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Adsorption and reactivity of hydrous iron oxide nanoparticles on boron-doped diamond

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Abstract

Hydrous iron oxide nanoparticles of 8–16 nm diameter are adsorbed from an aqueous sol onto the surface of polished boron-doped diamond electrodes. Boron-doped diamond acts as an inert substrate with low background currents and a wide potential window, allowing electrochemical and electrocatalytic properties of an electrically non-conducting material such as hydrous iron oxide to be studied. The electrochemical reduction of hydrous ferric oxide in aqueous phosphate buffer at pH 5 at a potential of ca. -0.2 V vs. SCE is accompanied by stripping of the deposit, which allows the determination of the approximate coverage of the oxide on the boron-doped diamond electrode, typically 1.4×10^{-9} mol cm^{-2} . Next, hydrous ferric oxide is shown to act as an efficient electrocatalyst for the oxidation of hydroxide to dioxygen. The process is proposed to occur with apparently one electron per hydroxide via a $C_{\text{het, rev}}E_{\text{rev}}C_{\text{het, irrev}}$ -type process, initiated by deprotonation of an active iron oxide surface site. It is also demonstrated that the reaction of hydrogen peroxide on hydrous ferric oxide surfaces (a heterogeneous Fenton-type process) is similarly triggered by the deprotonation of an active surface site.

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1. Introduction

Metal oxides are important catalysts in a wide range of technical and electrochemical processes. Iron oxide (usually mixed with other metal oxides) in particular, has been shown to be a very active (although unstable) catalyst for the oxygen evolution process [1,2] as well as other related processes, such as water splitting [3], chlorine evolution [4], the oxidation of organic molecules [5], the oxygen reduction process [6,7], and for the hydrogen peroxide decomposition [8]. Even more important are iron oxide-based catalysts in non-electrochemical processes [9,10]. In nature, nanoparticulate hydrous iron oxide is the iron source for metallo-proteins and therefore stored in form of ferritins [11] in the cells of animals, plants, fungi, and bacteria.

Nanoparticulate hydrous iron oxide readily adsorbs onto tin-doped indium oxide (ITO) electrodes [12] in

form of an electrochemically active layer. The amount of hydrous iron oxide nanoparticles is readily quantified by cathodic stripping to give the soluble $\text{Fe}^{2+}(\text{aq})$ [13]. For comparison, nanoparticulate hydrous ruthenium oxide undergoes facile adsorption onto both, ITO [14] and boron-doped diamond [15]. It is shown here that hydrous ferric oxide also undergoes adsorption onto both ITO and boron-doped diamond. Boron-doped diamond may be regarded as a chemically inert and topographically well-defined substrate, on which nanoparticle-based redox processes are readily studied. The low (capacitive) background currents and the wide accessible potential window in aqueous media [16] make boron-doped diamond extremely versatile.

In this report, preliminary results on the electrochemical characteristics of hydrous iron oxide nanoparticles adsorbed onto boron-doped diamond electrodes are reported. It is shown that with boron-doped diamond as an inert substrate, well-defined voltammetric responses for the oxidation of hydroxide anions are obtained. A fast preceding interfacial deprotonation step in a $C_{\text{het, rev}}E_{\text{rev}}C_{\text{het, irrev}}$ -type process is

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proposed to be responsible for reactive sites on the surface of the hydrous iron oxide.

2. Experimental

2.1. Chemical reagents

Demineralised and filtered water was taken from an Elga water purification system (Elga, high Wycombe, Bucks) with a resistivity of not less than 18 MΩ cm. Colloidal hydrous ferric oxide (ca. 8–16 nm particle size, ca. 2 mM in Fe, stabilised with perchloric acid at pH 3) was prepared from FeCl₃ (Aldrich) following a literature procedure [17–19]. The colloidal material is formed by drop-wise addition of an aqueous 20 mM FeCl₃ solution into boiling water. The material formed initially is believed to be hydrous ferric oxide, but a slow structural transition from hydrous ferric oxide to α-Fe₂O₃ might occur [20]. Therefore freshly prepared nanoparticle solutions were employed. A detailed structural investigation of similar Fe₂O₃ nanoparticle materials by X-ray absorption near-edge structure (XANES) analysis has been reported recently by Chen et al. [21]. KOH, KNO₃ (analytical grade, Aldrich), and hydrogen peroxide (Aldrich) were used without further purification.

2.2. Instrumentation

For electrochemical experiments a PGSTAT 30 Autolab system (Eco Chemie, Netherlands) was employed in conventional three-electrode configuration. The counter electrode was a platinum gauze, the reference electrode was a saturated Calomel electrode (SCE, Radiometer, Copenhagen), and the working electrode was a boron-doped diamond electrode (polished boron-doped diamond, De Beers Industrial Diamond, distributed by Windsor Scientific, Slough) mounted in a Teflon holder. Unless stated otherwise, the modification of the boron-doped diamond electrode surface was carried out by immersion of the polished boron-doped diamond electrode into a sol of hydrous ferric oxide (2 mM in Fe) for 30 s followed by thorough rinsing with water. The coating with hydrous iron oxide was removed by polishing with wet alumina (Buehler, 0.3 μm).

A bulk electrolysis experiment was carried out to rule out the formation of hydrogen peroxide during the oxidation of hydroxide. For this experiment, a solution of 10 mM KOH in aqueous 1.0 M KNO₃ was electrolysed at a hydrous iron oxide decorated electrode (5 cm²) in a stirred divided cell reactor at a potential of 1.2 V vs. SCE. The formation of products was monitored in situ with a 25 μm diameter platinum microdisk electrode. This procedure was validated independently by addition of known amounts of hydrogen peroxide. There was no

indication of traces of hydrogen peroxide being formed during hydroxide oxidation.

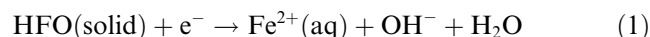
For electron microscopy experiments, a field emission gun system (FEGSEM, Leo 1530 field emission gun scanning electron microscope) was used. Prior to measurements samples were gold coated with a sputter coating unit. Digital simulation investigations of voltammetric curves were carried out with *Digisim*TM (BAS) and with a simulator [22] for a E_{rev}C_{het, irrev}-type processes coded in Delphi 5 (Borland).

3. Results and discussion

3.1. Adsorption of hydrous ferric oxide onto boron-doped diamond

The adsorption of hydrous iron oxide nanoparticles onto the surface of a polished boron-doped diamond electrode occurs rapidly from a colloidal solution 2 mM in iron at pH 3. The adsorption process is confirmed directly by scanning electron microscopy. Fig. 1 shows the featureless surface of the polished boron-doped diamond decorated with a deposit of nanoparticles typically 8–16 nm in diameter.

In phosphate buffer solution, hydrous ferric oxide (HFO) is electrochemically reduced and stripped from the electrode surface in form of Fe²⁺(aq) [13]. This reduction process may be written as a one electron reduction process (Eq. (1))



This process allows the characteristic reduction signal associated with the stripping of iron oxide to be detected

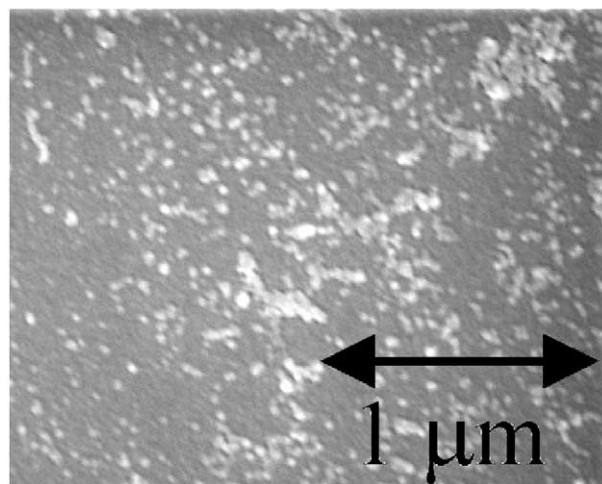


Fig. 1. FEGSEM image showing hydrous iron oxide nanoparticles of 8–16 nm size adsorbed onto the surface of a polished boron-doped diamond electrode. The surface of a bare boron-doped diamond electrode imaged under the same conditions was featureless.

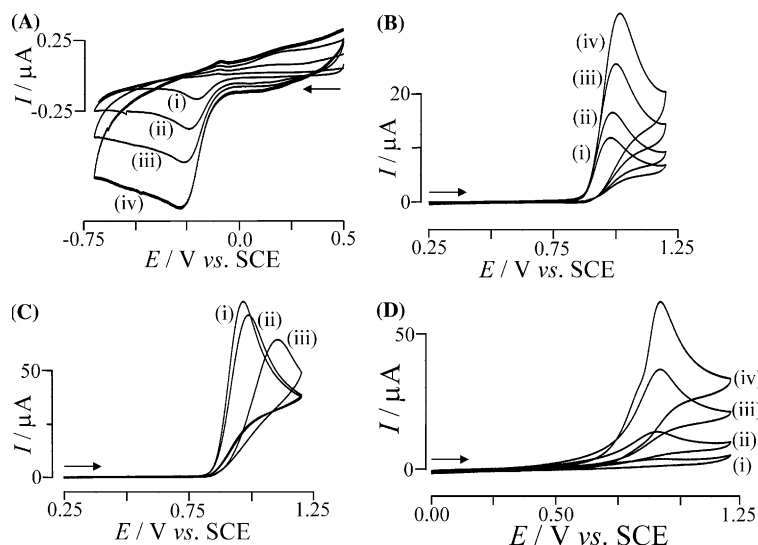


Fig. 2. (A) Cyclic voltammograms (scan rate (i) 2, (ii) 5, (iii) 10, and (iv) 20 mV s^{-1}) for the reduction of hydrous ferric oxide adsorbed onto boron-doped diamond (0.25 cm^2) and immersed in aqueous 0.1 M phosphate buffer at pH 5. (B) Cyclic voltammograms (scan rate (i) 0.01, (ii) 0.02, (iii) 0.05, and (iv) 0.1 V s^{-1}) for the oxidation of 0.3 mM KOH in aqueous 1.0 M KNO_3 at a boron-doped diamond electrode (0.25 cm^2) modified with hydrous ferric oxide. (C) Cyclic voltammograms (scan rate 0.05 V s^{-1}) for the oxidation of 1 mM KOH in aqueous 1.0 M KNO_3 at a boron-doped diamond electrode (0.25 cm^2) modified with hydrous ferric oxide (hydrous ferric oxide adsorbed from a sol (i) 2 mM, (ii) 0.2 mM, and (iii) 0.02 mM in Fe). (D) Cyclic voltammograms (scan rate 0.02 V s^{-1}) for the oxidation of 1 mM hydrogen peroxide in the presence of (i) 0.1 mM, (ii) 0.4 mM, (iii) 1.0 mM, and (iv) 2.0 mM KOH in aqueous 1.0 M KNO_3 at a boron-doped diamond electrode (0.25 cm^2) modified with hydrous ferric oxide.

and at least approximately quantified. In Fig. 2(A), the reduction of hydrous ferric oxide adsorbed to boron-doped diamond and immersed in phosphate buffer at pH 5 is shown for experiments conducted at a range of different scan rates. At a scan rate of 2 mV s^{-1} the reduction peak at -0.20 V vs. SCE can be integrated to give a charge of 33 μC . This corresponds to a surface coverage of 0.34 nmol (area 0.25 cm^2) or, assuming 10 nm diameter particles, an average spacing of 40 nm between individual particles (assuming a density of 5.12 g mol^{-1}). This result is in good agreement with the electron microscopy observation (see Fig. 1).

3.2. Oxidation of hydroxide at nanoparticulate hydrous ferric oxide

Iron oxide is a well-known catalyst for the oxidation of water in alkaline media [1]. This process is used here to explore the reactivity of nanoparticulate hydrous ferric oxide adsorbed onto boron-doped diamond in the otherwise apparently featureless positive potential range. The oxidation of hydroxide anions in aqueous 1.0 M KNO_3 is readily detected as a voltammetric peak at ca. 1.0 V vs. SCE. Fig. 2(B) shows the voltammetric signals for the oxidation of 0.3 mM hydroxide at various scan rates. In the absence of hydrous ferric oxide no oxidation peak is detected. The peak current scales proportional to the square root of the scan rate, which is indicative for a diffusion controlled process. From the peak current and the appropriate Randles–Sevcik ex-

pression [23] (Eq. (2); this equation is valid for $\text{EC}_{\text{solution-type}}$ processes, but may be applied in the limiting case of a diffusion controlled $\text{EC}_{\text{het,irrev}}$ process) the number of electrons transferred per hydroxide anion diffusing to the electrode, n , can be estimated

$$I_p = 0.4956Ac\sqrt{\frac{n^3F^3vD}{RT}} \quad (2)$$

In this equation the current at the peak potential, I_p , is related to the geometric electrode area, A , the bulk concentration, c , Faraday's constant, F , the scan rate, v , the diffusion coefficient, D , the constant for ideal gases, R , and the temperature, T . With the literature value for the diffusion coefficient of hydroxide in 1.0 M KNO_3 , $D = 4.45 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [24], and the geometric electrode area, $A = 2.5 \times 10^{-5} \text{ m}^2$, the number of electrons can be estimated from data in Fig. 2(B) as $n = 0.85$, or ≈ 1 . However, the oxidation of hydroxide should yield the two electron product dioxygen. Bulk electrolysis experiments (see experimental) were conducted to confirm the formation of dioxygen and to rule out the formation of hydrogen peroxide. Therefore, the formation of two equivalents of H_2O per O_2 can be postulated.

Based on the number of electrons consumed per hydroxide anion reacting at the anode, the following reaction scheme consistent with a $\text{C}_{\text{het,rev}}\text{E}_{\text{rev}}\text{C}_{\text{het,irrev}}$ -type process is proposed (Eqs. (3a) and (3b))



Reactive sites on the surface of hydrous ferric oxide are created by deprotonation (Eq. (3a)). In agreement with this process, the point of zero charge of iron oxides is commonly found in the pH range between 7 and 9 [25]. The oxidation (Eq. (3b)) of the nanoparticle surface sites as well as the chemical follow-up reaction step are fast enough to make the diffusion process rate determining. The reactive surface sites may be located at or close to the three phase boundary electrode – hydrous ferric oxide – solution. Attempts to electrochemically identify the oxidation of the iron oxide surface site by increasing the scan rate (up to 20 V s^{-1}) failed. However, the oxidation of Fe(III) at the deprotonated interface is plausible [26]. The formation of oxidised Fe(IV) intermediates during hydroxide oxidation has been postulated for SrFeO_3 catalysed processes [27]. However, unequivocal experimental proof by fast scan voltammetry and/or spectroelectrochemical methods will be required to proof the speculative idea of Fe(III) oxidation. The overall electrochemical process is converting two equivalents of hydroxide into one equivalent of water and half of an equivalent dioxygen.

Although a match of the experimental voltammogram with digitally simulated voltammetric curves can be obtained (see experimental), the high rate of the chemical reaction step rules out the determination of the rate constant from voltammetric data. For the $C_{\text{het, rev}}E_{\text{rev}}C_{\text{het, irrev}}$ reaction scheme (Eqs. (3a) and (3b)) only a lower limit for the rate constant for the irreversible chemical reaction step, $k_c > 1.3 \times 10^{-4} \text{ ms}^{-1}$, can be estimated (Eq. (4))

$$k_c = \sqrt{\frac{vFD}{RT}}. \quad (4)$$

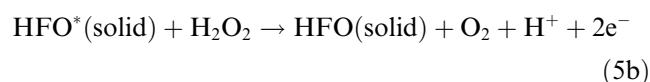
It is possible to further reduce the coverage of hydrous ferric oxide on the surface of the boron-doped diamond electrode by dilution of the sol. Fig. 2(C) shows the effect of a reduced electrocatalyst loading on the voltammetric signal for the oxidation of hydroxide. A tell-tale change in the shape of the voltammogram is indicating that slow electron transfer, probably between boron-doped diamond and the electrocatalyst, is limiting the overall rate in the presence of insufficient amounts of electrocatalyst.

3.3. Interaction of hydrous ferric oxide with hydrogen peroxide

The reaction of hydrogen peroxide with the surface of hydrous ferric oxide is of considerable importance in Fenton-type processes [28], biological processes [29,30], and technical procedures for the clean-up of organic wastes [31]. It is shown here that this process also depends on the presence of hydroxide.

Fig. 2(D) shows the voltammetric responses obtained for the oxidation of 1 mM hydrogen peroxide at a bo-

ron-doped diamond electrode modified with hydrous ferric oxide. Control experiments without electrocatalyst and over the same potential range show no comparable voltammetric peaks. Perhaps surprisingly, in the absence of hydroxide, hydrogen peroxide is not detected. Addition of 0.1 mM KOH (Fig. 2(D(i))) leads to a small oxidation peak at ca. 0.8 V vs. SCE. Addition of more hydroxide causes the signal for hydrogen peroxide oxidation to further increase, and in the presence of excess (2 mM KOH, see Fig. 2(D(iv))) both the hydrogen peroxide oxidation signal and the hydroxide oxidation signal are detected superimposed. Based on these observations, the hydrogen peroxide oxidation process may also be tentatively expressed as $C_{\text{het, rev}}E_{\text{rev}}C_{\text{het, irrev}}$ -type process (Eqs. (5a) and (5b))



However, from the shape of individual voltammograms it can be seen that mechanistic details for this system are more complex. The peak current estimated for the hydrogen peroxide oxidation process in the presence of excess OH^- (Fig. 2(D(iv))) is too low for a two electron process. Also, the voltammetric signal in the potential range between 0.5 and 0.7 V vs. SCE is indicating the formation of $\text{Fe}^{2+}(\text{aq})$ possibly from HFO^* in a chemical reaction with hydrogen peroxide (Fenton process). Further work will be required to resolve the overall mechanism

4. Conclusions

It has been shown that the electrochemical characteristics of nanoparticulate hydrous ferric oxide may be studied when adsorbed onto the surface of a boron-doped diamond electrode. Due to the low background current of boron-doped diamond and the wide accessible potential window, this approach is versatile. The electrocatalytic oxidation of hydroxide on hydrous ferric oxide has been demonstrated and analysed in terms of a $C_{\text{het, rev}}E_{\text{rev}}C_{\text{het, irrev}}$ -type process. Attempts to also identify intermediate reactive surface sites by fast scan voltammetry were unsuccessful, but may in future provide a powerful complementary analytical tool for iron oxide or other types of nanoparticulate solids.

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