Electrochemical Pseudo-Capacitance and Electric Reduction Treatment of Zn$_x$Fe$_{3-x}$O$_4$ Spinel Ferrite Electrodes

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Abstract
Zn$_x$Fe$_{3-x}$O$_4$ spinel ferrite nanoparticles were prepared by the coprecipitation technique. This research studied the effects of the $x$ value and electric reduction on the electrochemical properties of Zn$_x$Fe$_{3-x}$O$_4$ spinel ferrite electrodes. Results showed the pseudo-capacitances of Zn$_x$Fe$_{3-x}$O$_4$ electrodes decreased with an increase in the $x$ value and these capacitances increased after electric reduction at the -0.7V vs. Ag/AgCl reference electrode. In addition, the pseudo-capacitance after electric reduction decreased with repetition of the charge-discharge cycles. However, pseudo-capacitance increased again due to the re-treated electric reduction.

Key Words: Spinel ferrite, Electric reduction, Electrochemical properties, Pseudo-capacitance

I. INTRODUCTION
Electrochemical pseudo-capacitors utilize both an electrical double layer and interfacial redox processes to store energy in an electrode/electrolyte interface. Ruthenium oxide electrodes for electrochemical capacitors with aqueous electrolyte have been found to possess highly specific capacitance [1]. However, alternative materials are required because ruthenium is very expensive. It has been reported that transition metal oxide materials such as manganese oxide or iron oxide etc. have large pseudo-capacitance [2, 3]. We reported that the pseudo-capacitance of Fe$_2$O$_3$ electrodes increased after electric reduction at the -0.7V vs. Ag/AgCl reference electrode. [4] However, both the redox mechanisms of Fe$_2$O$_3$ and the cause of the increase in the pseudo-capacitance subsequent to the reduction treatment in Fe$_2$O$_3$ are not yet clear. To understand the presence of the mechanism in the pseudo-capacitance of crystallite active materials such as Fe$_2$O$_3$ it is important to recognize the relationship between the kinds of metal ions in each crystal structure site and the pseudo-capacitance. There are two sites in the spinel structure: the tetrahedral and octahedral. The selectivity properties of metal ions in these sites are determined by the kinds of ion. It is known that Zn$^{2+}$ ion found in zinc ferrite occupies the tetrahedral site. Our research investigated the effects of the $x$ value and electric reduction on the electrochemical properties of Zn$_x$Fe$_{3-x}$O$_4$ spinel ferrite electrodes.

II. EXPERIMENTAL METHOD
A. Synthesis of Electrode Materials and Measurement of Physical Properties
The raw materials used in this experiment were FeSO$_4$·6H$_2$O, FeCl$_3$ and ZnCl$_2$ powders. The chemical composition was chosen according to the formula Zn$_x$Fe$_{3-x}$O$_4$ when $x$ varies between 0 and 1. First, a 200g/L solution was prepared to dissolve these raw materials with purified water. These solutions were then weighed according to the aforementioned formula. After the solutions were mixed and degassed, a NaOH solution was poured slowly into a mixed solution and stirred for 20hrs. Aqueous suspensions containing the precipitated products were washed, filtered and dried. The crystal structure analysis of prepared powders was carried out by X-ray diffraction device and specific surface area measured using the Brunauer-Emmitt-Teller (BET) method.

B. Electrochemical Measurements
Electrochemical measurements were carried out by chrono-potentiometry and cyclic-voltammetry in 1 mol/L KCl electrolyte with a three-electrode type cell. The working electrode was prepared by mixing the obtained active materials (70wt.%), conductive carbon (30wt.%) and a small amount of polytetrafluoroethylene. These electrodes then underwent pressure bonding on a Ti mesh current collector. Activated carbon functioned as a counter electrode and the Ag/AgCl electrode in a saturated KCl solution was used as the reference electrode.

III. RESULTS AND DISCUSSION
The XRD technique was used to confirm all specimens in this experiment consisted of a spinel single phase. Fig.1 shows the effect of the $x$ value on the lattice constants of the a-axis comprising Zn$_x$Fe$_{3-x}$O$_4$ compounds. The lattice constants...
increase with a greater amount of Zn substitution. This result matches well with the known values of lattice constants with Zn$_x$Fe$_{3-x}$O$_4$ compounds.

Fig.2 shows chrono-potentiograms of a Zn$_x$Fe$_{3-x}$O$_4$ electrode at $x=0$. Line (a) indicates that chrono-potentiometry was measured after being kept at -0.7V vs. Ag/AgCl reference electrode for 20hrs in a constant voltage mode. Line (b) in this figure indicates that chrono-potentiometry was measured without this treatment. The constant current value was 50mA/g and the cycle number was measured in seconds. As seen in this figure, we found that the measuring time of potentiogram after being kept at -0.7V vs. Ag/AgCl reference electrode for 20hrs was longer than that of the non-treated electrode. Additionally, a low potential gradient region appeared in the proximity of the -0.2V vs. Ag/AgCl electrode after being kept for 20hrs at -0.7V vs. the Ag/AgCl reference electrode. We concluded the pseudo-capacitance of the Fe$_3$O$_4$ electrode was generated by this treatment. This treatment is referred to as an electric reduction treatment. The chrono-potentiograms of Zn$_x$Fe$_{3-x}$O$_4$ electrode at $x=1$ as electric reduction (a) or non-treated (b) are shown in Fig.3. The potential gradient of $x=1.0$ electrode in high potential region was higher than that of $x=0$ electrode. Moreover, as is the case with an $x=0$ electrode, electric reduction treatment significantly reduced the lapse time per single cycle of chrono-potentiogram.

For calculation of electrochemical capacitance per unit surface area, the specific surface areas were measured using the Brunauer-Emmitt-Teller (BET) method with N$_2$ gas. Fig.4 shows the effect of the $x$ value on a specific surface area of Zn$_x$Fe$_{3-x}$O$_4$ electrodes before and after electric reduction treatment. As seen in this figure, the specific surface area increased with an increase in the $x$ value of Zn$_x$Fe$_{3-x}$O$_4$. Moreover, we found electric reduction treatment did not alter specific surface areas of Zn$_x$Fe$_{3-x}$O$_4$ electrodes. Fig.5 shows the effect of the $x$ value on electrochemical capacitance per
unit surface area of Zn$_x$Fe$_{3-x}$O$_4$ electrodes after electric reduction or non-treatment. We found the capacitances per unit surface area increased through electric reduction treatment regardless of the amount of Zn substitution and capacitances per unit surface area decreased with an increase in the amount of Zn substitution.

Fig. 6 shows the cyclic voltammograms of Zn$_x$Fe$_{3-x}$O$_4$ electrodes (x=0-1) at a scan rate of 1 mV/s. We found anodic peaks were observed at about -0.2V vs. Ag/AgCl electrode and the value of the anodic peak current decreased with an increase in the amount of Zn substitution. It is known that pseudo-capacitance of redox reaction between Fe$^{2+}$ and Fe$^{3+}$ is obtained at the proximity of -0.2V vs. Ag/AgCl electrode [3]. Therefore, we concluded that the pseudo-capacitance of Zn$_x$Fe$_{3-x}$O$_4$ electrodes decreased with an increase in the amounts of Zn substitution. Additionally, it is well known that the Zn$^{2+}$ ions exist at a tetragonal site in the spinel structure. In other words, the amounts of Fe ion at the tetragonal site decreased with an increase in the amounts of Zn substitution. We think this result shows the amount of Fe ion present at the tetragonal site in the spinel structure exerts an influence on the pseudo-capacitance of the spinel ferrite electrode.

Fig. 7 shows the variation of electrochemical capacitance with the number of cycles for Zn$_x$Fe$_{3-x}$O$_4$ electrodes. As seen from this figure, the capacitance decreased with an increase in the number of cycles. Consequently, electric reduction was treated again for electrodes after a 20-cycle of chrono-potentiometry and then measured. Fig. 8 shows the effect of the cycle number on electrochemical capacitance. The cycle numbers of chrono-potentiometry after the re-reduction treatment
were defined as 22-40 cycles. After additional re-reduction treatment, the chrono-potentiometry cycle numbers were defined as 42-60 cycles. We found the decreased capacitance with cycle running increased again through re-reduction treatment. From this result, it is considered that electric reduction treatment has the effect of facilitating the redox reaction between Fe$^{2+}$ and Fe$^{3+}$, increasing cycle numbers that reduce the effectiveness of electric reduction treatment and that re-reduction treatment facilitated redox reaction. However, we were unable to obtain evidence of the above concerns in this experiment and require further detailed research.

IV. CONCLUSION

In this study we investigated the effects of the x value and electric reduction on electrochemical properties of Zn$_x$Fe$_{3-x}$O$_4$ spinel ferrite electrodes. Electric reduction treatment increased the electrochemical capacitance of Zn$_x$Fe$_{3-x}$O$_4$ electrodes. The capacitance per unit surface area decreased with an increase in the amount of Zn substitution and the anodic peak current at about -0.2V vs. Ag/AgCl electrode in cyclic voltammograms decreased with an increase in the x value of Zn$_x$Fe$_{3-x}$O$_4$ electrodes. This result suggests the amount of Fe ion present at the tetragonal site in spinel structure exerts influence on the pseudo-capacitance of the spinel ferrite electrodes. In addition, we found capacitances decreased with an increase in the number of cycles after the electric reduction treatment and increased again through the re-reduction treatment.

REFERENCES