YSZ PHASE PURITY AND STABILITY
IN CHEMICALLY PREPARED SOFC ANODES

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ABSTRACT
Phase pure, dual phase NiO-YSZ and CuO-YSZ have been synthesized by the co-precipitation method. Sample systems involving the synthesis of these materials at various pH levels, and at varying Ni, Cu and yttria content have been described. The nickel system shows a relatively simple precipitation pathway in which Ni\(^{2+}\) precipitates out of solution as Ni(OH)\(_2\). In contrast, Cu\(^{2+}\) precipitates as Cu\(_2\)(OH)\(_3\)Cl, followed by a conversion to CuO with increasing pH. Phase separation of monoclinic zirconia can be avoided by an appropriate choice of metal to base concentration ratios during precipitation or by the addition of additional yttria. The effect of the different preparations on conductivity suggests a small effect on short term performance. Large increases in conductivity and lower temperatures required during methane adsorption for Cu-YSZ make copper an attractive alternative to nickel for SOFC applications once optimal precipitation conditions have been established.

INTRODUCTION
The anode substrate should satisfy the following requirements: 1) porosity, so fuel and water vapour can flow in and out; 2) proper electrode microstructure to reduce polarization and 3) thermal expansion compatibility between the anode and the other cell components (1-3). Since the activation polarization is related to charge transfer processes and depends on the area of electrode/electrolyte/gas triple-phase boundaries (TPB), the material properties of the anode are of particular interest (4). In particular, the purity and stability of the electrolyte phase can have a substantial impact on the TPB, and the aging properties of the fuel cell. In this study, we will explore the phase properties of yttria stabilized zirconia (YSZ) for copper and nickel based anode materials.

Dual phase materials involving yttria stabilized zirconia (YSZ) and an active metal oxide precursor have been extensively studied due to their interesting catalytic, electronic and mechanical properties (5). Ni-YSZ is the most commonly used material for SOFC anodes because a) nickel serves as an excellent reforming catalyst for the oxidation of hydrogen; b) Ni provides electronic conductivity for the anode; and c) the thermal expansion coefficient of the anode can be managed by mixing with YSZ (4). The primary difficulty encountered with Ni-YSZ during the direct oxidation of hydrocarbons is the tendency to deactivate the Ni based anode due to carbon formation. Other metals such as copper are able to resist such coking (6) making it an attractive alternative to Ni based anodes, particularly for medium and low temperature SOFCs. In addition, complete conversion of
methane to CO$_2$ at relatively low temperatures (approximately 400°C) over Cu-YSZ catalysts has been reported (7).

Traditionally mixed metal oxides have been obtained by mechanical mixing of their components or by impregnation of the metal salts into a porous matrix (6, 8). These are simple methods which allow for accurate chemical composition but may lead to inhomogeneities. In contrast, co-precipitation by ammonia or buffer solution methods were described as assuring homogeneity and a uniform distribution of NiO particles within the matrix by controlling NiO and YSZ particle size distributions, but have been found to have a negative effect on the accuracy of composition (9, 10). The low yield of NiO within the final product was attributed to the formation of nickel-ammonia complexes, but synthesis with NaOH resulted in all of the Ni$^{3+}$ precipitating quantitatively as Ni(OH)$_2$ (10-12). These observed nuances for the co-precipitation of NiO-YSZ have prompted a closer look at CuO-YSZ materials obtained by this method.

Precipitation of metal hydroxides represents a very complex chemical process. A metal may form oxides, hydroxides and complexes with additional anionic species that can precipitate in different orders. The morphology of the particles is influenced by the conditions of precipitation, such as the concentration of reacting components, pH, temperature, etc. For example, it has previously been reported that depending on the concentrations of Cu(NO$_3$) or CuSO$_4$ and final pH, the solid phase which separates from solution consists of either copper(II) hydroxide, complex basic salts or copper(I) oxide (13). The co-precipitation method relies on the precipitation of multiple metals within the same pH range. There is a direct effect of metal concentration, pH and yttria content on the stabilization of zirconia in mixed metal oxides. In particular, separation of monoclinic zirconia has been observed. The resulting zirconium precipitate and final crystal structure of the calcined powder has also been linked to the concentration of precursor in solution (14).

In this work we have prepared dual phase NiO-YSZ and CuO-YSZ powders with various metal concentrations (10-90 %w/w), and evaluated the effects of pH and yttria content. Since the co-precipitation method relies on the precipitation of multiple metals, sometimes within the same pH range, the evaluation of the resulting powders under various conditions is of interest. We show the direct effect of metal concentration, pH and yttria content on the stabilization of zirconia in mixed metal oxides. The dual phase, high metal content samples were examined for differences in composition, zirconia phase stability and conductivity. Surface areas and porosities of the reduced powders were measured, as well as the ability of the metals to chemisorb methane at various temperatures.

EXPERIMENTAL

Anode Preparation

The YSZ-supported NiO and CuO anode materials were prepared by dissolving the appropriate amounts of ZrCl$_4$, Y$_2$O$_3$ (dissolved in 10 ml of 37 wt% HCl) and NiCl$_2$*6H$_2$O or CuCl$_2$*2H$_2$O (Aldrich) in 164 ml of distilled water. The precipitation was achieved through the introduction of a base. Sodium hydroxide (Aldrich) was introduced drop-
wise as a 2 M solution until the desired pH was achieved. Following the precipitation, the product was filtered, washed three times in 500 ml of water and dried at 120°C overnight. A portion of the dried product was then calcined at 950°C for 2 hours using a ramp speed of 25°C/min.

**Characterization**

The contents of nickel, copper, yttrium and zirconium were obtained using a Philips PW2400/00 X-ray fluorescence (XRF) instrument which was calibrated using a concentration gradient of NiCl₂ or CuO in a mixture of YSZ. Powder crystal composition was determined by X-ray diffraction (XRD) (Phillips PW1830) using Cu Kα radiation with a wavelength of 1.54 Å. Crystalline phases were assigned using the Powder Diffraction File (PDF) database (ICCD, 2001, Dataset 1-51).

In addition, a variable temperature PXRD (VT-PXRD) attachment (Anton Parr) was used to determine the order of crystallization for the powders. Cu Kα radiation was used from 2θ of 25° to 75° at 100°C intervals from 25°C to 1000°C. Vibrational characterization of the powders prior to calcination was determined using ATR Fourier transform infrared spectroscopy (FTIR) (Bruker Equinox 55). The BET surface area of the calcined powders were determined after reduction in flowing H₂ (99.9%) at 600°C for 2 hours using a Quantachrome Autosorb 1-C instrument. Conductivities of each cermet were measured using the four-probe method in the temperature range of 25°C-1000°C in He after reduction with flowing H₂ (99.9%) for 30 minutes at 800°C.

Methane adsorption FTIR studies were performed with samples that were pressed into a self-supporting disk with a weight of approximately 125 mg. An IR cell with KBr windows was connected to a gas handling and vacuum system. The sample disk in the cell can be treated in various ways such as degassing and reduction at a wide temperature range from room temperature to 400°C. Pre-treatment of the sample was performed by reduction in flowing H₂ (50 sccm) at 400°C for 6 hrs and then evacuated until the desired temperature was reached. Methane was then added to the sample cell to a pressure of 200 Torr and the spectra were taken at temperatures ranging from room temperature to 400°C. The spectra were recorded with an RS 1000 FTIR spectrometer (Mattson Instruments) using 64 scans and 1 cm⁻¹ resolution.

**RESULTS AND DISCUSSION**

**YSZ Stabilization and Co-precipitation with Cu²⁺ and Ni²⁺**

The degree of segregation of monoclinic zirconia has been studied as a function of metal concentration (Figure 1). The figure shows the percent stabilization of YSZ (%w/wYSZ:%w/wmZrO₂) with respect to nickel and copper metal content for samples precipitated at pH=13 and calcined to 950°C. At low metal concentrations the percent stabilization is low at approximately 65%. With increasing NiO content stabilization increases and reaches 100% at an oxide content of 50%w/w. Stabilization of YSZ also increases with increasing amounts of Cu, but does not reach full stabilization, instead it plateaus at approximately 75%. This puzzling observation suggested that perhaps the final pH of the solution played a role in the segregation process.
Percent stabilization with respect to final pH was measured for 10%w/w MO-YSZ mixtures. Figure 2 shows this dependence for both CuO and NiO samples. At pH <6 full stabilization of zirconia does not occur due to the incomplete precipitation of yttria out of solution. Above pH 7, stabilization for the NiO-YSZ-mZrO₂ system is pH dependant, complete stabilization occurs at pH 7 but rapidly decreases with increasing OH⁻ concentrations. This behaviour indicates that at high pH zirconia partially re-dissolves and the solubility product is independent of yttria, forming the m-ZrO₂ phase.

The CuO-YSZ-mZrO₂ system shows the opposite trend, increasing stabilization for increasing pH. At low pH, the precipitate which forms is a copper hydroxychloride (15), more specifically Cu(OH)₃Cl (as observed by FTIR and XRD, not shown), and as pH increases, the formation of CuO is expected and has been documented for many copper salts, including Cu(NO₃)₂ through the formation of Cu₂(OH)₃NO₃ and CuSO₄ through the formation of Cu₄(OH)₆SO₄ (13, 16). Additionally FTIR shows that the formation of copper (I) oxide does not occur during the precipitation procedure regardless of pH. The only other bands in the IR spectra are associated with zirconium hydroxide (17).

Figure 1. Percent stabilization of YSZ to monoclinic zirconia as a function of metal content at pH = 13

Figure 2. Percent stabilization of YSZ to monoclinic zirconia as a function of pH with a MO content of 10%w/w.
As the pH increases with respect to Cu$^{2+}$ concentration, the order of precipitation and subsequent conversion to CuO has been established for copper during co-precipitation. In contrast, precipitation of nickel does not form complex basic species and therefore precipitates as a hydroxide and must be calcined to NiO (equations 1 and 2).

\[
\text{Ni}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Ni(OH)}_2(s) \tag{1}
\]

\[
2\text{Cu}^{2+}_{(aq)} + 3\text{OH}^-_{(aq)} \rightarrow \text{Cu}_2(\text{OH})_3\text{Cl}(s) \leftrightarrow \text{CuO}_2(\text{s}) + \text{Cl}^-_{(aq)} + 2\text{H}_2\text{O} \tag{2}
\]

Although full stabilization of YSZ is achieved for a wider range of metal content and pH values for the NiO system, complete YSZ stabilization for CuO-YSZ can only be accomplished with increasing amounts of yttria. However, as stabilization of YSZ increases, Cu is lost during calcination. Figure 3a shows PXRD patterns of CuO-YSZ-mZrO$_2$ precipitated at a pH of 9.5 with increasing amounts of yttrium. The absence of $Y_2O_3$ peaks indicates the complete solubility of yttria in the zirconia lattice for all concentrations studied. However, at normal yttria content (8.5 mol%), the monoclinic zirconia phase is clearly visible. As yttria content increases, YSZ becomes fully stabilised but CuO content decreases as shown by XRF studies. Figure 3b shows the quantitative relationship between the gain of stabilization and the loss of Cu content (all samples were treated equally, as described in the experimental section). The loss of Cu at high temperatures may be corrected for by the addition of excess Cu salt in the starting solution. A possible explanation of the effects observed may be the strong interaction of copper with pure zirconia phases (18). However, further investigation of how to negate the loss of CuO is required.

![Figure 3. a) PXRD patterns of 10%w/wCuO-YSZ with differing yttria contents; i) 8.5 mol% YSZ; ii) 19 mol% YSZ; iii) 24 mol% YSZ; and iv) 29 mol% YSZ. b) Quantitative relationship between YSZ stabilization (PXRD) and the loss of Cu (XRF).](image)

**Crystallization Pathways**

Figure 4 shows the crystallization pathway of 30%w/w NiO-(8.5 mol%) YSZ. The dried powders show no peaks and indicate amorphous structures for both the nickel and yttrium/zirconium phases. As the temperature is increased, the formation of YSZ and NiO phases occurs at approximately 400°C. At temperatures above 400°C the full width at half maximum of the YSZ and NiO peaks continues to narrow, indicating a growth in
crystallite size. However, at elevated temperatures, the monoclinic crystalline phase of zirconia appears.

The formation of monoclinic zirconia could occur as a phase transformation of YSZ into mZrO₂ or as an independent crystallization. The intensity of the YSZ peaks remains constant during the appearance of the mZrO₂ peaks, and the fraction of YSZ/mZrO₂ is not temperature dependent (above 1000°C). Additionally, the fraction YSZ/mZrO₂ is dependent on the metal content. These observations suggest that the mZrO₂ phase does not segregate from stabilized YSZ but is crystallizing independently. The same crystallization pathway with more prominent mZrO₂ peaks is evident for lower NiO content and for all CuO-YSZ-mZrO₂ samples.

Figure 4. Crystallization pathway of 30% w/w NiO-(8.5 mol%) YSZ. ▲: YSZ, ■: NiO.

The coexistence of the monoclinic and cubic forms of zirconia has been extensively studied in the literature. A recent review by Yashima et al. shows phase diagrams that suggest the co-existence of both phases is expected in this temperature range and that complete stabilization at 1000°C occurs at approximately 20 mol% YO₁.₅ and not 14.8 mol% YO₁.₅ (19). Additionally, it has been suggested that it is possible to stabilize zirconia into the cubic phase by introducing CuO or NiO into the lattice. The addition of NiO and CuO by the sol-gel technique to zirconia resulted in fully stabilized zirconia at concentrations above 10 mol% Ni and 10 mol% Cu (7).

The formation of monoclinic zirconia in the presence of low concentrations of CuO and NiO suggests that it is not the interaction between the metals and zirconia that causes destabilization to occur, but it is the relative concentrations of metals with respect to the hydroxide concentration that plays the major role in YSZ phase purity. To obtain phase pure NiO-YSZ, precipitation at pH 9.5 ensures the full precipitation of all components with complete phase purity of the YSZ regardless of metal content. However CuO-YSZ phase pure substances must have a higher yttria content to obtain pure YSZ and an increased amount of copper precursor to correct for copper losses during heating.

Ni-YSZ and Cu-YSZ Anode Materials

Once complete stabilization of CuO-YSZ and NiO-YSZ was established, a comparison of powder characteristics was performed. Table 1 shows the conditions for precipitation,
composition by XRF, BET surface areas and whether complete stabilization of YSZ was achieved.

Table 1. The experimental conditions for the preparation of NiO-YSZ and CuO-YSZ materials and the resulting powder characteristics.

| Sample   | Metal | Yttria mol% | Expected metal oxide %w/w | Measured metal oxide %w/w | Final pH during precip. | Destabilization of the YSZ phase to YSZ+m-ZrO2 | BET surface area (m²/g) a |
|----------|-------|-------------|---------------------------|---------------------------|-------------------------|-----------------------------------------------|---------------------------|
| Sample-1 | Ni     | 8.5         | 80                        | 68                        | 13                      | No                                            | 4.5                       |
| Sample-2 | Ni     | 8.5         | 90                        | 75                        | 13                      | No                                            | 4.4                       |
| Sample-3 | Ni     | 8.5         | 80                        | 65                        | 9.5                     | No                                            | 8.2                       |
| Sample-4 | Ni     | 8.5         | 80                        | 65                        | 9.5                     | No                                            | 8.2                       |
| Sample-5 | Cu     | 8.5         | 80                        | 68                        | 13                      | No                                            | 4.5                       |
| Sample-6 | Cu     | 8.5         | 90                        | 75                        | 13                      | No                                            | 4.4                       |
| Sample-7 | Cu     | 8.5         | 90                        | 75                        | 13                      | No                                            | 1.8                       |
| Sample-8 | Cu     | 24          | 80                        | 68                        | 13                      | No                                            | 1.3                       |

a BET surface areas were measured after reduction with H₂ at 600°C for 2 hrs.

The NiO-YSZ powders show full stabilization in the YSZ phase. The four CuO-YSZ powders with higher yttria content exhibit full stabilization, while the CuO-8.5 mol% YSZ shows destabilization of the YSZ as described above. Compositions of CuO are higher than predicted at intermediate pH of 9.5, while the NiO composition is lower. This phenomenon may be explained by the order of precipitation for each of the mixtures. When precipitating Ni²⁺ with OH⁻, nickel is the last metal to come out of solution, while copper precipitates very early on. Therefore without an excess of OH⁻, especially at the relatively low pH of 9.5 it is expected that some zirconium and yttrium ions will remain in solution.

The BET surface areas range from approximately 1-8 m²/g with samples 3 and 4 showing the highest surface areas. This suggests that pH variations during precipitation affect the surface areas of the reduced powders, while increasing yttria content has no significant effect on surface area (cf. samples 6 and 7). Choice of metal also significantly changed the surface area, with Cu-YSZ exhibiting a smaller area than nickel, which may be attributed to the low melting point of copper and therefore the increased tendency for copper to form larger particles at high temperatures.

Conductivity of the powders shown in Figure 5 shows a significant difference in conductivity between the metals, but only a small effect due to stability and phase differences. Figure 5 shows the conductivity of Samples-2, 4, 6 and 7 after reduction at various temperatures. All composites show electrical conductivity behaviour with Cu-YSZ and Ni-YSZ exhibiting conductivity at approximately 20,000S/cm and 2,000S/cm respectively, in the high temperature region. The large difference may be attributed to the low NiO yield in the precursor powder and the intrinsic difference in conductivity between copper and nickel (~6:1) (20). Because the only significant difference in conductivities within the high temperature regime were observed with variations in metal type, at these high metal content conductivity is not affected by either pH during precipitation of nickel or yttria content within the copper samples. However, it is interesting to note in the figure that at lower temperatures differences in conductivity can be significant due solely to structural differences in the YSZ-mZrO₂ phase.
Ni-YSZ and Cu-YSZ anodes have significantly different behaviour; we show here the different and complementary modes of activation of methane by in situ FTIR. Analysis of the adsorption of methane on the reduced M-YSZ materials show that adsorption of methane on the metal surface increases with increasing temperature, but also significantly differs between each metal. There are four vibrational modes $v_1$-$v_4$ whose frequencies are 2917, 1533, 3019, 1306 cm$^{-1}$ respectively (21). Of these modes, only $v_3$ and $v_4$ are infrared active. For adsorbed methane, the bands at 3008 and 2998 cm$^{-1}$ are attributed to the $v_3$ mode which shows a red shift, and a band at 1305 cm$^{-1}$ (not shown) is due to the $v_4$ mode. Figure 6 shows the results for the adsorption of CH$_4$ on the reduced metal supported on YSZ in the presence of 200 Torr of methane at various temperatures. Both of the IR spectra of the adsorbed methane are very similar and are consistent with methane absorption values seen on Ni/Al$_2$O$_3$ and pure MgO (22, 23). The presence of bands at 2998 cm$^{-1}$ and 3008 cm$^{-1}$ indicates that there are two forms of adsorbed methane on reduced copper or nickel. The increase in the intensity of adsorption bands with respect to the 3019 cm$^{-1}$ band shows that the amount of adsorbed methane increases with increasing temperature and therefore requires activation, which is indicative of the chemisorption of methane. For methane adsorption on copper, the adsorption trend of the two species is slightly altered. Both the 2998 cm$^{-1}$ and 3008 cm$^{-1}$ bands increased significantly between 25°C and 100°C and the change becomes less pronounced as the temperature increases, suggesting that most of the available sites on copper are occupied at the early stages of heating and require very little activation. For nickel, the 2998 cm$^{-1}$ band does not begin to increase significantly with respect to the main gaseous band at 3019 cm$^{-1}$ until a temperature of 200°C is reached, while the 3008 cm$^{-1}$ band begins to increase immediately. The methane species formed on Ni at 2998 cm$^{-1}$ requires more activation and seems to be continuously filled throughout the temperature range. The methane peak at 3008 cm$^{-1}$ seems to require very little energy and indeed is quite large even at room temperature for the nickel-YSZ powder.

These differences in activation between metals indicate that methane adsorption on copper requires lower temperatures to achieve chemisorption for and indeed tapers off between 300-400°C, while methane on Ni chemisorption does not taper off so dramatically and requires a significant amount of energy to allow for the chemisorption of both of the methane species.

![Figure 5. Conductivity of Sample-2(●), Sample-4(▲), Sample-6(--), Sample-7(---).](image-url)
CONCLUSIONS

Phase pure, dual phase NiO-YSZ and CuO-YSZ have successfully been synthesized by the co-precipitation method. Sample systems involving the synthesis of these materials at various pH levels, Ni/Cu metal content and yttria content have been described and show that Ni-YSZ phase pure synthesis relies on proper choice of metal to hydroxide ratios. The copper system which shows the complete stabilization of yttria only after the addition of 24 mol% yttria suggests a more complicated pathway of precipitation. The loss of Cu during calcination also suggests some surface energy differences between YSZ, m-ZrO2 and the copper species present in the solid solution.

Conductivity of Cu-YSZ was superior to that of Ni-YSZ at all temperatures and was not significantly affected by the presence of m-ZrO2. Surface areas were also significantly different between copper-YSZ and nickel-YSZ, but remained constant within metal systems. Methane adsorption experiments suggest that Cu requires a lower temperature to activate methane onto the surface and elucidation of the two chemisorbed species on copper and nickel surfaces suggest that it is only the chemisorbed methane reflected by the 2998 cm\(^{-1}\) band that requires significant activation energies to form.

Overall, we have established the deleterious effects that low metal content and excess hydroxide concentrations have on the purity of stabilized zirconia. It is possible to obtain fully stabilize zirconia for CuO-YSZ but only after the addition of 24 mol% yttria. Phase separation of m-ZrO2 from YSZ has a small but significant effect on conductivity of the reduced anode material, and it is expected to influence aging performance significantly.

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