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Methane Internal Reforming over $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ -SDC Anode Material At Intermediate Temperatures

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The overall goal of this work is to develop a coking resistant $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ -SDC anode for IT-SOFCs. The $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ samples were prepared using 1) a one-step co-precipitation method and 2) a two-step co-precipitation/impregnation method. For the first method, $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ is synthesized via co-precipitation of Ni, Mg and Cu. In the two-step method, $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ is first prepared by co-precipitation of Ni and Mg, followed by addition of copper by impregnation. The materials were characterized using XRD, BET, TPO, and TPR. The activities toward methane steam reforming (MSR) were tested in a fixed-bed reactor. For the materials prepared from the one-step method, the MSR activity decreased when increasing Cu content even with only 5% Cu. With the two-step method, the MSR activity was not affected by the presence of Cu for concentration up to 5%. However, above 5% Cu the activity started to decrease. It was concluded that the two-step method is more effective.

Introduction

Currently, the barriers for full-scale commercialization of solid oxide fuel cells (SOFCs) are the high cost and relatively poor long-term stability. A solution is to attempt decreasing the operating temperature from the conventional 800-1000°C to 550-800°C. To further reduce the cost, it is desirable to limit the number of fuel pre-processing steps and, if possible, to feed the fuel directly (e.g. natural gas) to the SOFCs. Temperature limitations and fuel conditions; however, significantly affect material options because, on the one hand, the ohmic and electrode overpotential resistances increase rapidly when decreasing the operating temperature and, on the other hand, anode deactivation is associated usually with carbon formation when hydrocarbons are fed to the cell.

The overall goal of this research is to develop a coking resistant intermediate temperature $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ -SDC composite anode. The $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ -SDC anode has been chosen based on the premise that doped-ceria is suitable for intermediate temperature operations (550-750°C); that Ni-Cu alloy plays an important role in increasing resistance to coking (as well as raising sulphur tolerance) (1-2); that MgO is a promoter to avoid agglomeration during reduction, to increase Ni-Cu alloy activity and to stabilize doped-ceria material (3-6). This paper first describes how $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ has been prepared. It also reports on physical and chemical properties of $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ -

SDC characterized by x-ray diffraction (XRD), Brunauer-Emmett-Teller surface analysis (BET), and temperature-programmed techniques including temperature programmed oxidation (TPO) and temperature programmed reduction (TPR). To illustrate the reforming activities of these materials, the results for methane steam reforming are then presented. A Mg content of 10% ($y = 0.1$) was chosen because the literature indicates that this composition provides the highest electronic conductivity on Ni-Mg-O (7). For reference, NiO was also prepared and tested.

Experimental

Material Preparation

The $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ samples were prepared using two different methods: a one-step co-precipitation method and a two-step co-precipitation/impregnation method.

One-Step Co-precipitation Method. In this method, $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ was synthesized via co-precipitation of Ni, Mg and Cu. To start, a metal nitrate aqueous mixed solution composed of 0.2M of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.2M of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2M of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, was prepared for a given desired content of Ni, Cu and Mg. This mixture was added drop wise with a 30% ammonium hydroxide solution to a vessel maintained at a pH of 9. The solution was then stirred for 30 min in a closed system and aged for 24 h. The solid cake was washed, filtered with distilled water, and dried at 115°C overnight, resulting in a powder. Finally, the powder was transformed into a metal oxide form by calcination in air at 750°C for 4 h.

Two-Step Co-precipitation/Impregnation Method. In the two-step method, $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ was first prepared by co-precipitation of Ni and Mg, similar to the one-step preparation and was calcined in air at 800 °C for 4 h, followed by the addition of copper to $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ using incipient wetness impregnation. The material was then dried at 115°C overnight. Finally, the coated $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ was calcined at 750°C for 4 h.

Material Characterization

X-ray diffraction (XRD) patterns of the $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ powder samples were determined using a Bruker D8 FOCUS for 2θ of 30 to 80° using a step size of 0.02° and a count time of 0.5 sec. For BET analysis, the samples were pre-treated in N_2 at 300°C for 1 h to remove physisorbed moisture, followed by 30 min of cooling to room temperature. The BET surface was measured over the range of $0.05 \leq P/P_0 \leq 0.3$ using a Micromeritics Gemini™ V-Series surface analyzer.

Two temperature-programmed techniques (TP) were used to determine the calcination temperature and the reduction temperature: temperature-programmed oxidation (TPO) and temperature-programmed reduction (TPR), respectively. The TPO and TPR (5% H_2/N_2) of powder materials were carried out in a thermogravimetric analyzer (Cahn TG-2151 thermobalance). TPO was conducted by heating the un-calcined $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y$ powder samples at a heating rate of 10°C min⁻¹ from room temperature to 800°C and held for 30 min in air. Through this process, materials were transformed into oxide form and lost weight. The temperature, at which the sample weight remains

constant, represents the minimum calcination temperature to convert the material into a metal oxide. TPR is a similar technique where the materials are exposed to hydrogen in order to reduce a metal oxide to its pure metal form. Here, we used a ramping rate of $10^{\circ}\text{C min}^{-1}$ up to 800°C and dwell for 30 min in 5% hydrogen balanced with nitrogen (5% H_2/N_2). The TPR results allowed the determination of the minimum reduction temperature for a given reducing gas.

Methane Steam Reforming

Methane steam reforming (MSR) involves catalytic conversion of methane into a hydrogen rich gas. It is an endothermic reaction and is normally carried out at temperatures of approximately $700\text{--}800^{\circ}\text{C}$ in the presence of a suitable catalyst. In addition to the steam reforming reaction (global reaction illustrated in Equation 1), the water-gas shift reaction (Equation 2) is inevitable.

The water-gas shift (WGS) reaction converts carbon monoxide (CO) to carbon dioxide (CO_2) and hydrogen (H_2) through a reaction with steam (H_2O). Methane steam reforming is affected by operating pressure, temperature, and the ratio of steam to carbon (S/C) in the feed gas. Methane steam reforming is favoured at low pressure and high temperature. The most likely reactions leading to the formation of carbon/coke deposition are the following:

The formation of carbon can be an important problem in solid oxide fuel cells, when operated directly with hydrocarbon fuels. Carbon deposition results in anode deactivation because deposited carbon can plug gas flow and block the active site which leads to a loss of cell performance and fast degradation.

To evaluate the activity of the developed anode material for methane steam reforming (MSR) and water gas shift reaction (WGS), a fully automated catalytic fixed-bed reactor, capable of handling both gas and liquid feeds, was used. The catalyst was placed in a downflow quartz reactor. The reactor was comprised of a 10 mm I.D. quartz tube with a highly porous quartz frit. In the test, 60 mg (35-45 mesh) of 50 wt% $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}/50$ wt% SDC dispersed in 160 mg (35-50 mesh) of SiC (inert) were packed in the reactor. The exiting gases were analyzed online by a gas chromatograph (GC), Varian 3800 GC.

Several 50 wt% $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}/50$ wt% SDC samples were tested at different steam to carbon ratios. The conditions of S/C were first chosen at 2, and then progressively decreased. Results for S/C of 2 and 1 are presented here for the temperature of 750°C . The samples were pre-reduced at 750°C for 1 h in 10% H_2/N_2 . Then, the tests were conducted for about 20 h.

Methane conversion, yield, and selectivity were calculated using Equations 5, 6 and 7, respectively.

$$\% \text{conversion} = \frac{\text{molar flow rate of CH}_{4(\text{in})} - \text{molar flow rate of CH}_{4(\text{out})}}{\text{molar flow rate of CH}_{4(\text{in})}} \quad [5]$$

$$\text{species i yield} = \frac{\text{molar flow rate of species i}_{(\text{out})}}{\text{molar flow rate of CH}_{4(\text{in})}} \quad [6]$$

$$\text{species i selectivity} = \frac{\text{molar flow rate of species i}_{(\text{out})}}{\text{total molar flow rate of all product species}} \quad [7]$$

Results and Discussion

In this paper, the properties of $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ are reported including the phase of the material (XRD), the surface area analysis (BET), the calcination properties (TPO) and the reduction properties (TPR). The activity of 50 wt% $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ / 50 wt% SDC on MSR are also presented in terms of methane conversion, hydrogen yield, and hydrogen selectivity.

Properties of Prepared Materials

Phase Identification. The XRD patterns (Figure 1) were obtained using samples prepared by the one-step method. The results reveal that the XRD pattern of pure NiO and that of the mixture $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ are similar, as shown in the literature, for example, by Moon and Ryu (4). The same patterns were also obtained for $\text{Ni}_{0.9-x}\text{Cu}_x\text{Mg}_{0.1}\text{O}$ when Cu is less than 10 mol% ($x \leq 0.1$). However, the XRD patterns of samples containing more than 15 mol% copper have distinct peaks associated with CuO. Although the XRD patterns of $\text{Ni}_{0.9-x}\text{Cu}_x\text{Mg}_{0.1}\text{O}$ when $x \leq 0.1$ correspond to one-phase material, the TPR results (reported later in this paper) indicated the presence of multi-phases in $\text{Ni}_{0.9-x}\text{Cu}_x\text{Mg}_{0.1}\text{O}$. For example, $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ and $\text{Ni}_{0.85}\text{Cu}_{0.05}\text{Mg}_{0.1}\text{O}$ have the fingerprints of NiO and Ni-Mg-O solid solution. It implies that, in these cases, the Ni-Mg-O solid solution is dispersed into the NiO matrix and that Ni-Mg-O (and also CuO) pattern were hidden because of their significant lower amount compared to that of NiO. The XRD patterns of the samples prepared by the two-step method are similar to those obtained from the one-step method (Figure 2).

Surface Area Analysis. Total surface areas of the samples analysed by the BET technique are reported in Table I. The comparison between the samples containing 10% of Mg indicates that the surface area of the samples decreases somewhat when the copper content increases; from $9.6 \text{ m}^2/\text{g}$ for $\text{Ni}_{0.85}\text{Cu}_{0.05}\text{Mg}_{0.1}\text{O}$ to $8.1 \text{ m}^2/\text{g}$ for $\text{Ni}_{0.45}\text{Cu}_{0.45}\text{Mg}_{0.1}\text{O}$. The samples prepared from a two-step co-precipitation/impregnation method have similar, or slightly lower, surface area.

Figure 1. XRD patterns of $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ from the one-step method after calcination at 750°C for 4 h.

Figure 2. XRD patterns of 3, 5 and 10 mol% Cu impregnated on $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ made from the two-step method after calcination at 750°C for 4 compared with $\text{Ni}_{0.85}\text{Cu}_{0.05}\text{Mg}_{0.1}\text{O}$, $\text{Ni}_{0.80}\text{Cu}_{0.10}\text{Mg}_{0.1}\text{O}$ made from the one-step method.

Calcination Properties. For the one-step co-precipitation method, the peak of the weight loss rate for the un-calcined sample occurs at approximately 270°C for $\text{Cu}_{0.90}\text{Mg}_{0.10}$, whereas it occurs at 350°C for $\text{Ni}_{0.90}\text{Mg}_{0.10}$ (results not shown here). The results also show that no further weight loss happens after 400 °C for $\text{Cu}_{0.90}\text{Mg}_{0.10}$ and after 600°C for $\text{Ni}_{0.90}\text{Mg}_{0.10}$. For copper content up to 10 mol%, the TPO profiles are similar to that of $\text{Ni}_{0.9}\text{Mg}_{0.1}$. For 15% and more of Cu; however, the peak is shifted to lower temperature; for example for $\text{Ni}_{0.75}\text{Cu}_{0.15}\text{Mg}_{0.10}$, the peak occurs about 310 °C. The sample with 15% Cu also corresponds to the appearance of CuO in the XRD pattern (see Figure 1). For the two-step method, the $\text{Ni}_{0.9}\text{Mg}_{0.1}$ was first prepared and calcined at 800°C, before impregnating Cu. Therefore, Ni and Mg were already oxidized before impregnation of Cu. The TPO profiles of the un-calcined Cu impregnated samples from the two-step method indicate that above 400°C, the samples were completely oxidized.

Reduction Properties. The reduction properties of the oxide materials were analysed at a ramping rate of 10°C min⁻¹ up to 800°C and held for 30 min in 5% hydrogen balanced with nitrogen. From Equation 8, the theoretical weight loss can be determined. Comparison between the observed and theoretical weight loss indicates agreement within 3%. Note that when calculating the theoretical weight loss, it was assumed that MgO is not reduced and remains in its oxide form (3,5). Figure 3 represents the rate of weight change as a function of temperature for different compositions of the oxide material. The oxygen in $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ begins to be released at approximately 350°C, and by 750°C the Ni oxide is completely reduced into metallic Ni. $\text{Cu}_{0.9}\text{Mg}_{0.1}\text{O}$ released the oxygen at 200 °C and Cu oxide was fully reduced at 430°C. As seen in Figure 3, $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ shows two peaks; the first one at about 500 °C and the second one at about 650°C, which we attribute to the reduction of Ni in NiO and in Ni-Mg-O solid solution, respectively. In the present work the amount of Mg is small compared to that of Ni (10 mol% Mg vs. 90% Ni) resulting in MgO being dissolved in the NiO matrix. Comparing the TPR results for the 5% Cu prepared from the two different methods reveals that when Cu is co-precipitated with Mg and Ni, much higher temperatures are required to fully reduce the sample; when 5% Cu is impregnated, the sample is fully reduced at temperatures close to 700°C, whereas when it is co-precipitated, it requires temperatures close or greater than 800°C. This implies that $\text{Ni}_{0.9-x}\text{Cu}_x\text{Mg}_{0.1}\text{O}$ made from the one-step method is more difficult to reduce than when prepared using the two-step method.

TABLE I. Results for BET and TPR analysis.

Sample	BET surface area (m ² /g)	TPR weight loss	
		Experimental	Theoretical
$\text{Ni}_{0.90}\text{Mg}_{0.10}$	10.7	20.8%	20.2%
$\text{Ni}_{0.85}\text{Cu}_{0.05}\text{Mg}_{0.1}$	9.6	20.7%	20.1%
$\text{Ni}_{0.8}\text{Cu}_{0.1}\text{Mg}_{0.1}$	8.9	20.1%	20.1%
$\text{Ni}_{0.75}\text{Cu}_{0.15}\text{Mg}_{0.1}$	8.5	20.0%	20.0%
$\text{Ni}_{0.45}\text{Cu}_{0.45}\text{Mg}_{0.1}$	8.1	19.5%	19.6%
3%Cu impregnated on $\text{Ni}_{0.90}\text{Mg}_{0.10}\text{O}$	10.5	19.8%	20.2%
5% Cu impregnated on $\text{Ni}_{0.90}\text{Mg}_{0.10}\text{O}$	9.2	19.8%	20.2%
10% Cu impregnated on $\text{Ni}_{0.90}\text{Mg}_{0.10}\text{O}$	8.4	20.0%	20.2%

Figure 3. Rate of weight loss in TPR test for different $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ materials.

Methane Steam Reforming

Methane conversions, obtained from MSR tests at 750°C for S/C of 2 and 1 are shown in Figures 4a and 4b, respectively. At these conditions, the samples without copper, namely NiO/SDC and $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}/\text{SDC}$, provide the highest methane conversion. Also, the methane conversion decreases with increasing copper content. For example, for S/C of 2 at 750°C, the conversion with $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}/\text{SDC}$ is around 75%, whereas the conversion decreases to around 40% for 5% co-precipitated Cu. With 10% co-precipitated Cu, the conversion is only about 13%, but the conversion remains similar (around 10-15%) for Cu content above 10%.

Comparing the results between 5% Cu prepared from two different methods, the two-step co-precipitation/impregnation indicates considerable improvement in the conversion. The conversion of 5% Cu impregnated on $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}/\text{SDC}$ is around 60%, whereas the conversion of $\text{Ni}_{0.85}\text{Cu}_{0.05}\text{Mg}_{0.1}\text{O}/\text{SDC}$ is 40%. For the impregnation method, the conversion continues to decrease when the Cu content is increased. However, with the 3% Cu impregnated on $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}/\text{SDC}$, the conversion achieved was the same as $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}/\text{SDC}$.

The results from S/C of 1 (Figure 4b) indicates that up to 5% Cu, the Cu content does not affect the conversion for the catalyst prepared by the two-step method. However, for the one-step co-precipitation method, the trend for S/C of 1 is similar to the trend for S/C of 2, in that the conversion decreases with increasing Cu content. The lower activity obtained with the one-step method may be due to the decrease in reducibility as seen from the TPR results.

When comparing Figures 4a and 4b, the methane conversions of all samples with S/C of 1 are lower than with S/C of 2 (by approximately 20% point).

In conclusion, the two-step method resulted in higher methane conversion compared to the materials prepared using the one-step co-precipitation method.

Figure 4. Methane conversion at 750°C for a) S/C of 2 and b) S/C of 1.

The hydrogen yield is the amount of hydrogen produced per amount of methane fed and the trend of the hydrogen yield is equivalent to that of the methane conversion. Therefore, higher hydrogen yields were obtained from the samples without copper and 3% Cu impregnated on $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}/\text{SDC}$, and decreases when the copper content increased, especially for S/C of 2. Similarly, the hydrogen yields for S/C of 2 (highest yield around 2.4) were higher than those for S/C of 1 (highest yield around 1.8).

From Equation 1, the expected H_2 selectivity, if no water-gas shift reaction takes place, is 0.75. If all of the CO would be converted to CO_2 via the WGS reaction; then, the H_2 selectivity would reach 0.8. The H_2 selectivity at 750°C for S/C of 2 (Figure 5) shows that the H_2 selectivity lies between 0.75 and 0.8, still with most data toward 0.75. Yet, it can be seen that, as the Cu content increases, the H_2 yield increases, indicating that Cu favours the WGS reaction. At S/C of 1, the selectivity did not go as high as in S/C of 2, which is expected since higher water content would favour the WGS reaction, which in turn would increase the H_2 selectivity.

Some preliminary results seems to indicate that less coking occurs on the 3% Cu impregnated on $\text{Ni}_{0.90}\text{Mg}_{0.10}\text{O}$ than on the Cu free materials. More work is currently underway to clarify the benefit of Cu, especially at lower S/C ratios.

Figure 5. Hydrogen selectivity at 750 °C and S/C of 2.

Conclusions

The $\text{Ni}_{1-x-y}\text{Cu}_x\text{Mg}_y\text{O}$ anode materials were prepared using two different methods: a one-step co-precipitation method and a two-step method where Ni and Mg were first co-precipitated, followed by Cu impregnation. It was found that the surface area of the material decreases when the copper content increases. TPO results showed that if the anode material contains nickel, magnesium, and copper, the calcination temperatures must be greater than 600°C for the material to be completely oxidized. In the same way, to completely reduce Ni-Mg-Cu-O to Ni alloy, the reduction temperature should be equal to or greater than 750°C .

Although only NiO pattern can be seen clearly in the XRD patterns of the samples containing 10 mol% Cu or less, the TPR results disclosed the presence of NiO oxide and Ni-Mg-O solid solution. The results from MSR tests also showed that the samples from the one-step method are less active than those from the two-step method. $\text{Ni}_{0.90}\text{Mg}_{0.10}\text{O}/\text{SDC}$, NiO/SDC and 3%Cu impregnated on $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}/\text{SDC}$ all yielded similar methane conversions in the MSR tests at 750°C and S/C of 2 and 1. It was concluded that the two-step method was more appropriate.

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