Electrochemical Study of H_2O_2 Decomposition on the Magnetite Bulk Electrode

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Abstract

The high operating temperature and pressure in the heat transport system of Supercritical Water Reactors (SCWRs) can induce fouling in coolant tubes. Magnetite as a major component of foulants has large impacts on the water chemistry and corrosion of these systems since it is known as a catalyzer for decomposition of hydrogen peroxide. This study aimed to investigate the electrochemical kinetics of hydrogen peroxide decomposition on bulk magnetite electrodes using open circuit potential measurement, potentiodynamic and electrochemical impedance spectroscopy methods. Tafel slope and diffusion coefficient were estimated for different concentrations of hydrogen peroxide at pH=9.5 in the 0.1M $NaClO_4$ solution containing 0.01M $Na_2B_4O_7$ as a buffer.

Keywords: Magnetite, SCWR, Hydrogen peroxide

1. Introduction

The high operating temperature and pressure in the heat transport system of Supercritical Water Reactors (SCWRs) can induce fouling in coolant tubes due to the changes in water properties which occur at the sub- to supercritical conditions [1]. Because of major changes in water characteristics along with irradiation effects (which results in the generation of hydrogen peroxide and other radicals in water) corrosion mechanisms of constructural materials become more complex for SWCRs [2]. However, comprehensive data on radiolysis, kinetics, corrosion and thermodynamics have not been reported due to severe experimental condition of SCWR.

Characterizations of corrosion products in nuclear power plants have been presented in many recent publications [3,4 and 5]. It has been reported that magnetite and hematite are the main components of corrosion products in the heat transfer system of power plants._Iron oxides (especially magnetite) are known to be catalysts for hydrogen peroxide decomposition. For example, the catalytic decomposition of hydrogen peroxide on magnetite can form the hydroxyl radical (OH.) which is a strong oxidant and used for remediation of contaminated soils and groundwater [6,7].

From the kinetic perspective previous studies have evaluated hydrogen peroxide decomposition in the presence of magnetite by means of adding different concentration of H_2O_2 to a slurry of magnetite powders followed by measurement of the concentration of H_2O_2 at different intervals of time. However, electrochemical studies of H_2O_2 decomposition on magnetite have not yet been presented[7].

There have been several electrochemical studies of magnetite electrodes [8,9 and 10]. Allen et al. [8] studied the capacitance and resistance of magnetite admixed with carbon in $NaClO_4$ solution. They measured capacitance over potential changes at pH 3-9 and attributed shifts in the capacitance peak with pH tomagnetite dissolution. Jung et al. [11] studied the electrochemical behaviour of sintered magnetite electrodes in alkaline LiOH solution. They concluded that OH^- ions can be strongly adsorbed on the magnetite surface and are responsible for changes in the potential.

The present paper aimed to investigate the electrochemical decomposition of hydrogen peroxide on magnetite electrodes at different concentration of hydrogen peroxide and alkaline pH at room temperature by means of electrochemical techniques including open circuit measurement (OCP), potentiodynamic (PD) and electrochemical impedance spectroscopy (EIS).

2. Experimental procedure

2.1. Electrode preparation

The manufacturing of a solid magnetite electrode was an initial objective of this work. Commercial magnetite powder with a purity of more than 99.92% was purchased. A Malvern Instruments Mastersizer was used for particle size measurement. The average size of the magnetite particles was in the range of 100 nm to 10 μm. Magnetite powders were compressed first by cold isostatic pressing (CIP) at the pressure of 50K psi and room temperature, they werethen sintered for 5hr at 1100C in an argon gas atmosphere. Finally hot isostatic pressing (HIP) was performed at a temperature of 1100C and pressure of 25K psi on the magnetite rod to decrease micro porosity.

Quantitative phase analysis of the sample was carried out using the Rietveld method and x-ray powder diffraction data. Hence, the sample was reduced into fine powder to the optimum grain-size range for X-ray analysis (<10μm) by grinding under ethanol in a vibratory McCrone Micronising Mill for 7 minutes. Step-scan X-ray powder-diffraction data were collected over a range 3-80°2θ with CoKa radiation on a Bruker D8 Focus Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°.

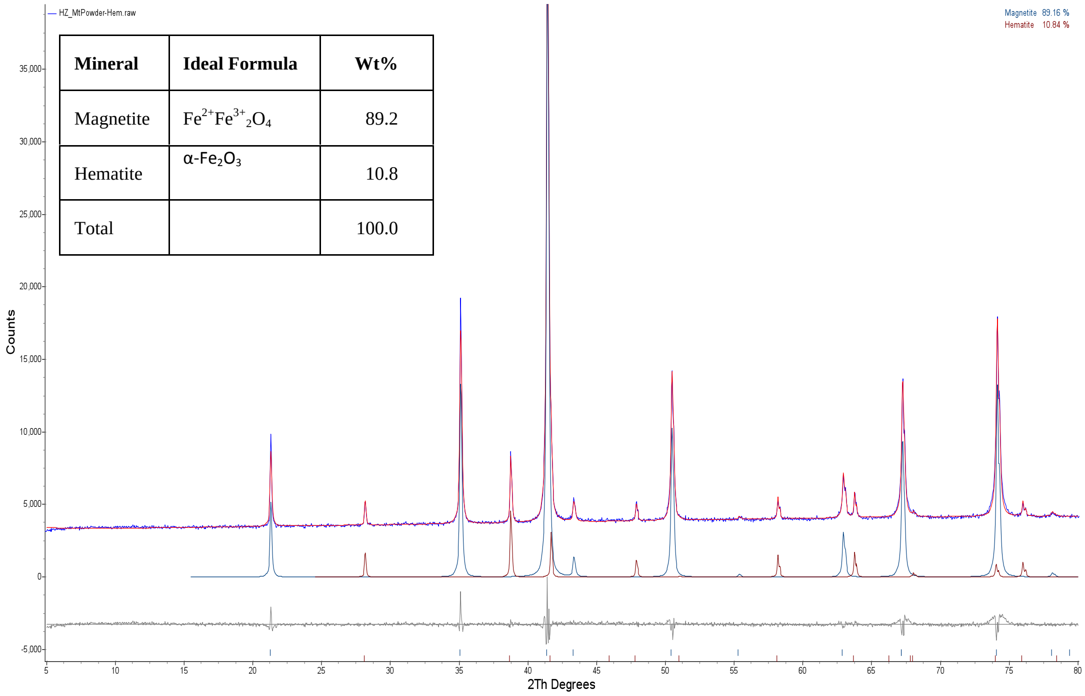
The X-ray diffractogram was analyzed using the International Centre for Diffraction Database PDF-4 and Search-Match software by Siemens (Bruker). X-ray powder-diffraction data of the sample were refined with Rietveld program Topas 4.2 (Bruker AXS). The results of quantitative phase analysis by Rietveld refinements are given in figure 1. It can be seen that 10.8 percent of the electrode is hematite. Although the atmosphere was fully controlled by inert argon gas, even pure magnetite particles might become partially surface oxidized.

2.2. Electrochemical methods

A Princeton Applied Research Versastat 3F potentiostat/galvanostat was used for all the electrochemical measurements. The OCP measurements were carried out for 30 minutes or until a steady state potential with changes no more than 5 mV per 5min was obtained. The kinetics of decomposition of H_2O_2 on the magnetite electrode was studied through the cathodic polarization tests from OCP down to -1.6 V vs. the reference electrode and at different concentration of H_2O_2. Electrochemical Impedance Spectroscopy (EIS) experiments were carried out at open circuit potential (OCP) after stabilization with an amplitude of 10 mV (peak to peak) in the frequency range of 50 mHz to 20 KHz and a sampling rate of 10 points per decade. A conventional three-electrode cell was used for all experiments. The cell consists of a Ag/AgCl reference electrode (RE), a graphite as a counter electrode (CE), and a 10mm OD magnetite disk as a working electrode (WE). The magnetite disc was connected to a wire with the use of conductive silver epoxy paste, mounted in epoxy resin. Surface conditioning of the magnetite electrode used in our experiments consisted of: grinding to 1200 SiC emery paper, followed by degreasing with ethyl alcohol and finally rising in deionized water in an ultrasound bath for 5 min.

2.3. Materials and preparation

Studies of H_2O_2 containing systems usually use $NaClO_4$ as the supporting electrolyte, since the ClO_4^- ion does not show specific adsorption to the surface as the molecule is large enough which cannot pass the Helmholtz layer on the surface. Thus, in this work 0.1M $NaClO_4$ solution used as the supporting electrolyte. Nuclear power plant primary coolant pH is adjusted by the addition of LiOH to pH 6.9- 7.4 for the pressurized water reactors (PWRs) and pH 10.2-10.8 for the CANDU (CANada Deuterium Uranium) [5]. Thus in this work pH was adjusted to 9.5 by addition of NaOH. Furthermore, the solution contained 0.01 M borate ($Na_2B_4O_7$) to provide a good buffer capacity. Deionized water (18.2 MΩ NANOpure DIamond, Barnstead, USA) was used in the preparation of all the solutions. Electrochemical experiments were carried out at different concentration of H_2O_2 (0, 10^{-4}, 10^{-2} and 1 M).



Mineral	Ideal Formula	Wt%
Magnetite	$Fe^{2+}Fe^{3+}{}_2O_4$	89.2
Hematite	α-Fe_2O_3	10.8
Total		100.0

Figure 1. Rietveld refinement plot of sample. blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

3. Results and discussion

3.1. Open circuit potential measurements

Figure 2 shows the changes of open circuit potential vs. time as a function of hydrogen peroxide concentration. It can be seen that OCP is increased from -183 mV to 258 mV vs. Ag/AgCl reference electrode when the concentration of H_2O_2 was increased from 0 to 1M, respectively. Therefore, possible reactions on the surface of magnetite are considered:

$$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O \qquad (1)$$

$$H_2O_2 \leftrightarrow O_2 + 2H^+ + 2e^- \qquad (2)$$

$$3Fe_2O_3 + H^+ + 2e^- \leftrightarrow 2Fe_3O_4 + 2H_2O \qquad (3)$$

The calculated equilibrium potentials for these reactions at pH=9.5 and various concentration of hydrogen peroxide using the Nernst equation show that all measured values fall between the three theoretical potentials, indicating a mixed potential on the magnetite surface.

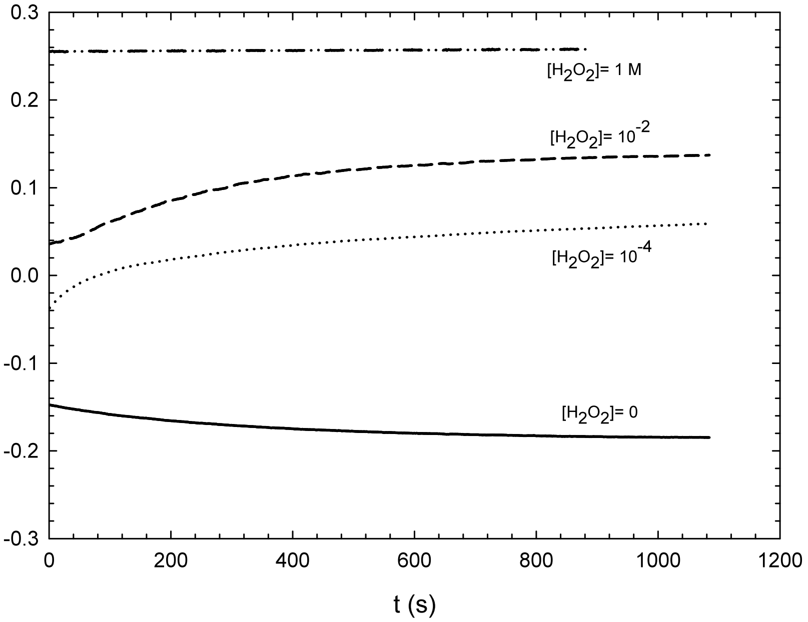


Figure 2. Open circuit potential of magnetite electrode vs. time in 0.1M NaClO4, pH=9.5 and different concentrations of hydrogen peroxide.

3.2. Cathodic polarization

The kinetics of hydrogen peroxide decomposition on the magnetite electrode were evaluated by the potentiodynamic method. Figure 3 shows the cathodic polarization curves for different concentrations of hydrogen peroxide at pH=9.5 at room temperature. It can be seen that all curves show a restricted region of activation controlled reduction, followed by mixed control and finally a mass transfer controlled region for reduction of hydrogen peroxide followed by reduction of H^+ at the more negative potentials. It is evident that the limiting current density is increased as the bulk concentration of hydrogen peroxide is increased. It is seen also that the onset of reduction of protons is delayed by increasing the concentration of hydrogen peroxide as it is a strong oxidant.

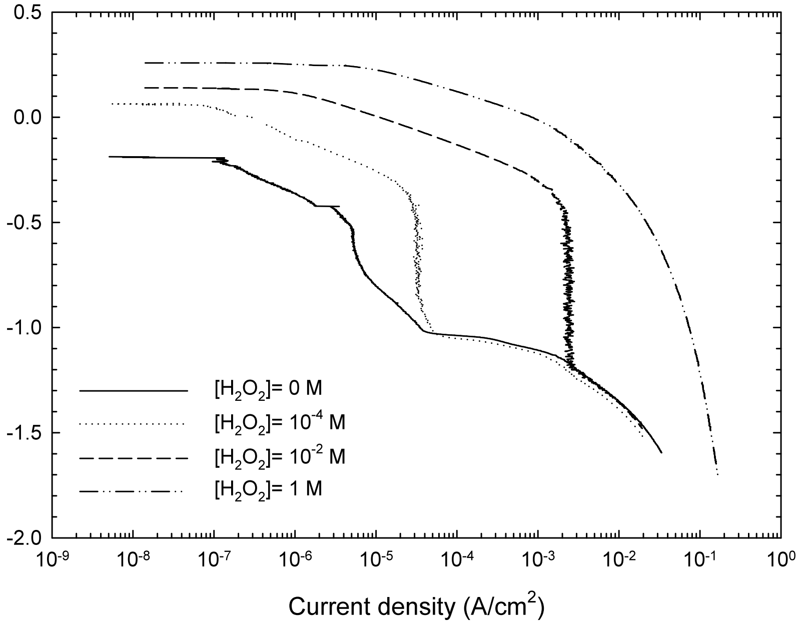


Figure 3. The cathodic polarization curves of magnetite bulk electrode in 0.1M NaClO4, pH=9.5 and different concentrations of hydrogen peroxide.

Because the onset of mixed control region is located at low overpotentials, Tafel extrapolation method cannot be used for extracting the kinetic data. Therefore, assuming the same cathodic and anodic charge transfer coefficient of hydrogen peroxide reduction on the magnetite electrode, kinetic parameters were extracted using the extended Butler-Volmer equation as given by:

□=□0□□□−□□□□□□□−□□□□□□□□□□1+□0□□□−□□□□□□□□□□2□2

Where, i_0 is the exchange current density, α_c and α_a are the transfer coefficients for cathodic and anodic reactions, respectively and η is the overpotential. After extraction of data from eq. 4 a Tafel slope of 135±15 mV/decade was found for reduction of hydrogen peroxide on the magnetite for all the concentrations. Furthermore, diffusion coefficients of hydrogen peroxide were calculated from limiting current density and bulk concentration data. The magnitude of diffusion coefficient was found to be in the range of 3.4E-5 cm^2s^{-1} for $[H_2O_2]$ =10^{-4} M to 8.7E-6cm^2s^{-1} for $[H_2O_2]$ =1 M.

3.3. Electrochemical impedance spectroscopy

The effect of hydrogen peroxide decomposition was also studied by means of EIS after OCP measurements. Figure 4 and 5 shows the nyquist and bode phase impedance curves of magnetite electrode at different concentrations of hydrogen peroxide. It can be observed that the radius of the semi-circular capacitive loop tends to decrease with an increase in hydrogen peroxide concentration. A large capacitive loop at low concentration might be attributed to the mass transfer control mechanism in which reduce the surface concentration of hydrogen peroxide on the magnetite, results in the increase of charge transfer resistance. It was observed from polarization experiments in 1M hydrogen peroxide that the limiting current density is nearly large which can be confirmed from small charge transfer resistance (4K Ω cm^{-2}) of impedance data. Likewise, reduction of ferric/ferrous ions to the metallic iron is also possible at higher concentrations.

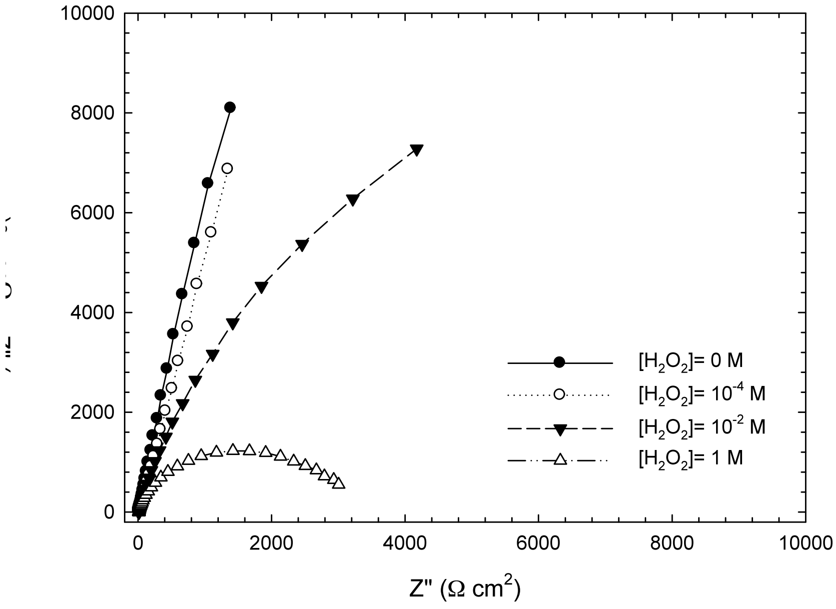


Figure 4. The nyquist curves of magnetite bulk electrode in 0.1M NaClO4, pH=9.5 and different concentrations of hydrogen peroxide.

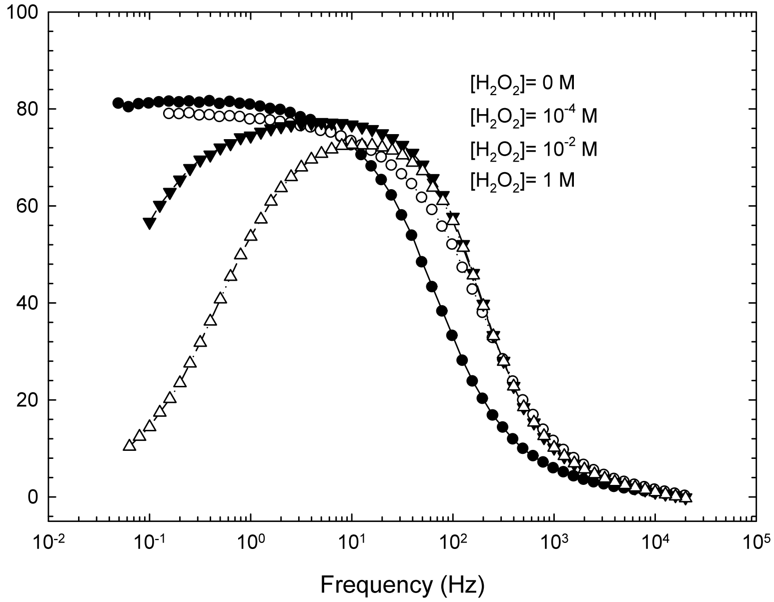


Figure 5. The bode-phase curves of magnetite bulk electrode in 0.1M NaClO4, pH=9.5 and different concentrations of hydrogen peroxide.

4. Conclusion

In this work the electrochemical kinetics of hydrogen peroxide decomposition were studied at different concentration of H_2O_2 in the range of 10^{-4} M to 1 M at pH=9.5. Open circuit potential measurement was used to evaluate the responsible reactions taking place at the surface of a bulk magnetite electrode. It was concluded that the OCP is more likely due to the decomposition of hydrogen peroxide than oxygen gas. Furthermore, Tafel slopes and diffusion coefficients were also estimated for magnetite in the presence of hydrogen peroxide by the use of the extended Butler-Volmer equation. The EIS data showed that charge transfer resistance can be facilitated by increasing hydrogen peroxide concentration.

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