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Solution Plasma Synthesis of Nanomaterials

ナノ材料の液中プラズマ合成

インターネット公表保留版

(論文投稿中のため、一部内容は公表を保留しています。)

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CHAPTER 1

General Introduction

1.1 NANOMATERIALS

The research fields of nanomaterials in the past decades are rapidly developed because of their unique electronic structures and large surface areas¹. In particular, pure metallic and metallic alloy nanoparticles have been applied as catalyst material, microelectronics material, optoelectronics material, magnetic material, conductive paste, fuel cells, battery electrodes and so on². Well size-controlled nickel and copper fine nanoparticles are applicable to conductive paste and electrode materials of multilayered ceramic capacitors^{3, 4}. Additionally, Ni-Cu bimetallic nanoparticle is an attractive material for a catalyst in a fuel cell and magnetic materials^{5, 6}. For the Li-ion battery field, the metal nanoparticles of Sn and Si can improve battery capacity dramatically^{7, 8}. As well as metal nanoparticles, the oxide nanomaterials of TiO₂ and ZnO have gained much more importance as an attractive semiconductor material^{9, 10}.

1.2 NANOMATERIALS SYNTHETIC METHOD

Nanomaterials have been produced by gas-phase or liquid phase methods. Gas-phase method is continuous process suitable for mass production with highly purity. Commercially-available nanomaterials have been produced by gas-phase method. Nevertheless, gas-phase method requires the complex equipment such as high-vacuum chamber. In contrast, liquid phase method can produce less aggregated particles with uniform particle size, but liquid phase method is a batch process and requires complex procedures and rigorous experimental conditions.

1.3 SOLUTION PLASMA FOR NANOMATERIALS SYNTHESIS

* I deferred the Internet publication of this section.

1.4 DIAGNOSTIC METHOD OF SOLUTION PLASMA

* I deferred the Internet publication of this section.

1.5 PURPOSE OF THIS STUDY

As mentioned above introduction, the solution plasma has many advantages to produce nanomaterials. Especially, the using of metal electrode as raw materials of nanomaterials enables continuous synthesis without any contaminations from electrode. However, it still has many problems, despite its quite significance in nanotechnology.

Problems

- (1) The parameters that are essential for controlling the size and composition of various nanomaterials have not been well understood.
- (2) Synthesis of nanomaterials using alloy electrode as a raw material has not been reported.
- (3) The electrochemical property of the synthesized nanomaterials has not been characterized.
- (4) The relationship between the properties of the plasma, such as the excitation temperatures, and synthesized nanomaterials has not been clearly understood.

Purpose of this study

The purpose of this study is to solve the above-mentioned problems of solution plasma synthesis of nanomaterials. This thesis includes seven chapters:

Chapter 1 presented a general introduction. The generations, applications and diagnostics of various solution plasmas were reviewed.

Chapter 2 described the Ni nanoparticles formation and surface morphology of Ni electrode in a solution plasma. The effects of electrolysis time, solution temperature, voltage, electrolyte concentration, and surface area on the size of Ni nanoparticles formed, amount of nanoparticles produced, and surface morphologies of the electrodes were examined. Additionally, the relationship between the surface morphology and crystal orientation of the electrode was investigated.

Chapter 3 described the synthesis of Cu, CuO, and Cu-based alloy nanoparticles via solution plasma. The effect of the electrolyte and electrolysis time on the morphology of the products was mainly examined.

Chapter 4 described the synthesis of ZnO nanoflowers. The effects of the applied voltage, concentration of the electrolyte, reaction temperatures, and agitation on the morphology of the products were examined. Photoluminescence and photocatalytic activity of the products were also characterized.

Chapter 5 described the optimum experimental conditions required for the synthesis of Sn nanoparticles (Sn-NPs) using K_2CO_3 or KCl as the electrolyte. The effects on the products of the solution temperature, the use of surfactants, and applied voltage were investigated. Electrochemical properties of SnO plates and Sn-NPs were analyzed for use as an anode material in Li-ion batteries.

Chapter 6 described the diagnostic of solution plasma using spectroscopic measurements, electrical measurement, and high-speed camera observation. The effects of edge shielding, applied voltage, and electrode material on the plasma were investigated. The excitation temperature was estimated by applying the Boltzmann plot method. The change in current and voltage during plasma initiation were analyzed to optimize the experimental conditions.

Chapter 7 presented the general conclusions of this study.

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CHAPTER 2

Ni nanoparticles formation and surface morphology of Ni electrode

ABSTRACT : This chapter describes the surface morphology of a glow discharge electrode in a solution. In the experiments detailed in the chapter, the effects of electrolysis time, solution temperature, voltage, electrolyte concentration, and surface area on the size of nanoparticles formed and their amount of nanoparticles produced were examined. The surface morphologies of the electrodes was also studied. The results demonstrated that the amount of nanoparticles produced increased proportionally with the electrolysis time and current. When the voltages were below 140 V, surfaces with nanoparticles attached, called “Particles” type surfaces, were formed on the electrode. These surfaces changed and displayed ripples, turning into “Ripple” type surfaces and the nanoparticles sizes increased with an increase in the amount of nanoparticles produced. In contrast, at voltages over 160 V, the surfaces of the electrodes were either “Random” or “Hole” type, and the particle sizes were constant at different amount of nanoparticles produced. Additionally, we have investigated the relationship between the ripple formation and crystal orientation of the electrode. As a result, the ripple patterns were formed on all planes, except (111)- and (100)-oriented planes; their direction was [001].

2.1 INTRODUCTION

When a high direct current (DC) voltage is applied to a conductive electrode in a solution, a plasma layer is generated at the interface between the electrode and the solution. The formation of the plasma layer is due to the heating of the solution near the electrode. The electrode under such conditions was named “*a contact glow discharge electrode*” by Hickling and Ingram¹, who studied light emission from such electrodes. They performed a conventional electrolysis of water and increased the current by increasing the voltage from a low value. Since the heating of the solution due to electrical resistance was concentrated at the electrode/solution

interface, the solution near the cathode heated to its boiling point and a gas layer containing hydrogen gas and steam was generated. If the voltage was sufficiently high, the gas layer formed a glow discharge plasma that was accompanied by light emission. The emission spectra of this radiation depended on the constituent elements of the electrolyte and electrode materials²⁻⁴. A glow discharge electrode can be used for the synthesis of organic-inorganic superabsorbent composition⁵ and degradation of pollutants⁶.

Recently, a solution plasma was applied in the synthesis of nanoparticles⁷. Gold nanoparticles were synthesized from the solution of HAuCl_4 ^{8, 9}. Paulmier et al. reports the synthesis of TiO_2 nanorods using contact glow discharge electrolysis¹⁰. The nanoparticles of Ni, Ti, Ag and Au were produced by the electrode dissolution during a solution plasma using a glow discharge electrode¹¹. This method for producing nanoparticles has many advantages: (1) it requires a simple experimental setup without the need for a vacuum chamber; (2) there is no need to supply any gas; (3) a conductive electrode is used as the raw material, and harmful reductants or expensive agents are not required; and (4) it can be applied to any electrically conductive metal/alloy. To produce nanoparticles for various applications, control of the particle size and efficient production are essential. However, in spite of their importance, the parameters that are essential for controlling the formation of nanoparticles have not been well understood. Further, the relationship between the surface morphologies of the electrode and the experimental conditions has not been reported. The surface morphologies may be helpful in understanding the mechanism of nanoparticles formation. In this study, we investigated the surface morphology of a glow discharge electrode in a solution. In the experiments detailed in the chapter, the effects of electrolysis time, solution temperature, voltage, electrolyte concentration, and surface area on the size of nanoparticles formed and their amount of nanoparticles produced were examined to study the surface morphologies of the electrodes. The dependence of the ripple formation on the crystal orientation of the electrode was also investigated.

2.2 EXPERIMENTAL SECTION

2.2.1 Experimental Setup

The experimental setup consisted of two electrodes in a glass cell with a capacity of 300 ml as shown in Fig. 2-1. The cathode consisted of a Ni wire with a diameter of 1.0 mm and purity of more than 99.9 mass% (Kojundo chemical, Saitama, Japan) placed at the center of the glass cell. The upper and lower parts of the cathode were shielded by a quartz glass tube to keep the exposed length constant. The exposed portion functioned as the actual electrode. The anode consisted of a Pt wire with a length of 1000 mm, diameter of 0.5 mm, and purity of 99.98 mass% (Nilaco, Tokyo, Japan), and it was bent into a semicircular mesh. The distance between the electrodes was maintained at 30 mm. A glow discharge plasma was generated around the cathode and was maintained by applying a voltage using a direct current power supply (ZX800H, Takasago, Tokyo, Japan). A NaOH solution was used as the electrolyte. The solution temperature was recorded every 5 s at a depth of 10 mm using a polymer-coated thermistor thermometer (Ondotori TR-71Ui, T&D, Nagano, Japan). The current and voltage were recorded every 2 s using a DC power supply.

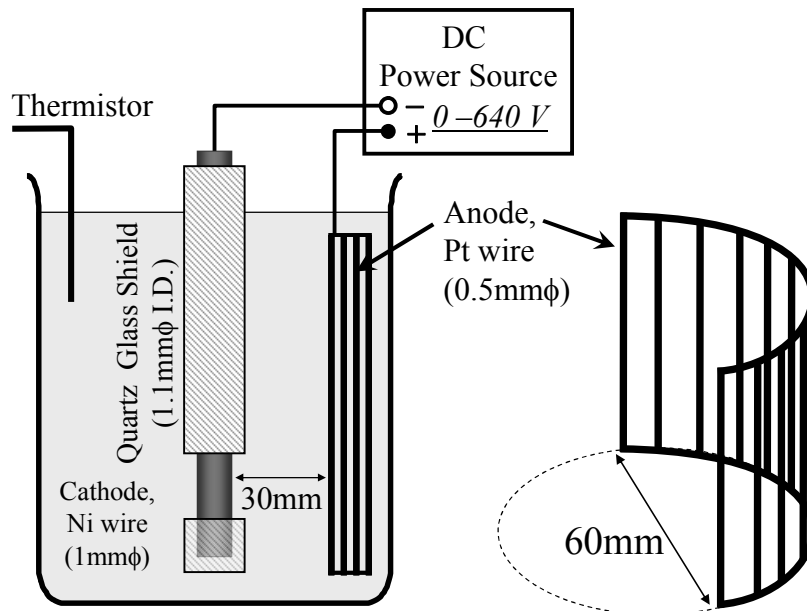


Figure 2-1. Schematic diagram of the experimental apparatus of plasma electrolysis for the synthesis of Ni nanoparticles. The only exposed part worked as an electrode. Anode of a platinum wire, which was bent into a half-round mesh with a length of 1000 mm, a diameter of 0.5 mm and the distance between both electrodes was kept to be 30 mm, as shown in the corresponding cubic diagram.

2.2.2 Experimental Conditions

The standard conditions were an electrolysis time of 60 min, voltage of 140 V, electrolyte concentration of 0.1 M, and exposed length of 10 mm without any agitation. To study the effect of the experimental conditions on the nanoparticles produced, we changed the electrolysis time, voltage, electrolyte concentration, solution temperature, and exposed length from their standard condition values. Table 2-1 shows the experimental conditions. There were samples with the same experimental conditions, and these are denoted by asterisks. For example, the conditions for T-60, V-140, and I-10 were the same. To change the solution temperatures, the solutions were cooled or heated.

Table 2-1. Experimental conditions. Samples with the same experimental conditions are denoted by asterisks.

Sample name	Time (min.)	Temperature Control	Maintained Voltage (V)	Electrolyte	Electrode Length (mm)
t-1	1	Natural cooling in air	140	0.1 M NaOH	10
t-5	5				
t-30	30				
t-60*	60				
t-360	360				
T-1	60	Quenched using ice water	140	0.1 M NaOH	10
T-2		Quenched using 25 °C water			
T-3		Natural cooling in air			
T-4		Heated using hotplate			
T-5		Strongly-heated using heater			
V-80	60	Natural cooling in air	80	0.1 M NaOH	10
V-100			100		
V-120			120		
V-140*			140		
V-160			160		
V-180**			180		
V-200			200		
0.001M	60	Natural cooling in air	600	0.001M NaOH	10
0.005M			490	0.005M NaOH	
0.01M			400	0.01M NaOH	
0.1M**			180	0.1M NaOH	
1.0M			70	1.0M NaOH	
I-10**	60	Natural cooling in air	180	0.1 M	10
I-20				NaOH	20
I-30					30

2.2.3 Experimental Procedure

The experimental procedures are as follow. First, the solution was heated to 60 ± 3 °C. Then, the voltage was increased from 0.0 V to a preset level at a rate of 0.5 V/s, and the electrolysis voltage was maintained at the preset level for a preset time. In the case of changing the electrolyte concentration, we determined the rate of voltage increase needed to increase the voltage to the preset level in less than 300 s, because the pre-warmed solution tended to cool down. Finally, after electrolysis, the products of the process were collected by centrifugation and washed with deionized water. Subsequently, the products were observed using an H-700 (Hitachi High-Technologies, Japan) transmission electron microscope. The collected particles were characterized by X-ray diffractometry (XRD) using a Miniflex II (Rigaku, Tokyo, Japan) diffractometer. The post-experiment cathode wires were also observed using a JSM-7001F (JEOL, Tokyo, Japan) field-emission scanning electron microscope. To investigate the dependence of the pattern formation on the crystal orientation of the electrode, the electrode was characterized using an electron backscatter diffraction (EBSD) technique. For the EBSD analysis, the surface of the electrode wire was mechanically polished using a rotary sander before electrolysis.

2.2.4 Analytical Method

In order to determine the mean diameter of the nanoparticles, four photographs of the spherical particles were taken for each experiment with the same magnification. From these four photographs, we measured the diameters of over 1000 particles whose diameters were greater than 10 nm. We calculated the volume mean diameter from this data. The volume mean diameter D_v differs from the number mean diameter D_n as shown by equations (2.1) and (2.2). Here, the d_i stands for the diameter of particle i and V_i mean the volume of the spherical particle with the diameter d_i .

$$D_n = \frac{\sum d_i}{n} \quad (2.1)$$

$$D_v = \frac{\sum (d_i \cdot V_i)}{\sum V_i} \quad (2.2)$$

We selected the volume mean diameter rather than number mean diameter because we could obtain a Gaussian distribution of the particle diameters by using a volume mean diameter.

The amount of nanoparticles produced (or Production) was calculated from the difference in the weight of the electrode before and after the experiments. We measured the electrode weight 5 times and calculated the average value. The nanoparticles production M (mg), production density d (mg/cm²), and production rate v (mg/s) were derived by the equations listed below. Here, M_b is electrode weight before electrolysis and M_a is the weight after electrolysis. S is a surface area of the exposed part of the electrode, and t means the electrolysis time.

$$M = M_b - M_a \quad (2.3)$$

$$d = \frac{M_b - M_a}{S} \quad (2.4)$$

$$v = \frac{M_b - M_a}{t} \quad (2.5)$$

2.3 RESULT AND DISCUSSIONS

2.3.1 Electrolysis Time

The electrolysis times were changed in the range from 1 to 360 min. [Figure 2-2](#) shows the SEM images of the Ni wire after electrolysis for different electrolysis times. When the electrolysis times were less than 5 min, surfaces with particles attached to them were generated. We named such electrode surfaces “Particle” in order to categorize the different surface morphologies. After more than 30 min of electrolysis time, a rippled pattern was formed on the electrode surface, leading to what we have termed as a “Ripple” surface. A Ripple surface on the electrode during an electrode-melted solution plasma was first found, and it was probably

caused by the sputtering effect. The orientation of these patterns was different at different areas of the electrode. Some areas did not have any Ripple patterns. These patterns probably depended on the crystal grains and the spacing of the ripple became wider with time. According to the SEM image shown in Fig.2-3, the obtained particles were spherical. The diameter of the nanoparticles produced in the early stages of the electrolysis is small. Figure 2-4 (a) shows the relationship between the electrolysis time and nanoparticles production. This result indicates that the production increases in proportion to the electrolysis time. Figure 2-4 (b) shows the plot of the mean diameter against the produced amount. The particle size tends to increase with an increase in the production. This tendency was in agreement with the results of a previous paper in which the electrolysis time had been changed from 10 to 30 min¹¹. From the XRD pattern, products were metallic nickel and didn't contain the nickel oxide. These results suggest that coarse particles were formed due to the rough surface. These results also suggested that the particle size depended on the amount of nanoparticles produced. Therefore, when the effects of the experimental conditions on the particle size are investigated, the total amount of nanoparticles produced should be carefully considered.

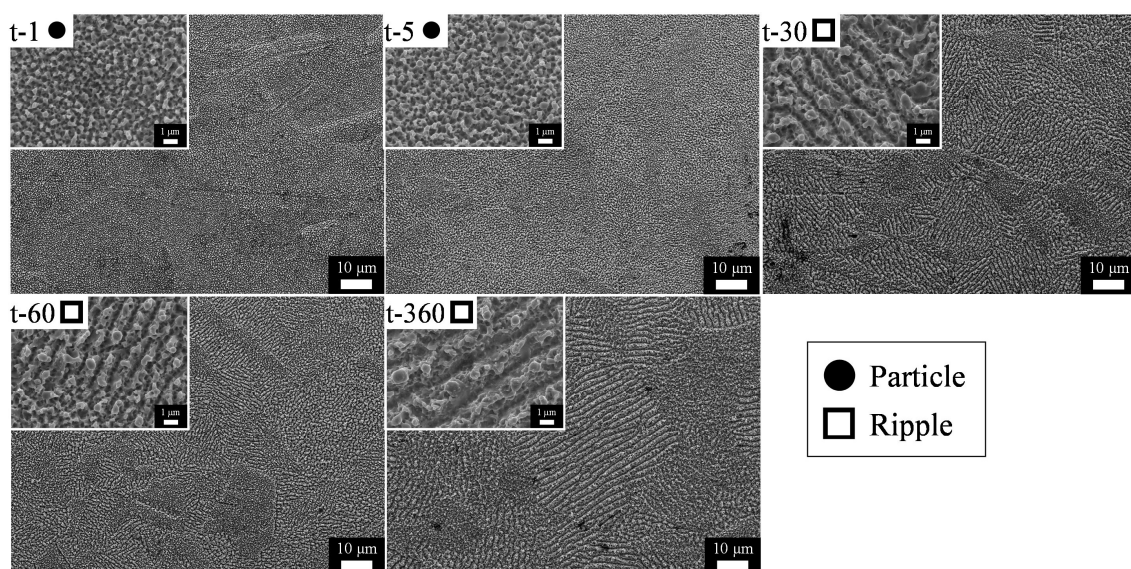


Figure 2-2. SEM images of the Ni cathode wire observed after electrolysis for different electrolysis times.

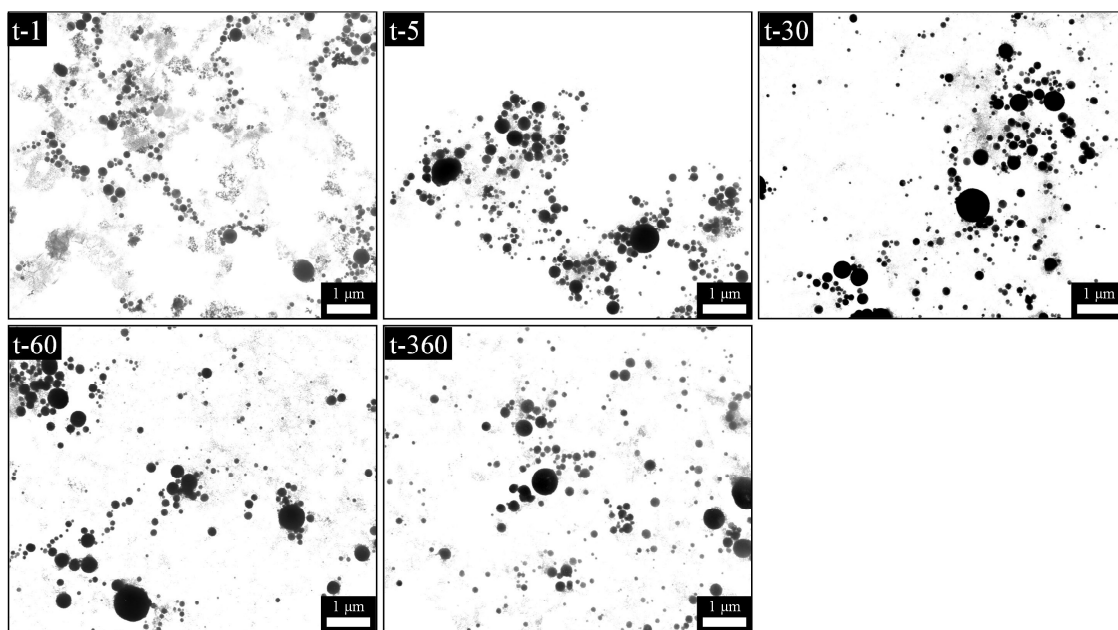


Figure 2-3. TEM images of the product at different electrolysis time.

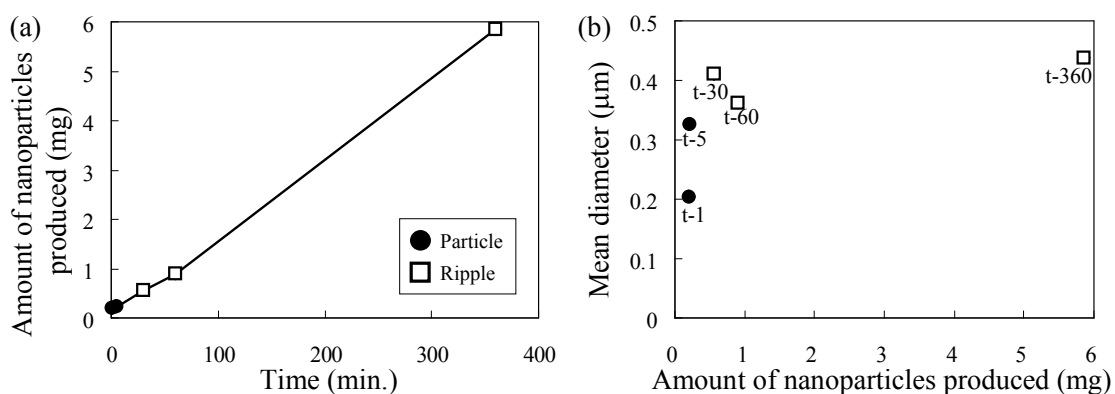


Figure 2-4 (a) Plot of nanoparticles production against electrolysis time. The amounts of nanoparticles produced were calculated using the difference in the weight of the electrode before and after electrolysis. (b) Plot of mean diameter against the production at different electrolysis times. The mean diameter was measured from the TEM images.

Figure 2-5 shows the size distribution of the product for each electrolysis time. Here, the diameter is the volumetric based value. The most frequent diameter was 0.2 μm and this tendency did not change for different electrolysis times. However, the ratio of the coarse particles over 0.5-μm in diameter increased with time. Therefore, the increase in diameter was caused by the formation of coarse particles. XRD pattern of the products indicated that the obtained products were metallic Ni particles (Fig. 2-6).

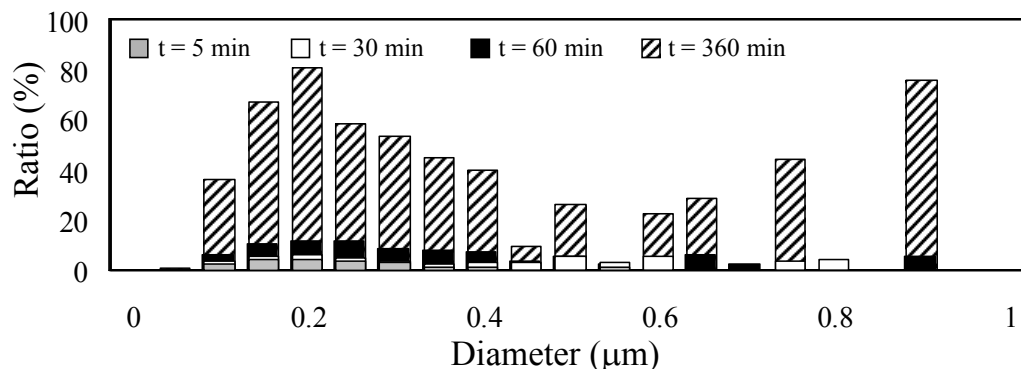


Figure 2-5 Size distribution of the produced nanoparticles. The ratio is normalized using the total amount of particles produced.

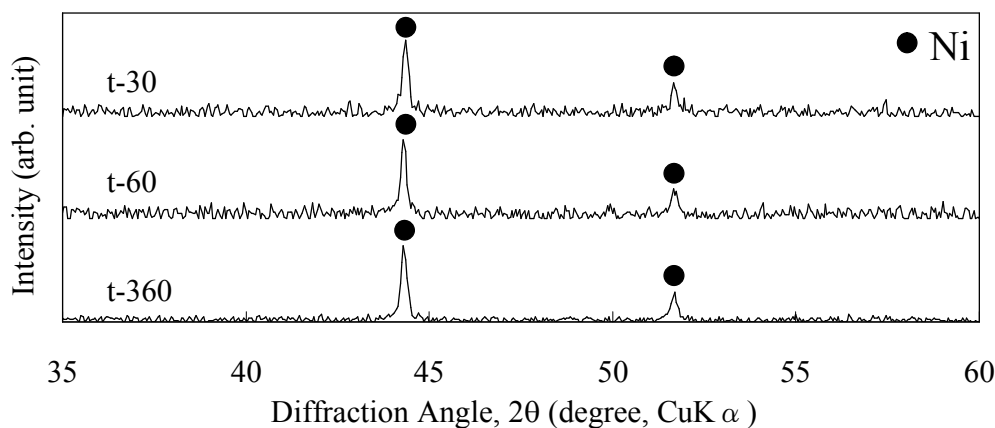


Figure 2-6 XRD patterns of the product at different electrolysis time.

2.3.2 Electrolysis Temperature

In order to control the solution temperatures, the electrolysis solution was either cooled or heated. For the T-1 condition, the electrolysis solution was cooled using ice water. In contrast, the electrolysis solution was heated with a heater for the T-5 condition. In the case of the T-3 condition, the electrolysis solution was cooled in the air. We measured the solution temperature at a certain point. There was a temperature distribution in the electrolysis solutions without agitation. Figure 2-7 shows the SEM images of the electrode surface after the experiment. The labels show the average temperatures of the solution during 60 min. For solution temperatures below 80 °C, the Ripple pattern was formed, similar to the pattern seen in the t-30, t-60, and

t-360 conditions. At solution temperatures over 92 °C, the surfaces were Particle type. This difference in the surfaces can be explained by the nanoparticles production. Figure 2-8 (a) shows a plot of the amount of nanoparticles produced against the mean diameter. The nanoparticles production decreased at high solution temperatures. The particle size was also decreased with a decrease in the nanoparticles production. Thus, in the case of less nanoparticles production, the electrode surface was Particle type. Figure 2-8 (b) shows a plot of the mean diameter against the average current over 60 min. The high temperatures caused a decrease in the current because the gas layer completely covered the electrode and prevented the current from flowing. XRD patterns shown in Fig. 2-9 indicate the solution temperature did not affect the composition of the products. From these results, it can be seen that the production can be controlled by current and not by the solution temperature. A high current produces a large amount of particles. However, in the case labeled 64 °C, the production decreased despite the high current. This was because the electrolysis solution was too cold to fully form a plasma layer, and the electrolysis of water occurred at the interface between electrode surface and solution. This result also suggested that the suitable range for the solution temperature is from 69 to 80 °C.

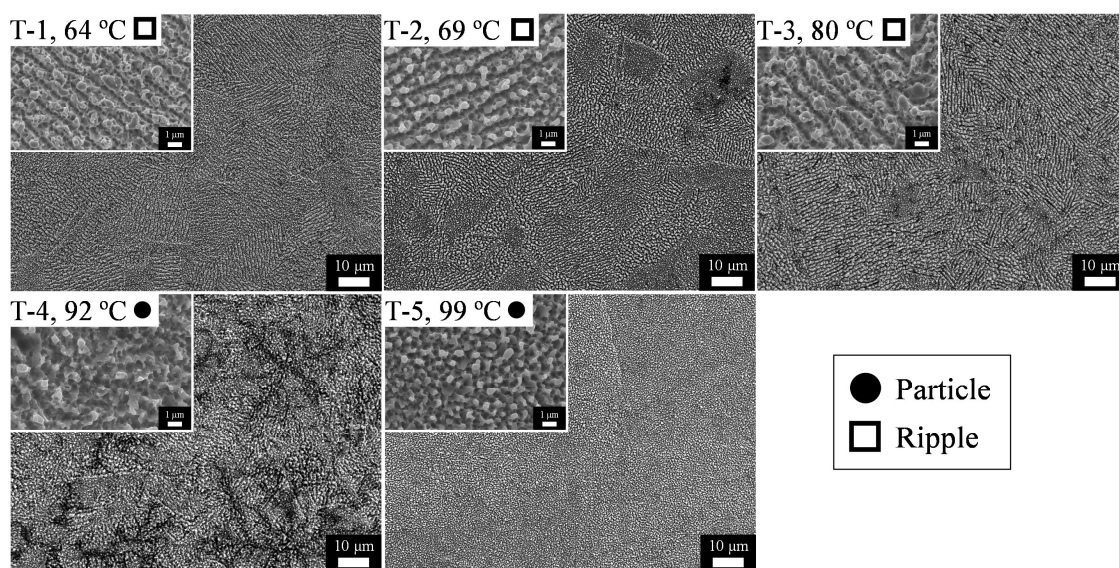


Figure 2-7 SEM images of the cathode Ni wire observed after electrolysis at different solution temperatures.

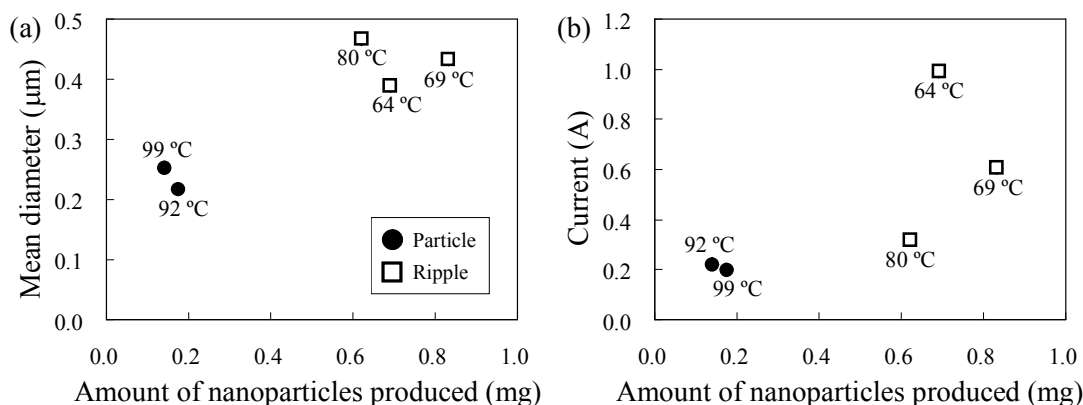


Figure 2-8 (a) Plot of nanoparticles production against the mean diameter. The labels show the average temperatures of the solution over 60 min. (b) Plot of the mean diameter against the average current over 60 min.

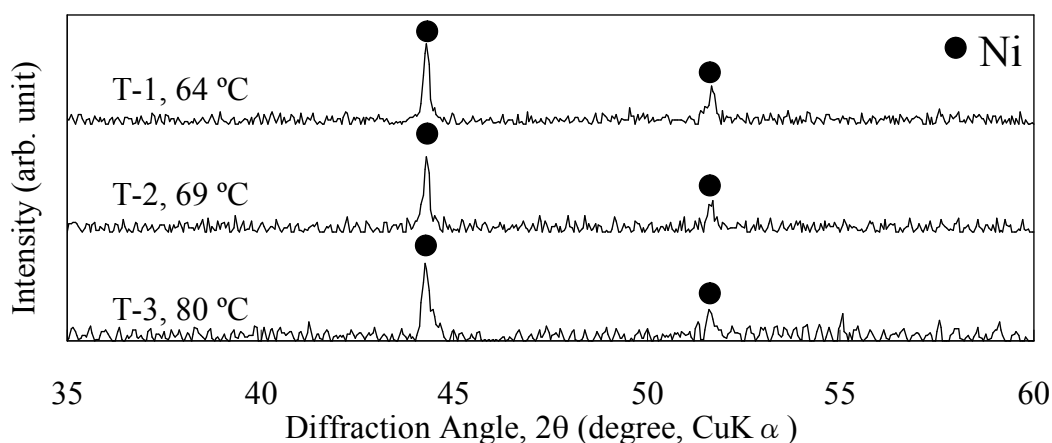


Figure 2-9 XRD patterns of the product at different at different solution temperatures.

2.3.3 Voltage

We investigated the effect of voltage on the particle size and production by changing the voltage from 80 to 200 V. The edge of the electrode was shielded by using a quartz glass tube. As we described in Chapter 5, the edge-shield maintains a partial plasma region. After transition from partial-plasma region to full-plasma one, the products are oxidized and agglomerated. In the case of voltages from 80 to 120 V, the light emissions with a glow discharge were not clear. For the range from 140 to 180 V, the light emissions were observed, and the intensity of the light emission increased with an increase in the voltage. Therefore, an increase in the light emission means that the net area of the discharge expands with an increase in the voltage. At

200 V, in spite of the use of the edge-shield, the discharge condition of the plasma transitioned to that of a full plasma, in which the particles were partially oxidized and agglomerated due to an increase in the surface temperature. The current was probably concentrated at the interface between the electrode and the quartz glass tube.

Figure 2-10 shows SEM images of the electrode after the experiments. When a voltage of 80 V was applied, an undulating surface was generated. This undulating surface is probably related to the crystal grains. Under the high temperature condition caused by the high voltage, the electrode surface changed due to thermal expansion. Melted particles were also observed. For the range from 100 to 120 V, Particle type surfaces were formed. At 140 V, a Ripple type surface was formed. When the voltage was 160 V or 180 V, the surface had a random shape, which we have named “Random” for the purpose of classification. The high voltage caused a transition to the Random type surface. At 200 V, with a transition to full plasma, the electrode surface was quite rough. This is due to an increase in the surface temperature.

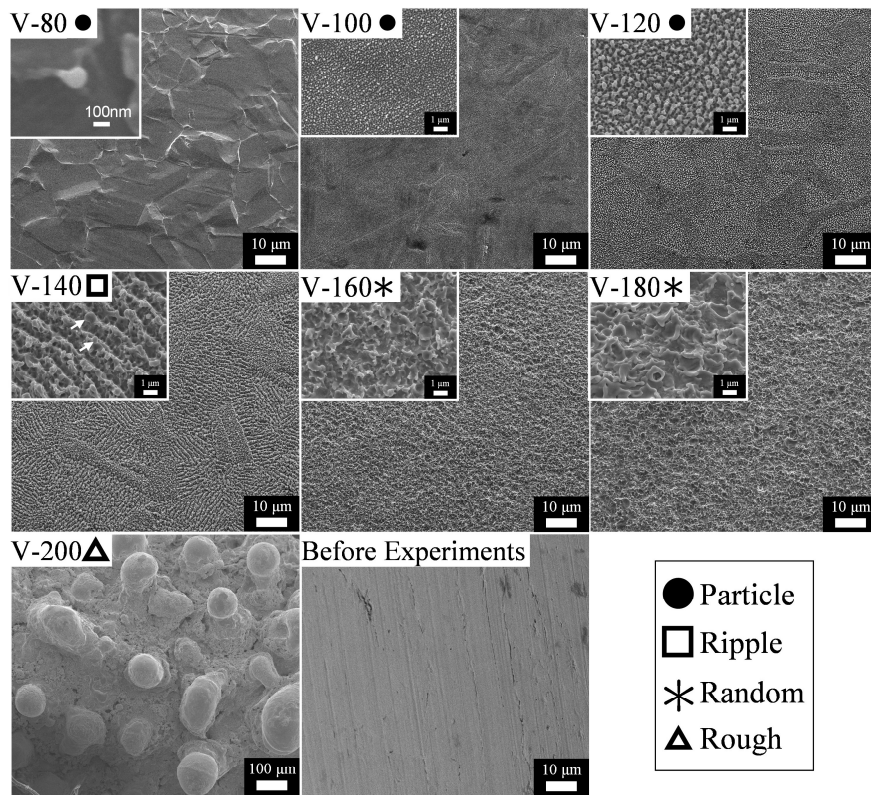


Figure 2-10 SEM images of the Ni cathode wire observed after electrolysis at different voltages.

Over 60 min at different voltages. In the range from 80 to 180 V, the current decreased with an increase in the voltage. As in the cases of changing the electrolysis time and solution temperature, described above, the nanoparticles production increased with an increase in current. However, the high voltage values caused a low current and high production. The nanoparticles were formed by the concentration of the current¹¹. Therefore, the nanoparticles production increases with an increase in the current. High voltages accelerate the electrons and ions in the plasma sheath¹². The energy of the electrons increased owing to this acceleration under high voltage. Hence, the production increased with a decrease in the current at high voltages. The electric power needed to maintain the plasma tends to be a constant value. Based on this, the current was decreased with an increase in the voltage. We predict that the heat balance determines the electric power needed to maintain the plasma. When the solution is cooled, the electric current increases in order to make up for the heat loss, as shown in section 6.

Figure 2-11 (b) shows a plot of the nanoparticles production against the mean diameter at different voltages. In the range from 80 to 120 V, a small amount of particles was obtained. This result indicated that the particles can be formed at 80 V. The nanoparticles production increased with an increase in the voltage. At voltages below 140 V, the mean diameter increased with an increase in the production. This is because the electrode surface became rough with an increase in the nanoparticles production. However, in the range from 140 V to 180 V, the mean diameter decreased with an increase in the production. This result suggested that the voltage affected nanoparticles formation. In the case of the Ripple surface at 140 V, coarse particles were attached to the electrode surface (see arrows, Fig.2-10). We have also observed coarse particles in the products as shown in Fig.2-12. The formation of these coarse particles increased the mean diameter. In contrast, the Random surface, which was formed at 160 and 180 V, does not have any coarse particles. This is the reason for the decrease in the particle size with an increase in the voltage. According to a previous report in which the voltage was changed from 100 to 160 V¹¹, the particle size decreased with an increase in the voltage in the case of not only Ni but also other elements. At 200 V, the particle size increased because of the transition to a full plasma. Figure 2-13 summarizes the XRD patterns of the products. The full plasma at 200V produced

both metallic nickel and nickel oxide. This was exactly the same as the result obtained in the reported data^{13, 14}. The measurement of the surface temperature of the electrode indicated that the temperature of full plasma was more than 2000 °C, in contrast, the temperature without transition to full plasma was less than 100 °C. The transition to full-plasma increased the surface temperature, and the products were oxidized as a result of high-temperature corrosion. The increase of the products size at the full plasma can be explained by the increase of a gas volume and a high temperature. According to the report¹⁵, the size of the product produced by wire explosion is increased with increasing the gas volume over the cathode. Therefore, the large size of particles produced in the full plasma might be caused by the large volume of plasma zone.

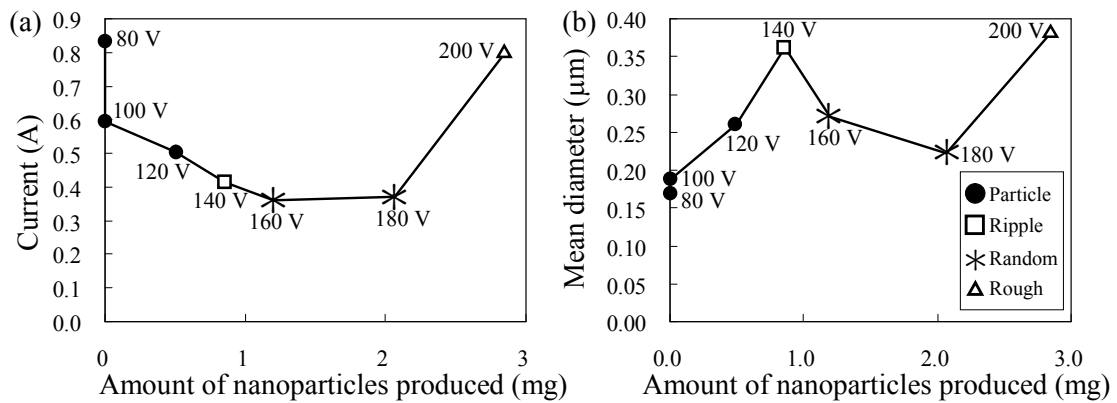


Figure 2-11 (a) Plot of the average current over 60 min against the nanoparticles production. (b) Plot of the mean diameter at different applied voltages against the nanoparticles production.

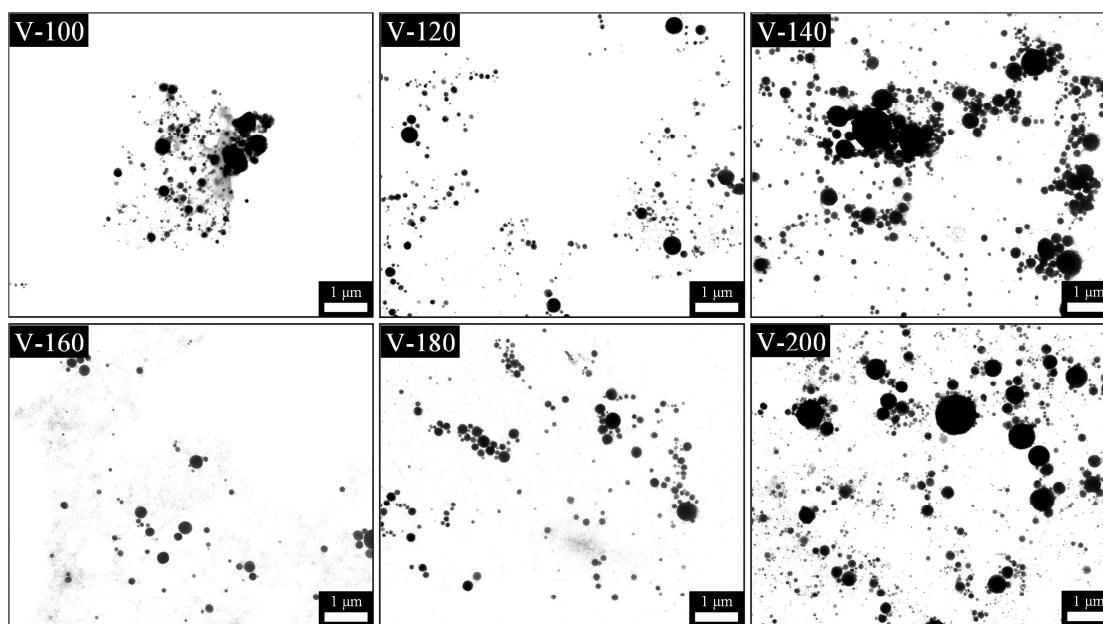


Figure 2-12 TEM images of the products at different applied voltages.

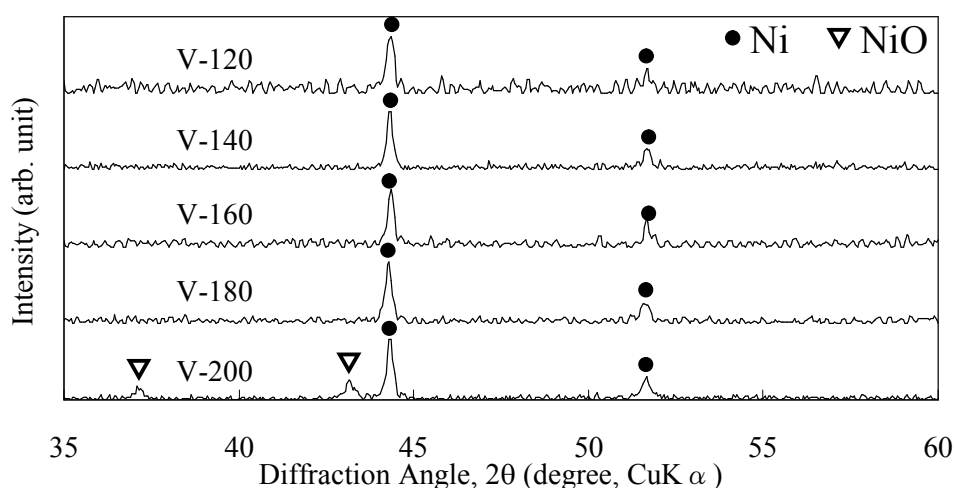


Figure 2-13 XRD patterns of the products at different applied voltages.

2.3.4 Electrolyte Concentration

As above mentioned in section 2.3.3, the transition to a full-plasma due to an increase in the voltage happened at 200 V, in spite of the use of an edge-shield. The solution for using higher voltages without a transition to full-plasma is to use low electrolyte concentrations. When the concentration of the electrolysis solution is low, the current decreases due to an increase in the solution resistance. We previously reported that the use of low electrolyte concentrations could enable the use of high voltages¹⁶. The mean diameter decreased with a

decrease in the production, as shown in Table 2-2. During the change in the electrolyte concentration from 0.001 to 1.0 M, the highest nanoparticles production occurred at 180 V with an electrolyte concentration of 0.1 M. In the case of concentrations of 0.001 M and 1.0 M, the amounts of particles produced were too small to be able to collect any. Figure 2-14 shows the SEM images of the electrode after this set of experiments. When the electrolyte concentrations were 0.001 M at 600 V and 0.005 M at 490 V, pores were formed on the electrode surface (arrows show), which we have named “Hole” for the purpose of classification. These pores on the electrode were also formed in other reported experiments^{2, 16}. These surfaces were of the Random type in the case of 0.01 M and 0.1 M. At 1.0 M, the surface was of the Particles type. As mentioned in section 2.3.3, the high voltage probably accelerates the charged particles such as electrons, Na^+ , and OH^- . There is a possibility that pores formed on the surface of the electrode at high voltage due to sputtering rather than the melting of the electrode surface.

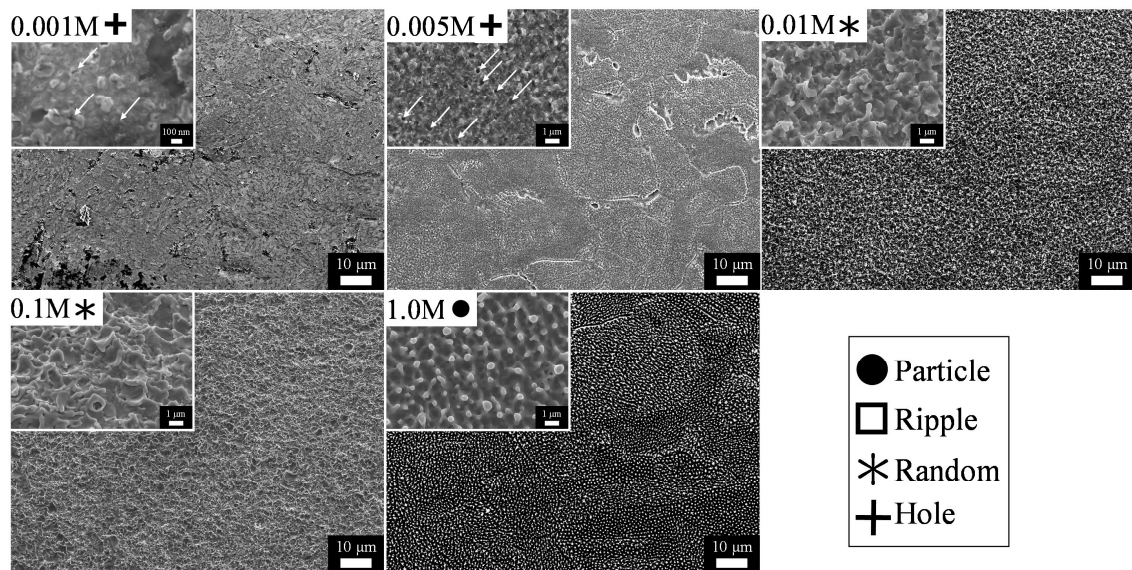


Figure 2-14 SEM images of the Ni cathode wire observed after electrolysis at different concentrations.

Table 2-2. Experimental results. The breakdown voltage corresponds to the highest value of the current. The maintained current, power, and temperature are the average values during electrolysis. The production rate and density were derived by dividing the production by the electrolysis time and surface area, respectively.

Sample name	Breakdown				Maintained			Production (mg)	Particle size		
	Voltage (V)	Current (A)	Power (W)	Temp. (°C)	Current (A)	Power (W)	Temp. (°C)		N	Volume mean diameter (nm)	Number mean diameter (nm)
t-1	53.8	3.12	167	62.0	0.438	61.4	84.9	0.20	673	205	90
t-5	49.8	2.80	139	64.5	0.484	67.7	83.4	0.21	712	326	108
t-30	52.8	2.88	152	62.7	0.438	61.4	84.9	0.56	912	410	108
t-60*	52.7	2.87	151	64.7	0.431	60.3	76.2	0.90	1950	361	113
t-360	50.8	2.76	140	64.3	0.424	59.3	69.2	5.86	777	439	119
T-1	71.9	2.54	183	48.8	0.991	138	64.3	0.69	842	389	115
T-2	60.9	1.86	113	53.0	0.606	84.8	68.5	0.83	1050	433	101
T-3	59.9	1.95	117	59.9	0.319	44.6	80.2	0.62	995	465	110
T-4	45.9	1.60	73.4	66.3	0.219	30.7	92.0	0.14	1005	253	104
T-5	43.9	1.21	53.1	65.4	0.200	28.0	99.1	0.18	1384	215	102
V-80	49.8	2.78	138	63.4	0.831	66.4	87.4	0.01	1076	168	61
V-100	52.8	2.59	137	60.1	0.593	59.3	85.9	0.01	664	187	61
V-120	51.8	2.90	150	62.3	0.503	60.3	84.2	0.50	796	261	87
V-140*	51.8	2.74	142	64.5	0.413	57.8	85.3	0.86	1950	361	113
V-160	51.8	2.74	142	64.9	0.360	57.6	83.6	1.20	501	271	102
V-180**	51.8	2.76	143	60.1	0.371	66.7	81.3	2.07	1257	222	61
V-200	46.6	2.99	139	63.7	0.801	160	93.3	2.85	921	380	133
0.001M	479	0.40	192	74.3	0.125	75.3	87.8	0.17	-	-	-
0.005M	275	0.63	174	67.7	0.130	63.8	85.8	0.47	2072	129	56
0.01M	176	0.99	174	72.5	0.176	70.2	85.6	0.70	465	198	77
0.1M**	79.8	0.87	69.4	68.2	0.371	66.7	81.3	2.07	1257	222	61
1.0M	21.5	2.91	62.6	62.7	0.544	38.1	73.2	0.32	-	-	-
l-10*	51.8	2.74	142	64.5	0.431	60.3	76.2	0.90	1950	361	113
l-20	53.8	4.94	266	65.2	0.590	82.5	89.0	2.15	1210	630	66
l-30	55.8	6.86	383	61.4	0.718	100	89.7	2.53	837	611	120

2.3.5 Surface Area

One way to increase the nanoparticles production is to extend the plasma area by using an electrode with a large surface area. The exposed length of the cathode wire was varied to 10 mm, 20 mm, and 30 mm. We predicted that the nanoparticles production would increase in proportion to the surface area. However, this did not happen because the current did not triple, as shown in Table 2-2. The heat balance determines the electric power consumed. When the surface area tripled, the heat loss is also required to triple. However, the solution temperatures increased from 76 to 90 °C with the tripling of the surface area. If the solution temperature were to remain constant for each surface area, the production would have increased in proportion to the surface area. This result also suggested that cooling of the solution is essential to extend the plasma area.

2.3.6 Summary of the Results

As mentioned in sections 2.3.1–2.3.5, the key factors affecting the formation of nanoparticles are the current and voltage. The other factors such as solution temperature, electrolyte concentration, and surface area affect the current and voltage. For example, the solution temperature and surface area of the electrode just change the current. The high temperature caused a decrease in the current because the gas layer fully covered the electrode and prevented the flow of current. The voltage also affected the current and particle size. At high voltages, the current decreased and the production increased. Low electrolyte concentration can increase the voltage, which probably causes sputtering of the electrode.

The role of the current is to control the amount of nanoparticles produced. [Figure 2-15](#) shows the plot of current against the production rate. The shapes in the inset show the morphology of the electrode surface. This plot does not contain the t-1, t-5, V-80, and V-100 conditions because the amounts of nanoparticles produced in these cases were too small. The T-1 and T-2 conditions were also removed because a conventional electrolysis of water occurred at the interface between the electrode and the solution interface. From this plot, the current increased with the production rate because the current concentration produces a nanoparticles.

[Figure 2-16](#) shows the plot of the mean diameter against the production density, i.e., the amount of nanoparticles produced per unit area. Interestingly, the surface morphologies affected the mean diameter and the production density. In addition, voltage changed the electrode surface. In the case of voltages below 140 V, the surfaces were either Particle or Ripple type. For voltages over 160 V, the surfaces changed to Random or Hole types, and these surfaces produced particles that were smaller than those produced from Ripple surfaces. The difference between Particle and Ripple type surfaces is in the production density; the production density was below 1.7 mg/cm² for Particle type surfaces and over 1.7 mg/cm² for Ripple type. Compared to Ripple surfaces, the Particle surfaces produced particles with a smaller diameter. The Particle surfaces probably change into Ripple surfaces during particle production. The spacing of the ripples became wider at a high production density and the mean diameter increased with an increase in the production density. In contrast, the sizes of the particles

produced from Random type surfaces were constant at different production densities.

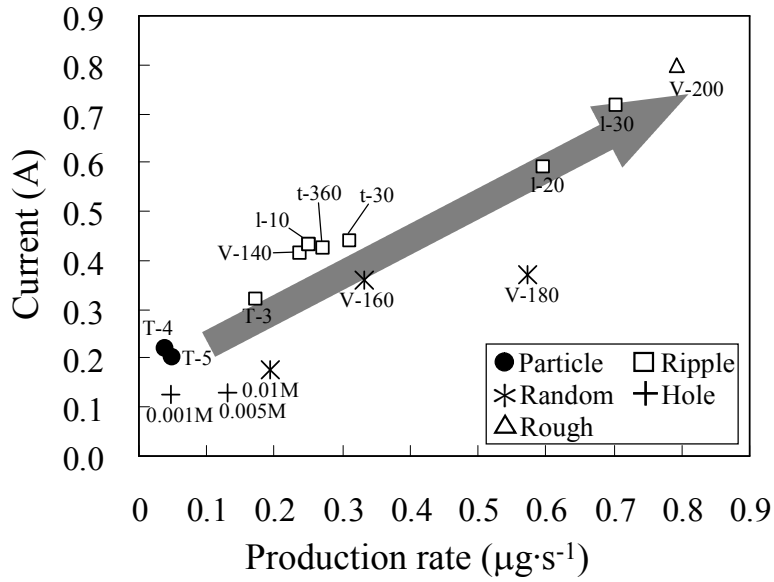


Figure 2-15 Plot of mean current against the production rate. The inset shapes are a guide to the different morphologies of the electrode surface. The current increased with an increase in the production rate.

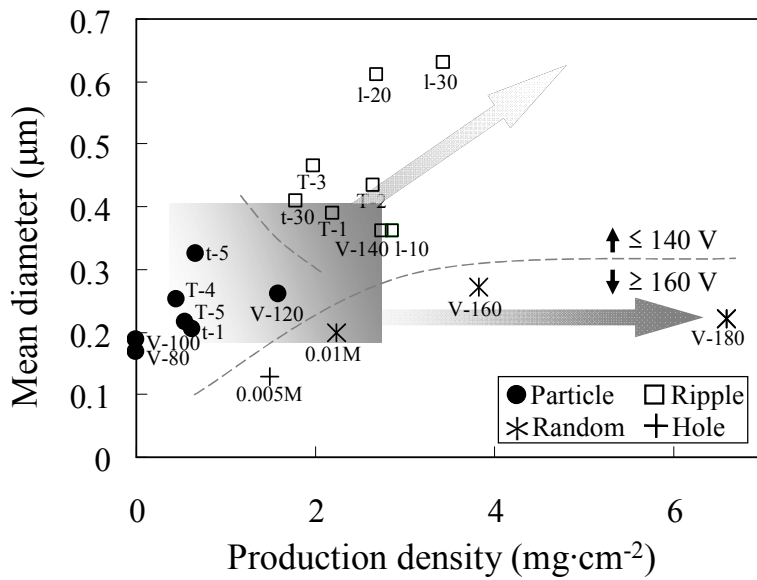


Figure 2-16 Plot of the mean diameter against the production density. The inset shapes are a guide to the different morphologies of the electrode surface. The surface morphology affected the mean diameter and production density. The most suitable condition for the production of nanoparticles was the one in which the particle diameter was small and the production density was high. The Random type surface has a small diameter and high production density.

2.3.7 Formation mechanism of Ripple surface

To investigate the ripple formation mechanism, the electrode surface after 30 min of electrolysis was characterized using an EBSD technique. Figure 2-17 (a) shows a SEM image of the nickel electrode before electrolysis. The electrode surface was mechanically polished and marked, as shown in the right side of Fig.2-17 (a), to locate the same area after electrolysis. The electrode surface was quite smooth and defect free. Figure 2-17 (b) shows an EBSD orientation map of the nickel electrode surface before electrolysis. The grains are color-coded based on the crystal direction perpendicular to the measured surface plane (normal direction, ND). The black lines indicate grain boundaries. The inset shows a standard triangle of a partial inverse pole figure. This inverse-pole-figure indicates that the nickel electrode had a polycrystalline structure with the grain size of less than 50 μm and that no crystal orientation anisotropy existed in the electrode. Figure 2-17 (c) shows a SEM image of the nickel electrode after 30 min of electrolysis. We observed both a rippled surface and a particle-coated surface on the electrode. Regions with the same surface pattern are enclosed by black lines. It is noteworthy that the surface patterns agreed well with the crystal grains. This result indicates that the surface pattern depended upon the crystal orientation of the electrode; the black lines in Fig.2-17 (c) correspond to the grain boundaries.

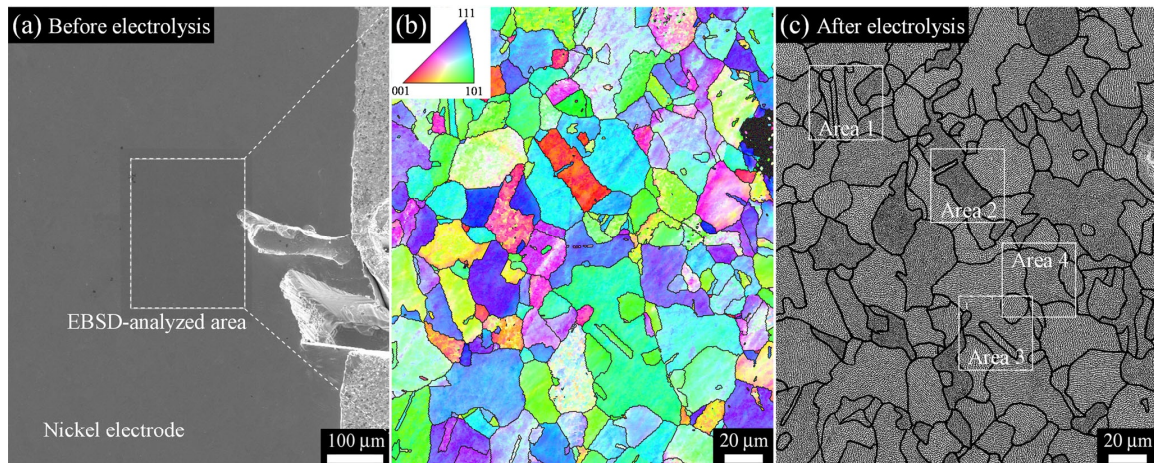


Figure 2-17 (a) SEM images of the nickel electrode before electrolysis. (b) Electron Back-Scattering Diffraction (EBSD) orientation map of the nickel electrode surface before electrolysis, in which the grains are color-coded by the crystal direction normal to the measured surface plane, and grain boundary is shown by a black solid line. (c) SEM image of the nickel electrode after electrolysis of 30 minutes. The regions with a same surface pattern are enclosed by a black line.

Figure 2-18 shows enlarged SEM images and EBSD maps corresponding to Area 1 to 4 in Fig.2-17 (c). The arrows overlaid on the SEM images show the direction of the ripple pattern. The cubes in the EBSD maps show the crystal lattice of a nickel sample at each grain. These cubes were drawn based on the calculation of the crystallographic tilt, as taken from the inverse-pole-figure. From these results, we know that the ripple patterns were formed on all planes except (111)- and (100)-oriented planes. The particle-coated surfaces were formed on the (111) plane and the (100) plane. The center grain in Area 2 is the (100) plane. The center of Area 4 contains a region in the (111) plane orientation. The direction of the ripple pattern depended upon the lattice orientation, as indicated by arrows in the EBSD maps, the lattice direction was [001].

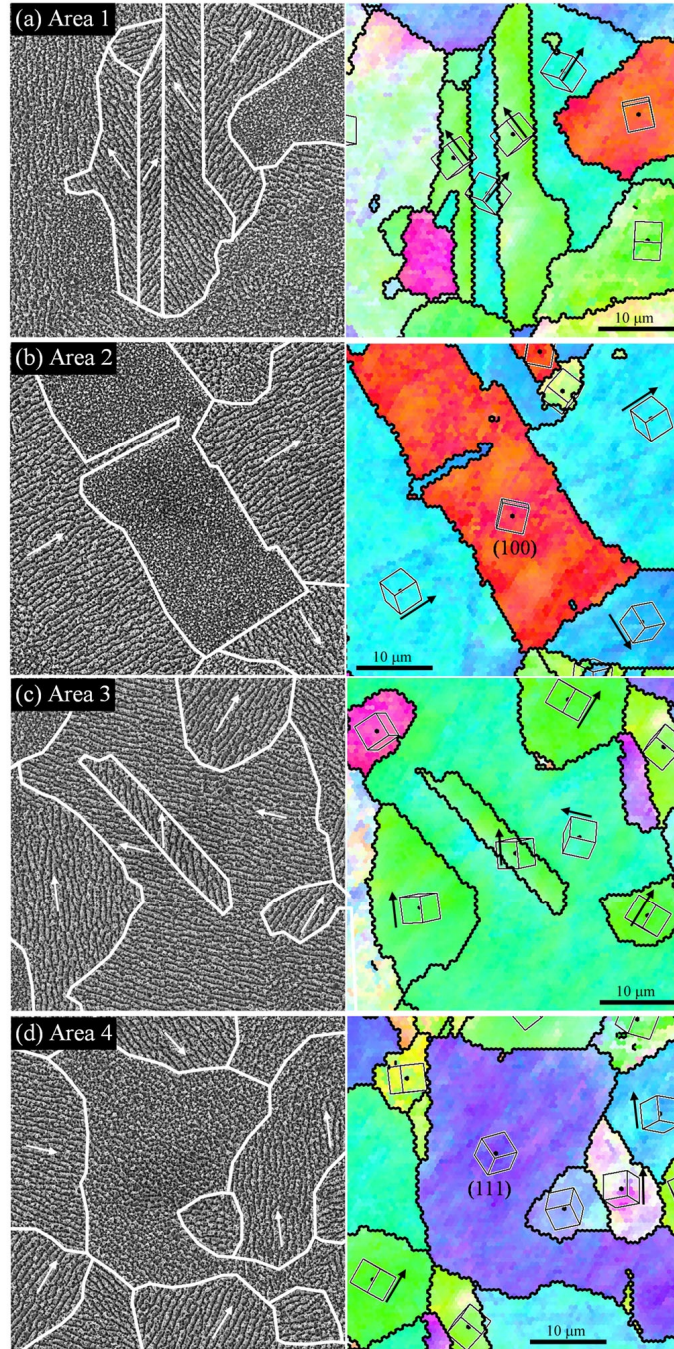


Figure 2-18 Enlarged SEM images and EBSD maps corresponding to the Area 1 to 4 in Fig. 2-17 (c). The arrows in SEM images show a direction of a ripple pattern. The cubes in EBSD maps show a crystal lattice of a Face Centered Cubic (FCC) at each grain. The cubes are based on the calculation of the crystallographic tilt from inverse-pole-figure

Previous reports indicate that the nanoparticles are produced via two mechanisms in the solution plasma: local melting of an electrode because of the current concentration, which is induced by the electrothermal instability¹¹, and uniform sputtering in the form of a bombardment of charged particles in the plasma². The agglomeration of molten metals probably produced the particle-coated surface. However, ripple formation on the glow discharge electrode has not previously been reported. In the case of ion beam sputtering¹⁷⁻²⁰, Xe⁺, Ar⁺, Kr⁺, and Ne⁺ ions have been used with an accelerating voltage of 1–60 kV. The incident angle and substrate temperature have an influence on the ripple formation. In the solution plasma, the main species in the plasma are OH⁻, Na⁺, H⁺, and ionized Ni³. These ions seem to be too small to bombard the electrode surface. Additionally, the applied voltage of 140 V is relatively small, as compared to the ion beam irradiation. It is unlikely that ripple formation on the glow discharge electrode was induced by the ion sputtering process.

We are also considering the possibility of thermal etching, in which facets and grooves are generated on a surface via the evaporation, surface diffusion, and body diffusion of an electrode²¹. Faceting is a phenomenon in which a plane with a low surface energy grows on the sample surface under high temperature conditions. Grooves are generated at the grain boundaries. In certain cases, the thermally-etched plane grows a rippled surface²¹. In the case of a face-centered-cubic (FCC) like nickel, the surface energy increases in the following order; (111), (100), (110), and (210). According to the literature, the (111) and (100) facets have been observed on FCC surfaces^{21, 22}. EBSD maps in [Fig.2-18](#) indicate that the direction of the ripple pattern is the [001] direction. If we denote the facet plane by (k,l,m), the following relation will hold: $(1,1,0) \times (k,l,m) = [0,0,1]$. We can calculate the facet planes: $k - l = 1$, $m = 0$. From these equations, the facet planes should be (100), (210), (310), etc. If the (111) facet is generated, the ripple pattern will be in the $[\bar{1}10]$ direction. Generally, the facet plane is determined by the crystallographic tilting; the plane near the (111) plane generates the (111) facet. However, in the case of a glow discharge electrode, all facet planes probably consisted of the (100) plane. There is a possibility, that is, that the surface oxidation changed the surface stability so as to selectively stabilize the (100) plane.

2.4 CONCLUSIONS

In this chapter, we investigated Ni nanoparticles formation and surface morphology of Ni electrode in a solution plasma. From these results, the morphologies of the electrodes were changed according to the experimental conditions. It was determined that the current and voltage are the main factors. The following conclusions were drawn:

- (1) The production increased proportionally with electrolysis time and current.
- (2) When the voltages were below 140 V, surfaces with nanoparticles attached were formed on the electrode. These surfaces changed, and displayed ripples and the sizes of the particles produced increased with an increase in the production.
- (3) For voltages over 160 V, the surfaces of the electrodes were Random or Hole type, and the particle sizes were constant at different production densities.
- (4) EBSD maps indicated that the ripple patterns were formed on all planes except the (111)- and (100)-oriented planes. The direction of the ripple pattern was [001]. The ripple pattern was likely generated because of the thermal etching during the glow discharge in a solution.

In this study, we found a strong connection between the production and the electrode surface. Additionally, results suggested that the particle size is controllable by changing the crystallographic face of an electrode. These findings can help not only in the optimization of the experimental conditions but also in investigation of the formation mechanism of the nanoparticles in a solution plasma.

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CHAPTER 3

Synthesis of Cu, CuO, and Cu-based alloy nanomaterials

ABSTRACT : This chapter describes the synthesis of Cu, CuO and Cu-based alloy nanoparticles via solution plasma, in which the effect of the electrolyte and electrolysis time on the morphology of the products was mainly examined. In the experiments, a pure metallic copper and Cu-Ni alloy wire as a cathode were immersed in an electrolysis solution. When pure metallic electrode was used, electrolyte was K_2CO_3 with the concentration from 0.001 to 0.50 M or a citrate buffer (pH = 4.8). The results demonstrated that by using the K_2CO_3 solution, Cu wire produced CuO nanoflowers with many sharp nanorods, the size of which decreased with decreasing the concentration of the solution. Spherical particles of copper with/without pores formed when the citrate buffer was used. The pores in the copper nanoparticles appeared when the applied voltage changed from 105 V to 130 V, due to the dissolution of Cu_2O . The solid solution alloy nanoparticles of Ni-Cu prepared in this study have a uniform distribution of composition. These results demonstrate that the solution plasma technique is applicable not only for the synthesis of pure metals but can also be used for the synthesis of alloy nanoparticles.

3.1 INTRODUCTION

Presently, nanostructured Cu-based materials, including metallic copper, copper oxide and copper-based alloy, have been used in a broad range of areas. For instance, metallic nanoparticles of copper attract attention not only in the scientific field but also in industry because of their application in electronic devices such as printed circuit boards¹⁻³ and multilayer ceramic capacitors.^{4,5} CuO, is an important p-type transition-metal-oxide semiconductor with a narrow band gap of 1.2 eV, and it has been widely used as a heterogeneous catalyst, gas sensor, electrode materials for lithium-iron battery^{6,7}, and field emission emitter. Moreover, many recent efforts have been directed toward the fabrication of nanocrystalline CuO to enhance its

performance⁸⁻¹¹ and develop new functions.^{12, 13} As a Cu-based bimetallic nanoparticles, Ni-Cu nanocrystal is an attractive material that is being extensively used as a catalyst in fuel cells¹⁴, glucose sensor¹⁵, and magnetic material¹⁶. Thus far, Ni-Cu nanoparticles have been synthesized via hydrothermal reaction¹⁴, hydrazine reduction¹⁷, polymeric precursor method¹⁶, microemulsion method¹⁸, and chemical vapor deposition¹⁹ using metallic chloride^{14, 16-18}, sulfate¹⁸, and acetylacetonate¹⁹ as precursors.

In the past decade, laser-irradiation, microwave, and solution plasma have been extensively used for the synthesis of nanoparticles. To this end, several reports have demonstrated the use of plasma and microwave methods to synthesize various metallic nanoparticles, including Au^{20, 21}, Ag²² and Pt²², from the metal ions in solution. Typically, metallic rods, plates, and powders have been used as the starting materials for the synthesis of Au²³⁻²⁵, Ag²⁴, Ni²⁵⁻²⁷ nanoparticles via solution plasma method. In addition, alloy nanoparticles have also been synthesized using this method. For example, Pt-Au nanoparticles have been synthesized from H₂PtCl₆, NaAuCl₄, and HClO₄ solutions²⁸. Similarly, FePt nanoparticles were synthesized in molten LiCl-KCl-CsCl electrolyte containing metallic ions of Fe and Pt²⁹. Pootawang et al. reported the formation of Ag/Pt nanocomposites via electrode erosion, taking advantage of the effects of electric arc at the cathode (Ag rod) and sputtering at the anode (Pt rod)³⁰. Furthermore, Zhang et al. demonstrated the synthesis of Ag-Au alloy nanoparticles in solution by laser irradiation of a metal powder suspension³¹. However, to the best of our knowledge, the Cu-based nanoparticles formation from Cu or Cu alloy electrode as raw materials has not been studied. Herein, the purpose of this study is to investigate the Cu-based nanoparticles formation from Cu or Cu alloy electrode. In fact, we investigated the effect of the electrolyte solution on formation of Cu-based nanoparticles. In the case of metallic Cu electrode, the electrolysis solution was K₂CO₃ with a concentration from 0.001 to 0.50 M or citrate buffer (pH = 4.8). As an alloy electrode, Cu-Ni alloy wires with different Cu content were used. Finally, a possible mechanism for the synthesis of copper, copper oxide and copper alloy nanoparticles was discussed.

3.2 EXPERIMENTAL SECTION

3.2.1 Experimental Setup

Figure 3-1 shows the experimental setup, which consists of two electrodes in a glass cell with a capacity of 300 ml. A cathode placed in the center of the glass cell was a metallic copper wire, Cu-43%Ni constantan wire (Ni 42.6 wt%, Cu 56.6 wt%, Mn 0.8 wt%) and Cu-66%Ni monel wire (Ni 66.3 wt%, Cu 31.3 wt%, Fe 1.5 wt%, Mn 0.9 wt%) of 1.0 mm in diameter (Nilaco, Tokyo, Japan). The upper part of the cathode electrode was shielded by a quartz-glass tube to obtain an exposed length of 10 mm; the exposed part functioned as the actual electrode. The anode was a platinum wire, which was bent into a half-round mesh with a length of 1000 mm, a diameter of 0.5 mm, and a purity of 99.98 mass% (Nilaco, Tokyo, Japan). The cubic diagram in the right side of Fig.3-1 shows the shape of the anode electrode. The surface area of the anode was 50 times larger than the cathode. The distance between the electrodes was kept at 30 mm. The glow discharge plasma was generated around the cathode and was maintained by applying a voltage from a direct-current power supply (ZX800H, Takasago, Tokyo, Japan).

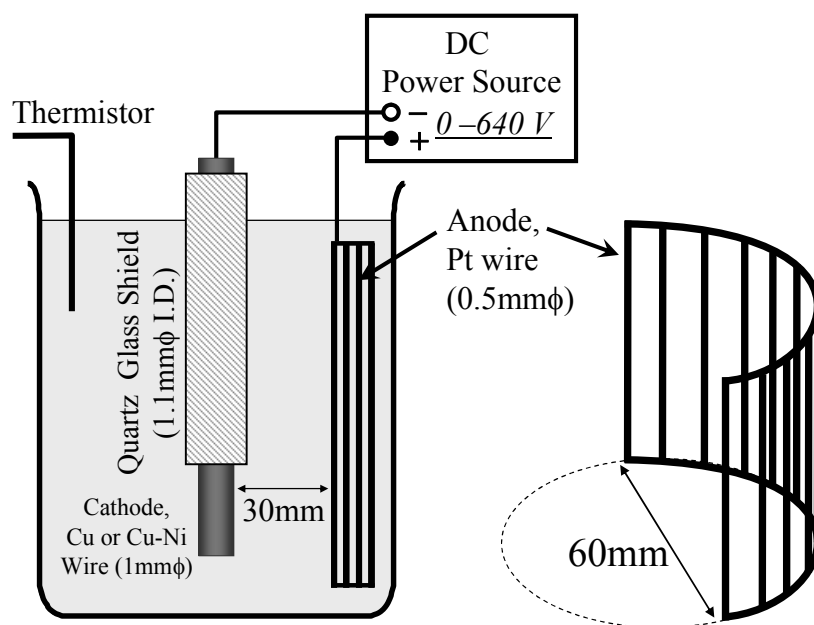


Figure 3-1. Schematic diagram of the experimental apparatus of plasma electrolysis for the synthesis of Cu nanoparticles. The only exposed part worked as an electrode. Anode of a platinum wire, which was bent into a half-round mesh with a length of 1000 mm, a diameter of 0.5 mm and the distance between both electrodes was kept to be 30 mm, as shown in the corresponding cubic diagram.

3.2.2 Experimental Procedure and Characterizations

In the case of metallic Cu wire as a cathode, the electrolyte was K_2CO_3 solutions with concentrations of 0.5 to 0.001 M or citrate buffer (pH = 4.8). When the electrolyte was citrate buffer, the effects of the electrolysis time and applied voltage on the product morphology were investigated; the electrolysis times were 60 and 5 min, and the applied voltages were 105 and 130 V. For Cu-Ni alloy, the electrolyte was 0.1 M NaOH and the applying voltage was 160 V. The solution temperature was recorded every 5 s at the position of 10 mm below the surface using a polymer-coated thermistor thermometer (Ondotori TR-71Ui, T&D). The current and voltage were recorded every 2 s using a DC power supply.

After the experiments, the products were collected by the centrifugation. The collected particles were washed with a deionized water to remove solidified salts. After drying, the particles were characterized by XRD using a Miniflex II (Rigaku, Tokyo, Japan) diffractometer. The surface of the cathode after the experiments and the products were observed by FE-SEM using a JSM-7001F (JEOL, Tokyo, Japan) microscope, transmission electron microscopy (TEM) using a H-700 (Hitachi High-Technologies, Japan) microscope, High-resolution TEM (HR-TEM), and selected area electron diffraction (SAED) patterns using a JEM-2010F (JEOL, Tokyo, Japan) microscope. The alloys synthesized in this study were observed by using scanning transmission electron microscope (STEM, HD-2000, Hitachi High-Technologies). The composition of the alloys was determined by energy dispersive X-ray analysis (EDX) using the genesis microanalysis system (EDAX) attached to the STEM.

3.3 RESULT AND DISCUSSIONS

3.3.1 Metallic Cu electrode

Electrolytes of 0.5 to 0.001 M K_2CO_3 solution and citrate buffer (pH = 4.8) were used to investigate the influence of the electrolyte. According to the XRD patterns of the products (Fig. 3-2), metallic copper formed when using the citrate buffer solution. When a K_2CO_3 solution was used, copper oxide formed in all concentrations of the electrolyte. Figure 3-3 shows the copper E-pH diagram and explains which phase is electrochemically stable. Before the electrodes were

connected to the power supply, the potential was zero. The copper cathode was charged negatively during the electrolysis, which stabilized metallic copper. When the cathode surface was melted to generate nanoparticles, the particles peeled from the surface had zero potential. Plots show the pH of solutions used in the experiments: (a) citrate buffer (pH = 4.8); (b) 0.001 M K_2CO_3 ; (c) 0.01 M K_2CO_3 ; (d) 0.01 M K_2CO_3 ; and (e) 0.5 M K_2CO_3 . According to this diagram, copper is easily forms CuO in the case of (c), (d) and (e). In addition, Cu_2O becomes stable in (b). In case of (a), the citrate buffer solution (pH = 4.8), metallic copper is generated. The theoretical results agree well with the XRD patterns (Fig.3-2). These results revealed that the phase of the product is controlled by the solution pH.

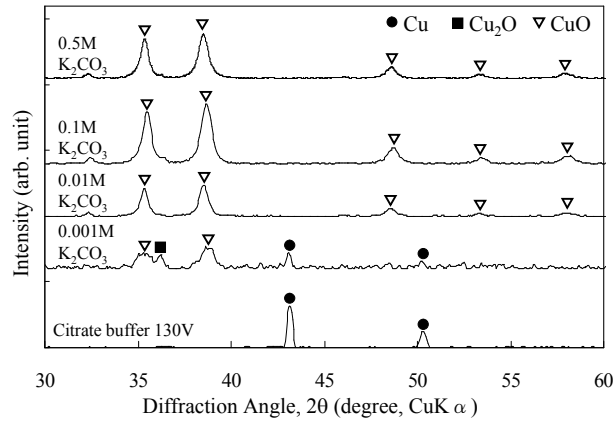


Figure 3-2. XRD patterns of the products, which were collected by centrifugation, washed with deionized water, and dried. When a citrate buffer solution was used as an electrolyte with a pH of 4.8, only metallic copper formed.

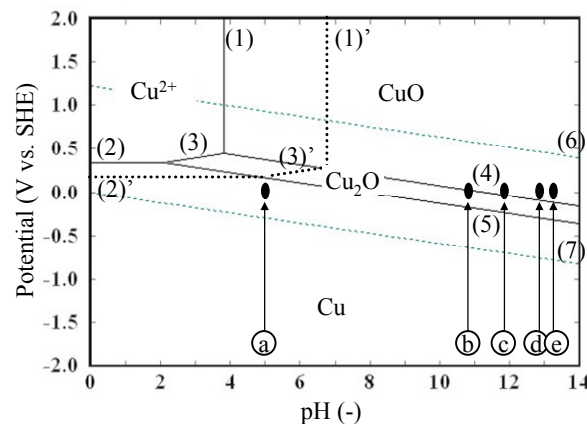


Figure 3-3. Cu E-pH diagram under the assumption of $[Cu^{2+}] = 1.0 \text{ mol/kg}$ (solid line) and $[Cu^{2+}] = 1.0 \times 10^{-6} \text{ mol/kg}$ (dotted line); (1) $CuO + 2H^+ = Cu^{2+} + H_2O$; (2) $Cu^{2+} + 2e^- = Cu$; (3) $Cu_2O + 2H^+ = 2e^- + 2Cu^{2+} + H_2O$; (4) $2CuO + 2H^+ + 2e^- = Cu_2O + H_2O$; (5) $Cu_2O + 2H^+ + 2e^- = 2Cu + H_2O$; (6) $2H_2O = O_2 + 4H^+ + 4e^-$; and (7) $2H^+ + 2e^- = H_2$. The plots show the pH of solutions which were used in the experiments; a) citrate buffer (pH = 4.8), b) 0.001 M K_2CO_3 ; c) 0.01 M K_2CO_3 ; d) 0.01 M K_2CO_3 ; and e) 0.5 M K_2CO_3 . SHE means standard hydrogen electrode.

Figure 3-4 shows the SEM and TEM images of the products, in which the use of K_2CO_3 solution yielded flower-like products including many nanorods (Fig 3-4 a - b). Interestingly, the product size decreased with the decrease in the electrolyte concentration because of the high applied voltage³². Figure 3-5(a) shows a typical TEM image of the nanorod peeled from the CuO nanoflowers (0.01-M K_2CO_3 , 200 V), the inset of which is an SAED pattern taken from one of the nanorods. This confirmed the single crystal of the CuO grown along the [010] direction. Further, an HR-TEM image, shown in Figure 3-5(b), revealed a lattice fringe of approximately 0.25 nm, which corresponded to the (11 $\bar{1}$) plane of the CuO. Previously, the solution plasma had produced spherical nanoparticles as

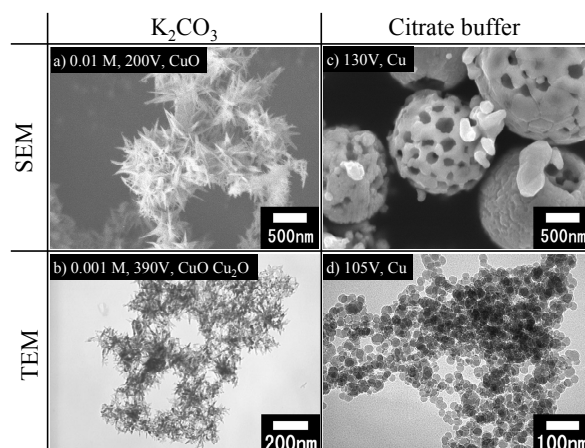


Figure 3-4 SEM and TEM images of the products. The upper captions show the concentration of the electrolyte, the applied voltage, and phase. The phase of the product was identified by X-ray and electron diffraction.

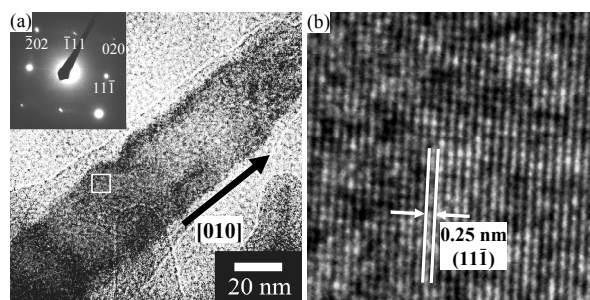
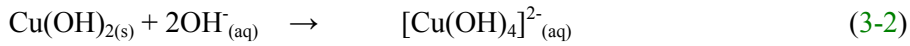


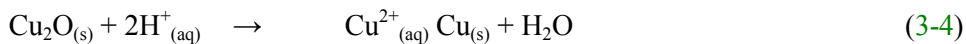
Figure 3-5 (a) TEM image of a CuO nanorod peeled from the CuO nanoflower (0.01-M K_2CO_3) and its corresponding SAED pattern. (b) High-resolution TEM image.

following steps; first, the surface of the cathode melted. Secondary, the molten metal formed sphere due to the surface tension in the solution, and then was solidified to form spherical nanoparticles^{25, 32, 33}. However, the flower-like products formed due to another mechanism, which was not solidification after melting but nucleation and crystal growth. The flower-like CuO have been produced through a hydrothermal synthesis^{7, 34-37}, solution routes^{9, 13, 38-43} and microwave irradiation⁴⁴. The growth unit of CuO nanoflowers in these methods is a $[Cu(OH)_4]^{2-}$ ions. Here, we consider the formation mechanism of the flower-like CuO in the following three steps. First, the surface of the Cu electrode forms $Cu(OH)_2$ by steam corrosion at a high temperature, as shown in equation (3-1). The reaction proceeds at over 260 °C because the

temperature of the solution surrounding the cathode is high enough to melt copper. Second, the product $\text{Cu}(\text{OH})_2$ reacts with the hydroxide ion to produce so-called “tetrahydroxocuprate (II) anions”, $[\text{Cu}(\text{OH})_4]^{2-}$ ^{36, 40}, [equation (3-2)]. Then, solid CuO precipitates with a decrease in temperature via reaction (3-3). The growth rates of CuO are different for each crystal plane as reported by Li-Xia Yang et al.⁴⁰; growth rates is $[010] > [100] > [001]$. Because of the high growth rate along the $[010]$ direction, CuO crystals grew preferentially along the $[010]$ direction to form flower-like particle.



Spherical particles of copper were also produced when using citrate buffer as the electrolyte [see Figs.3-5 c-d]. In addition, the particles synthesized by applying a voltage of 130 V had many pores with a particle diameter of less than 100 nm. The partially melt of the electrode led to the formation of spheres. A higher voltage increased the temperature of the electrode surface, and thereby the electrode oxidized. The oxidized electrode melted to produce copper melt containing oxygen (Fig.3-6). Molten copper containing oxygen remains liquid until the temperature reaches the liquidus line, as shown in the phase diagram⁴⁵ [see Fig.3-7a⁴⁶]. At the liquidus [see T_1 in Fig.3-7a], the liquid solidifies to form crystals of pure copper [Fig.3-6 (2)]. As the temperature decreases, the liquid becomes richer in oxygen [Fig. 3-6 (3)]. When it reaches the eutectic temperature E , there are two phases, solid copper and molten copper containing Cu_2O with a concentration of 3.4 mass%. When the solidification is complete, the eutectic microstructure of $\text{Cu-Cu}_2\text{O}$ appears [Fig.3-6 (4)]. Solid Cu_2O is dissolved as shown in following equation (3-4), which reaction proceeds at under 290 °C, and a pH of 4.8 to produce porous particles.



Moreover, the proportion of pores in the particles varies. This difference in product morphology is explained by the oxygen concentration. When molten copper slightly oxidizes, as shown by the B arrow in Fig. 3-7 (a), the ratio of Cu_2O decreases to form spherical particles having few pores. Conversely, with a high concentration of oxygen, as shown with the C arrow, particles with many pores form. Figure 3-7 b and c show the SEM images of the porous Cu product obtained at different concentrations of oxygen, as shown in arrows B and C in Fig. 3-7 a.

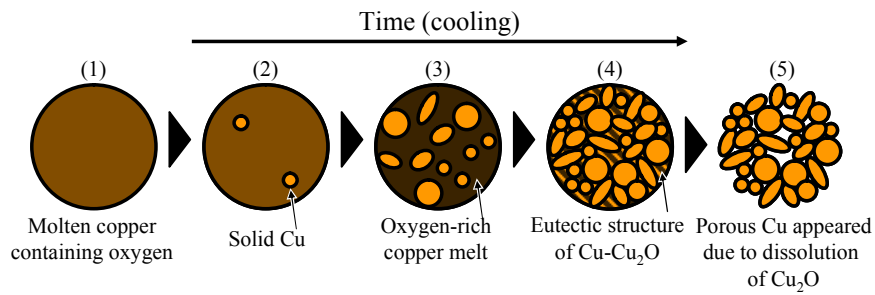


Figure 3-6. Formation mechanism of porous copper particles. The liquid solidifies to form crystals of pure Copper (2). As the temperature decreases, the liquid becomes richer in oxygen (3). When solidification is complete, the eutectic microstructure of Cu- Cu_2O appears as shown in (4). The phase of Cu_2O dissolved to produce porous particle.

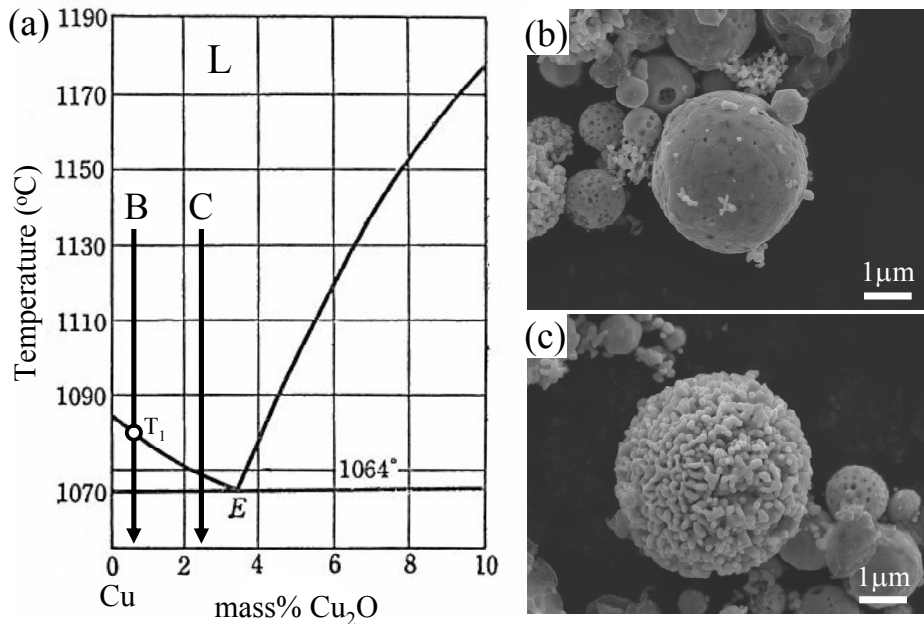


Figure 3-7. (a) Cu- Cu_2O phase diagram.⁴⁶ The difference in the product morphology is explained by the oxygen concentration. When a molten copper slightly oxidizes as shown with arrow B, the ratio of Cu_2O decreases to form spherical particles with a few pores. Conversely, with a high concentration of oxygen shown with arrow C, the particles with many pores form. Corresponding SEM images were shown in (b) and (c).

3.3.2 Influence of electrolysis time

We also controlled the time of plasma electrolysis at 60 min and 5 min under the condition of citrate buffer solutions as the electrolyte. According to the SEM images of the products produced at the different times of electrolysis (Fig.3-8 a), it was found that the particle size became larger with time; the product size reached 500 nm after 5 min and 2 μm after 60 min. Figure 3-8 b shows the histories of the cathode electrodes during electrolysis, in which the edge of the cathode was gradually consumed with time. The results indicated that products were mainly generated at the tip of the electrode. To understand why particles became larger with time, we observed the electrode surface after the experiments using FE-SEM. Figure 3-9 shows the SEM images of the cathode surface which were observed after experiments. The SEM images revealed that the wire tip became thinner, and the larger particles with a diameter of over 1 μm were attached to the edge of the electrode (see arrows). The current was concentrated on the tip due to the highly inhomogeneous electric field, and then, the tip of the electrode was heated up to form the coarse particles. The experimental conditions for the preparation of Cu and CuO nanostructures are summarized in Table 3-1.

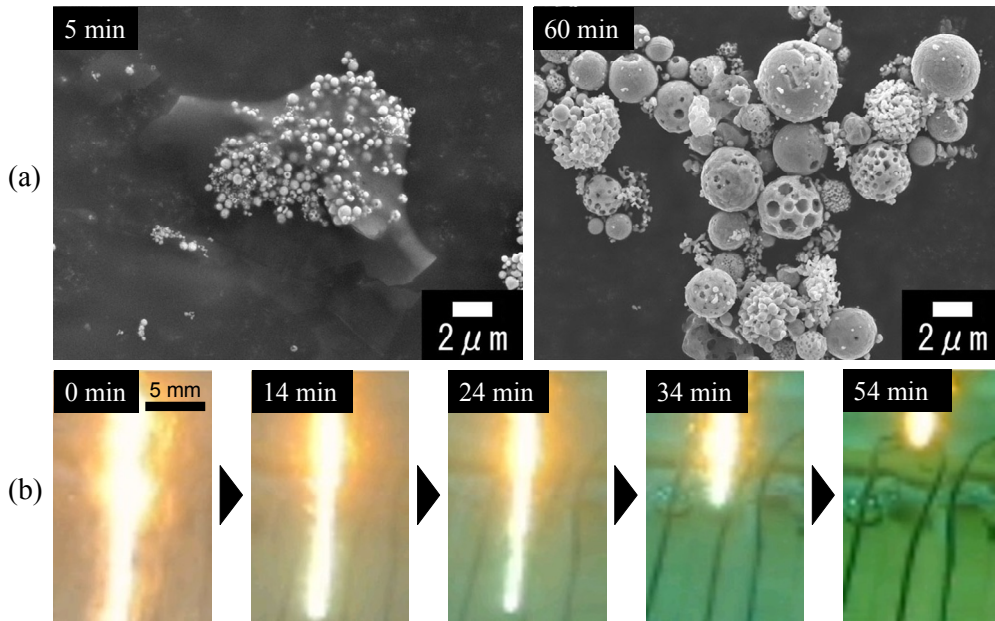


Figure 3-8. (a) SEM images of the product at different periods during electrolysis: 5 min and 60 min. The product became larger in size. (b) Histories of cathode electrodes during electrolysis. The edge of the cathode was gradually consumed.

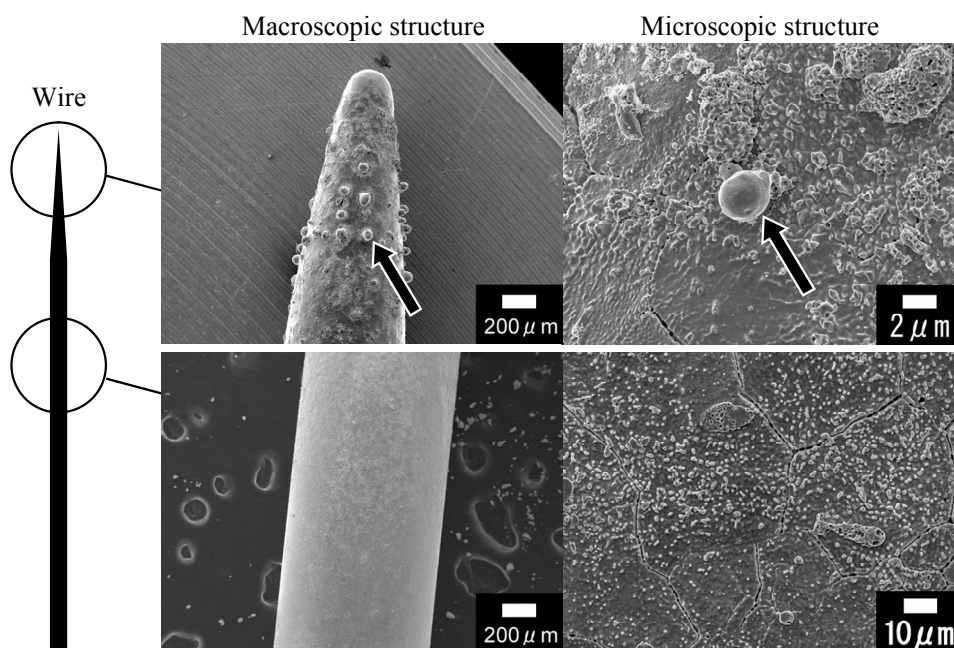


Figure 3-9. SEM images of the cathode surface, which were observed after the experiments. Coarse particles with a diameter over 1 μm attached to the edge of the electrode (see arrows).

Table 3-1 Summary of experimental conditions and products morphologies

Electrolyte	Electrolysis Time (min.)	Applied Voltage (V)	Morphology
0.5M K_2CO_3	60	80	Flower-like CuO
0.1M K_2CO_3	60	130	Flower-like CuO
0.01M K_2CO_3	60	200	Flower-like CuO
0.001M K_2CO_3	60	390	Flower-like CuO
Citrate buffer (pH = 4.8)	60	105	Cu Sphere
Citrate buffer (pH = 4.8)	60	130	Cu Porous sphere
Citrate buffer (pH = 4.8)	5	130	Cu Porous sphere

3.3.3 Cu-Ni alloy

The use of solid solution alloys of Cu-43%Ni, Cu-66%Ni, Ni-21%Cr, and Ni-9%Cr, as the cathode resulted in the generation of plasma with light emission, which further led to the formation of nanoparticles in the solution. The average temperature of each solution and the electrical current used are summarized in [Table 3-2](#). It reveals a gradual increase in the solution temperature, which eventually becomes constant.

Table 3-2. Average solution temperature and current during electrolysis.

Sample	Solution Temperature (°C)	Current (A)
Cu-43%Ni	68.02	0.63
Cu-66%Ni	68.88	0.65
Ni-21%Cr	68.15	0.62
Ni-9%Cr	69.35	0.64

Figure 3-10 shows the high angle annular dark field (HAADF) STEM images and the corresponding EDX mapping images of the alloys. The HAADF images of the alloys shown in (a-1) and (b-1) indicate the formation of spherical particles. In the plasma, the heat induced by the locally concentrated electrical current melted the surface of the electrode. The melted metal assumed spherical shape due to the effect of surface tension, and solidified in the form spherical particles. Furthermore, the EDX analysis of the alloys indicates the uniform distribution of Cu and Ni without segregation in the sphere. The corresponding XRD patterns of the alloys shown in Fig. 3-11 indicate the formation of metallic Ni-Cu. In addition, the diffraction pattern of Cu-43%Ni alloy indicated the formation of small amount of CuO. In section 3.1.1, we reported that the precipitation of CuO from Cu rod in plasma in an alkaline solution proceeds via the formation of $\text{Cu}(\text{OH})_4^{2-}$ ions, as per the equation (3-3). Use of neutral solution might prevent the oxidation of Cu. The composition of the alloy was estimated by averaging the compositions of 50 particles, as determined by using EDX. Figures 3-12 (a) and (b) show the distributions of Ni with respect to Cu in Cu-43%Ni and Cu-66%Ni, respectively. Here, N represents the number of the particles measured. The composition of the alloys was found to be similar to that prepared using wire as the raw material. The enlarged XRD pattern of the alloys shown in Fig. 3-12 (c) indicates that the Cu and Ni are mixed at the atomic level, with no pure phases of Cu and Ni. Furthermore, the lattice parameters were calculated from the XRD patterns and listed in Table 3-3 and Fig. 3-13.

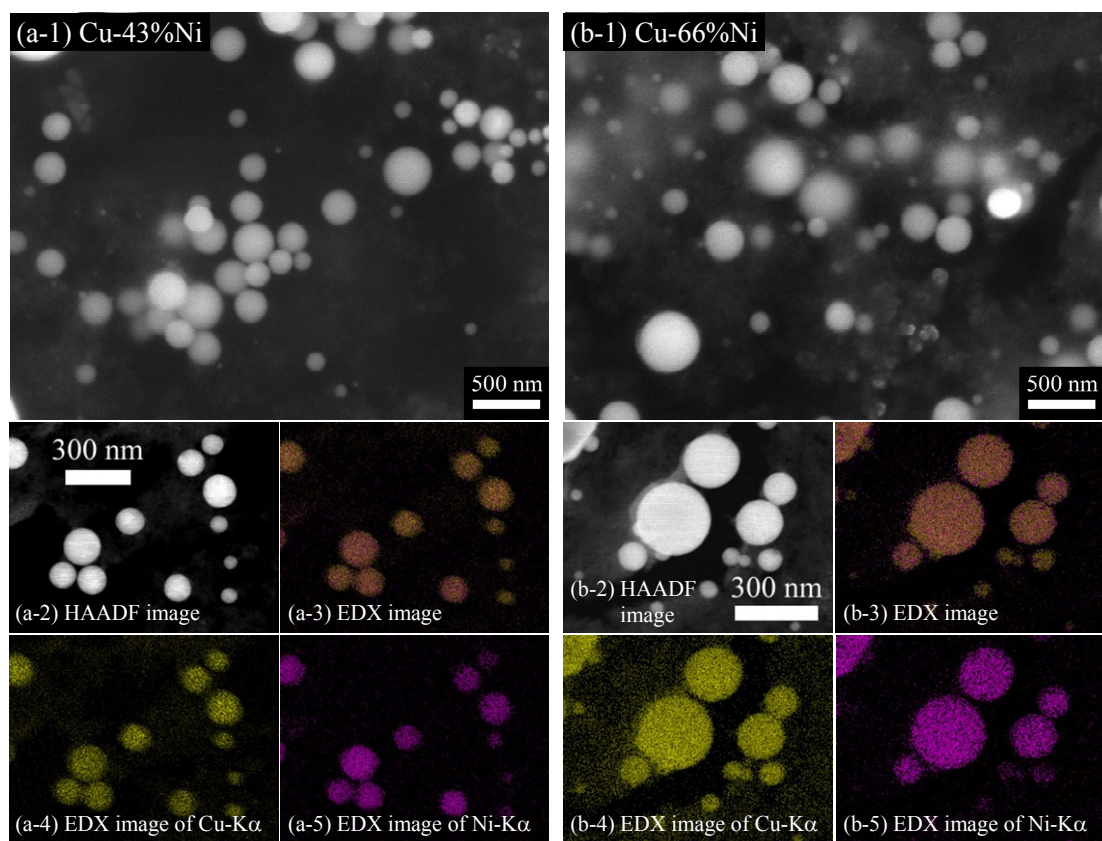


Figure 3-10. STEM-HAADF images and corresponding EDX mapping images of (a) Cu-43%Ni and (b) Cu-66%Ni nanoparticles. (a-3) and (b-3) show combined EDX images of Cu-K α and Ni-K α .

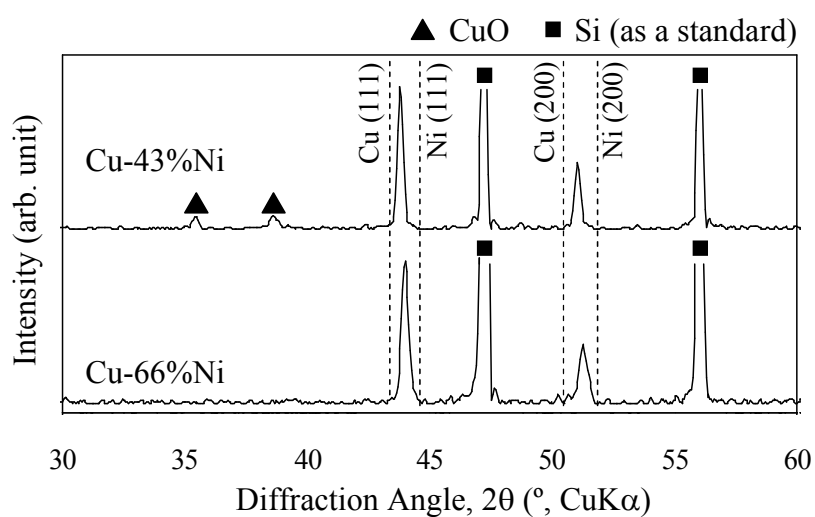


Figure 3-11. XRD patterns of the Ni-Cu products. Silicon powder was mixed to the products to be a standard material.

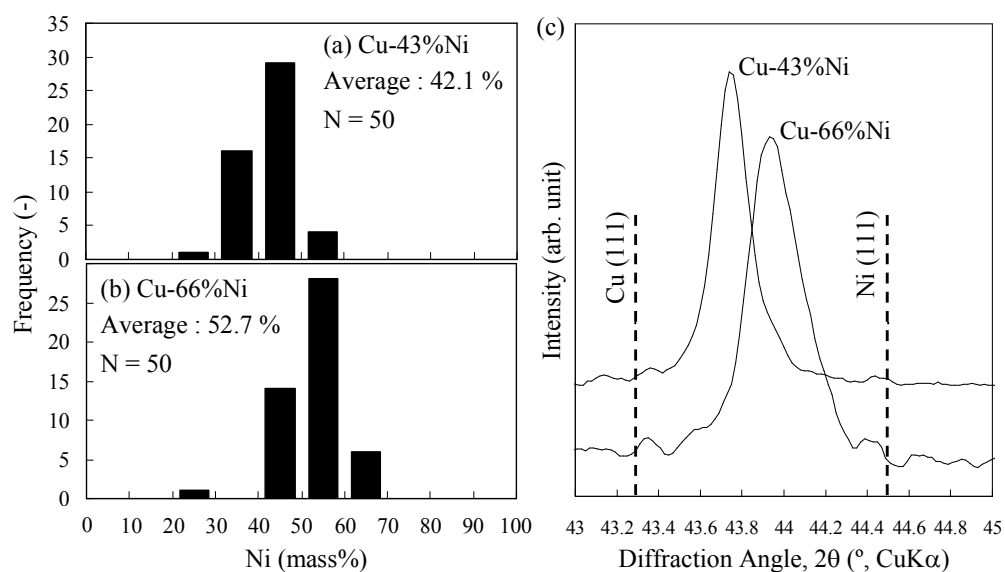


Figure 3-12. (a, b) Distribution of Ni compositions against Cu at Cu-45%Ni and Cu-66%Ni products. (c) enlarged XRD patterns of the products.

Table 3-3 Lattice parameters of Cu-43%Ni and Cu-66%Ni calculated by the XRD patterns.

Sample	Lattice parameter (Å)
Pure Cu	3.615
Cu-43%Ni	3.573
Cu-66%Ni	3.556
Pure Ni	3.524

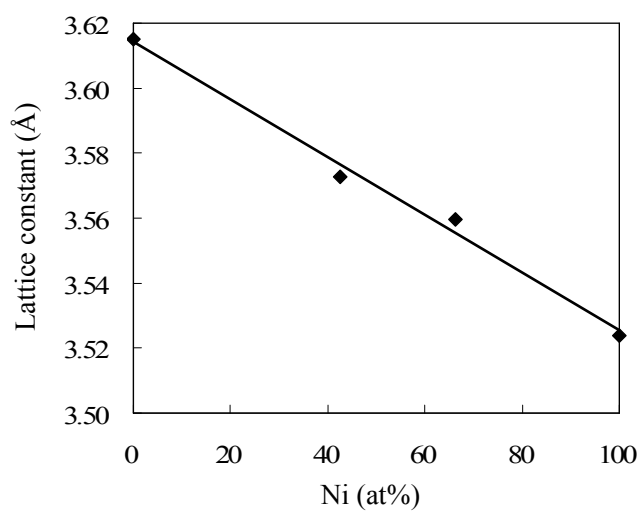


Figure 3-13 Lattice constant of Cu-43%Ni and Cu-66%Ni products.

3.4 CONCLUSIONS

In this chapter, we studied the relationship between the experimental conditions and the formation of Cu, CuO and Cu-Ni alloy nanoparticles via solution plasma, and concluded the following:

- 1) Flower-like CuO with many nanorods under 100 nm in diameter and a [010] orientation in the growth direction were synthesized because of the formation of $[\text{Cu}(\text{OH})_4]^{2-}$ ions and oriented crystal growth. In addition, the particle size of CuO decreased with decreasing concentration of the K_2CO_3 electrolyte.
- 2) The application of the citrate buffer solution yielded metallic copper nanoparticles, whose shape changed according to the applied voltage: spherical particles at an applied voltage of 105 V and porous spherical nanoparticles at 130 V.
- 3) The size of the porous copper nanoparticles increased with electrolysis time due to the thinning of the electrode tip with time.
- 4) The solid solution alloy nanoparticles of Cu-43%Ni and Cu-66%Ni synthesized in this study had uniform distribution of the composition. The Cu-43%Ni alloy, in particular, contained a small amount of CuO due to the reaction with the electrolyte.

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CHAPTER 4

Synthesis of ZnO flowers and their photoluminescence properties

ABSTRACT : In this chapter, ZnO nanoflowers were synthesized using a solution plasma. We examined the effects of the applied voltage, concentration of the electrolyte, reaction temperatures and agitation on the morphology of the products. In the experiments, the zinc wire (cathode) was immersed in an electrolysis solution of K_2CO_3 (concentration: 0.01 to 5.00 M) and was electrically melted by a glow discharge at different voltages ranging from 42 to 200 V. The results revealed that the products were nanoflowers having many nanorods (size: <100 nm). The ZnO nanoflowers had a wurtzite structure with the [0001] orientation in the growth direction. ZnO nanoflowers were synthesized at a high electrolyte temperature in a static system (no agitation). On the other hand, the use of agitation led to both amorphous ZnO nanospheres and spherical metallic zinc particles. The excitation temperature of plasma was 4000 K from the light emission using spectrometer. From these result, melting and vaporization of the Zn electrode produced particles. Photoluminescence (PL) measurement indicated that as-synthesized ZnO flowers and amorphous ZnO nanospheres showed strong green emissions, which was attributable to their surface defect structure. Furthermore, the annealing at 700 °C led to a reduction in green emissions, attributable to a decrease in the number of surface defects. Photocatalytic activity of ZnO nanoflowers was increased by the annealing.

4.1 INTRODUCTION

Zinc oxide (ZnO) has a wide direct band gap and a large exciton binding energy (3.37 and 60 eV, respectively, at room temperature), which make it an important electronic and photonic semiconductor. It has been demonstrated that ZnO is useful in a wide range of applications, including solar cells, ultraviolet lasers, light-emitting diodes, transparent conductors, photocatalytic materials, gas sensors, and luminescence materials. Various ZnO

nanostructures, such as nanorods, nanowires, nanospheres, nanodisks, and nanoflowers, have been fabricated by thermal evaporation^{1, 2}, hydrothermal synthesis,³⁻⁵ solution routes,^{6, 7} microwave irradiation^{8, 9}, vapor-liquid-solid growth,¹⁰ pulsed laser ablation,^{11, 12} plasma,^{13, 14} and electric discharge.¹⁵⁻¹⁷

While there are several ZnO nanostructures, the flower-like morphology, as a special three-dimensional structure, has received the most attention in recent years because of its unique photoluminescence (PL) and photocatalytic properties.^{5, 18, 19} The optical and electrical properties of ZnO are related to its structural defects. It has been reported that the visible emission of ZnO is mainly related to intrinsic defects such as oxygen vacancies (V_o), interstitial oxygen (O_i), zinc vacancies (V_{Zn}) and interstitial zinc (Zn_i).²⁰ These defects can affect photocatalytic performance; that is, acting as active centers, they can capture photo-induced electrons, thereby inhibiting the recombination of photo-induced electrons and holes.⁵

Recently, plasma-assisted techniques based on the electrical discharge in a liquid have become a focus of many studies for the synthesis of nanoparticles^{16, 17, 21-23}. The solution plasma causes a supercritical state of water in which the surface of the cathode is partially heated by a glow discharge at a high temperature^[22]. The solution plasma offers many advantages: (1) simple experimental setup, (2) no need to supply gas, (3) easy mass production, and (4) use of easy-available zinc wire as a raw material of nanoparticles. The solution plasma seems to be considerably attractive for the synthesis of ZnO nanocrystals from not only a scientific point of view but also an engineering one. However, to the best of our knowledge, few papers have been published on the ZnO production using the solution plasma. Therefore, we have studied the production of ZnO nanocrystals from a Zn wire (cathode) by using solution plasma; further, the effects of the applied voltage, concentration of electrolysis solution, solution temperature and agitation on the morphology of the products in the solution plasma were mainly examined. The products recovered were characterized by using a field-emission electron microscope (FE-SEM), a transmission electron microscope (TEM), and selected area electron diffraction (SAED) patterns. The mechanisms of nanoparticles formation have also been discussed on the basis of the results. In addition, the photoluminescence and photocatalytic properties of the products and

the effect annealing were studied, in an effort to determine the types of defects present.

4.2 EXPERIMENTAL SECTION

4.2.1 Experimental Setup

Figure 4-1 shows the experimental apparatus used for the electrolysis experiments under stable power supply conditions (ZX800H, Takasago, Tokyo, Japan). A platinum wire of length 1000 mm, diameter 0.5 mm, and purity 99.98 mass% (Nilaco, Tokyo, Japan) was used as the anode; this wire was bent into a half-round mesh and fixed in a glass frame. A zinc wire of diameter 1.0 mm and purity 99.99 mass% (Nilaco, Tokyo, Japan) was used as the cathode. It was shielded by an electrically insulated polytetrafluoroethylene (PTFE, TX-1, Sanplatec, Osaka, Japan) tube or glass tube in order to obtain an exposed length of 10 mm; the exposed part functioned as the net actual electrode. The distance between the electrodes was kept at 30 mm. The electrolytes were solution of K_2CO_3 with 99.5% in purity (Kishida Chemical, Osaka, Japan) having concentrations ranging from 5.0 to 0.01 M. When the effect of solution temperature and agitation were studied, the electrolyte was a 0.5 M K_2CO_3 solution. The solution temperature at a depth of 10 mm was recorded every 5 s by using a polymer-coated thermistor thermometer (Ondotori TR-71Ui, T&D, Nagano, Japan). The light emission from plasma was measured using a visible light spectrophotometer (USB 2000+, Ocean Optics).

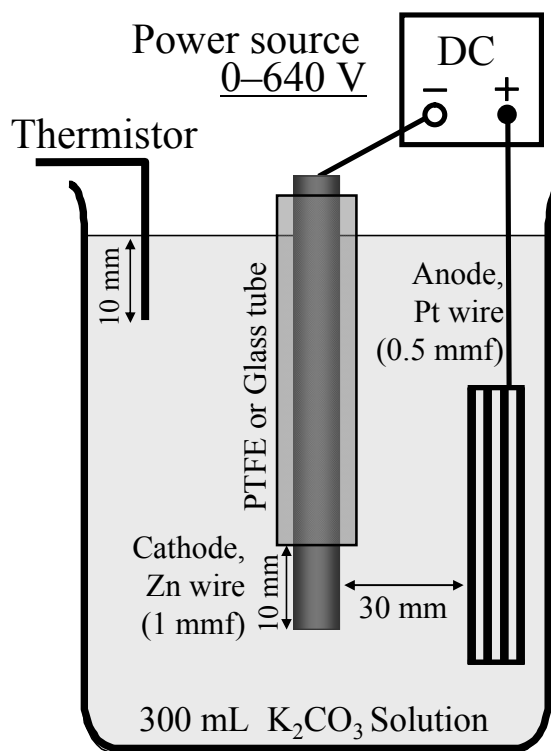


Figure 4-1 Schematic representation of the experimental apparatus of plasma electrolysis for the synthesis of Zn nanoparticles.

4.2.2 Experimental Procedure and Characterizations

The experimentals for producing nanoparticles were performed as a following procedure. First, the anode and cathode wire were washed by deionized water and ethanol by using an ultrasonic washer. Secondary, the voltage was applied at a rate of 0.5 V/s until the formation of plasma under the constant-voltage control. Then, the voltage was fixed at a constant value for 1 h. After the experiments, products were collected by the centrifugation and washed with deionized water. When the electrolyte temperature was changed, the reaction temperature was fixed by controlling the electrolyte temperature as shown in the [Table 4-1](#). The temperature was changed stepwise in three steps using water at 25 °C and a hotplate. Afterward the products were collected by centrifugation, then washed with deionized water. Subsequently, the products were characterized using a JSM-7001FA (JEOL) scanning electron microscope (SEM), a Miniflex II (Rigaku) X-ray diffractometer (XRD), and a JEM-2010 and JEM-2010F (JEOL) transmission electron microscope (TEM). Photoluminescence (PL) measurements were performed at room temperature using a Xe lamp line (FP-6400, JASCO) at a wavelength of 325 nm. The photocatalytic activities of the products were determined by measuring the rate of degradation of methylene blue under UV light, at an applied power of 30 W. In a typical photocatalytic experiment, 40 mg of dried product was added to 200 ml of a solution of 5.0×10^{-4} mg L⁻¹ methylene blue in water. The mixture was first sonicated for 12 hours in the dark to reach the adsorption equilibrium, then irradiated with UV light at room temperature. Before and after UV irradiation, the concentration of methylene blue was measured using a visible light spectrophotometer (USB 2000+ USB-ISS-VIS, Ocean Optics).

[Table 4-1](#). Experimental conditions for different solution temperature with/without agitation.

Sample name	Agitation	Temperature Control
S-1	No	Cooling using 25 °C water
S-2		Cooling using 25 °C water
S-3		Cooling in air
A-1	1500 rpm	Cooling using 25 °C water
A-2		Cooling in air
A-3		Heating using a hotplate

4.3 RESULT AND DISCUSSIONS

4.3.1 *Effect of voltage and concentration of electrolyte*

Table 4-2 shows the experimental parameters and the corresponding morphology of the products, which were evaluated by SEM images as shown in Fig.4-2, at different solution concentrations ranging from 5.0 to 0.01 M. The voltages of plasma formation were increased with decreasing the concentration of electrolyte owing to the low electro-conductivity of the solution; the voltage was 50 V with the concentration of 2.0 M, and it was 190 V with the concentration of 0.01M. This tendency agreed with the reported data²³. Here, the voltages of plasma formation have a margin of error because the voltages of plasma formation were determined by the observation of the cathode. The maintained voltages were selected in order to keep glow discharge. The voltage was changed to investigate the effect of voltage at the concentration of 1.0M and 0.01M. When gas-layer was generated at the surface of the cathode, the breakdown occurred because the current cannot increase any more. Thus, the power of breakdown was higher than the maintained power. With increasing the concentration of the solution, the maintained power decreased, and interestingly, the morphology of the products changed by the maintained power; no product less than 30 W, nanoflowers in the range from 44 to 48 W and coarse particles more than 66 W. We observed light emission when the maintained powers were more than 44W. With more than 66 W, the light emission became strong. These results suggested that the input voltage was not sufficient for producing particles in the case of under 30W. At an electric power of more than 66 W, the cathode melted and generated coarse particles because of overheating.

Figure 4-2 shows the SEM images of the products. Nanoflowers generated in the range of 44 to 48 W, having many nanorods with a diameter of less than 100 nm. With an increase in the concentration of the solution, the flowers were smaller: that is, 0.5–1.0 μm in diameter at 1.0 M (see Fig. 4-2(a)), 0.5–3.0 μm in diameter at 0.5 M (see Fig. 4-2(b)), and 0.5–5.0 μm in diameter at 0.1 M (see Fig. 4-2(c)). In contrast, an electric power of over 66 W generated coarse and agglomerated particles with the diameter of over 1 μm . Figure 4-3(a) shows a typical TEM image of the ZnO nanoflowers, the inset of which is an SAED pattern taken from one of the

nanorods. This confirmed the single crystal of the ZnO grown along the [0001] direction. Further, an HR-TEM image, shown in Fig.4-3 (b), revealed a lattice fringe of approximately 0.52 nm, which corresponded to the (0001) plane of the wurtzite ZnO.

Table 4-2 Experimental parameters and corresponding morphology of final products.

Concentration (M)	Voltage/V		Power/W		Morphology
	Plasma Formation	Maintained	Breakdown	Maintained	
5.00	-	42	-	29	No product
2.00	50	50	52	28	No product
1.00	54	60	97	30	No product
1.00	48	66	98	44	Nanoflowers
0.50	75	80	160	48	Nanoflowers
0.10	89	105	112	47	Nanoflowers
0.10	84	110	103	66	Coarse particles
0.01	190	200	245	168	Coarse particles

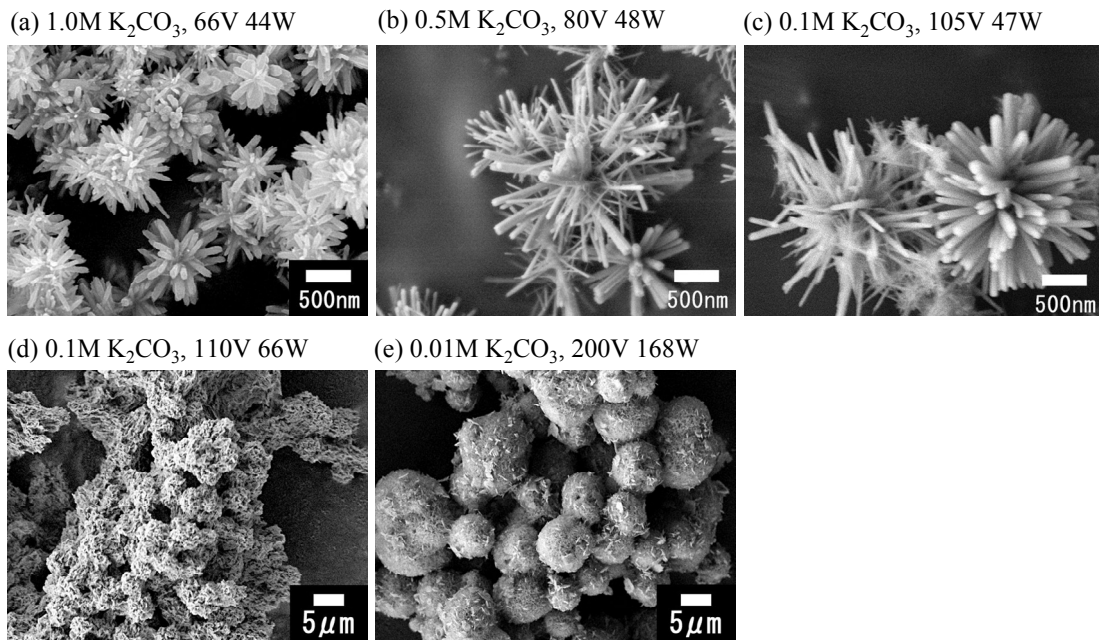


Figure 4-2. SEM images of products obtained under different conditions of K_2CO_3 concentration and charged electric voltage. High K_2CO_3 concentration and low electric voltage induced the production of ZnO nanoflowers.

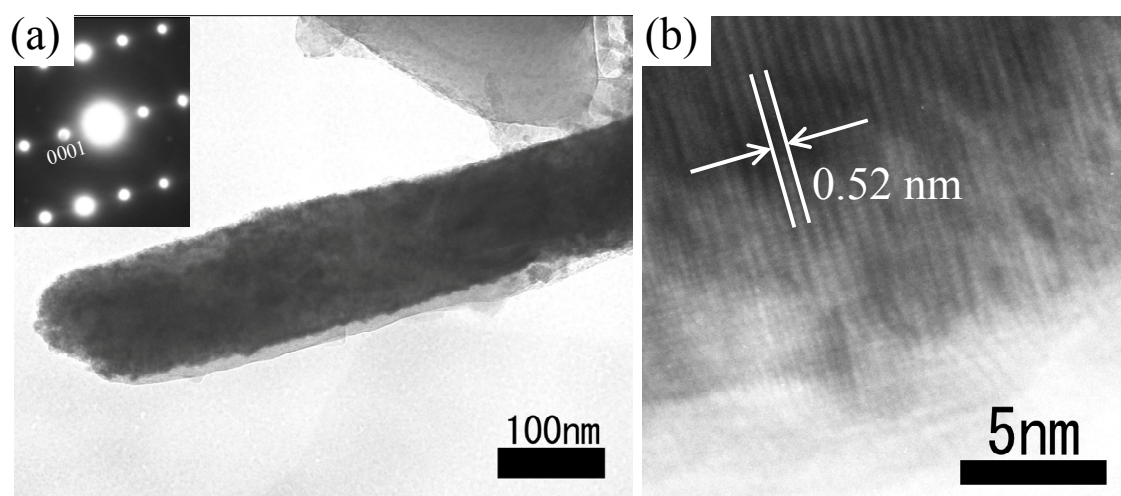


Figure 4-3. (a) TEM image of a ZnO nanorod peeled from the ZnO nanoflower (1.0-M K₂CO₃, 66 V 44 W) and its corresponding SAED pattern. (b) High-resolution TEM image.

4.3.2 Effects of solution temperature and agitation

Experimental results are shown in Table 4-3. The current was increased at high temperatures. As we observed in previous work, at high temperature a gas layer completely covered the electrode, preventing current flow²⁴. High current flow led to production of a large amount of particles.

Table 4-3. Summary of the experimental results. The temperature and power are the average values. The amount of nanoparticles produced (Production) was calculated from the difference in the weight of the electrode before and after the experiment.

Sample	Temperature (°C)	Power (W)	Current (A)	Production (mg)
S-1	61	92	1.15	35.3
S-2	69	86	1.08	22.0
S-3	81	52	0.65	24.3
A-1	54	97	1.21	20.1
A-2	65	74	0.93	20.0
A-3	77	51	0.64	13.5

SEM images and XRD patterns of the products are shown in Fig. 4-4 and Fig. 4-5, respectively. From the XRD results, the ratio of ZnO to Zn increased with increasing temperature under static conditions. Sample S-3 contained primarily ZnO nanoflowers, with only a small number of Zn particles, while S-1 consisted solely of Zn particles. Sample S-2

contained many horn-shaped structures on the particle surfaces, which grew into the rod-shaped structures seen in S-3. According to the TEM observation, rod-like crystals grew in the [0001] direction on the surface of the spherical particles (see Fig.4-6). When the solution was agitated, all products were spherical in shape and no flower-like structures formed. The XRD patterns in Fig. 4-5 indicate that these products were mainly metallic Zn; no ZnO peaks were observed.

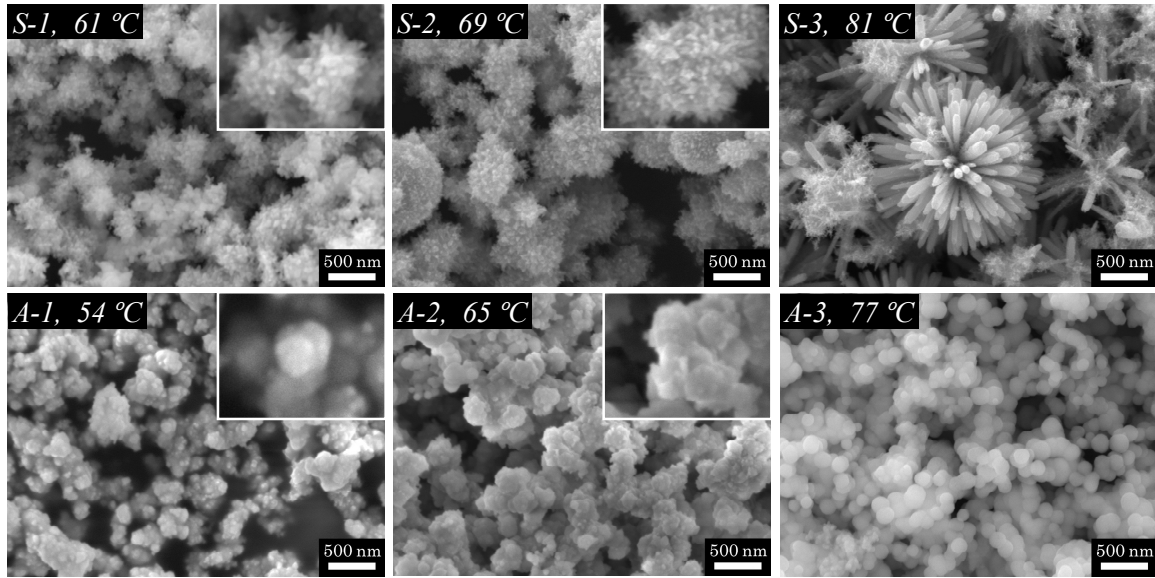


Figure 4-4. SEM images of the products made with and without agitation at different electrolyte temperatures. The labels show the average solution temperatures during electrolysis.

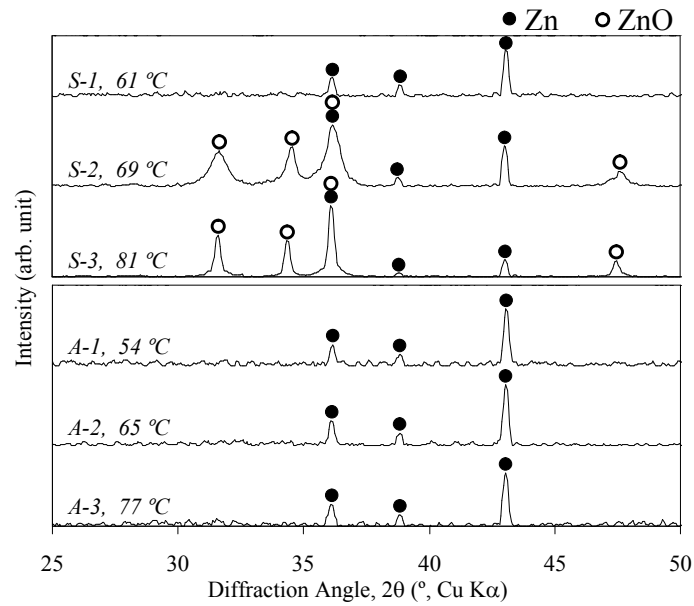


Figure 4-5. XRD patterns of the products made with and without agitation at different electrolyte temperatures.

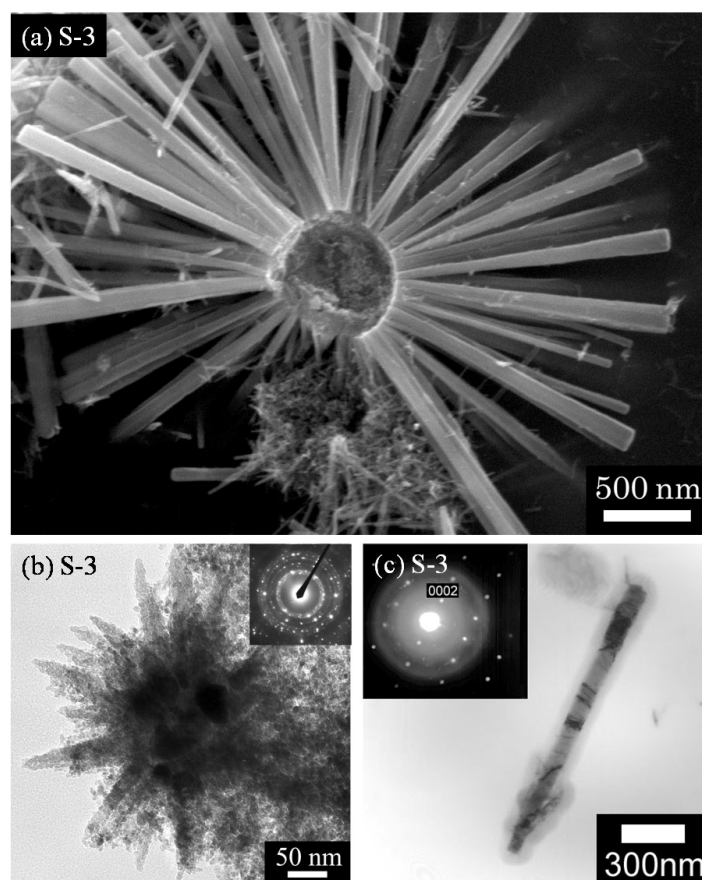


Figure 4-6. SEM and TEM images of the ZnO nanoflower (S-3): (a) cross-sectional SEM image; (b) bright-field TEM image and corresponding electron diffraction pattern; (c) TEM image of a ZnO nanorod peeled from the ZnO nanoflower and its corresponding SAED pattern.

TEM images and energy dispersive X-ray spectroscopy (EDS) results obtained with a sample prepared using agitation (A-3) are shown in Fig. 4-7. As seen in Fig. 4-7 (a), both coarse (diameter: >500 nm) and fine particles were formed in the A-3 condition. From the EDS result shown in Fig. 4-7 (b), the coarse particles consisted mainly of metallic zinc, while the fine particles contained 50 at% oxygen. Fig. 4-7 (c-e) show fine particles and their corresponding selected-area electron-diffraction (SAED) patterns. According to Fig. 4-7 (d), the fine particles had an amorphous structure. However, upon irradiation with a strong convergent electron beam, the applied heat caused the structure to change to polycrystalline ZnO.

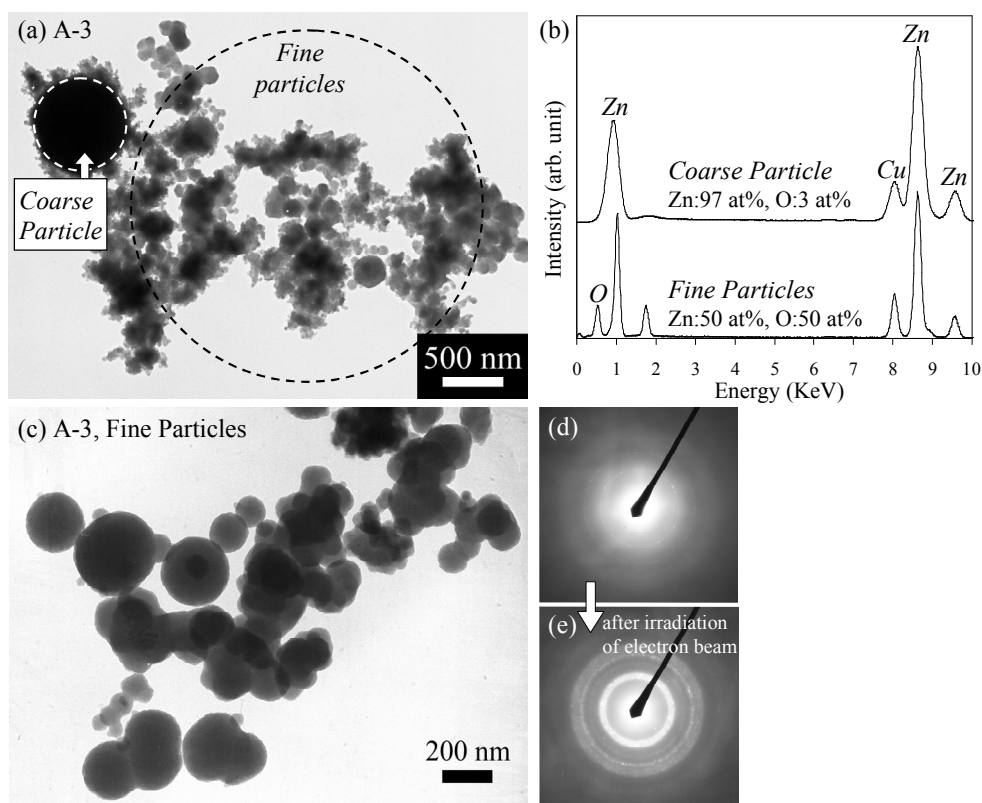


Figure 4-7. TEM images and EDS analysis of the A-3 nanoparticles: (a) bright-field TEM image; (b) EDS analysis corresponding to the highlighted region in (a); (c) bright-field TEM image of the fine particles; (d) electron diffraction pattern from (c); (e) electron diffraction after irradiation with strong convergent electron beam.

4.3.3 Formation mechanism of the products

Light emission with glow discharge was observed in all experiments. Fig. 4-8 shows the optical emission spectrum from the solution plasma using Zn electrode at S-3 condition. The emissions from OH and Zn were observed. These strong emissions from Zn suggested that the electrode was partially ionized. The excitation temperature is calculated using the Boltzmann plot method under the assumption of local thermodynamic equilibrium (LTE) as shown in the following equation (1-1). Here, I_{ij} is the emission intensity (330 nm, 334 nm, 468 nm, 472 nm and 481 nm), λ_{ij} is the wavelength, g_i is the statistical weight of the upper level, A_{ij} is the transition probability, E_i is the upper level energy, k is the Boltzmann constant, $N(T)$ is the total number density of neutrals, and $U(T)$ is the partition function. The excitation temperature is found to be 4000 K as shown in Fig.4-9. Hattori et al.²⁵ have reported that excitation temperature was 3200 ± 500 K from Zn electrode using microwave plasma in water.

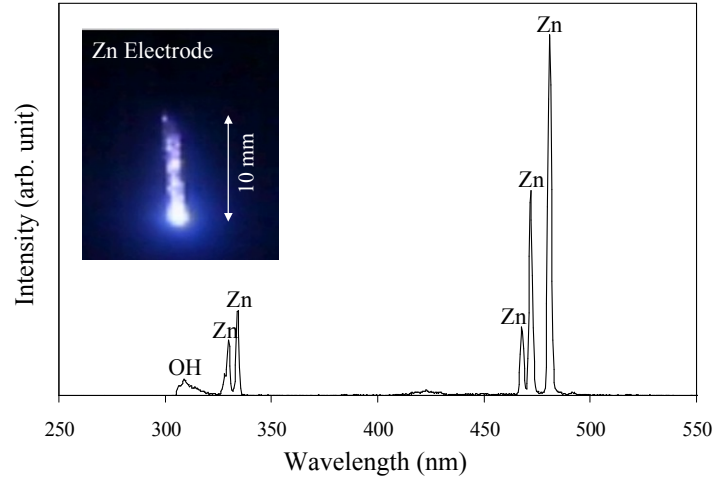


Figure 4-8. Optical emission spectrum from the solution plasma using Zn electrode.

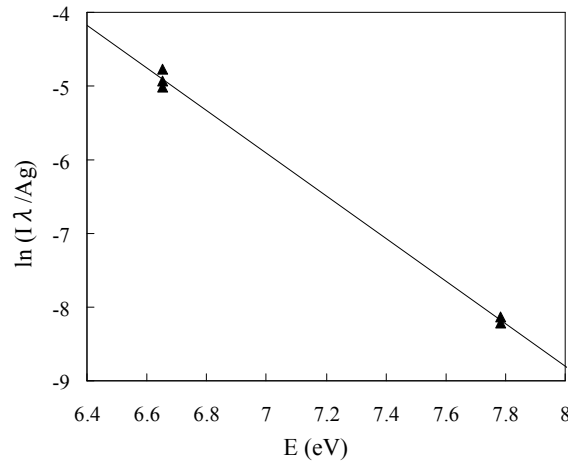
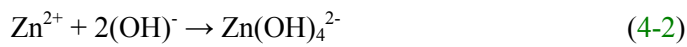
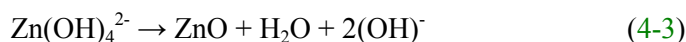


Figure 4-9. Boltzmann plots for the measured intensity of the zinc lines.

Proposed formation mechanisms with and without agitation are shown in Fig. 4-10. During the plasma, the electrode is partially melted or vaporized by the current concentration. Melted Zn is peeled from electrode surface to form spherical Zn particles due to interfacial tension. Vaporized zinc was ionized in the plasma to form $\text{Zn}(\text{OH})_4^{2-}$, according to the following reactions:



The unstable $\text{Zn}(\text{OH})_4^{2-}$ ions reach supersaturation, then precipitate as ZnO crystals according to Eq. (4-3).



In this manner, ZnO nanoflowers grew on the surface of the remaining spherical particles, preferentially along the [0 0 0 1] direction^{4, 8, 26}. Ionization was enhanced at high temperature; in the absence of agitation (e.g., the S-3 sample), this resulted in long ZnO nanorods. However, when agitation was applied, Zn(OH)_4^{2-} ions were immediately cooled to form amorphous ZnO nanoparticles without crystal growth.

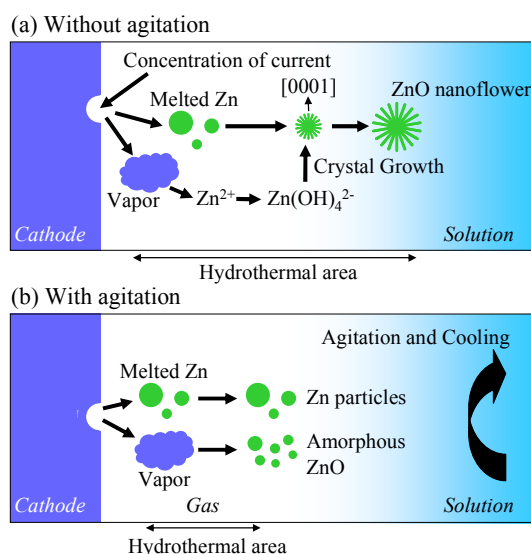


Figure 4-10. Formation mechanisms of the products. (a) Without agitation, the produced particles partially melted or vaporized. The ZnO then ionized to form Zn(OH)_4^{2-} , and ZnO nanoflowers grew by precipitation from the ions. (b) With agitation, the thickness of the hydrothermal area decreased. The produced particles were immediately cooled, without melting or ionization, to form Zn particles and amorphous ZnO.

4.3.4 Photoluminescence and Photocatalytic properties

To study the effect of annealing on defect evolution, the ZnO nanoflowers (S-3) were annealed at 500 °C or 700 °C in the air for one hour. After annealing at 500 °C, the ZnO peaks in the XRD patterns of Fig.4-11 became sharp and some metallic zinc remained. On the other hand, at 700 °C, virtually all the Zn was oxidized to ZnO. The SEM observations of the samples after annealing indicated that although some particles were agglomerated, the flower-like structure was largely preserved (Fig.4-12). Fig. 4-13 shows the PL spectra of the A-3 spherical particles, S-3 ZnO nanoflowers, and annealed nanoflowers, obtained using an excitation wavelength of 325 nm. A broad green emission ranging from 480 to 580 nm was observed in

case of the spherical particles and the ZnO nanoflowers. The peak positions in case of the samples comprising of the spherical particles and ZnO nanoflowers were evaluated as 539 nm and 545 nm, respectively. This green emission from ZnO, reported by many researchers^{20, 27}, originates from V_o , O_i , V_{Zn} and Zn_i . The green emission at 520–550 nm is related to the electron transition from the conduction band to O_i (2.28 eV, 544 nm) and V_o (2.30 eV, 539 nm). The difference in the peak positions observed in the PL spectra acquired from spherical particles and ZnO nanoflowers was probably induced by differences in the defect structure. Annealing led to a reduction in green emissions, attributable to a decrease in the number of defects²⁸. Note that the small peaks in the starting samples at 460–470 nm remained after annealing. According to the literature⁵, PL peaks at 468 nm are related to the defects V_{Zn} , Zn_i and V_o . Some researchers have reported the PL measurements at different excitation wavelengths^{29, 30}. If there is variation in the origins of the asymmetry of the broad PL band, the PL spectra may shift when different excitation wavelengths are used. Figure 4-14 shows the PL spectra acquired from ZnO nanoflowers at different excitation wavelengths ranging from 300 to 360 nm. In this study, any peak-shift was not observed.

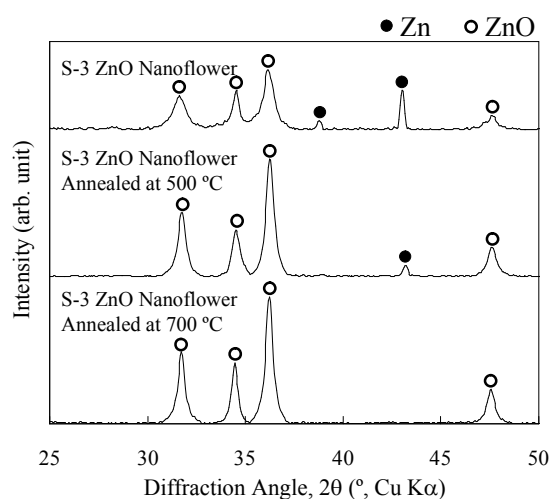


Figure 4-11. XRD patterns of the products at different annealing temperatures.

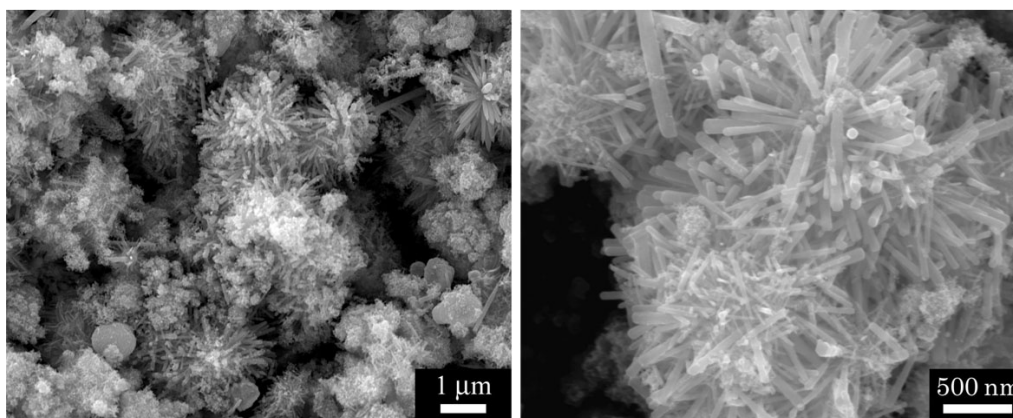


Figure 4-12. SEM image of the ZnO nanoflowers annealed at 700 °C.

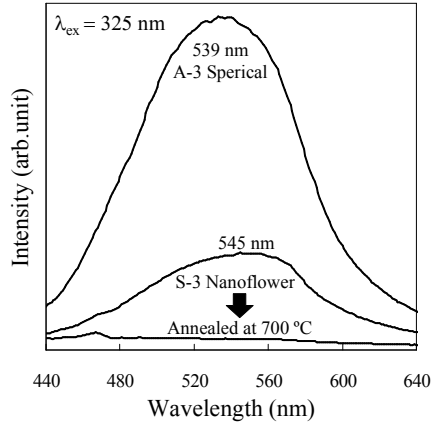


Figure 4-13. Photoluminescence spectra ($\lambda_{\text{ex}} = 325$ nm) of spherical particles, ZnO nanoflowers, and nanoflowers annealed at 700 °C for 60 minutes.

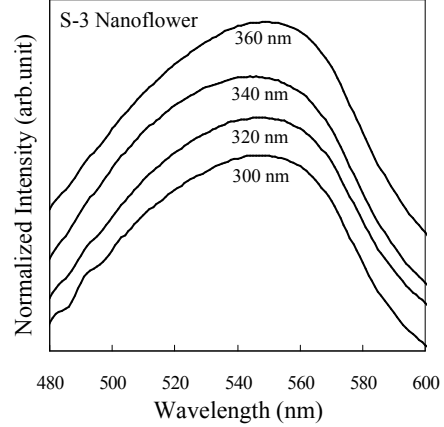


Figure 4-14. PL spectra acquired from ZnO nanoflowers at different excitation wavelengths ranging from 300 to 360 nm.

To determine photocatalytic activity, degradation of methylene blue was measured under UV light irradiation; results are shown in Fig.4-15. In general, the dependence of photocatalytic reaction rates on the concentration of organic pollutants is described well by the Langmuir–Hinshelwood kinetic model³¹.

$$r = \frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (4-4)$$

Equation (4-4) can be simplified to a pseudo first order equation represented in equation (4-5).

$$-\ln\left(\frac{C}{C_0}\right) = kKt = k't \quad (4-5)$$

In the above equations, r is the rate of the reaction, C_0 is the initial concentration, C is the concentration of the reactant at time t (min), k is the reaction rate constant (min^{-1}), and K is the adsorption coefficient. The apparent rate constants k_{app} were calculated from the linear transform $-\ln(C/C_0) = kt + b$, as shown in Fig. 4-15 (b). The apparent rate constants shown by the S-3 ZnO nanoflowers, commercial ZnO particles, and ZnO nanoflowers annealed at 700 °C were 0.0034, 0.028, and 0.049 min^{-1} , respectively. Compared to the commercial ZnO particles, ZnO nanoflowers with no annealing showed lower photocatalytic activity, because the nanoflowers contained defects and significant levels of metallic Zn. After annealing at 700 °C, the photocatalytic activity of ZnO nanoflowers increased, as a consequence of their highly

crystalline structure and high surface area.

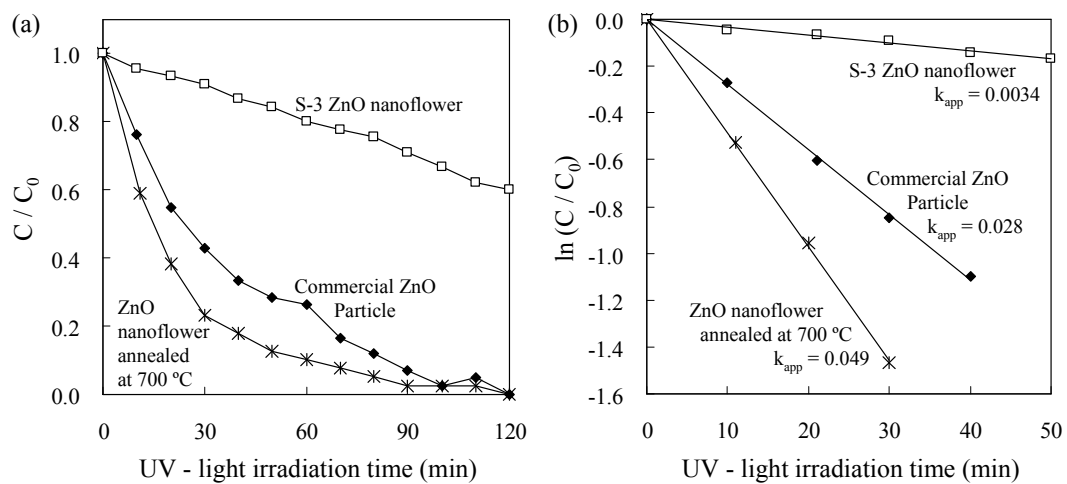


Figure 4-15. (a) Photocatalytic degradation of ethylene blue under UV light irradiation using different photocatalysts. (b) First order linear transforms of (a).

4.4 CONCLUSIONS

In this chapter, the synthesis of ZnO nanocrystals using plasma in liquid was studied. In the experiments, we applied an electric voltage from 42 to 200 V to the electrodes of both Zn and platinum in a K_2CO_3 solution with different concentrations ranging from 0.01 to 5.00 M, and the effects of temperature and agitation on product morphology and composition were investigated. The photoluminescence and photocatalytic activity of the products were also studied. The following conclusions were drawn:

- (1) A high voltage was required to maintain the plasma near the Zn electrode at a low electrolyte concentration. The SEM and TEM observations demonstrated that the product morphology depended strongly on the concentration, C , and the voltage, V ; that is, no product was obtained when $(C, V) = (\geq 1.0 \text{ M}, \leq 60 \text{ V})$, nanoflowers when $(C, V) = (1.0 \text{ M}, 66 \text{ V}), (0.5 \text{ M}, 80 \text{ V}), (0.1 \text{ M}, 105 \text{ V})$, and coarse particles when $(C, V) = (\leq 0.1 \text{ M}, \geq 110 \text{ V})$.
- (2) When the electrolyte temperature was high and there was no agitation, flower-like ZnO precipitated. Use of agitation led to spherical products, i.e., coarse metallic Zn and amorphous ZnO nanospheres.
- (3) Melting and vaporization of the electrode produced particles. ZnO nanoflowers grew on the surface of spherical particles by precipitation from $Zn(OH)_4^{2-}$ ions.
- (4) Because of their defects, ZnO nanoflowers and amorphous ZnO showed strong green emissions when irradiated at 325 nm. The 700 °C annealed ZnO nanoflowers had higher photocatalytic activity than as-prepared product.

These findings are applicable not only to zinc but also to other metals and alloys. We hope that the results will lead to further development of the use of solution plasma for nanoparticle synthesis, with enhanced ability to control product morphology and composition.

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CHAPTER 5

Synthesis of Sn-based nanoparticles for Li-ion batteries

ABSTRACT : This chapter investigates the optimum experimental conditions required for the synthesis of Sn nanoparticles (Sn-NPs) via direct-current electrolysis using K_2CO_3 or KCl as the electrolyte. Metallic Sn wire was used as a cathode, which was melted by the local concentration of current upon the application of a direct-current voltage. The effects on the products of the solution temperature, the use of surfactants and applied voltage were investigated. When the applied voltage was 400 V in a 0.001 M K_2CO_3 solution without surfactant, single-crystalline tin oxide (SnO) plates were synthesized. Quenching the solution affected the product size. The addition of poly(vinyl alcohol) (PVA) significantly stabilized the $Sn_6O_4(OH)_4$ octahedrons. The Sn-NPs were synthesized in the presence of the surfactant, cetyltrimethylammonium bromide (CTAB). Electrochemical properties of SnO plates and Sn-NPs were analyzed for use as an anode material in Li-ion batteries. A composite of Sn-NPs and graphite enhanced the cyclic stability owing to the buffer space provided by the graphite for volume expansion. In the case of the 30 wt% loaded Sn-NPs, the capacity was measured to be $414 \text{ mAh}\cdot\text{g}^{-1}$ after 20 cycles. With the KCl electrolyte without surfactant, the Sn-NPs were also synthesized. The optimum KCl concentration required for the formation of smaller particles was determined to be 0.05 M. Subsequently, the effective production energy of 45 Wh/g was obtained at the voltages ranging from 110 to 130 V.

5.1 INTRODUCTION

Sn and Sn-based alloy nanoparticles are being widely used in lead-free solder paste^{1,2} and as anode materials in batteries^{3,4} owing to their low melting point and high surface area. For instance, Sn-based eutectic alloys such as Sn-Pb, Sn-Bi and Sn-Zn are used as a solder. Current Li-ion batteries, with graphite and other carbonaceous materials as standard anode materials,

have a maximum theoretical capacity of $372 \text{ mAh}\cdot\text{g}^{-1}$. Although this capacity is not considered very low, new anode materials with higher capacities are required to produce lightweight batteries with high energy density. Recently, Sn anodes have attracted much attention because of their high theoretical capacity of $992 \text{ mAh}\cdot\text{g}^{-1}$ to form a $\text{Li}_{4.4}\text{Sn}$ alloy⁵⁻⁷. However, during lithium insertion/extraction process, a large volume change ($>300\%$) inevitably occurs. This leads to pulverization of the tin anode and loss of electric contact to current collector, resulting in poor cycling performance^{8,9}. Consequently, several strategies, including the formation of tin-based alloy^{10,11}, reducing the particle size to nanoscale, and dispersion of nano-Sn in conductive carbon matrix to form tin/carbon composite¹²⁻²⁰, have been proposed to mitigate this volume change issue. Nanoparticles of intermetallic compounds such as SnSb , Cu_6Sn_5 and Ni_3Sn_4 can increase the energy density of Li ion battery^{21,22}.

Recently, solution plasma technique has been applied for nanoparticles synthesis. In the solution plasma technique, a cathode made of metal wire is used as a raw material for the synthesis of the nanocrystals. In general, this technique offers many advantages: (1) simple equipment, (2) no requirement for a gas supply, (3) higher productivity than conventional solution processes, and (4) applicability to continuous production. However, experimental conditions required for the synthesis of Sn nanoparticles (Sn-NPs) have not been reported. In addition, controlling method of morphologies and composition of the products is not established.

In this chapter, we have adopted a solution plasma technique for preparing Sn-based nanoparticles. Firstly, the effect of surfactant and the cooling rate on the products was investigated for Sn-NPs synthesis, in which the K_2CO_3 electrolyte was used. The electrochemical performance as anode material for Li-ion battery was measured. Secondary, as a surfactant-free synthesis route, the KCl solution was applied to the electrolyte. We have analyzed the optimum electrolyte concentration and voltage conditions required to achieve smaller particle size, high purity, high yield, and highly energy efficient production of Sn-NPs. Finally, the synthesis of Sn-based alloy nanoparticles was studied.

5.2 EXPERIMENTAL SECTION

5.2.1 Experimental Setup and Procedure

The experimental setup consisted of two electrodes in a glass cell shown in Fig.5-1. The cathode consisted of an Sn wire of diameter 1.0 ~ 2.0 mm and 99.9 mass% purity (Nilaco, Tokyo, Japan) placed at the center of the glass cell. A glow discharge plasma was generated around the cathode and was maintained by applying a voltage using a direct-current power-supply (ZX800H, Takasago, Tokyo, Japan).

When the effect of surfactant was studied, a 0.001 M or 0.005 M K₂CO₃ solution was used as the electrolyte. Before electrolysis, the solution was heated to 80 ± 3 °C on a heating plate equipped with a magnetic stirrer. The applied voltage was 400 V or 250 V, with voltage control, and the electrolysis time was approximately 30 min. The solution was stirred using a magnetic stirrer at a rate of 1200 rpm during electrolysis. Table 5-1 shows the experimental conditions for study the effect of surfactants. To study the effect of solution temperature on the products, the solution temperatures were controlled in Runs 1–3. In Runs 4, 5, and 6, the effect of surfactants on the product was investigated by addition of 0.01 mass% poly(vinyl alcohol) (PVA, average degree of polymerization: 1400), 0.001 M SDS, and CTAB with concentration ranging from 0 to 200 × 10⁻⁶ g·ml⁻¹, respectively. The cooling rates after electrolysis were also varied; the glass cell with the solution containing the products and ions was either immediately quenched in ice-water (0 °C, 30 L) after the experiments or allowed to cool gradually in air (Run 7). Sn-NP/graphite composites were prepared by adding graphite powder of diameter 15 μm (Expanded Graphite EC1000, Ito Kokuen) to the Sn-NP-dispersed solution.

Table 5-1. Experimental conditions for study the effect of surfactants.

Run	Temperature Control	Surfactants	Cooling after Electrolysis
1	Natural cooling in air	No	Quenched using ice-water
2	Quenched using 25 °C water		
3	Quenched using ice-water		
4	Natural cooling in air	SDS	
5		PVA	
6		CTAB	
7		No	Natural cooling in air

For surfactant-free synthesis, the electrolyte was composed of 300 ml of KCl solution with concentrations varied from 0.01 to 1.0 M. The voltage was fixed to a constant value for a time period of 1 h, during which the electric power W was kept at 40 W. When the effect of voltage was investigated, the applied voltage was varied from 70 to 190 V. During electrolysis, the solution was stirred using a magnetic stirrer at a rate of 600 rpm. The values of current, voltage and solution temperature were recorded every 2 s. Figure 5-1 (b) shows the experimental procedure adopted in this study for the synthesis of Sn-NPs. As the first step of the process, the weight of the electrode was measured. Subsequently, Sn-NPs were synthesized by applying appropriate voltage. Finally, after consumption of the electrode tip, the electrode weight was measured once again. This procedure was repeated until 0.5 g of Sn-NPs was obtained.

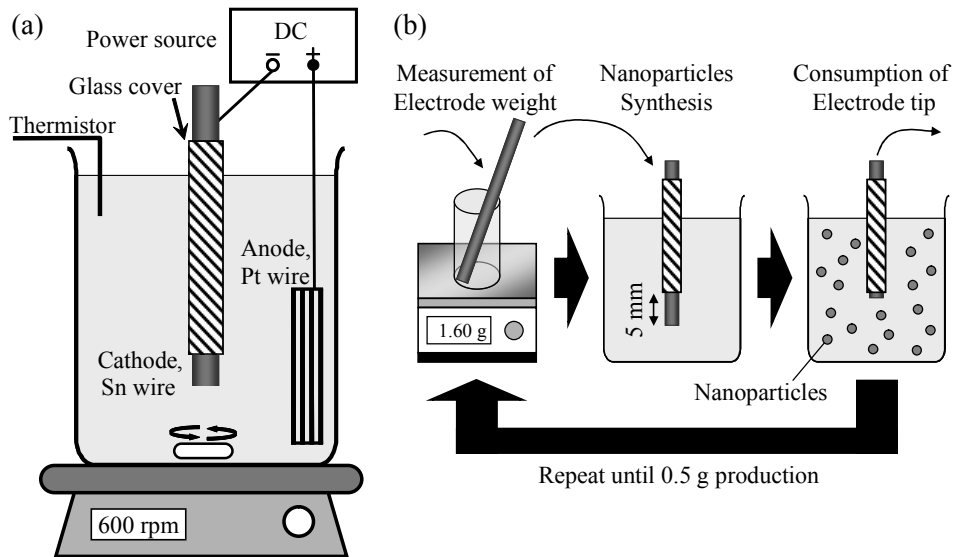


Figure 5-1. (a) Schematic diagram of the experimental setup used for the synthesis of Sn-NPs. Sn wire was used as the cathode. During electrolysis, the KCl solution with different concentrations was stirred using a magnetic stirrer at a rate of 600 rpm. (b) Experimental procedure adopted for the synthesis of Sn-NPs. As the first step, the weight of the electrode was measured. Subsequently, Sn-NPs were synthesized by applying voltage. Finally, after the consumption of the electrode tip, the electrode weight was measured once again. This procedure was repeated until the synthesis of 0.5 g of Sn-NPs.

For alloy nanoparticles synthesis, Sn-35%Pb tin-lead solder (Pb 35 wt%, Sn 65 wt%), Bi-30%Sn alloy (Sn 30 wt%, Bi 70 wt%), and Sn-25%Zn alloy were used as raw materials. The

Sn-25%Zn alloy was prepared by mixing pre-determined quantities of pure Sn and Zn. Furthermore, we investigated the effect of crystal grain size of the electrode on the properties of the synthesized nanoparticles. For this, Sn-35%Pb, Bi-30%Sn, and Sn-25%Zn alloys were heated up to their melting point, followed by quenching with ice water. The intermetallic SnSb alloy was prepared by melting Sn and Sb grains in a crucible. The Cu_5Sn_6 and Ni_3Sn alloys were synthesized by arc melting. The obtained bulk alloys were cut into thin sticks of diameter < 3 mm.

5.2.2 Characterization

The products were collected by centrifugation and dried. Subsequently, the particles were characterized by X-ray diffraction (XRD) using a Miniflex II (Rigaku, Tokyo, Japan) diffractometer. The products were observed by a JSM-7001F (JEOL, Tokyo, Japan) field emission scanning electron microscope (FE-SEM) and a JEM-2010F (JEOL, Tokyo, Japan) transmission electron microscope (TEM). The particle size analysis was performed using dynamic light scattering measurements performed on Nanotrac UPA-UT151 (Microtrac Inc.).

5.2.3 Preparation of cell and Electrochemical measurements

The electrochemical characterizations were carried out in two-electrode Swagelok-type cells (Fig.5-2)²³. The working electrode consisted of an active material, conductive carbon (acetylene black), and a polymer binder (polyvinyl alcohol) in the weight ratio of 75:15:10. The well-blended slurry was pasted onto a copper foil and dried at 60 °C for 12 h in vacuum. The dried electrode was punched into a disc of diameter 10 mm and pressed under a pressure of 20 MPa. A metallic lithium disc of diameter 10 mm was used as the counter and reference electrode. The cells were assembled in an Ar-filled glove box (UNICO), using a solution of 1 M LiPF_6 dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v) as electrolyte and polypropylene membrane as a separator. The cells were galvanostatically cycled from 0.01 to 2.0 V versus Li/Li^+ at 0.2 C in the constant current mode using a battery tester (PFX2011, Kikusui). Cycling voltammograms (CV) were measured at a scanning rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$ using a

potentiostat (PGSTAT 128N, Metrohm Autolab).

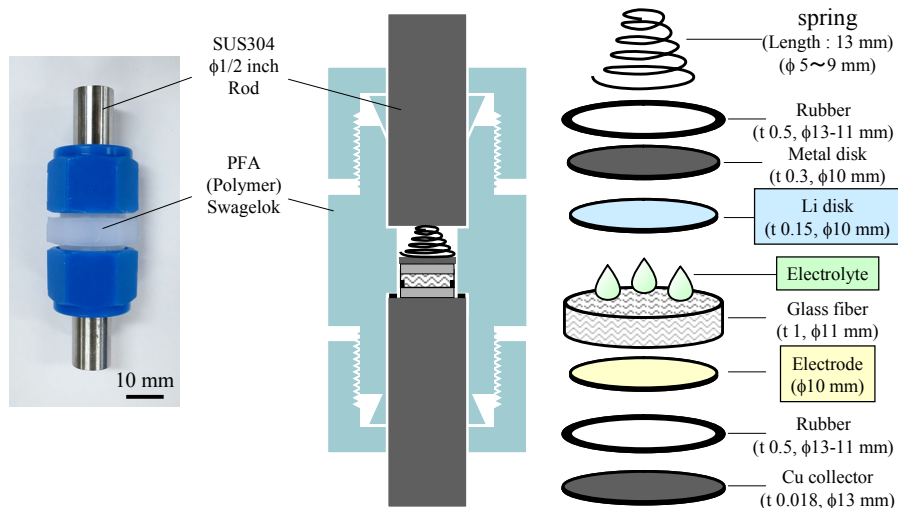


Figure 5-2 Two-electrode Swagelok-type cells for electrochemical measurement.

5.3 RESULT AND DISCUSSIONS

5.3.1 Effect of surfactants and cooling

Figure 5-3 shows the XRD patterns of the products, and Fig. 5-4 shows the SEM images of the products. Runs 1–7 correspond to the experimental conditions shown in Table 5-1. The XRD patterns shown in Fig. 5-3 indicate that the products were SnO, $\text{Sn}_6\text{O}_4(\text{OH})_4$, and Sn. Interestingly, SnO_2 was not formed, although it is more stable. This suggests that the product was formed not from Sn^{4+} but from Sn^{2+} ions. Tetragonal SnO is a thermodynamically metastable phase. The solution plasma sometimes produces a metastable phase as a result of a high cooling

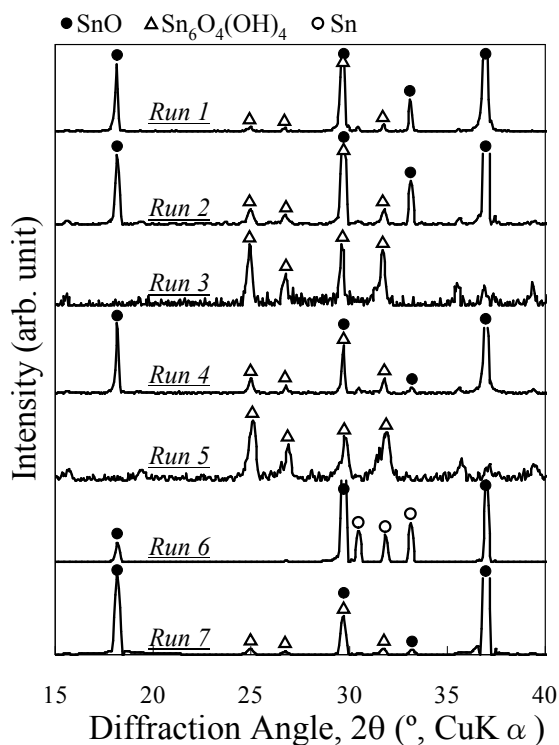


Figure 5-3 XRD patterns of products from Runs 1–7 in Table 5-1.

rate. The solubility diagram of Sn species in water at 25 °C²⁴ shows that the solubilities of Sn(IV) and Sn(II) species change with pH. There is a possibility that the solution plasma technique produces the SnO₂ phase by changing the pH. According to the SEM images shown in Fig. 5-4, oriented crystals were mainly produced under the conditions used for Runs 1, 2, 4, 6, and 7, and these showed strong SnO peaks in the XRD patterns. Detailed observations of these crystals (Fig. 5-5) show that the crystal thicknesses were less than their widths. We therefore called these oriented crystals “plate-like crystals.” These results suggest that the plate-like crystals are SnO.

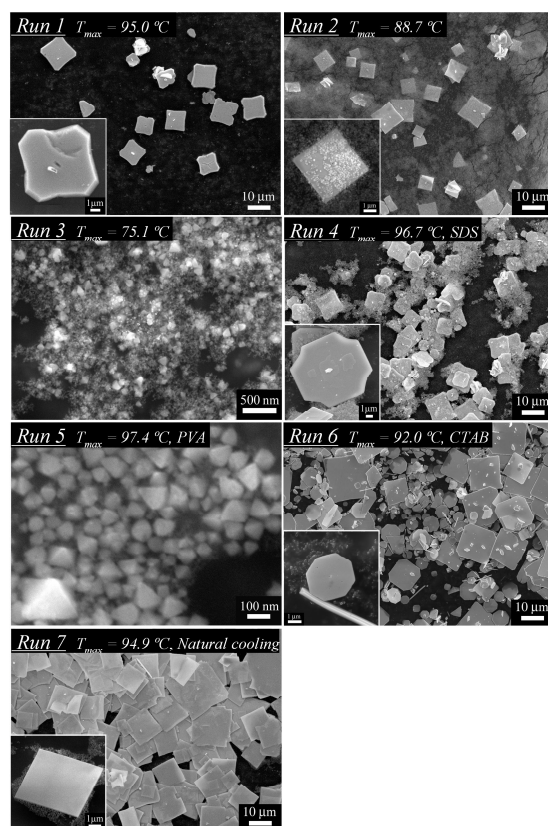


Figure 5-4 SEM images of products synthesized under different conditions (Table 1) using 0.001 M K₂CO₃ solution as the electrolyte. $T_{\max}$ is the maximum temperature (°C) during electrolysis..

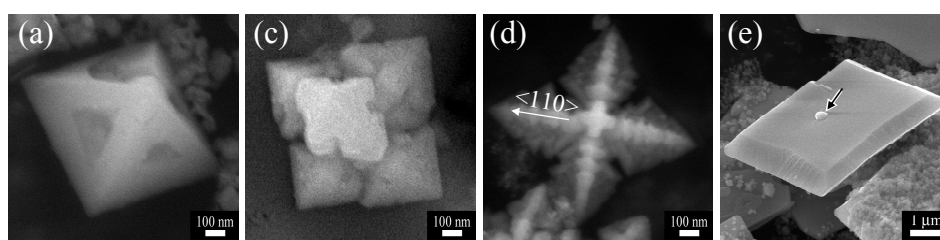


Figure 5-5 SEM images of the product (obtained by Run 3) having different morphologies.

In order to control the solution temperatures, the electrolysis solutions were cooled. For Run 3, the electrolysis solution was cooled using ice-water. The electrolysis solution was cooled using water at 25 ± 5 °C for Run 2. In Run 1, the electrolysis solution was allowed to cool naturally in air. We measured the solution temperatures at certain points. Figure 5-4 shows SEM

images of the products; $T_{\max}$ is the maximum temperature ($^{\circ}\text{C}$) during electrolysis. Without cooling, the solution temperature increased to $95.0\text{ }^{\circ}\text{C}$ (Run 1). SnO plates were synthesized under this condition. When the electrolysis solution was cooled using ice-water (Run 3), the main phase of the products was $\text{Sn}_6\text{O}_4(\text{OH})_4$ nanoparticles. In the case of cooling using water at $25 \pm 5\text{ }^{\circ}\text{C}$ (Run 2), both SnO plates and $\text{Sn}_6\text{O}_4(\text{OH})_4$ nanoparticles precipitated. These results show that the product phase was controlled by the solution temperature. A solution temperature above $95.0\text{ }^{\circ}\text{C}$ was effective for producing SnO plates.

Compared to the case without surfactants (Run 1), the addition of SDS (Run 4) did not affect the morphology and composition of the product. The products produced using SDS were SnO plates, similar to the products produced in Run 1. When PVA was used as the surfactant (Run 5), $\text{Sn}_6\text{O}_4(\text{OH})_4$ octahedrons were precipitated, in spite of the solution temperature being above $95.0\text{ }^{\circ}\text{C}$. This is because PVA affected the crystal growth of the product. SDS is an anionic surfactant and has no hydroxyl groups. In contrast, PVA is a crystalline polymer with many hydroxyl groups. Previous papers have reported that the hydroxyl groups in PVA form hydrogen bonds with other hydroxyl groups,^{25, 26} as shown in Fig. 5-6. We speculate that PVA attaches to a specific crystal plane of $\text{Sn}_6\text{O}_4(\text{OH})_4$ as a capping agent, forming octahedrons. PVA probably prevented dehydration of $\text{Sn}_6\text{O}_4(\text{OH})_4$ by forming a coating on the $\text{Sn}_6\text{O}_4(\text{OH})_4$ surface. In the case of CTAB addition (Run 6), SnO and Sn were formed. The SEM image in Fig. 5-4 shows that plate crystals, particles, and rods were formed. As described in section 3.5, SnO and $\text{Sn}_6\text{O}_4(\text{OH})_4$ are probably formed from $\text{Sn}(\text{OH})_3^-$ ions. CTAB is a cationic surfactant, and ionizes completely in water to form CTA^+ . The CTA^+ cations form $\text{CTA}^+-\text{Sn}(\text{OH})_3^-$ ion pairs by electrostatic interactions. These $\text{CTA}^+-\text{Sn}(\text{OH})_3^-$ ion pairs are known to be seeds for rod crystal formation.²⁷ This is why rods were formed on addition of CTAB. CTA^+ probably also became attached to the metallic Sn surface to stabilize the metallic particles.

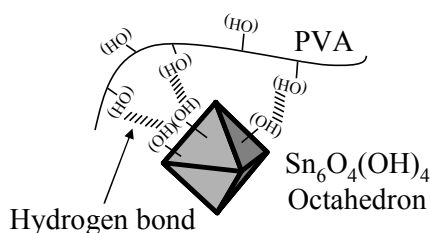


Figure 5-6 Schematic diagram of the effect of PVA on the $\text{Sn}_6\text{O}_4(\text{OH})_4$ surface.

Two methods of cooling the solution after electrolysis were used: natural cooling in air (Run 7) and quenching in ice-water (Run 1). Figure 5-7 shows the changes in solution temperature for the different cooling methods. When the solution was naturally cooled in air (Run 7), the SnO plates grew larger than those produced when the solution was quenched using ice-water (Run 1). These results indicated that the Sn ions remained in solution, without precipitation, after electrolysis, and they gradually precipitated as SnO as the solution temperature decreased. With the slower rate of cooling, the SnO plates grew larger because the rate of crystal growth was higher than the rate of nucleation. The slow cooling rate decreased the number of crystal nuclei, and these nuclei grew large crystals. When the solution was cooled quickly, many crystal nuclei precipitated, and formed small crystals.

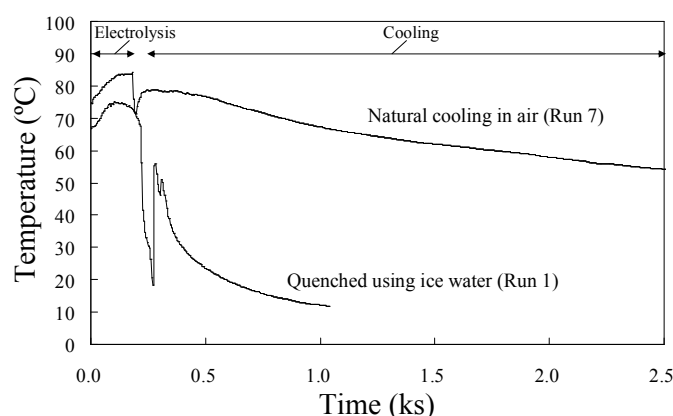


Figure 5-7 Changes in solution temperature. The temperature decrease at around 0.2 ks was induced by reconnection of the thermocouple.

In chapter 3 and 4, we reported the preparation of ZnO and CuO nanocrystals using a solution plasma technique, in which the nanocrystals were precipitated from metal hydroxide ions such as $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Cu}(\text{OH})_4^{2-}$ using an alkaline solution. Similarly, there is a possibility that, in the present study, the SnO nanocrystals were formed from $\text{Sn}(\text{OH})_3^-$ ions. Sn^{2+} ions form $\text{Sn}(\text{OH})_3^-$ ions by the following reaction with hydroxyl ions (equation 5-1):



When the solution becomes saturated with $\text{Sn}(\text{OH})_3^-$ ions, precipitation of solid $\text{Sn}_6\text{O}_4(\text{OH})_4$ or SnO occurs, as shown in equations 5-2 and 5-3.



When the solution temperature is high, $\text{Sn}(\text{OH})_3^-$ ions tend to form SnO, as in equation (5-3). At low temperatures, the $\text{Sn}(\text{OH})_3^-$ ions immediately precipitate as $\text{Sn}_6\text{O}_4(\text{OH})_4$ (equation 5-2) because $\text{Sn}(\text{OH})_3^-$ ions cannot exist as stable ions in solution.

TEM observations were carried out to investigate the crystal structures of the SnO plates and $\text{Sn}_6\text{O}_4(\text{OH})_4$ crystals. Figures 5-8 (a–c) show the TEM images of the SnO plates obtained in Run 1. The insets show the corresponding selected area electron diffraction (SAED) patterns. The SAED patterns show that the square plates were single-crystalline tetragonal SnO, with the plate faces on the (001) plane. This crystal structure is consistent with those of other SnO plates produced by different methods.²⁸ However, the sides of the square plates had different planes at each plate. The sides of plate-like crystals (Fig. 4a) were along the (110) plane, and the sides of plates (Fig. 4b) were on the (200) plane. We assumed that the (001) plane of SnO was the most stable and that the growth rate in the $\langle 001 \rangle$ direction was much slower than that in the $[110]$ and $\langle 100 \rangle$ directions as a result of the differences in surface energy. The SnO crystals grew to form a plate-like crystal. There have been few reports on the surface energy of SnO crystals. Generally, in a solution synthesis, oriented crystals are synthesized as a result of the differences in growth rates at each plane. In the case of ZnO, the $[0001]$ surface has a high surface energy and the $\langle 0001 \rangle$ direction has a high growth rate. Similarly, the $[001]$ plane of SnO probably has the lowest surface energy. This is why the SnO crystals grew to form plate-like crystals.

SEM and TEM were used to observe a crystal of the intermediate product $\text{Sn}_6\text{O}_4(\text{OH})_4$, which was formed along with the SnO plates in Run 7. Figures 5-8 (d–f) show the SEM and TEM images of the $\text{Sn}_6\text{O}_4(\text{OH})_4$ skeleton crystal. The SEM images of the $\text{Sn}_6\text{O}_4(\text{OH})_4$ skeleton crystal in Fig. 5-8 (d) show a square morphology. This skeleton crystal probably grew into an SnO plate. Figure 5-8 (e) shows the TEM image of a skeleton crystal similar to the skeleton crystal shown in Fig. 5-8 (d). The SAED patterns shown in Fig. 5-8 (f) are consistent with the $\text{Sn}_6\text{O}_4(\text{OH})_4$ crystal structure, and the growth direction was along the $[110]$ direction. Subsequently, an octahedron grew in the $[110]$ direction, and new octahedrons attached to the tip of the first

octahedron. The octahedrons have rough surfaces with many peaks because many octahedrons agglomerate epitaxially. According to the literature,²⁹ $\text{Sn}_6\text{O}_4(\text{OH})_4$ has a tetragonal structure with $a = 7.9268 \text{ \AA}$ and $c = 9.1025 \text{ \AA}$. The growth rate along the z -axis is probably different from those along the x -axis and the y -axis. This difference resulted in growth of the $\text{Sn}_6\text{O}_4(\text{OH})_4$ octahedron to give a plate-like skeleton crystal.

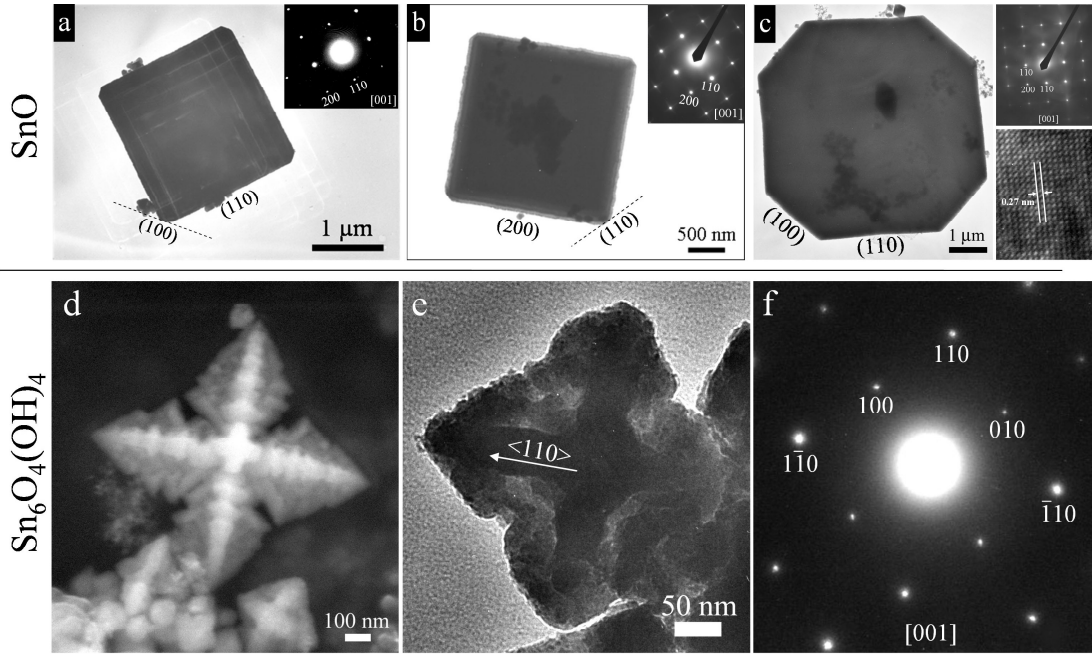


Figure 5-8 (a–c) TEM images of the SnO plates. The insets show the SAED patterns of the SnO plates recorded with an electron beam parallel to the [001] crystal direction. (d) SEM images of the $\text{Sn}_6\text{O}_4(\text{OH})_4$ skeleton crystal in the SnO plates. (e) TEM images of the $\text{Sn}_6\text{O}_4(\text{OH})_4$ skeleton crystal. (f) SAED patterns taken from the $\text{Sn}_6\text{O}_4(\text{OH})_4$ skeleton crystal with the electron beam parallel to the [001] direction.

5.3.2 Effect of CTAB concentration

Figure 5-9 shows the XRD patterns of the different samples prepared with various concentrations of CTAB. Figure 5-10 shows the corresponding microstructural analysis performed using SEM. In case of sample prepared without the addition of CTAB (labeled as “CTAB-0” in Fig. 5-9), the XRD pattern and SEM image revealed the formation of SnO plates containing $\text{Sn}_6\text{O}_4(\text{OH})_4$ particles. The TEM observation of this sample shown in Fig. 5-8 indicated the formation of single-crystalline tetragonal SnO plates, with the plate faces on the (001) plane. In addition, the systematic characterization revealed that the SnO plates and

$\text{Sn}_6\text{O}_4(\text{OH})_4$ particles were precipitated from $\text{Sn}(\text{OH})_3^-$ ions, as described by the equations 5-2 and 5-3. In case of sample synthesized in the presence of 10 and $30 \times 10^{-6} \text{ g}\cdot\text{ml}^{-1}$ of CTAB, the size of the SnO plates was found to decrease, with the formation of a small amount of metallic Sn. On further increasing the CTAB concentration to $200 \times 10^{-6} \text{ g}\cdot\text{ml}^{-1}$, we could obtain 150 mg of Sn nanoparticles (Sn-NPs) of diameter $<200 \text{ nm}$, upon 7 min of electrolysis with average current of 0.43 A .

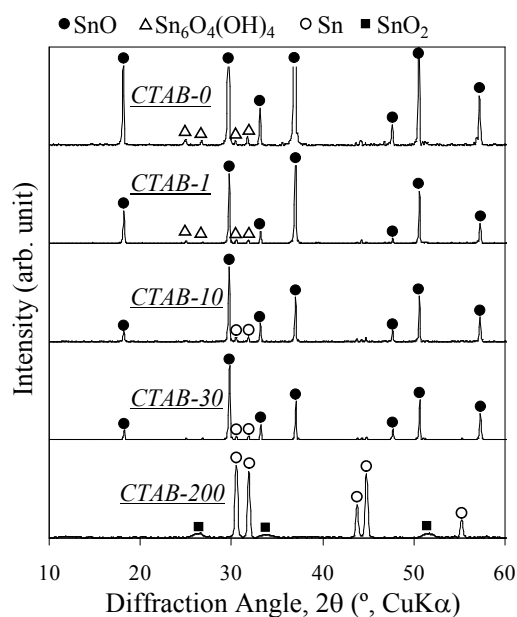


Figure 5-9 XRD patterns of the samples synthesized with different concentrations of CTAB (0 to $200 \times 10^{-6} \text{ g}\cdot\text{ml}^{-1}$).

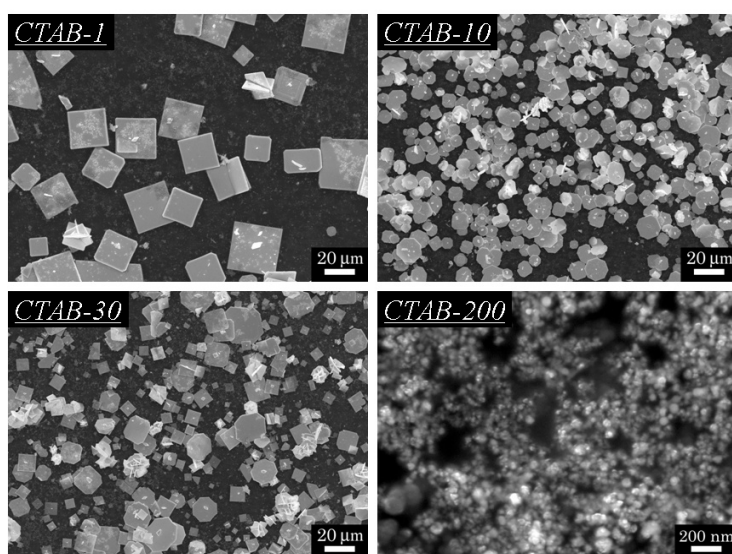


Figure 5-10 SEM images of samples synthesized with different concentrations of CTAB.

The crystal structure of the prepared Sn-NPs was analyzed by using TEM to clarify the location of the oxide SnO_2 . Figure 5-11 (a) shows the bright-field TEM image of the prepared Sn-NPs and Fig. 5-11(b) shows the selected area electron diffraction (SAED) pattern corresponding to the area (b), shown with a dotted line in Fig. 5-11 (a). From TEM images, the mean diameter of the Sn-NPs was 48 nm. The SAED pattern confirmed the formation of single-crystalline tetragonal Sn-NPs. Besides, we could also observe the formation of multi-crystalline Sn particles and colloidal SnO_2 particles of diameter of <10 nm. Figures 5-11 (c) and (d) show the high-resolution TEM images taken from the area (c) and (d) shown with a solid line in Fig. 5-11 (a). As evidenced from Fig. 5-11 (d), an oxide layer was formed on the surface of Sn particles. These SnO_2 phases were probably produced as a result of the high-temperature atmosphere surrounding the Sn electrode surface. After the experiments, the oxide phase might have been formed during the drying process.

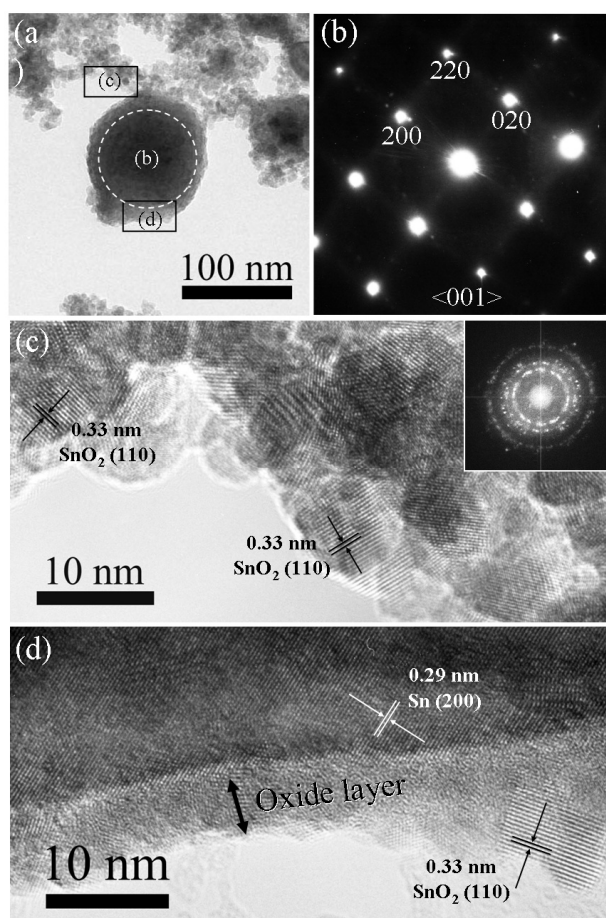


Figure 5-11 TEM images of the sample obtained by the addition of $200 \times 10^{-6} \text{ g}\cdot\text{ml}^{-1}$ of CTAB.

Figure 5-12 shows the possible formation mechanism underlying the formation of Sn-NPs upon the addition of CTAB. The solution near the cathodic plasma is heated to the boiling point and a vapor was generated. When the sample was synthesized without CTAB, the resulting sample was SnO plates, which was precipitated from Sn(OH)_3^- ions formed from the oxidation and ionization of Sn-NPs. On the other hand, when the sample was synthesized with CTAB, Sn-NPs were formed in addition to SnO plates. This could be attributed as the effect of CTAB, explained as follows. CTAB is a cationic surfactant, which ionizes completely in water to form CTA^+ . The CTA^+ formed in the aqueous solution might have probably attached to the surface of Sn-NPs, to stabilize the metallic particles. If the solution contains large quantities of CTAB sufficient to cover whole surface of Sn-NPs, the formation of Sn(OH)_3^- ions on the Sn-NPs surface is prevented. According to our experiments, 1 mg of CTAB was needed to produce 1 g of Sn-NPs. In addition, the optimum temperature range was determined to be 70–84 °C. The surface area of particles and adsorption area of CTAB molecules were calculated for comparison. When all particles are spheres with 48 nm diameter, surface area of these particles can be calculated from amount of production and density of metallic Sn as shown in Table 5-2. Actual surface area will be increased due to surface roughness of particles and existence of colloidal SnO_2 nanoparticles shown in Fig.5-11 (c) with the particle size less than 10 nm.

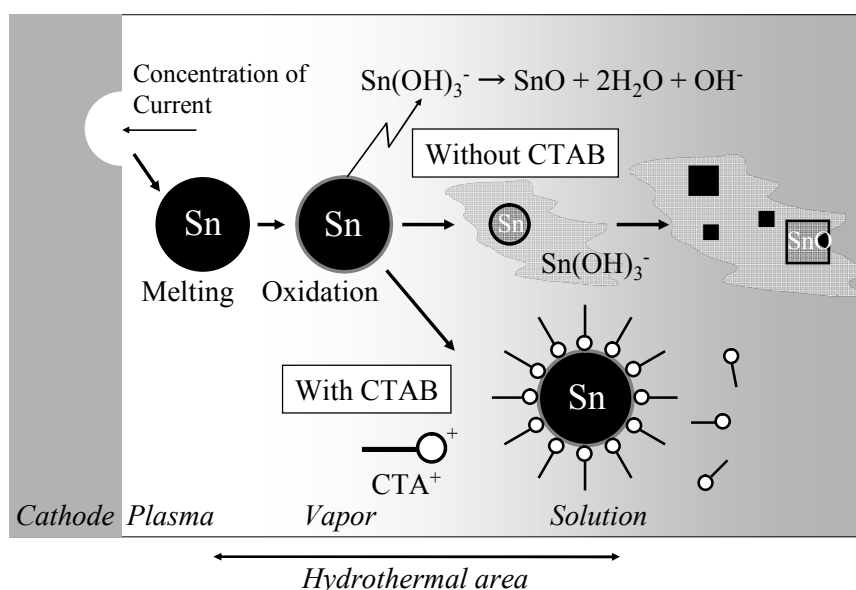


Figure 5-12 Mechanism proposed for the formation of Sn nanoparticles in the presence of CTAB.

Table 5-2. Surface area of particles calculated from the mean diameter, amount of production and density of Sn.

Mean diameter	48 nm
Production amount	150 mg
Density of metallic β -Sn	7.365 g·cm ⁻³
Surface area of particles	2.55 m ²

According to the literature³⁰, the adsorption area of one CTAB molecule is 0.35 nm². On the assumption of monomolecular adsorption of CTAB, the total absorption area of CTAB was estimated. Table 5-3 shows the adsorption area of CTAB molecules at each concentration. In the case of 200×10^{-6} g·ml⁻¹ of CTAB, the adsorption area was 34.68 m² which is larger than the surface area of Sn-NPs.

Table 5-3 adsorption area of CTAB molecules at each concentration.

Concentration (g·ml ⁻¹)	Adsorption area (m ²)
1×10^{-6}	0.17
10×10^{-6}	1.73
30×10^{-6}	5.20
200×10^{-6}	34.68

5.3.3. Electrochemical properties for Li-ion batteries

The electrochemical properties of the SnO plate, prepared without the addition of CTAB, was studied using constant current charge/discharge measurement. For that, the anode was formed by preparing a composite of SnO plates and graphite. During the first charge/discharge process, Li₂O and metallic Sn were formed, according to the following equation (5-4).



Figure 5-13 shows the cyclic performance of the SnO plates and SnO plate/graphite composite. In both the samples, the decrease in capacities was induced by large volume expansion during the lithium-ion insertion process, in which the SnO-plate was mechanically damaged, cracked, and pulverized. Inset of Fig. 5-13 is merely the corresponding SEM image of the sample. It was observed that the flat SnO plate was pulverized to particles after 20 cycles. These pulverized particles might have peeled from the electrode or lost the connection with copper collector, which lead to the observed decrease in capacity³¹.

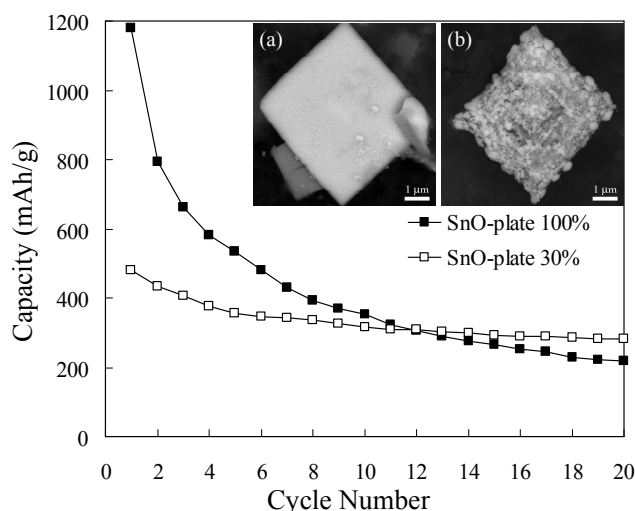


Figure 5-13 Discharge capacity of the SnO products in the range of 0.01 - 2 V at a cycling rate of 0.2 C with the binder of PVDF. The product of SnO –plate 30% is a mixture of SnO plate and graphite. Inset images show the SEM images of SnO plates of (a) as-prepared electrode and (b) after 20 cycles.

The electrochemical properties of the synthesized Sn-NP/graphite composite (Sn-NPs 30%) were also evaluated. For comparison, the cyclic performances of pure graphite and pure Sn-NPs (Sn-NPs 100%) were also recorded. [Figure 5-14](#) shows the cyclic performance of the samples. In the case of Sn-NPs 100%, the discharge capacity was found to decrease dramatically. The decrease in capacities was induced by large volume expansion during the lithium-ion insertion process. In contrast, it was found that the discharge capacity of Sn-NPs 30% was $414 \text{ mAh}\cdot\text{g}^{-1}$ after 20 cycles owing to the buffer space provided by the graphite for volume expansion. The charge/discharge voltage curves of Sn-NPs 30% are illustrated in [Fig. 5-15](#). A typical voltage profile related to alloying-dealloying of lithium with Sn-NPs and graphite was observed. In the first cycle, the coulombic capacity was calculated to be 66 %, based on the discharge capacity of $653 \text{ mAh}\cdot\text{g}^{-1}$ and charge capacity of $433 \text{ mAh}\cdot\text{g}^{-1}$. This is usually due to the irreversible reactions, such as the formation of a solid electrolyte interface (SEI) layer and the decomposition of solvent in the electrolyte¹⁷. Low coulombic efficiency in the first cycle might have been caused by the formation of SEI layer owing to the high surface area of Sn-NPs. Additionally, the irreversible reduction of SnO_2 on the Sn-NP surface to metallic Sn occurred by following equation (5-5).



In the 2nd cycle, the efficiency was increased to 93 % and above 95 % after 18 cycles. Compared to the theoretical capacity of 559 mAh·g⁻¹ in Sn-NPs 30%, the discharge capacity after 20 cycles decreased to 414 mAh·g⁻¹, owing to the formation of SnO₂ and weak bonding force between Sn-NPs and graphite. According to the SEM image shown in Fig.5-14, the Sn nanoparticles attached to the graphite surface. However, in this study, the Sn and graphite were just simply mixed together, and they may be lack of good adhesion or contact. The method for composite preparation requires further improvement in order to enhance the capacity and cyclic properties.

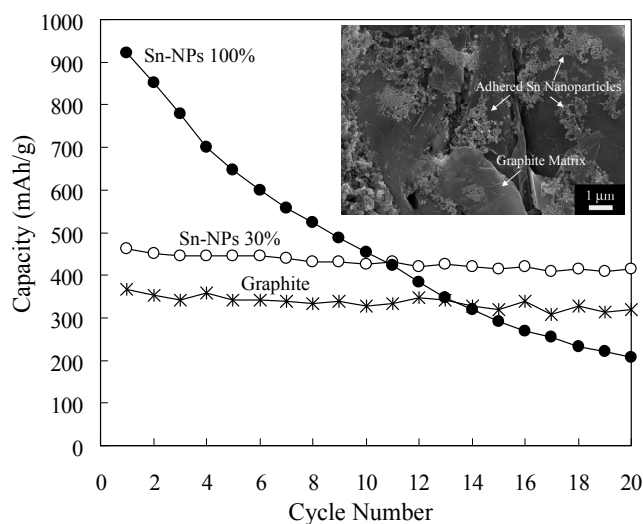


Figure 5-14 Discharge capacity of the Sn-NPs 30%, Sn-NPs 100% and graphite composite with the binder of PVA in the range of 0.01–2 V at a cycling rate of 0.2 C. Inset images show the SEM images of the composite.

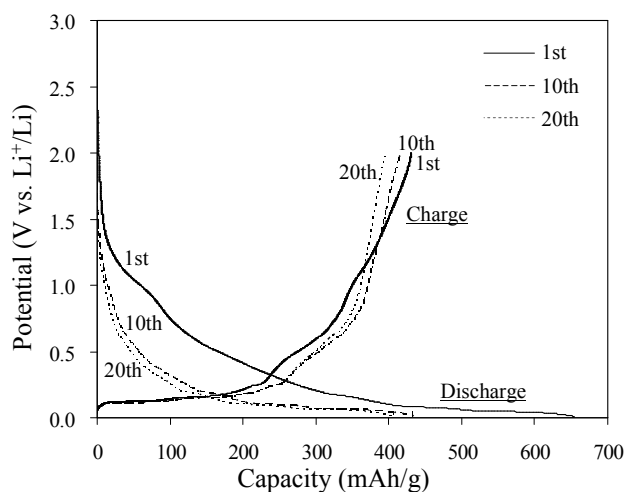


Figure 5-15 Voltage profiles of Sn-NPs 30% and graphite composite with the binder PVA. The cycling rate was 0.2 C.

Figure 5-16 shows the typical cyclic voltammograms of Sn-NPs 30% and graphite with PVA binder, obtained at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$ between 0.0 and 2.0 V. In the first negative scan, a broad reduction band was observed at $1.4 \sim 0.8 \text{ V}$ (peak 1), corresponding to the irreversible reduction of SnO_2 and the decomposition of solvent to form SEI film³². However, this disappeared in next scan. The peaks 2 and 3 shown in the 5th cycle could be related to the formation of Li_xSn . According to the literature, Li_2Sn , LiSn , Li_7Sn_3 , Li_5Sn_2 , and $\text{Li}_{13}\text{Sn}_5$, are typically obtained in the potential range of $0.76\text{--}0.38 \text{ V}$ ¹⁸. Similarly, the peaks 4 and 5 below 0.3 V , which were observed in both reduction and oxidation curves, could be attributed to the reversible intercalation of lithium into graphite^{18,33}. The 4 individual peaks (peaks 6–9) on the positive side could be related to the extraction of Li from Sn^{12, 34}.

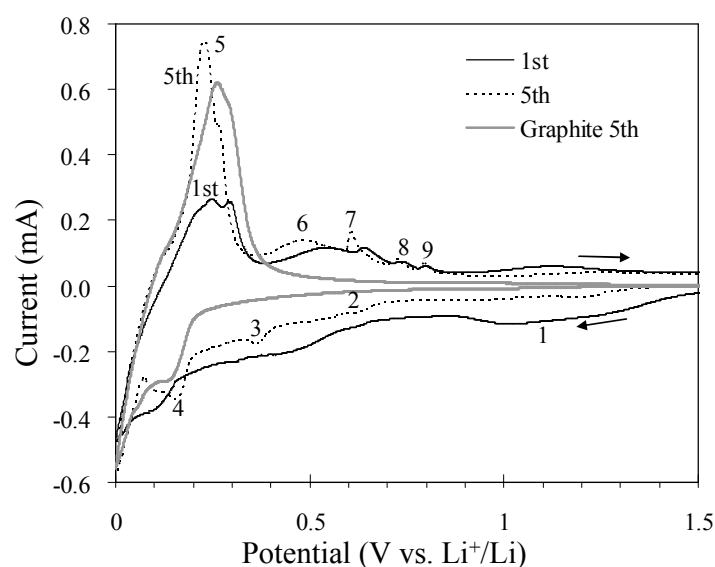


Figure 5-16 Cyclic voltammograms of Sn-NPs 30% with the binder PVA. The scan speed was 0.1 mV/s .

5.3.4. Effective formation of Sn nanoparticles via KCl solution

In this section, formation of Sn nanoparticles (Sn-NPs) via KCl solution route without surfactant addition is discussed. In chapter 2, we have reported that the electrolyte concentration greatly affects the formation of the nanoparticles. In the case of nickel cathode, the voltage required for producing the discharge tends to decrease at high electrolyte concentrations, due to an increase in the electrical conductivity of the solution. Consequently, higher electrolyte

concentration results in high current flow, which in turn leads to the formation of bigger-sized particles. This suggests that a lower concentration of the electrolyte is desired for the synthesis of smaller-sized particles. Therefore, in this study, we varied the electrolyte concentrations from 0.01 to 1.0 M to arrive at the optimum condition suitable for the synthesis of Sn-NPs. Here, the electric power was fixed at a constant value of 40 W. Table 5-4 summarizes the applied voltages and the resulting current for different concentrations of the electrolyte. Similar to the trend observed in case of Ni electrode, the applied voltages for plasma formation decreased at higher concentrations of the electrolyte.

Table 5-4. Applied voltage and resulting current for different electrolyte concentrations.

Concentration (M)	0.01	0.05	0.1	0.5	1.0
Voltage (V)	200	170	140	100	80
Current (A)	0.20	0.25	0.30	0.42	0.50

Figure 5-17 shows the XRD patterns of the Sn samples synthesized under different concentrations of the KCl electrolyte. As can be seen from the diffraction patterns, the samples synthesized with the electrolyte concentrations in the range of 0.05 to 1.0 M exhibited mixed Sn and SnO₂ phases. For the electrolyte concentration of 0.01 M, the XRD pattern indicated the formation of Sn₆O₄(OH)₄. The samples were further analyzed by using SEM. As can be seen from the SEM images shown in Fig.5-18, particles produced from 0.05 to 1.0 M were spherical, in which the particle size decreased at lower concentrations. These particles were formed as the result of melting of the Sn electrode surface. The surface of the particles was partially oxidized under the plasma condition. On the other hand, at the electrolyte concentration of 0.01 M, octahedral crystals of Sn₆O₄(OH)₄ were precipitated in the equations (5-1) and (5-2). It is assumed that the higher accelerating voltage used in the electrolysis process led to the ionization of the Sn electrode, resulting in the formation of Sn(OH)₃⁻ ions, as shown in Eq. (5-1). The Sn(OH)₃⁻ ions in solution was further transformed to Sn₆O₄(OH)₄, as shown in Eq. (5-2). Figure 5-19 shows the particle size distribution of the Sn-NPs prepared in this study. Results indicate that the particle size tends to decrease with a decrease in the concentration of the electrolyte. At

the electrolyte concentration of 0.01 M, the particle size was larger because of the formation of $\text{Sn}_6\text{O}_4(\text{OH})_4$ crystals. Of all the different concentrations of the electrolyte used in this study, the smallest particle size of 258.5 nm was obtained at the concentration of 0.05 M.

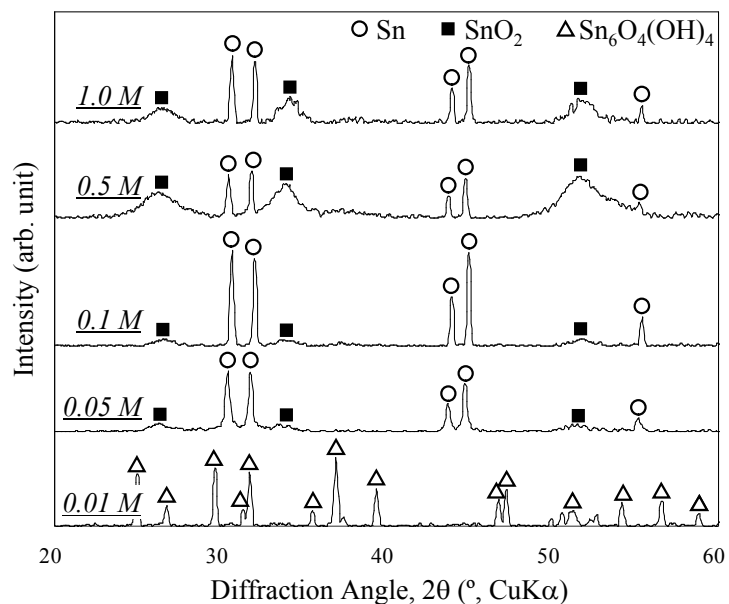


Figure 5-17 XRD patterns of the products synthesized at different KCl concentrations of the electrolyte. From 0.05 to 1.0 M of KCl, Sn and SnO_2 phases were formed. In contrast, the 0.01 M concentration of KCl, the $\text{Sn}_6\text{O}_4(\text{OH})_4$ were synthesized.

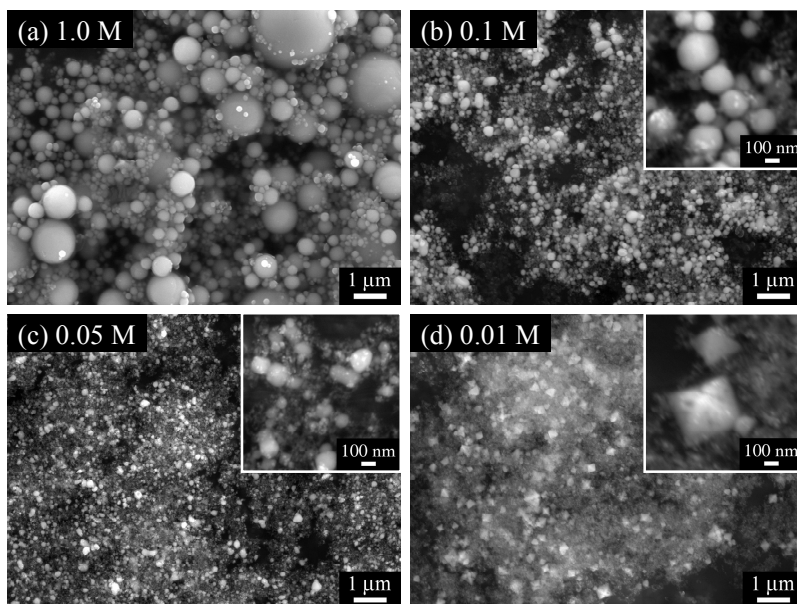


Figure 5-18 SEM images of the products at different electrolyte concentrations. Particles produced from 0.05 to 1.0 M were spherical, in which the particle size decreased at lower concentration. In contrast, at the 0.01 M concentration, the octahedral shapes were precipitated.

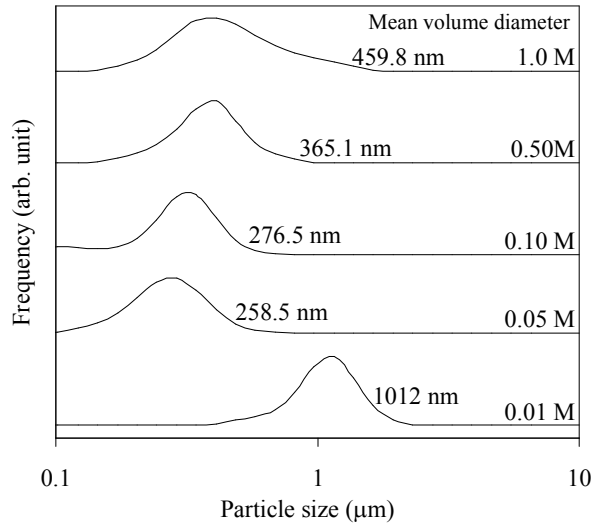


Figure 5-19 Particle size distributions of the products at different electrolyte concentrations. Particle sizes were measured by dynamic light scattering. The particle size was decreased with decreasing the electrolyte concentrations. At 0.01 M, particle size was big because of the $\text{Sn}_6\text{O}_4(\text{OH})_4$ crystals formation.

Furthermore, we evaluated the production energy Q (Wh/g), which indicates the amount of energy required for the synthesis of Sn-NPs. The input power W (Wh) can be calculated from the recorded voltage and current, using the following equation (5-6).

$$\text{Power, } W(\text{Wh}) = E(V) \int I(A) dt / 3600 \quad (5-6)$$

The amount of Sn-NPs M (g) synthesized in the process was measured by calculating the difference in weight of the electrode wire before and after electrolysis. Accordingly, the production energy Q (Wh/g) was derived from W (Wh) and M (g), using the following relation.

$$\text{Production Energy, } Q(\text{Wh} / \text{g}) = W(\text{Wh}) / M(\text{g}) \quad (5-7)$$

Figure 5-20 shows the plot between the amount of Sn-NPs synthesized M (g) and the input power (Wh), for different concentrations of the electrolyte. As shown in the equation (4), the gradient of the linear line indicates the production energy (Wh/g). As can be seen from the plot, the electrolyte concentration of 0.1 M exhibits the lowest production energy of 51.1 (Wh/g). The

electrolyte concentration of 0.05 M required the production energy of 65.9 (Wh/g). From these results, it can be concluded that the optimum electrolyte concentration is 0.05 M because of the smallest particle size.

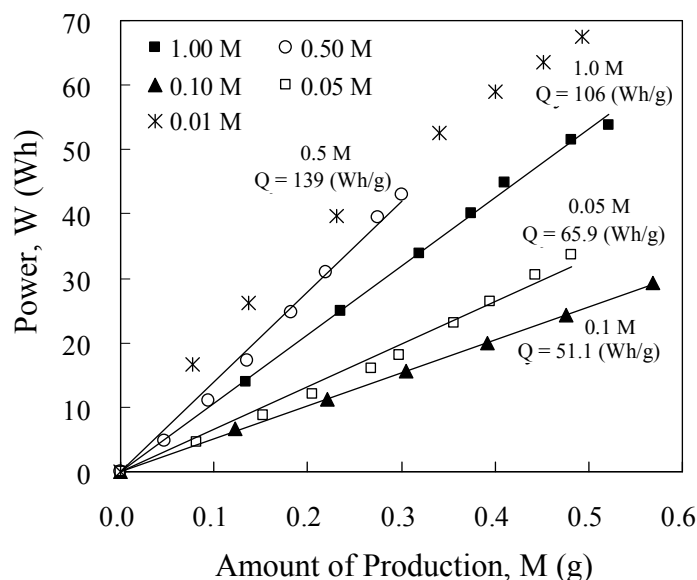


Figure 5-20 Plot between the amount of Sn-NPs synthesized in the process M (g) and the input power (Wh). The gradient of linear line indicates the production energy (Wh/g). The KCl concentration of 0.1 M required the lowest production energy.

We investigated the effects of applied voltage on the composition, production energy, and particle size of the sample, at the fixed electrolyte concentration of 0.05 M. **Figure 5-21** shows the XRD pattern of the samples obtained by varying the voltage from 70 to 190 V. In the high-voltage range of 170 to 190 V, the resulting Sn-NPs were partially oxidized to SnO₂ because of the high temperature induced under the high-voltage conditions. At voltages below 150 V, the oxide phase was not observed because of the decrease in temperature.

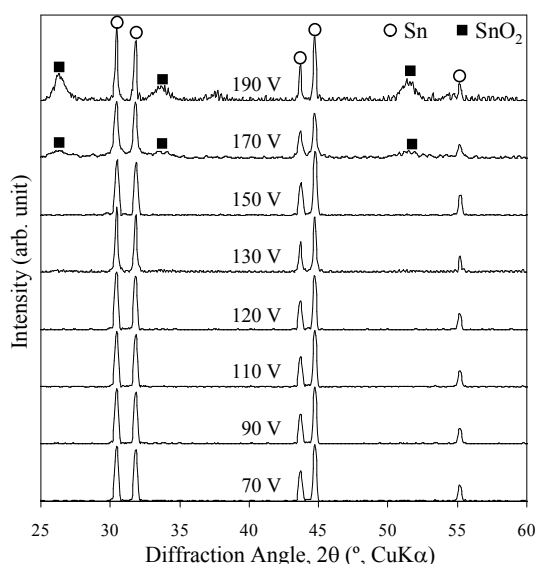


Figure 5-21 XRD patterns of the products synthesized at different voltages with the electrolyte concentration of 0.05M.

Fig. 5-22 shows the production energy and particle size of the samples obtained under different voltage conditions. As can be seen from the figure, effective production energy of around 45 (Wh/g) was obtained for voltage conditions ranging from 110 to 130 V. The value of 45 (Wh/g) indicates that the input power of 45 Wh is required for the synthesis of 1 g of Sn-NPs. At high voltages above 170 V, the temperature surrounding the Sn electrode exceeded too high, making it unsuitable for the effective synthesis of Sn-NPs. On the other hand, at voltages below 90 V, the production energy required for the process was high because of the lack of heat under low voltage conditions. Furthermore, we evaluated the mean diameter of the samples obtained at different voltage conditions. As can be seen from Fig. 5-22, the applied voltage of 190 V resulted in the formation of coarse particles with oxide phase due to the high-voltage conditions. For applied voltages below 170 V, the resulting particle size increased with a decrease in the production energy. When the production energy was low, large amount of particles were generated. Consequently, the particles tend to agglomerate and result in larger particle size.

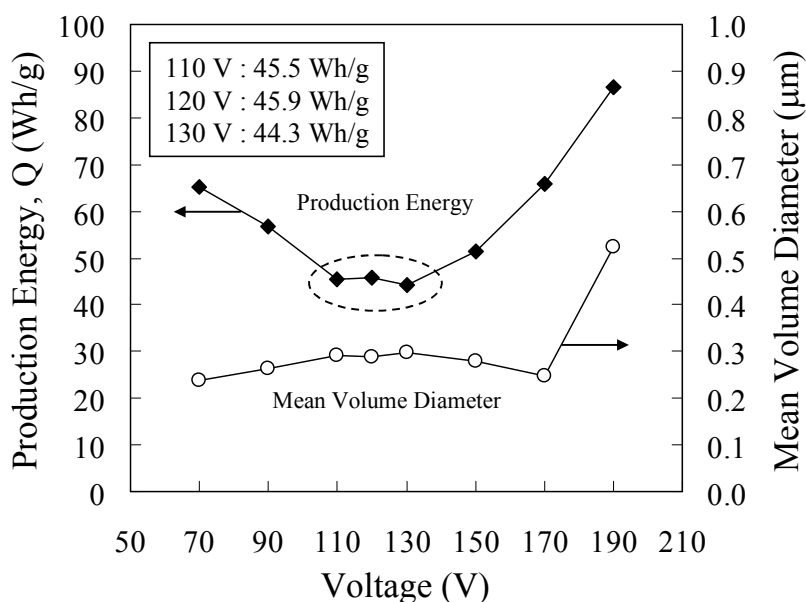


Figure 5-22 The amount of Sn-NPs synthesized in the process M (g) plotted as a function of the input power (Wh) and mean particle diameter (nm). The voltages ranging from 110 to 130 V are considered to be suitable for the effective production of Sn-NPs.

5.3.5. Synthesis of Sn-based Alloy nanoparticles

(i) Sn-Pb Eutectic alloy

In contrast to the solid solution alloy, the eutectic alloy is a phase-separated alloy, in which the crystal grains with different compositions exist in a bulk material. Therefore, in this study, we analyzed the effect of crystal grain size of the electrode on the properties of the synthesized nanoparticles. It is well known that the size of the crystal grains depends on the cooling temperature. In principle, quenching of the melted eutectic alloy results in the formation of smaller crystal grains. Figure 5-23 shows the cross-sectional SEM images of the electrode, obtained by detecting the backscattered electrons during SEM observation. Here, heavier elements such as Pb appear brighter. Compared to the as-received (not quenched) electrode, the crystal grain size of the quenched electrode was found to be relatively smaller. After the solution plasma synthesis of nanoparticles, the surface of the electrode was observed by using SEM. As can be seen from the SEM image, the surface of the as-received (not quenched) electrode became rough after electrolysis. On the other hand, the SEM image of the quenched electrode revealed a smooth surface after electrolysis.

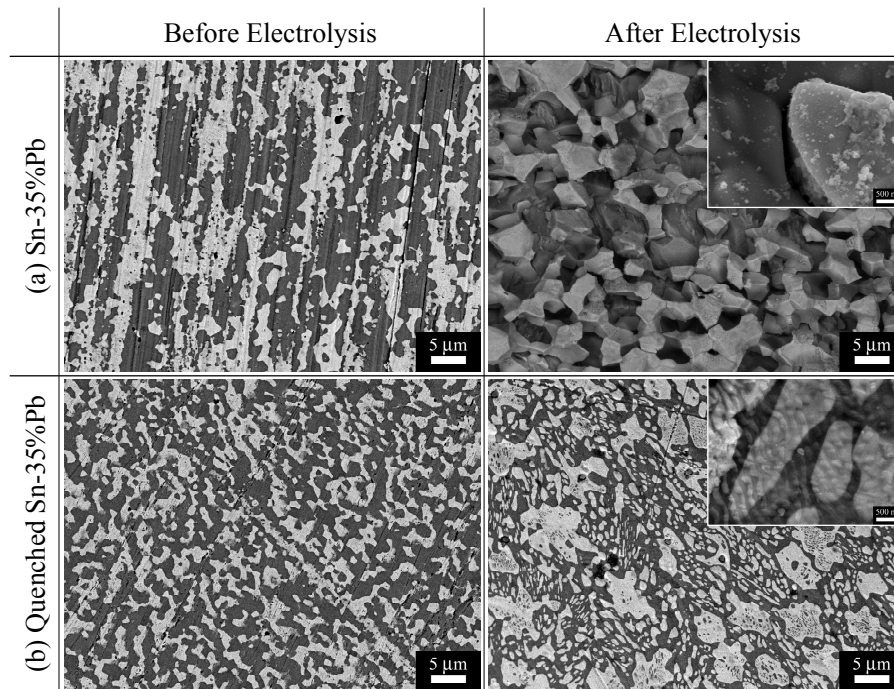


Figure 5-23 Cross-sectional SEM images of the Sn-35%Pb and quenched Sn-35%Pb electrode before/after electrolysis.

The particles synthesized from quenched and as-received electrodes were further characterized by using STEM. Figures 5-24 (a) and (b) show the STEM-HAADF images of the Sn-35%Pb nanoparticles. Similar to the backscattered composition image of SEM, the brightness of the STEM-HAADF image depends on the atomic number of the element. Therefore, the bright parts in the Fig. 5-24 (a) and (b) correspond to the Pb-rich phase. The EDX mapping of the particles shown in Fig. 5-24 (c) indicated the coexistence of both Pb-rich and Sn-rich phases in each particle. The particles were found to have a lamellar structure, which is one of the typical eutectic structures. Figures 5-25 (a) and (b) show the distributions of Pb composition with respect to Sn. In case of as-received electrode, the obtained particles were found to have a wide distribution of composition, with the average Pb content ranging from 35.0–46.9%. These results indicate that the Pb-rich grains were preferentially consumed, while the Sn-rich phases were remained on the surface of the electrode, due to the lower melting point of Pb when compared to Sn. In contrast, the composition of the particles synthesized from the quenched electrode was found to be similar to the starting composition of the wire owing to the small size of crystal grains. The XRD pattern of the particles shown in Fig. 5-25 (c) revealed the formation of metallic Sn and Pb, without any oxide phase.

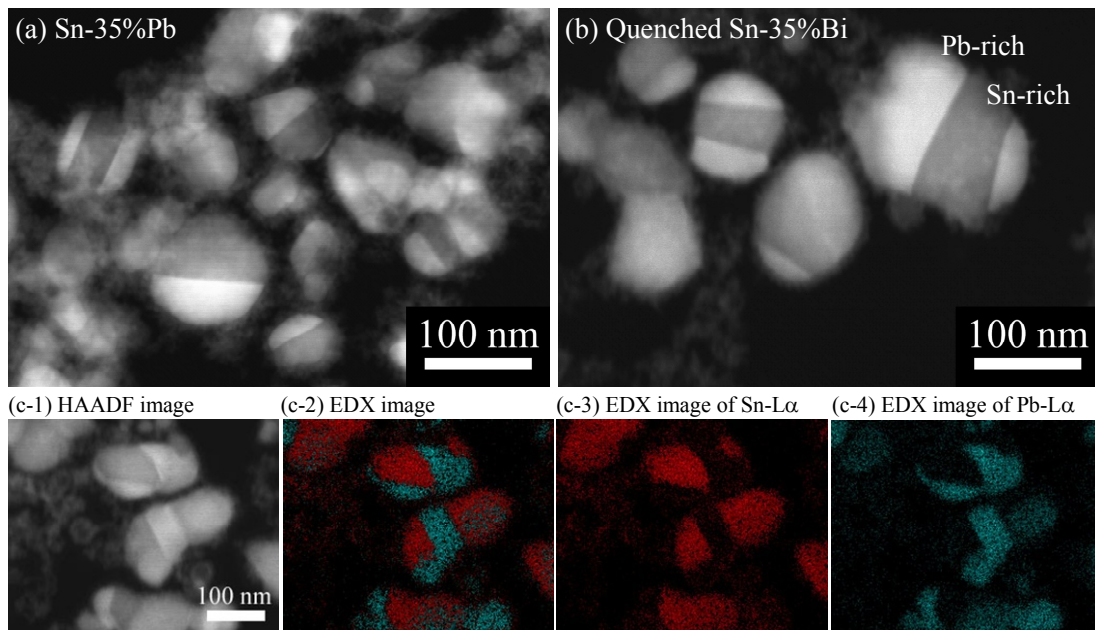


Figure 5-24 STEM-HAADF images of (a) Sn-35%Pb and (b) Quenched Sn-35%Pb nanoparticles. (c) HAADF image and corresponding EDX image of Quenched Sn-35%Pb nanoparticles.

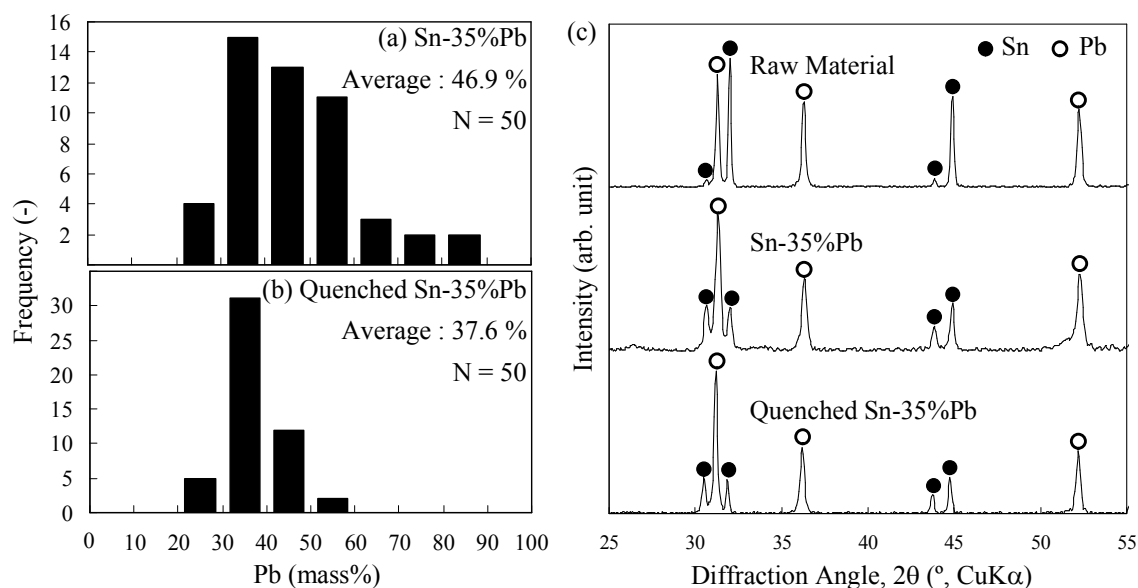


Figure 5-25 (a, b) Distribution of Pb compositions against Sn at Sn-35%Pb and quenched Sn-35%Pb products. (c) XRD patterns of the raw material, Sn-35%Pb and quenched Sn-35%Pb products.

(ii) Sn-Bi and Sn-Zn Eutectic alloy

Figure 5-26 shows the SEM images and XRD patterns of Bi-30%Sn and Sn-25%Zn. In both the cases, the obtained nanoparticles were spherical in shape, with the diameter being < 300 nm. In the case of Bi-30%Sn, the XRD pattern revealed the formation of metallic Bi and amorphous $\text{Bi}_2(\text{Sn}_2\text{O}_7)$. However, metallic Sn was not detected from the XRD pattern. On the other hand, the EDS analysis indicated that the amorphous phase consists of Sn and oxygen. Conversely, metallic Sn and ZnO were synthesized when Sn-25%Zn was used as a cathode. These oxides were precipitated during galvanic corrosion³⁵ of the cathode, after the formation of nanoparticles. When two metals are in direct contact in a conductive electrolyte, a process of galvanic corrosion occurs in which one metal acts as an anode and the other as a cathode. The electro-potential difference between the two metals provides the driving force for corrosion. According to the literature³⁶, standard oxidation-reduction potentials of Sn, Pb, Bi, and Zn are: $E^\circ_{\text{Sn}} (\text{V vs. SHE}) = -0.1375 [\text{V}]$, $E^\circ_{\text{Pb}} (\text{V vs. SHE}) = -0.1263 [\text{V}]$, $E^\circ_{\text{Bi}} (\text{V vs. SHE}) = 0.3172 [\text{V}]$ and $E^\circ_{\text{Zn}} (\text{V vs. SHE}) = -0.7626 [\text{V}]$. The electro-potential difference of 0.0112 [V] for the Sn-Pb couple is much lower than the 0.9 [V] of the Sn-Zn couple, and since the element with a lower oxidation-reduction potential is more readily oxidized, this explains why metallic Sn and

Zn oxide were formed from the Sn-Zn electrode. Similarly, metallic Bi and Sn oxide were formed in the case of the Sn-Bi electrode. In addition, the composition and temperature of the electrolyte, and the applied voltage also affects the oxidation of the products.

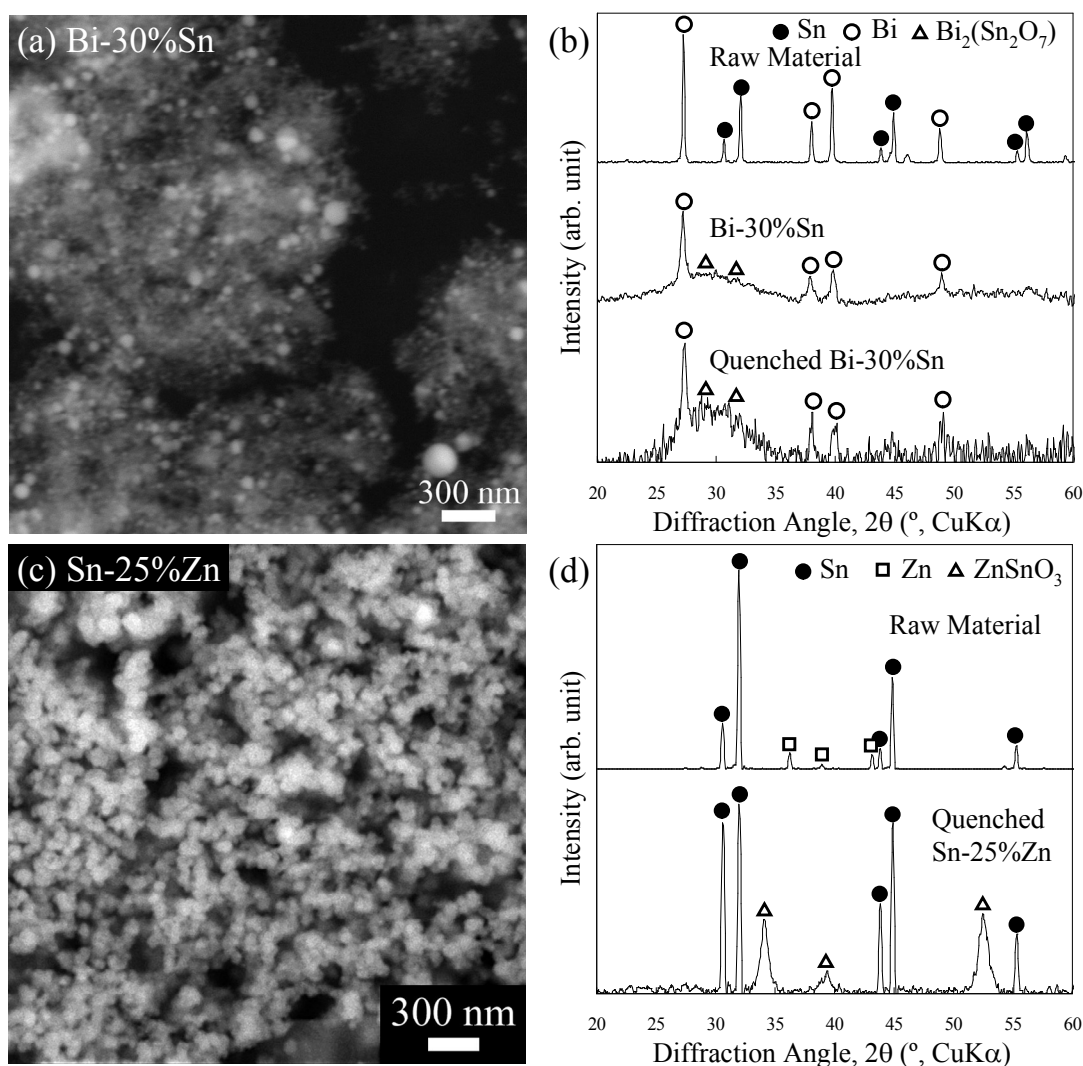


Figure 5-26 SEM image of the (a) Bi-30%Sn and (c) Sn-25%Zn nanoparticles . (b) XRD patterns of the raw material, Bi-30%Sn and quenched Bi-30%Sn products. (c) XRD patterns of the raw material and Sn-25%Zn products.

(iii) Sn-based Intermetallic Alloys

Furthermore, we investigated the powder processing for the Sn-based intermetallic alloys of SnSb, Cu₅Sn₆, and Ni₃Sn. In case of intermetallic alloys, wire electrode could not be fabricated due to its brittle nature. Therefore, electrodes were synthesized by arc melting and

were cut into thin sticks of dimension 2-3 mm x 2-3 mm x 30-50 mm. With the voltage of 150 V applied to the SnSb, Cu₅Sn₆, and Ni₃Sn electrodes, we could observe light-emission from the discharge plasma. Subsequently, nanoparticles were obtained by plasma solution synthesis using SnSb and Ni₃Sn electrodes. However, Cu₅Sn₆ electrode did not generate nanoparticles, as the experimental conditions, such as applied voltage, electrolyte, and so on, did not favor the formation of nanoparticles. The STEM-HAADF images of the SnSb particles shown in Figures 5-27 (a-d) indicate the formation spherical SnSb and colloidal oxide particles. In addition, the XRD analysis of the SnSb particles shown in Fig. 5-27 (e) reveal the presence of SnSb, metallic Sn, and SnO₂. The formation of SnO₂ phase could be attributed to the corrosion of the electrode with the oxidation-reduction potential of $E_{\text{sb}}^{\circ} = 0.1504$ [V]. In the case of SnSb, the color of the as-prepared sample was black. When the solution containing the sample was exposed to air for 24 h, the color of the sample turned white. In contrast, the use of ethanol reduces the oxidation of the sample. When Ni₃Sn was used as the electrode, spherical Ni₃Sn nanoparticles were obtained, as shown in Fig. 5-28 (a). Contrary to the case of SnSb, the XRD pattern (Fig. 5-28 (b)) of this sample indicated the formation of Ni₃Sn without any metallic Ni phase. These results suggest that some alloys tend to be oxidized by corrosion during the synthesis of nanoparticles, which needs to be circumvented.

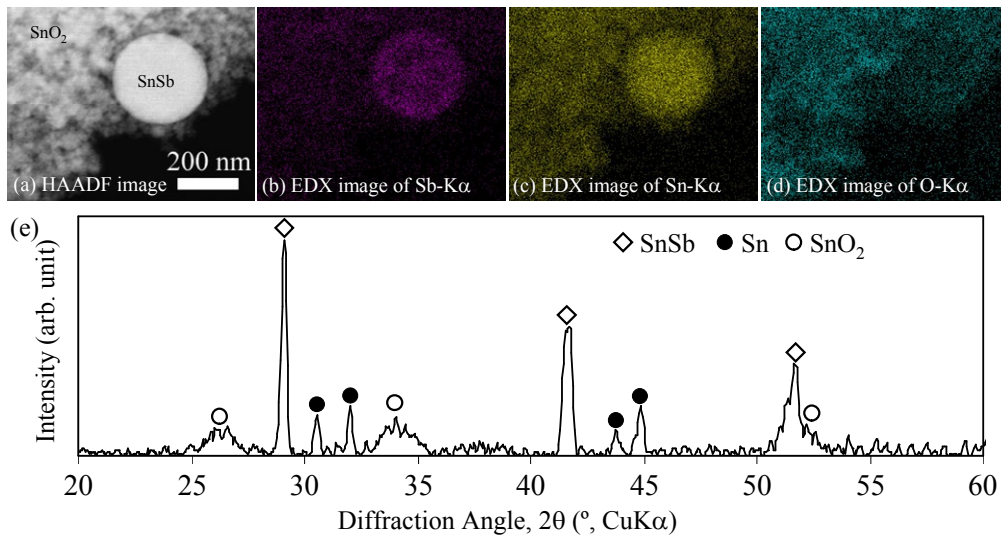


Figure 5-27 (a-d) STEM-HAADF image and corresponding EDX mapping of SnSb nanoparticles. (e) XRD pattern of the SnSb products.

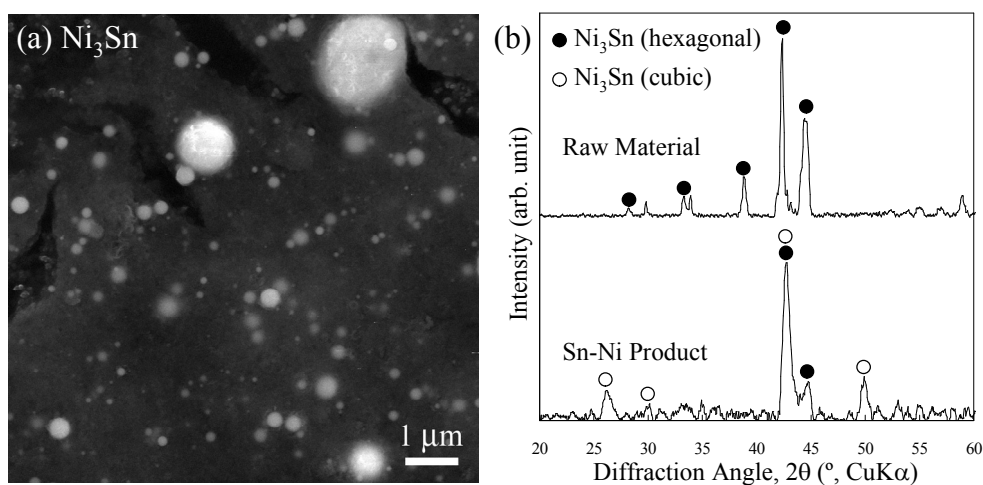


Figure 5-28 (a) SEM image of the Ni_3Sn nanoparticles. (b) XRD patterns of the raw material and Ni_3Sn products.

5.4 CONCLUSIONS

In this chapter, SnO plates, $\text{Sn}_6\text{O}_4(\text{OH})_4$ nanoparticles, Sn-NPs , and Sn -based alloy nanoparticles were synthesized by solution plasma using a metal wire. In the experiments, we adapted two routes; surfactant-assisted route and the use of KCl solution, for synthesis of Sn-NPs . The following conclusions were derived:

Surfactant-assisted route

1. At any cooling rate, a solution temperature above 95.0°C was effective for producing single-crystal SnO plates. In contrast, below 75.1°C , the products were colloidal nanoparticles of $\text{Sn}_6\text{O}_4(\text{OH})_4$.
2. SDS addition did not significantly affect the product. PVA addition significantly stabilized $\text{Sn}_6\text{O}_4(\text{OH})_4$ octahedrons.
3. Sn-NPs were synthesized in the presence of different concentrations of surfactant (CTAB). At a high concentration of $200 \times 10^{-6} \text{ g}\cdot\text{ml}^{-1}$ of CTAB , the yield of Sn-NPs was found to be 150 mg. SEM and TEM observations indicated that the diameter of prepared Sn-NPs was $<200 \text{ nm}$, and the particle surface was partially oxidized.

4. Electrochemical studies revealed that the discharge capacity of the sample Sn-NPs 30% was $414 \text{ mAh}\cdot\text{g}^{-1}$ after 20 cycles.

KCl solution route

1. The particle size of Sn-NPs decreased with a decrease in the concentration of the electrolyte. The optimum concentration required for the formation of small Sn particles was determined to be 0.05 M.
2. At the optimum concentration of 0.05 M, effective production energy of 45 Wh/g was obtained for the applied voltages ranging from 110 to 130 V. Higher voltages over 170 V induced the oxidation of the particles.
3. The alloy particles of Bi-30%Sn, Sn-25%Zn, and SnSb were found to be oxidized due to galvanic corrosion. However, when the electro-potential difference between the metals is small, as in the case of Sn-Pb, this oxidation of the product is significantly reduced.
4. The compositional analysis of the eutectic Sn-35%Pb nanoparticles prepared in this study showed the coexistence of Pb-rich and Sn-rich phases. The uniformity in the composition of the alloy was found to depend on the size of the crystal grains of the electrode. More qualitatively, electrode with smaller grain size favored the formation of nanoparticles with uniform compositions.

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CHAPTER 6

Solution plasma diagnostics during nanoparticles synthesis

ABSTRACT : The solution plasma during nanoparticles formation was analyzed using a spectroscopic measurements, electrical measurement, and high-speed camera observation to investigate the effects of edge shielding, applied voltage, and electrode material on the plasma. When the edge of the Ni electrode wire was shielded by a quartz glass tube, a plasma was uniformly generated while metallic Ni nanoparticles were generated. The emission spectrum from this electrode contained OH, H α , H β , Na, and O lines. Without an edge-shielded electrode, infrared radiation continuously radiated at the electrode edge such that the products were partially oxidized owing to the high temperature. The excitation temperature was estimated by applying the Boltzmann plot method. When the voltages were varied with different electrolyte concentrations, the excitation temperature increased with an increase in the voltage: (voltage, concentration, excitation temperature) = (50 V, 5.0 M, 3400 K), and (250 V, 0.05 M, 7000 K). The size of the Ni nanoparticles decreased at high excitation temperature. According to the high-speed observation, many light-emitting points appeared on the metallic plate and immediately disappeared when a certain point was strongly heated to produce nanoparticles. Additionally, light emission points moved in a chain reaction; after the first emission point was generated, the next emission point tended to be generated in the space surrounding the first emission point. The change in current and voltage during plasma initiation were analyzed to optimize the experimental conditions. Pre-warming of the electrolyte is quite effective in generating plasma at lower electric power. Additionally, Plasma generation required higher electric power than that for maintaining the plasma. These findings will contribute to the upscaling of discharge electrolysis.

6.1 INTRODUCTION

Plasma generation in a liquid is currently being investigated for application in a variety of fields such as nanoparticles synthesis¹⁻³, hydrogen production⁴, surface modification⁵, polymerization⁶, and the decomposition of harmful dissolved substances⁷⁻¹⁰. For controlling and developing solution plasma, plasma diagnosis has become much more important. Many methods for plasma diagnosis, such as electrical measurement, optical emission spectroscopy (OES) containing the broadening of a spectral line, Langmuir probes, and laser irradiation have been proposed in a past¹¹. Among the various methods, OES is one of the most used diagnostics for a liquid plasma¹². The emission spectra depended on the constituent elements of the electrolyte and electrode materials^{13, 14}. The analysis of a light emission spectrum from a plasma has revealed the excitation temperature, current density, and active radicals that constitute the plasma. Furthermore, the plasma behavior can be clarified through high-speed imaging. High-speed imaging has been applied for observing plasma in liquid^{3, 15-18}. However, it is difficult to observe the surface of a wire electrode by using a high-speed camera because the surface of conventional wire electrodes is very small and not flat. Meanwhile, in the light of initiation and maintaining plasma under limiting conditions, the understanding of the relationships between conductivity, electric power, and current has become very important. However, in spite of their importance, the relationships between such parameters have not been well understood.

In this study, spectroscopic measurements of a solution plasma using direct current were performed during nanoparticle synthesis. In the experiments, the effects of edge-shielding, applied voltage, and electrode material on the plasma were mainly investigated. The excitation temperature was estimated from the emission spectrum by applying the Boltzmann plot method with the assumption of local thermodynamic equilibrium (LTE). Observations by a high-speed camera were carried out to investigate the plasma generation on a flat metallic plate. Furthermore, the electric power and voltage required for plasma formation were investigated at different electrolyte temperatures and concentrations. Based on the obtained results, plasma formation method for large electrode surface areas was proposed.

6.2 EXPERIMENTAL SECTION

6.2.1 Experimental Setup

(i) Effect of edge-shielding

When the electrode has an edge similar to the tip of a wire, the transition from a partial-plasma region to a full-plasma region occurred with the strong emission of light. This transition might be caused by the current concentration at the edge induced by a highly inhomogeneous electric field. In this study, the effect of edge-shielding on the plasma condition and products was investigated. Figure 6-1 shows the experimental apparatus used for the experiments under stable power supply conditions (ZX800H, Takasago). A platinum wire of length 1000 mm, diameter 0.5 mm, and purity 99.98 mass% (Nilaco) was used as the anode. A nickel wire of diameter 1.0 mm and purity 99 mass% (Nilaco) was used as the cathode. It was shielded by a quartz glass tube of inner diameter 1.1 mm in order to obtain an exposed length of 10 mm; the exposed part functioned as the actual electrode. We used two types of cathode: (a) without an edge-shield, or (b) with an edge-shield [see Figs. 6-1(a) and 6-1(b)]. We shielded the tip of the electrode as shown in Fig. 6-1(a) to suppress the transition. The distance between the electrodes was kept at 30 mm. The electrolytes used were 0.1 M NaOH solutions. The solution temperature at a depth of 10 mm was recorded every 5 s using a polymer-coated thermistor thermometer (Ondotori TR-71Ui, T&D, Nagano, Japan).

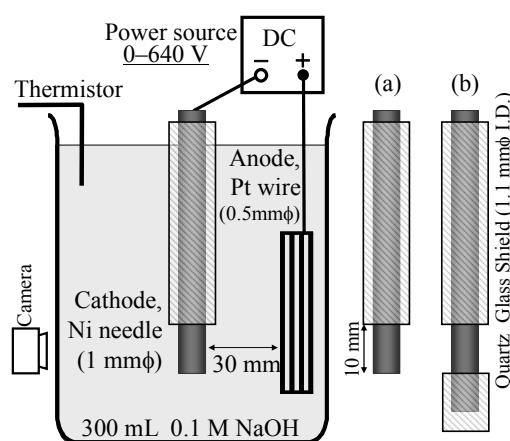


Figure 6-1 Schematic diagram of the experimental apparatus. As the cathode, one of two nickel needles, (a) no edge-shield, or (b) with an edge-shield, was immersed and a voltage was applied up to 180 V. In case (b), the shield resulted in only an exposed part of length 10 mm acting as an electrode. The anode was a platinum wire of length 1000 mm and diameter 0.5 mm; the distance between the electrodes was kept at 30 mm.

(ii) Effect of applied voltage

When the applied voltage was investigated, the electrode was Ni wire with the edge-shield. The concentrations of the NaOH solutions varied from 0.001 to 5.0 M for changing the applied voltages. The applied voltages were varied at each concentration.

(iii) Effect of electrode materials

When the effects of the electrode material were investigated, the cathode materials were wires comprised of Ti, Fe, Ni, Cu, Zn, Zr, Nb, Mo, Pd, Ag, W, Pt, Au, and various alloys of stainless steel and Cu–Ni alloys. The upper and lower parts of the cathode were shielded by a quartz glass tube to maintain the exposed length at 10 mm. The electrolyte was 0.1 M NaOH solution.

(iv) Metal plate electrode for camera observation

To realize the observation of the electrode using a high-speed camera, DC discharge plasma was generated on a flat metallic plate. The experimental setup consisted of two electrodes in a square-shaped glass cell to eliminate the effect of light refraction. When the metallic plate without any covers was directly immersed in an electrolyte, the discharge primarily occurred at the edge of the plate because the current tends to concentrate on the edge of the electrode. To limit the area of plasma discharge on the electrode plane, a quartz glass holder was used to cover the whole surface of the cathode electrode plate, except for the hole on the electrode plate, which had a 14-mm diameter, as shown in Fig.1. Metallic plates of Au, Ni, Ti, and Zn with thicknesses of 0.2 mm were inserted in this glass holder. The counter electrode was a platinum wire of length 1000 mm and diameter 0.5 mm. A 0.1 M NaOH solution was used as the electrolyte.

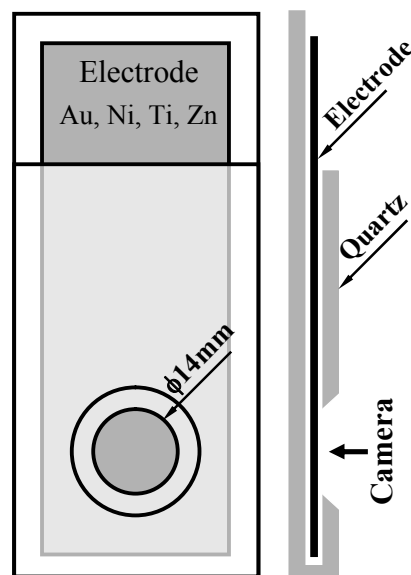


Figure 6-2 Schematic diagram of the cathode electrode. The quartz glass holder covers the whole area of the electrode plate, except for a hole on the electrode plate of diameter 14 mm.

(v) Electrical measurement

* I deferred the Internet publication of this section.

6.2.2 Characterizations

Light emission from the plasma was measured using a visible-light spectrophotometer (USB 2000+, Ocean Optics) with an observation range from 200 to 850 nm. A high-speed camera (Photoron FASTCAM SA5, 1/20000 s) was used to reveal the plasma conditions. After electrolysis, the products were collected by centrifugation and washed with deionized water. Subsequently, the products and post-experiment cathode wires were observed using a JSM-7001F (JEOL) field-emission scanning electron microscope (SEM). The particles were characterized by XRD using a Miniflex II (Rigaku, Tokyo, Japan) diffractometer. Particle size-distributions were obtained from TEM images of the products by using a H-700 (HITACHI, Tokyo, Japan) microscope. To measure the particle diameter, the four samples for TEM observation were prepared. The mean diameters were evaluated on the basis of volume.

6.3 RESULT AND DISCUSSIONS

6.3.1 Effects of edge shielding on the Ni electrode

The experiments were repeated each three times at same condition and named “No Edge-Shield-1”, “No Edge-Shield-2”, “No Edge-Shield-3”, “Edge-Shield-1”, “Edge-Shield-2” and “Edge-Shield-3” to guarantee the reproducibility. Figure 6-4 shows the histories of the currents for different electrodes. For both electrodes, a glow discharge with light emission occurred at approximately 120 V. Figure 6-5 (a) shows the spectra of the plasma and the photographs of the Ni electrode. The intensity of light emission increased with increasing voltage, which means that the net area of the discharge increased with increasing voltage. As with other reports^{13, 14, 19}, the strong emissions of H_{α} (656 nm) and H_{β} (486 nm) as the Balmer atomic hydrogen lines and the OH A $^2\Sigma^+-X^2\Pi$ (0, 0) band (309 nm) and O (777 nm) were detected. The strong emission of Na (589 nm) was derived from the NaOH electrolyte solution. The emissions from the Ni electrode (341, 357, 362 and 386 nm) relatively increased at a higher voltage because of the increase in the electrode temperature. Without edge shielding, the transition to a full plasma occurred at approximately 173 V. After the transition to a full plasma, the current increased from 0.37 A to 0.51 A. The emission spectra at 180 V under full-plasma conditions exhibited strong infrared radiation, which suggested that the Ni electrode was strongly heated owing to the high input power induced by the higher current flow.

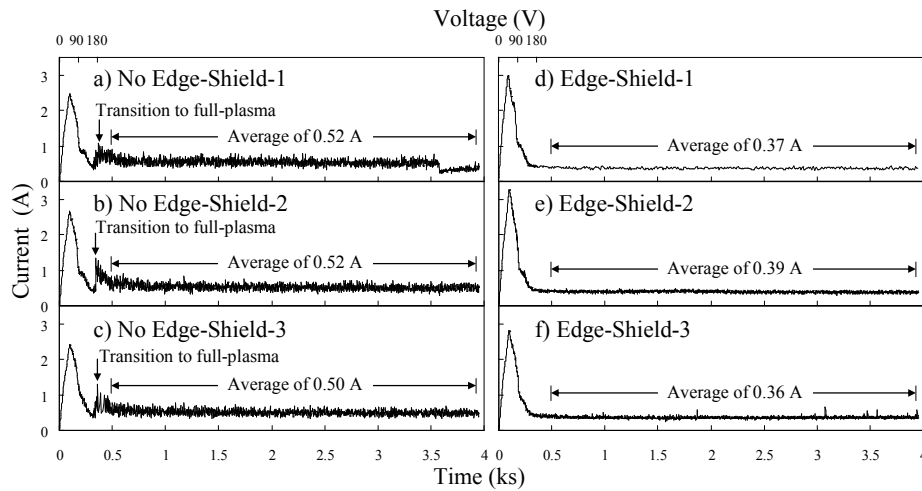


Figure 6-4 Histories of current. The voltage was applied at a rate of 0.5 V/s up to 180 V. [(a)-(c)] The transition to full-plasma from the electrode tip occurred at 173 ± 2 V. The average current was 0.51 ± 0.01 A. [(d)-(f)] The transition to full-plasma was suppressed by the edge-shield. The average current was 0.37 ± 0.02 A.

* I deferred the Internet publication of this section.

Figure 6-7 summarizes the XRD patterns of the products. The no-edge-shielded electrode produced both metallic nickel and nickel oxide. In contrast, the products produced by using the edge-shielded electrode didn't contain the nickel oxide. Obviously, the transition to full-plasma enhanced oxidation of the product due to higher temperature and the edge-shielded electrode was effective in suppressing the transition.

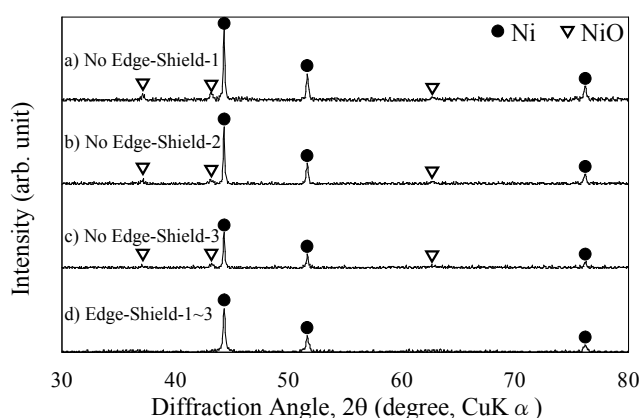


Figure 6-7 XRD patterns of the products from the two cathodes without the edge shielded (a)-(c), and with the edge shielded (d). The no-edge-shielded electrode produced both metallic nickel and nickel oxide. In contrast, the products produced by using the edge-shielded electrode didn't contain the nickel oxide.

Figure 6-8 shows TEM images of the products (left) and the electrode nickel needles (right). All the products were spherical, and the smallest particle-size was less than 20 nm. The results suggested that the electrode surface was locally heated and momentarily exceeded the melting point, and the molten metal yielded to a spherical shape due to surface tension. In using no edge-shielded electrode, particles with the diameter of more than 1 μm were contained and the surface of the wire showed many cracks, which were probably caused by thermal expansion due to the transition to full-plasma. Coarse particles with a diameter over 1 μm attached to the electrode surface. In contrast, in using edge-shielded electrode never had any cracks or coarse particles. We also observed that regular patterns appeared on the electrode surface in the edge-shielded. This implied that nanoparticles grew at projections (see white arrows in Fig.6-8) and then peeled from the projections to become particles. Figure 6-9 shows particle

size-distributions of the products which were evaluated by TEM images. The use of an edge-shielded electrode decreased the volume mean diameter of the product, to 220 nm, in contrast to the use of an electrode without an edge-shield, where the one was 890 nm, in which mean diameters were calculated using three dates. The suppression of coarse particles had an influence on the mean diameters. The number mean diameter was 85 nm in using edge-shielded electrode, which diameter was small compared to the reported data by Toriyabe et al.(2007)¹. Toriyabe et al. reported that the product size decreased with increasing the voltage, but the transition to full-plasma easily occurred when voltage was high. Thus, the edge-shield was quite effective for the decrease of product size. Transition to full-plasma influenced not only the product size, but also nanoparticles production, which was reduced in the no-edge-shield case, as shown in Fig. 6-10. The mass of production after 1 hour were 15 ± 2 mg in no-edge-shield case, and 1.7 ± 0.5 mg in edge-shield case. This difference can be explained by the increasing a gas volume and a high temperature.

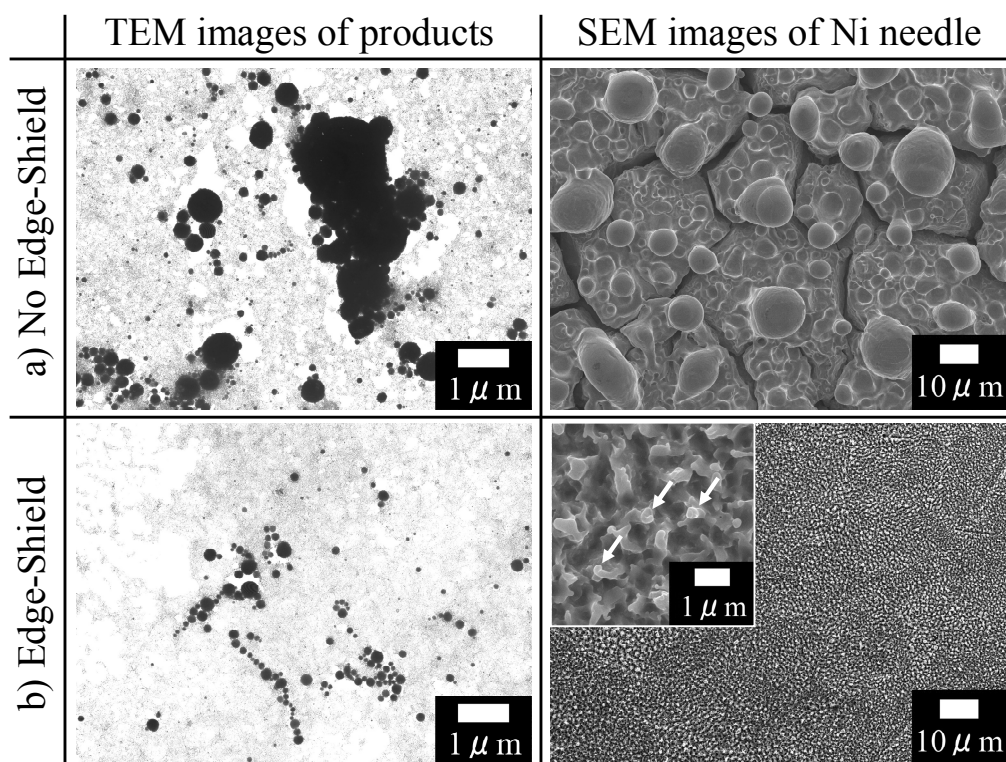


Figure 6-8 TEM images of the product (left) and SEM images of the surface of the nickel needle (right) when the edge-shield was used/not used. All the products were spherical, and the smallest particle-size was less than 20 nm.

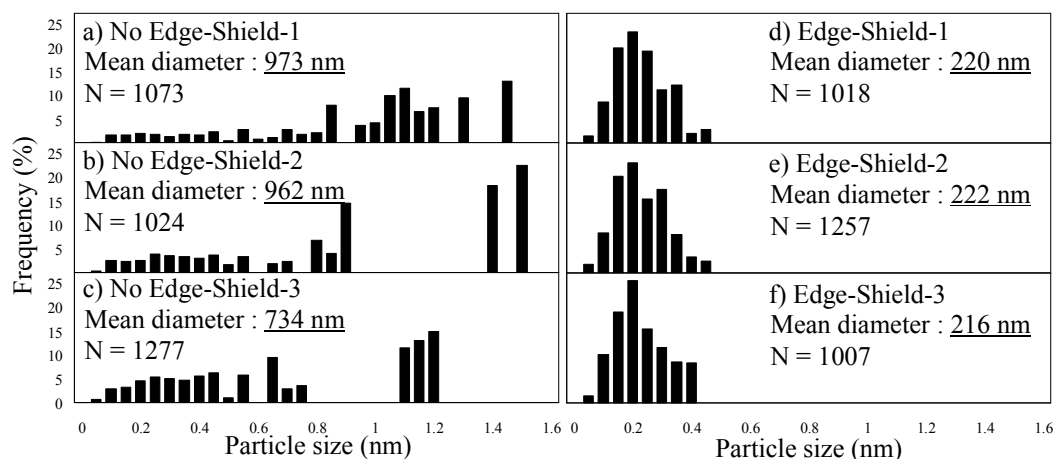


Figure 6-9 Particle size-distributions of the products, measured from TEM images of the products, together with the mean diameter based on volume and the sample number N. The use of an edge-shielded electrode decreased the volume mean diameter of the product, to 220 nm, in contrast to the use of an electrode without an edge-shield, where the one was 890 nm, in which mean diameters were calculated using three dates.

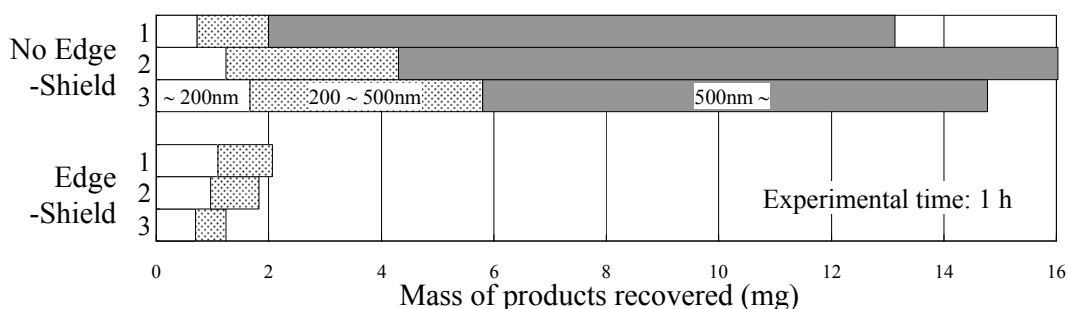


Figure 6-10 mass of products recovered after 1 hour were 15 ± 2 mg in no-edge-shield case, and 1.7 ± 0.5 mg in edge-shield case. Large particles of diameter over 500 nm reached as much as 73 ± 12 mass% without the edge-shield.

Possible effect of transition to full-plasma was discussed on the basis of the experimental data. According to the experiments results, the current increased to 0.51 ± 0.01 A from 0.37 ± 0.02 A with transition to full plasma. In addition, a video of electrode surface taken by using a high-speed camera revealed that the net area of plasma is small before transition to full-plasma. But after the transition to full-plasma, the whole area of electrode emitted light. Without edge-shield, the edge of the electrode was heated higher than the side of the electrode since the electric field concentrated to the edge. After that, the full-plasma was generated from the edge, and it expanded to the whole area of the electrode. On the other hand, the surface of the

electrode with the edge-shield was uniformly heated because of avoiding the concentration of the electric field to the edge. Partially shielding of the cathode suppressed the transition to full plasma. In using edge-shielded, the net area of plasma is small and plasma area moves quickly to keep the surface temperature low. In such case, formed nanoparticles were cool-downed quickly without agglomeration.

6.3.2 Effects of the Electrolyte Concentration and Voltage

* I deferred the Internet publication of this section.

6.3.3 Effects of the electrode material

* I deferred the Internet publication of this section.

6.3.4 High-speed Camera Observation of plate electrode

In this section, the DC discharge plasma was generated on a flat metallic plate to realize the observation of the electrode using a high-speed camera. The typical changes in current and voltage are shown in [Fig.6-17 \(a\)](#); [Fig.6-17 \(b\)](#) shows the corresponding condition of the surrounding cathode. When the applied voltage was relatively low, a type of electrolysis of water occurs at the interface between the cathode and the solution. The current is increased with increasing voltage in accordance with Ohm's law. Because the resistance heating is concentrated at the cathode/solution interface, the solution near the cathode is heated to the boiling point and a gas layer containing hydrogen gas and vapor is generated. Once the gas layer is generated at the surface of the cathode, the current cannot increase any more and thereafter decreases because the cathode electrode and the solution do not touch each other. If the voltage is sufficiently high, a glow discharge with intense light emission starts in the gas-layer. The electrons in the plasma layer are accelerated under

a high electric field and impact a neutral atom to excite it. This excited atoms drop down immediately to a stable energy level by emitting light. The surface of the electrode partially melts to produce nanoparticles owing to the concentration of current causes by the electrothermal instability^{16,17}. Fig. 6-17(c) shows the concentration mechanism of current. If the temperature at a certain point is larger than that in the surrounding area, the conductivity of plasma becomes high. The current increases due to the high conductivity of the plasma. The spot, where the current concentration occurs, is heated exclusively. Eventually, the cathode melts or ionizes at the spot to form nanoparticles.

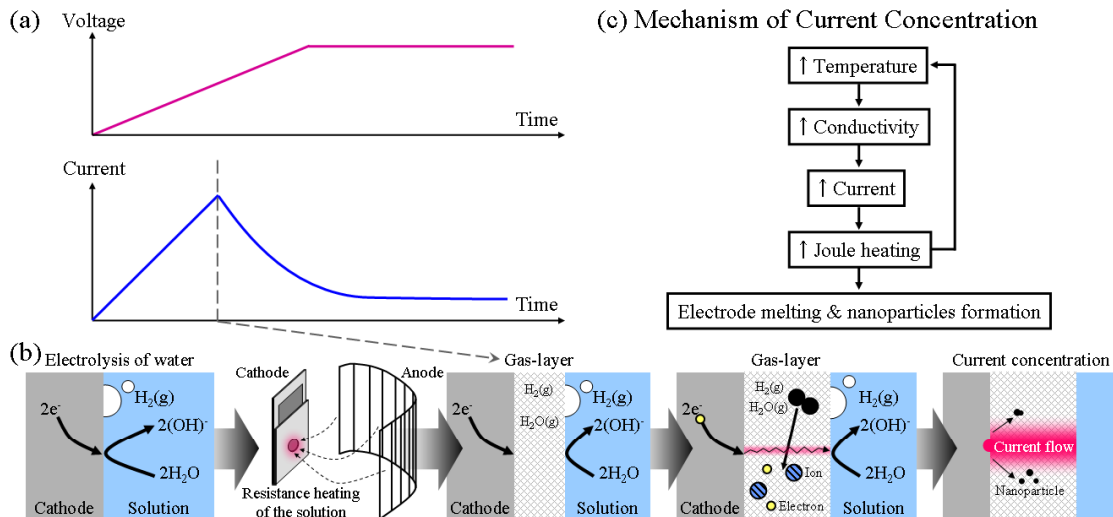


Figure 6-17 (a) Typical changes in current and voltage during electrolysis. (b) Formation mechanism of nanoparticles during solution plasma. (c) Concentration mechanism of current. If the temperature at a certain point is larger than in the surrounding area, the conductivity of plasma becomes high. The current increased induced by the high conductivity. The spot of current concentration was heated extra. Eventually, the cathode melted and formed nanoparticles.

The photographs shown in Fig.6-18 display the light emission from the Au, Ni, Ti, and Zn electrodes. From these photographs, it is clear that the discharge plasma was successfully generated on the electrode surface. Generated water vapor was attached to the upper part of the hole, which prevented the plasma generation at this part. Therefore, the emission intensity from the upper part was lower than that of the lower part. In the optical emission spectroscopy results shown in Fig.6-19, strong emissions of H_α (656 nm), H_β (486 nm) (Balmer atomic hydrogen

lines), OH A $^2\Sigma^+-X^2\Pi$ (0, 0) band (309 nm), and O (777 nm) were detected. Strong emissions of Na (589 nm) derived from the NaOH electrolyte solution. The emissions from Au (312 nm), Ni (341, 357, 362, 386 nm), Ti (324, 334 nm), and Zn (330, 335, 468, 472, 481 nm) were also detected. The emission intensity from the elements changed for each electrode material. In the cases of Au and Ni, the intensities from H and OH were stronger than the emission from the electrode element. In contrast, strong emission lines from Ti and Zn were observed with the Ti and Zn electrodes. This difference is probably caused by the properties of each element.

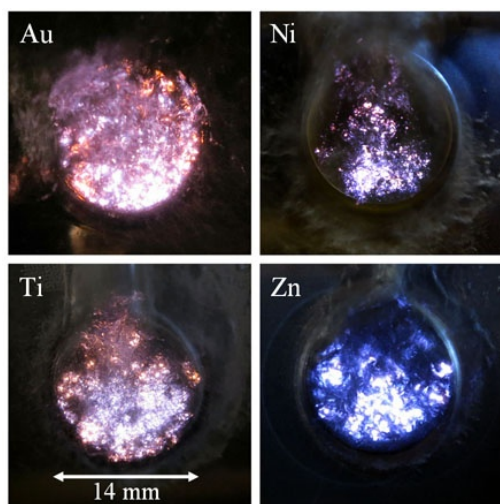


Figure 6-18 Photographs of each electrode plate taken using a digital camera during discharge. The quartz glass holder covers the whole area of the electrode plate, except for a hole on the electrode plate of diameter 14 mm.

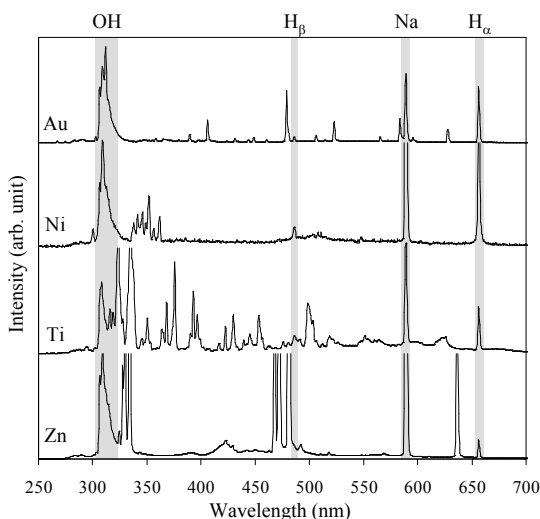


Figure 6-19 Spectra of plasma for each electrode material observed with 0.1 M NaOH and 190 V conditions.

Figure 6-20 shows sequential images of the electrodes taken using the high-speed camera with a frame rate of 20000 fps. In these images, the plasma appears as points, rather than as a layer structure. The total discharge area is very small. These light-emitting points correspond to current-concentration points depicted in **Fig.6-17 (b)**. The large current is concentrated at a certain point, which induces the ionization of various species. From the videos taken using the high-speed camera, the starting point of light emission seems to be random, and emission points disappeared very quickly, within a few hundred microseconds and there was regularity in the

movement of light emission. After the first emission point was generated, the next emission point tended to be generated in the space surrounding the first emission point. In the Ni case, the light-emitting points moved in a linear manner. The light emission from Zn slowly spread in a circle. These results revealed that the current-concentration occurred in a chain reaction.

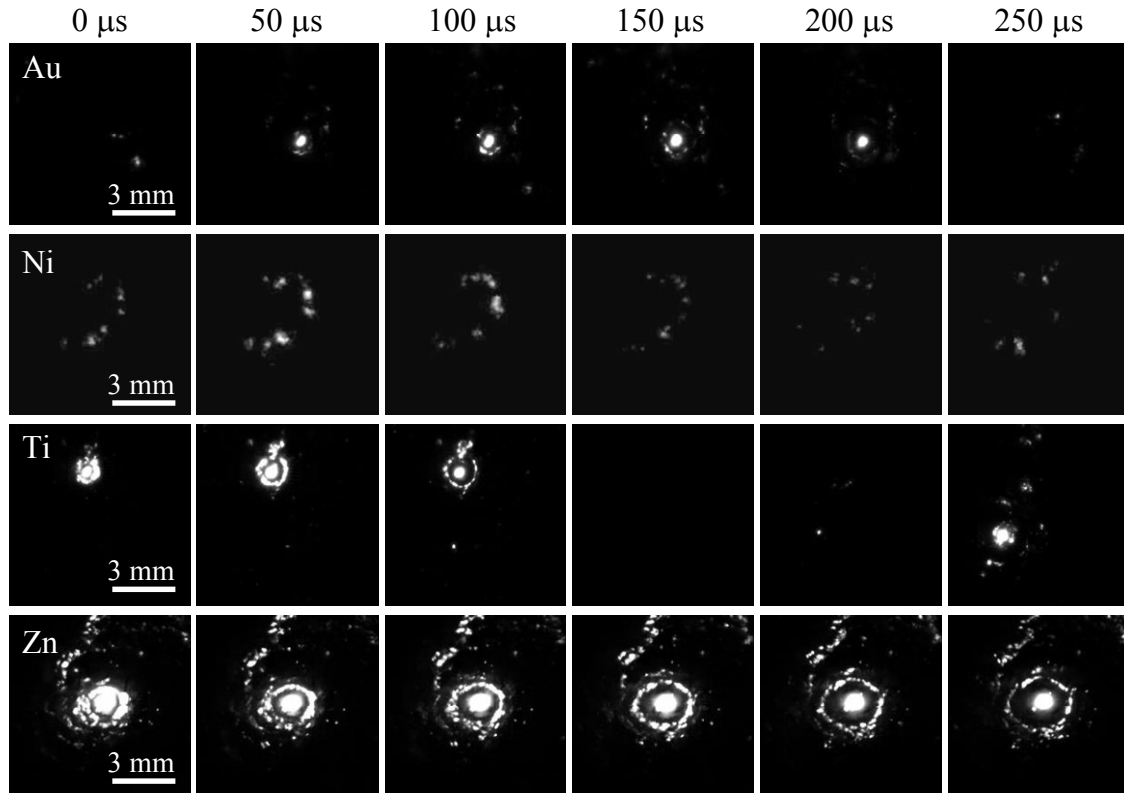


Figure 6-20 Sequential images of the plasma generated on the electrode plate, taken using a high-speed camera with a frame rate of 20000 fps.

From the high-speed observation, we predicted the formation and extinction mechanism of plasma emission, as shown in Fig.6-21 (a). First, the current concentration occurred at a certain spot. If the current at a certain spot is larger than the current in the surrounding area, the temperature of this spot increases because of the higher current, and then the conductivity of the plasma increases because of the high temperature. The increase in temperature at a certain spot induces a large current flow, which increases the temperature further. When the temperature exceeds the melting point of the electrode material, the electrode melts and nanoparticles form (STEP 1). Second, heat diffusion extends the concentration spot (STEP 2). Subsequently, the

current concentration spot disappears because the temperature distribution becomes uniform owing to the heat diffusion (STEP 3).

After producing particles in the experiment, the electrodes were observed through SEM and TEM. According to Fig.6-21 (b), holes were formed on the surface of Au, Ni, and Ti electrodes (see arrows). The current concentration strongly heated a certain spot of the electrode, and the electrode momentarily melted or vaporized. This condition is more similar to a microscale arc or spark region than a glow discharge plasma³². In the case of Zn, rod-like structures were attached to the electrode surface. From the TEM observation of the products, it is clear that the Au, Ni, and Ti electrodes produced spherical nanoparticles. From the X-ray and electron diffraction, it can be seen that Au and Ni have a metallic phase. The product from the Ti electrode was oxidized because of high-temperature corrosion. The Zn electrode produced rod-like ZnO particles. As reported previously³³, the precursor of rod-like ZnO is $\text{Zn}(\text{OH})_4^{2-}$, which is formed around the electrode at high temperatures. When the ZnO precipitated, ZnO crystals grew preferentially along the $[0\ 0\ 0\ 1]$ direction. The ZnO nanorods also grew on the surface of the Zn electrode.

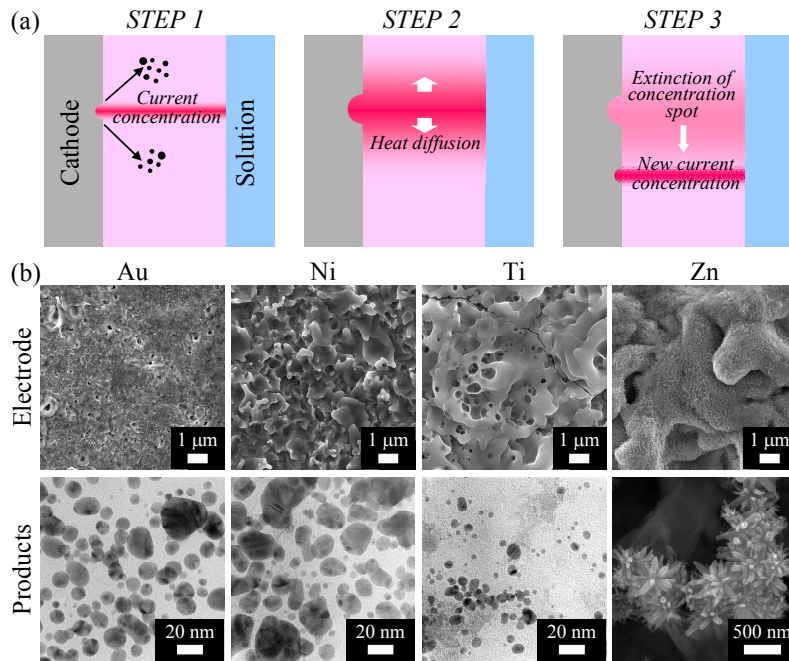


Figure 6-21 (a) Formation and extinction mechanism of the current concentration. (b) Images of the electrode surface after discharge and particle production, obtained through SEM and TEM.

6.3.5 Controlled plasma generation at different electrolyte temperatures

* I deferred the Internet publication of this section.

6.4 CONCLUSIONS

Optical Emission Spectroscopy

* I deferred the Internet publication of this section.

High-speed Camera Observation

1. Solution plasma is not a layer structure but consists of points that appeared and disappeared within a few hundred microseconds.
2. The current concentration strongly heated a certain spot of the electrode, which momentarily melted or vaporized.
3. Microscopic phenomenon of solution plasma in liquid is more like a microscale spark or arc plasma, rather than glow discharge plasma.

Electrical measurement

* I deferred the Internet publication of this section.

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General Conclusion

The large number of papers published over the last few years on atmospheric solution plasmas emphasizes the increasing interest in this particular field of plasma physics and chemistry. Plasma in liquids is currently being investigated for application in a variety of fields such as nanomaterials synthesis, hydrogen production, polymerization, and decomposition of dissolved harmful substances. These methods offer the following advantages: (1) use of simple equipment without the stringent need of vacuum chamber, (2) no requirement of gas supply, (3) use of readily available precursors, (4) facile separation of the products in solution. However, it still has many problems, despite its quite significance in nanotechnology. Methods for controlling the size and composition of the various nanomaterials have not been well understood. Additionally, the solution plasma during nanomaterials synthesis has not been fully characterized. Thus, the control of plasma is still difficult. In this thesis, the controlled synthesis of various metal, oxide and alloy nanomaterials was reported. The electrochemical properties of the synthesized nanomaterials were analyzed. Finally, the control of plasma initiation and maintaining were investigated based on the plasma diagnosis.

In Chapter 1, a general introduction was provided. The generations, applications and diagnostics of various solution plasmas were reviewed.

In Chapter 2, the Ni nanoparticles formation and surface morphology of Ni electrode was investigated. When the voltages were below 140 V, surfaces with nanoparticles attached, called “Particles” type surfaces, were formed on the electrode. These surfaces changed and displayed ripples, turning into “Ripple” type surfaces and the nanoparticle sizes increased. In contrast, at voltages over 160 V, the surfaces of the electrodes were either “Random” or “Hole” type, and the particle sizes were constant at different amount of nanoparticles produced. The ripple patterns were formed on all planes, except (111)- and (100)-oriented planes; their direction was [001]. In this study, we found a strong connection between the production and the

electrode surface. Additionally, results suggested that the particle size is controllable by changing the crystallographic face of an electrode.

In Chapter 3, the Cu, CuO, and Cu-based alloy nanoparticles were synthesized, in which the effect of the electrolyte and electrolysis time on the morphology of the products was mainly examined. The results demonstrated that by using the K_2CO_3 solution, Cu wire produced CuO nanoflowers with many sharp nanorods, the size of which decreased with decreasing the concentration of the solution. Spherical particles of copper with/without pores formed when the citrate buffer was used. In the case of Ni-Cu wire, synthesized nanoparticles have a uniform distribution in composition.

In Chapter 4, the synthesis of ZnO nanocrystals using solution plasma was studied. The product morphology depended strongly on the concentration, C , and the voltage, V ; that is, no product was obtained when $(C, V) = (\geq 1.0 \text{ M}, \leq 60 \text{ V})$, nanoflowers when $(C, V) = (1.0 \text{ M}, 66 \text{ V})$, $(0.5 \text{ M}, 80 \text{ V})$, $(0.1 \text{ M}, 105 \text{ V})$, and coarse particles when $(C, V) = (\leq 0.1 \text{ M}, \geq 110 \text{ V})$. Use of agitation led to spherical products, i.e., coarse metallic Zn and amorphous ZnO nanospheres. Melting and vaporization of the electrode produced particles. ZnO nanoflowers grew on the surface of spherical particles by precipitation from $Zn(OH)_4^{2-}$ ions. Because of their defects, ZnO nanoflowers and amorphous ZnO showed strong green emissions when irradiated at 325 nm. The 700 °C annealed ZnO nanoflowers had higher photocatalytic activity than as-prepared product. These findings are applicable not only to zinc but also to other metals and alloys.

In Chapter 5, the optimum experimental conditions required for the synthesis of Sn nanoparticles (Sn-NPs) was examined. When the applied voltage was 400 V in a 0.001 M K_2CO_3 solution without surfactant, Single-crystalline tin oxide (SnO) plates were synthesized. Quenching the solution affected the product size. The addition of poly(vinyl alcohol) (PVA) significantly stabilized the $Sn_6O_4(OH)_4$ octahedrons. The metallic Sn nanoparticles were synthesized in the presence of the surfactant, cetyltrimethylammonium bromide (CTAB).

Electrochemical properties of SnO plates and Sn-NPs were analyzed for use as an anode material in Li-ion batteries. A composite of Sn-NPs and graphite enhanced the cyclic stability owing to the buffer space provided by the graphite for volume expansion. In the case of the 30 wt% loaded Sn-NPs, the capacity was measured to be $414 \text{ mAh}\cdot\text{g}^{-1}$ after 20 cycles. With the KCl electrolyte without surfactant, the Sn nanoparticles were also synthesized. The optimum KCl concentration required for the formation of smaller particles was determined to be 0.05 M. Subsequently, the effective production energy of 45 Wh/g was obtained at the voltages ranging from 110 to 130 V.

In Chapter 6, the solution plasma during nanoparticles formation was analyzed using a spectroscopic measurements, electrical measurement, and high-speed camera observation to investigate the effects of edge shielding, applied voltage, and electrode material on the plasma. When the edge of the Ni electrode wire was shielded by a quartz glass tube, a plasma was uniformly generated while metallic Ni nanoparticles were generated. The emission spectrum from this electrode contained OH, $\text{H}\alpha$, $\text{H}\beta$, Na, and O lines. Without an edge-shielded electrode, infrared radiation continuously radiated at the electrode edge such that the products were partially oxidized owing to the high temperature. The excitation temperature was estimated by applying the Boltzmann plot method. When the voltages were varied with different electrolyte concentrations, the excitation temperature increased with an increase in the voltage. The size of the Ni nanoparticles decreased at high excitation temperature. According to the high-speed observation, many light-emitting points appeared and immediately disappeared when a certain point was strongly heated to produce nanoparticles. The change in current and voltage during plasma initiation were analyzed to optimize the experimental conditions. Plasma generation required higher electric power than that for maintaining the plasma. These findings will contribute to the upscaling of discharge electrolysis.

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