Journal of Power Sources 183 (2008) 682–686

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Thermodynamic analysis of ammonia fed solid oxide fuel cells: Comparison between proton-conducting electrolyte and oxygen ion-conducting electrolyte

Meng Ni, Dennis Y.C. Leung, Michael K.H. Leung*

Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

ARTICLE INFO

Article history:
Received 1 March 2008
Received in revised form 8 May 2008
Accepted 8 May 2008
Available online 16 May 2008

Keywords:
Solid oxide fuel cell (SOFC)
Proton-conducting ceramics
Electrolyte
Electrochemical thermodynamics
Ammonia fuel

ABSTRACT

A thermodynamic analysis has been performed to compare the theoretical performance of ammonia fed solid oxide fuel cells (SOFCs) based on proton-conducting electrolyte (SOFC-H) and oxygen ion-conducting electrolyte (SOFC-O). It is found that the ammonia fed SOFC-H is superior to SOFC-O in terms of theoretical maximum efficiency. For example, at a fuel utilization of 80% and an oxygen utilization of 20%, the efficiency of ammonia fed SOFC-H is 11% higher than that of SOFC-O. The difference between SOFC-H and SOFC-O becomes more significant at higher fuel utilizations and higher temperatures. This is because an SOFC-H has a higher hydrogen partial pressure and a lower steam partial pressure than an SOFC-O. In addition, an increase in oxygen utilization is found to increase the efficiency of ammonia fed SOFCs due to an increase in oxygen molar fraction and a reduction in steam molar fraction. With further development of new ceramics with high proton conductivity and effective fabrication of thin film electrolyte, the SOFC based on proton-conducting electrolyte is expected to be a promising approach to convert ammonia fuel into electricity.

1. Introduction

Solid oxide fuel cells (SOFCs) have been identified as efficient and environmentally friendly electricity generators [1–8]. One of the main advantages of SOFCs is their fuel flexibility. In practice, hydrogen and hydrocarbons, such as methane and ethanol, can be used as fuels in SOFCs to generate electricity [9–12]. Recent research works show that ammonia is also a feasible fuel for electricity generation by SOFCs [13–22]. Ammonia emerges as a promising fuel for fuel cells because it is relatively cheap, easy to store and transport, less flammable compared with other fuels and relatively safe due to any leakage being easily detectable by odor. In addition, the infrastructure of ammonia technology has been well established. Therefore, there is increasing interest in using ammonia in fuel cells, especially in SOFCs [13–22].

Conventional SOFCs are based on oxygen ion-conducting electrolyte (SOFC-O), such as the commonly used yttria-stabilized zirconia (YSZ). Alternatively, an SOFC can be built with a proton-conducting electrolyte (SOFC-H). Previous thermodynamic analyses have shown that an SOFC-H running on hydrogen or hydrocarbon (methane, methanol, or ethanol) has a higher maximum energy efficiency than an SOFC-O counterpart [23–27]. Those thermodynamic analyses designed for hydrocarbon fuels cannot be directly applied to study ammonia fuel due to different electrochemical mechanisms. For example, steam is required for an SOFC running on methanol, but not for an SOFC running on ammonia. When methanol is used as a fuel, the steam-to-methanol ratio is critical for determining both the carbon formation boundary and the SOFC efficiency. On the other hand, ammonia fuel used in SOFC undergoes thermal crack to produce hydrogen and nitrogen at the anode and, therefore, no steam is needed to prevent carbon formation.

In this paper, a thermodynamic analysis is conducted to study the theoretical performance of ammonia fed SOFCs. Theoretical analyses have been performed to study both conventional SOFC-O and advanced SOFC-H. The results of both SOFC-O and SOFC-H are compared and discussed in terms of energy conversion efficiency.

2. Thermodynamic analysis

2.1. Principles of ammonia fed SOFC

2.1.1. SOFC-O

In an SOFC-O (Fig. 1(a)), ammonia undergoes decomposition over a Ni catalyst at the anode chamber as

$$2NH_3 \leftrightarrow N_2 + 3H_2 \qquad (1)$$

---

* Corresponding author. Tel.: +852 2859 2628; fax: +852 2858 5415.
E-mail address: mkhleung@hku.hk (M.K.H. Leung).

0378-7753/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2008.05.022

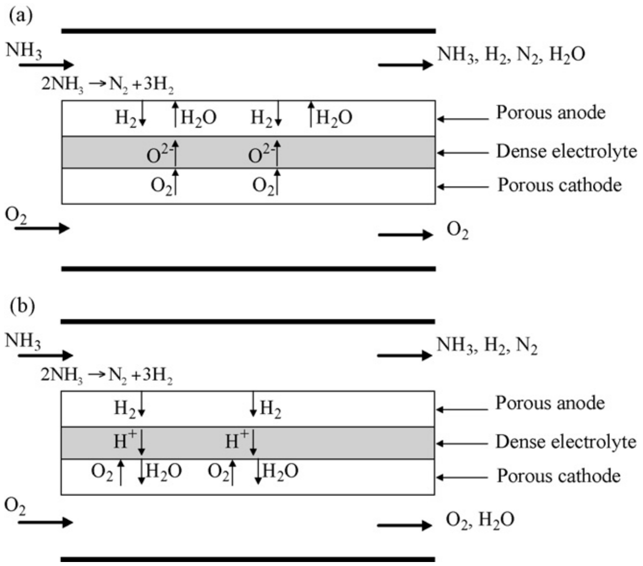

Fig. 1. Schematic of ammonia fed SOFC: (a) SOFC-O and (b) SOFC-H.

The oxygen supplied at the cathode is reduced to O^{2-}. The O^{2-} ion is subsequently transported through the dense electrolyte to the porous anode, where it reacted with the hydrogen generated from ammonia to form H_2O. The electrochemical reactions taking place in the electrodes of an SOFC-O are summarized as

Cathode:

$$0.5O_2 + 2e^- \rightarrow O^{2-} \tag{2}$$

Anode:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{3}$$

Wojcik et al. [13] made the first attempt to use ammonia as a fuel in YSZ-based SOFC-O and obtained a maximum power density of about 50 mW cm^{-2}. It was believed that toxic NO might be formed at the anode due to the following reaction [13]:

$$2NH_3 + 5O^{2-} \leftrightarrow 2NO + 3H_2O + 10e^- \tag{4}$$

However, recent theoretical and experimental investigations show that NO generation is thermodynamically unfavorable and the concentration of NO is negligibly small (up to only a few ppm) [15,17,18]. Thus, the NO formation reaction in ammonia fed SOFC is assumed negligible in the present study.

2.1.2. SOFC-H

In an SOFC-H (Fig. 1(b)), ammonia is decomposed into nitrogen and hydrogen over Ni catalysts at the anode chamber, similar to an SOFC-O [15]. The N_2 is removed from the anode chamber, while the H_2 produced undergoes a subsequent electrochemical reaction at the anode as

$$H_2 \rightarrow 2H^+ + 2e^- \tag{5}$$

The produced electrons traveling from the anode to the cathode through an external circuit yield an electrical power output. The protons are transported through dense electrolyte to the cathode chamber and undergo electrochemical reactions with oxygen molecules to form H_2O at the cathode as

$$2H^+ + 0.5O_2 + 2e^- \rightarrow H_2O \tag{6}$$

The overall reaction can be written as

$$2NH_3 + 1.5O_2 \rightarrow N_2 + 3H_2O \tag{7}$$

2.2. Equilibrium potential of ammonia fed SOFC

The equilibrium potential of an SOFC cell is the maximum voltage that drives charges through an electric circuit in an SOFC. In practice, the voltage of an SOFC is less than the theoretical value due to different overpotential losses, such as activation, concentration, and ohmic overpotentials [7,28]. In this paper, only the equilibrium potential of the SOFC is considered with an aim to investigate the theoretical maximum performance of the SOFC fed with ammonia.

According to thermodynamics of fuel cells, the voltage (E) of a fuel cell can be expressed as

$$E = -\frac{\Delta G}{nF} \tag{8}$$

where n is the number of electrons involved per electrochemical reaction, F is the Faraday constant, and ΔG is the change in Gibbs free energy.

In an SOFC fed with ammonia, the species involved in electrochemical reactions are H_2 and O_2, and the product is H_2O. The voltage can be written in the Nernst form as

$$E = E^0 + \frac{RT}{2F}\ln\left[\frac{P_{H_2}(P_{O_2})^{1/2}}{P_{H_2O}}\right] \tag{9}$$

where E^0 is the voltage at standard pressures; P_{H_2}, P_{H_2O} and P_{O_2} are the partial pressure of hydrogen, steam, and oxygen, respectively. The above equation is applicable to both SOFC-O and SOFC-H. However, it should be mentioned that P_{H_2O} refers to partial pressure of H_2O at the anode side of an SOFC-O, while it refers to partial pressure of H_2O at the cathode side of an SOFC–H.

2.3. Determination of gas composition in the SOFC

The calculation procedures developed by Assabumrungrat et al. [29] are adopted in the present study to determine the partial pressure of each gaseous component. It is also assumed that the gaseous species are under equilibrium at the SOFC inlet.

For both SOFC-O and SOFC-H, the number of moles (n) of each component at the SOFC outlet can be calculated as

$$n_{NH_3} = a - 2x \tag{10}$$

$$n_{N_2} = x \tag{11}$$

$$n_{H_2} = 3x - b \tag{12}$$

$$n_{H_2O} = b \tag{13}$$

$$n_{O_2} = 0.21c - 0.5b \tag{14}$$

where a and c are the mole numbers of inlet ammonia and air (containing 21% oxygen), respectively; b is the extent of electrochemical reaction of hydrogen, which is related to current density J; $2x$ is the number of moles of NH_3 converted as in reaction (1).

Assuming ideal gas and equilibrium conditions, the partial pressure of each gas component can be related with the equilibrium constant as (taking NH_3 as an example):

$$K_{NH_3} = \frac{(P_{H_2})^3 \cdot (P_{N_2})}{(P_{NH_3})^2} \tag{15}$$

where P_{NH_3} and P_{N_2} are partial pressure of NH_3 and N_2, respectively.

The equilibrium constant can also be determined by its definition:

$$K_{NH_3} = \exp\left(-\frac{\Delta G_f}{RT}\right) \tag{16}$$

where ΔG_f is the change in Gibbs free energy between the products and the reactants for chemical reaction at a standard state.

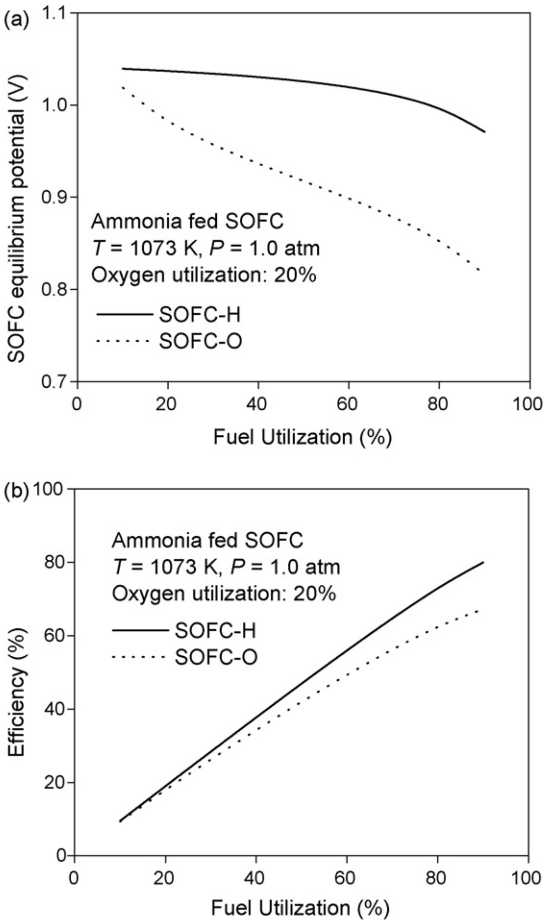

Fig. 2. Theoretical performance of ammonia fed SOFC-H and SOFC-O at different fuel utilizations: (a) equilibrium potential and (b) efficiency.

Based on the equilibrium constant and the mass balance, the partial pressure of each gaseous species can thus be determined. Detailed calculation procedures for Eq. (10) to Eq. (16) can be found elsewhere [25,29]. After obtaining the gas partial pressure, the theoretical potential of SOFC fed with ammonia can be calculated with the average partial pressures of H_2, H_2O and O_2 through the Nernst equation (Eq. (9)).

2.4. Efficiency of ammonia fed SOFC

When a current is drawn from an SOFC, the maximum electrical work (W) generated by the SOFC can be calculated as

$$W = qE \tag{17}$$

where q is the electrical charge passing through the SOFC. The efficiency of ammonia fed SOFC can be defined as the ratio of the maximum electrical work (W) extracted from the SOFC to the maximum conversion of the chemical energy of the fuel fed to the SOFC [24,25]:

$$\eta(\%) = \frac{W}{-\Delta H^\circ} \times 100 \tag{18}$$

where ΔH° is the lower heating value (LHV) of the feeding ammonia at the standard condition (320.1 kJ mol^{-1}). It should be mentioned that the theoretical efficiency has no absolute significance and is attributed to given fuel utilization and working temperature [24]. The fuel utilization and oxygen utilization are defined as the ratio of consumed fuel (ammonia) and oxidant (oxygen) to the feeding fuel and oxidant, respectively.

3. Results and discussion

In this section, the results of theoretical performance of ammonia fed SOFC are presented, with a focus on comparison of the proton-conducting electrolyte and the oxygen ion-conducting electrolyte.

3.1. Comparison between ammonia fed SOFC-H and SOFC-O at different fuel utilizations

The efficiency and equilibrium potential of ammonia fed SOFCs using different electrolyte types with different fuel utilizations at 1073 K are shown in Fig. 2. It is found that the equilibrium potential of SOFC-H is significantly higher than that of SOFC-O (Fig. 2(a)). As a result, the efficiency of SOFC-H is higher than that of SOFC-O (Fig. 2(b)). In addition, the difference between the efficiency of SOFC-H and that of SOFC-O becomes larger as the fuel utilization increases. At typical fuel utilization of about 80–90% [23], the efficiency of ammonia fed SOFC-H is about 10% higher than that of SOFC-O (Fig. 2(b)). It is also found that the SOFC efficiency increases with increasing fuel utilization, which is consistent with previous thermodynamic analyses [23,25].

In order to understand the theoretical performance of ammonia fed SOFC-H and SOFC-O, the partial pressures of the gaseous species are shown in Fig. 3. It is found that the hydrogen partial

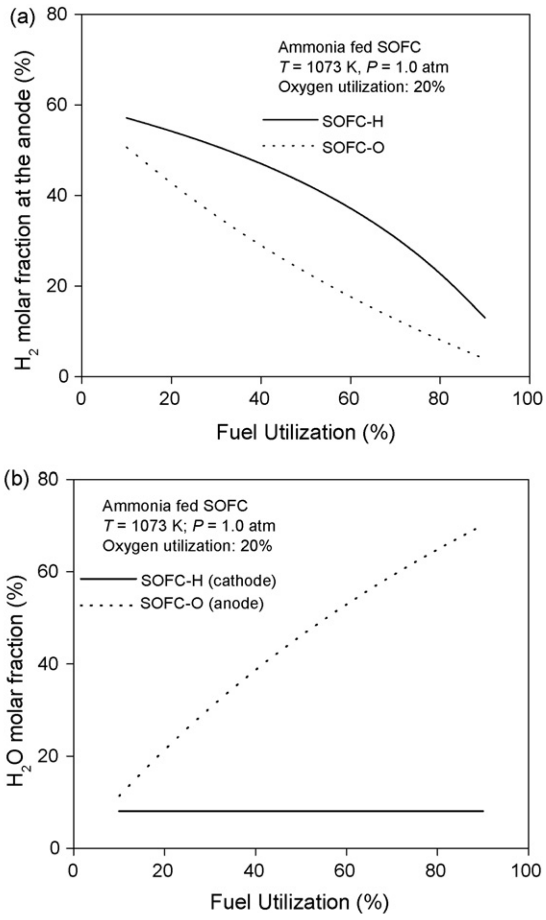

Fig. 3. Effect of electrolyte type on gas composition at different utilizations: (a) H_2 molar fraction and (b) H_2O molar fraction.

pressure in SOFC-H is significantly higher than that in SOFC-O, especially for medium fuel utilization (Fig. 3(a)). This is because steam is produced at the anode in an SOFC-O, which in turn could dilute the concentration of hydrogen fuel at the anode. However, for an SOFC-H, steam is generated at the cathode and, thus its molar fraction of hydrogen could be higher compared with an SOFC-O. At a higher fuel utilization, the difference in hydrogen partial pressure between an SOFC-H and an SOFC-O becomes smaller since both partial pressures approach to zero. In addition, the partial pressure of steam in an SOFC-H (cathode) is lower than that in an SOFC-O (anode) and the difference becomes more significant at higher fuel utilization (Fig. 3(b)). In an SOFC-O, steam is generated at the anode side and the molar consumption of reactant gas (H_2) is equal to the molar generation of product gas (H_2O). Therefore, both steam molar fraction and steam partial pressure increase with fuel utilization in an SOFC-O. For an SOFC-H, steam is generated at the cathode side and its molar fraction depends on oxygen utilization. Since the oxygen utilization is constant in the present study, the steam molar fraction is invariant in an SOFC-H (Fig. 3(b)). Therefore, as the ammonia fed SOFC-H has higher H_2 partial pressure and lower H_2O partial pressure than the SOFC-O, the SOFC-H has a higher theoretical performance.

3.2. *Comparison between SOFC-H and SOFC-O at different temperatures*

The effects of temperature on the theoretical performance of the ammonia fed SOFC-H and an SOFC-O are shown in Fig. 4(a) and (b). As the temperature increases, both SOFC-H and SOFC-O perform with lower efficiency and equilibrium potential. This is because the potential at the standard condition (E^0 in Eq. (9)) decreases significantly with increasing temperature. Thus, the reduced equilibrium potential results in lower theoretical efficiency of SOFCs. It should be mentioned that the overpotentials of an SOFC decrease with increasing temperature. Therefore, the optimal operating temperature depends on both the reversible potential and the overpotentials. Electrochemical modeling analyses are important

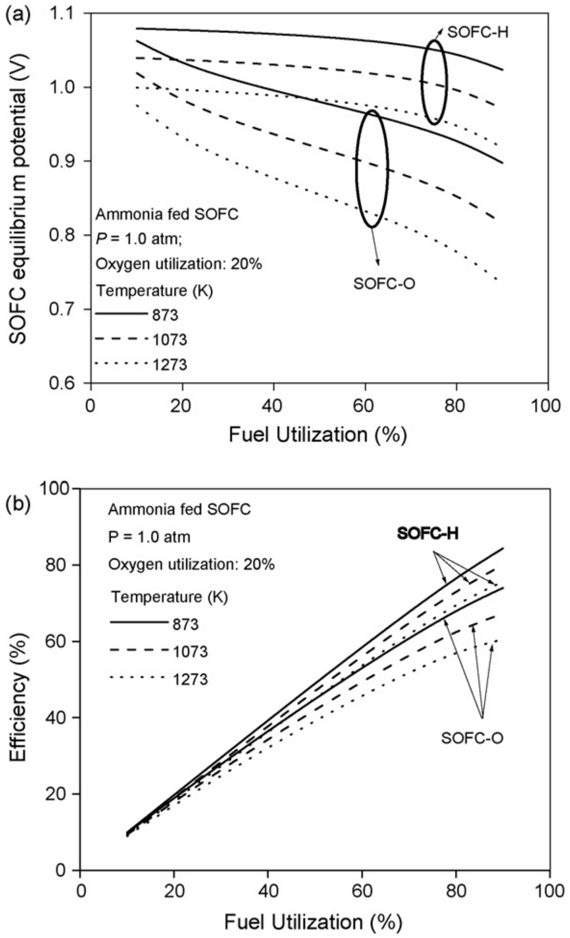

Fig. 4. Effect of electrolyte type on ammonia fed SOFC performance at different temperatures: (a) equilibrium potential and (b) efficiency.

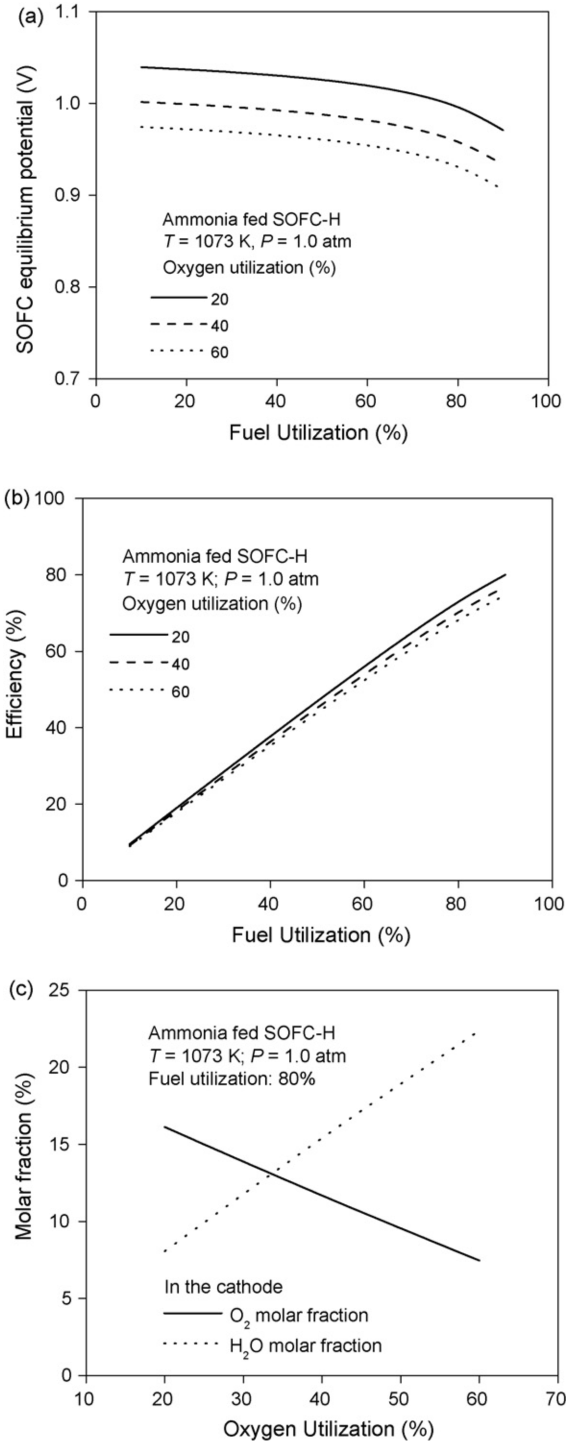

Fig. 5. Effect of oxygen utilization on performance of ammonia fed SOFC-H: (a) equilibrium potential, (b) efficiency and (c) molar fractions of steam and oxygen.

to quantify the overpotentials involved in operation of the ammonia fed SOFCs. Detailed model development and analyses of the ammonia fed SOFC-H will be presented in another paper [30].

3.3. *Effect of oxygen utilization on performance of ammonia fed SOFC-H*

In addition to fuel utilization and working temperature, oxygen utilization is yet another important parameter governing the performance of the ammonia fed SOFC-H. It is found that the equilibrium potential and the theoretical maximum efficiency of the ammonia fed SOFC-H decrease with increasing oxygen utilization (Fig. 5(a) and (b)). This is because the oxygen molar fraction decreases while the steam molar fraction increases with increasing oxygen utilization (Fig. 5(c)), which can in turn decrease the equilibrium potential (Eq. (9)). Therefore, in order to maintain high performance of the ammonia fed SOFC-H, low oxygen utilization is desired. However, low oxygen utilization means over-supply of oxygen gas (air) at the cathode side of the SOFC, which can take away heat from the SOFC system and may reduce the energy efficiency of the practical SOFC system. Therefore, in order to obtain the optimal oxygen utilization, detailed thermodynamic analysis of the complete SOFC system considering all possible energy losses needs to be performed.

3.4. *Implication for practical applications*

The above analyses reveal that the maximum efficiency of the ammonia fed SOFC-H is higher than the SOFC-O without considering any irreversible losses. In practice, the actual SOFC efficiency is lower than the theoretical value because of the presence of various overpotentials. Using similar electrode materials, the activation overpotentials of an SOFC-H and an SOFC-O can be similar. The concentration overpotentials are also insignificant at a low or medium current density and they may play an important role only at a high current density. The ohmic overpotentials deserve special attention as the electrolytes used for SOFC-H and SOFC-O could have very different ionic conductivities. So far, the ionic conductivity of typical proton conductors (i.e. $BaCe_{0.8}Sm_{0.2}O_{2.9}$) is much lower than that of the oxygen ion conductors (i.e. YSZ) [31,32], indicating that the advantage of an SOFC-H will be offset by the ohmic loss at the electrolyte. Therefore, it is important to search for solid oxides with high proton conductivity and high stability. Alternatively, the ohmic overpotentials can be minimized by fabricating thin film electrolyte [33]. It has been demonstrated that thin film electrolyte with thickness of about eight microns could achieve high SOFC performance [33]. With further development in material science and thin film fabrication technology, the SOFC based on proton-conducting electrolyte will be a promising technology for converting ammonia to electricity.

4. Conclusion

In this study, a thermodynamic analysis has been conducted to compare the theoretical performance of ammonia fed SOFC based on different types of electrolytes. It has been demonstrated that an SOFC-H could potentially perform better than an SOFC-O under typical operating conditions. This is mainly because of higher hydrogen partial pressure and lower steam partial pressure in an SOFC-H in comparison with an SOFC-O counterpart. Low temperature and low oxygen utilization are found to be beneficial to enhance the theoretical maximum efficiency of the ammonia fed SOFCs. However, detailed electrochemical modeling analyses as well as energy and exergy analyses of the practical SOFC system are needed in order to quantify the optimal operating parameters. Development of new materials with high proton conductivity and high stability as well as advanced thin-film fabrication of electrolyte will be important to achieve high efficiency of ammonia fed SOFC-H for electricity generation.

Acknowledgements

The authors would like to thank the financial support by the Research Grants Council of Hong Kong, PR China (HKU7150/05E) and the CRCG of the University of Hong Kong. The authors also would like to thank Prof. A.K. Demin (Institute of High Temperature Electrochemistry, Russia) and Prof. Suttichai Assabumrungrat (Chulalongkorn University, Thailand) for discussions and suggestions.

References

[1] Y.H. Huang, R.I. Dass, Z.L. Xing, J.B. Goodenough, Science 312 (2006) 254–257.
[2] Z.P. Shao, S.M. Haile, J. Ahn, P.D. Ronney, Z.L. Zhan, S.A. Barnett, Nature 435 (2005) 795–798.
[3] S.L. Douvartzides, F.A. Coutelieris, A.K. Demin, P.E. Tsiakaras, Int. J. Hydrogen Energy 29 (2004) 375–379.
[4] A.K. Demin, V. Alderucci, I. Ielo, G.I. Fadeev, G. Maggio, N. Giordano, V. Antonucci, Int. J. Hydrogen Energy 17 (1992) 451–458.
[5] S.H. Chan, H.K. Ho, Y. Tian, Int. J. Hydrogen Energy 28 (2003) 889–900.
[6] M. Ippommatsu, H. Sasaki, S. Otoshi, Int. J. Hydrogen Energy 21 (1996) 129–135.
[7] M. Ni, M.K.H. Leung, D.Y.C. Leung, Energy Convers. Manage. 48 (2007) 1525–1535.
[8] M. Ni, M.K.H. Leung, D.Y.C. Leung, J. Power Sources 168 (2007) 369–378.
[9] S.H. Chan, O.L. Ding, Int. J. Hydrogen Energy 30 (2005) 167–179.
[10] E. Hernandez-Pacheco, M.D. Mann, P.N. Hutton, D. Singh, K.E. Martin, Int. J. Hydrogen Energy 30 (2005) 1221–1233.
[11] C.O. Colpan, I. Dincer, F. Hamdullahpur, Int. J. Hydrogen Energy 32 (2007) 787–795.
[12] J. Staniforth, K. Kendall, J. Power Sources 71 (1998) 275–277.
[13] A. Wojcik, H. Middleton, I. Damopoulos, J. Van herle, J. Power Sources 118 (2003) 342–348.
[14] Q.L. Ma, R.R. Peng, Y.J. Lin, J.F. Gao, G.Y. Meng, J. Power Sources 161 (2006) 95–98.
[15] Q.L. Ma, R.R. Peng, L.Z. Tian, G.Y. Meng, Electrochem. Commun. 8 (2006) 1791–1795.
[16] G.G. Fournier, I.W. Cumming, K. Hellgardt, J. Power Sources 162 (2006) 198–206.
[17] Q.L. Ma, J.J. Ma, S. Zhou, R.Q. Yan, J.F. Gao, G.Y. Meng, J. Power Sources 164 (2007) 86–89.
[18] N.J.J. Dekker, G. Rietveld, J. Fuel Cell Sci. Technol. 3 (2006) 499–502.
[19] N. Maffei, L. Pelletier, J.P. Charland, A. McFarlan, J. Power Sources 162 (2006) 165–167.
[20] L. Pelletier, A. McFarian, N. Maffei, J. Power Sources 145 (2005) 262–265.
[21] N. Maffei, L. Pelletier, J.P. Charland, A. McFarlan, J. Power Sources 140 (2005) 264–267.
[22] N. Maffei, L. Pelletier, J.P. Charland, A. McFarlan, Fuel Cells 7 (2007) 323–328.
[23] A. Demin, P. Tsiakaras, Int. J. Hydrogen Energy 26 (2001) 1103–1108.
[24] A.K. Demin, P.E. Tsiakaras, V.A. Sobyanin, S.Y. Hramova, Solid State Ionics 152–153 (2002) 555–560.
[25] S. Assabumrungrat, W. Sangtongkitcharoen, N. Laosiripojana, A. Arpornwichanop, S. Charojrochkul, P. Praserthdam, J. Power Sources 148 (2005) 18–23.
[26] W. Jamsak, S. Assabumrungrat, P.L. Douglas, N. Laosiripojana, S. Charojrochkul, Chem. Eng. J. 119 (2006) 11–18.
[27] W. Jamsak, S. Assabumrungrat, P.L. Douglas, N. Laosiripojana, R. Suwanwarangkul, S. Charojrochkul, E. Croiset, Chem. Eng. J. 133 (2007) 187–194.
[28] M. Ni, M.K.H. Leung, D.Y.C. Leung, Fuel Cells 7 (2007) 269–278.
[29] S. Assabumrungrat, N. Laosiripojana, V. Pavarajarn, W. Sangtongkitcharoen, A. Tangjimatee, P. Praserthdam, J. Power Sources 139 (2005) 55–60.
[30] M. Ni, D.Y.C. Leung, M.K.H. Leung, Electrochemical modeling of ammonia-fed solid oxide fuel cells based on proton conducting electrolyte, Journal of Power Sources 183 (2008) 687–692.
[31] R.R. Peng, Y. Wu, L.Z. Yang, Z.Q. Mao, Solid State Ionics 177 (2006) 389–393.
[32] J.W. Fergus, J. Power Sources 162 (2006) 30–40.
[33] F. Zhao, A.V. Virkar, J. Power Sources 141 (2005) 79–95.