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FABRICATION OF NANOPARTICLES BY ELECTRIC DISCHARGE PLASMA IN LIQUID

NANOCZĄSTKI WYTWORZONE METODĄ WYŁADOWAŃ ELEKTRYCZNYCH W CIECZY

The electric plasma discharge method involves the application of a voltage between a cathode and anode in a conductive electrolytic solution to create a discharge plasma at the cathode. When certain material is used as the cathode, small droplets are emitted with the plasma discharge, and the melted droplets are rapidly cooled in the solution to form nanoscale particles of the material. In this work, nanoparticles of Al, Au, Si, and various alloys of between 100 nm and less than 10 nm in size were produced and characterized. Characterization of Si nanoparticles is especially important because their use in lithium batteries greatly influences battery performance. It was found by high resolution electron microscopy and microstructural surface analysis that oxidation layers of a few nm in thickness were formed on the surface of the Si nanoparticles.

Keywords: nanoparticles, plasma discharge, electrolysis, silicon

W metodzie wyładowań elektrycznych w cieczy pod wpływem przyłożonej różnicy potencjałów pomiędzy anodą i katodą zanurzonymi w elektrolicie dochodzi do wyładowania plazmy na katodzie. Gdy zastosuje się materiał jako katodę, podczas wyładowania plazmy tworzą się małe krople ciekłego materiału, które gwałtownie krzepną w elektrolicie. W ten sposób wytwarzane są cząstki nanometrycznej wielkości. Przy użyciu tej metody możliwe jest wytwarzanie nanocząstek różnych materiałów. Wytworzone nanometryczne cząstki Al, Au, Si oraz stopów miały wymiary od 100 nm do poniżej 10 nm. W szczególności nanocząstki Si stosowane do wytwarzania baterii litowych znacząco wpływają na wydajność baterii, z tego też powodu bardzo ważne jest scharakteryzowanie tych cząstek. Obserwacje przy użyciu wysokorozdzielczej transmisyjnej mikroskopii elektronowej i analiza mikrostruktury nanocząstek Si wskazują, że na powierzchni cząstek znajduje się warstwa tlenków o grubości kilku nm.

1. Introduction

Recently, nanoparticles have attracted attention because of their excellent chemical and physical properties, and a great deal of studies on them have been reported [1,2]. Nanoparticles are expected to be especially useful in the fields of IT [3], environment/energy [4], and bio/life science [5]. The following methods of nanoparticle fabrication are generally well known: the vapor phase, liquid phase, and solid phase methods, and synthesis using laser, arc RF plasma, and ion beam [6-12]. These methods have disadvantages such as complicated processes and expensive equipment. Glow plasma discharge in electrolytic solution has been proposed as a unique method of nanoparticles synthesis, in which the materials used to produce the nanoparticles are used as the cathode [13-14]. In this method, the current increases simultaneously with the voltage of the electric cell, and plasma discharge occurs at a critical voltage point so that small droplets from the cathode surface are emitted and then quenched in the solution. This plasma discharge method has the following advantages: (a) it is a simple method in principle; (b) the cell operates in air; (c) it enables

easy mass production; (d) control of nanoparticle; and (e) it is applicable to conductive materials including alloy systems; therefore, it is possible to apply this method to semiconductor materials such as Si and its alloys.

Si nanoparticles have recently attracted interest for use in practical applications [15] because when Si nanoparticles are used as a Li ion battery material, the capacity of the battery could be greatly increased compared with the batteries that are in general use. Therefore it is expected that production of high quality Si nanoparticles will be an important challenge.

In the present paper, we report the production of various types of nanoparticles by plasma discharge in liquid and the characterization of Si nanoparticles.

2. Experiments

An electrolytic cell was used to produce the nanoparticles. The principle of the cell is shown schematically in Fig. 1 [14,16], in which a Pt anode and nanoparticle precursor mater-

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ial cathode were set in the electrolytic solution. The prototype cell that was actually used is shown in Fig. 2.

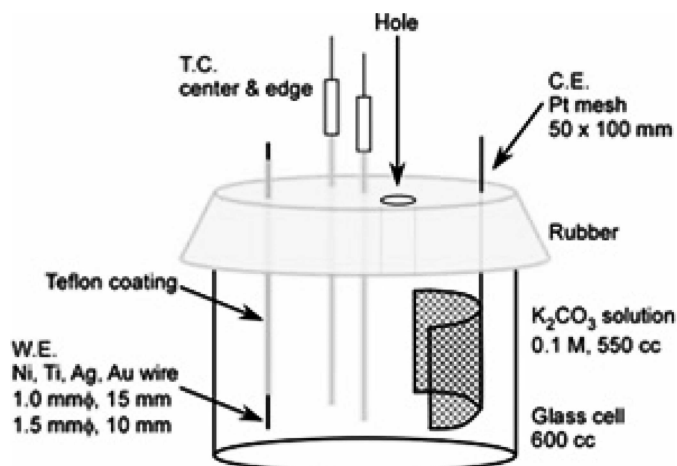


Fig. 1. Schematic of the electrolysis experimental apparatus[14,16]

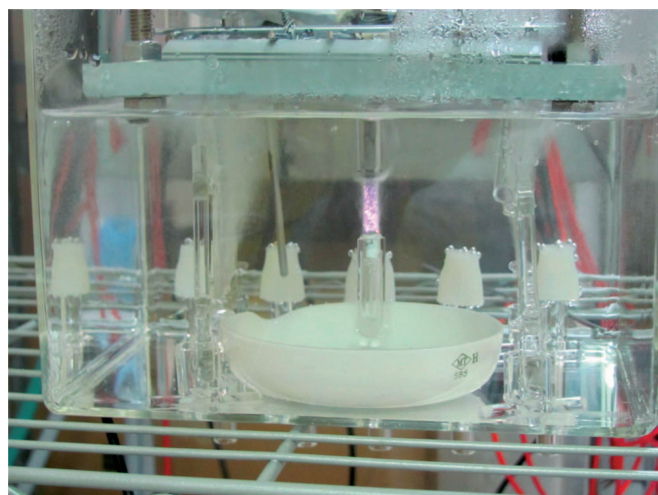


Fig. 2. The prototype electrolysis cell used in the present study

The range electrolysis conditions was as follows: the aqueous electrolyte solution contained 0.1 M potassium carbonate, potassium citrate, or lithium citrate acid, the temperature was 80-95°C and the applied voltage and current were respectively 100-200 V and 0.1-1.0 A.

The electrolysis conditions were changed depending on the cathode material. The materials used to produce nanoparticles were Al, Fe, Cu, Ni, Au, Ti, and W pure metals, and CuNi, NiTi, 304 stainless steel, and Sn-3.5Ag alloys. The obtained nanoparticles were observed by transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDS) and analyzed by X-ray diffraction (XRD) and mass spectroscopy.

3. Results and Discussion

3.1. Plasma discharge characteristics

The current increased with voltage until the voltage critical point was reached and plasma discharge occurred. **Fig. 3** shows a typical current-voltage curve for the electrolytic cell

[14,17]. The current increased linearly with voltage (region (1) and (2)) according to Ohmic law until the critical voltage, after which the current sharply dropped with increasing voltage. In this transitional region plasma discharge occurred at tip of cathode, as shown in Figure 3.

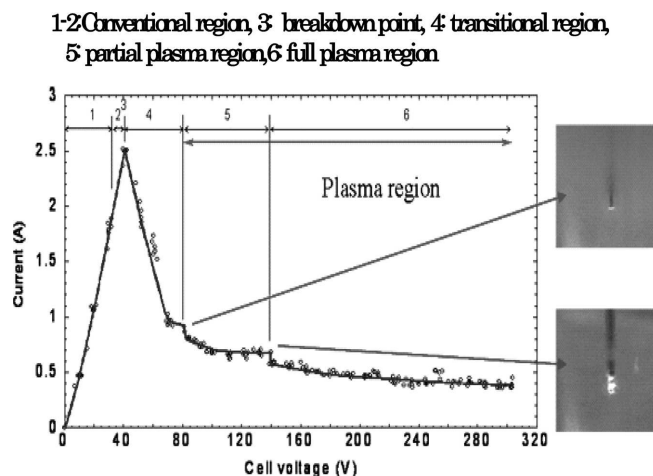


Fig. 3. Relationship between plasma generation and the current-voltage Characteristics of the cell[14,17]

During this process, the temperature of the electrolyte rose to about 80-95°C owing to Joule heating, and the cathode material was shielded with a layer of mixed gas of water vapor from boiling at the cathode surface and hydrogen gas through electrolysis. When voltage continued to increase, the plasma discharge expanded to the whole area of cathode. Subsequently, small droplets were emitted into the electrolyte from the cathode surface and were rapidly quenched in the aqueous solution to produce nano-sized particles. Accordingly, the size of the nanoparticles is controlled by the droplet mass. It is reported that the nanoparticle size is also influenced by the applied voltage [18] and the concentration of electrolytic solution.

3.2. Nanoparticles of pure metals

Fig. 4(a-f) shows typical microstructures of pure metal nanoparticles produced by the method of plasma discharge in liquid. All of the obtained nanoparticles exhibited fcc and bcc structures and were spherical and well defined. The size distribution was different depending on the metal, with larger sizes observed for metals with lower melting point even under the same electrolysis conditions. Furthermore, nanoparticles produced from metals such as Al and Ni that have strong affinity with oxygen often formed an oxide layer on the particle surface.

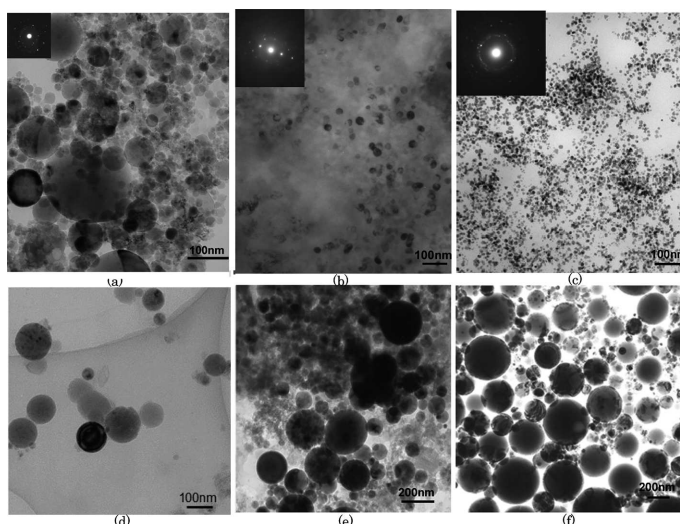


Fig. 4. TEM images of pure metal nanoparticles produced by plasma discharge method; (a) Al, (b) Cu (c) Au, (d) W, (e) Ti, and (f) Fe

3.3. Distribution and characterization of alloy nanoparticles

Fig. 5(a-d) shows the nanoparticles of alloys. The nanoparticles obtained using each alloy were in spherical shape like those obtained from the pure metals. The size distribution of the as-produced nanoparticles was wide for each alloy; those of the Sn-3.5at%Ag, CuNi, and NiTi alloys and stainless steel were about 10–20 nm, 10-500nm, 50-400nm, and 50-200 nm, respectively. These results may have been caused by variation in the plasma discharge conditions as well as the melting point of the electrode material.

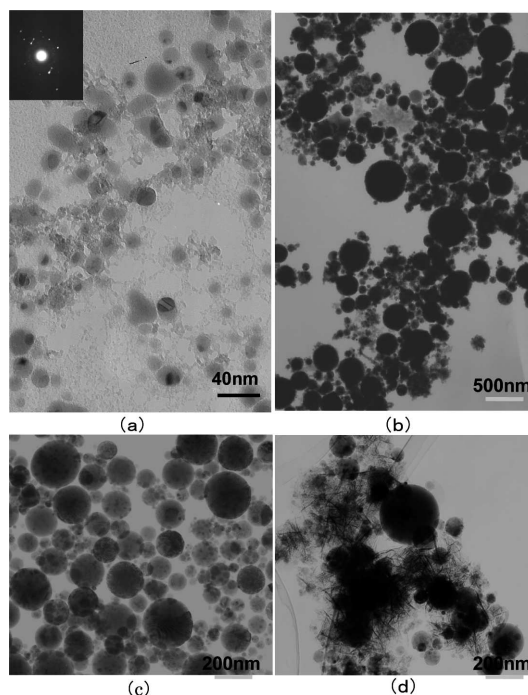


Fig. 5. TEM images of alloy nanoparticles; (a) Sn-3.5Ag, (b) 316 stainless steel, (c) CuNi alloy, and (d) NiTi alloy

Fig. 6 shows the more detailed structure of a nanoparticle of Sn-3.5at%Ag alloy. A eutectic structure was observed which was composed of epsilon phase and Sn component according to the phase diagram of the Sn-Ag alloy system.

It was found that the 316 stainless steel nanoparticles had a catalytic effect. Fig. 7 shows the spectral absorbance of a solution containing soil extract and stainless steel nanoparticles compared with those containing pure metal nanoparticles of each alloying element. It was clearly observed that the stainless steel nanoparticles had a catalytic effect, but the mechanism of this effect was not clarified.

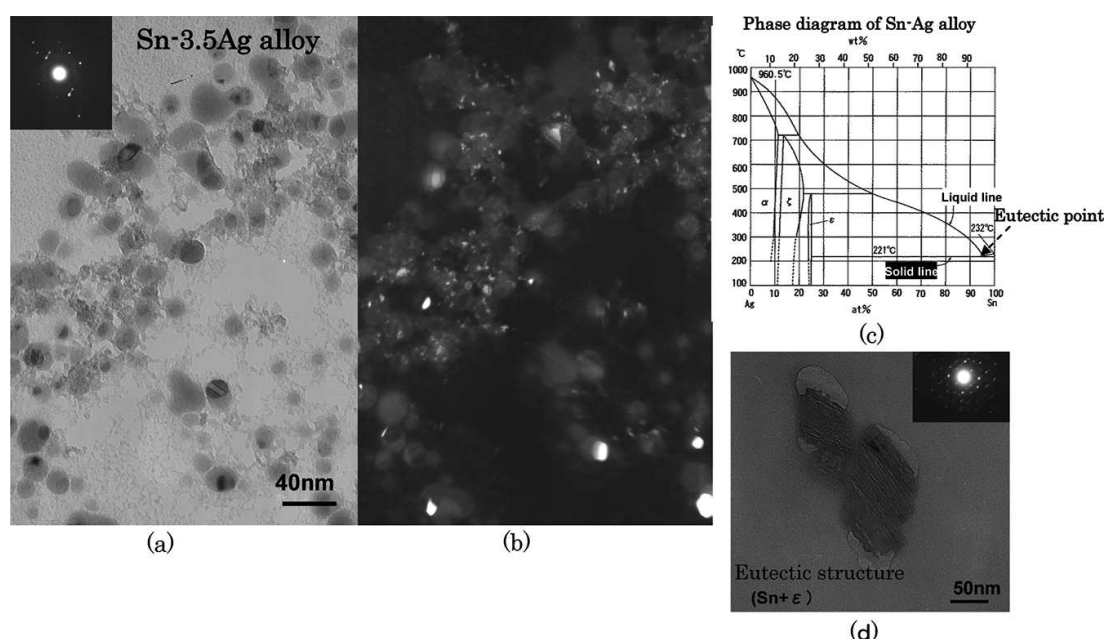


Fig. 6. Structure of the Sn-3.5Ag nanoparticles: (a) Bright field image of the alloy, (b) dark field image, (c) phase diagram of the Sn-Ag alloy system, and (d) eutectic structure produced in the nanoparticle

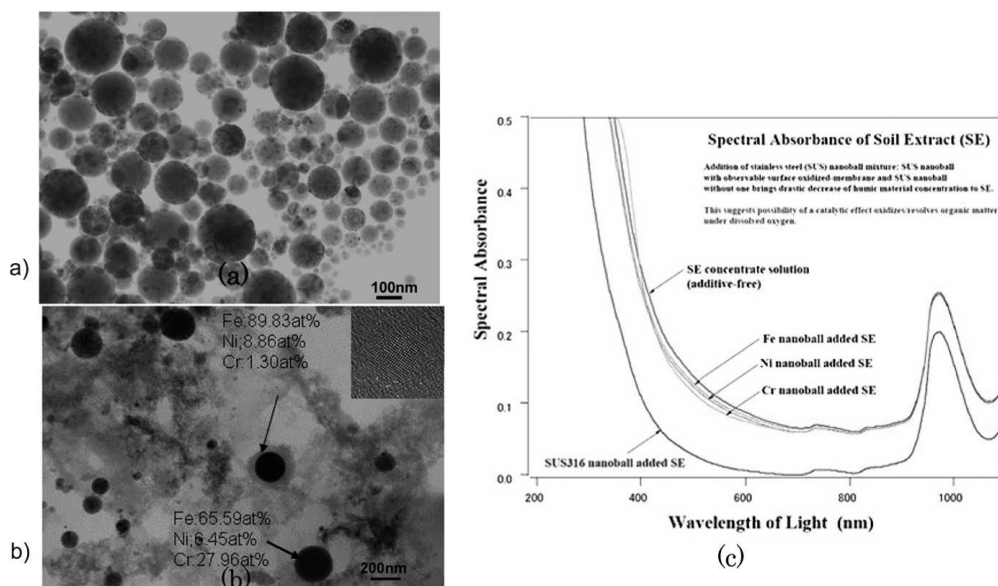


Fig. 7. (a) TEM image of 316 stainless steel nanoparticles and their (b) EDS compositional analysis, and (c) catalytic effect on the spectral absorbance of soil extract

3.4. Characterization of Si nanoparticles

Si nanoparticles are expected to be beneficial for lithium ion batteries because their use results in higher battery capacity [19]. The performance of such a Si lithium battery is largely controlled by the size and surface structure of the Si nanoparticles [20]. It is expected that the capacity of the battery would increase with decreasing Si nanoparticle size because the amount of lithium ions which will interact with the Si depends on the effective Si surface. **Fig. 8(a-b)** shows

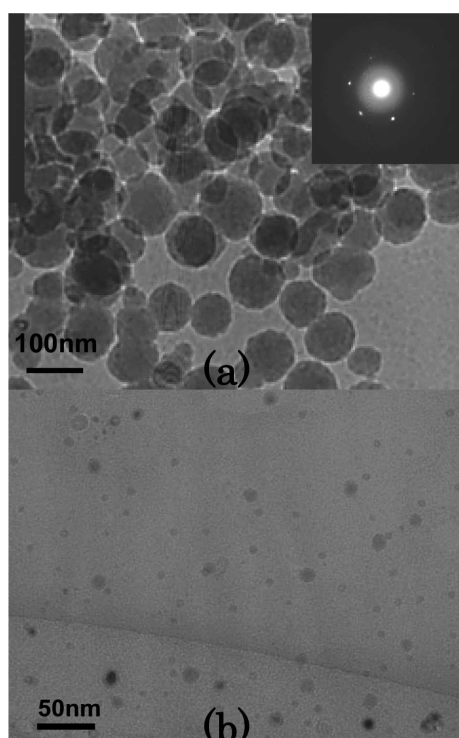


Fig. 8. Si nanoparticles with different size distribution; (a) relatively larger nanoparticles and (b) smaller nanoparticles

that the present Si nanoparticles were obtained with average sizes of 30–50 nm and less than 20 nm.

The size of the Si nanoparticles was controlled by the electrolysis conditions; very small Si particles were produced when the plasma discharge occurred at high applied voltage [18] and lithium citrate was used.

Fig. 9 shows a high resolution TEM image of a Si nanoparticle. It was clarified from TEM and EDS analysis that an oxide layer was often formed on the Si nanoparticles. It was difficult to identify the type of oxide film but the EDS analysis data suggested the presence of SiO. Such an oxidation of the surface may influence the Si lithium battery performance, and therefore it is important to suppress oxidation during nanoparticle production. However, it has also been suggested that battery performance is not greatly decreased when SiO_x oxide layers are formed [15].

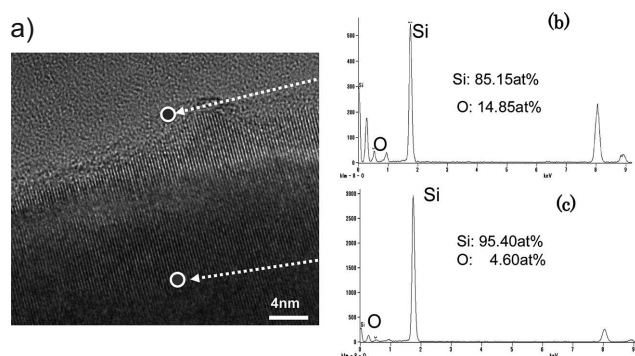


Fig. 9. (a) High resolution TEM image near the surface of a Si nanoparticle, (b) and (c) EDS analysis spectrum of the oxide layer and inside of the crystallite, respectively

4. Conclusion

In this work, nanoparticles of pure metals and many kinds of alloys were produced by plasma discharge in liquid. Most

of the particles were spherical in shape. The size distribution of the nanoparticles depended on the electrolysis conditions, and the particle size tended to become smaller with increasing plasma discharge voltage, and when using lithium citrate solution. In particular, the minimum size obtained for Si nanoparticles was less than 20 nm. Oxide surface layers were often formed during the production process on nanoparticles of materials which had strong oxygen affinity.

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