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The electrochemical generation of ferrate at porous magnetite electrode

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Abstract

In this work, ferrate(VI) was generated by the electrochemical oxidation of porous magnetite electrodes, made by melting pure magnetite grains. Pretreatment of the anode by cathodic polarization was necessary for ferrate(VI) generation and the achievement of high current efficiency. A electrolyte composition was found to be 16 M NaOH. In this electrolyte, the effect of anode current density J on Fe(VI) synthesis rate, current efficiency, and internal cell temperature were studied. An optimum result was obtained at $J = 3.3\,\mathrm{mA\,cm^{-2}}$, 30 °C in 16 M NaOH for 5 h.

Keywords: Porous magnetite; Ferrate; Cathodic polarization; Current efficiency

1. Introduction

Ferrate is an iron species in an unusual valence state (>3) and therefore, a very powerful oxidizing agent that has been considered for several applications [1–3]. For instance, ferrate can be used as an oxidant: (i) in organic synthesis as a substitute and safer alternative to other highly toxic oxidizing compounds (e.g. CrO_3, $K_2Cr_2O_7$) and (ii) for the destruction of organics and for water treatment to replace chlorine, hydrogen peroxide or ozone. Ferrate has also been recently used in a new class of batteries, referred to as super-iron batteries, which use the Fe(VI)/Fe(III) system as cathode material in alkaline medium (with a zinc anode) [2,4–7].

Ferrate can be chemically and electrochemically synthesized. The chemical synthesis involves the oxidation of $Fe(NO_3)_3$ with an oxidant such as alkaline hypochlorite [8]:

$$\begin{aligned}&2Fe(OH)_3 + 3ClO^- + 4OH^-\\&\quad\rightarrow 2FeO_4{}^{2-} + 3Cl^- + 5H_2O\end{aligned} \tag{1}$$

or of $Fe_2(SO_4)_3$ with Oxone™, which is a triple salt mixture of monoperoxosulfate ($HSO_5{}^-$), containing K_2SO_4, $KHSO_4$, and $KHSO_5$ [9]. Ferrate can also be electrochemically generated by oxidation of an iron electrode in alkaline media [10–22]. Poggendorf [23] was the first one to observe the formation of ferrate(VI) by anodic oxidation of an iron electrode in a concentrated alkaline hydroxide solution. These studies were continued by Haber [24] and Pick [25], who found that a necessary condition for the formation of ferrate(VI) was pH ≥ 14; the results were better in NaOH than in KOH solutions.

Previous studies on the electrochemical synthesis of ferrate focused on various iron electrodes: grey cast iron, white cast iron, steel, mild steel, etc. The anodic oxidation reaction of an iron electrode is:

$$Fe + 8OH^- \rightarrow FeO_4{}^{2-} + 4H_2O + 6e^- \tag{2}$$

The current yield for ferrate generation on iron electrodes was in the range 20–60%. An optimum current yield of about 60% at a low concentration (about 1 mM) was observed at a pressed iron powder electrode for a 1 h electrolysis in 14–16 M NaOH solutions [26]. In the search for higher current efficiencies, we studied the current yield for ferrate generation at various electrodes other than iron and observed an exciting result at magnetite electrode. Ferrate was successfully generated by the electrochemical oxidation of magnetite electrode in a high concentration alkaline solution. The anodic oxidation reaction of magnetite is:

$$Fe_3O_4 + 16OH^- \rightarrow 3FeO_4{}^{2-} + 8H_2O + 10e^- \tag{3}$$

Compared with oxidation of iron electrode, Eq. (2), the number of electrons per ferrate ion produced, Eq. (3), is only 3.33.

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This study focuses on the electrochemical synthesis of ferrate by oxidation of porous magnetite electrodes. The aim is to use these high surface area magnetite electrodes to generate ferrate in high yield and in high concentration compared with iron electrodes. The use of a porous electrode was successfully applied in previous studies with iron where it was shown that iron passivation was diminished and iron dissolution was enhanced upon increasing the porosity of the iron electrode [26,27]. Similarly, the porous magnetite electrode influenced the formation of the passive layer in such a way that it led to an increase in current yield for ferrate generation and to a higher concentration of ferrate.

2. Experimental

The synthesis was carried out in a divided two-compartment aboratory cell separated by sulfonic acid substituted perfluorocarbon polymer membrane (surface area 40 cm^2). The anode was a 30 cm^2 slab of porous magnetite prepared by melting pure magnetite grains (FeO 31.01%, Fe_2O_3 68.97%). A 30 cm^2 (apparent area) sheet of high surface area platinum gauze acted as the cathode. The volumes of the anode and cathode electrolytes were 80 and 150 ml, respectively. Anode pretreatment included 2 min sonication in 1:10 (v/v) H_2SO_4, followed by de-ionized water washing to

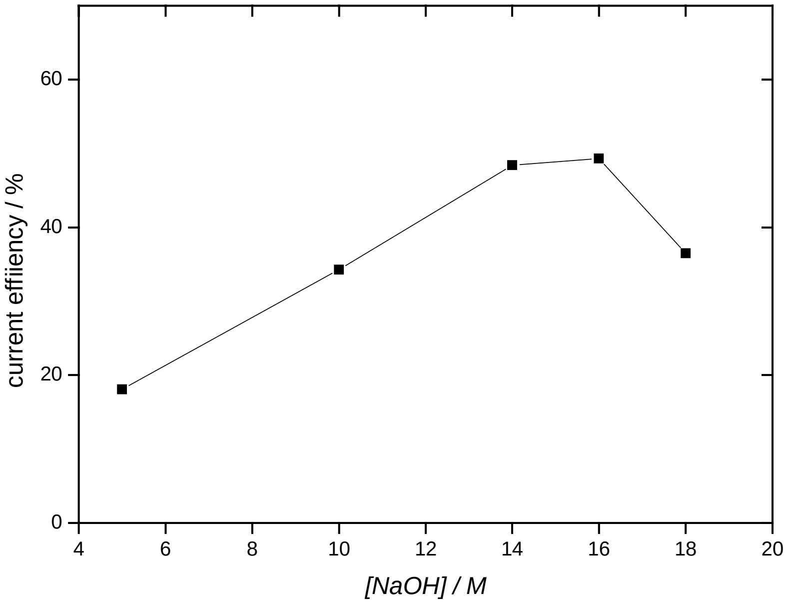

Fig. 1. Current efficiency as a function of NaOH concentration for 1 h electrolysis of magnetite electrode at a current of 100 mA and room temperature.

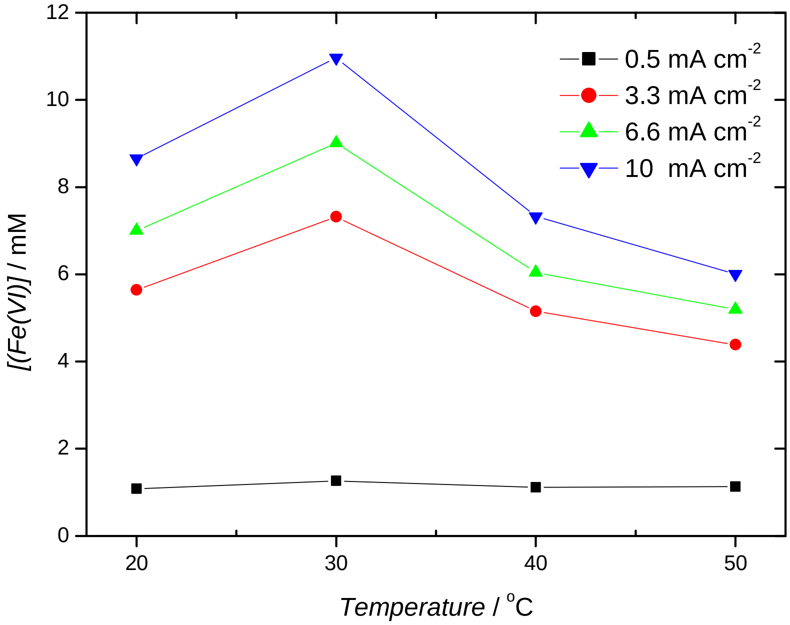

Fig. 2. Concentration of Fe(VI) as a function of cell temperature in 16 mol l^{-1} NaOH at different current densities for 1 h electrolysis.

pH 7 and cathodic polarization in the range, 15–20 mA cm^{-2} for 15 min. All electrolytes were prepared from analytical grade reagents and de-ionized water. Electrolyte pretreatment was carried out as suggested in [28]. The electrolyte in both compartments was 16 M NaOH solution. Cell temperature was controlled within ±1 °C by a large water bath. Constant direct current was supplied by YJ83/2 DC power sources (Precision & Scientific Instrument Co. Ltd., Shanghai, China). The stirring near the electrode surface was necessary in the anode compartment. The synthesis was carried out for 5 h when the formation of a passivation layer significantly decreased the generation yield of ferrate. The solution phase FeO_4^{2-} concentration was probed by UV-Vis photodiode array spectrophotometer at $\lambda = 505$ nm [29].

3. Result and discussion

Pretreatment of the magnetite anode by cathodic polarization is a necessary condition for the achievement of high current efficiency. The passive layer was destroyed and the electrode was activated during cathodic polarization. A maximum current efficiency for 1 h electrolysis was observed in 14–16 M NaOH solutions, as shown in Fig. 1. The high current efficiency indicated higher anode corrosion rate and

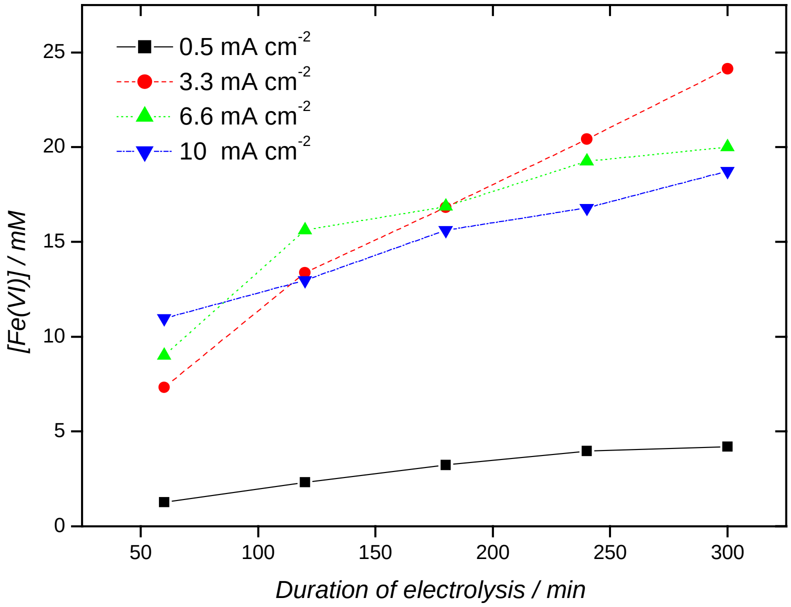

Fig. 3. Concentration of Fe(VI) as a function of duration of electrolysis in 16 mol l^{-1} NaOH at different current densities and at 30 °C.

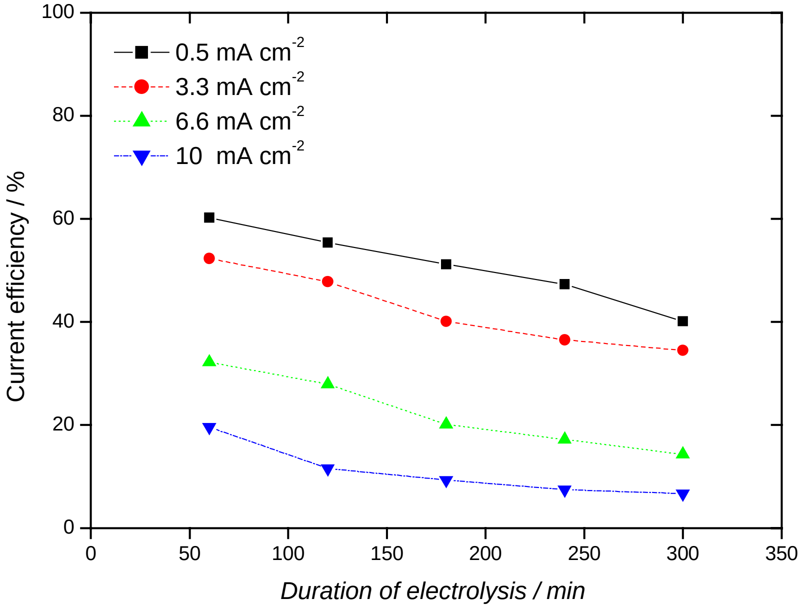

Fig. 4. Current efficiency as a function of duration of electrolysis in 16 mol l^{-1} NaOH at different current densities and at 30 °C.

lower ferrate decomposition rate. An abrupt decrease in current efficiency was observed upon increasing the NaOH concentration to 18 M. In this study, a 16 M NaOH solution was used as electrolyte. In this electrolyte, the effect of anode current density J on Fe(VI) synthesis rate, current efficiency, and internal cell temperature were probed. Increasing the cell temperature generally results in faster rates of Fe(VI) generation and higher current efficiency. However, this trend is diminished or reversed for temperatures higher than 30 °C, resulting in a maximum at 25–35 °C, as shown in Fig. 2. At higher current densities, the cell potential is so high that an increase in the rate of ohmic heating is observed. The cell temperature increasing accelerates the Fe(VI) decomposition reaction, and the surface of porous magnetite electrode is passivated rapidly, which leads to a low current efficiency and gradually decreases the rate of Fe(VI) generation. Although lower current densities retard the passivation process and increase the current efficiency for Fe(VI) generation, lower synthesis rates are obtained. The Fe(VI) synthesis rate and current efficiencies, as shown in Figs. 3 and 4, at $J = 0.5$ and $3.3\,\mathrm{mA\,cm^{-2}}$ for 1 h are: $1.5\,\mathrm{mM\,h^{-1}}$ and 70.2%; $7.3\,\mathrm{mM\,h^{-1}}$ and 52.3%, respectively. A current density of $3.3\,\mathrm{mA\,cm^{-2}}$ is observed as an optimal compromise between these phenomena supporting a high synthesis rate and a high current efficiency.

The porouse magnetite electrode made by melting pure magnetite grains was initially characterized by scanning electron microscopy. Fig. 5. shows that these pores were not distributed evenly and their shape was irregular. The XRD patterns for a porous magnetite electrode before electrolysis

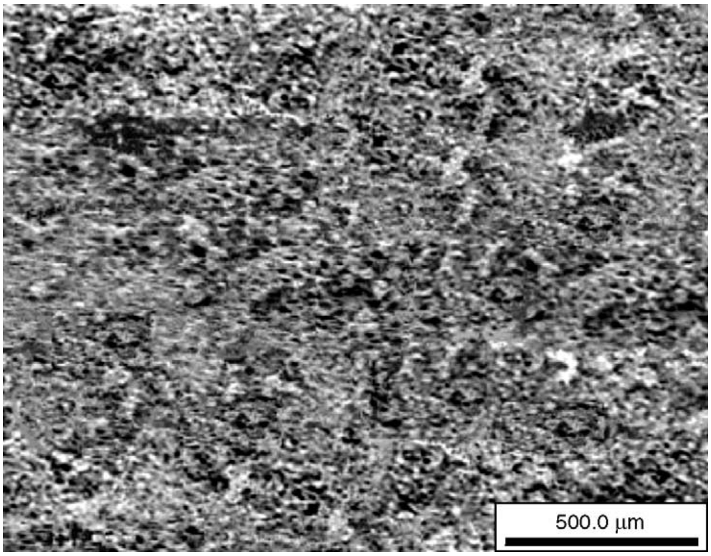

Fig. 5. Scanning electro micrograph (SEM) of the surface of a porous magnetite electrode.

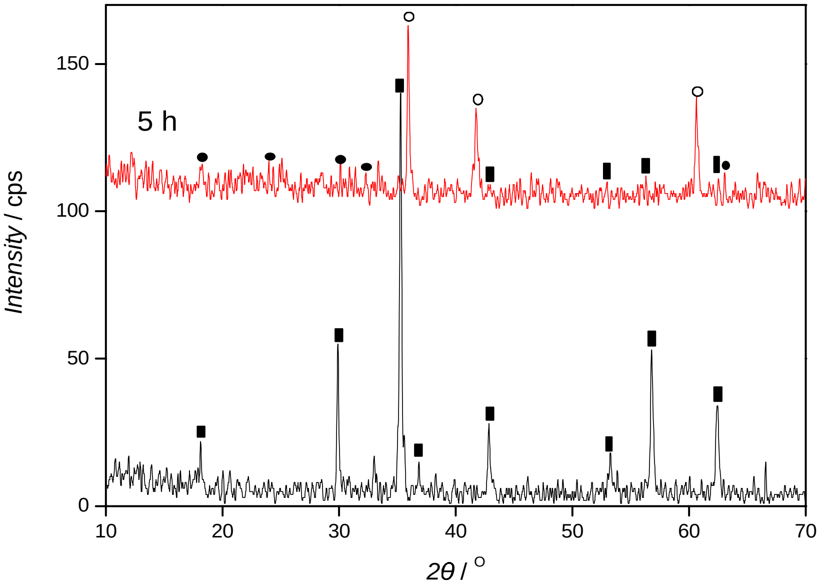

Fig. 6. X-ray diffraction histograms for a porous magnetite electrode before electrolysis and after 5 h electrolysis: Fe_3O_4 (■); FeO (○); Fe_2O_3 (●).

and after 5 h electrolysis were shown in Fig. 6. The XRD pattern for porous magnetite electrode exhibited some characteristic diffraction peaks. The XRD peaks were very sharp, which suggested a pure well-crystalline magnetite. Nevertheless, new diffraction peaks were visible at 36.1, 41.94, and 60.88° after 5 h, and were characteristic to FeO. A close examination of the XRD pattern after 5 h electrolysis might revealed the presence of Fe_2O_3. Fe_3O_4 almost disappeared after 5 h.

4. Conclusion

The electrochemical generation of ferrate at a porous magnetite electrode has been demonstrated. The electrolysis conditions were investigated and optimized. A ferrate solution about 25 mM was obtained under the optimum conditions: NaOH concentration (16 M), $J = 3.3\,\mathrm{mA\,cm^{-2}}$, $I = 100\,\mathrm{mA}$, 30 °C, electrolysis duration (5 h). The optimal current efficiency was 52.3%. The result of this study suggests that this approach is very promising to improve the yield for ferrate generation. On the other hand, even under the optimum conditions tested, the formation of a passive layer of magnetite electrode was not completely avoided. Thus, it will be crucial to improve this particular aspect in order to achieve a more attractive method of ferrate generation.

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