탄화수소의 직접산화를 위한 고체산화물 연료전지 전극 개발

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Development of Solid Oxide Fuel Cell Anode for Direct Oxidation of Hydrocarbons

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Introduction

Fuel cell is one of the promising clean energy technologies in the future. It can generate much higher power than general combustion system. Most fuel cell systems use hydrogen that is clean but hard to get and handle. Solid Oxide Fuel Cell (SOFC) has a flexibility of fuel selection due to its high operation temperature. An SOFC generates power through the reduction of oxygen to oxygen ion at the cathode, oxygen ion conduction through the oxide electrolyte, and the oxidation of fuel by the ion at the anode. When the fuel is oxidized, the electron is generated at the anode. Direct, electrochemical oxidation of any fuel, without reforming the fuel, is theoretically possible in the SOFC since oxygen ion is transferred. The conventional anode is a cermet of Ni and yttria-stabilized zirconia (YSZ). Ni works as an electronic conductor and YSZ does as an ionic conductor. However, Ni induces carbon formation from hydrocarbons. To prevent this problem, the SOFC must be operated in a narrow range of temperatures or internal reforming by additional steam feeding is necessary. The fuel must be small hydrocarbons such as methane, since the amount of steam is increased significantly for bigger ones. Recently, Several groups tried direct oxidation of methane and light hydrocarbons in the system [1-3]. Our work has centered on examining Cu-based anodes for SOFCs. When Ni is replaced with Cu, the anode can oxidize hydrocarbons directly to produce electrical energy without carbon formation.

Experimental

The fuel cells were prepared using a dual tape casting method. One layer of YSZ(Tosoh-zirconia, 8% Y_2O_3) was prepared by tape casting. On the green tape of YSZ, the mixture of YSZ and pore formers was tape-cast. After calcination at 1800K, the two layers were a dense YSZ wafer, 60 um thick, as an electrolyte and a porous YSZ support, 400 um thick, as an anode structure. Alternatively, the porous layers were prepared from mixture of YSZ and NiO (Alpha Aesar) powders. The samples were exposed to hydrogen at 973K for 10 hrs to reduce NiO into Ni, and placed in 2.2 M nitric acid at 353K for 2 hrs to leach Ni.

Cathode material, a 1 : 1 mixture of YSZ and Sr-$LaMnO_3$ (Praxair Surface Technologies), was painted onto the dense side of the wafer, then sintered at 1500K. Ceria was added on the porous YSZ layer by wet impregnation of $Ce(NO_3)_6H_2O$. In the case of Cu incorporation, a solution of $Cu(NO_3)_2H_2O$ was impregnated on the layer. Heat treatment to form the oxides was done at 750 K. The final concentration was 10 wt% of ceria and 20 wt% of Cu. For the single cell test, Pt line was attached on the cathode and Au line was attached on the anode. Finally, The cell was sealed onto Al_2O_3 tubes and heated up to the operation temperature. The cathode was left open to air. Liquid fuels were introduced using a syringe pump, and the liquids were vaporized in the oven used to maintain the temperature of the cell at 973 K.

The composition of the outlet gas from the anode was analyzed by on-line gas chromatograph. The porosity of the sample was taken by the water immersion method and mercury porosimetry (AutoPore Mercury Porosimeter).

Results and Discussion

In our previous work, we demonstrated that stable power generation was possible by direct oxidation of small hydrocarbons, including methane and butane[4], when Ni was replaced with Cu. For higher hydrocarbons, liquid fuels, toluene was first examined, varing the flow rate of carrier gas N_2 to change the toluene concentration. It was found that OCV did not change with the concentration of toluene down to 2.5 vol%, the maximum current density increased significantly with increasing concentration. For low concentrations, the maximum current density is limited by diffusion of toluene through the anode. At higher concentrations, the current density is likely controlled by oxidation kinetics at the electrolyte interface and ion conductivity in the electrolyte. Evidence that toluene is being electrochemically oxidized is the effluent containing CO_2 and water in quantities corresponding to the amount of the oxygen ions passed through the electrolyte. The stability of electrocatalytic oxidation is further demonstrated for decane, toluene, and a synthetic diesel by at 973 K. The performance remained steady with reasonable power output of 0.1 W/cm^2 without any deactivation.

Since most hydrocarbon fuels have some level of sulfur, it is important to demonstrate power generation through the direct oxidation of sulfur containing fuels. Fig. 1 shows the performance of the cell upon switching from 50 mol% n-decane(0 ppm S) to 50 mol% n-decane (5000 ppm S), while holding the cell potential at 0.5V. The current density dropped much by the introduction of sulfur and could not show the original value by switching back to pure decane. However, the cell could be restored completely by introducing steam with N_2. As seen in Fig. 1, the cell could be poisoned and restored repeatedly without showing any decrease of cell performance. The phase diagram (Fig. 2) for ceria shows the likely cause for the sulfur poisoning[5]. From the calculated value, cerium of Fig. 1 should be around point 1 and lose its activity. Heating the phase with steam should oxidize cerium back. The phase diagram gives us a hint that modest level of sulfur should not affect the ceria in the anode. Fig. 3 is the demonstrated result of cell performance in 5 mol% n-decane (100 ppm S). The calculated position is point 2. Stable performance was observed for 100 hrs in this range. Sulfur concentration at this level is not likely to have any effect on the anode performance.

Compared to hydrogen or higher hydrocarbons, methane is a relatively stable gas. In order to obtain a high power density, the oxidation rate of methane must be improved by catalytic or thermodynamic approach. Our catalytic design for an anode in a SOFC is based on Cu and ceria. Assuming that small amount of addition of Ni to Cu improves the methane activation without carbon formation and stabilizes Cu structure due to Ni's higher melting temperature, for stable and reasonable performance it is worth to add small amount of Ni into our cermet. To demonstrate Cu-Ni alloy application in the anode cermet, we made the model cell of YSZ cermet impregnated with different ratio of metal and reduced the samples with hydrogen at 1173K for 3 hrs, followed by exposure to a flow of methane at 1073K for 1.5 hr. The results are shown in the photographs of Fig. 4. The results of the alloy cermet were dependent of its composition. Cu-Ni (5:5) did not show any crack or breakage, however, the surface of anode cermet was covered by large amount of carbon. While the colors of Cu-Ni (9:1) and Cu-Ni (8:2) were slightly changed by carbon, there was no evidence of carbon generation on the surface. In the range of Ni concentration lower than 20%, the decomposition of hydrocarbon into carbon formation can be suppressed not to affect the stability of the cermet structure. To determine the possibility of Cu-Ni cermet anode in a SOFC, the real cell was made by incorporating Cu and Ni with the weight ratio of 8 : 2 on ceria/YSZ layer. At 973K the maximum power density for methane was 0.07 W/cm^2 , which was 25% of hydrogen based power density. When the temperature was increased to 1073K, the maximum power density of methane reached almost 75% as much as that of hydrogen generated. The Cu-Ni cell did not undergo carbon formation and showed the reasonable power density for the long run test over 20 days. It indicates that there was no sintering or evaporation of metal phase.

Recent work on high-performance SOFCs has tended to favor the use of thin electrolyte films supported on the Ni-YSZ anode and a great deal of work has gone into optimizing the structure of the anode[6,7]. To apply the information to our system, we tired a leaching method to exchange Ni with Cu in conventional SOFCs and measured the porosity changes during the procedure. The results are given in Table 1. The values in second and third column were taken before and after reduction by hydrogen at 937K for 10 hrs. The values in fourth column were taken after leaching the reduced samples by nitric acid. All the samples with NiO showed significant increase of porosity after reduction by hydrogen and leaching by nitric acid. In the case of the NiO/YSZ cermet of 1:1 ratio, the final porosity reached 70%. Compared to the porosity (around 60%) of cermets by the addition of pore formers in our previous work[8], the value obtained from NiO/YSZ cermet is significantly higher, indicating that NiO can do the role of pore formers much better. The cell manufactured using the leaching process was prepared. The maximum power densities of butane (0.15 W/cm^2) and hydrogen (0.26 W/cm^2) are even slightly higher than those reported in our earlier works. It indicates that the anode structure made with NiO/YSZ cermet provides sufficient pore volume to introduce active materials, resulting in high active catalytic area by good dispersion.

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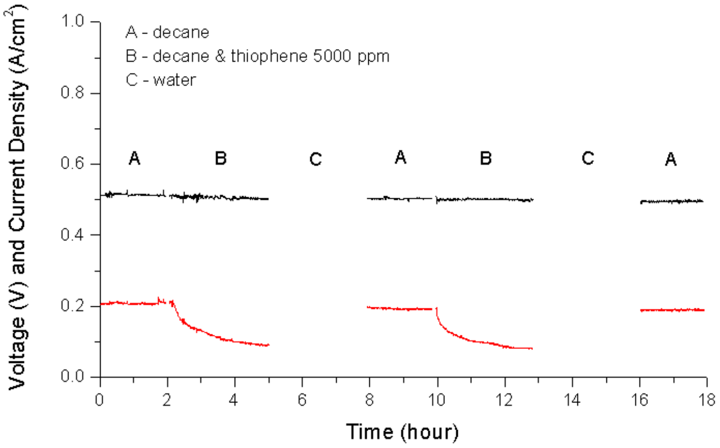

Fig. 1. Single cell performance as a function of time at 973K, holding the cell potential at 0.5V. The feed to the anode was: (A) 50mol% n-decane in N_2; (B) 50 mol% n-decane, having 5000 ppm S; (C) 50 mol% H_2O in N_2.

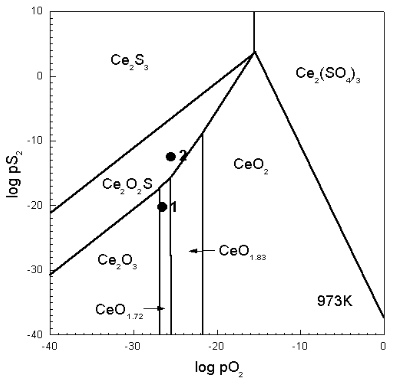

Fig. 2. The Ce-O-S phase diagram at 973K. Points 1 and 2 correspond to the experimental conditions described in the text.

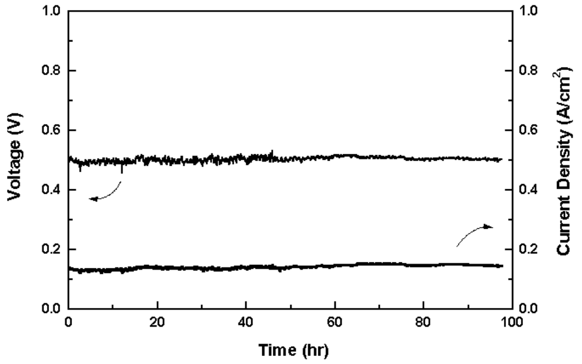

Fig. 3. Single cell performance as a fuction of time at 973K, holding the cell potential at 0.5V. The feed to the anode was 5 mol% n-decane containing 100 ppm S.

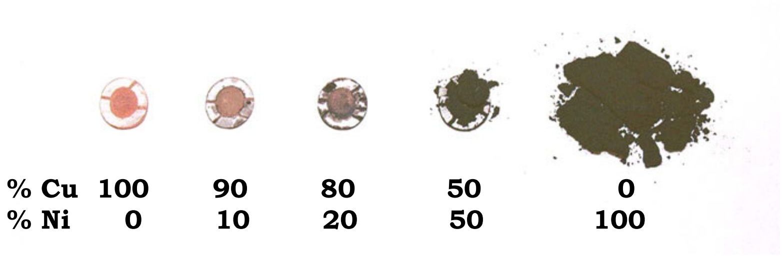

Fig. 4. Samples exposed to dry methane at 800°C for 3 hrs.

Table 1. The porosity change of the cermets by reduction with hydrogen and leaching in nitric acid.

YSZ:NiO mass ratio	Initial porosity (%)	Porosity (%) after H_2 reduction	Porosity (%) after leaching
100:0	33	33 (33)	32 (33)
80:20	38	42 (41)	47 (47)
60:40	46	54 (54)	64 (64)
50:50	51	59 (60)	69 (72)