Over the past few decades, there has been a great deal of interest in the electrochemical generation of ferrate, Fe(VI) or FeO₄²⁻. Such interest arises from a pure scientific curiosity and also from its possible applications such as high energy density rechargeable batteries, and destruction of various environmental pollutants. Published studies on the electrochemical generation of ferrate have utilized highly alkaline media, such as 14 M NaOH, in which ferrate is stable. Its preparation or observation as an intermediate species in acidic aqueous media has not been reported in the past due to its very high standard potential. Electrochemical preparation of ferrate in non-alkaline media would open up the new chemistry of Fe(VI) and facilitate the electrochemical treatment of wastes and pollutants due to its high oxidation potential and extremely high instability.

Boron-doped diamond (BDD) electrodes have received much interest due to their unique electrochemical properties including a low capacitive background current, wide potential window, chemical inertness, and high mechanical strength. These properties have allowed the BDD electrodes to be used in a wide variety of electrochemical applications. Its wide potential window and chemical inertness are especially appealing characteristics for studying electrochemically generated oxidants and/or reductants. Here we report electrochemical generation of ferrate in an acidic aqueous medium for the first time utilizing BDD electrodes to oxidize Fe²⁺ to ferrate.

The preparation of BDD electrodes used in this study has been described elsewhere. The electrochemical cell was a single compartment cell made from Teflon, with the surface of the BDD working electrode exposed at the bottom of the cell through an O-ring supported opening. The counter electrode was a Pt mesh, the reference electrode was a home-made Ag/AgCl (in saturated KCl) electrode for aqueous solutions, while a Pt wire was used as the pseudo-reference electrode in organic solvents. Electrochemical measurements were made using an EG&G Princeton Applied Research model 273A potentiostat/galvanostat controlled with an IBM compatible PC. Aqueous solutions were prepared using doubly distilled deionized water.

Fig. 1 shows the cyclic voltammograms (CVs) of 6.0 mM FeSO₄ in 0.10 M HClO₄ on BDD electrodes at different scan rates. Three peaks, two anodic (AI and AII) and one cathodic (CI), are seen in the CVs. While peaks AI and CI are assigned to the Fe³⁺/Fe⁴⁺ redox pair, peak AII at 2.3–2.75 V depending on the scan rate, has not been reported in the literature. We assign peak AII to the oxidation of Fe³⁺ to ferrate, Fe(VI), according to eqn. (1).

\[
\text{Fe}^{3+} + 4 \text{H}_2\text{O} \rightarrow \text{FeO}_4^{2-} + 8 \text{H}^+ + 3 \text{e}^- \tag{1}
\]

are the thermodynamic potential of which is consistent with the observed value.

An extremely strong oxidant, ferrate (Fe(VI) or FeO₄²⁻), has been produced electrochemically in an acidic aqueous medium for the first time.

The standard reduction potential of ferrate (2.20 V vs. NHE) is well above that of water oxidation (1.23 V vs. NHE), leading to the evolution of oxygen. Thus, the absence of a Fe(vi) reduction peak must be due to a fast catalytic reaction (EC: E = electrochemical and C = chemical/catalytic), summarized in Scheme 1.

\[
\text{2FeO}_4^{2-} + 5 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{3+} + 13/2 \text{O}_2 + 10 \text{H}^+ \tag{2}
\]

Scheme 1 EC mechanism of ferrate(VI) generation.

To show that reaction (1) requires water, CVs recorded in acetonitrile solutions with and without water are shown in Fig. 2. Addition of water not only reduces the overpotential for the Fe³⁺/Fe⁴⁺ redox pair, but also leads to a new anodic peak, AII.
The obtained are shown as a function of electrolysis time in Fig. 3.

This observation indicates that reaction (1) requires water, as indicated by its stoichiometry. Also, peak AI increases rapidly with increasing water concentration, confirming the catalytic character of the reaction.

To show that the mechanism of the electrocatalytic reaction is at work from another point of view, the apparent number of electrons transferred ($n_{\text{app}}$) was obtained for reaction (1) under potentiostatic conditions at +2.6 V. The $n_{\text{app}}$ values were calculated from eqn. (3)

$$n_{\text{app}} = \frac{1}{1 + \gamma} \left[ 1 + \frac{\gamma}{1 - e^{-p(1+\gamma)}} \right]$$

which was derived for the EC$^-$ reaction mechanism. Here $n$ is the number of electrons transferred; $p$ is the mass transport coefficient defined as $p = m_0A/V$ with $m_0$ being the mass transport constant, $A$ being the electrode area, and $V$ being the solution volume; and $\gamma$ is obtained from eqn. (4)

$$\frac{I_{\text{ss}}}{I_{\text{t}=0}} = \frac{\gamma}{1 + \gamma}$$

Here $I_{\text{ss}}$ is the steady state current reached during potentiostatic electrolysis. The coefficient $p$ is obtained from eqn. (5)

$$I_{\text{t}=0} = I_{\text{t}} - e^{-pt}$$

where $I_{\text{t}}$ is the current at time $t$, $I_{\text{t}=0}$ is the initial current obtained at $t = 0$ upon potential step. The $n_{\text{app}}$ values thus obtained are shown as a function of electrolysis time in Fig. 3. The $n_{\text{app}}$ value starts at 3, which is expected for reaction (1), and continue to increase with increasing time. The initial $n_{\text{app}}$ value of 3 and the steady increase over electrolysis time is positive evidence that an EC$^-$ reaction is occurring with a very large turnover rate.

In conclusion, we report electrochemical generation of ferrate for the first time in acidic aqueous solution and organic solvent using a BDD electrode. The observation of this electrochemistry previously not reported was made possible due to the unique nature of the BDD electrode, which has a very large overpotential for oxygen evolution. The electrochemically generated ferrate rapidly oxidizes water to produce oxygen and regenerate Fe$^{3+}$. This reaction is expected to open up a new area comprising the rich chemistry of Fe(vi) and also to lead to indirect electrochemical generation of a variety of compounds having large anodic overpotentials, as well as electrochemical destruction of organic wastes, using electrogenerated ferrate.

More detailed studies on the mechanism of electrochemical generation of ferrate and its optimization and stabilization are currently in progress in our laboratory.

A grateful acknowledgement is made to the Korea Science and Engineering Foundation for supporting this research through the Center for Integrated Molecular Systems located at POSTECH and to the Ministry of Education for providing graduate stipends to J. W. L.

Notes and references