Production of Reduced Aluminum Nanoparticles from Aluminum oxide by applying high voltage pulses to solutions

T. Saiki1, S. Taniguchi2

1. Electrical, Electronic and Information Engineering, Faculty of Engineering Science,
Kansai University, 3-3-35 Yamate, Suita, Osaka 564-8680, Japan
2. Institute for Laser Technology,
1-8-4Utsubo-honmachi, Osaka, Osaka 550-0004, Japan

E-mail address: tsaiki@kansai-u.ac.jp

Abstract

Metal nanoparticles has been attracted as raw materials for nanoinks and nanopastes, which are used to Printed Electronics. Synthesizing various metal nanoparticles has been researched. We investigated possibility of reducing metal oxide to metal by high-voltage pulses in this paper. This method should save electrical consumption power compared to conventional methods using high-temperature and high-pressure plasma such as arc discharge. Reduced Al nanoparticles were obtained by applying high voltage pulses to solutions. It was found from hydrogen generation using reduced Al nanoparticles by applying high voltage pulses to solutions to evaluate reduction rate that a high reduction efficiency of 97% was obtained at maximum. We concluded that using high voltage pulses for reduction is suitable for application to printed electronics because oxide film on reduced Al nanoparticles is thin. Also, because this method is similar to laser ablation in liquids using pulse lasers, the similarities were discussed in this paper.

Keywords: High voltage repetitive pulses, Reduction of metal oxide, Metal nanoparticls, Printed Electronics, Laser ablation in liquids

1. Introduction

Metal nanoparticles are a raw material of nano-ink and nano-paste of printed electronics for manufacturing electric and electronic circuits at low temperature, low cost and in a short time, and are currently attracting attention. Until now, silver has been attracting attention as a material, but copper is currently attracting attention because of its low cost among metals3). In this study, we investigated the possibility of large electron emission to the solvent by high voltage pulse and the reduction of metal oxide by solvated electrons. This reduction method does not use an arc discharge that generates a high temperature, consumes low power, and requires only a simple device. In this paper, aluminum oxide was used as a material, and research was conducted to determine whether it can be used as a printed wiring. Aluminum is not yet considered for printed electronics. Research has already been conducted on metal-air batteries using metal plates made of Al nanoparticles. In addition, research and development for practical use of hydrogen production using aluminum fine particles are also being conducted.

2.Experiment

In this time, we conducted experiments on reduction of metal oxide fine particles using pulsed high voltage and nanoparticle formation. Fig. 1 shows the reduction experiment apparatus. The reason for using a pulse is that a current larger than the DC high voltage flows through the solvent at the time of rising of the high voltage pulse. A glass bottle having a needle electrode (300 μm in diameter) in a solution having a size of 21 mmφ and a height of 49 mm as shown in Fig. 1 was used as a load for applying a high voltage in the reduction experiment. Aluminum oxide (α-alumina 400mg, average size 5μm, high-purity chemical) was used for reduction experiments. The solvent and the aluminum oxide fine powder were placed in a glass bottle. Pure water (ion-exchanged water, 4 mL) or acetonitrile (ACN) (5 mL) was used as a solvent for the reduction experiment.

In the pulse high-voltage reduction experiment, an AC high voltage was generated from a DC low-voltage power supply (PR18-5A, TEXIO) and a high-voltage generation circuit, which was input to a two-stage Cockcroft-Walton circuit, and the ground side was set to-. Then, the output side of the capacitor with the gap was made positive and a high voltage pulse was generated at the output.

A high voltage probe and an oscilloscope (TDS2012C, Tektronix) were used to measure the pulse high voltage. In the reduction experiment with the application of a high pulse voltage, a stair-like high voltage pulse with a rising time of 200 ns was applied to the solvent. The repetition of the high voltage pulse was 0.3 Hz and a pulse high voltage of 3.6 kV peak was momentarily applied to the solvent. Thereafter, the voltage gradually decreased to 1.6 kV, and the gap attached to the capacitor was discharged to 3.6 kV again, and this was repeated in time. The voltage increase at the rise of this sawtooth high voltage pulse was 2.0 kV. Cockcroft output from the high-voltage AC power supply was 5.6 kV with no load, and 4.0 kV with the load (solvent and electrode) connected. With respect to the current flowing through the circuit, the time average output current was measured from the voltage waveform at the 120Ω resistor connected to the circuit using an oscilloscope. The time average output current of the Cockcroft-Walton circuit was 0.05 mA and 0.04 mA when the solvent was pure water and ACN, respectively. At this time, when the solvent was ACN, the average output power of the pulse generation circuit was 0.2 W.

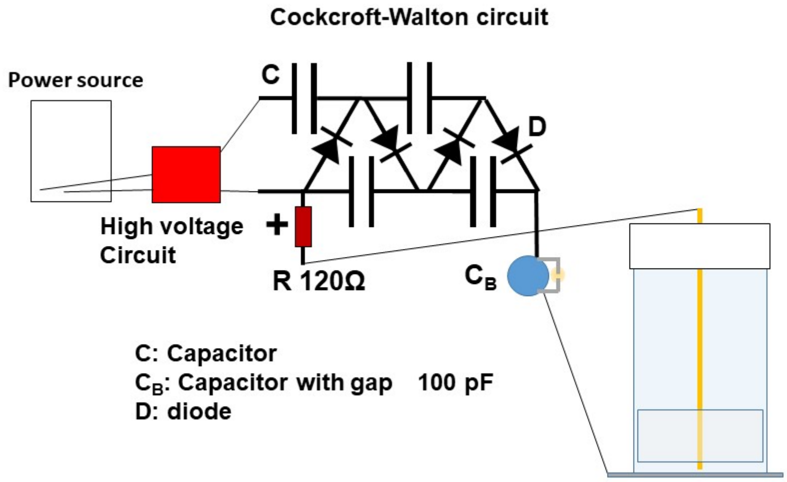

Fig.1. Experimental setup for reducing metal oxide. Adding pulse high voltage.

3.Results

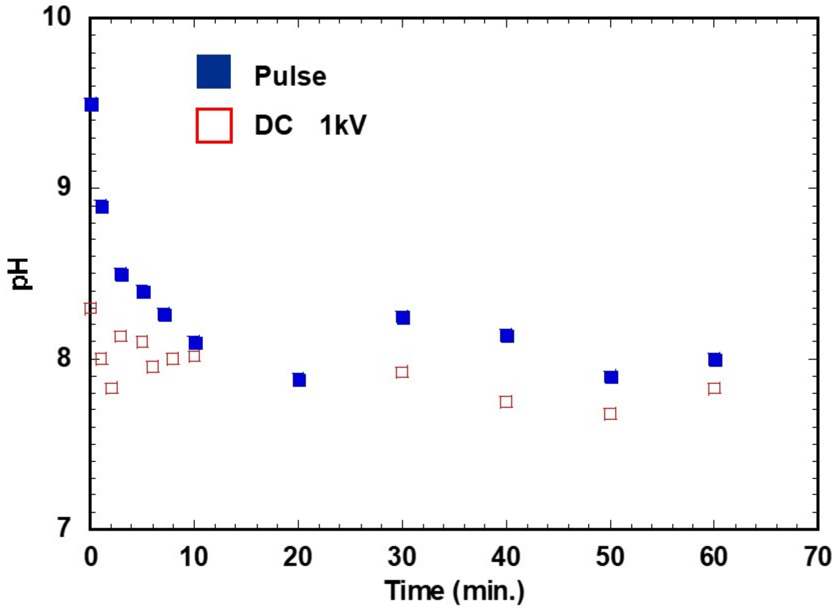

Fig.2. Result on measured pH of pure water. Blue square: added high voltage

pulses, square and red square and white: added DC 1kV.

The measurement results of the passage of the pH time is shown in Fig.2. The square blue indicates the pulse change voltage application, and the hollow square red indicates the time change measurement result when 1 kV DC high voltage is applied. When the solvent was pure water, the pH was measured immediately after the application of the pulse high voltage, and the pH was found to be pH = 11.

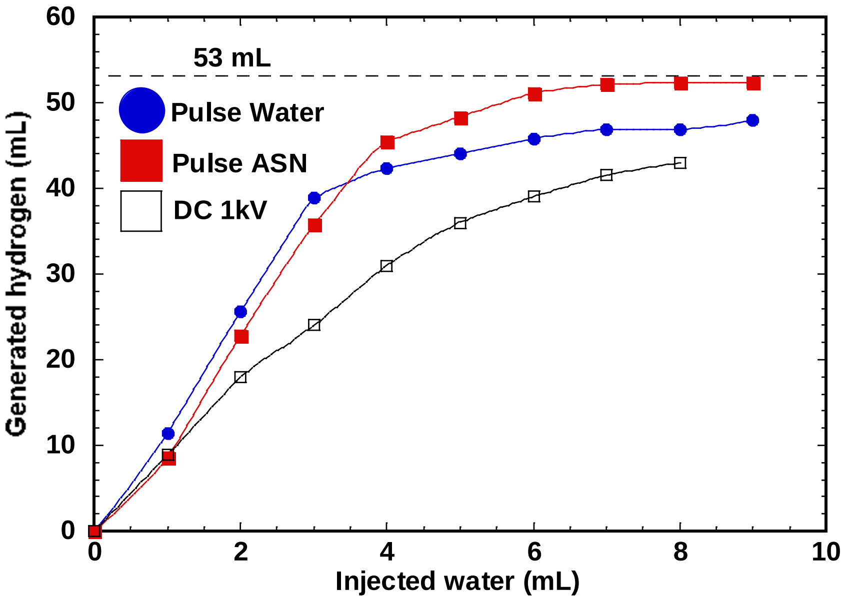

Fig. 3. Comparison of generated hydrogen. Circle: added high voltage pulses. Liquid was pure water. Square: added high voltage pulses. Liquid was ACN. White square: added DC 1kV.

It was confirmed that if Al nanoparticles produced were produced. Fig. 3 shows a comparison of the amount of hydrogen generated. The hollow squares are the results of experiments using reduced Al nanoparticles generated by reduction with a DC high voltage of 1 kV for hydrogen generation. The open squares indicate the case where the solvent is pure water when a high DC voltage is applied, the open squares indicate the case where the solvent is pure water when the high voltage pulse is applied, and the squares indicate the case where the solvent is ACN when the high voltage pulse is applied. From Fig. 3, it can be seen that when hydrogen is produced using nanoparticles generated by reduction by applying a pulsed high voltage, the reaction rate with water vapor increases, and the reaction rate becomes almost 100% with less water injection. On the other hand, it was found that the reaction rate of the reduced alumina particles obtained by applying a high DC voltage of 1 kV with water vapor was inferior to the case of applying a high pulse voltage.

As a result of the hydrogen production experiment, it was found that the generated fine particles were almost aluminum. The weight of the reduced aluminum fine powder used for hydrogen generation was 40 mg, and the amount of hydrogen generated when the reduced aluminum fine powder was completely reduced was 53 mL (break line in Fig.3.). When the solvent was pure water or ACN under pulsed high voltage application, the reduction rates were estimated to be 94% and 97%, respectively, from the experimental results. The Al nanoparticles generated in the reduction experiment with a DC high voltage of 1 kV were evaluated to have a lower reduction ratio of 92%.

References

1) A. L. Dearden, P. J. Smith, D. Y. Shin, N. Reis, B. Derby and P. Brien: A low curing temperature silver ink for use in ink-jet printing and subsequent production of conductive tracks, Micronol. Rapid Commun., **26** (2005) 315.

2) J. W. Chung, S. H. Ko, N. R. Bieri, C. P. Grigopoulos and D. Poulikakos: Conductor micro structures by laser curing of printed gold nanoparticle ink, Appl. Phys. Let., **84** (2004) 801.

3) J. Lee, B. Lee, S. Jeong, Y. Kim: Microstructure and electrical property of laser-sintered Cu complex ink, Appl. Surf. Sci., **307** (2014) 42.

4) O.Takai, N.Saito, N.Sano, K.Imasaka and J. Suehiro: Material Processing Using Underwater Discharge Plasma, Plasma Fusion Res, **84**(10) (2008) 674.

5) M. Kawasaki and N. Nishimura: Laser-induced fragmentative decomposition of ketone-suspended Ag2O micropowders to novel self-stabilized Ag nanoparticles, J. Phys. Chem. C, 112 (2008) 15647.

6) M. Shoji, K. Miyajima, and F. Mafune: Ionization of gold nanoparticles in solution by pulse laser excitation as studied by mass spectrometric detection of gold cluster ions, J. Phys. Chem. C,112 (2008)1929.

7) U. Naher, S. Bjornholm, S. Frauendorf, F. Garcias, C. Guet, “Fission of metal clusters”, Phys. Rep. 285 (1997) 245.

8) P. E. Mason, F. Uhlig, V. Vaněk, T. Buttersack, S. Bauerecker, P. Jungwirth, “Coulomb explosion during the early stages of the reaction of alkali metals with water”, Nature Chemistry, 7 (2015) 250.

9)D. G. Rowe: Solar-powered lasers, Nature Photonics, **4** (2010) 64.

10)T. Yabe, T. Okubo, S. Uchida, K. Yoshida, M. Nakatuska, T. Funatsu, A. Mabuti, A. Oyama, K. Nakagawa, T. Oishi, K. Daito: High-efficiency and economical solar-energy-pumped laser with Fresnel lens and chromium codoped laser medium, Appl. Phys. Lett., 90 (2007) 261120.

10)T. Saiki, S. Taniguchi, K. Nakamura, Y. Iida: Development of Solar-Pumped Lasers and Its Application, Electrical Engineering in Japan, **199**(2) (2017) 3.

11) T. Saiki, “High-voltage Pulse Generation Based on Relaxed Self-Excited Oscillation Using Electrostatic Induction in External Capacitors”, (2018), [arXiv:1806.08905].

12) T. Okada, T. Saiki, S. Taniguchi, T. Ueda, K. Nakamura, Y. Nishikawa, and Y. Iida: Hydrogen Production using Reduced-iron Nanoparticles by Laser Ablation in Liquids, ISRN Renewable Energy, vol. 2013 (2013) ID 827681-1-7.