
Recyclable metal air fuel cells using sintered Magnesium paste with reduced Mg nanoparticles by high-repetitive ns pulse laser ablation in liquid

Taku Saiki^{1,*}, Shigeaki Uchida², Tatsuya Karita¹, Kazuhiro Nakamura¹, Yuusuke Nishikawa¹, Shinji Taniguchi³, Yukio Iida¹

¹Department of Electrical and Electronic Engineering, Faculty of Engineering Science, Kansai University, 3-3-35 Yamate, Suita, Japan

²The Graduate School for the Creation of New Photonics Industries, 1955-1 Kurematsu-cho, Nishiku, Hamamatsu, Shizuoka, Japan

³Institute for Laser Technology, 1-8-4 Utsubo-honmachi, Nishi-ku, Osaka, Japan

Email address:

tsaiki@kansai-u.ac.jp (T. Saiki)

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Abstract: An energy cycle using solar power and metals has been proposed. High repetitive laser pulses are generated by a solar-pumped laser or a laser generated using solar power, and the laser pulses are irradiated to metal oxides in liquid. We can obtain reduced metal nanoparticles with this method, and solar power is effectively stored as chemical energy. We succeeded in producing sintered Mg metal paste. The sintered Mg nanopaste reduced Mg nanoparticles from pure MgO or Mg(OH)₂ powder, collected from used Mg air cells, by laser ablation in liquid using a high-repetitive ns pulse Nd:YAG laser. We also fabricated metal air fuel cells using sintered Mg plates as negative electrodes. Electricity was successfully produced from these cells. A light-emitting diode and a motor were connected to the Mg paste air fuel cells and the output voltage and current of the cells were measured. The observed output voltage was 1.4 V when they were connected to a low load, which is the same as conventional Mg air cells. Metal oxides were reduced with high efficiency and at a noticeably low cost by using lasers generated from solar energy. This makes it possible to recycle Mg plates. The new recyclable Mg paste air fuel cells are expected to become common power supplies with high-energy density and high output power.

Keywords: Magnesium, Recycle, Solar Power, Solar-Pumped Pulse Laser, Laser Ablation in Liquid

1. Introduction

Using renewable energy, such as solar power, wind power, thermal power, and biomass, has become attractive due to the depletion of fossil fuels and the environmental issues with nuclear power. In previous experiments, metal oxide powders were reduced to metal powders by using solar power. This means that chemical energy is stored in the reduced metals. Hydrogen was produced using reduced metal powders [1]. Reduction of metal oxides by solar power has been commonly conducted one decade ago. However, this system has yet to be made practical. The reduction efficiency was low of a few percentage points heated metal oxides by solar power. Reduction occurs by separation of the oxide and metal atoms by heating metal oxides at a high temperature. Metal oxides are heated at only 3000 K by using solar light. By using solar light, the powder density of focused solar light is limited by

the divergence angle of the solar light, which is not adequate for reducing and evaporating metal oxides. The power density of focused solar light is required to vaporize metal oxides resulting from the reduction of these metal oxides. A temperature of close to 5000 K is required to efficiently reduce metal oxides to metals. Reducing metal oxides by continuous wave (CW) laser light converted from solar light [2,3,5-7] instead of solar light directly has been proposed and research on this reduction has been conducted [2-4]. However, metal oxides are reduced by heating them at a high temperature when using a CW laser. The mechanism for this reduction is the same as that using solar light. Efficient reduction must be done using a high-power laser with an output power of over 100 W. In fact, reduction efficiency of metal oxides degrades due to the decrease in the temperature of heated metal oxides at a position where the intensity of the beam is weak. The average reduction efficiency was up to a few percentage points

during the experiments owing to recombination of generated oxygen with Mg vapor. The solar light was effectively converted to chemical energy with less than 1% [4]. Preventing to recombine oxygen with Mg vapor in reducing metal oxides by continuous wave (CW) laser light is future object.

We have been conducting experiments on the reduction of metal oxides with high reduction efficiency by using a method different from that described above [8,9]. Collected solar light is converted to high repetitive laser pulses by using a solar-pumped laser, and the laser pulses are irradiated to metal oxides in liquid. We can obtain reduced metal nanoparticles with this method, and solar power is effectively stored as chemical energy. Reduction of metal oxides by using laser ablation in liquid does not occur by separation of metals and oxides at high temperature. It has been suggested that the reduction process occurs due to separation with a high electrical field generated by ejection of electrons from metal oxides [10-15]. We previously succeeded in reducing Fe and Al metal oxides with high reduction efficiency [8,9]. Figure 1 shows the instrument for mass-producing reduced metal nanoparticles from metal oxides using a solar pumped high-repetitive laser. One hundred grams of metal oxide were reduced per day using this instrument.



Fig. 1. Instrument for producing reduced metal nanoparticles from metal oxides using solar-pumped high-repetitive laser in action.

Research on hydrogen reacting with these reduced metal nanoparticles with steam has been conducted [9]. These reduced metal nanoparticles are applicable to metal air fuel cells, which generate electricity by metal chemically reacting with oxygen [8,16,17].

Air fuel cells are expected to become common power supplies with higher energy density than that of Li-ion batteries. Air fuel cells are used as recyclable primary batteries. The used metals in the metal fuel cells can be collected and recycled at anytime. The used metal plates can be changed into metal oxides finally. These metal oxides should be recycled into metals. We also must reduce the amount of metal oxides to metals at low cost and high efficiency to construct a system that satisfies the requirements of air fuel cells. Magnesium exists abundantly on the earth's surface and in the

oceans. Its Clark number is 8th among all materials and is ideal as energy storage material.

The energy storage efficiency from solar power to metals is low. However, this is not correct because there is a special mechanism for reducing metal oxides into metals using irradiating laser pulses with high intensity. In commercial systems for storing solar energy and generating electricity using solar panels and Li-ion batteries, the maximum storage efficiency is commonly up to 7%. This storage efficiency should degrade due to the temporal dependence on the generated electricity. Moreover, the system has issues of high cost and following the loads. The solar power system has a fundamental and principle issues. While, the system we propose may solve the above problems. Pure MgO powder and Mg(OH)₂ powder were reduced by laser ablation in liquid using a high-repetitive pulse laser, producing reduced Mg nanoparticles. Magnesium nanopastes with Mg nanoparticles were sintered, and Mg metal plates with low resistivity and a multi-crystalline structure were obtained. We also fabricated metal air fuel cells using the sintered Mg paste plate and measured the output voltages and currents.

2. Experimental methods

2.1. Fabrication of Metal Nanopastes

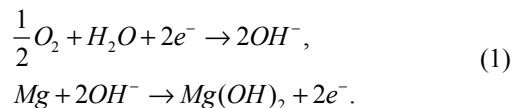
We used MgO powder (mean diameter was 1 μm, purity 99.9%, Koujyunndo chemical co. Ltd, Japan) as a metal oxide. We also used Mg(OH)₂ powder obtained from Mg air cells that generate electricity for comparison. The reduced Mg nanopowders from MgO and Mg(OH)₂ powders were used to produce Mg nanopastes. The Mg(OH)₂ powder can change to MgO powder by heating. However, a large amount of energy is required for this chemical reaction. We investigated if Mg(OH)₂ powder can be reduced to Mg nanoparticles by using a laser and that sintered Mg paste can be metalized with adequate low resistance. High-repetitive laser pulses with a wavelength of 1064 nm and pulse duration of 8 ns were focused using a lens [8,9]. The focused laser pulses were directly irradiated in water with MgO powder from the side surface of a glass bottle. Also, the focused laser pulses were irradiated in water with Mg(OH)₂ powder in the same way. The volume of the used water in a glass bottle was 10 mL.

Irradiation with laser pulses was done for ten minutes. The weights of both the MgO and Mg(OH)₂ powders were 1.0 g. However, metal oxide powders over 1 g can be reduced to metal powders. For the glass bottle with the Mg(OH)₂ powder, the water was first wasted after laser irradiation, and the powder was dried. For the MgO powder, the powder was mixed with the water and dried. The obtained Mg nanoparticles were mixed with Ag nanopaste, (Ag 82 wt. %, Daiken chem. Co. Ltd, Japan). The weight of the mixed Ag nanopaste was around 10 mg. The Mg nanoparticles was mixed with the Ag nanopaste as much as possible. After that, the produced Mg nanopastes were pasted onto common Mg metal plates and heated using an electrical hot plate. The main reasons for mixing Mg nanoparticles with Ag nanopaste are 1)

to remove the oxygen on the surface of the reduced Mg nanoparticles and 2) incorporating Mg nanoparticles into a metal coordination bond, resulting in a stable dispersion property. Also, Ag is difficult to oxidize. The Mg nanopastes were heated at 200°C for one minute then at 260°C for 5 min to metalize it. The Mg nanopastes were then sintered, as mentioned above, and the sintered Mg nanopastes with low resistance were used as negative metal electrodes in the metal air fuel cells. An x-ray diffraction (XRD) instrument (MAXima_X XRD-7000, Shimadzu, Japan) was used to analyze the materials of the MgO powder, Mg(OH)₂ powder, and sintered Mg nanopastes.

2.2. Metal Air Fuel Cells

We fabricated metal air cells. The structure of a metal junctional metal air cell is shown in Fig. 2. We used paper saturated with salt water as an electrolyte of the metal air cells. In these cells, the Mg nanopastes in Fig. 2, thus only the reduced Mg metal nanoparticles, were resolved into the salt water, and electricity was produced. The chemical reaction between Mg metal and oxides in the Mg metal air cells is shown below.



Electrons generated when Mg nanoparticle is ionized were collected using conventional, Mg metal plates, as shown in Fig. 2. After generating electricity, Mg(OH)₂ powder was produced between the Mg paste and paper. The base metal plate behind the Mg paste to extracting electrons must have an adequate high reference potential to obtain a high output voltage because of decreasing the loss of the ionization energy. The stored energy density of the Mg air cells was theoretically evaluated to be 4500 Wh/kg without oxygen in the atmosphere.

The sintered Mg nanopastes were used as the negative electrodes of the Mg paste air cells. The size of the two sintered Mg nanopastes was 14×16 mm² and thickness was 0.3 mm. A porous carbon electrode of 14×16 mm² (JS-7900MG, Elekit, Japan) and 0.5-mm thickness was used for collecting oxygen. In the experiment, the Mg nanopaste air cells were connected to two kinds of loads, and the temporal dependence on the output voltage of the cells were measured. White light-emitting diode (LED) illumination (3 LED touch light mini, Green Ornament, Japan) was used as one load. The circuit of white LEDs consisted of a cascade connection of three LEDs and a resistance. A power supply with an output voltage of 3.0 V was required for the three LEDs. Because this voltage was high, a DC-DC converter (MCP1640, Strawberry Linux, Japan) was used for boosting the output voltage of the Mg nanopaste air cells up to 3.0 V. The electrical conversion efficiency of the DC-DC converter was close to 90%. A motor (Solar Motor 02, 76005, Tamiya, Japan) with a propeller was chosen as the second load. Finally, the voltage-current (V-I) properties of the Mg nanopaste air cells

were measured to determine their output current.

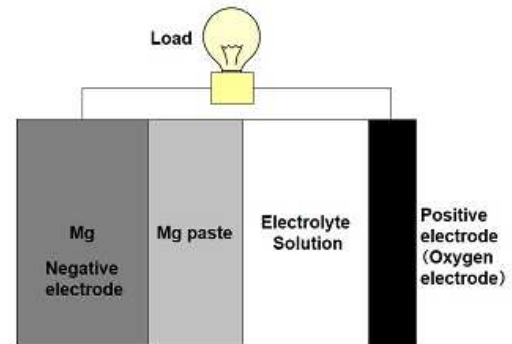


Fig. 2. Air fuel cells using sintered Mg paste

3. Results and Discussion

3.1. Sintering of Metal Nanopastes

The reduced Mg nanopowders are shown in Figs. 3 and 4. The MgO powder is shown in Fig. 3(a), and that after irradiating with laser pulses is shown in Fig. 3(b). The Mg(OH)₂ powder obtained from the Mg air cells is shown in Fig. 4(a), and dried powder after irradiating with laser pulses is shown in Fig. 4(b). As shown in Fig. 3(a), the MgO powder was white, but the color slightly changed to gray, as shown in Fig. 3(b). The color was close to the metal powder. For reduction efficiency, we conducted an experiment to produce hydrogen by using the reduced Mg powder, similar to what we did [9]. We used an iron oxide, Fe₃O₄ powder, which was reduced to iron metal by laser ablations in liquid; the evaluated reduction efficiency was over 97%. However, the metal nanoparticles had a very thin oxide shell. The reduction efficiency of both reduced Mg nanopowders were evaluated from the volume of the generated hydrogen. The evaluated reduction efficiency was over 95% and close to perfect.



Fig. 3. (a) MgO powder and (b) after laser irradiation.



Fig. 4. (a) Mg(OH)₂ powder collected from Mg air cells and (b) after laser irradiation

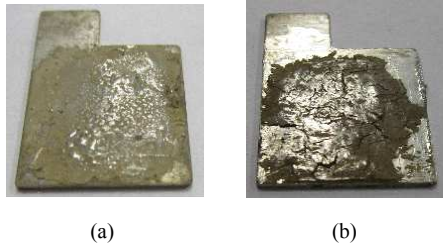
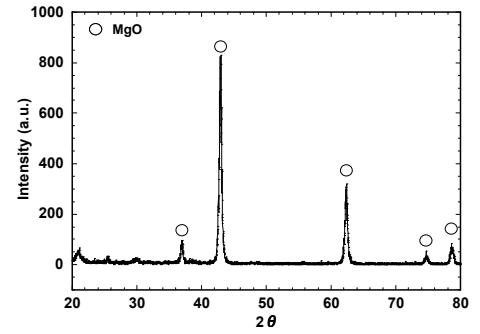


Fig. 5. Sintered Mg plates (a) using MgO powder and (b) using Mg(OH)₂ powder obtained from Mg air cells

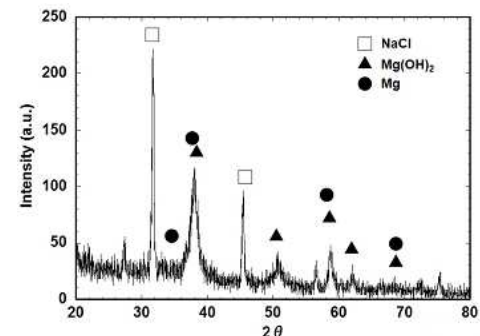
We evaluated the mean size of the generated Mg nanoparticles by using Scherrer's equation and the width of the angle for obtained X ray spectrum. The evaluated mean size of the produced Mg nanoparticles was evaluated to be 4 nm. The produced Mg nanoparticles had hydroxide shells due to using water for laser ablation. The core of the nanoparticles was very close to pure Mg metal. Thus, there was no problem producing the Mg nanopastes. A sintered Mg nanopaste made from MgO powder is shown in Fig. 5(a), and a sintered Mg nanopaste made from Mg(OH)₂ powder collected from Mg air cells is shown in Fig. 5(b). As shown in Fig. 5, both sintered Mg nanopastes had lusters and low resistivity. The volume resistivity evaluated by four-terminal method was ten times higher than that of common Mg metal.

3.2. XRD Analysis

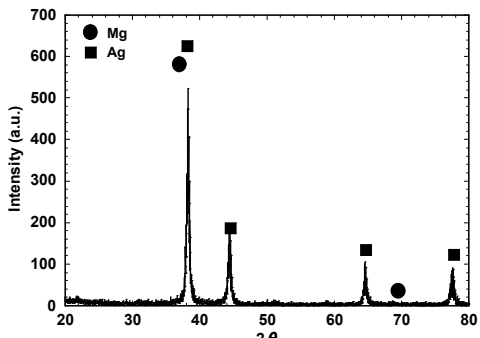
The results of XRD analysis for the MgO and Mg(OH)₂ powders obtained from Mg air cells, and the sintered Mg nanopastes are shown in Fig. 6. The results of XRD analysis for the MgO powder are shown in Fig. 6(a), and those for the Mg(OH)₂ powder are shown in Fig. 6(b). The results in Fig. 6 (b) suggest that the Mg(OH)₂ powder initially contained Mg powder and NaCl before laser irradiation. The results of XRD analysis for the sintered Mg nanopaste made from MgO powder are shown in Fig. 6(c), and those for the sintered Mg nanopaste made from Mg(OH)₂ powder are shown in Fig. 6(d). The results in Figs. 6(c) and (d) suggest that both sintered Mg nanopastes had less MgO or Mg(OH)₂. The results shown in Fig. 6(d) also suggest that the sintered Mg nanopaste made from Mg(OH)₂ had less NaCl. A weak broad X ray spectrum exists near the angle of 36.6 degrees, as shown in Figs. 6(c) and (d). The X ray spectrums should show the existence of Mg. It was assumed that the spectral intensity would be weak because the sintered Mg nanopastes had a nano-sized crystalline structure. We evaluated the mean size of the metal crystals for the sintered Mg nanopastes by using Scherrer's equation and the width of the angle for the obtained X ray spectrum, as shown in Fig. 6(c). The evaluated mean size was also 4 nm. Conventional Mg metal bulk, which is made in blast furnaces, has no magnetism because the sizes of the metal crystals are large and random, and the magnetism is concealed inside. However, these sintered Mg nanopastes are ferromagnetic and flame retardant. Thus, they have less risk of a fire.



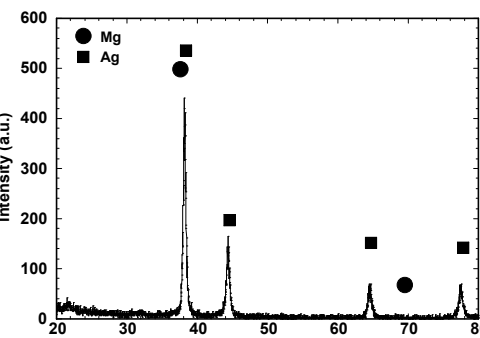
(a)



(b)



(c)



(d)

Fig. 6. Analyzed XRD patterns. (a) MgO powder, (b) Mg(OH)₂ powder obtained from air cells after generating electricity, (c) sintered Mg nanopaste from MgO powder, (d) Sintered Mg nanopaste from Mg(OH)₂ powder obtained from air cells after generating electricity.

3.3. Fabrication of Mg Paste Air Cells

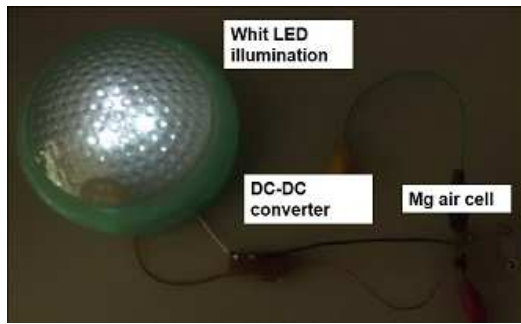


Fig. 7. Photo of white LEDs illuminated using Mg paste metal air cell

The Mg nanopaste air cells were connected to white LEDs, and the output voltage of the cells were measured using a data logger (VR-71, T and D, Japan). A photo of white LEDs illuminated using the Mg nanopaste air cells is shown in Fig. 7. The temporal dependencies on the output voltage of the Mg nanopaste air cells when the white LEDs were connected are shown in Figs. 8(a) and (b). The measured output voltage of the air cell using Mg nanopaste made from MgO powder is shown in Fig. 8(a), and the measured output voltage of the air cell using Mg nanopaste from Mg(OH)₂ powder is shown in Fig. 8(b). The output voltages of the cells were measured for 150 minutes. The output voltages of the cells were compared with that when using a conventional Mg air cell. The white squares show the use of a conventional Mg air cell. As shown in Fig. 8(a), the initial output voltage was 1.45 V. After that, it was constant at 1.4 V. The output voltage of the Mg nanopaste air cell using Mg nanopaste made from MgO powder was almost the same as that using Mg nanopaste made from the Mg(OH)₂ powder, as shown in Figs. 8(a) and (b). The output voltages of the Mg nanopaste air cells using Mg nanopastes were almost the same as when using a conventional Mg air cell. The output current of both Mg nanopaste air cells and a conventional Mg air cell was 4 mA.

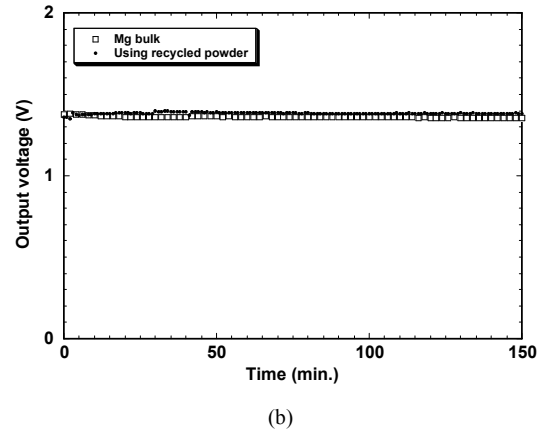
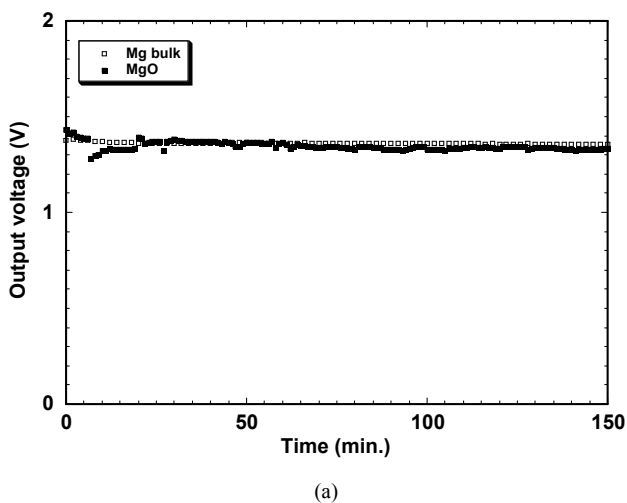


Fig. 8. Measured output voltages of Mg nanopaste air cells. (a) Using Mg nanopaste made from MgO powder and (b) using Mg nanopaste from Mg(OH)₂ powder.

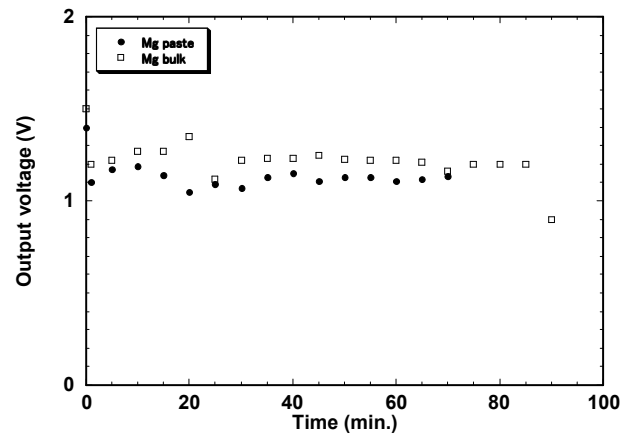


Fig. 9. Measured output voltages of Mg nanopaste air cells when solar motor was connected.

The measured output voltages of Mg nanopaste air cells when a solar motor with a propeller was connected are shown in Fig. 9. A sintered Mg nanopaste made from MgO was used as the metal air cell because the electrical property was almost the same as when using a sintered Mg nanopaste made from Mg(OH)₂ powder. The measured output voltages were 0.05 V lower than when using a conventional Mg air cell. However, the Mg nanopaste air cells could run the solar motor for 90 minutes. The initial output current of the conventional Mg air cell was 28 mA, and the output current of the Mg nanopaste air cells was 24 mA. The results could be obtained because the effective surface area of the Mg nanopaste air cells is smaller than that of the Mg plate used as a negative electrode.

Finally, the output V-I properties for Mg air and Mg nanopaste air cells are shown in Fig. 10. The data shown in Fig. 10 were obtained when electricity generated from the Mg nanopaste air cells began. The output current and output voltage of the Mg nanopaste air cells increased with time and became close to that of the conventional Mg air cell, as shown in Fig. 10. The measured maximum output current of the conventional Mg air and Mg nanopaste air cell made from MgO powder was 150 and 120 mA, respectively. This is because the effective surface area of the Mg nanopaste was

smaller than that of the Mg plate used as the negative electrode in the conventional Mg air cell. The reason was already mentioned above. Another reason seems to be that the reaction of the Mg nanopaste with salt water does not initially proceed well. Also, judging from the slope of the output voltage to current, as shown in Fig. 10, the internal resistance was evaluated to be 3 ohms. We found that internal resistance was almost equal to that of the conventional Mg air cell. The resistance depends on the positive porous carbon electrode. The evaluated volume resistivity was ten as high as that of the conventional Mg metal bulk, and the resistances did not degrade the output voltage of the Mg air cell when the output current was large. The output voltage of the both Mg nanopaste air cell was 0.1 V lower than that of the conventional Mg air cell. The difference in the output voltage is thought due to the difference in the crystal structure between the conventional Mg plate and sintered Mg nanopastes. The degradation in output voltage should occur at the boundary between the Mg plate and sintered Mg nanopaste.

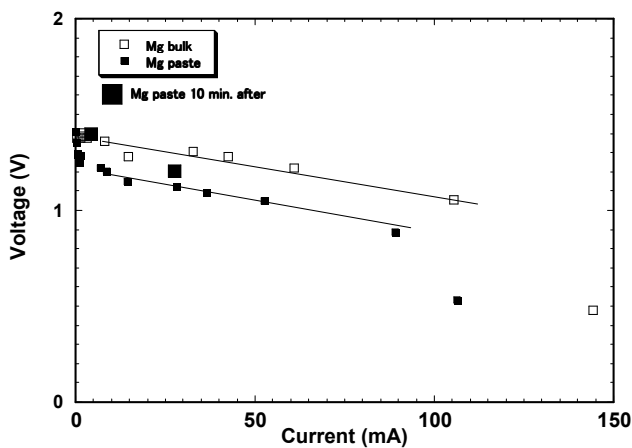


Fig. 10. Voltage- current property for Mg air cell and Mg nanopaste air cell. The large black square data were one for the Mg nanopaste air cell obtained after ten minutes when the power generation was started.

3.4. Future Objects

If metal air cells are used as recyclable primary cells, which will be alternatives to secondary batteries, Mg plates used as negative electrodes will be set into cartridge. Such air cells will be used as disposable primary cells. The experimental results discussed in this paper suggest that Mg metal can be recycled from MgO or Mg(OH)₂ powder. Magnesium metal plates are changed into Mg(OH)₂ powder after using metal air cells. Also, Mg(OH)₂ powder can be changed into MgO powder through additional heating.

The amount of MgO or Mg(OH)₂ powder must be used to reduce at low cost and quickly for Mg metals to be used in air cells. It will be possible to modify the output laser power of the solar-pumped pulse lasers or lasers generated using solar power and to increase the number of instruments for reducing metal oxides. The wavelength of the laser pulses used in this experiment was 1064 nm, which is the same as the laser wavelength of the Nd/Cr:YAG ceramic, which uses solar-pumped lasers [6,7].

We must then conduct experiments to determine how many times a Mg plate can be recycled and still produce electricity. The experiments should be close to actual use conditions.

4. Conclusion

We produced sintered Mg metal paste with reduced Mg metal nanoparticles on conventional Mg plates. The Mg nanoparticles were produced from MgO or Mg(OH)₂ powder collected from used Mg air cells by laser ablation in liquid using high-repetitive ns pulse Nd:YAG laser with a wavelength of 1064 nm. We also fabricated metal air fuel cells using sintered Mg plates as negative electrodes. These cells generated electricity. The electrical properties, such as output voltage or currents, for these cells were investigated. The temporal dependence on the output voltage of the Mg paste air cells was also observed. The observed output voltage was 1.4 V when connecting to a low load. The output voltages of the Mg paste air cells were slightly lower than that of a conventional Mg air cell. However, the obtained current density was almost the same. These results suggest that recycling of Mg plate is possible by irradiating high-repetitive laser pulses with high intensity in liquid, which was generated using solar power. This means that solar energy can be effectively stored in Mg plates anytime.

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