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Optimization of Flow Rate for Improving Performance and Stability of Ni-YSZ based Solid Oxide Fuel Cells Using CH_4 Fuel

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The advantages of solid oxide fuel cells (SOFCs), compared with other types of fuel cells, include their high energy conversion efficiency and their utilization of hydrocarbon fuels without reformers. Although conventional Ni-based cermet anodes have commonly been used as an anode material with high catalytic properties for H_2 fuel, the carbon deposition in Ni-YSZ anodes when hydrocarbon fuels are used directly is a critical problem that results in the destruction of the anode microstructure and abrupt decline in cell performance. Our research focuses on optimizing the flow rate of CH_4-fueled Ni-YSZ anode/YSZ electrolyte/LSM-YSZ cathode type SOFC unit cells for improving cell performance and better durability. A high power density of 0.75 Wcm^{-2} at 800 ^oC, 0.5 Wcm^{-2} at 700 ^oC and 0.4 Wcm^{-2} at 650 ^oC using CH_4 fuel as well as excellent durability were obtained via optimization of CH_4 flow rate at 800 ^oC, 700 ^oC, and 650 ^oC operating temperatures. The different types of carbon that cause an increase or decrease in cell performance under certain operating conditions was also investigated.

Keywords: Solid oxide fuel cell, Ni-based anode supported unit cell, durability test, CH_4.

1. INTRODUCTION

Solid oxide fuel cells (SOFCs) with low emission and high energy conversion efficiency can use hydrocarbon fuels directly without the use of a reformer, making them a very attractive energy device [1]. For hydrocarbon fuels, conventional Ni-based cermet anodes have commonly been used as an anode material because of their catalytic properties. However, carbon deposition is a critical problem that causes loss of cell performance and poor stability during internal reforming reactions [2-6]. Changing the composition of the fuel, the operating temperature, the catalyst support, the Ni

particle size, and the addition of various catalysts to prevent carbon formation all affect the rate of carbon deposition. Moreover, carbon has diverse structures including adsorbed polymeric, vermicular filaments, carbide, and graphitic, which affect carbon reactivity and result in degradation in catalytic activation [7-8]. Several studies of the characteristics of carbon deposited on Ni-YSZ have been sought to overcome carbon deposition. Alzate-Restrepo et al. [9] found that when current density was increased, less carbon was deposited and that, with increased operating time and anode thickness, deposited carbon became more difficult to remove. Lin, Zhan et al. [10] found that Ni-YSZ anode-supported SOFCs can be operated stably with high applied current density. It is also well known that carbon deposition is suppressed at high S/C ratios, lower operating temperatures, and when new anode catalysts such as ceria, ceramic anode and Alkali metals are used [11-19]. The utilization of carbon as a fuel for solid oxide fuel cells was further investigated by Ihara et al [20]. The CO_2 generated by the electrochemical oxidation of carbon reacted with the deposited carbon and produced CO. In turn, this CO can be used as fuel.

In this study, we fabricated Ni-YSZ anode-supported unit cells with a thin YSZ electrolyte using the dip-coating method and examined their maximum power density and durability at various CH_4 flow rates at temperatures between 650 ^oC and 800 ^oC. The results suggest that some useful small ball carbon may be deposited on the anode and the rate of carbon deposition can be minimized for improved cell performance by optimizing CH_4 flow rates at a given operating temperature.

2. EXPERIMENTAL

2. 1. Fabrication of unit cells

Conventional Ni-YSZ anode-supported unit cells were fabricated by uni-axial pressing, dip-coating and screen printing methods. The anode raw materials were NiO (Nickelous Oxide Green, J.T. Baker, USA), coarse YSZ (FYT13.0-010H, Unitec Ceramics, UK), fine YSZ (TZ-8Y, Tosoh, Japan), and carbon black (Raven 430, Columbian Chemical, USA) as pore former. The anode was produced with a mixture of 58.4 wt% NiO, 15.8 wt% coarse YSZ, 15.8 wt% fine YSZ and 10 wt% carbon black by uni-axial pressing method. The pre-sintered anode supports manufactured at 1200 ^oC were then dipped into fine YSZ slurry to coat them with a thin electrolyte layer. A thinner electrolyte reduces the ohmic resistance associated with the oxygen transport across the electrolyte and minimizes carbon formation on the anode side through a maximal carbon oxidation reaction. The thickness (6-10 ㎛) of YSZ electrolyte was controlled by withdrawal speeds during the dip-coating process, followed by sintering at 1350 ^oC to obtain a dense YSZ electrolyte. A cathode having a composition of 50 wt% LSM and 50 wt% fine YSZ was screen-printed to obtain 1 cm^2 active area on one side of the anode support electrolyte, while the other side was polished to remove the electrolyte coating. Finally, it was sintered at 1150 ^oC.

2. 2. Cell performance tests

In tests, unit cell performance was measured with apparatuses designed and built by our laboratory; this is described in detail in our previous study [21].

The performance of the Ni-YSZ anode supported unit cells that has 1 cm^2 active area was evaluated at various temperatures (650-800 ^oC) in reactive gases of H_2 (200 $ccmin^{-1}$ in standard ambient temperature and pressure) with either 3 % H_2O or CH_4 (20-75 $ccmin^{-1}$ in standard ambient temperature and pressure) with 3 % H_2O at the anode and air (500 $ccmin^{-1}$ in standard ambient temperature and pressure) at the cathode. The I-V characterization and durability were measured with a multi-functional electronic load module (3315D, Taiwan). AC impedance measurements were conducted with a Solatron 1260 frequency analyzer and a Solatron 1287 interface.

2. 3. Characteristics of deposited carbon

The microstructures of Ni-YSZ anode were observed with a scanning electronic microscope (SEM: Model S4200, Hitachi, Ltd., Japan) to compare the different forms of carbon deposited. The different forms of carbon on the anode were further examined by using temperature-programmed oxidation (TPO: Telcat-M). TPO was measured with a ramping temperature rate of 5 $^oCmin^{-1}$ and gas flow rate of 30 $ccmin^{-1}$ (20 % O_2 and 80 % He).

Carbon that leads to degradation of cell performance and to cracking of the anode microstructure was revealed to be a form of fiber, graphite, or amorphous carbon that is oxidized at 400~700 ^oC. In contrast, small ball carbon, which can enhance electrical conductivity in metallic phases and greatly improve power density, is oxidized at over 700 ^oC.

However, if the rate of carbon deposition is not controlled, the small ball carbon can transform into “flower-like” or poly-aromatic carbon through agglomeration [22-24]. Therefore, the optimal operating conditions for using CH_4 can be found by distinguishing between these two classes of deposited carbon.

3. RESULTS AND DISCUSSION

3.1. Evaluation of initial cell performance using H_2 and CH_4

The unit cells were successfully fabricated with a thin electrolyte to obtain high power density by uni-axial pressing and dip-coating methods as shown in the SEM image in figure 1. The unit cell with 10 ㎛-thick YSZ electrolyte showed a maximum power density of 0.4 Wcm^{-2} with H_2 at 800 ^oC.

However, the unit cell fabricated with 6 ㎛-thick YSZ electrolyte showed a 50 % improvement in maximum power density of 0.6 Wcm^{-2}, and showed maximum power density of 0.75 Wcm^{-2} for 30 $ccmin^{-1}$ of CH_4 fuel as shown in figure 2.

Even though the CH_4 flow rate increased to 75 $ccmin^{-1}$, the cell performance deteriorated as illustrated in figure 3. As a result, the 30 $ccmin^{-1}$ CH_4 flow rate was chosen for the durability test.

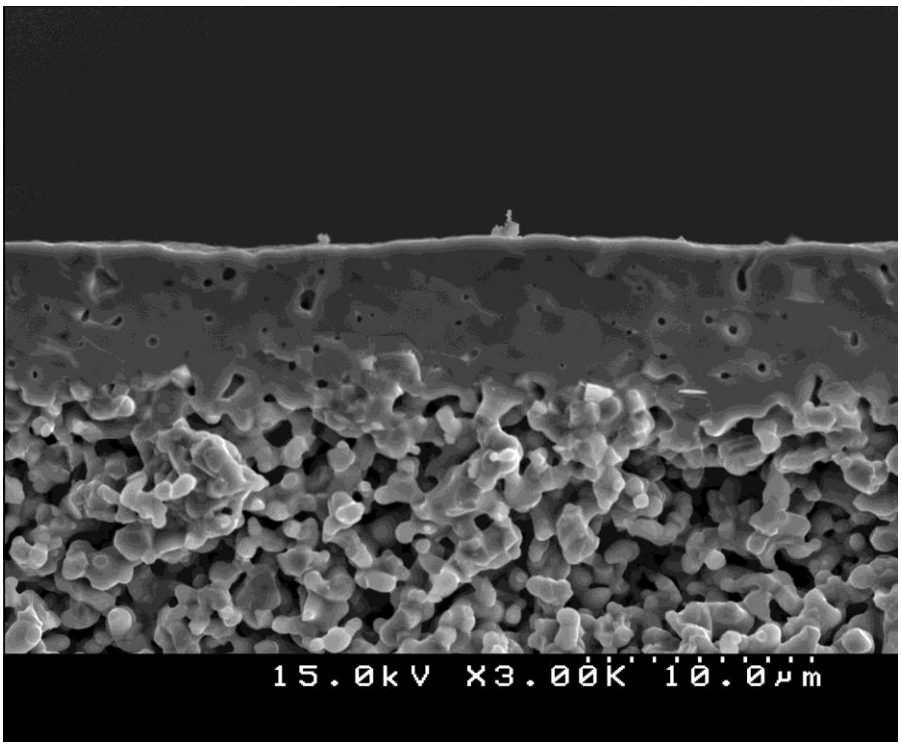

Figure 1. SEM image of a cross-sectional area of anode supported electrolyte fabricated by uni-axial pressing and dip-coating methods.

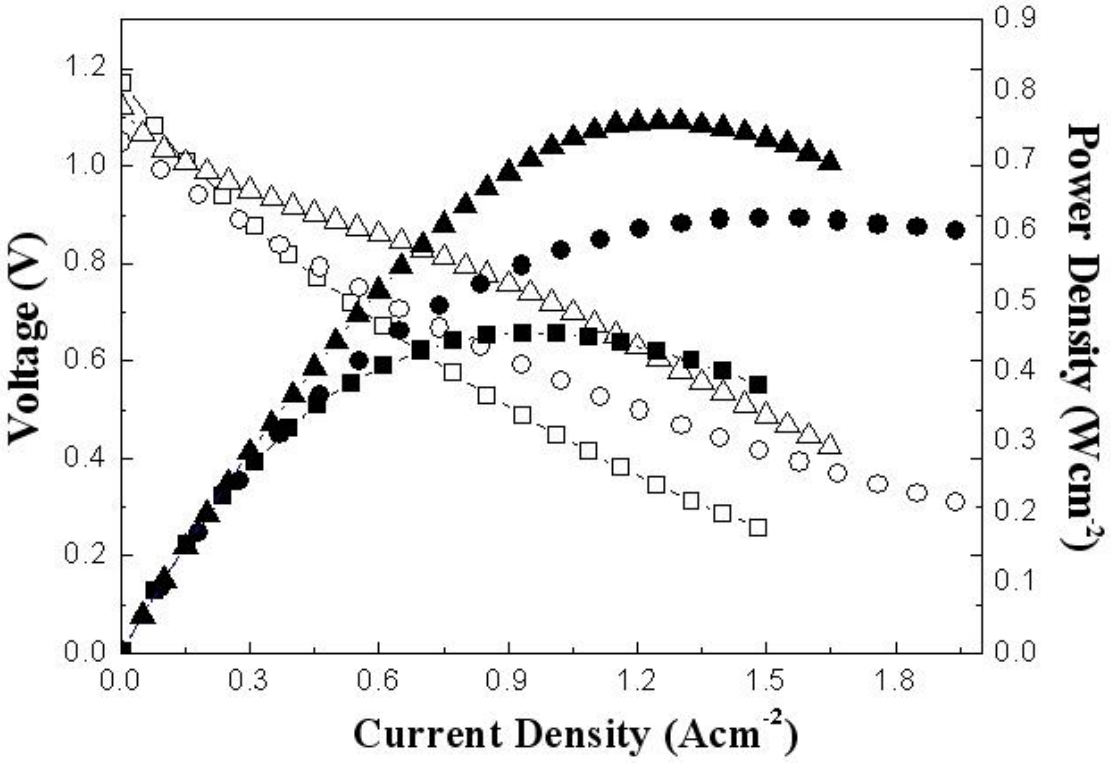

Figure 2. The I-V characteristics of the unit cell with 10 ㎛ thickness of YSZ electrolyte (■), the unit cell with 6 ㎛ thickness of YSZ electrolyte using humidified H_2 (200 $ccmin^{-1}$) with 3% H_2O and air (500 $ccmin^{-1}$) (●), and using CH_4 (30 $ccmin^{-1}$) with 3% H_2O (▲).

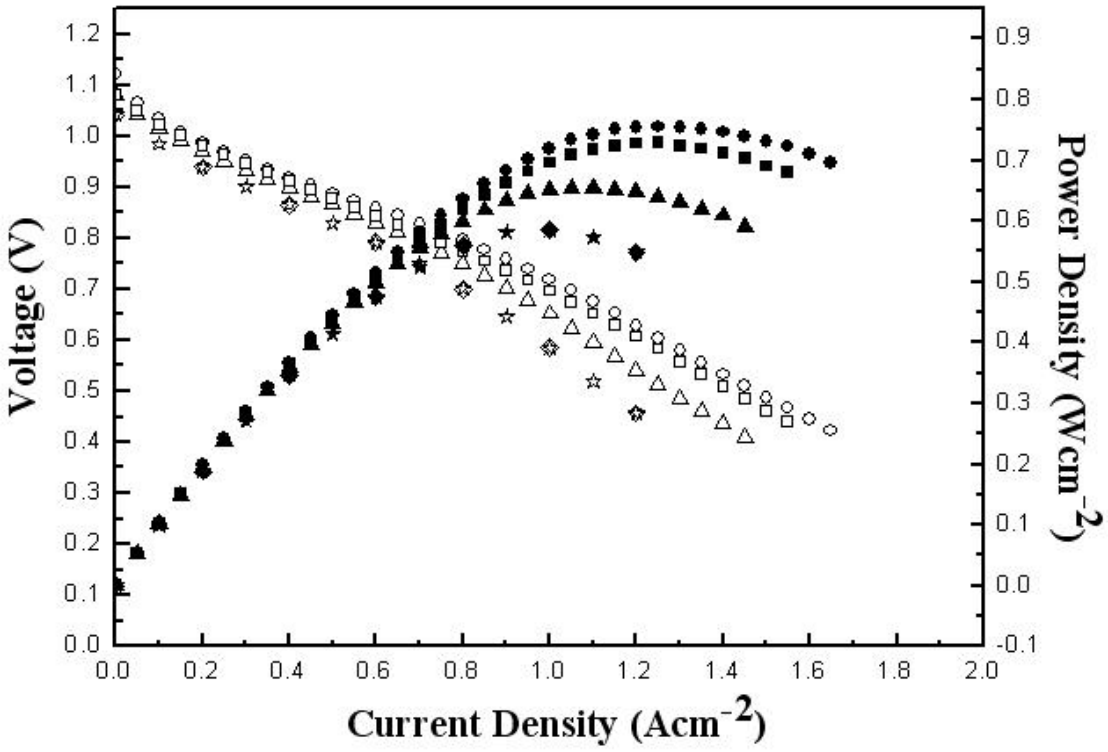

Figure 3. The I-V characteristics of the unit cell with various CH_4 flow rates, 25 (■), 30 (●), 35 (▲), 55 (♦), 75 (★) with 3% H_2O at 800 ^oC.

3.2. Conditions when fuels are changed ($H_2 \rightarrow CH_4$)

To operate Ni-YSZ based SOFCs using CH_4 with minimal cell degradation, they must be operated under polarization conditions to reduce carbon deposition [25-26]. As well, CH_4 concentrations must be gradually increased in order to not affect stability. Moreover, a thinner electrolyte is a major factor to attain higher current densities and reduce carbon formation rates by increasing oxygen transport. The case of a conventional Ni-YSZ unit cell with a 10 ㎛-thick electrolyte is supplied with 50 ccmin^{-1} of CH_4 flow rate showed rapid degradation in cell performance. However, the stability of a unit cell supplied with an optimized CH_4 flow rate (30 ccmin^{-1}) was improved despite lower voltage. On the other hand, a unit cell with a 6 ㎛ minimized thickness of electrolyte at a 30 ccmin^{-1} CH_4 flow rate showed highest initial voltage and better durability as shown in figure 4.

After stabilization, the unit cells with 6 ㎛ minimized thickness of electrolyte at a 30 ccmin^{-1} CH_4 flow rate showed much smaller ohmic resistance and anodic polarization resistance than did those using H_2, as shown in figure 5. Usually, anodic polarization resistance using CH_4 fuel is higher than that using H_2, because of the higher mass of CH_4 molecules, slower electrochemical oxidation and deposited carbon [13, 27]. However, in this case, if the amount of CH_4 supplied is optimized under applied current, the anodic polarization resistance can be reduced through increased electrical conductivity and the carbon oxidation reaction by oxygen ion transfer. As well, the rate of carbon

removal as well as the amount of carbon formed during the gas phase reaction is optimized and the resulting minimized carbon deposits enhance electrical conductivity [28].

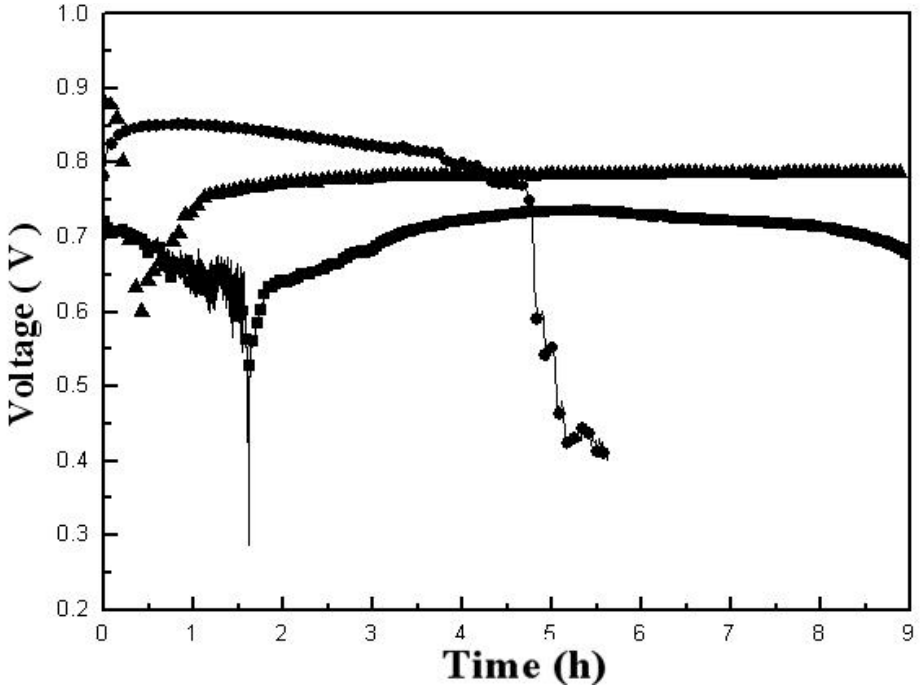

Figure 4. Long-term stability test of the unit cell with 10 ㎛ thickness of YSZ electrolyte (■), the unit cell with 6 ㎛ thickness of YSZ electrolyte (▲) using CH_4 (30 $ccmin^{-1}$) with 3% H_2O, and the unit cell with 10 ㎛ thickness of YSZ electrolyte using CH_4 (50 $ccmin^{-1}$) with 3% H_2O (●).

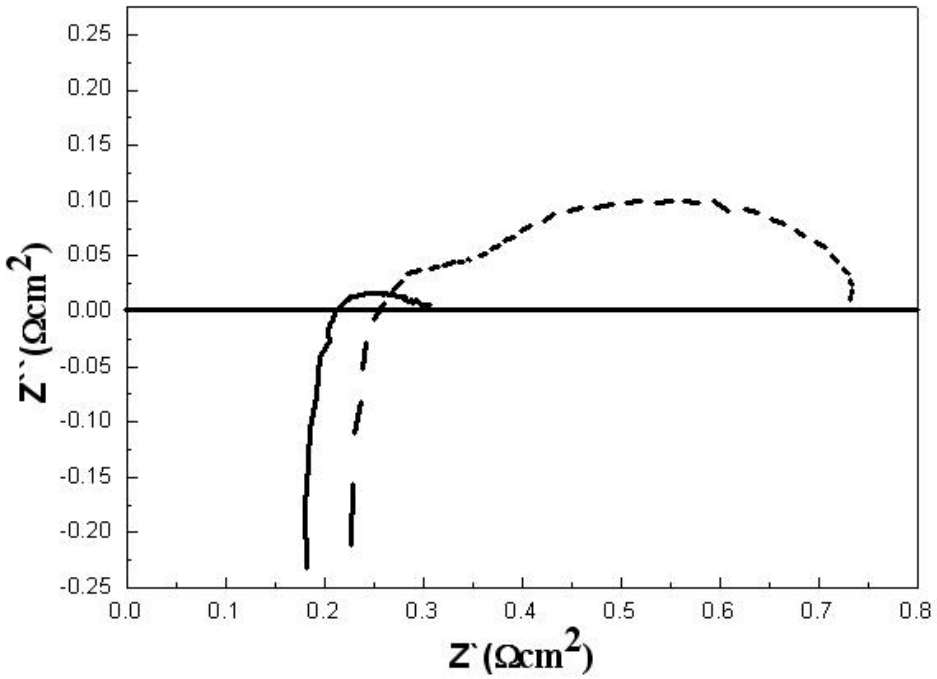

Figure 5. Impedance spectra for the unit cell using H_2 (---) and CH_4 (—).

3.3. Evaluation of cell performance at various operating temperatures and CH_4 flow rates

The maximum power density for 30 ccmin^{-1} of CH_4 with applied 0.4 current density at 800 ^oC is 0.71 Wcm^{-2} for 54 hours of operation without degradation in performance.

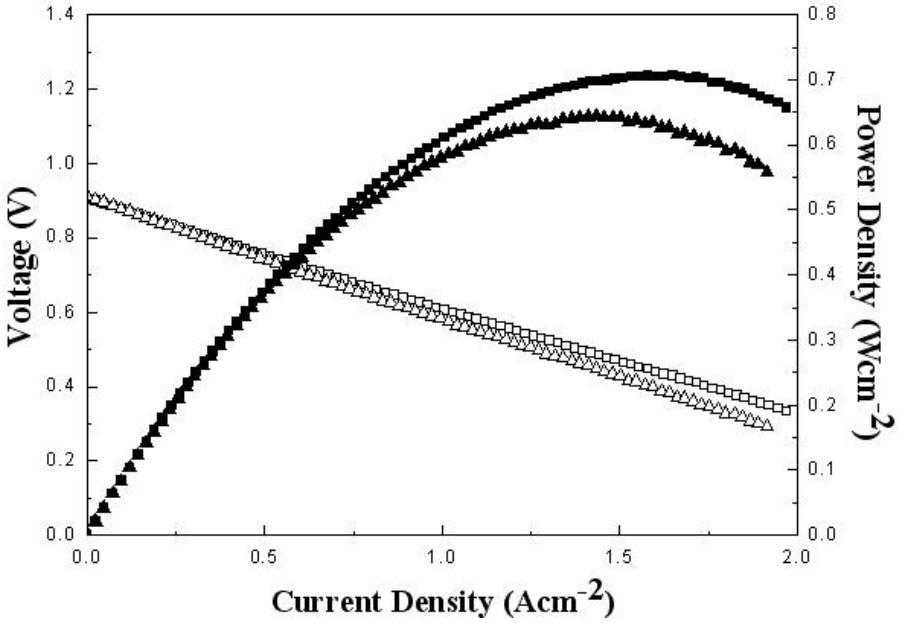

Figure 6. The I-V characteristics of the unit cell using 30 ccmin^{-1} CH_4 flow rates (■), 25 ccmin^{-1} CH_4 flow rate after 96 hours of total operation (▲) with 3% H_2O at 800 ^oC.

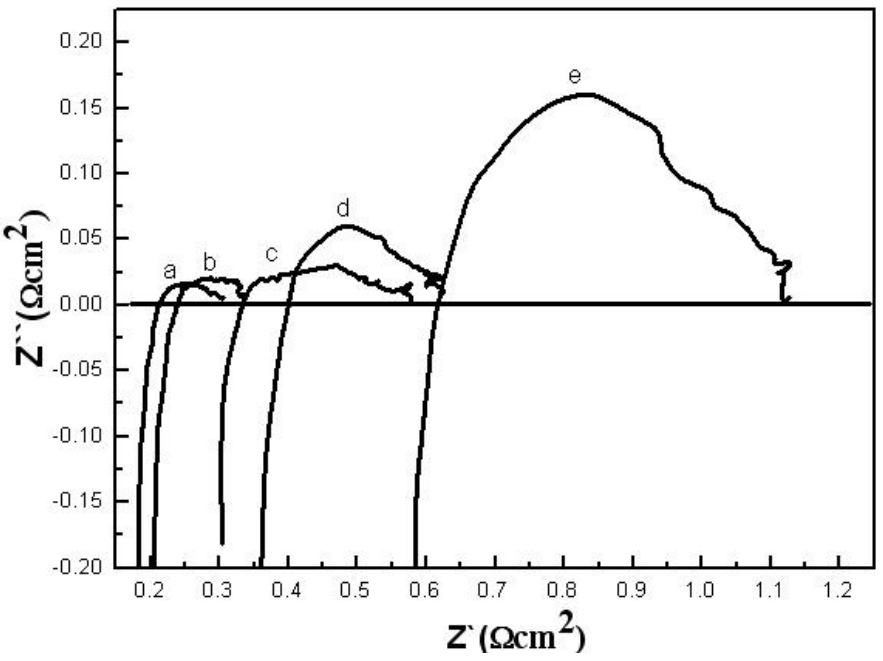

Figure 7. Impedance spectra for initial (a), after 54 hours for 30 ccmin^{-1} CH_4 flow rates (b), and initial (c), after 15 hours (d), after 27 hours (e) for 25ccmin^{-1} CH_4 flow rates with 3% H_2O at 800 ^oC.

However, a 25 ccmin^{-1} CH_4 flow rate showed 0.65 Wcm^{-2} of maximum power density and degradation in performance as carbon deposition increased in figure 6. Looking at the impedance spectra data in figure 7, a CH_4 flow rate of 30 ccmin^{-1} showed similar ohmic resistance and anodic polarization resistance for 54 hours of operation.

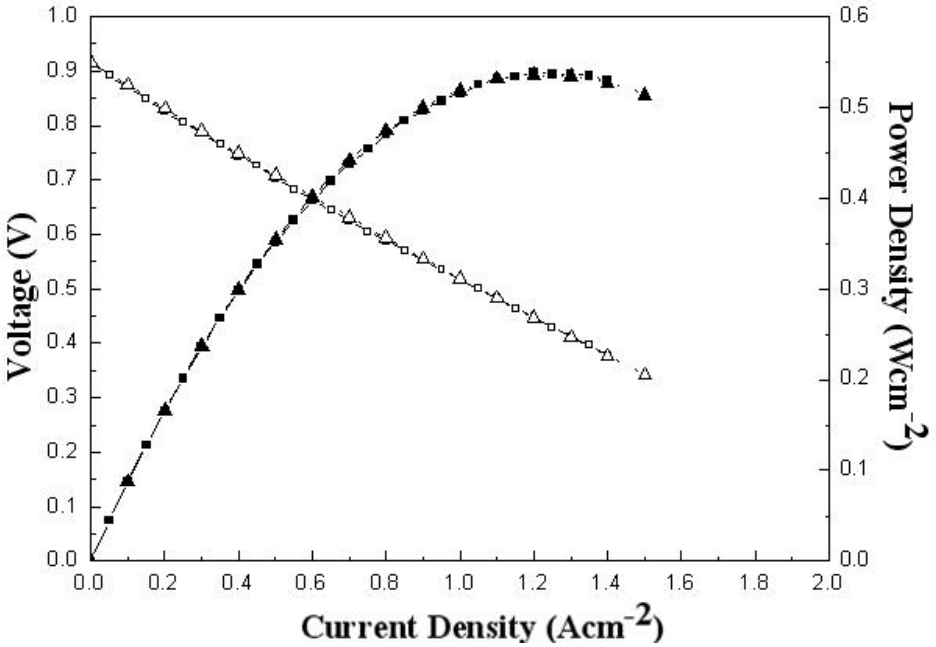

Figure 8. The I-V characteristics of initial (■) and after 120 hours of operation (total operation, 200 hours) (▲) for 25 ccmin^{-1} CH_4 flow rates with 3% H_2O at 700 ^oC.

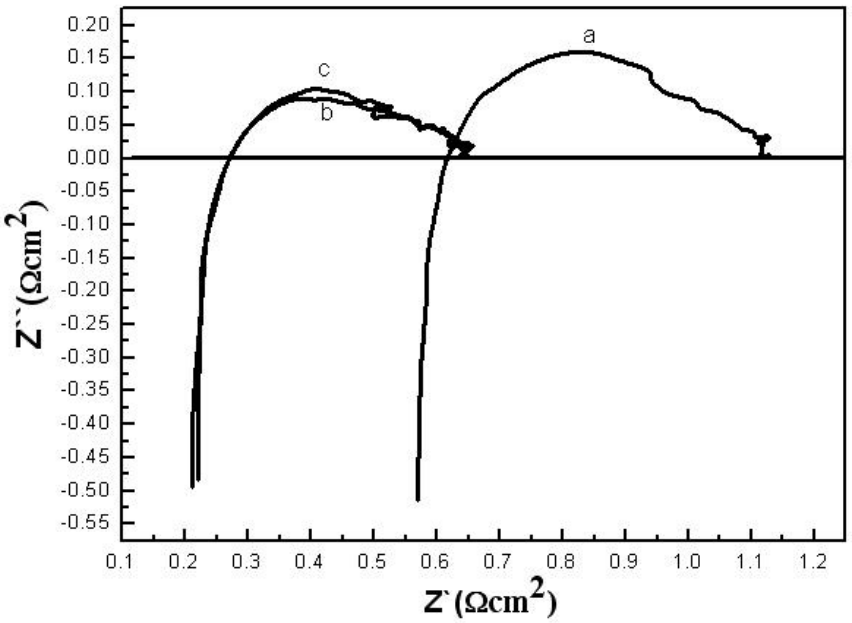

Figure 9. Impedance spectra after 96 hours of total operation for 25 ccmin^{-1} CH_4 flow rates at 800 ^oC (a), and initial (b) and after 120 hours (c) of operation for 25 ccmin^{-1} CH_4 flow rates with 3% H_2O at 700 ^oC.

However, ohmic resistance and anodic polarization resistance gradually increased in the case of 25 ccmin^{-1} of CH_4 at 800 ^{o}C. This is because both the rate of carbon removal through electrochemical reaction and the rate of carbon formation during the gas phase reaction are equilibrant and optimal by 30 ccmin^{-1} flow rate at 800 ^{o}C.

We then lowered the operating temperature to 700 ^{o}C and then again to 650 ^{o}C. The ohmic resistance reduced from 0.58 Ωcm^{-2} at 800 ^{o}C to 0.25 Ωcm^{-2} at 700 ^{o}C despite the decrease in operating temperatures, because the equilibrant condition is reset by 25 ccmin^{-1} flow rate at 700 ^{o}C. As well, after the cell operated for 120 hours at 700 ^{o}C with 25 ccmin^{-1} of CH_4, no degradation in cell performance was observed in the I-V curve and impedance spectra as shown in figures 8 and 9.

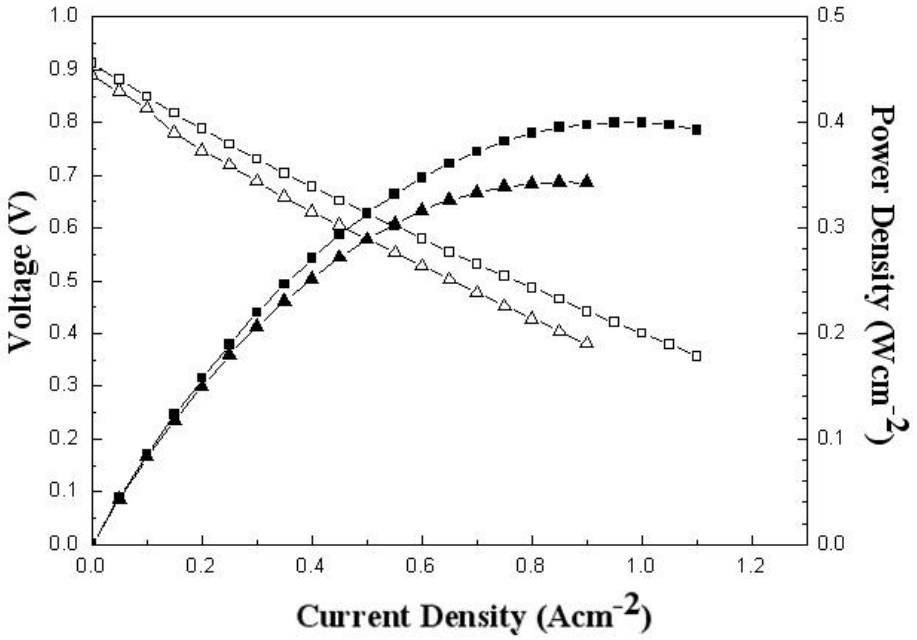

Figure 10. The I-V characteristics of the unit cell using 25 ccmin^{-1} CH_4 flow rates at initial (■) and after 170 hours of operation (total operation, 370 hours) (▲) with 3% H_2O at 650 ^{o}C.

However, in the I-V curve and impedance spectra at 650 ^{o}C of figures 10 and 11, cell power density slowly decreased to 0.35 Wcm^{-2} after 170 hours. Figure 12 summarizes the long-term stability results obtained for conventional Ni-YSZ based SOFCs using CH_4 at various temperatures and with different CH_4 flow rates. At 800 ^{o}C, 30 ccmin^{-1} of CH_4 was more stable than 25 ccmin^{-1}, but the cell is re-stabilized when the operating temperature was lowered and CH_4 was supplied at 25 ccmin^{-1}. Then, cell performance at 650 ^{o}C degraded gradually for 170 hours due to carbon deposition. From the results, it is found that the stability of CH_4-fueled SOFC is relative with the rate of carbon removal and it of carbon formation. If the removal rate is faster than the formative rate, it leads to oxidize the deposited carbon has electrical conductivity. In the other case, the formative rate is faster than the removal rate, which accelerates to deposit carbon that blocks the anode pore and crack the anode micro-structure.

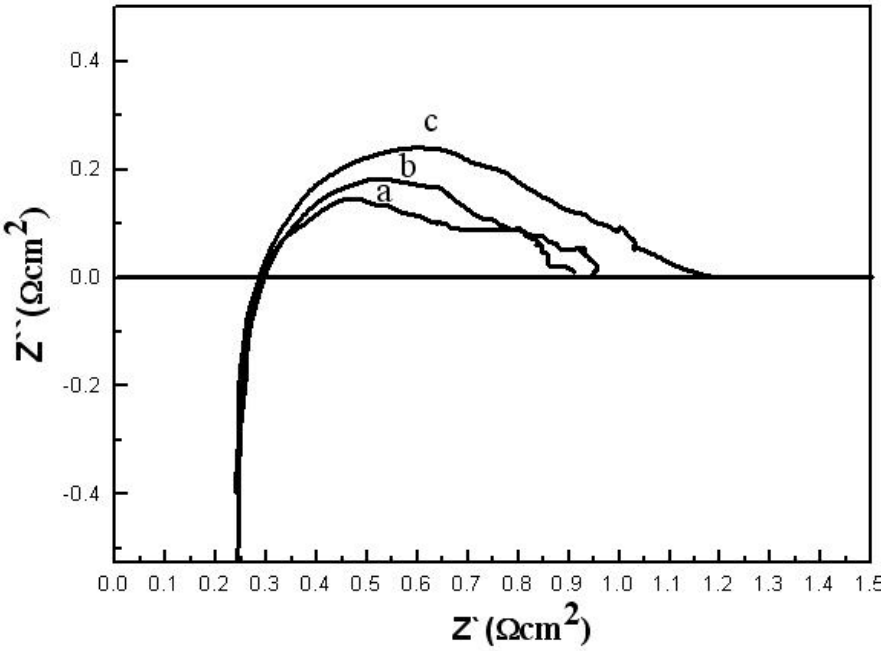

Figure 11. Impedance spectra for initial (a), after 27 hours (b), after 170 hours (c) for 25 ccmin^{-1} CH_4 flow rates with 3% H_2O at 650 ^oC.

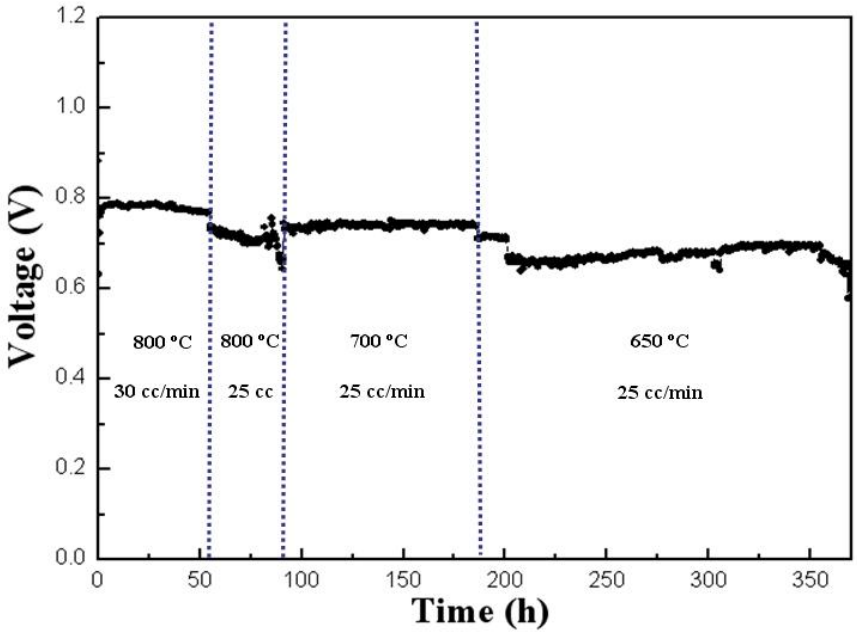

Figure 12. Summarized result of long-term stability test for various temperatures and CH_4 flow rate with 0.4 applied current density.

3. 4. Anode analysis after CH_4 fueled operation

The characteristics of the carbon deposited on the anode surface were investigated by analyzing the conventional Ni-YSZ both under and in the absence of optimized operating conditions. The SEM

images in figure 13 show the different types of carbon that were formed on in the anode near electrochemically active region.

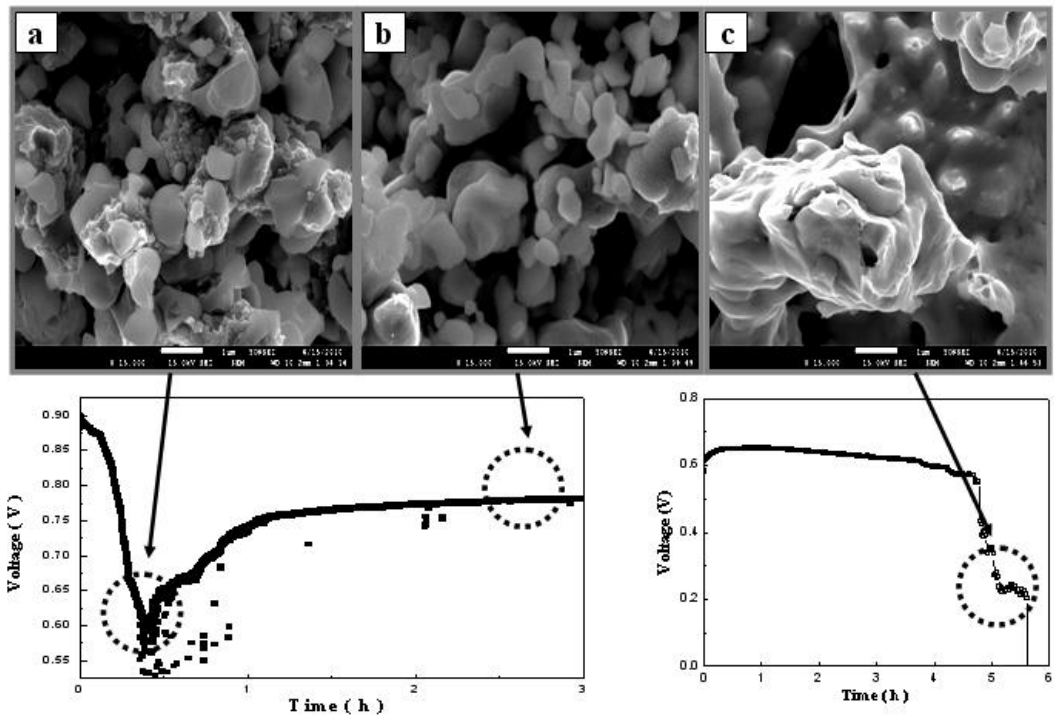

Figure 13. SEM images of the anode section with 30 ccmin^{-1} CH_4 flow rate at initial degradation (a) and under stable operation (b) and the anode section with 75 ccmin^{-1} after operation stop (c).

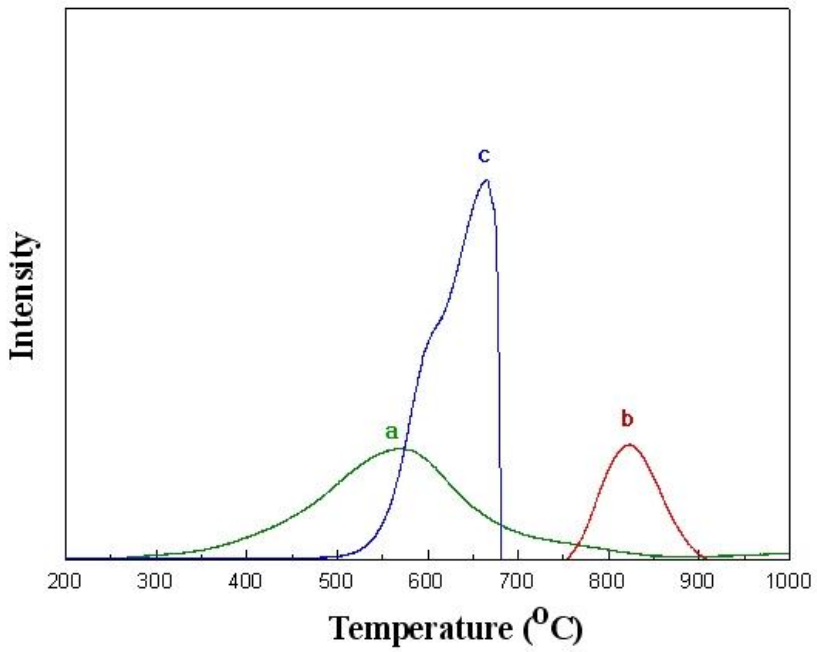

Figure 14. Temperature-programmed oxidation results for the anode at initial degradation (a), under stable operation (b) and after operation stop (c).

The graphite carbon causes cell expansion and provokes a crash in the microstructure of the anode, which is oxidized at around 700 ^{o}C. In the case of Ni-YSZ unit cells operated outside of particular operating conditions which are not with optimal CH_4 flow rate and under polarization conditions, graphite carbon was deposited on the anode as the SEM image as figure 13c illustrates. Figure 13a shows that fiber or amorphous carbon that is usually oxidized under 600 ^{o}C was deposited during initial degradation.

During stable operation, small ball carbon that enhances power density and electrical conductivity is deposited on the anode. Furthermore, small ball carbon did not accumulate and form the poly-aromatic carbons that block the microstructures of anodes during the period of optimized testing as figure 13b illustrates. As shown in figure 14, it is confirmed that the fiber or amorphous carbon at initial degradation is changed to small ball carbon after stabilizing condition. If excessive CH_4 supplied in the unit cell, the fiber, amorphous carbon, and graphite are deposited in the anode. The quantities of these carbons are much larger than it of small ball carbon that is deposited at stable condition. The TPO, SEM and voltage graph results illustrate that cell stability and power density gradually improved under optimized CH_4 flow rate through the transformation of amorphous carbon into small ball carbon without increasing in the amount of carbon

4. CONCLUSION

Thin YSZ electrolytes (6 ㎛ thick) can be successfully fabricated on Ni-YSZ anode supports to obtain higher oxygen ionic conductivity by dip-coating them in YSZ slurry. These conventional Ni-YSZ unit cells showed much lower ohmic and anodic polarization resistance and higher performance and improved stability by controlling CH_4 flow rates. It was confirmed that the optimal CH_4 flow rates for operating CH_4-fueled cells are 30 ccmin^{-1} at 800 ^{o}C, 25 ccmin^{-1} at 700 ^{o}C, and 20 ccmin^{-1} at 650 ^{o}C by controlling the amount and the type of carbon deposited under given operating conditions. The CH_4 fueled unit cell showed maximum power densities of 0.75, 0.53, and 0.4 Wcm^{-2} at 800 ^{o}C, 700 ^{o}C, and 650 ^{o}C, respectively, in CH_4 humidified with 3 % H_2O and operated for over 370 hours without serious degradation.

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References

1. S.A. Barnett In: W. Vielstich, A. Lamm, H. Gasteiger, Editors, Handbook of Fuel Cell Technology IV, *Fundamentals of Technology and Applications*, p. 1098, Wiley, San Francisco (2003).
2. J. Mermelstein, M. Millan, N.P. Brandon, *Chem Eng Sci* ., 64, (2009) 492.
3. M. Ni, D.Y.C. Leung, M.K.H. Leung, K. Sumathy, *Fuel Processing Technol*., 87, (2006) 461.
4. P. McKendry, *Bioresource Technol* ., 83, (2002) 55.
5. Y. Cao, Y. Wang, J.T. Riley, W.-P. Pan, *Fuel Processing Technol*., 87, (2006) 343.

6. A.L. Dicks, *J. Power Sources*., 61, (1982) 113.
7. C.H. Bartholomew, *Catal. Rev. -Sci. Eng*., 24, (1982) 67.
8. P.G. Menon, J. Mol. *Catal*., 59, (1990) 207.
9. Alzate-Restrepo, J. M. Hill, *Appl Catal A Gen*., 342, (2008) 49.
10. Y. Lin, Z. Zhan, J. Liu, S.A. Barnett, *Solid State Ion*., 176, (2005) 1827.
11. T. Hibino, A. Hashimoto, T. Inoue, J.-I. Tokuno, S.-I. Yoshida, M. Sano, *Science*, 288, (2000) 2031.
12. B.C.H. Steele, *Solid State Ion*., 86, (1996) 1223.
13. E.P. Murray, T. Tsai, S.A. Barnett, *Nature*, 400, (1999) 649.
14. S. Park, J.M. Vohs, R.J. Gorte, *Nature*, 404, (2000) 265.
15. R.H. Cunningham, C.M. Finnerty, R.M. Ormerod In: U. Stimming, S.C. Singhal, H. Tagawa, W. Lehnert, Editors, Proceedings of Fifth International Symposium on Solid Oxide Fuel Cells, p. 973, *The Electrochemical Society Proceedings Series*, Pennington, NJ (1997).
16. H. Praliaud, M. Primet, G.A. Martin. *Appl. Surf. Sci*., 17, (1983) 107.
17. H. Praliaud, J.A. Dalmon, C. Mirodatos, G.A. Martin. J. Catal., 97, (1986) 344.
18. J.R. Rostrup-Nielsen, L.J. Christiansen. *Appl. Catal. A: General*., 126, (1995) 381.
19. J. H. Myung, J. J. Lee, S. H. Hyun, Electrochem. *Solid-State Lett*., 13, (2010) B43.
20. S. Hasegawa, M. Ihara, *J. Electrochem. Soc*., 155, (2008) B58.
21. S.D. Kim, H. Moon, S.H. Hyun, J. Moon, J. Kim,H.W. Lee, *Solid State Ion*., 177, (2006) 931.
22. H. He, J.M. Vohs, R. J. Gorte, *J. Power Sources*., 144, (2005)135.
23. J. Mermelstein, M. Millan, N. P. Brandon, *Chem. Eng. Sci*., 64, (2009) 492.
24. C. M. Finnerty, N. J. Coe, R. H. Cunningham, R. M. Ormerod, *Catal. Today*., 46, (1998) 137.
25. M. Pillai, Y. Lin, H. Zhu, R. J. Kee, S. A. Barnett, *J. Power Sources*., 195, (2010) 271 .
26. Y. Lin, Z. Zhan, J. Liu and S.A. Barnett, *Solid State Ion*., 176, (2005)1827.
27. J. Liu, S. A. Barnett, *Solid State Ion.*, 158, (2003)11.
28. H. Kim, C. Lu, W. L. Worrell, J. M. Vohs, R. J. Gorte, *J. Electrochem. Soc*., 149, (2002) A247.