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Electrochemical generation of ferrate in acidic media at boron-doped diamond electrodes

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An extremely strong oxidant, ferrate (Fe(VI) or FeO_4^{2-}), has been produced electrochemically in an acidic aqueous medium for the first time

Over the past few decades, there has been a great deal of interest in the electrochemical generation of ferrate, Fe(VI) or FeO_4^{2-}.[1] Such interest arises from a pure scientific curiosity and also from its possible applications such as high energy density rechargeable batteries,[2] and destruction of various environmental pollutants.[3] 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.[1] 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[4] 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.[5] These properties have allowed the BDD electrodes to be used in a wide variety of electrochemical applications.[6] 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 aqueous acidic medium for the first time utilizing BDD electrodes to oxidize Fe^{2+} to ferrate.

The preparation of BDD electrodes used in this study has been described elsewhere.[7] 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 an Ag 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 $FeSO_4$ in 0.10 M $HClO_4$ 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 Fe^{3+}/Fe^{2+} 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 Fe^{3+} to ferrate, Fe(VI), according to eqn. (1),

$$Fe^{3+} + 4\,H_2O \rightarrow FeO_4^{2-} + 8\,H^+ + 3\,e^- \qquad (1)$$

the thermodynamic potential[4] of which is consistent with the observed value.

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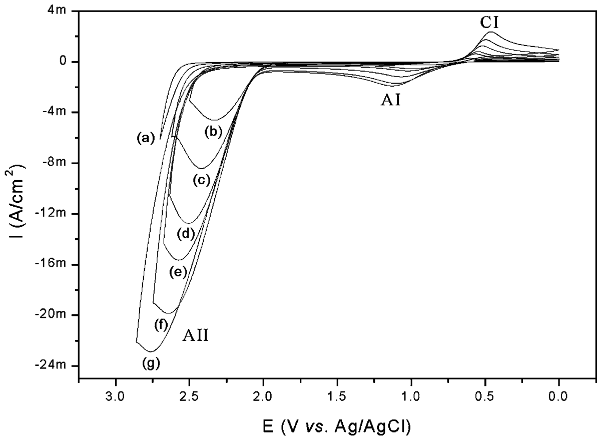
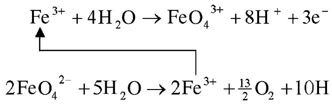


Fig. 1 Cyclic voltammograms (CVs) at a boron-doped diamond electrode in (a) 0.1 M $HClO_4$, and with 6 mM $FeSO_4$ at scan rates of (b) 10, (c) 50, (d) 100, (e) 250, (f) 500 and (g) 1000 mV s^{-1}. The electrochemical cell was a single compartment cell, with the surface of the BDD electrode exposed at the bottom of the cell through an O-ring supported opening with a Pt mesh counter electrode, and Ag/AgCl reference electrode (in saturated KCl).

No cathodic peak was observed for the reduction of Fe(VI) to Fe^{3+} even at scan rates higher than those used in Fig. 1. Aeration or deaeration did not affect the peak, indicating that oxygen is not involved and does not affect the reaction. One characteristic of peak AII is that it is excessively large compared to that expected from reaction (1). The AI:AII ratios for the CVs shown in Fig. 1 vary between 1:8 to 1:10 depending on reaction conditions, which are much larger than the expected ratio of 1:3. We thus conclude from these observations that the electrochemically generated ferrate undergoes a rapid decomposition reaction with water to produce O_2 and regenerate Fe^{3+} according to eqn. (2),

$$2\,FeO_4^{2-} + 5\,H_2O \rightarrow 2\,Fe^{3+} + 13/2\,O_2 + 10\,H^+ \qquad (2)$$

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),[8] summarized in Scheme 1.



$$Fe^{3+} + 4H_2O \rightarrow FeO_4^{3+} + 8H^+ + 3e^-$$

$$2FeO_4^{2-} + 5H_2O \rightarrow 2Fe^{3+} + \tfrac{13}{2}O_2 + 10H^+$$

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 Fe^{3+}/Fe^{2+} redox pair, but also leads to a new anodic peak, AII.

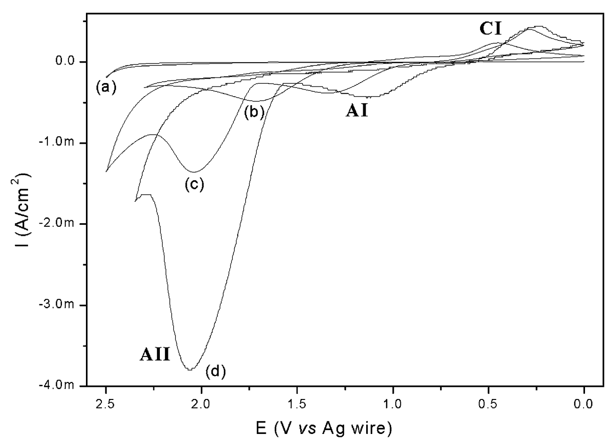


Fig. 2 Cyclic voltammograms (CVs) at a boron-doped diamond electrode in (a) acetonitrile with 0.1 M $LiClO_4$ only, (b) as in (a) but with addition of 6 mM $FeSO_4$, (c) as in (b) but with addition of 1.13 M of water, and (d) as in (b) but with addition of 2.83 M of water, at a scan rate of 100 mV s^{-1}. A Pt mesh counter electrode and Ag wire pseudo-reference electrode were used.

This observation indicates that reaction (1) requires water, as indicated by its stoichiometry. Also, peak AII 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_{app}) was obtained for reaction (1) under potentiostatic conditions at +2.6 V. The n_{app} values were calculated from eqn. (3)[7]

$$n_{app} = n[\frac{1}{1+\gamma} + \frac{p\gamma t}{1-e^{-p(1+\gamma)t}}] \qquad (3)$$

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 γ is obtained from eqn. (4)

$$\frac{I_{ss}}{I_{(t=0)}} = \frac{\gamma}{1+\gamma} \qquad (4)$$

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

$$I_{(t)} = I_{(t=0)}e^{-pt} \qquad (5)$$

where $I_{(t)}$ is the current at time t, $I_{(t=0)}$ is the initial current obtained at $t = 0$ upon potential step. The n_{app} values thus obtained are shown as a function of electrolysis time in Fig. 3. The n_{app} value starts at 3, which is expected for reaction (1), and continue to increase with increasing time. The initial n_{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.

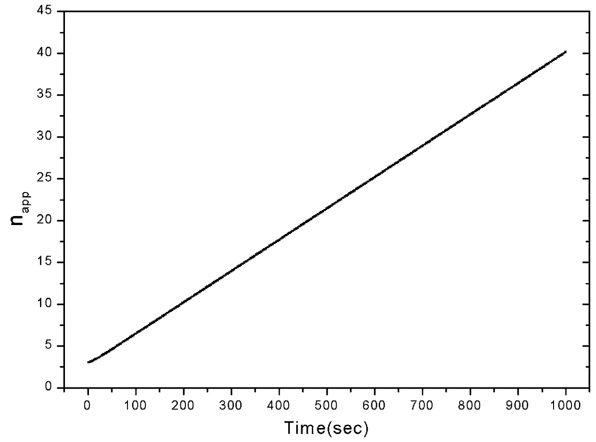


Fig. 3 Apparent number electrons transferred (n_{app}) during the controlled potential electrolysis.

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.

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