy (Chi604a, Shanghai Chenhua) was performed on the cell under open-current conditions from 500 °C to 700 °C. Anode off-gas was determined by gas chromatography (N-2000, Zhejiang).

# 4. Results and discussion

Ni-SDC from top to bottom.

Fig. 3 presents open circuit voltages (OCVs) of the cell at different temperatures. Line A indicates OCVs with hydrogen as the fuel, about 0.935, 0.880 and 0.835 V at 500, 600 and 700 °C, respectively. Line  $\alpha$  gives the OCVs with ammonia as the fuel, which is 0.900 V at 500 °C, 0.875 V at 600 °C, 0.834 V at 700 °C. Compare line A and line  $\alpha$ , OCVs of hydrogen and ammonia as fuel were quite similar, and the difference between them is figured in line B. At 500 °C, the difference is much higher than that at 600 and 700 °C, which is possibly because that ammonia does not completely decompose at this temperature, and the specific will be discussed afterwards (See Table 1).

Shown in Fig. 4 are the I-P and I-V curves for the cell fueled with ammonia or hydrogen at different temperatures. Maximum power densities were 65.1 and 82.3 mW cm<sup>-2</sup> at 500 °C, 168.1 and 191.8 mW cm<sup>-2</sup> at 600 °C, and 252.8 and 271.2 mW cm<sup>-2</sup> at 700 °C, with ammo-

nia and hydrogen as the fuel, respectively. The cell performances for ammonia and hydrogen are quite close, especially at temperatures over 600 °C. This suggests that ammonia is a good substitute for  $H_2$ . The difference of cell performances for ammonia and hydrogen decreased with temperature, which is partly because that ammonia-cracking reaction is positive at high temperature, which leads to high hydrogen partial pressure. But as the differences of OCVs are much smaller than cell performances, the affection of inherent resistance should be main factor, which will be discussed in Fig. 5.

Fig. 5 gives the comparisons of impedance spectra of the single cell fuelled by ammonia and hydrogen 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 electrode polarization resistance. The electrode polarization resistances were 4.20 and 2.20  $\Omega$  cm<sup>2</sup> at 500 °C, 0.52 and 0.39  $\Omega$  cm<sup>2</sup> at 600 °C, and 0.18 and 0.17  $\Omega$  cm<sup>2</sup> at 700 °C with ammonia and hydrogen as the fuel, respectively. Obviously, the values with ammonia and hydrogen as the fuel are more similar at higher temperatures, because the ammonia-cracking process is more active at higher temperatures. The electrolyte resistances with ammonia and hydrogen as fuel were 2.22 and 1.93  $\Omega$  cm<sup>2</sup> at 500 °C, 1.00 and 0.95  $\Omega$  cm<sup>2</sup> at 600 °C, and 0.51 and 0.50  $\Omega$  cm<sup>2</sup> at 700 °C, respectively. Since the difference of electrolyte and electrode polarization resistance between ammonia and hydrogen as the fuel both decreased with temperature, the difference of cell performances should also decrease with temperature, as has been validated in Fig. 4.

Although  $H_2O$ ,  $N_2$  and  $H_2$  are expected in the anode off-gas,  $NH_3$  and NO are still possible unpleasant components, the former may be the result of incomplete decomposition of  $NH_3$ , and the latter can come from over oxidation of  $NH_3$ . Table 1 is the anode off-gas composi-

Fig. 3. OCVs of the cell at different temperatures. A: OCVs with hydrogen as fuel.  $\alpha$ : OCVs with ammonia as the fuel. B: OCV difference with ammonia as the fuel and hydrogen as the fuel.







Fig. 4. I-V (solid) and I-P (hollow) curves for a fuel cell consisting of a Ni–SDC anode, a SDC electrolyte, and a SSC–SDC cathode, fuelled by ammonia ( $\bullet$ ) and hydrogen ( $\blacksquare$ ) at a: 500 °C, b: 600 °C and c: 700 °C with air as oxidant.

tions tested by gas chromatography at different temperatures with different ammonia flow rates. All tests were carried under short current circumstance with maximum flux of oxygen ions across the SDC electrolyte to the anode, so that the conditions at the anode become most oxidizing. But at all situations, no NO was detectable, just as the theoretical predication. Off-gas was not smelly only



Fig. 5. Comparisons of impedance spectra of the single cell with ammonia ( $\bullet$ ) and hydrogen ( $\blacksquare$ ) as fuel under open-current conditions at a: 500 °C, b: 600 °C, and c: 700 °C.



Fig. 6. Long-term stability of the cell tested at 600  $^{\rm o}{\rm C}$  with ammonia as fuel.

Table 1

The compositions of anode off-gas of the single cell operated at different temperatures and fuelled with ammonia in different flow rates

Conditions (different temperatures with different ammonia flow rates)		$H_2\%$	$N_2$ %	$\mathrm{NH}_3$ %	NO %
500 °C	30 ml/min	51	28	21	Not detectable
	5 ml/min	28	67	5	Not detectable
600 °C	30 ml/min	57	43	<1	Not detectable
	5 ml/min	8	92	<1	Not detectable
700 °C	30 ml/min	55	45	<1	Not detectable
	5 ml/min	8	92	<1  ppm	Not detectable

at 700 °C with the flow rate of 5 ml/min, and higher concentration of ammonia in off-gas was detected at lower the temperature with the higher flow rate. Since ammonia is also a toxic, direct emission of anode off-gas is unbefitting. But as the content of ammonia in anode off-gas is very small at the main operating temperatures for cells (600–700 °C), and the solubility of which is huge, ammonia is quite easy to be recycled by water, which will almost add no cost at all.

Shown in Fig. 6 is the endurance test of the fuel cell with ammonia as the fuel carried out at 600 °C under the voltage of 0.45 V and current density about 360 mA cm<sup>-2</sup>. After operating for 50 h, no detectable decay in performance occurred.

# 5. Conclusions

Ammonia may be the substitute fuel for H<sub>2</sub>, but the toxic NO is doubted to be generated over the electrode reactions. By thermodynamic analysis, NO formation was investigated as the function of ammonia conversion rate and the operating temperature. More NO was formed at higher current and temperature, but the amount was negligible even at 800 °C with the ammonia conversion rate of 0.99. With ammonia as the fuel, OCVs of the cell with construction of Ni–SDC/SDC (50  $\mu$ m)/SSC–SDC were 0.900, 0.875, and 0.834 V at 500 °C, 600 °C and 700 °C, respectively, and maximum power densities were 65.1 mW cm<sup>-2</sup> at 500 °C, 168.1 mW cm<sup>-2</sup> at 600 °C, and 252.8 mW cm<sup>-2</sup> at 700 °C, respectively, which were quite similar with those

of hydrogen. NO was not detectable in the off-gas of anode with ammonia as the fuel, though the decomposition of ammonia was not complete, especially in lower temperature and higher ammonia flow rate. Test of long-term stability for the fuel cell showed good endurance of anode materials in ammonia atmosphere.

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### References

- J.J. MacKenzie, W.H. Avery, Ammonia fuel: the key to hydrogenbased transportation, in: Energy Conversion Engineering Conference, vol. 3, Washington, DC, 1996, p. 1761.
- [2] R. Metkemeijer, P. Achard, Int. J. Hydrogen Energy 19 (1994) 535.
- [3] R. Metkemeijer, P. Achard, J. Power Sources 49 (1994) 271.
- [4] A. Wojcika, H. Middletona, I. Damopoulosa, J. Van herleb, J. Power Sources 118 (2003) 342.
- [5] Qianli Ma, Ranran Peng, Yongjing Lin, Jianfeng Gao, Guangyao Meng, J.Power Sources, in press.
- [6] Changrong Xia, Meilin Liu, Solid State Ionics 144 (2001) 249.
- [7] Zongping Shao, Sossina M. Haile, Nature 431 (2004) 170.
- [8] Yaohui Zhang, Xiqiang Huang, Zhe Lu, Zhiguo Liu, Xiaodong Ge, Jiahuan Xu, Xianshuang Xin, Xueqing Sha, Wenhui Su, J. Power Sources, in press.