Electrochemical Reduction of Perchlorate Ion on Porous Carbon Electrodes Deposited with Iron Nanoparticles

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1. Introduction

Perchlorate ion, which is a known toxic compound and is listed as a serious environmental pollutant is generally considered to be very stable in aqueous solutions due to its tetrahedral structure and charge distribution within the polyatomic anion. As a result, it is very difficult to reduce or remove ions in solution. Currently, there are several methods for the removal of perchlorate from water, including biological reduction, chemical reduction, and physical methods based on anion exchange techniques. Membrane filtration methods have been utilized, too. However, the aforementioned methods have drawbacks such as the need for disposal of perchlorate and/or by-products, high cost and low efficiency.

Electrochemical reduction is an attractive alternative because the toxic \( \text{ClO}_4^- \) ion is converted into the non-toxic \( \text{Cl}^- \) ion according to the reaction below:

\[
\text{ClO}_4^- + 4e^- + 4H^+ \rightarrow \text{Cl}^- + 2H_2O
\]
The electrodegradation of the perchlorate ion has been previously investigated using a variety of transition metal electrodes. According to these studies, the rate of reduction depends on the nature of the metal as well as other experimental conditions, including pH. Additionally, these studies showed that hydrogen promotes $\text{ClO}_4^-$ reduction via catalysis by a metal ion, rendering the rigorous evolution of hydrogen during the application of a high reductive potential unavoidable. This caused several experimental difficulties, including fast dwindling of sample volume and increasing resistance.

In recent years, zero-valent iron (ZVI) has attracted increasing interest for the reduction of perchlorate. Perchlorate in both fresh water and brine can be rapidly and completely destroyed by low concentrations of stabilized ZVI nanoparticles at moderately elevated temperatures. However, chemical generation of ZVI with NaBH$_4$ is expensive and not reusable. In this study, the preparation of ZVI by electrochemical reduction of iron (II) on a porous carbon electrode is investigated as an alternative to the use of expensive NaBH$_4$. ZVI nanoparticles prepared by the present method are well distributed on a polypyrrole conducting polymer film. Therefore, aggregation of ZVI was prevented and surface area was increased, which resulted in better surface reactivity. Additionally, a mild reducing condition was applied to enhance the efficiency of the degradation reaction of perchlorate with ZVI without the evolution of hydrogen.

2. Experimental

Electrochemical experiments were performed using a three electrode system, which consists with a porous carbon (0.5 $\times$ 0.5 $\times$ 0.1 cm: Deuocel Co.) working electrode, a platinum foil (0.5 $\times$ 2 cm) counter electrode and an Ag/AgCl reference electrode. The reference electrode was separated from the working solution by a bridge containing a 2 M solution of NaClO$_4$, which prevented contamination of the working solution with chloride ions. All potentials below are quoted with respect to this reference electrode. For voltammetry and deposition, an EG&G Princeton Applied Research (PAR) 263A instrument equipped with Model M250/270 electrochemistry software was used. All solutions were purged with nitrogen for 30 min to remove dissolved oxygen.

All chemicals were obtained from commercial sources and used as received: sodium sulfate anhydrous (Duksan, 99.0%), iron(II) sulfate heptahydrate (Sigma-aldrich, 99.0%), and pyrrole (Aldrich, 98%).

Film morphology and composition were obtained by scanning electron microscope (SEM, Jeol Model 6700F) equipped with an energy dispersive X-ray analysis (EDX) probe. The perchlorate anion was analyzed using Dionex ion chromatography (DX 300) with a suppressed conductivity detector.

3. Results and Discussion

ZVI nanoparticles are electrochemically deposited on the porous carbon electrode modified with a polypyrrole film. For this, the polypyrrole conducting polymer was previously deposited on a porous carbon electrode using cyclic voltammetry (CV). Electrodeposition was performed by 20 cycles of a potential scan between -0.7 ~ -1.1 V at 50 mV/s in a 0.1 M pyrrole solution. Fig. 1 shows a cyclic voltammogram of polypyrrole modified porous carbon electrode in a 0.1 M sodium sulfate solution containing in 0.1 M iron sulfate. Scan rate : 20 mV/s.
cyclic voltammogram (CV) of polypyrrole modified porous carbon electrode in a 0.1 M sodium sulfate solution containing in 0.1 M iron sulfate. The CV clearly demonstrated iron deposition at more negative potential of ~-1.0 V and oxidation during the reverse anodic scan. ZVI nanoparticles were electrodeposited on the polypyrrole surface at the constant potential of -1.2 V for 300 s using a mixed solution of 0.1 M iron sulfate and 0.1 M sodium sulfate. The total amount of iron deposited during the chronoamperometric experiment can be calculated using the Faraday’s law. According to the total charge, it was calculated that $4.06 \times 10^{-6}$ mol of iron was electrodeposited on the electrode surface, which is equivalent to $2.265 \times 10^{-3}$ g of iron.

The morphology and composition were determined by SEM and EDX analysis. Fig. 2 shows SEM images for the bare porous carbon electrode before deposition of polypyrrole (Fig. 2A) and after modification with polypyrrole (Fig. 2B). Fig. 2B shows that morphology of the porous carbon was maintained after electrodeposition of polypyrrole. As seen in the figure, polypyrrole film is very homogeneous and no aggregation is observed. Surface morphology was dramatically changed after electrodeposition of ZVI on the electrode surface. Electrodeposition of ZVI was confirmed by EDX analysis (Fig. 3) and color change of the electrode. The ZVI surface was dark black when freshly deposited on the electrode surface.

It is well known that two overall processes occur simultaneously during the electrochemical reduction of perchlorate by iron:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (2)$$

$$4Fe + ClO_4^- + 8H^+ \rightarrow Cl^- + 4Fe^{2+} + 4H_2O \quad (3)$$

Electrochemical degradation of perchlorate was performed at -0.3 V using a solution containing 10 ppm of ammonium perchlorate and change of perchlorate concentration with degradation time was monitored with ion chromatography. Fig. 4 depicts ion chromatograms showing the change in

![Fig. 2. SEM images for (A) a porous carbon electrode, a polypyrrole modified porous carbon electrode (B) before and (C) after electrodeposition of ZVI.](image1)

![Fig. 3. EDX spectrum for a polypyrrole modified porous carbon electrode after electrodeposition of ZVI.](image2)
perchlorate concentration, before (Fig. 4A) and after 10 min (Fig. 4B) the degradation of perchlorate with electrochemically generated ZVI. Preliminary results showed that ~12.7% of perchlorate was reduced in just 10 min. and it is expected that efficiency can be increased with area of the carbon electrode, amount of ZVI, and reaction temperature.

In summary, we developed a facile and efficient method for the preparation of ZVI on the polypyrrole modified porous carbon electrode and the electrode was successfully used to destroy perchlorate ions. Further studies on the effects of conditions including electrolysis time, potential, perchlorate concentration on the degradation efficiency are under investigation in our laboratory. Additionally, methods to recycle ZVI after experiments will be investigated in the future.

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