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Air Cells Using Negative Metal Electrodes Fabricated by Sintering Pastes with Base Metal Nanoparticles for Efficient Utilization of Solar Energy

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Abstract

Research on the produce of renewable energy as a source of solar power has continuously advanced. We have proposed an energy cycle that uses solar-pumped pulse lasers and base metal nanoparticles. Here, Fe and Al nanoparticles were prepared by laser ablation in liquid for the energy cycle. Solar power was confined in base metal nanoparticles. Metal plates were fabricated by sintering metal paste with base metal nanoparticles. Electricity was generated by air cells using the sintered metal plate. A highly repetitive laser pulse, which was an alternative to lasers driven by solar power, was used for laser ablation in liquid, and metal oxides (Fe_3O_4 or Al_2O_3) were reduced and metal nanoparticles were fabricated. Metal plates with a low electrical resistance were fabricated by sintering them at a low temperature of 520 K.

The electrical properties of the air cells fabricated using sintered paste with nanoparticles as negative electrical cathodes were the same as those of the air cells fabricated in a blast furnace. It was found that the sintered metal nanopaste could be used for air cells.

Keywords

Solar Power; Laser; Renewable Energy; Air Cells; Nanoparticles

Introduction

Recently, concerning the desire to develop methods for the reduction in the amounts of gases that causes the global earth warming, low-cost and energy-saving method are encouraged. Also, research on the production of renewable energies has continuously advanced [1-3].

High temperatures are generated by focusing solar light on metal oxides, thereby reducing the metal oxides by the generated high temperatures. As a result of this process, chemical energy is stored as the difference of chemical potential between metal and metal oxide, and hydrogen is generated [1]. In previous research, CW lasers have been generated using solar energy is used for the reduction of magnesium oxides. Here, an energy cycle in which reduced magnesium is used as a renewable energy is proposed [3, 4]. Our group is also developing solar-pumped lasers [3, 5-7] that employ solar light for pumping laser materials. We propose an energy cycle using base metallic nanoparticles and solar-pumped pulsed lasers.

A Nd/Cr:YAG ceramic laser has been used as a solar-pumped laser [6, 7]. Its lasing wavelength is 1064 nm, which is the same as that of the Nd:YAG laser. The ceramic laser has a special lasing mechanism because its photon energy includes thermal energy due to the phonon-assisted cross-relaxation effect [8]. The maximum theoretical optical-optical (from solar light to laser) conversion efficiency reaches close to 80%. Very high opt.-opt. conversion efficiency close to 60% has been achieved in experiments. The generation of efficient high peak-power and highly repetitive laser pulses from solar-pumped lasers, whose conversion efficiency is close to that of CW laser [6], has been realized.

The reduction and production of metal nanoparticles using laser ablation in liquid and solar-pumped pulsed lasers has been performed here. The method is different from that adopted by Yabe et. al [4].

Laser ablation in liquid with a high fluence and a high intensity of laser pulses can produce nanoparticles and reduce metal oxides [9-13]. The physics of thermal ablation and coulomb explosion [14-16] have been proposed for the ablation of metal oxides in liquid, which is remarkably different from that using a CW laser.

It has been considered that reduced metal oxides can be used as a negative electrode of air cells. Electricity can be obtained by reacting metals with oxygen in air. Research on air cells has been carried out for 40 years since Ferro developed Zn air cells [17, 18]. Air cells are expected as a future electrical power source because their energy storage density per unit weight is higher than that of the Li ion battery. Metal oxides, such as Fe_3O_4 and Al_2O_3, exist in large quantities in the ground.

Our aim in this paper is to develop primary air cells [17, 18]. The electrical property of air cells using sintered metal paste was investigated and compared with that of air cells using conventional metals. No such researches have been performed previously. The possibility of using sintered paste with reduced metal oxide particles fabricated by laser ablation in liquid as a negative electrode was investigated.

Experimental

Reduction of metal oxide powder and production of nanoparticles

By using pulse laser ablation in liquid, metal oxides were reduced, and metal nanoparticles such as Fe and Al were fabricated. The chemical formulas for the reduction are shown. We first show the chemical formula for Fe_3O_4 and Fe:

$$\frac{1}{3}Fe_3O_4 \rightarrow Fe + \frac{2}{3}O_2, \quad \Delta H = 373 \text{ kJ/mol.} \qquad (1)$$

The chemical formula for Al_2O_3 and Al is shown next:

$$\frac{1}{2}Al_2O_3 \rightarrow Al + \frac{3}{4}O_2, \quad \Delta H = 838 \text{ kJ/mol.} \qquad (2)$$

Fe oxides are resolved and vaporized at a temperature of above 1600 K. Furthermore, Al oxides are resolved and vaporized at a temperature of above 3300 K.

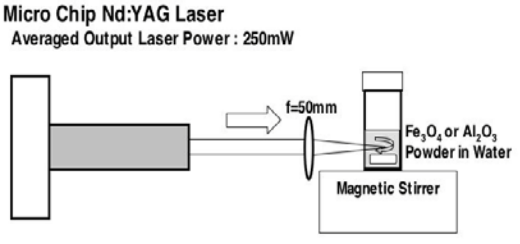


FIG. 1 LASER SYSTEM FOR LASER ABLATION IN LIQUID USING MICROCHIP LASER

The laser ablation method in liquid is described in the paragraph below. When laser pulses are irradiated onto metal oxides in liquid, the metal oxides melt and resolve and the melted oxides are set outside the metal nanoparticles. The surrounding liquid cools the metal nanoparticles rapidly. The merits of the use of this method are as follows: 1) We do not need to use specific materials for reduction. 2) A high reduction rate of metal oxides is obtained because the recombination between oxygen and metals is prevented. 3) The re-collection of nanoparticles is easier than in other methods. 4) It has a very low cost. We obtained reduced Fe nanoparticles with 20 nm diameters by this method [13]. The experimental setup for laser pulse ablation is shown in Fig. 1. A microchip Nd:YAG laser was used in this experiment. The maximum output averaged laser power was 250 mW, the laser wavelength was 1064 nm, the repetitive rate of the laser pulses was 18 kHz, and the pulse duration was 8 ns. A beam with a diameter of 6 mm ($1/e^2$) was focused using a lens with a focal length of 50 mm. Thus, the diameter of the focused beam was 20 μm at the front of each glass bottle. Glass bottles with a size of 20 mmΦ x 5 mm were used in the experiment.

Fe_3O_4 andα-Al_2O_3 powders (Koujyundo Chemical Laboratory) were mixed with water in each glass bottle for the experiment. The mean size of each Fe_3O_4 andα-Al_2O_3 was 1 μm. Each glass bottle was set after the focused laser beam. The weight of the Fe_3O_4 andα-Al_2O_3 powders was measured using an electronic force balance. Their measured weight was 200 mg. 4mL of pure water was placed in each glass bottle. Laser pulses were irradiated to the water with the metal oxide in glass bottle for 20 minutes. Here, the fluence of the irradiated laser pulse was estimated to be 4.5 J/cm^2. Ketones, such as acetone, are used as liquids for laser ablation in liquid. Here, we neglect the oxidation at the surface of metal nanoparticles. A magnetic stirrer was used to mix the liquid. After the irradiation of the laser pulses for 20 minutes in the case of Fe_3O_4, the surface of the nanoparticles was black. Thus, it has been presumed that the surfaces of metal nanoparticles were surrounded by Fe_3O_4. In the case of α-Al_2O_3 powder, its color changed to gray, which is close to the color of Al powder. The powder after irradiating laser pulses in the water was dried to not change chemically.

Fabrication of metal plates by sintering paste

(a)

(b)

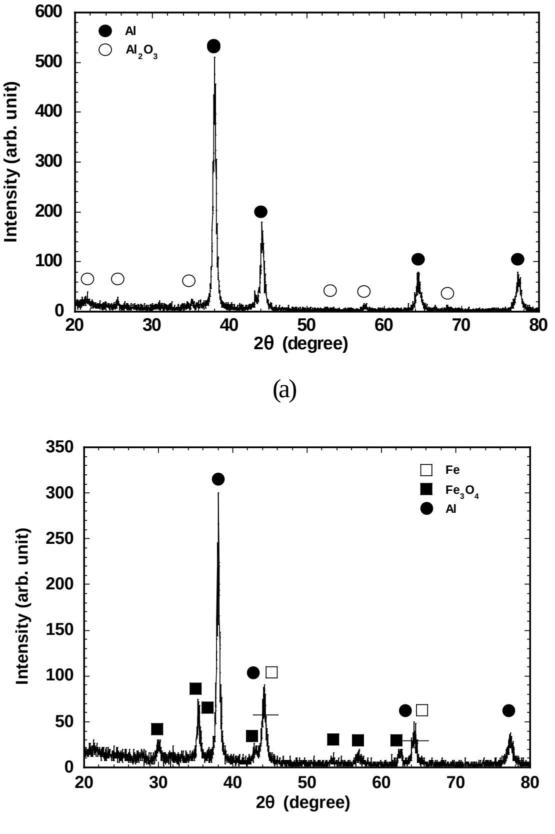
FIG. 2 SINTERED METAL PASTE. (A) FE AND (B) AL

TABLE I MEASURED ELECTRICAL RESISTANCE

	Original powder[Ω]	Paste[Ω]	Paste after sintering[Ω]
Fe	Large (unmeasurable)	Large (unmeasurable)	0.0
Al	Large (unmeasurable)	Large (unmeasurable)	0.0

The dried Fe and Al nanopowders were mixed with 3mg of Ag nanopastes (NAG-10 Daiken Chemical); the viscosity of the paste was high. Fe paste was sintered using an electrical hot plate for 5 minutes (1 minute at 520 K, 4 minutes at 570 K). In the case of the Al paste, the paste was also sintered for total 5 minutes (1 minute at 510K, and 4 minutes at 550K) to generate less gas per unit time. The sintered metal plates are shown in Figs. 2(a) and 2(b). The sintered Fe plate is shown in Fig. 2(a), and the sintered Al plate is shown in Fig. 2(b). The opposite surface of either plate was not metalized by oxidation.

A tester measures the electrical resistance of the metal oxide, and the metal paste, and sintered metal paste. The Fe_3O_4 and α-Al_2O_3 powders, and Fe and Al pastes were set on a glass sheet with 1 mm thickness and sintered. The results are shown in Table II. The distance between the needles of the tester was 8 mm. The electrical resistances of the Fe_3O_4 and α-Al_2O_3 powders were very high; they could not be measured because both powders are insulators. The electrical resistances of the metal pastes mixed with reduced Fe and Al nanoparticles by irradiating laser pulses were also measured. However, they were also very high and thus could also not be measured. Finally, after sintering the metal pastes, the measured electrical resistance is 0.0Ω. It was prospected that the Fe and Al pastes were both metalized. For the sintered Al paste prepared by this method, a weak ferromagneticity was observed, and thus it was presumed that the metal structure of Al is markedly different from the structure of common metals. Crystal structure analysis using XRD was performed to check the quantities of Fe_3O_4 and α-Al_2O_3 in the sintered metal paste samples. The results are shown in Figs. 3(a) and 3(b). An XRD instrument (MAXima_X XRD-7000 Shimazu Japan) was used for the experiment. K-α X ray radiation of Cu was irradiated onto the samples. The results for analyzing Al and Fe plates are shown in Fig. 3(a) and Fig. 3(b), respectively. In the case of Al, a large spectrum of Al and a small of spectrum of α-Al_2O_3 were slightly observed. The Al spectrum contained components of a little Ag nanoparticles and the Al stage. Thus, the quantity was not determined.



(a)

(b)

FIG. 3 RESULTS OF XRD ANALYSIS: (A) AL AND (B) FE

Moreover, determining the quantity of Fe was difficult because, normally, the peak spectrum of the Fe_3O_4 is larger than that of Fe at the same quantity [19]. However, we can see the two components at angles of 45 and 65 degrees in Fig. 3(b), but the Fe component was clearly recognized. The spectrum peak of Fe at 44.7 degrees evaluated by extracting the Al background component is nearly three times higher than that of Fe_3O_4 at 43 degrees, and it was found that the sintered Fe paste contains negligible quantity of Fe_3O_4 [19]. Additionally, the sintered structure was observed by a microscopy, and it was found that the porous structure consisted of small metal particles in the metal plates.

Air cell

An experimental setup for testing air cells is shown in Fig. 4. Fe (JIS G3141) and Al (JIS 1050) plates were used as the metal plates in the negative electrodes. The dimensions of the metal plates were set to be 20 mm x 15 mm x 0.5 mm. However, the size of the metal paste was set to be 8 x15 mm^2, which is almost half of the metal plate, because of the difference in duration of the output voltage between the use of the metal pastes and that of the conventional metal plates. The electrical property of the sintered metal pastes on the metal plates was compared with that of the conventional metal plates. Here, a Pt-doped carbon electrode with a layer for diffusing oxygen was used as the positive electrode. A separator made of 8 pieces of papers piled up was set between the positive electrode and the negative metal electrode. The thickness of each piece of paper was 0.1 mm. Saturated salt water was injected into each piece of papers at intervals of 5 minutes. The chemical formulas of Fe air cells are shown below:

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-,$$

$$Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e^-. \qquad (3)$$

The chemical formulas of Al air cells are also shown:

$$\frac{3}{4}O_2 + \frac{3}{2}H_2O + 3e^- \rightarrow 3OH^-,$$

$$Al + 3OH^- \rightarrow Al(OH)_3 + 3e^-. \qquad (4)$$

The theoretical electromotive forces of Fe and Al air cells are 1.2 and 2.7 V, respectively. However, using NaCl dissolved in water, the output voltages of the cells were 0.4 and 0.7V, respectively. Because the valence of the Al ion is 3 and 3 electrons are emitted from the negative electrodes per chemical reaction, the electrical power density per unit weight is high. Metal nanopaste could help to connect different metal tightly. It is expected that the output voltage of the air cells will be improved by using different metal junctions. The air cells using different species of metal junctions utilize the phenomenon of galvanic corrosion. For example, new local cells are constructed between Fe nanopaste and an Al plate, and a new electromotive force is generated. Here, Fe corrosion occurred before Al corrosion occurred resulting in the generation of a high output voltage depending on the use of Al as a total air cell.

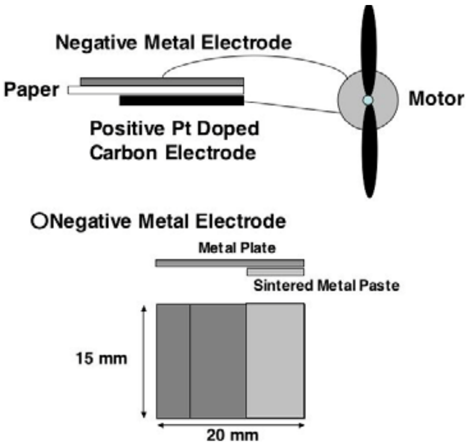


FIG. 4 EXPERIMENTAL SETUP FOR METAL AIR CELLS

Electrical Property of Air Cells

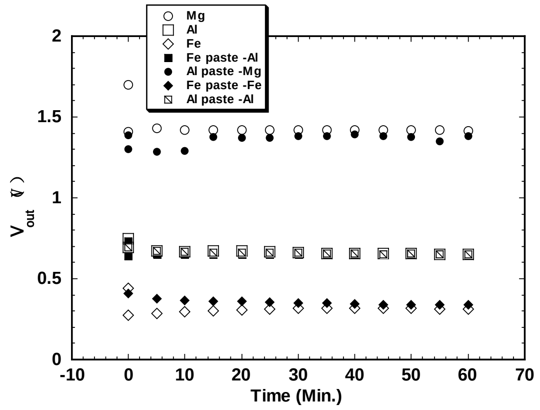
Previously, as shown in section 2, metal pastes with Fe and Al were sintered on metal plates, and air cells were fabricated. The electrical properties of the air cells were then investigated. The open output voltage of air cells using a negative Mg electrode was 1.8 V, and that of air cells using negative Al electrode was 1.2 V. That of air cells using a negative Fe electrode was 0.6V. Fe paste on a Fe plate was sintered. Al paste on an Al plate was also sintered. The measured shortcut currents of the air cells using Fe and Al plates were both 70 mA. In the case of Fe and Al pastes, the extracted shortcut current was 40 mA because the area was half of that using Fe and Al plates.

Small connecting load

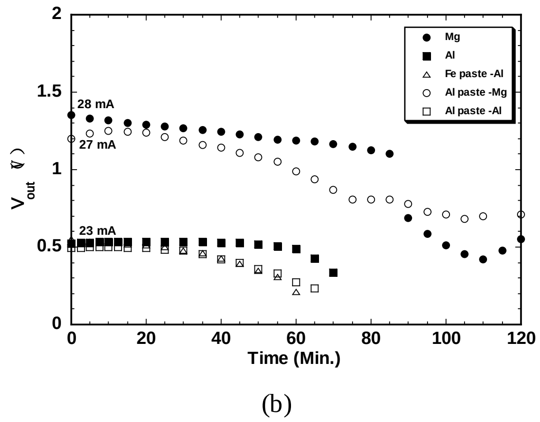
The temporal property of the output voltage when the electrical load connected to the air cells is small is shown in Fig. 5(a). A 1.0 kΩ resistor was connected to the constructed air cell, and their output voltages were measured. The obtained output voltages of the Fe, Fe paste–Fe and Fe paste–Al, air cells were all 0.4V, one of the Al and Al paste–Al air cells were all 0.7V, and that of the Mg and Al paste–Mg air cell were all 1.4V. Current can be evaluated by dividing the output voltage by the 1.0 kΩ resistance. The evaluated output current of the Mg air cell was 1.4mA, that of one of the Al air cells was 0.7 mA, and that of one of the Fe air cells was 0.4 mA.

Large connecting load

A large load, which was applied using an electrical motor (Solar motor, Mabuchi RF-500TB Tamiya, Japan) with a propeller, was connected to the air cells to induce the flow of large currents. The temporal property of the output voltage is shown in Fig. 5(b). The motor rotated normally. However, when connected to the Fe air cells, the motor did not rotate owing to low output voltage. The temporal property of the output voltages was measured when the motor was connected to the air cells. In the case of the Fe paste –Al air cell, the initial output voltage was 0.7 V. In the case of the Al paste –Al air cell, the initial output voltage was also 0.7 V. The output current was 26 mA. The duration of the output voltage was 60 minutes for the Al air cell, and that for the Al paste –Al air cell was 30 minutes, half of that for the Al air cell. Moreover, that for the Fe paste –Al air cell was 30 minutes, which was also half that for the Al air cell. The initial output voltage in the case of the Mg air cell was 1.4 V, and that in the case of the Al paste –Mg air cell was also 1.4 V. The output currents were 28 and 27 mA, respectively. The duration of the output voltage was 80 minutes for the Mg air cell, and that for the Al paste –Mg air cell was 40 minutes, which was also half of that for the Mg air cell.



(a)



(b)

FIG. 5 MEASURED OUTPUT VOLTAGE OF METAL AIR CELLS. THE LOAD WAS (A) 1K Ω AND (B) A MOTOR

DISCUSSION

We conducted experiments to produce nanoparticles and reduce metal oxides by laser ablation in liquid. It has been proved in the experiments that metal plates prepared by sintering metal pastes can be obtained, and that the electrical resistances of the metal plates are close to those of conventional metal plates. The Clarke numbers of Al and Fe are 3 and 4, respectively. They exist abundantly in the ground of the earth. The proposed method of reducing and metalizing metal oxides is an alternative to the conventional electrolysis method in aluminium refining. Reduction is performed in two steps; laser ablation and sintering. Ag nanopaste has less ability to reduce metal oxides. Ag paste with only Fe_3O_4 powder could not be sintered, and no perfect metal plate was fabricated in fact. The inner surface of the paste was not sintered into the metal.

Some heat sources or the solar light can sinter the metal paste. When sintering metal paste, the degradation of surface energy induces heat generation during the chemical reaction. When the paste reaches a given temperature, sintering starts automatically with the generated heat. No heat is required to melt a common metal plate. Required energy to start sintering is adequately lower than the stored energy in the sintered metals owing to the vanishing surface energy.

Here, we consider the input-output energy balance. The injected total laser energy determined by calculation was 290 J when the averaged laser power was 250 mW and the irradiation time was 20 minutes, considering surface loss of each glass bottle. The minimum chemical energy per mol to reduce Fe_3O_4 to Fe is 373 kJ, that to reduce Al_2O_3 to Al is 838 kJ. In the case of Fe, when its weight is 200mg, the required minimum energy to reduce it is evaluated to be 960 J. This energy is 3.3 times as large as the injected total laser energy in liquid. In the case of Al, when its weight is 200 mg, the required minimum energy to reduce it is evaluated to be 3300J. This energy is 11 times as large as the injected total laser energy. Moreover, more energy for reduction is needed because the generated metal and oxide atoms must be removed far away from metal atoms. These results strongly show that the physics of the reduction process does not depend on conventional thermal ablation. Because the estimated irradiated laser fluence was 4.5J/cm^2 in this case, the ablation of the metal oxides occurred by the coulomb explosion. Also, it has been thought that reduction of 200 mg of Fe_3O_4 or Al_2O_3 powder can be almost perfectly performed when the averaged laser power is 250 mW, and the irradiation time is 10 minutes. In coulomb explosion, avalanche ionization occurs in metal oxides. Some of the electrons of Fe_3O_4 are ejected into water. Fe and O atoms are ionized and exploded by the coulomb repulsion between ions. Finally, local plasma is generated. Air cells using sintered metal nanopaste were constructed and their electrical property was investigated. It was clarified that the fabricated air cells using sintered metal nanopaste can be used as primary air cells.

If the weight of oxygen is neglected, the potential electrical energy density per unit weight of Fe used in air cells is estimated to be 1160 Wh/kg, and that of Al is estimated to be 8100 Wh/kg. The potential energy of Al is 7 times higher than that of Fe. The atomic weight of Fe is 55.6, and that of Al is 27. Thus, the potential current of Al is higher than that of Fe, indicating that Al has an advantage for generating electricity.

The electrical resistance of metal plates must be adequately low because currents are extracted from such plates. A large plate made from sintered paste may have a high electrical resistance, resulting in the degradation of the output voltage. Because we did not fabricate large-scale metal plates, the sintered metal plates had lower electrical resistances, and their resistance could not be estimated. However, the resistance is as low as that of common metal plates. A dissimilar metal joint is important for improving the electromotive force of air cells.

By sintering metal paste on common metal plate, a more rigid connection between them is obtained, and contact resistance is reduced. From the experimental result, it has been thought that a dissimilar metal joint between the Al and Mg plates for the negative metal electrode has a low contact resistance. When using a Mg plate, the output voltage of air cells decreased 80 minutes after connecting electric codes. However, when using Al paste and a Mg plate as an air cell, the output voltage was sustained 40 minutes after connecting the codes. Because the output voltages of the Al paste -Al air cells are the same as that of the Al air cells when the load is low, the output voltage will be maintained near 1.4 V for 80 minutes if the area of the metal paste is twofold. After using Fe and Al in air cells, metal oxides are generated. These metal oxides return to Fe and Al by laser ablation in liquid. The negative metal electrode used is exchanged to new ones. In this experiment, to improve the electromotive force of air cells, we had used a Mg plate as a base metal plate. Using Li plates will improve the electromotive force when sintered Al paste is used, and a higher electrical stored energy per unit weight of the air cells will be obtained.

Solar energy or other natural energies are considered as the sources of laser power for laser ablation in liquid. However, the most suitable lasers for energy cycles are considered to be solar-pumped lasers because common lasers have a low electro-optical conversion efficiency and their generated energy gains are vanished.

Repetitive usage of metal oxide by laser ablation and researching the maximum stored energy gain of metals are the future objects.

Conclusions

As an example of renewable energies for utilizing solar energy efficiently, a renewable energy obtained using metallic nanoparticles fabricated by laser ablation in liquid was proposed in this study. Laser pulses are generated using solar power. It has been clarified that metal nanoparticles can be used in metal air cells to generate electricity.

By using high repetitive laser pulses, an alternative to pulsed solar-pumped lasers, Fe_3O_4 and Al_2O_3 were reduced, and Fe and Al nanoparticles were fabricated. Metal plates were obtained by sintering paste with Fe and Al nanoparticles at around 520 K. It was found that Fe and Al metal plates have low electrical resistances.

The electrical properties of the air cells using Fe and Al plates fabricated by sintering Fe and Al nanopaste had been compared with those using Fe and Al plates fabricated in a blast furnace. Very close output voltages and currents were obtained. Different species of junction metal plates were used as negative electrodes for the air cells. A higher output voltage of the Al paste–Mg air cells than that of the Al air cells has been obtained. Al was connected to Mg tightly by sintering Al nanopaste. The measured out put voltage of Al paste-Mg air cell was 1.4 V when an electrical motor was connected, which is the same as that of the Mg air cell. Also, a high output voltage of the Fe paste-Al air cell than that of the Fe air cell was obtained.

REFERENCES

[1] P. Charvin, S. Abanades, F. Lemort, and G. Flamant, "Hydrogen Production by Three-Step Solar Thermochemical Cycles Using Hydroxides and Metal Oxide Systems", *Energy & Fuels*, vol. 21, pp.2919-2928, July 2007.

[2] D. G. Rowe, "Solar-powered lasers", *Nature Photonics*, vol. 4 pp.64-65, Feb. 2010.

[3] 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.*, vol. 90 pp.261120-261122, June 2007.

[4] M. S. Mohamed, T. Yabe, C. Baasandash, Y. Sato, Y. Mori, L. Shi-Hua, H. Sato, and S. Uchida, "Laser-induced magnesium production from magnesium oxide using reducing agents", *J. Appl. Phys.*, vol. 104 pp.113110-113116, Dec. 2008.

[5] M. Weksler and J. Shwartz", Solar-pumped solid-state lasers", *IEEE J. Quantum. Electron*, vol. 24 pp.1222-1228, July 1988.

[6] T. Saiki, S. Motokoshi, K. Imasaki, K. Fujioka, H. Yoshida, H. Fujita, M. Nakatsuka, and C. Yamanaka, "Highly-repeated laser pulses amplified by Nd/Cr:YAG ceramic amplifier under CW arc-lamp light pumping", *Opt. Comm.*, vol. 282, pp.2556-2559, May 2009.

[7] T. Saiki, S. Motokoshi, K. Imasaki, K. Fujioka, H. Yoshida, H. Fujita, M. Nakatsuka, and C. Yamanaka, "Nd3+- and Cr3+-doped yttrium aluminum garnet ceramic pulse laser using Cr4+-doped yttrium aluminum garnet crystal passive Q-Switch", *Jpn. J. Appl. Phys.*, vol. 48 pp.122501-1-7, Jan. 2009.

[8] T. Saiki, M. Nakatsuka, K. Imasaki, "Highly efficient lasing action of Nd3+- and Cr3+-doped yttrium aluminum garnet ceramics based on phonon-assisted cross-relaxation using solar light source", *Jpn. J. App. Phys.*, vol. 49 pp.082702-1-8, Aug. 2010.

[9] A. Henglein, "Physicochemical properties of small metal particles in solution: "microelectrode" reactions, chemisorption, composite metal particles, and the atom-to-metal transition", *J. Phys. Chem.*, vol. 97 ©pp.5457-5471, May 1993.

[10] M. S. Sibbald, G. humanov, and T. M. Cotton, "Reduction of cytochrome c by halide-modified, laser-ablated silver colloids", *J. Phys. Chem.*, vol. 100 ©pp.4672-4678, Mar. 1996.

[11] M. Kawasaki and N. Nishimura,"Laser-induced fragmentative decomposition of ketone-suspended Ag2O micropowders to novel self-stabilized Ag nanoparticles", *J. Phys. Chem. C*, vol. 112 pp.15647-15655, Sep. 2008.

[12] H. Q. Wang,, A. Pyatenko, K. Kawaguchi, X. Y. Li , Z. Swiatkowska-Wackocka, and N. Koshizaki, "Selective pulsed heating for the synthesis of semiconductor and metal submicrometer spheres", *Angew. Chem. Int. Ed.*, vol. 49 pp.6361-6364, Aug. 2010.

[13] S. Taniguchi, T. Saiki, T. Okada, T. Furu, "Synthesis of reactive metal nanoparticles by laser ablation in liquids and its applications", Report on The 421th Topical Meeting of The Laser Society of Japan, Laser Technology for 21st Century, No. RTM-11-56, (2011) pp.25-30 [in Japanese].

[14] J. Purnell, E. M. Snyder, S. Wei, and A. W. Castleman, Jr, "Nuclear fusion induced by coulomb exprosion of heteronuclear clusters", *Chem. Phys. Lett.*, vol. 229 pp.333-339, Nov. 1994.

[15] K. Yamada, 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, vol. 111, pp.033401-1-4, July 2007.

[16] 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*, vol. 112 pp.1929-1932, Jan. 2008.

[17] K. Ikawa, T. Horiba, Air Cells, Japan Patent 258782, Oct. 8, 1993.

[18] Y. Kudo, M. Suzuki, Al slid-stage Air Cells, Japan Patent 147442, July 20, 2006.

[19] Y. Kataoka, and S. Itushiki, For Analysis by X radiation, Production Research vol. 12 (1960) p.311 [in Japanese].