Effect of Reduction Agent on ZnO Reduction by Radio-frequency Dielectric Heating

Shinobu MUKASA†, Yuki UDACA, Koudai MATSUZAWA, Nobuyuki DOI, Hiromichi TOYOTA, and Shinfuku NOMURA

(Received January 23, 2017)

Metal air battery attracts attention as an automobile battery, because of its high energy density. In order to reuse the battery, it is necessary to undertake reduction of metal oxide which is generated at the cathode without large environment load. We conducted the reduction of ZnO powder by radio-frequency dielectric heating. The ZnO powder and a reducing agent of organic liquid is put into a reaction vessel, and the tip of the electrode inserted from the top of the vessel is in contact with the surface of the powder. By measuring the spectrum of the black-body radiation, the temperature was found to be approximately 2000 K. The reduction amount of ZnO increased remarkably when 0.7 to 1.4 mL of methanol was added as a reduction agent to 2.0 g ZnO powder, with a maximum of 27.6 mg at 1.1 mL reached. The reduction amount was smaller when ethanol, acetone, furfural, cyclohexane or dodecane were added as a reduction agent. The maximum energy efficiency is 3.3% without taking the reaction energy of the reduction agent into consideration, whereas it becomes 1.0% when taking it into consideration.

Key Words
Reduction, Dielectric Heating, Radio-frequency, Reduction agent, Air battery

1. Introduction

The problems of global warming, air pollution, depletion of fossil fuels and such arise due to the increasing energy demand brought on by the economic growth in the world today. As one solution to these problems, the air battery is attracting increased attention. An air battery has an energy density greater than that of the conventional lithium ion battery, is filled with metals, such as Zn, Al, Mg and Li as an anode active material, and uses oxygen from air as a cathode active material. It is used as a battery for electronic devices, and is expected to be used in electric vehicles. However, since it is usually a primary battery, that is, it cannot be recharged, exchange of the battery after use is required, and recycling is necessary to mitigate its environmental impact, which in this case, means reducing the metal oxide to the original metal.

Reduction of zinc oxide has usually been conducted by two methods, pyrolysis and electrolysis. In pyrolysis, zinc oxide is reduced over 2100 K spontaneously without adding any reducing agent. However, by adding reducing agent, for instance, solid carbon, carbon monoxide, methane and hydrogen, the temperature to cause the reduction decreases to approximately 1100 K. In recent years, pyrolysis using solar power of 300 kW adding biomass as a reducing agent was conducted, and the energy...
efficiency was reported to be 30%\(^9\). On the other hand, electrolysis using an ionic liquid was conducted, and the efficiency was reported to be over 80%\(^17\).

Reduction of metal oxide by in-liquid plasma has been studied\(^18\). The in-liquid plasma reduction is the method by which plasma is generated in an alcohol in which the metal oxide powder is dispersed. By inducing radio-frequency and microwaves to the submerged electrode, plasma is generated in bubbles in the liquid, and the interior of these bubbles provide a high temperature and highly active reaction field\(^19\) ~ \(^21\).

There are three advantages of this technique. The first is its relatively small environmental impact, the second is separating the reaction area from air and the last is the efficient supply of alcohol as a reducing agent to the reaction area. When experiments were conducted on alcohol in which zinc oxide (ZnO) powder is dispersed using a microwave of 2.45 GHz\(^18\) and radio-frequency of 27.12 MHz, the reduction amount was much smaller than expected. This is because the surface tension prevents ZnO powder from penetrating the reaction area in the bubble. Meanwhile, reduction of ZnO powder by plasma in gas phase was difficult, because temperature of the apparatus was increased without heat absorption by evaporation of liquid around the plasma. However, even if the power of radio-frequency was lowered until plasma could not be sustained, the ZnO powder around the electrode was found to be heated enough for the reduction by dielectric heating.

In this research, a radio-frequency electrode of 27.12 MHz inserted into a container filled with a methanol vapor was brought into contact with the surface of ZnO powder in a sample bottle set in the container, and then the reduction of ZnO by radio-frequency dielectric heating was conducted. First, the product was analyzed by using a transmission electron microscope (TEM) and X-ray diffraction (XRD) and energy dispersive X-ray spectrometry (EDS). The sample is analyzed by using TEM (JEM-2100, JEOL), XRD (RAPIDII-V/DW, Rigaku) and EDS. The accelerating voltage of TEM and EDS is 200 kV. Incident X-ray of XRD is CuK\(\alpha\) (0.154 nm). The reduction amount is measured from the amount of hydrogen gas generated when the sample is dissolved at the end of the experiment into an aqueous hydrochloric acid. The reaction equations of Zn and ZnO in an aqueous hydrochloric acid are the followings:

\[
\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2 \quad (3)
\]
\[
\text{ZnO} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O}. \quad (4)
\]

Only Hydrogen is generated by the reaction of Zn.

2. Experimental

The outline of the experimental device is shown in Fig. 1. In the sealed container made of polycarbonate tube of 55 mm inside diameter, a sample holder which is filled with ZnO powder (JIS Special Grade, Wako) and a reduction agent is fixed in a base made of Teflon. In addition to the reduction agent, methanol for substitution of air is injected in the container. The container is filled with vapor of methanol by decompressing the container using an aspirator to 10 kPa. A Cu electrode of diameter \(\phi\) 3 mm is inserted from the top of the container, and the electrode tip comes in contact with the ZnO powder surface. ZnO powder is heated by applying 27.12 MHz radio-frequency of 30 W from a power supply (T161-6066TLQ, Thamway) to the electrode.

When assuming that the reduction agent was fully oxidized with the reduction of ZnO, the reaction equation is expressed as follows:

\[
\text{ZnO} + n\text{C}_3\text{H}_7\text{O} \rightarrow \text{Zn} + n\text{CO}_2 + \frac{ny}{2}\text{H}_2\text{O}, \quad (1)
\]

where

\[
n = \frac{1}{2x + y/2 - z}, \quad (2)
\]

The sample is analyzed by using TEM (JEM-2100, JEOL), XRD (RAPIDII-V/DW, Rigaku) and EDS. The accelerating voltage of TEM and EDS is 200 kV. Incident X-ray of XRD is CuK\(\alpha\) (0.154 nm).

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\]

3. Results and Discussion

A heat-resisting glass test-tube 6 mm in inner diameter used as a sample holder was filled with 0.5 g of ZnO powder without a reduction agent. After the radio-frequency power supply was turned on, the ZnO powder in contact with the electrode turned black and red heat was also observed indicating radio-frequency dielectric heating. The emission spectrum from the heating was measured. In order to retain stable heating, 0.3 mL of methanol is added into the sample holder. The spectrum is shown in Fig. 2.
Continuous black-body radiation from a visible region to an infrared region with some peaks of Zn was confirmed. By applying the spectral radiance equation of Planck's law, the temperature was found to be approximately 2000 K. In wavelength longer than approximately 600 nm, the difference from the Planck's law is caused due to the spectral emissivity of ZnO. The peaks of Zn were identified from NIST Atomic Spectra Database.

The black-colored area in the ZnO powder caused by dielectric heating expanded in approximately 30 s from the start of heating. The TEM picture of the black-colored powder is shown in Fig. 3. Polygonal particles of 10 to 40 nm were confirmed. Because oxygen was barely detected from EDS measurement of these particles, they are considered to be Zn particles synthesized by reduction of ZnO powder.

Diffraction spectrum of XRD is shown in Fig. 4. Although peaks of ZnO existed, peaks of Zn were confirmed in addition. Peaks of Zn were confirmed from the gray products as well, however their strength was much smaller than that from the black product. The gray products which were provided by heating the black product continuously was considered to be yielded by re-oxidization.

The reduction agent was added to the ZnO powder directly into the sample holder. To investigate the relationship between the reduction agent and the reduction amount, the sample holder is exchanged to a 5 mL sample bottle made of heat-resistant glass, and 2.0 g of ZnO powder is supplied. When 0.9 mL of methanol was added to the powder, the amount of reduction by heating time was measured. As shown in Fig. 5, the amount of reduction increases with elapsed time and reaches 25.4 mg at 120 s. After that, though there is a slight decrease, the amount remains almost constant. This is because the reduction agent in the sample holder was evaporated fully at approximately 120 s.

According to visual observation, the gray-colored area expanded from the ZnO surface in contact with the electrode in approximately 90 s, and the area started to become darker at approximately 120 s. Moreover, movement of the powder close to the surface in a radial direction is observed. This is because the evaporated methanol in the bottle expands and decomposes thermally around the
electrode tip where the dielectric heating occurred, and such a gas flow affects the surrounding powder. The black-colored powder was mixed with the original white ZnO powder, and therefore the mixed powder turns gray.

Fig. 6 shows the reduction amounts for methanol, ethanol or dodecane used as a reducing agent for a heating time of 120 s. When the 0.7 to 1.4 mL of methanol was supplied, reduction increased remarkably, reaching a maximum of 27.6 mg at 1.1 mL. When ethanol was supplied, the reduction amount reached a maximum of 6.2 mg at 0.9 mL, however the change for ethanol was relatively small compared with the case for methanol. When dodecane was supplied as a reducing agent, although the reduction amount reached a maximum of 3.8 mg at 0.9 and 1.2 mL, its effect as a reducing agent was almost negligible. It is supposed that the agent evaporated fully before 120 s, when the amount of the reduction agent is smaller than 1 mL, while the temperature increase is suppressed when the amount is larger than 1 mL, because the powder remains to be in wet condition.

In addition to the reducing agents mentioned above, 0.9 mL of acetone, furfural, and cyclohexane of were used. The reduction amounts are shown in Fig. 7, and are relatively small in comparison with those for alcohols. The boiling point and permittivity of these reducing agents are shown in Table 1. The boiling point of acetone is lower than that of methanol, and the permittivity of furfural is higher than that of methanol. Therefore, it is thought that these physical properties do not affect the reductions. As another reason, the amount of carbon materials which are generated by thermal decomposition of the reduction agent is the lowest when using methanol. It is supposed that the carbon materials adhered onto the surface of ZnO powder, and obstructed reduction of the powder.

Energy efficiency is calculated from the ratio of the enthalpy change of the reduction reaction to the supplied energy. Two kinds of energy efficiency were calculated. One was the case where only the reaction of ZnO is taken into consideration, and another where the reaction of the reducing agent is also taken into consideration. The enthalpy change of reduction reaction of ZnO (348.3 kJ/mol) was used when taking only the reaction of ZnO into consideration. The equation of the energy efficiency is as follows:

\[
\eta_0 = \frac{348.3 \text{ kJ mol}^{-1} \cdot m [\text{mg}]}{81.41 \text{ g mol}^{-1} \cdot 30 \text{ W} \cdot 120 \text{ s}} \times 100% \quad (5)
\]

where, \( m \) means the mass of the reduced ZnO. The maximum of the efficiency became 3.3, 0.7 and 0.5%, when methanol, ethanol and dodecane were used, respectively.

The equation of the energy efficiency where the reaction of the reducing agent is taken into consideration is as follows:

\[
\eta_1 = \frac{(348.3 \text{ kJ mol}^{-1} + n\Delta H) \cdot m [\text{mg}]}{81.41 \text{ g mol}^{-1} \cdot 30 \text{ W} \cdot 120 \text{ s}} \times 100% \quad (6)
\]

where the \( \Delta H \) indicates the combustion heat of the reduction agent, for instance methanol of -725.7 kJ mol\(^{-1}\). The maximum of the efficiency became 1.0, 0.3 and 0.2%, when methanol, ethanol and dodecane were used, respectively.

This energy efficiency is much smaller than that for electrolysis. This experiment was conducted simply to confirm whether reduction of ZnO by radio-frequency dielectric heating was possible. The easiest way to increase
these energy efficiencies is to put the powder into a thermal insulating container. Further consideration of the thermal properties of the layout of the apparatus is essential for practical use. In addition, an appropriate layout for electromagnetic waves is necessary. Towards these ends, investigation into the way electromagnetic waves travel in the materials as well as the physical mechanisms of interactions between the electromagnetic waves and the materials should be conducted. One advantage of this method is its potential for a wider scope of application. This method is considered to be applicable to the reduction of other metal oxides, for instance, magnesium, as well.

4. Conclusion
Radio-frequency dielectric heating of ZnO powder with a reduction agent was conducted. The frequency and power of the radio-frequency is 27.12 MHz and 30 W, respectively. The temperature of the dielectric heating was approximately 2000K as taken from the black-body radiation spectrum. The reduction amount of ZnO is remarkably increased when adding 0.7 to 1.4 mL of methanol as a reduction agent to 2.0 g ZnO powder, and reached a maximum of 27.6 mg at 1.1 mL. The reduction amount was small when adding ethanol, acetone, furfural, cyclohexane or dodecane as a reduction agent. The maximum energy efficiency ignoring the reaction energy of the reduction agent is 3.3%, whereas that when taking the reaction energy of the reduction agent into consideration is 1.0%.

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