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Properties of Anode Materials Based on $Ce_{0.8}Sm_{0.2}O_{1.9}$ and Ni-Cu Alloys

S. Koutcheiko[1], Y. Yoo[1], I. Davidson[1], D. Ghosh[2]
[1]National Research Council Canada, Ottawa, Ontario, Canada
[2]National Research Council Canada, Vancouver, BC, Canada

The cost and efficiency of solid oxide fuel cells could be improved significantly if the cell could be fuel by dry natural gas directly at temperatures in the range 500-600 °C without the need for conversion to syngas by external or internal reforming. For solid oxide fuel cells operating at this intermediate temperature range, ceria doped with Sm (SDC) or Gd (GDC) is typically used as the electrolyte and as a component of the anode. Doped ceria itself is a poor catalyst and poor electronic conductor and, therefore, additions of metal catalysts to the anode are necessary (1). The most common anode materials for solid oxide fuel cells are Ni-containing cermets (2). However, nickel solid oxide fuel cell anodes are unsuitable for operation with dry natural gas because of carbon deposition (3). Therefore, controlling the catalytic properties of metal and of the carbon formation/gasification equilibrium is of great importance. One method of controlling the catalytic activity is by alloying the Ni with a metal inactive for the decomposition of methane. Copper appears to be such a metal, as it does not chemisorb methane, shows no activity for carbon deposition from aliphatic hydrocarbons at temperatures < 800 °C, and decreases the tendency for deactivation (4). It has been shown previously that the rate of carbon formation for alloys of Ni with more than 10 at% Cu is more strongly decreased than the rate of steam reforming (5).

In the present work we report some properties of SDC-$Ni_{1-x}Cu_x$ cermets and their behavior as anodes in dry methane. Alloying Ni (m.p. 1453 °C) with Cu (m.p. 1083 °C) has the added advantage of bypassing processing problems associated with low melting point of copper and its oxides.

The samples containing 50 wt% of $Ce_{0.8}Sm_{0.2}O_{1.9}$ and 50 wt% of $Ni_{1-x}Cu_x$, where x=0, 0.09, 0.28, 0.48 were prepared by impregnation followed by calcinations and reduction. The required amounts of $Ni(NO_3)_2{*}6H_2O$ (Aldrich) and $Cu(NO_3)_2{*}3H_2O$ (Aldrich) were dissolved in water. The solution and SDC nanopowder (20 nm, Microcoating Technology Ltd.) were mixed together and dried. The mixture was then calcined at 500 and 900 °C for 5h at each temperature in air. Then the samples were reduced at 900 °C in forming gas (8% H_2 in Ar).

X-ray powder diffraction measurements were carried out on Bruker D8 diffractometer using Cu K_α radiation. The lattice constants of the metals and alloys were calculated from the (111), (200), and (220) reflections.

Thermal expansion coefficients of the cermets under reducing and oxidizing atmospheres were measured with Setaram Setsys-Evolution apparatus in the temperature range 200-900 °C at a heating/cooling rate of 5°/min. Small disks (∅ ~ 5 mm, h ~ 3 mm) sintered at 900 °C were used for the measurements.

An electrolyte supported (YSZ, 150 μm, Kerafol Gmbh) single cell was prepared by screen printing. A mixture of YSZ and Pt (40 wt%) was used as the cathode. The $Ce_{0.8}Sm_{0.2}O_{1.9}$- $Ni_{1-x}Cu_x$ anode was prepared by heating at 1000 °C for 1h in air and than reduced in forming gas in situ at 900 °C. Gold and platinum grids were printed on the surface of anode and cathode, respectively, for current collection. A certified gas mixture of CH_4 (5%) in Ar (Air Products) was used as the fuel. The effluent gas from the anode compartment was analyzed with a QME 200 mass spectrometer.

Fig 1. shows X-ray patterns for SDC-supported $NiO_{1-x}Cu_xO$ powders calcined at 900 °C for 5h in air. It is clear that only one composition, with x=0.09, is a single phase solid solution, and this had a cubic rock salt structure with a lattice parameter of 0.4180 nm. Traces of tenorite CuO were detected in the sample with x=0.28. With increasing CuO concentrations, above x=0.28, the segregation of the tenorite phase is clearly observed. The crystallographic unit cell parameter of

$Ni_{1-x}Cu_xO$ increases with increasing copper content due to the difference in the ionic radii for Ni^{2+} (0.69) and Cu^{2+} (0.73 A) (6). The nominal composition at x=0.48 exceeded the solubility limit of CuO in NiO, which is about 30 mol% at 1000 °C (7).

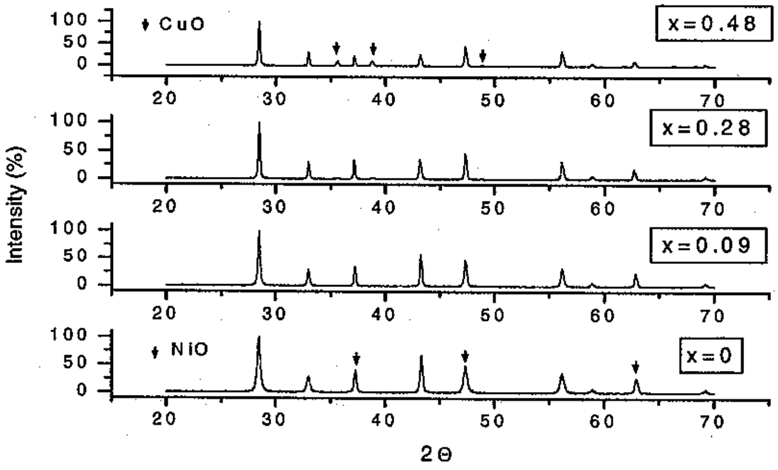

Fig. 1 X-ray patterns for SDC –$NiO_{1-x}CuO_x$ calcined at 900 °C for 5h in air

It was found that all mixed oxides of $NiO_{1-x}CuO_x$ supported on SDC could be reduced in forming gas in the temperature range 200-350 °C. However, only the reduction at 900 °C produced single phase $Ni_{1-x}Cu_x$ alloys in the range $0 < x \leq 0.48$. Fig. 2 shows the dependence of cell parameters of $Ni_{1-x}Cu_x$ alloys obtained after reduction of the SDC- $Ni_{1-x}Cu_xO$ powders in forming gas at 900 °C for 5h. One can see that at all concentrations a solid solution of Ni-Cu is formed. The cubic unit cell parameters increase almost linearly with increasing Cu content. Thus it seems that single -phase alloys are formed despite the segregation of Ni(Cu)O and CuO phases mentioned above. The freshly reduced samples showed pyrophoric behavior and were deactivated in flowing Ar, containing trace amounts of oxygen, at 100 °C. Complete oxidation of alloys in air was observed in the temperature range 200-500 °C and resulted in segregation of tenorite in the case of the x=0.28 and 0.48 samples. Only the sample of SDC-$Ni_{1-x}Cu_x$ containing 9 mol% of Cu could be reversibly

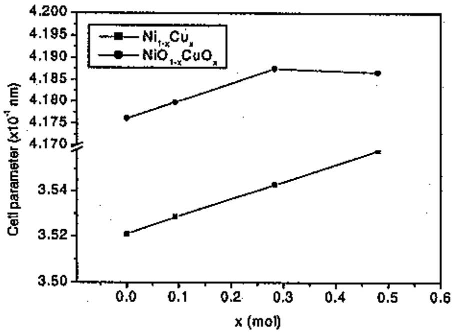

Fig 2. Cell parameters for $Ni_{1-x}Cu_x$ and $NiO_{1-x}Cu_xO$ supported on SDC prepared at 900 °C in forming gas and air, respectively.

oxidized and reduced below 600 °C without copper phase segregation. It is worth noting that reduction of the SDC support was detected at temperatures above 600 °C.

The thermal expansion of the SDC-$NiO_{1-x}Cu_xO$ ceramics was measured during the process of cermet fabrication by reduction in forming gas. For comparison the curve for a pure SDC-CuO ceramic is also presented in Fig 3. Measurement of the thermal expansion coefficients (TECs) of the cermets was performed at a cooling rate of 5 °C/min from 900 °C to 200 °C. It can be seen from Fig. 3 that the NiO-CuO oxides show a drastically reduced change in size on reduction in the temperature range 200-400 °C in comparison to that for pure CuO. The very sharp expansion (by about 2.6 %) of the SDC-CuO ceramic at 300 °C makes the anode fabrication process extremely challenging. The expansion observed in the temperature range above 600 °C seems to be mainly due to reduction of Ce^{4+} to Ce^{3+} in the SDC. The TECs for the SDC-$Ni_{1-x}Cu_x$ cermets measured in forming gas are presented in Table 1. The TECs of the cermets increase with increasing Cu content from $13.3x10^{-6}$ K^{-1} for x=0 to $14.9x10^{-6}$ K^{-1} for x =0.48. The sample with x=0.09 had the closest TEC to that of the potential electrolyte, SDC ($12.6x10^{-6}$ K^{-1}), among the Ni-Cu containing cermets studied. The expansion behavior of the SDC–$Ni_{1-x}Cu_x$ cermets was also tested under oxidizing conditions.

Table 1. Characterization of SDC-$Ni_{1-x}Cu_x$ cermets

x	Cell parameter for $Ni_{1-x}Cu_x$, x 10^{-1}, nm	TEC in FG (200-900 °C), x 10^{-6} K^{-1}	TEC in FG at 500±100 °C, x 10^{-6} K^{-1}
0	3.5210	13.3	13.3
0.09	3.5285	13.5	13.6
0.28	3.5428	14.6	14.6
0.48	3.5579	14.9	15.2

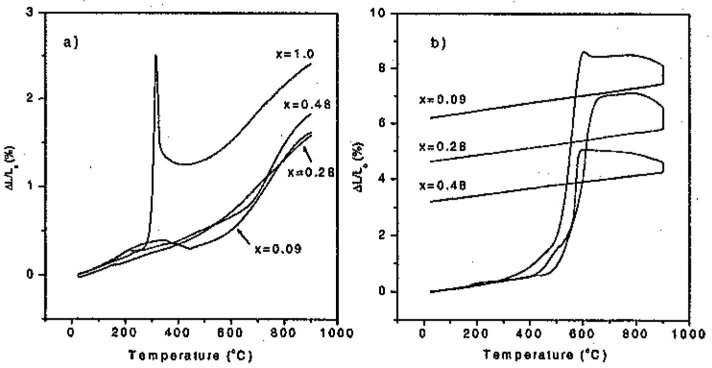

Fig. 3. Thermal expansion behavior (a) of SDC- $NiO_{1-x}CuO_x$ samples during reduction in forming gas and (b) of SDC-$Ni_{1-x}Cu_x$ samples during thermal cycle measurements in air (dwell time at 900 °C is 1h).

The results of measurements are presented in Fig. 3 (b). All the samples showed very large expansion at 450-600 °C. However, the expansion decreased with increase in Cu content from 8.4% for x=0.09 to 4.8% for x=0.48. The shrinkage on heating for 1h at 900 °C was probably due to partial sintering of oxide ceramics. Given that the SDC-$Ni_{0.81}Cu_{0.09}$ cermet showed no tendency for phase segregation during the cell fabrication process and had the lowest TEC among the compositions investigated, it was chosen for the evaluation of CH_4 conversion in single cells. However, in our experiments relatively low OCV values (-0.2-0.3 V) were obtained at 500-600 °C for a single cell supported on SDC electrolyte when dry CH_4 was supplied as the fuel. Therefore, finally YSZ was used for the electrolyte, and the operating temperature for the cell was increased to 750 °C. YSZ has greater resistance to reduction at this temperature than SDC. In the cell with a YSZ electrolyte an OCV of -0.5 V was obtained at 750 °C using dry methane and the OCV increased to -1.06 V when traces of oxygen (~0.1%) were added to the fuel by controlled leakage into the anode chamber to initiate the partial oxidation of the CH_4. The product distribution from electrochemical methane conversion over the SDC-$Ni_{0.91}Cu_{0.09}$ anode at 750 °C and at different currents is shown in Fig. 4. It should be emphasized that under open-circuit conditions (zero current) conversion of CH_4 proceeds via partial oxidation as evidenced mainly by the formation of H_2 and CO and a small amount of CO_2. The H_2/CO ratio observed is closed to 2. Applying negative (anodic) current which draws oxygen ions through the electrolyte to the anode results in consumption of H_2 by electrochemical oxidation. An increase in CO_2 concentration in the effluent gas is also observed, but at the same time, the amount of CO is almost unaltered under anodic conditions. This indicates that the additional CO_2 is produced via electrochemical oxidation of carbonaceous species formed from CH_4 absorbed on the anode surface rather than via oxidation of CO. Reversing the current, applying a positive (cathodic) current, draws oxide ions away from the anode surface and leads to a remarkable decrease in CO_2 concentration from 550 ppm at 0 mA/cm^2 to 0 ppm at +20 mA/cm^2. However, the amount of CO and H_2 is practically unaltered at +20-30 mA/cm^2 indicating that they are produced by catalytic partial oxidation.

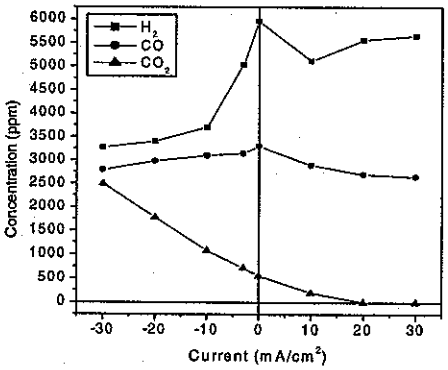

Fig. 4. Anode conversion of dry methane as a function of current at 750 °C

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