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Oishi, Naoki; Yoo, Yeong

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# Low polarization resistance of Ni–Cu–Ce oxide anode synthesized by coprecipitation with tetramethylammonium carbonate for intermediate temperature SOFC

Naoki Oishi\*, Yeong Yoo

*Institute for Chemical Process and Environmental Technology, National Research Council Canada, 1200 Montreal Rd, Ottawa, Ontario, Canada K1A 0R6*

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## ABSTRACT

With little deviation from the metal cation stoichiometry in a starting metal nitrate solution, Ni–Cu–Ce oxide powders for intermediate temperature SOFC anodes were synthesized by coprecipitation using tetramethylammonium carbonate and decomposition of coprecipitated metal carbonates. The synthesized oxide powder was found to have a high surface area. A 30% Ni–30% Cu–40% Ce anode fired at a low temperature of 900 °C on a  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  electrolyte provided low electrode polarization with an estimate of less than  $0.1 \Omega \text{ cm}^2$  at temperatures over 600 °C on wet 50%  $\text{H}_2$  despite the Ni–Cu metallic phase in the anode was only 30% by volume.

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## 1. Introduction

In powder synthesis of cerium oxide by coprecipitation, ammonium carbonate is used as a precipitating agent to prepare high surface area powders [1], which are desirable for catalyst applications. When this method is applied to the synthesis of nickel based ceria powders having high surface areas for the anode of solid oxide fuel cell (SOFC), there is a problematic issue regarding controllability of the metal cation stoichiometry; the cation ratio in a metal oxide synthesized by coprecipitation with ammonia carbonate departs from its original cation ratio in the starting metal cation solution because metal cations such as  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  form soluble amine complexes in the presence of ammonia.

Substituted ammonia such as tetramethylammonium hydroxide is known to hinder the formation of complexes due to steric effects [2–5], and the carbonate of substituted ammonia also hinders complexing [6], in addition, it would produce high surface area oxides by decomposition of coprecipitated metal carbonates.

In order to obtain Ni–Cu–Ce oxide powders with high surface areas for intermediate temperature SOFC anodes, the oxide powder was synthesized by coprecipitation of a metal nitrate solution with tetramethylammonium carbonate and decomposition of the coprecipitated metal carbonate phase. In this study, we report consistent stoichiometry of the metal cation between the starting metal nitrate solution and the synthesized oxide powder, and low electrode polarization resistance of the anode material, which is well suited to

intermediate temperature SOFCs that can be manufactured at lower temperature.

## 2. Experimental

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Fluka: 98%),  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (Sigma-Aldrich: 98%) and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich: 99%) were used as starting materials. Metal nitrates were mixed in a desired ratio and dissolved in deionized water (nominally,  $18.2 \times 10^6 \Omega \text{ cm}$ ) to give a 1.0 M metal cation solution. Since tetramethylammonium carbonate was not readily available, a method reported by Bunker et al. was modified to prepare a tetramethylammonium carbonate solution [6];  $\text{CO}_2$  was bubbled through a commercially available tetramethylammonium hydroxide solution (Sigma-Aldrich: 25%) until the pH showed a steady value (pH = 8.0–8.2). The solution was diluted to half by adding deionized water to be used as a tetramethylammonium carbonate solution for the precipitating agent in this study.

The 1.0 M metal cation solution was instantaneously poured into the tetramethylammonium carbonate solution in a beaker at room temperature. Assuming that the coprecipitated phase was made up of all metal carbonates, at least 2 times as much precipitating agent as the stoichiometrically required amount was used. Subsequently, the coprecipitated phase in a beaker was heated in a water bath controlled at about 70 °C for 3 h under gentle stirring. After the heat treatment, the coprecipitated phase was vacuum-filtered and washed with a sufficient amount of deionized water. The washed sample was then dried at over 90 °C in a vacuum oven. The dried sample, which was thought to be made up of not only carbonates, but also hydroxycarbonates and oxycarbonates (presumably in hydrated forms), was calcined in air at 600 °C for 1 h to form metal oxides by decomposition

\* Corresponding author. Tel.: +1 613 998 8379; fax: +1 613 991 2384.

E-mail address: [naoki.oishi@nrc-cnrc.gc.ca](mailto:naoki.oishi@nrc-cnrc.gc.ca) (N. Oishi).

of the carbonate related phases. For comparison, certain samples were synthesized with tetramethylammonium hydroxide as a precipitating agent in a similar manner.

BET surface area measurement (Model ASAP 2020, Micromeritics) by using N<sub>2</sub> was carried out on selected samples. Elemental analysis was performed by wavelength dispersive X-ray fluorescence spectrometer (Model S4 Pioneer, Bruker).

Polarization resistance of the prepared anode material was examined by impedance measurement on a symmetrical cell. Anodes were attached to a sintered Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> electrolyte pellet by spraying a suspension made with the anode material and firing. The dimensions of a Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> pellet measured about 13 mm in diameter and about 1 mm in thickness. Anode firing was performed at 900 or 1000 °C in air for 3 h. Impedance measurement was carried out at 500, 550, 600 and 650 °C in 50 or 8% H<sub>2</sub> humidified at room temperature (<3% H<sub>2</sub>O) by frequency response analyzer (Model PGSTAT100 with FRA2 module, Autolab) over a frequency range of 1 × 10<sup>-3</sup> to 1 × 10<sup>6</sup> Hz with an ac amplitude of 10 mV.

**3. Results and discussion**

As soon as the metal nitrate solution was poured into the tetramethylammonium carbonate solution, small bubbles were vigorously liberated, and a green–blue colored coprecipitated phase was formed; more blue with metal nitrate solutions having higher copper contents. After drying, the color of the coprecipitated phase remained similar, but it became dark after calcination at 600 °C, and the calcined powder was found to be easily crushed in an agate mortar with a pestle. It was found that a nominal 30% Ni–30% Cu–40% Ce (by cation) oxide powder was 34.3 m<sup>2</sup>g<sup>-1</sup> in BET surface area, which was higher than a corresponding oxide powder coprecipitated with tetramethylammonium hydroxide (15.3 m<sup>2</sup>g<sup>-1</sup>). In the case of tetramethylammonium hydroxide as a precipitating agent, the appearance of the precipitated phase was brown in color, and the calcined sample became dark, which was similar to the oxide powder made with tetramethylammonium carbonate, however, the grains of the calcined oxide powder were relatively hard to be ground.

Fig. 1 shows the comparison of the nominal concentration of metal cations in a metal nitrate solution and the analyzed concentration of metal cations in the corresponding metal oxide powder. In this study, the cerium concentration in nitrate solutions was fixed at 40%, while concentration of nickel and concentration of copper were depen-

dently varied from 0 to 60%, 60 to 0%. It was found that nickel and copper concentrations were linearly varied with individual nominal concentration with a R<sup>2</sup> value of 0.999 by linear regression, and that their analyzed concentrations fairly matched the nominal concentrations in the corresponding metal nitrate solution. Compared to the nominal concentrations of nickel and copper in a metal nitrate solution, the analyzed nickel content in the corresponding oxide powder was low by 4%, while the analyzed copper content was slightly high. Since the analyzed concentration and the nominal concentration showed good linear dependence, the difference in concentration could be attributed to the deviation of hydration and/or the purity of metal nitrates. It was therefore confirmed that nickel–copper–cerium oxide powders could be synthesized by coprecipitation using tetramethylammonium carbonate and decomposition of the coprecipitated phase with little deviation from the metal cation stoichiometry in a prepared metal nitrate solution.

Impedance spectra (Nyquist plots) obtained at different temperatures under two H<sub>2</sub> concentration conditions were found to have one distorted arc at low frequency and another arc at high frequency. A typical impedance spectrum of a symmetrical cell is shown in Fig. 2. The anode with a thickness of 30 to 40 μm was made of a nominal 30% Ni–30% Cu–40% Ce oxide powder (corresponding to 14% vol Ni–16 vol.% Cu–70 vol.% CeO<sub>2</sub>) and fired at 900 °C. The measurement was carried out in humidified 50% H<sub>2</sub> at 550 °C. It was found that the observed impedance spectrum was in good agreement with reported data on 65 vol.% Cu–35 vol.% Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> anodes on a Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> electrolyte, which showed a low frequency arc over a frequency range of 10<sup>-3</sup> to 1 Hz at about 550 °C [7]. The low frequency arc was thought to correspond to electrode polarization resistance, and a semi-circle was fitted to the low frequency arc in estimating the area specific polarization resistance, R<sub>p</sub>. In contrast, the resistance value that was obtained from the high intercept of the high frequency arc on the impedance spectrum, which was thought to be the sum of ohmic components (an electrolyte, two anodes and leads) appeared to be high. This could be explained that the resistance of the anode layers was high due to a high volume percent of the resistive undoped cerium oxide (70 vol.% CeO<sub>2</sub>).

Arrhenius plots of R<sub>p</sub> for 30% Ni–30% Cu–40% Ce anodes are summarized in Fig. 3. Area specific polarization resistance for the anode fired at 900 °C was not obtained at 650 °C in 50% H<sub>2</sub> because the magnitude of the measured impedance corresponding to a low frequency arc was very low so that the data points were scattered probably due to temperature fluctuation. The anode fired at 900 °C

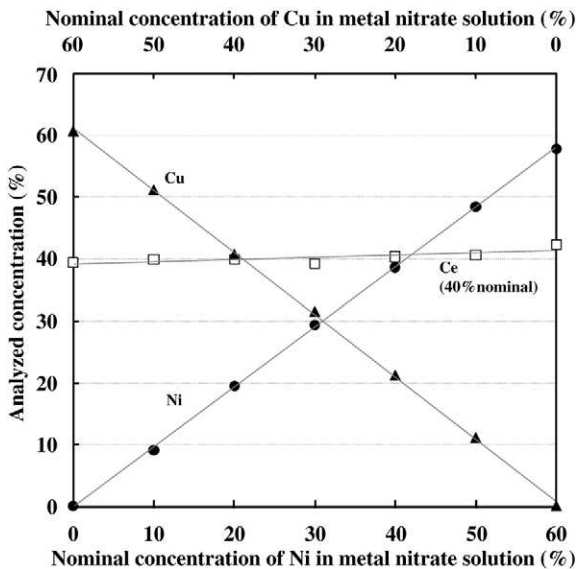


Fig. 1. Comparison of nominal metal cation concentrations in nitrate solutions and analyzed metal cation concentrations in synthesized powders.

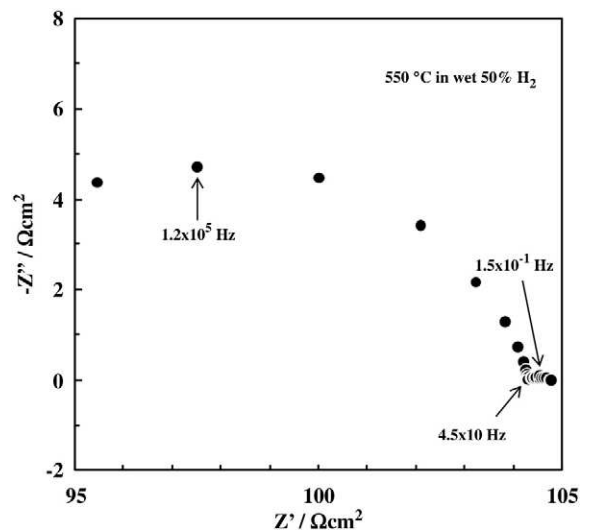


Fig. 2. A normalized impedance spectrum of an anode symmetrical cell made with a 30% Ni–30% Cu–40% Ce oxide powder; anode was fired at 900 °C, impedance measurement was performed at 550 °C in humidified 50% H<sub>2</sub>.

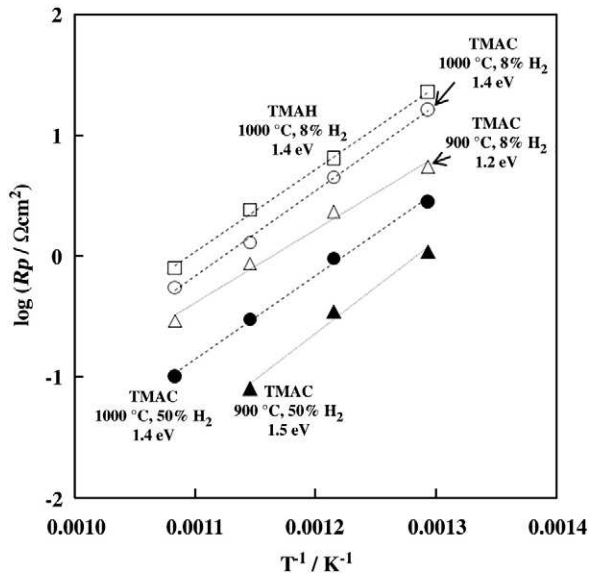


Fig. 3. Arrhenius plots of  $R_p$  for anodes made with a 30% Ni–30% Cu–40% Ce oxide powder under different conditions; firing temperature and anode gas are shown together with estimated activation energy. TMAC: tetramethylammonium carbonate, TMAH: tetramethylammonium hydroxide.

was found to have lower  $R_p$  than the anode fired at 1000 °C over the temperature range tested under both  $H_2$  concentration conditions. It was thought that lower firing temperature could retain higher surface area for electrode reaction. It was found that activation energy of  $R_p$  for the anodes fired at 900 and 1000 °C did not have large dependence on  $H_2$  concentration, and that activation energy lay within 1.2 to 1.5 eV, which was comparable to a literature data of 1.5 to 1.7 eV [7]. It was also confirmed that the anode synthesized with tetramethylammonium carbonate (TMAC) showed better area specific resistance than the anode made with tetramethylammonium hydroxide (TMAH) with no difference in activation energy, indicating that higher active area was achievable on anodes made with tetramethylammonium carbonate. Although the metallic phase of nickel and copper was

theoretically just about 30 vol.% in the 30% Ni–30% Cu–40% Ce anode, which was thought to provide a better redox stability, low polarization resistance ( $<0.1 \Omega \text{ cm}^2$ ) was found to be obtainable at temperatures over 600 °C. It should be noted that a 60% Ni–40% Ce anode fired at 1000 °C showed poor adhesion to the electrolyte, and that the copper addition in the anode was beneficial to reduce the temperature for anode firing.

#### 4. Conclusions

In order to obtain high surface area Ni–Cu–Ce oxide powders for intermediate temperature SOFC anodes, coprecipitation using tetramethylammonium carbonate and decomposition of the coprecipitated phase was employed. The metal cation stoichiometry in an oxide powder was almost consistent with that in the starting metal nitrate solution, and the oxide powder was high in surface area. The 30% Ni–30% Cu–40% Ce anode (14 vol.% Ni–16 vol.% Cu–70 vol.%  $\text{CeO}_2$ ) fired at a low temperature of 900 °C was found to provide low electrode polarization with an estimate of less than  $0.1 \Omega \text{ cm}^2$  at temperatures over 600 °C on 50%  $H_2$  in spite of a low volume% of the Ni–Cu metallic phase (30 vol.%).

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