様式第２号（第５条，第１１条関係）

「課程博士用」

学 位 論 文 の 要 旨

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学位論文題目	Study on Dry Methane Directly Oxidized and Power Generated Performance at Nickle Based Anode in SOFC（ニッケルベースアノードを持つ SOFC のドライメタン燃料による発電特性）		

Executive Summary

The reaction mechanisms of dry methane on the anode (Ni-YSZ or Ni-ScSZ) are investigated detailedly, utilizing a combined theoretical and experimental approach. The degradation mechanism of Ni- ScSZ anode in low concentration of dry methane is explored. Besides, the optimization of conventional Ni based anodes and development of alternative materials for direct utilization of hydrocarbon fuels SOFCs are focused.

Chapter 1 presents a brief introduction on basic concepts and the main component materials of SOFCs, as well as the utilization of methane mode.

Chapter 2 gives the flow process of material preparation, fabrication and measurements of single cells, as well as characterization techniques.

Chapter 3 evaluates the influence of dry methane concentration on reactions mechanism at Ni-YSZ anode in SOFC, and explores the mathematical relationship between the concentration of dry methane and the amount of oxygen ions. As the oxygen ion concentration at the anode three-phase boundary increasing continuously, the reaction route is shown in Fig.1, and the following reactions with low concentration methane occurs in sequence $CH_4 + O^{2-} \rightarrow CO + 2H_2 + 2e^-$, $CH_4 + 2O^{2-} \rightarrow CO + H_2O + H_2 + 4e^-$, $CH_4 + 3O^{2-} \rightarrow CO + 2H_2O + 6e^-$, $CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$, the first two or three reactions occur with intermediate methane concentration, and the first reaction occurs only with high methane concentration, both on Ni-YSZ and Ni-ScSZ anode. The judgment of methane in low, medium or high concentration depends on $v(CH_4) \leq I/(4F)$, $I/(4F) \leq v(CH_4) \leq I/(2F)$, $v(CH_4) \geq I/(2F)$ respectively, which are based on Faraday's first law and the relationship among reactant species.

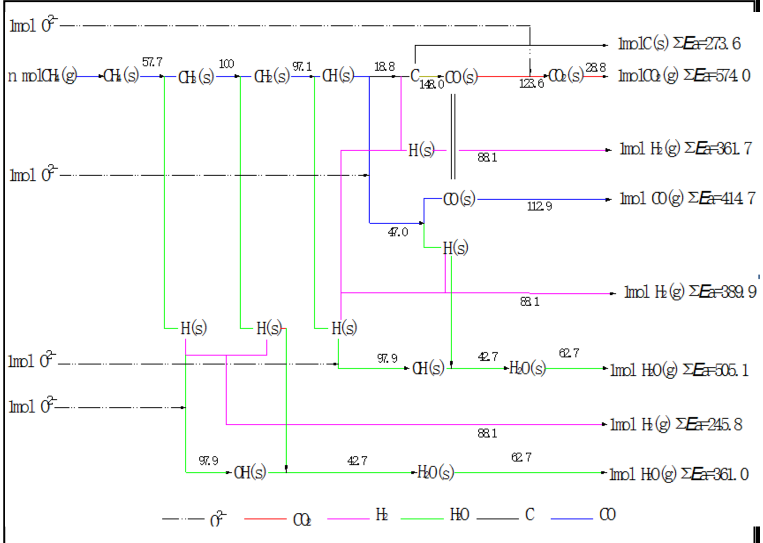

Fig.1　Reaction route

Chapter 4 clarifies the influence of dry methane concentration on the output performance of cells with Ni-ScSZ anode. The main reason for the output performance change was further discussed from electrochemical reaction kinetics. Especially in low concentrations of dry methane, the phenomenon of a rapid cell degradation at high current density was observed and further studied. Without mechanical damage and seal leakage, this phenomenon could be attribute to the production of H_2O in transition of reactions, resulting in the increase of $p(H_2O)/p(CH_4)$ at anode side, as well as the polarization, which caused the anode degradation.

Chapter 5 creates a Ni_xCu_{1-x} (x = 0.8, 0.5, 0.2) alloy anode with novel structure for the direct utilization of hydrocarbon fuels. The novel anode prepared directly by alloying the poor catalytically active Cu with Ni was elaborated in this chapter. The as-prepared material with cubic crystal structure (Fig. 2a) and a columnar shape was observed (Fig. 2b). The possibility of Ni-Cu alloy as a potential anode was investigated in dry CH_4, both in performance test and stability test. The cells with $Ni_{0.8}Cu_{0.2}$ anode achieved the highest value of 315 mW·cm^{-2} at 1073 K under methane (Fig. 2c). The Ni_xCu_{1-x} anodes showed a stable property after 10 h operation in dry methane.

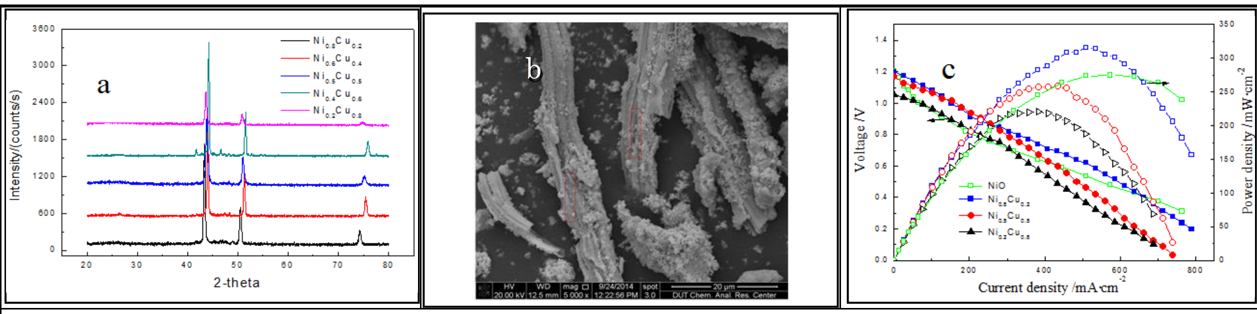

Fig.2　XRD,SEM and performance for NiCu alloys.

Chapter 6 the tubular YSZ with the stereo structure was firstly prepared by hard template method to form a three dimensionally porous anode framework（Fig.3 a）, and then $Ni_{0.5}Cu_{0.5}O_x$ as catalysts was impregnated into YSZ skeleton to fabricate $Ni_{0.5}Cu_{0.5}O_x$-YSZ composite anode. The performance and stability of $Ni_{0.5}Cu_{0.5}O_x$-YSZ anode was characterized when CH_4 was used as fuel, which will be discussed in detail. By comparing the results of the 100 h long-term stability tests under dry CH_4 and wet CH_4 (3%H_2O) respectively（Fig.3 a and b）, the cell with dry CH_4 showed an obvious voltage drop of 5.27% but the one with wet CH_4 showed the more stable property, indicating that the presence of 3%H_2O had an obvious impact on inhibiting carbon deposition on the anode（Fig.3 d）. SEM and EDS results confirmed that the porous anode structure was quite steady, as well as less carbon was formed in the anode using wet CH_4 (3%H_2O) as fuel after 100 h operation. Therefore, the stereo structure design with YSZ micro tube as skeleton and impregnated $Ni_{0.5}Cu_{0.5}O_x$ as catalyst is indeed an alternative and effective technique to enhance cell performance, stability and reliability for SOFCs.

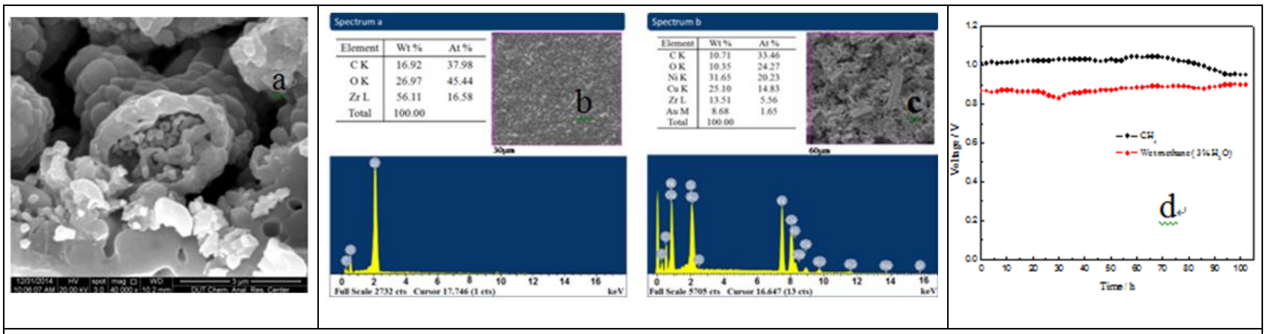

Fig.3 SEM, EDS and 100h test of Ni0.5Cu0.5Ox-YSZ stereo anode

Chapter 7 $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) was adopted to replace YSZ as anode scaffold and $Ni_{0.5}Cu_{0.5}Ba_{0.05}O_x$ was used as the impregnated catalyst to prepare three-dimensional $Ni_{0.5}Cu_{0.5}Ba_{0.05}O_x$/SDC anode. The anode microstructure effect on the cell performance was investigated by using a powdered $Ni_{0.5}Cu_{0.5}Ba_{0.05}O_x$-SDC anode, which was prepared by mixing $Ni_{0.5}Cu_{0.5}Ba_{0.05}O_x$ powder and SDC powder. The single cells with such contrastive anodes were fabricated for the power generation performance test and the long-term stability test. The cell with $Ni_{0.5}Cu_{0.5}Ba_{0.05}O_x$/SDC anode showed a good stability for 100 h operation in dry CH_4, while the cell with $Ni_{0.5}Cu_{0.5}Ba_{0.05}O_x$-SDC dropped rapidly after 10 h. SEM results shows $Ni_{0.5}Cu_{0.5}Ba_{0.05}O_x$/SDC anode presented a stable structure, suggesting that the fabrication of anti-carbon catalyst combined with three-dimensional electrode is potential measure to enhance durability for direct utilization of dry methane as fuel in SOFCs.

Chapter 8 discusses the possibility of the $SrMoO_4$ based materials as an alternative candidate for SOFC anodes. Considering the low catalytic activity of $SrMoO_4$-YSZ in preliminarily investigation, $Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC) was introduced into $SrMoO_4$ by wet impregnation to further improve its potential as SOFC anode materials. The introduction of GDC showed excellent effects of enhancing catalytic activity, resulting in a higher cell performance. When the mass ratio of $SrMoO_4$ to YSZ was 5:5, and the GDC impregnation loading reached an optimal value, 50wt% (relative to $SrMoO_4$ and YSZ), the cell exhibited a high performance, with a maximum power density of 361.01 $mW\cdot cm^{-2}$ in dry CH_4 at 1073 K.

Finally, a detailed conclusion in **Chapter 9** is presented on the general discussion of the results in the whole report. It emphasizes the most important conclusions in the study and finally comments on how the research of this topic could be continued.

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