

전기 화학적으로 변형된 자철광 단결정의 전기적 특성과 Verwey전이 이동

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Electrical Property and Verwey Transition Shift of the Electrochemically Modified Magnetite Single Crystals

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It was well established that the Verwey transition temperature (T_v) and electrical transport properties of magnetite ($\text{Fe}_{3(1-\delta)}\text{O}_4$) depend on the degree of nonstoichiometry (δ).^{1,2} High temperature (>1473 K) annealing in CO/CO_2 gas mixtures is a popular method to control the stoichiometry of magnetite.³ The electrochemical modification of metal oxides is a more convenient method to control the stoichiometry of metal oxide at room temperature.^{4,5} This work presents the Verwey transition and electrical transport property of magnetite single crystals which are electrochemically modified by continuous cyclic voltammetry (CV) treatment in aqueous 0.1 N KOH.

EXPERIMENTAL

Magnetite single crystals were prepared from Fe_2O_3 (99.999%) under 1 atm CO_2 circumstances using the cold crucible in a RF furnace (Skull melter)⁶ and labeled as-grown crystal (AS5N). To obtain stoichiometric magnetite (DF5N), $\delta=0.0000$ in $\text{Fe}_{3(1-\delta)}\text{O}_4$, as-grown crystal (2 mm thick) annealed under an appropriate CO/CO_2 mixtures at 1673 K, 24 hrs.³ The single crystals were checked by Laue back scattering and x-ray powder diffraction. All the peaks observed in the powder diffraction pat-

terns were attributed to the magnetite. Surface of the crystals was polished by alumina powder (1 μm in diameter).

A bar ($1 \times 1 \times 7 \text{ mm}^3$) shaped magnetite electrode was prepared by cutting the crystals. The sample was then polished with a 1200c abrasive paper and 1 μm alumina powder, successively, and cleaned with distilled water and acetone. AS5N and DF5N were electrochemically modified by CV treatment in 0.1 N KOH solution. The potential range of CV treatment was from -1.5 to 0 V (vs. SCE), and a sweeping rate was 50 mV/sec. The potential sweeping was continued for 20 hrs in order to obtain the electrochemically modified surface with sufficient thickness. The treatment was terminated either at 0 V to obtain the oxidized state of the magnetite surface, or at -1.5 V to obtain the reduced surface. After finishing potential sweeping, the final potential (0 or -1.5 V) was maintained for 10 minutes to complete electrochemical reaction. AS5N_{ox} and AS5N_{red} represent electrochemically oxidized and reduced as grown crystals, respectively. DF5N_{ox} and DF5N_{red} represent electrochemically oxidized and reduced stoichiometric magnetite crystals, respectively.

The electrical resistance of magnetite surfaces

was measured by the dc four wire method. Wires for resistance measurements were attached on the surface with Ag-paste. The surface properties of the magnetites were investigated using SEM, micro-Raman, FT-IR, and XPS.

RESULTS AND DISCUSSION

Fig. 1 shows the first ten consecutive voltammograms of AS5N in 0.1 N KOH solution. The voltammogram of a pure Fe obtained in this work was similar to that in the literature.⁷ It was found that the voltammograms of AS5N and DF 5N showed little difference. The redox peaks corresponding $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ were not observable in the very first scan because of low ionic conductivity of magnetite crystal,⁸ but became apparent in the following scans. There were three oxidation peaks and two reduction peaks observed in the following voltammograms. The peak O1 is due to $\text{Fe} \rightarrow \text{Fe}^{2+}$. The peak O2 is believed due to oxidation of Fe^{2+}

$\rightarrow \text{Fe}^{3+}$. The shoulder peak O3 could be explained as follows: once Fe metallic state was established by the first reduction process, the crystal structure of magnetite was destroyed. If then, the voltammogram would show two oxidation peaks. However, the peak O3 was still observed, which indicated that the Fe^{2+} ions in the crystal lattices participate in oxidation reaction.⁸ This explanation was also supported by the increasing magnitude of the redox peaks in the voltammograms as scan continued. When Fe^{2+} ions were oxidized, the surface rich in Fe^{3+} ions became more resistive than the original surface, which pushed the reduction peaks to more negative potential. Therefore, the two reduction peaks, R1 ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$) and R2 ($\text{Fe}^{2+} \rightarrow \text{Fe}$), were observed with a distorted shape. The reduction current observed at -1.5 V is due to reduction of hydrogen ions in the solution.

The CV diagrams of AS5N according to the number of scans (the 10th, the 120th and the 1200th) were compared in Fig. 2. At the 10th scan, the redox peaks were relatively sharp and small. The redox peaks of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ were enlarged

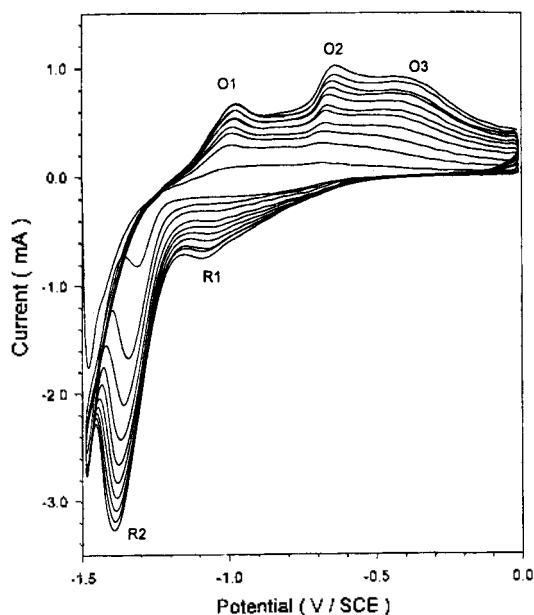


Fig. 1. The first 10 cyclic voltammograms of AS5N in 0.1 N KOH solution. There are two reduction peaks in reduction cycles (-1.1 V and -1.4 V) and three oxidation peaks in oxidation cycles (-0.35 V, -0.75 V and -1.0 V). Intensity of all peaks is growing with number of scans.

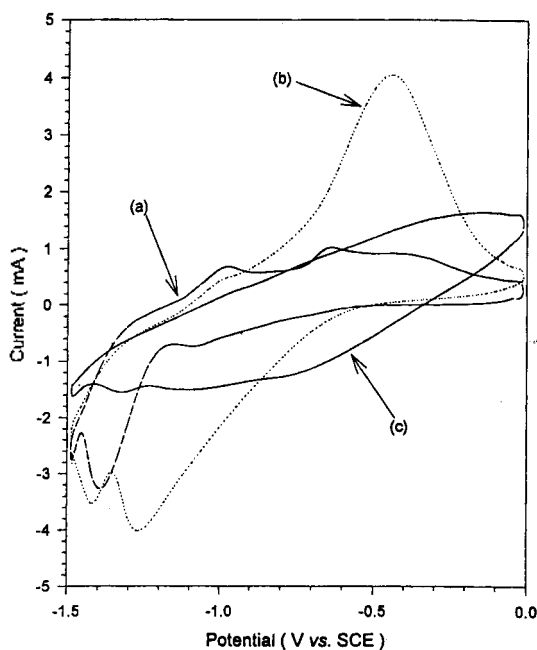


Fig. 2. Cyclic voltammograms of AS5N in 0.1 N KOH solution at 10 (a), 120 (b), 1200 (c) scan.

with a small potential shift in the 120th CV diagram. The maximum peak height (and area) for oxidation of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ was observed around this scan and the shoulder peak (O3 in Fig. 1) disappeared. This indicates that no more Fe^{2+} ions in the crystal lattices could participate in the redox reaction because of thick amorphous layer formed by continuous redox scan. From this, it could be deduced that the surface of magnetite can not sustain its crystal structure during CV treatment.

The redox peaks, especially those for $\text{Fe} \leftrightarrow \text{Fe}^{2+}$ were dispersed slowly and the final CV diagram shows no distinctive redox peaks as shown in Fig. 2(c). This could be due to slow formation of stable and irreversible ferric oxide compounds on the surface of the magnetite electrode, which plays a role as a resistive layer. Evidences for the formation of ferric oxides were confirmed by micro-Raman study, which is mentioned in the following discussion.

The surface morphology of the magnetites was completely changed after 1200th redox cycles, which was shown in the SEM picture of Fig. 3. Flake layer (FL) on the surface was formed by CV treatment. The shiny polished crystal surface before CV treatment was changed into non-reflective surface after CV treatment. FL was about 2 μm in thickness, and easily removed by a cotton tipped stick. According to the potential-pH diagram for

$\text{Fe-H}_2\text{O}$ system,⁹ FL can consist of $\text{Fe}(\text{OH})_2$, Fe_2O_3 , FeOOH and Fe_3O_4 . The Fe_2O_3 , FeOOH and Fe_3O_4 peaks¹⁰ evidently appeared in micro-Raman spectrum of FL, but $\text{Fe}(\text{OH})_2$ peak was not seen in micro-Raman (3673 cm^{-1})¹¹ and FT-IR (ATR) spectra (3632 cm^{-1}).^{7,11} The electrical resistance of FL was higher than 100 k Ω at room temperature due to the cracks and Fe_2O_3 and FeOOH phase in the FL. In order to avoid ohmic contact problem and other experimental errors, FL was removed by a cotton tipped stick with ethanol before attaching the lead wires to sample for electrical resistance measurements. Micro-Raman and FT-IR spectra of the cleaned surface of magnetites were basically identical with those of the polished surface of magnetite. XPS analysis also revealed the cleaned surfaces were magnetite. Therefore, the cleaned surface would be magnetite for all samples (AS5N_{red} , AS5N_{ox} , DF5N_{red} and DF5N_{ox}), even though $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of the surfaces would be slightly altered from the original ratio of bulk crystals by CV treatment.

Fig. 4 shows plots of the $\log(R/R_{200})$ vs. temperature of AS5N , AS5N_{ox} and AS5N_{red} , and Fig. 5 shows plots of the $\log(R/R_{200})$ vs. temperature of DF5N , DF5N_{ox} and DF5N_{red} , respectively; where R is resistance at a given temperature and R_{200} is resistance at 200 K.

The sudden jump in the plots is related to the Verwey transition.¹ It is generally accepted that be-

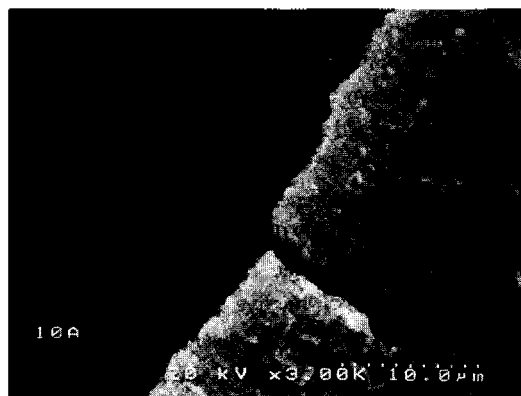


Fig. 3. SEM picture of AS5N_{red} . There are irregular cracks on the flake layer and this layer is easily removed.

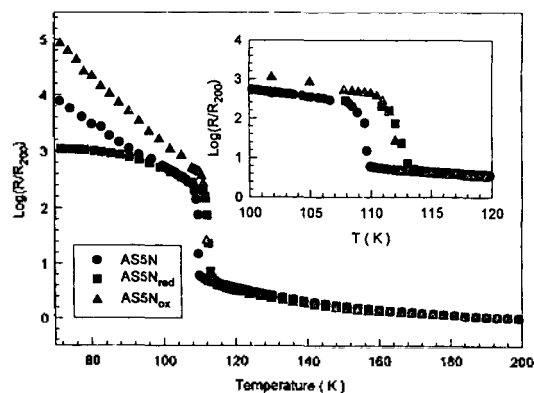


Fig. 4. Resistivity/Resistivity at 200 K (R/R_{200}) vs. temperature of AS5N , AS5N_{red} , AS5N_{ox} . T_v of AS5N shifted by electrochemical treatment.

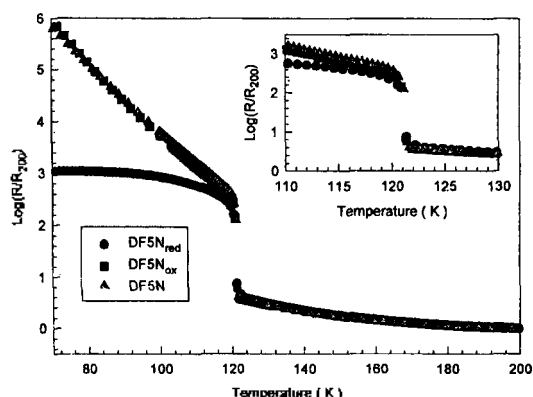


Fig. 5. R/R_{200} vs. temperature of DF5N, DF5N_{red}, DF5N_{ox}. Below Verwey transition the temperature dependence of R/R_{200} was changed by electrochemical treatment.

low T_v the distribution of Fe^{2+} and Fe^{3+} ions in the octahedral sites changes from dynamic disorder (electrons resonating on octahedral sites) to long-range order (LRO); the electrons on the Fe^{2+} ions freeze out, causing a substantial rise in resistivity.^{2, 13, 14} The stoichiometry should be close to the stoichiometric magnetite to have Verwey transition; $\delta < 3.5 \times 10^{-2}$ of $\text{Fe}_{3(1-\delta)}\text{O}_4$.²

Above T_v , the temperature dependence of $\log(R/R_{200})$ of all samples was same with stoichiometric magnetite within experimental error, which agreed well with the reported resistivity data.² The electrical properties of magnetite are not effected by small amount of impurities ($x=0.04$ in $\text{Fe}_{3-x}\text{M}_x\text{O}_4$; $\text{M}=\text{Ti}$, Zn or Fe vacancies) above T_v .¹² Therefore, one could expect that the stoichiometry of all the samples will be very close to a stoichiometric magnetite from the electrical and spectroscopic properties.

It has been reported that slight deviations from stoichiometry in magnetite crystals produce decrease in T_v , for example, for $\text{Fe}_{3(1-\delta)}\text{O}_4$, $T_v=115$ K when $\delta=1.7 \times 10^{-3}$, and $T_v=90$ K when $\delta=1.0 \times 10^{-2}$.^{2, 13, 14} For the ASSN sample T_v is about 109 K, where as for ASSN_{ox} and ASSN_{red} T_v is about 113 K, as shown in the inset to Fig. 4. The observed T_v shift relative to the value $T_v \approx 121$ K for stoichiometric Fe_3O_4 and the shift compared to ASSN_{ox} and ASSN_{red} samples could result from the

change of ASSN surface by CV modification. The as-grown magnetite crystal has metal vacancies, $\delta \sim 3.6 \times 10^{-3}$ for $\text{Fe}_{3(1-\delta)}\text{O}_4$. Therefore, when the scan was terminated at the reduction potential (-1.5 V), the surface was expected to be closer to the ideal stoichiometry than that of ASSN. In turn, T_v of ASSN_{ox} should be lower than those of ASSN and ASSN_{red} because ASSN_{ox} will have more metal deficient surface by terminating at the oxidation potential (0 V). In Fig. 4, ASSN_{red} specimen exhibited higher T_v than ASSN, but ASSN_{ox} sample showed the same T_v as ASSN_{red}, which did not coincide with the above expectation. One possible interpretation of this result might be that T_v shift is affected not by the terminating potential, but by T_v shift occurring during the entire CV process. It must be noted that CV treatment only alters the surface of crystals. Therefore, it may not be valid to compare T_v of the surface modified crystals to T_v of bulk $\text{Fe}_{3(1-\delta)}\text{O}_4$ and then infer the deviations in stoichiometry. Recently, however, Kozłowski *et al.* reported¹⁴ that inhomogeneous distribution of impurities (Zn and Al) in bulk magnetite affects T_v vs. composition relationship, and concluded T_v for a composite sample was representative for the lower impurities phase by a computer simulation of resistivity vs. T .¹⁴ Therefore, from the T_v shift (from 109 K to 113 K), we could conclude that the part of as-grown crystal surface was changed to more stoichiometric phase by CV treatment. The corresponding degree of nonstoichiometry to $T_v=113$ K approaches $\delta \sim 2.5 \times 10^{-3}$.

For stoichiometric magnetite (DF5N), T_v was ~ 121 K, as shown in Fig. 5. T_v of DF5N_{red} and DF5N_{ox} was observed basically identical with that of DF5N, $T_v \sim 121$ K. Even though Margulies *et al.* reported that nonstoichiometric surface of a stoichiometric magnetite thin film (less than $0.42 \mu\text{m}$ in thickness) could partly be the cause of the decrease of T_v ,¹⁵ there was no distinctive T_v shift of DF5N observed in this work. The disagreement probably comes from the differences of sample thicknesses. The properties of the thin films would be more effectively dependent on the nonstoichiometric surface than the bar shaped magnetite crystal used in

this work. According to the report of Kozłowski,¹⁴ we will have only T_v of more stoichiometric phase by resistivity measurements if composition of a sample is mixed phases. Therefore, it is expected that T_v of the electrochemically modified stoichiometric magnetite will be close to 121 K because CV treatment only provides the slightly altered nonstoichiometric surface. This expectation is well coincident with the experimental data, as shown in Fig. 5. We also found that T_v for the mixed phase consisting of Fe_3O_4 and Fe_2O_3 was ~ 121 K.¹⁶

A qualitative explanation for the temperature dependences of the R/R_{200} below T_v is as follows; Fe^{2+} ions formed on the surface during the final reduction process might be responsible for the more metallic characteristics of AS5N_{red} and DF5N_{red} than that of the original crystals. For AS5N_{ox} , reduced concentration of Fe^{2+} ions on the surface may result in the less metallic behavior below T_v . R/R_{200} of DF5N_{ox} was, however, nearly the same as that of DF5N . This is quite different from the results of AS5N_{ox} and AS5N . It should be noted that the stoichiometric magnetite has the most nonmetallic behavior below T_v .^{2,13} The effect of reduced concentration of Fe^{2+} ions to the temperature dependence of R/R_{200} could be canceled out by the effect of nonstoichiometric surface of DF5N_{ox} . Therefore, R/R_{200} of DF5N_{ox} would have the same temperature dependence as that of DF5N below T_v .

In summary, this work was carried out electrochemical modification of as-grown and stoichiometric magnetites by CV treatment in 0.1 N KOH solution, in order to alter the stoichiometry of the surfaces. The modified surfaces were nearly stoichiometric magnetite after cleaning. All samples had Verwey transition (T_v) in resistance measurements. Below T_v , R/R_{200} of modified magnetites was basically subject to the final terminating potential. And temperature dependence of R/R_{200} could be explained by the concentration of Fe^{2+} ions which was determined by the final potential of CV treatment. It was found that the T_v shift of the as-grown crystal was achieved by CV treatment. T_v of the modified surface approached ~ 113

K; the corresponding degree of nonstoichiometry, in $\text{Fe}_{3(1-\delta)}\text{O}_4$, approaches $\delta \sim 2.5 \times 10^{-3}$.

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16. We annealed Fe_2O_3 pellets under vacuum and 1 atm CO_2 circumstance. The XRD pattern of pellets was mixture of Fe_3O_4 and Fe_2O_3 patterns. The pellets had break point in the plot of resistivity vs. temperature around 121 K.