

## Application of Sol-gel Processing to Synthesis of Ni-YSZ Cermet Membrane

by

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### Abstract

Optimization of both the internal gelation process (IGP) and EDTA (ethylene-diamine-tetra-acetic acid) complexes-gel reduction process (CGRP) was carried out for manufacturing of Ni-YSZ (yttria-stabilized zirconia) cermet as the membrane electrode. For the IGP, we found the adequate amount of gelling agent and stabilizer such as HMTA (hexamethylenetetramine) and urea for the starting solution, so that precursor gels containing Ni content of 45-61.3 mol% were successfully synthesized. However, the samples prepared via IGP did not show the electronic conductivity but ionic one, although NiO in the samples was completely reduced to Ni. This might be caused by a decrease of Ni content during sintering at high temperatures. On the other hand, for the EDTA CGRP, precursor gels were successfully synthesized by controlling pH value in the preparation of soluble complexes. In addition, the sample synthesized via EDTA CGRP showed the electronic conductivity for Ni content of 60 mol%.

**Keywords:** Sol-gel synthesis, Internal gelation, EDTA complexes, Cermet, Electric property

### 1. Introduction

In the nuclear fuel reprocessing, reducing the volume of the waste solution including Na is one of the concerns to be solved. So we are applying an electro-osmotic phenomenon to separation of Na ions from the waste solution. To do so, the membrane with both cation (Na ion) permeability and the electrode performance should be needed. In addition, such a membrane is intended to be used in the radioactive field. Therefore, the Ni-YSZ (yttria-stabilized zirconia) cermet was chosen

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as a suitable material for above purposes.

Generally, the Ni-YSZ cermet has been widely used in the solid oxide fuel cell (SOFC) as an anode material<sup>1-3)</sup>, and also has been developed by various synthesis methods<sup>4-6)</sup>. The internal gelation is one of the sol-gel synthesis methods<sup>7,8)</sup>. We have so far developed the internal gelation process (IGP) in order to synthesize the novel nuclear fuel which is the zirconia-based microsphere doped with plutonium<sup>9,10)</sup>. In addition, we have been interested in the EDTA complexes-gel reduction process (CGRP) for the synthesis of Ni-YSZ cermet<sup>6,11,12)</sup>. This EDTA CGRP was applied to the synthesis of high  $T_c$  super conductor materials<sup>11)</sup>. The samples synthesized through both sol-gel processes have the atomic homogeneity and high purity, and can be prepared with the precise chemical composition.

In the present study, we performed the process optimization for both IGP and EDTA CGRP. Furthermore, the electric property of samples thus synthesized via such sol-gel processes were discussed.

## 2. Experiment

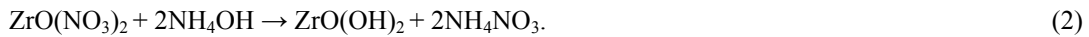
### 2.1 Sol-gel synthesis

#### 2.1.1 Internal gelation process

The internal gelation synthesis was performed through the following processes<sup>9,10)</sup>. The nitrate solution of  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were used to prepare the feed solution with a cation concentration of 1.6 mol/kg and a nitric acid concentration of 1 mol/kg. On the other hand, the solutions to cause the hydrolysis reaction were prepared by dissolving HMTA ( $\text{C}_6\text{H}_{12}\text{N}_4$ ) and urea ( $\text{CO}(\text{NH}_2)_2$ ) into deionized water with concentrations of 1.6 mol/kg and 1.4 mol/kg, respectively. Subsequently, the starting solution was prepared by adding the HMTA/urea solution little by little to the feed solution at a temperature of 270 K. For HMTA and urea solutions, optimum mole ratios of  $r_{\text{HMTA/metal}}$  and  $r_{\text{urea/metal}}$ , where metal means sum of cations, should be found here. The starting solution was dropped into silicone oil heated at ca. 368 K. The droplets solidified within one and a half minutes by hydrolysis caused at the “internal ” part of gel spheres. Ammonium hydroxide in hydrolysis is formed mainly from HMTA in the presence of urea according to the following reaction:



In Eq. (1), ammonium hydroxide causes the precipitation of the metal hydroxides and gelation. For example, Eq. (2) applies to zirconium hydroxide:



Gel spheres were washed with kerosene for removal of silicone oil, and were subsequently rinsed with 2 M of ammonium solution for removal of by-products such as ammonium nitrate. Then, gel spheres were dried at 313 K in a thermostatic chamber. Dried microspheres were calcined under the appropriate heat treatment in the flowing Ar gas to burn out by-products and residual organic compounds in these spheres. And then, the calcined spheres were grinded, and were subsequently pelletized by cold isostatic press (CIP) to form the disk. The pelletized specimens were sintered at 1473 K or 1673 K in air for 8 hours. Finally the sintered pellets were heated at 1123 K in the flowing Ar-5% $\text{H}_2$  gas for 3 hours in order to reduce NiO to Ni.

### 2.1.2 EDTA complexes-gel reduction process

In the EDTA CGRP, zirconium chloride (0.2 M, pH = ~1), yttrium chloride (0.2 M, pH = ~1) and nickel nitrate (0.2 M, pH = ~1) were prepared as the feed solution<sup>6)</sup>. On the other hand, EDTA acid was dissolved in deionized water (0.2 M) while ammonia was adding to adjust pH value (= 5.0)<sup>6)</sup>. The feed solution was little by little added into aqueous EDTA at room temperature while stirring continually. Also at this process, pH value was adjusted to ~5.0 by adding ammonia. The clear soluble complexes thus synthesized were heated at 393 K for a couple of days. At this process, it gradually changed into viscous gel, and finally the solid precursor was prepared. Subsequently the solid precursor was grinded to the powder, and was calcined at 873 K. Then, the pelletized sample was sintered at 1473 K in air. At the last process, sintered pellet was reduced at 1123 K in the flowing Ar-5%H<sub>2</sub> gas as mentioned above.

For comparison, we prepared the cermet sample via the conventional powder sintering process. Using commercially available powders such as ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub> and NiO, the cermet samples were synthesized through powder mixture, CIP, sintering and reduction.

## 2.2 Measurement and sample characterization

In order to optimize the thermal treatment of calcination process, TG (thermogravimetry) /DTA (differential thermal analysis) measurements were performed at temperatures from R.T. to ~800 K. The electric property was evaluated by DC method or AC impedance method. In the DC method, the electric resistance can be obtained by the current-voltage relationship. On the other hand, in the AC impedance method, the complex impedance of the sample can be obtained as a function of frequency (Cole-Cole plot).

The X-ray diffraction (XRD) measurement and the scanning electron microscopy (SEM) + energy-dispersive X-ray spectroscopy (EDS) were performed to further investigate the character of the synthesized samples. These measurements allowed to clarify the chemical state, the concentration and the distribution mainly of Ni in the sample.

## 3. Results and Discussion

### 3.1 Sample synthesized via internal gelation process

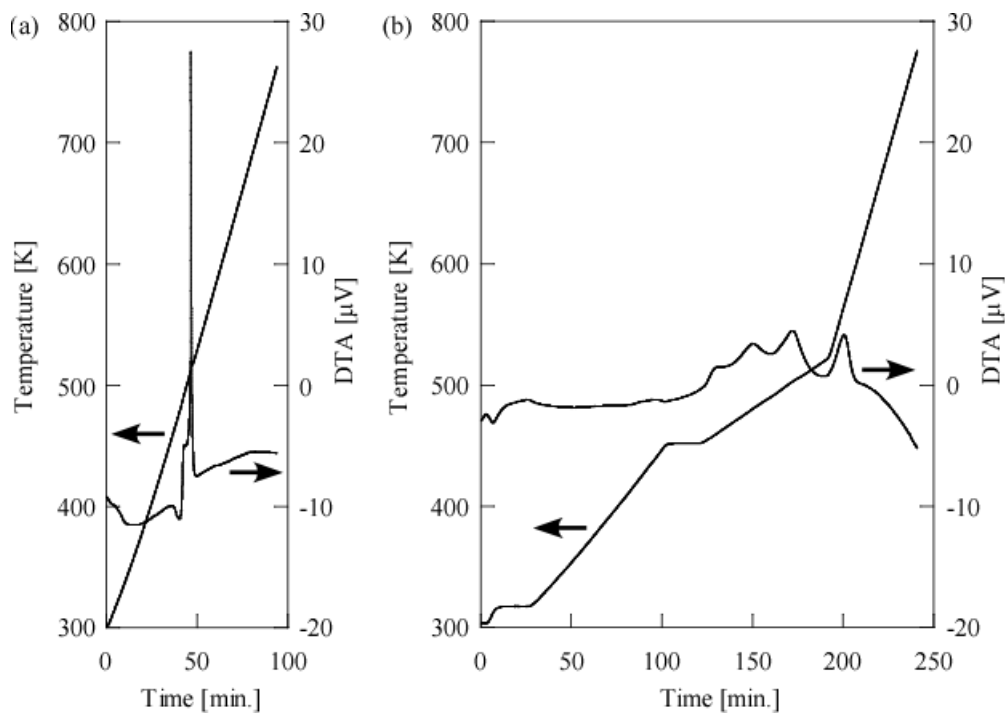
In the previous study, we pointed out the importance of ratio of HMTA (or urea) to metal, ( $r_{\text{HMTA/metal}}$  or  $r_{\text{urea/metal}}$ ) in solution for the internal gelation<sup>9,10)</sup>. For the system Zr-Y-Er-Ce-O,  $r_{\text{HMTA/metal}}$  and  $r_{\text{urea/metal}}$  are considered to be good for 1.2 and 1.05, respectively. So we determined optimum one by varying  $r_{\text{HMTA/metal}}$  (or  $r_{\text{urea/metal}}$ ) from 0.2 to 1.2 (or 1.05). The results for  $r_{\text{HMTA/metal}}$  of 0.4-0.5 and for 61.3 mol% of Ni were summarized in **Table 1**. In other cases ( $r_{\text{HMTA/metal}} < 0.4$ ,  $r_{\text{HMTA/metal}} > 0.5$ ), the following phenomena were often observed: (1) the gelation occurred in preparing the starting solution; (2) the gelation did not occurred in the hot bath; (3) the gelation occurred but gel spheres eroded in washing with kerosene and/or ammonium solution. We considered to be good for the cases that the gelation successfully occurred in the hot bath and the degree of erosion of gel spheres was small in washing. In the case of 45 mol% Ni, the gelation reactions almost successfully occurred. For both Ni contents,  $r_{\text{HMTA/metal}}$  and  $r_{\text{urea/metal}}$  were good in the ranges of 0.4-0.5 and 0.4-0.5, respectively. The cermet samples presented hereafter in this article were synthesized under the conditions of  $r_{\text{HMTA/metal}} = 0.5$  and  $r_{\text{urea/metal}} = 0.4$ .

The calcination of the samples through the sol-gel process was needed to remove water, by-products, residual organic matter and other impurities. Firstly, the well-gelled spheres were analyzed by DTA at a heating rate of 5 K/min up to 773 K (**Fig. 1 (a)**). The exothermic peak can be seen at about 520 K in the DTA curve, which is due to thermal decomposition of by-products such

as ammonium nitrate and formaldehyde or residual urea. Under this heating condition, the grinded powder blew up in an electrical furnace during calcination. In order to prevent such a phenomenon, it required the mild heat treatment in which the heating rate was 2 K/min, and the temperature was kept at 452 K for 20 min. Furthermore, the sample was heated at a rate 1 K/min, and the heating rate was change to 5 K/min at 533 K. It, therefore, appeared that calcination under this condition was well performed as shown in **Fig. 1** (b).

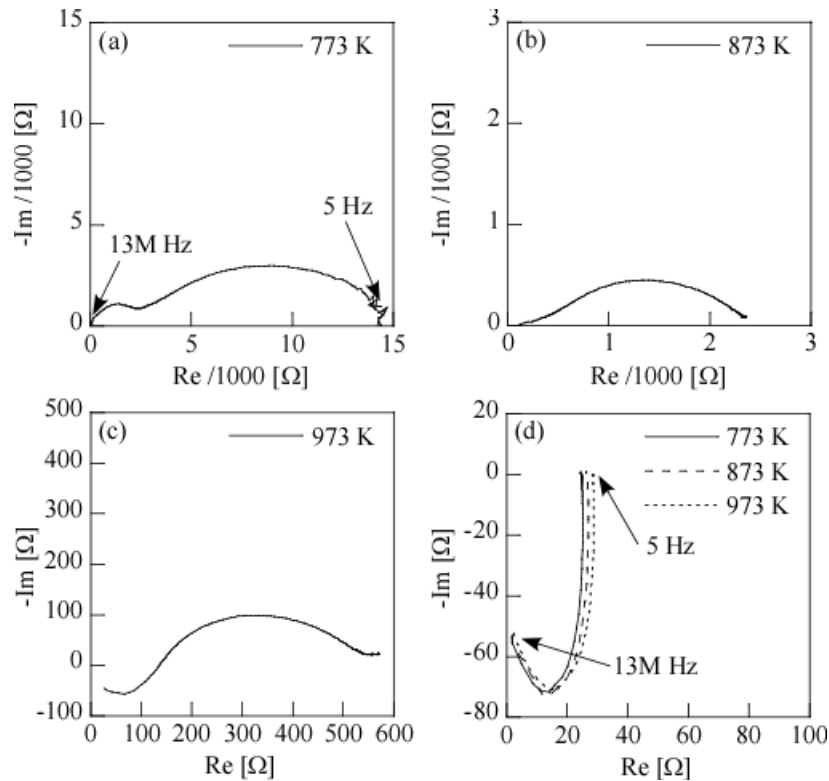
**Table 1** Gelation condition and behavior for solution with Zr:Y:Ni = 30.5:8.2:61.3 (mol%).

$r_{\text{HMTA/metal}}$	$r_{\text{urea/metal}}$	Gelation time [s]	Observation of gel spheres
0.5	0.8	40	Erosion during washing with kerosene
	0.7	70	Partial erosion in washing
	0.6	60	Good gelation and extremely small erosion in washing
	0.5	60	Partial erosion in washing
	0.4	60	Good gelation and extremely small erosion in washing
	0.3	60	Partial erosion in washing
0.4	0.8	60	Erosion during washing with kerosene
	0.7	90	Erosion in hot bath
	0.6	85	Erosion during washing with kerosene
	0.5	70	Good gelation and extremely small erosion in washing
	0.4	55	Partial erosion in washing
	0.3	90	<i>ditto</i>



**Fig. 1** DTA curves for heating rate 5 K/min (a) and for optimized heating condition (b).

For the Ni-YSZ cermet samples thus synthesized via the IGP, the AC impedance measurements were performed at 773 K to 973 K in the flowing Ar-5%H<sub>2</sub> gas to prevent the oxidation. The results obtained for the sample prepared via the IGP and the conventional powder sintering route were shown in **Figs. 2** (a-c) and **Fig. 2** (d), respectively. These cermet samples were prepared at Ni mol% of 61.3 and 60.0, respectively. The ionic conductivity is shown in **Figs. 2** (a-c) because one or two half circles and high resistance at low frequencies are observed in those figures. On the other hand, **Fig. 2** (d) shows the electronic conductivity because of low resistances at low frequencies. Based on the percolation model in Ref. [13], the cermet containing Ni amount over 28 vol% should show the electronic conductivity. For the samples provided for the AC impedance measurement, Ni molar ratio of 60% corresponds to ~32 Ni vol%. In order to clarify such an electric property, we performed X-ray diffraction measurements for these samples. The diffraction patterns shown in **Figs. 3** (a) and (b) were obtained for the surface and the inside of the sample prepared via the sol-gel synthesis route. Those in **Figs. 3** (c) and (d) were measured for the sample prepared via the conventional powder sintering. For the sample via the so-gel route, the diffraction intensity of Ni is weak not only for the surface but also for the inside of the sample. Furthermore, we observed the inside of the samples via the sol-gel route by SEM+EDS. **Figure 4** also shows that the intensity of Ni-K $\alpha$  line is weak and the amount of Ni decreases in the cermet sample via the sol-gel route. In fact, a weight loss of ~13 % during sintering at 1673 K was found for the sample synthesized via the sol-gel route.

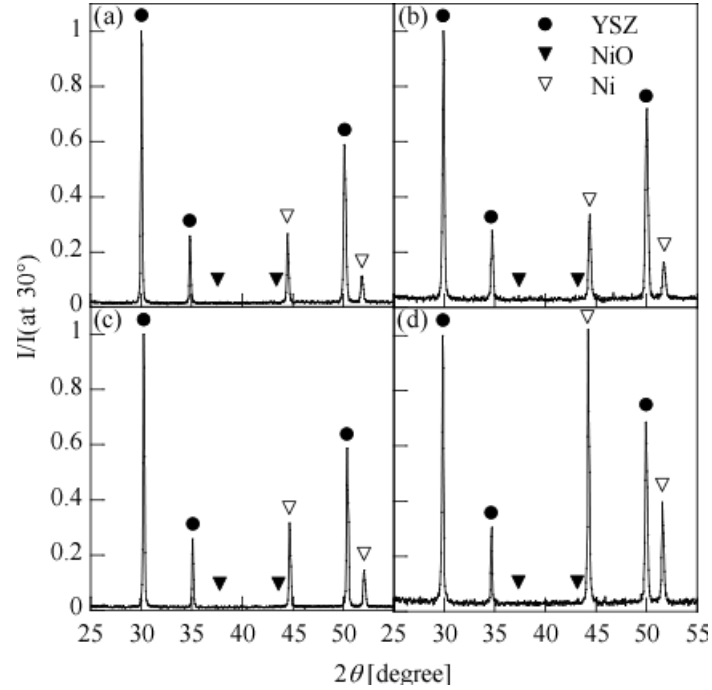


**Fig. 2** Cole-cole plots for Ni-YSZ cermet synthesized via IGP (a-c) and via conventional powder sintering method (d).

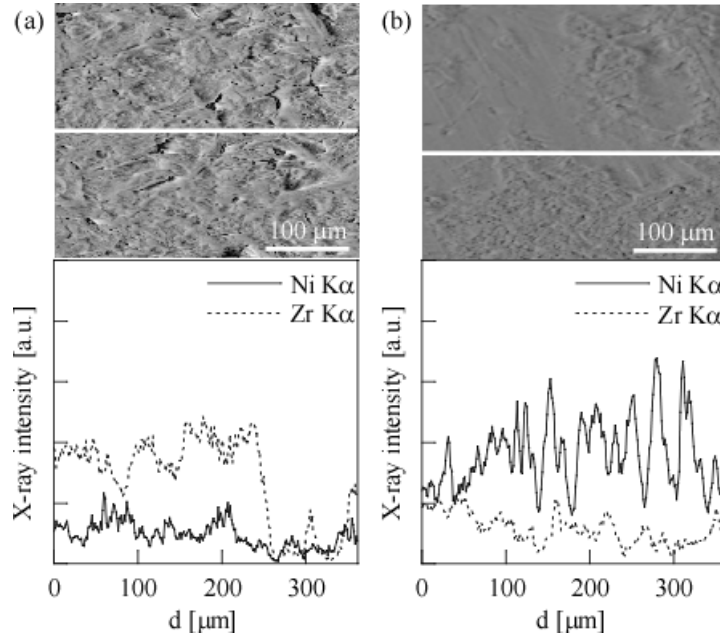
### 3.2 Sample synthesized via EDTA complexes-gel reduction process

According to Refs. [6,11,12], we could prepare the feed solution. In such a process, it was

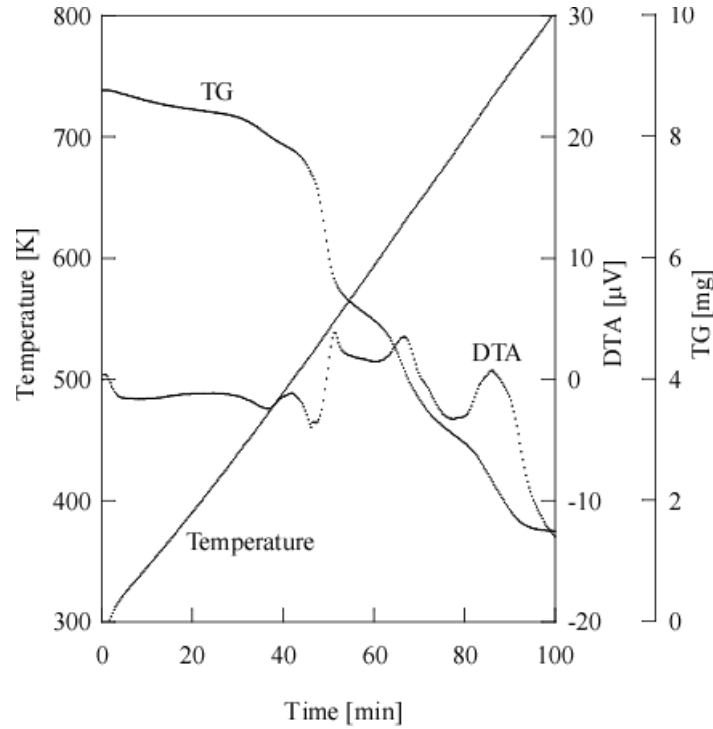
found that the key was pH adjustment for preparation of EDTA complexes (pH value =  $\sim 5$ ). Because, precipitate formation was observed without pH adjustment. That might lead to inhomogeneity of solution.



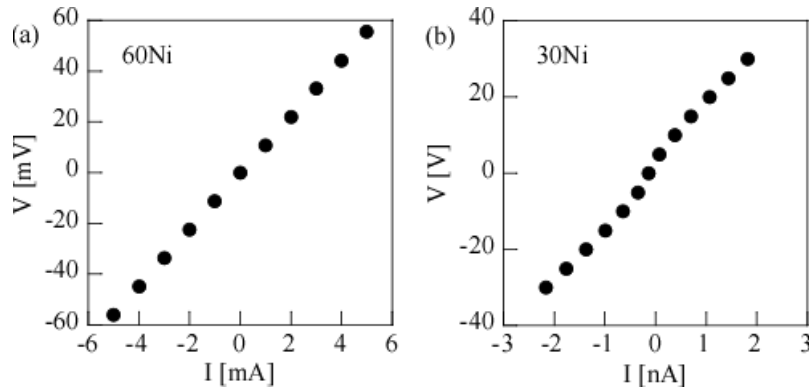
**Fig. 3** X-ray diffraction patterns from Ni-YSZ cermet synthesized via IGP, (a) surface; (b) internal and via conventional powder sintering method, (c) surface; (d) internal.



**Fig. 4** SEM images and EDS analyses of Ni-YSZ cermet synthesized via IGP (a) and via conventional powder sintering method (b).



**Fig. 5** TG/DTA curves of Ni-YSZ cermet synthesized via EDTA CGRP.



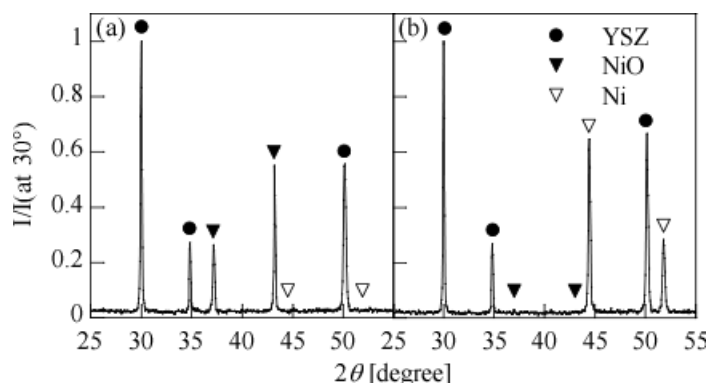
**Fig. 6** I-V relationship by DC method for Ni-YSZ cermet synthesized via EDTA CGRP with Ni content of 60 mol% (a) and 30 mol% (b).

TG/DTA curves is shown in **Fig. 5**. The rapid change of TG/DTA curves and exothermic peak can be found between 510-540 K. Therefore, the heating rate was 5 K/min, and the temperature was kept at 473 K for 20 min to depress the exothermic reaction. Subsequently, the temperature was risen up to 873 K at 5 K/min and was kept for 2 h. This was the thermal treatment of calcination for the EDTA CGRP.

The I-V curves taken by the DC method are shown in **Fig. 6**. **Figure 6 (a)** is the I-V curve for Ni content of 60 mol%. This result shows the good linearity between current and voltage, and consequently the resistance is estimated to be  $\sim 11 \Omega$  without the correction of measurement device. Reduced Ni is responsible for the electronic conductivity and electronic pathways connect with each other in such a sample. On the other hand, **Fig. 6 (b)** does not show the electronic conductivity

since the resistance seems to be very large ( $> \sim 10^{10} \Omega$ ). These results are consistent with the finding based on the percolation model<sup>13)</sup>.

**Figure 7** shows the XRD patterns from the surface of the sample before (a) and after (b) reduction. In **Fig. 7** (b), only metallic phase of Ni can be found, and the peak intensity is much stronger than that of the sample via IGP, although it was taken from the sample surface. Hence, the EDTA CGRP gave the favorable result for manufacturing of Ni-YSZ cermet compared to the IGP.



**Fig. 7** X-ray diffraction patterns from the sample synthesized via EDTA CGRP, (a) before and (b) after reduction.

#### 4. Conclusion

The sol-gel processes were applied to the synthesis of Ni-YSZ cermet. For the internal gelation process, precursor powders with 45 mol% and 61.3 mol% of NiO were successfully synthesized by optimizing quantities of HMTA and urea in the starting solution for gelation and the calcination condition. However, cermet samples thus synthesized showed the ionic conductivity but not the electronic one, although NiO in these samples was reduced to Ni. This is the reason why the amount of Ni in the sample decreased in the sintering process at high temperatures. Therefore, further improving the sintering condition allows the Ni-YSZ cermet synthesized via the internal gelation to have the electronic conductivity. On the other hand, for the EDTA complexes-gel reduction process, precursor powders were successfully synthesized by pH adjustment during preparation of soluble complexes and the calcination condition. Furthermore, the EDTA CGRP cermet sample with 60 mol% of Ni had the electronic conductivity, which means that showed the electrode performance.

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