

The Electrochemical Investigation of Dissolution of Nickel Ferrite in Aqueous Solutions

Jun-Young Jung*, Sang-Yoon Park, Mansoo Choi, Hui-Jun Won, Wang-Kyu Choi, Jei-Kwon Moon
Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 303-353, Republic of Korea
*Corresponding author: jjy87@kaeri.re.kr

1. Introduction

During operation of primary coolant system in PWR, iron oxide is formed on the inner surface. These deposits form a layer with other deposits that accelerate under deposit corrosion. In addition, they interfere with water flow in piping systems and decrease the transmission efficiency of heat in heat exchangers. Thus, these deposited oxide must be removed. Many formulations have been developed to dissolve or decontaminate oxide formed on the metal surface [1]. In a pressurized water reactor (PWR), the oxide layer formed on the surface of the reactor coolant system is generally known to be made of two different layers, a Fe rich (Fe_3O_4 , NiFe_2O_4) external layer and a Cr rich (FeCr_2O_4 , Cr_2O_3) inner layer [2].

In this study, we investigated the characteristics of dissolution to NiFe_2O_4 in HYBRID (HYdrazine Based metal Ion Reductive Decontamination) which was developed in KAERI used in reductive decontamination of the inner surface of PWR. HYBRID is consist of hydrazine, sulfuric acid and copper ion. We investigated the dissolution of NiFe_2O_4 when the hydrazine and copper sulfate added to the sulfuric acid solution. Potentiostatic electrochemical impedance spectroscopy (EIS) is a useful tool for the analysis of complex electrochemical systems [3]. We conducted the EIS for this study.

2. Experimental Methods

NiFe_2O_4 used for the experiment was prepared to electrodeposited on the surface of the specimen. The specimens were stainless steel 304 in the form of a small cylinder (15 mm diameter and 2 mm length). Surface of specimens was wet polished prior to each measurement using #800 grit and #1,200 grit emery paper and then conducted ultrasonic washing in ethanol and acetone. Electrodeposition speed of NiFe_2O_4 was 0.7 \AA/s . Thickness of electrodeposited NiFe_2O_4 was 500 nm. Experiment was carried out using a three electrode cell with a saturated calomel electrode (SCE) and a platinum electrode as reference and counter electrodes, respectively. Impedance measurements were carried out at open circuit potential using an alternating current (AC) potential sine wave signal of peak to peak amplitude of 10 mV. Frequency range used was 100 kHz to 5 mHz. Test solutions were prepared with deionized water and analytical grade reagents. Copper ions were added as copper(II) sulfate(CuSO_4). The Na_2SO_4 was added to maintain the concentration to

0.1M SO_4 . The temperature was maintained at 25°C . We purged in the solution with nitrogen gas for 30 minute before experiment. The composition of solution of the object of the experiment shown in the table I.

Table I. Chemical condition for EIS measurement

| | |
|------------|--|
| Solution 1 | 0.011M H_2SO_4 (pH=1.72) |
| Solution 2 | 0.011M H_2SO_4 (pH=3.0) |
| Solution 3 | 0.01M H_2SO_4 + 0.02M N_2H_4 + 0.5mM CuSO_4 (pH=3.0) |

3. Results

Figure 1 shows typical Nyquist plots of the reductive dissolution of NiFe_2O_4 obtained at open circuit potentials. The plot consists of an incomplete semicircle related to a charge transfer reaction and a straight line attached to the semicircle indicating the presence of a diffusion process. We conducted the EIS for this study. The EIS experimental results are interpreted in terms of the equivalent circuit in Figure 2. The impedance data were fitted using an iterative complex nonlinear least squares fitting program [4]. Figure 3 show that calculated data was similar with raw data.

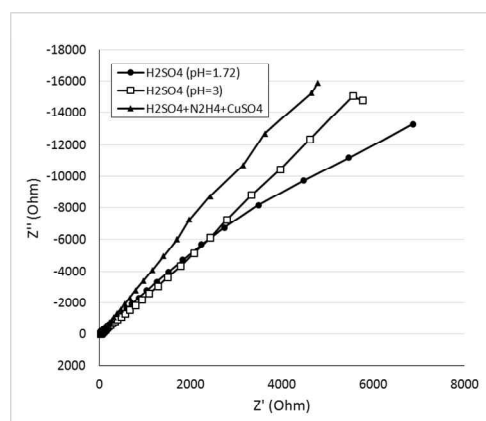


Fig. 1. Typical Nyquist plots of nickel ferrite in reductive decontamination solution.

Since the electron transfer reaction was of most interest, values of charge transfer resistance R_1 obtained from the fitting procedure were used for the remainder of this study. $1/R_1$ refers to the rate of dissolution. Table II shows values of $1/R_1$ obtained from the curve fitting. It is clear that $1/R_1$ depends on N_2H_4 , Cu^+ and pH of solution. The highest value of $1/R_1$ appeared in the solution 1. The lowest $1/R_1$ value was measured in the

solution 3. When pH is low, high $1/R_1$ value was obtained. Bode plots of nickel ferrite in reductive decontamination solution was shown in Figure 4.

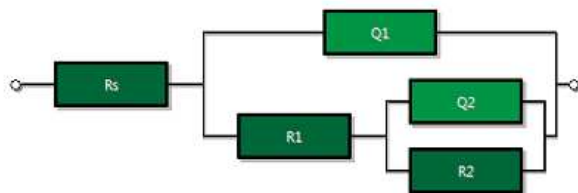


Fig. 2. Equivalent circuit used for impedance analysis.

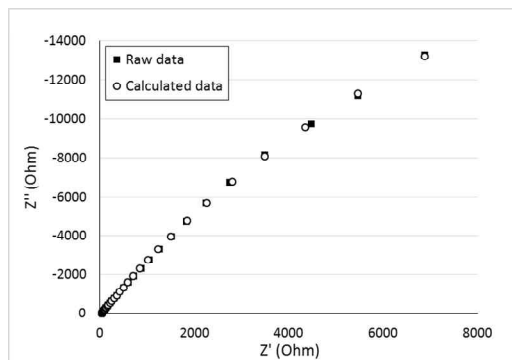


Fig. 3. Fitting of impedance spectrum of nickel ferrite using the equivalent circuit shown in Figure 2.

Table II. Values of charge transfer resistance R_1

| | Solution 1 | Solution 2 | Solution 3 |
|------------|------------|------------|------------|
| R_1 | 2306 | 3471 | 6179 |
| $1000/R_1$ | 43.37 | 28.81 | 16.18 |

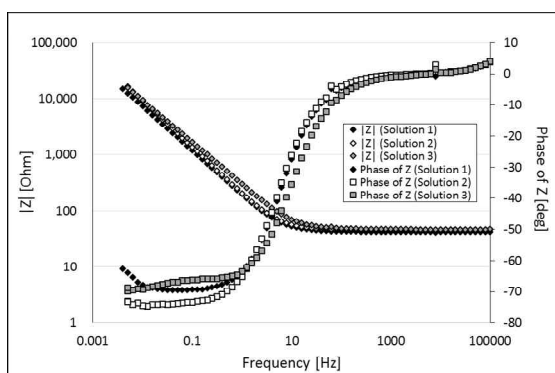


Fig. 4. Bode plots of nickel ferrite in reductive decontamination solution.

4. Conclusion

The behavior of NiFe_2O_4 in this study has been shown to depend on N_2H_4 and Cu^+ ion. From the analysis of EIS results, R_1 , taken as equal to the rate of reductive dissolution of magnetite, decreased when N_2H_4 and Cu^+ ion added. In practice HYBRID solution is used at 95°C . However, experiment was carried out at room temperatures in this study. So addition of N_2H_4

and Cu^+ did not help to dissolution of NiFe_2O_4 . In subsequent study, we will experiment the dissolution of NiFe_2O_4 at a high temperature.

ACKNOWLEDGE

The authors would like to express their appreciation to the National Research Foundation of Korea (NRF) for the award of a grant funded by the Ministry of Science, ICT and Future Planning (MSIP) of the Republic of Korea, in support of the authors' work through the Nuclear Research and Development Program (NRF-2012M2A8A5025655).

REFERENCES

- [1] R.M. Cornell, U. Schwertmann, "The Iron Oxides, Structure, Properties, Reactions, Occurrence, and Uses" Weinheim, Germany VCH, pp. 267, 1996.
- [2] Riess R, Odar S, Kysela J, "decontamination and steam generator chemical cleaning", International ANT LCC5 special topic report, 1st edn. Sweden, Skultuna, 2009.
- [3] A.M. Al-Mayouf, "Electrochemical Investigation of Magnetite Reductive Dissolution in Aqueous Solutions", NACE International, CORROSION SCIENCE SECTION, Vol. 58, No. 6, pp. 519-525, 2002.
- [4] B.A. Boukamp, "Equivalent Circuit Manual", 2nd ed. University of Twente, 1989.