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Review

Doped Diamond: A Compact Review on a New, Versatile Electrode Material

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The present paper gives an overview on the current development status of doped-diamond electrodes for electrochemical applications. It starts with a short discussion on the different types of diamond electrodes and their preparation methods. This is followed by a summary of the electrochemical properties of diamond electrodes in different electrolytes. Modification strategies for doped-diamond electrodes are discussed as an important technology to change their electrochemical properties. The second part of the paper deals with practical applications of diamond electrodes from water treatment to inorganic and organic electrosynthesis, electroanalysis and electrochemical energy technology to biotechnology.

Keywords: Diamond electrodes, boron-doped diamond

1. INTRODUCTION

The last great change in the area of technical electrode materials in industrial electrochemistry was the introduction of so-called dimensionally stable anodes (DSA®) in the 1960s and 1970s [1, 2]. Originally developed for use in chlor-alkali electrolysis they have now found widespread applications in many other areas such as oxygen evolution, cathodic corrosion protection, metal finishing industry among others. They lead to spectacular advancements in these industries.

With the current introduction of doped diamond electrodes we are witnesses of a similar technological leap. Therefore, it is no surprise that in the last years several review articles [3-10] and a book [11] on diamond electrodes have been published. However, these review articles generally feature only one or a few limited application areas of diamond electrodes (general electrochemical properties: [3, 10], water treatment: [4, 7, 8, 10], electrosynthesis: [4, 7, 8, 10], photoelectrochemistry

[3, 5], electroanalytical applications: [6, 9]). Therefore, this paper gives a short, up-to-date and compact review covering nearly all aspects of diamond electrodes.

2. TYPES OF CONDUCTING DIAMOND MATERIALS AND THEIR PREPARATION

Because of its large bandgap of more than 5 eV undoped diamond is normally electrically insulating and cannot be used as an electrode material. But as other large band-gap materials diamond can be made conducting by doping it with certain elements. Currently, in most cases boron is used as dopant. A p-semiconductor results. If phosphorus [12] or nitrogen are used as dopant a n-semiconductor is produced.

Two major methods for the production of doped diamond materials have been developed: chemical vapor deposition (CVD) of thin film doped-diamond and high pressure, high temperature HPHT doped-diamond particle production. Other methods reported for the production of conducting diamond electrodes are vacuum annealing of undoped diamond and so-called surface transfer doping of undoped diamond.

2.1 Thin film CVD doped diamond

Similar to DSA® or platinized electrodes for thin film diamond electrodes the doped diamond film is deposited on a conducting substrate [4, 13]. The deposition technique is plasma-assisted CVD. The plasma necessary for the deposition is activated either by hot filaments [4, 13, 14] or by microwave radiation [15]. In both cases the gas phase (about 10 to 50 mbar) typically consists of hydrogen as the carrier gas, methane (0.5% - 3% CH_4 in H_2) or acetone/methane mixture [15] as carbon source and other gases which provide the dopants [4, 13, 14, 15]. By use of either microwave or thermally by hot filaments (temperature of filaments: about 2200 - 2800°C) the gas phase is activated to form a plasma. For the coating of larger substrates currently only the hot filament process can be used. In this case multiple filaments are applied.

Before diamond coating the substrate has to be pretreated properly [4, 13]. One important pretreatment step is activation of the surface with nanoscale diamond particles [13]. These tiny diamond crystallites are the nucleation sites for the growth of the thin diamond film during CVD process. The surface activation (seeding pretreatment) can e.g. be performed by substrate polishing with diamond powder or by immersing the substrate into a suspension of nanoscale diamond particles accompanied by ultrasonication.

Substrate temperature during diamond film production is about 750 to 825°C. Typical growth rates are between 0.2 and 3 μm/h [4]. The thickness of diamond thin films is usually between 1 and 10 μm but other thicknesses are possible. The diamond thin films have a nanocrystalline or microcrystalline structure and a rough surface.

Substrates for doped diamond film deposition are usually either silicon (both single-crystalline and polycrystalline) or self-passivating metals such as titanium, tantalum, tungsten, molybdenum and niobium. Niobium seems to be the best suited of the metal substrate materials because it can withstand the deposition conditions (high temperature with hydrogen containing atmosphere) with the least changes in material structure.

The use of silicon as a substrate leads to more perfect, pore-free films. But for many practical applications the brittleness of silicon is prohibitive. In this case doped-diamond films on metal substrates are used. Another advantage of the use of metal substrates is the possibility to produce large area electrodes up to the square meter range. This is not possible with silicon substrates because they are not available in this size. However, large area diamond electrodes based on silicon substrates can be produced by a mosaic-like arrangement of diamond-coated silicon wafers on a metal substrate with subsequent passivation of the metal portions not protected by the silicon/doped diamond pieces [16].

Doped diamond films can be deposited directly onto silicon without any interlayer [7]. If the doped diamond films shall be deposited onto self-passivating metal substrates often interlayers (e.g. the corresponding metal carbide) are applied to enhance the adhesion of the diamond film at the substrate and to protect the substrate against hydrogen in the deposition gas mixture (danger of hydrogen embrittlement of the substrate) [7].

Other substrate materials for deposition of doped diamond are carbon materials such as graphite [7, 17], glassy carbon [7] or carbon fibre materials. CVD thin film diamond electrodes can be modified in multitude of ways to change their properties. This will be discussed in paragraph 3.4.

Free-standing doped-diamond films can be produced by deposition of relatively thick conductive diamond films on silicon or other substrates and subsequent removal of the substrate e.g. by chemical etching (see also paragraph 4.5.). The production of single-crystalline doped-diamond by CVD is also possible. For this purpose natural nonconducting diamond single crystals have been used as a substrate for CVD thin film deposition [18, 19].

2.2. HPHT doped diamond

A second type of diamond electrodes which seems to become more important is a diamond particle electrode. Diamond particle electrodes are produced by immobilisation of conducting diamond particles into a substrate [20-22]. For this purpose boron-doped HPHT (= high pressure, high temperature) – diamond particles with a particle size between about 100 and 200 μm are used. If the diamond particles are embedded into a conducting metal substrate [20, 21] the space between the single diamond particles has to be protected by some kind of non-conducting passivation layer. Inorganic materials or perfluorinated organic compounds are necessary. Such electrodes can be used such as usual thin film diamond electrodes on conducting substrates. However, it is also possible to immobilise the diamond particles into non-conducting substrates [22]. In this case the substrates should be very thin and the diamond particles have to face both surfaces of the substrate. This can be realised e.g. by fixing doped diamond particles in a thin PVDF film. In this case the diamond particle electrode can only be used as a bipolar electrode. The different types of diamond electrode materials currently in use are shown in figure 1.

The majority of doped-diamond electrodes currently in use are thin film boron-doped diamond electrodes.

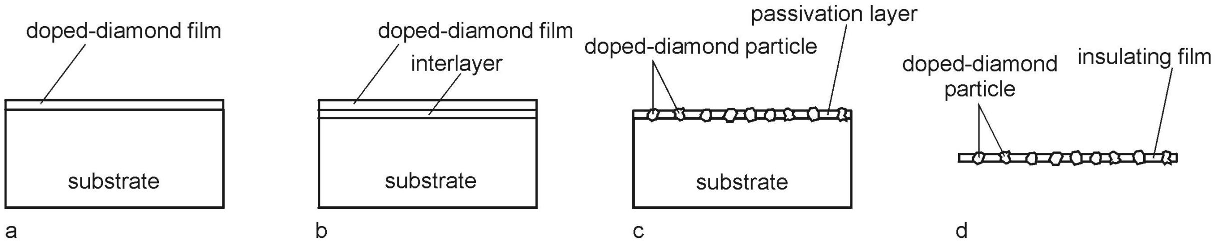

Figure 1. Schematic drawing of the different types of diamond electrodes currently in use: a) doped-diamond thin film electrode without interlayer between substrate and diamond film, b) doped-diamond thin film electrode with interlayer between substrate and diamond film, c) doped-diamond particle electrode, particles immobilised in conducting substrate with passivated surface, d) doped-diamond particle electrode, particles immobilised in an insulating film

2.3. Vacuum annealed undoped diamond

Recently, it has been reported that thin undoped diamond films prepared by microwave-assisted CVD can be made conducting by annealing them in vacuum at temperatures exceeding 1,550 ^{o}C [23, 24]. This result has been explained by the formation of a nondiamond carbon phase under these severe conditions. This conducting carbon phase is formed along the intercrystalline boundaries leading to a conducting network in the diamond film [23, 24]. In addition, structural defects in the bulk of diamond crystallites also provide some increased conductivity. The conducting phase is outcropping at the diamond film surface as an array of microelectrodes [23]. The practical usefulness of this approach to produce diamond electrodes remains questionable.

2.4. Surface transfer doping of undoped diamond

In the late 1980s a comparatively high surface conductivity on undoped hydrogenated diamond has been found by Ravi and Landstrass [25]. This phenomenon has been explained by a process called surface transfer doping [26-29]. Hydrogen termination of the diamond surface (see also paragraph 3.4.) leads to a reduced ionization potential and turns the diamond's electron affinity negative [28]. Therefore, undoped hydrogenated diamond can be doped by physisorbed surface adsorbates [28].

According to this electrochemical surface transfer doping model, solvated ions in a thin, aqueous, atmospheric layer can extract electrons from intrinsic diamond leaving behind holes as mobile charge carriers and thus causing a substantial surface conductivity with p-type conductivity [28].

Diamond electrodes making use of the surface transfer doping effect have been named surface conductive diamond (SCD) material [30]. The long term stability of the surface transfer doping effect is very limited because its depends on a hydrogen-terminated surface which is easily changed to an oxygen terminated surface during electrochemical processes which leads to degradation in electrical properties [30].

3. PROPERTIES

3.1. General properties of diamond

Diamond is well known for its unusual material properties such as the high hardness (1×10^4 kg mm $^{-2}$), high thermal conductivity (2600 W m^{-1} K^{-1}) and high charge carrier mobilities (electron mobility: 2200 $cm^2\ V^{-1}\ s^{-1}$, hole mobility: 1600 $cm^2\ V^{-1}\ s^{-1}$). With a bandgap of 5.45 eV undoped diamond is an excellent electrical insulator with resistivities in the order of 10^{20} Ω cm.

3.2. Properties of doped diamond electrodes

3.2.1. Dopants for diamond electrodes and their electrical properties

Boron is by far the most widely used dopant to produce conducting diamond electrodes [7]. This is because of boron has a low charge carrier activation energy of 0.37 eV [7]. Boron doping leads to a p-type semiconductor. At low doping levels, the diamond acts as an extrinsic semiconductor. At high doping levels the material acts as a semimetal. To introduce boron into the diamond material during film growth a boron containing substance has to be added to the deposition gas mixture. Substances such as diborane or trimethyl borane can be used. The majority of studies with doped-diamond electrodes uses boron-doped diamond.

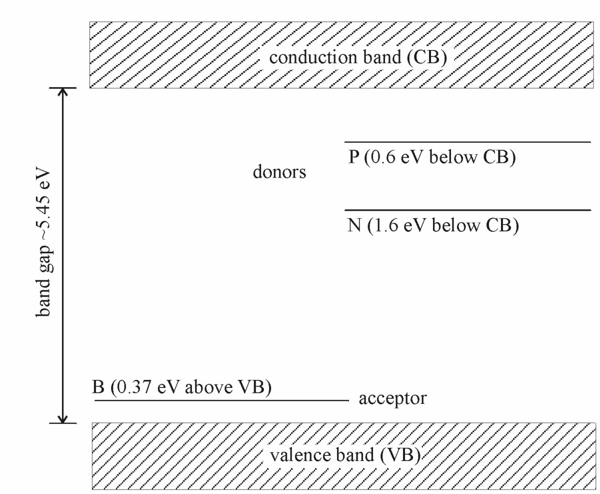

Figure 2. Energy diagram of selected states in the band gap of diamond (one dimensional representation)

But other dopants are also possible. They provide n-type conductivity: nitrogen (charge carrier activation energy 1.6 –1.7 eV) [7, 31, 32], phosphorus (charge carrier activation energy 0.6 eV) [12, 32] and sulfur [32, 33]. Also co-doped diamond thin film electrodes have been produced, such as nitrogen-boron [7] or boron-sulfur co-doped [32, 33] electrodes.

Sulfur can only be introduced as a dopant into diamond in the presence of boron [32, 33]. At low boron concentrations a n-type semiconductor results [32, 33]. It has also been suggested that heavily boron doped CVD diamond can switch its conductivity from p-type to n-type after deuterium plasma treatment [12]. The alternative dopants are introduced into the CVD diamond films by adding an appropriate gas to the deposition atmosphere. This is ammonia [7] or N_2 [31] in case of nitrogen doping , PH_3 for phosphorus [12] and H_2S for sulfur doping [32, 33]. Figure 2 shows an energy diagram of diamond with some selected states in the band gap.

The conductivity of doped diamond electrodes depends on the doping level. For boron-doped diamond electrodes with resistivities between 5 and 100 mΩ cm are usually produced [7, 13]. Typical and useful boron concentrations in diamond are between 500 ppm to about 10,000 ppm [7] or 10^{19} – 10^{21} atoms cm^{-3} [13]. Interestingly, boron-doped diamond has also been found to be superconducting at very low temperatures [34] with T_c depending on doping level.

3.2.2. Electrochemical properties in aqueous electrolytes

Doped-diamond has been introduced into electrochemistry by Pleskov et al. [35]. Since then, mainly the electrochemical behavior of diamond electrodes in aqueous electrolytes has been investigated. The most striking feature here is their very high overpotential for both oxygen and hydrogen evolution [3, 4, 8, 10, 13, 36-39]. Figure 3 shows cyclic voltammograms of a platinum and a diamond electrode in 0.2 M H_2SO_4 in the region between hydrogen and oxygen evolution. The much higher overpotential of diamond electrode for both reactions is obvious. This leads to a wide potential window (approx. 3.5 V) which can be used for other electrochemical reactions in aqueous electrolytes. Diamond electrodes have indeed the largest potential window so far measured in aqueous electrolytes . This makes them also totally different to common electrode materials such as gold, platinum or mixed metal oxide DSA® type electrodes.

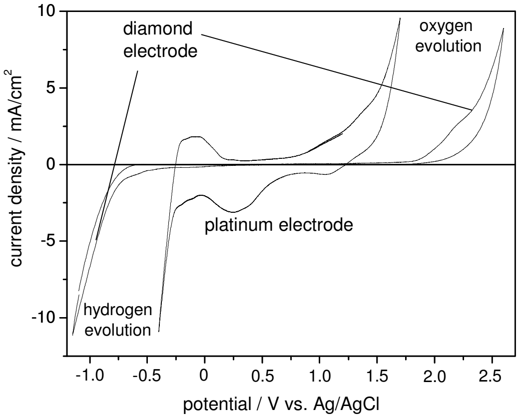

Figure 3. Cyclic voltammogram of a platinum and a diamond electrode (Diachem® from Condias) in 0.2 M H_2SO_4, v=100 mV/sec

Diamond electrodes are also distinguished from these conventional electrode materials by their very low capacitance and by the absence of surface oxide formation and reduction reactions which are found at conventional metal or metal oxide electrode materials between oxygen and hydogen evolution (see also figure 3). The electrochemical properties of diamond electrodes depend to some extent on doping level, on surface termination and nondiamond carbon content (see paragraph 3.4.1.).

High overpotentials on diamond electrodes are also found for halide (I^-, Br^-, Cl^-) oxidation [3, 40] and for the reduction of the corresponding halogens (I_2, Br_2, Cl_2) [40] as well as for oxyen reduction. In general, electrochemical reactions which require adsorption of reaction intermediates have a high overvoltage on diamond electrodes. Figure 4 and 5 display cyclic voltammograms of diamond electrode in comparsion with platinum for the redox couples I^-/I_2 and Br^-/Br_2 showing the much higher overpotential on diamond elctrodes for these reactions.

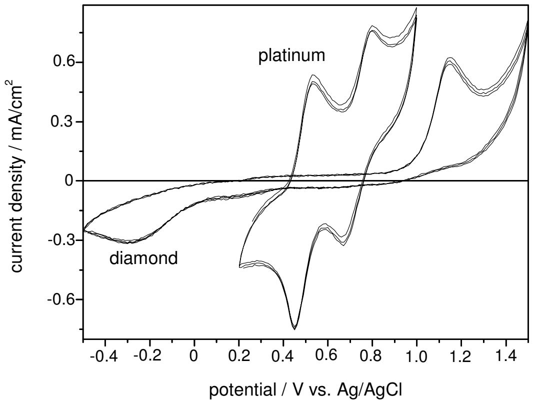

Figure 4. Cyclic voltammogram of a platinum and a diamond electrode (Diachem® from Condias) in 5 x 10^{-3} M KI + 1 M KCl, v=100 mV/sec

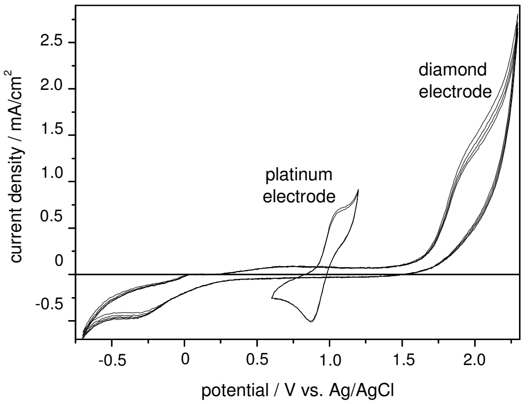

Figure 5. Cyclic voltammogram of a platinum and a diamond electrode (Diachem® from Condias) in 5 x 10^{-3} M TEAB + 1 M $NaClO_4$, v=100 mV/sec

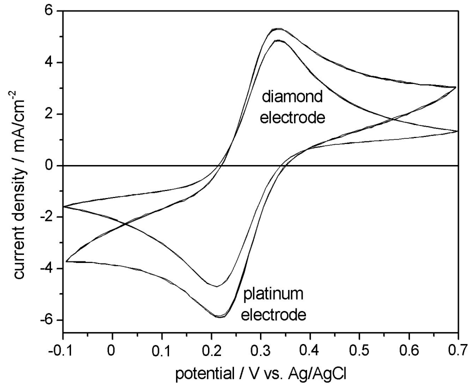

Figure 6. Cyclic voltammogram of a platinum and a diamond electrode (Diachem® from Condias) in 10^{-2} M $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$ + 1 M KCl, v=100 mV/sec

The high overpotential for oxygen evolution gives rise for the possibility for a very effective anodic OH· radical production in aqueous electrolytes [41-44] according to

$$H_2O \rightarrow OH\cdot + e^- + H^+ \qquad (1)$$

These OH· radicals can e.g. be used for water and wastewater treatment (see paragraph 4.1.).

A totally different electrochemical behavior can be found in the case of simple outersphere, one-electron transfer processes in which no adsorbed intermediates are involved. They can proceed more or less quasireversible on diamond electrodes [3, 19, 40]. This could e.g. be shown for $Fe(CN)_6^{3-/4-}$ [3, 6, 21, 31, 45-52], $Ru(NH_3)_6^{2+/3+}$ [3, 6, 17, 30, 31, 40, 46, 48, 50], $IrCl_6^{2-/3-}$ [31, 46], $Fe^{2+/3+}$ [46, 50], $Ce^{3+/4+}$ [53, 54] and $Eu^{2+/3+}$ [55] among others. Figure 6 displays cyclic voltammograms of a platinum and diamond electrode with the redox couple $Fe(CN)_6^{3-/4-}$, showing that the electrochemical behavior of both electrode materials is comparable in this case, although platinum is more reversible. Doping level and pretreatment of the diamond electrode have a considerable influence on the kinetics of charge transfer reactions of this material. Therefore, a more irreversible behavior of diamond electrodes especially at low doping levels and with oxygen terminated surface is possible [49, 52].

3.2.3. Photoelectrochemistry

Doped-diamond electrodes display also interesting photoelectrochemical properties [56-58]. Since diamond has a very wide bandgap, visible and long-wavelength ultraviolet (UV) radiation should not be able to excite electrons from the valence into conduction band. Nevertheless, some studies show significant photocurrents even with subbandgap illumination [35, 56], presumably due to impurity or surface states within the bandgap. Fujishima and coworkers [57] could show that on high-quality diamond electrodes with very low nondiamond carbon content only irradiation with suprabandgap illumination is able to excite electrons into the conduction band. They studied the photoelectrochemical behavior of boron-doped diamond electrodes 0.1 M KH_2PO_4 solution with excimer lasers of 3 different wavelengths: ArF (193 nm, 6.4 eV), KrF (248 nm, 5.0 eV), and XeF (351 nm, 3.53 eV). The photocurrent observed using the ArF laser was much greater than those observed with the KrF and XeF lasers. In addition, the photoelecrochemical properties of semiconducting diamond were found to be highly sensitive to the surface conditions [58] (see paragraph 3.4.1.).

3.2.3. Electrochemistry in nonaqueous electrolytes

The majority of electrochemical investigations with diamond electrodes has so far been performed in aqueous electrolytes. Only a few studies are concerned with the behaviour of diamond electrodes in nonaqueous electrolytes.

One group of non-aqueous electrolytes are liquid organic electrolytes. From this group reports on the electrochemistry of diamond electrodes in propylene carbonate [59, 60], acetonitrile [60, 61], γ-butyrolactone, *N*,*N*-dimethylformamide and diethyl carbonate – propylene carbonate mixtures [60] are available. Some investigations on the electrosynthesis of organic compounds with diamond electrodes have been performed in methanol [62-65] (see paragraph 4.3.). Generally, it has been found that boron-doped diamond film electrodes exhibited in non-aqueous organic electrolytes a 1.5–2.5 times wider potential window (approx. 5.0–7.5 V) than in aqueous electrolytes. But glassy carbon or graphite electrodes exhibited almost the same potential windows as that for diamond in the same organic electrolytes. This is contrary to the behaviour in aqueous electrolytes there diamond electrodes have a much wider potential window than all other electrode materials including graphite.

First results [66] indicate that diamond electrodes are probably an insoluble anode material for electrochemical processes in molten salt systems. They could replace commonly used graphite electrodes that are consumed during use in such electrolytes. This could be shown by electrolysis in a LiCl-KCl melt containing Li_2O [66]. But further investigations are necessary.

Electrochemistry of diamond electrodes in solvent-free solid polymer electrolyte [67, 68] and in liquid ammonia at temperatures between -70 to -35°C [69] has also been investigated.

3.3. Stability of diamond electrodes

The high chemical and electrochemical stability of diamond electrodes has been taken for granted for some years. Especially the high electrochemical stability under severe conditions has been emphasized [3, 4, 8, 10, 13, 38, 70, 71]. It has been considered as one of the major advantages of doped-diamond electrodes compared to conventional electrode materials. However, in the last years in some investigations it has been shown that diamond electrodes are etched electrochemically under certain experimental conditions [37, 72-74].

Until today, investigations on the anodic corrosion of doped-diamond were only performed in acidic aqueous electrolytes [37, 72-74]. Panizza et al. [72] did not found any loss of diamond material of diamond anodes during electrolysis 1M H_2SO_4 (1 A/cm^2, 40^{o}C). But if the electrolysis experiments were performed in 1M H_2SO_4 + 3M acetic acid a strong decrease of surface roughness has been measured.

But more detailed investigations with diamond thin film electrodes on silicon substrates by Katsuki et al. [37] and Comninelllis [73] did show that in sulfuric acid electrolytes corrosion rates of 0.4 µg [37] or 0.3 µg diamond per Ah [73] can be measured. Comninelllis [73] did also show that the corrosion rate strongly depends on electrolyte composition. If organic compounds are added to electrolytes such as 1M sulfuric acid or 1M perchloric acid corrosion rates are dramatically increasing: up to 12 µg diamond per Ah in 1M H_2SO_4 + 3M acetic acid (at 1 A/cm^2, 40^{o}C).

Schäfer et a. [74] reported that during electrolysis with thin film diamond anodes on niobium substrates (at 4 A/cm^2, 70^{o}C) in 1.3 M H_2SO_4 corrosion rates of about 0.4 µg/Ah cm^{-2} are reached. In this long-term electrolysis experiment in certain time intervals 1 g/L organic material has been added to the electrolyte (5 times). This organic material was destroyed during the electrolysis (see paragraph 4.1.1.). Therefore, in this experiment only part of the electrolysis time organic material was present in the acidic electrolyte. The corrosion rate measured by Schäfer et al. equals a loss of diamond film thickness of about 1 µm diamond per 900 Ah/cm^2. This means, that under these conditions and a current density of 200 mA/cm^2 an electrode lifetime (diamond film thickness of 1 µm) of 0.5 years can be expected. Lowering the current density to only 20 mA/cm^2 would give an electrode lifetime of roughly 5 years for a 1 µm thick electrode.

These corrosion rates of the diamond layer during anodic polarization are comparable to corrosion rates which are usually found with platinized or mixed metal oxide coated titanium electrodes [73]. By applying thicker diamond films (10 µm are possible) also with high current densities acceptable electrode lifetimes are possible.

However, certain electrolyte compositions lead to increased corrosion rates. The corrosion rate of 12 µg diamond per Ah (in 1M H_2SO_4 + 3M acetic acid at 1 A/cm^2, 40^{o}C) reported by Comninellis [73] would result in an electrode lifetime of 6 days at 200 mA/cm^2 or 6 months at 20 mA/cm^2 (thickness of the diamond film: 1 µm). In this case even a 10-fold increase of diamond film thickness would only allow to work with low current densities to reach acceptable service life.

Besides electrochemical etching also the detachment of diamond material from the substrate can be problematic. The mechanisms that can cause diamond film detachment are complex [75]. In addition to the nondiamond carbon content, also cracks and pores, the initial diamond nucleus density, the diamond film thickness, interlayer thickness, the nature of the substrate and the bonding between the substrate and the diamond film may affect electrode stability [75]. All these factors are associated with production conditions. Therefore, a proper selection and careful control of preparation conditions is very important in order to obtain long-term stable doped diamond thin film electrodes.

3.4. Modification of diamond electrodes

Doped-diamond electrodes can be modified in multitude of ways to adapt their properties to different uses. The most frequently used modifications are described in the following paragraphs.

3.4.1. Surface modification by anodic and cathodic treatment in aqueous electrolytes

As-produced diamond thin film electrodes possess a hydrogen terminated surface [3, 7, 18]. This is due to the hydrogen containing atmosphere during the production process [3, 7]. The unpolar hydrogen-terminated surface gives the electrodes a hydrophobic nature [3, 7, 18, 36]. The flatband potential of semiconducting diamond was found to be nearly independent on pH for electrodes with a hydrogen terminated surface [58]. Hydrogen-termination is stable on air at least for months [3] although a gradual replacement of hydrogen by oxygen from air has been reported [76].

Hydrogen-terminated surface is changed to an oxygen terminated during anodic oxidation (e.g. oxygen evolution) in aqueous electrolytes [7, 18, 37, 70, 77-79]. Oxygen-terminated diamond surface shows hydrophilic tendency [18, 37]. Anodic treatment of diamond photoelectrodes results also in a positive shift in both the photocurrent onset potential and the flatband potential indicating the displacement of the bandedges [58]. The flatband potential at the oxidized diamond shows a marked pH dependence [58]. An oxygen terminated surface can be changed back to a hydrogen terminated one by cathodic treatment in acidic aqueous electrolytes [76].

As-produced thin film diamond electrodes usually possess some non-diamond sp^2-carbon impurities [18, 42, 50, 78]. These impurities can be destroyed by anodic oxidation in aqueous electrolytes [39, 42, 78]. In cyclic voltammogramms they give rise to an anodic current wave starting before the oxygen evolution at diamond electrodes [4, 18, 50]. The height of this current peak is diminishing with subsequent scans and is almost absent from the third potential scan [4, 18, 42]. In general, the higher the sp^2-nondiamond carbon content the lower is the potential window between hydrogen and oxygen evolution in aqueous electrolytes [50, 78].

3.4.2. Surface modification by plasma treatment

Another possibility of surface modification of doped diamond electrodes is plasma treatment in different atmospheres:

Hydrogen plasma treatment of doped-diamond electrodes lead to a hydrogen-terminated surface [58] whereas short oxygen plasma treatment leads to oxygen-containing functional groups on the diamond electrode surface [77, 79]. Longer treatment of diamond electrodes in an oxygen plasma leads to a plasma etching of the diamond material [80]. This has been utilized to produce a nanostructured diamond honeycomb film by use of a porous alumina mask [80].

Fluorination of diamond electrode surface has been performed in a rf-plasma reactor with CF_4-He-atmosphere at 8 µbar for 5 min [80]. After this treatment a fluorine terminated diamond surface with extraordinary hydrophobic properties resulted. This led to a further increase of the hydrogen evolution overvoltage by more than 1 V and consequently to a wider potential window in aqueous electrolytes [81, 82]. Potential windows of more than 5 V have been reported [82]. It has been suggested that fluorinated diamond electrodes could be expected to be excellent cathodes for reactions requiring very negative potentials, such as deposition of some metals or nitrate reduction [81].

Ammonia plasma treatment of hydrogen terminated diamond electrodes resulted in doped-diamond with surface terminal amino groups [84]. This amin-termination of the diamond surface could be interesting for the immobilisation of biomolecules such as DNA molecules for biotechnological applications (see paragraph 4.7.).

3.4.3. Surface modification by chemical reactions

Chemical and electrochemical surface modifications of doped diamond electrodes with several organic substances have also been performed. For this purpose the benefit of the carbon chemistry for the design of chemically modified surfaces can be used [84].

Examples are the surface grafting of pyrenebutyric acid by esterification [84], 2,4-dinitrophenylhydrazine [85], 3-aminopropyltriethoxysilane [85] or quinone [86] modification and the covalently bonded 4-nitrophenyl groups on single-crystalline diamond via electrochemical reduction of 4-nitrobenzene diazonium tetrafluoroborate in acetonitrile solution [87]. The modification by 3-aminopropyltriethoxysilane is particularly important for possible applications, because the terminal amino group can be used to form a covalent bond with functional molecules such as DNA, enzymes, and immuno-compounds, and highly selective, highly sensitive electrode systems can be created [85].

3.4.4. Structuring of diamond film electrodes

For electroanalytical applications (see paragraph 4.4.) arrays of microelectrodes are often advantageous. Consequently, diamond microelectrodes arrays have been fabricated using photolithography to selectively deposit or etch thin films of doped diamond on a silicon substrate [88, 89].

Diamond film electrodes with highly ordered nanometer-scale cylindrical pores (so-called nano-honeycombs') have also been produced [80, 90] for the purpose to increase the diamond electrode surface area.

3.4.5. Deposition of nanosized metal or metal oxide clusters

Thin film diamond electrodes are also used as an inert and chemically and electrochemically stable substrate for the deposition of metal or metal oxide clusters with the aim to utilize the much higher catalytic activity of very small particles (nanoparticles) compared to the conventional bulk material [91]. For some applications these nanoparticles have to be immobilised on a conducting substrate. And this substrate has be not electrochemically active at potentials at which the corresponding electrochemical processes proceed. Because of its unique electrochemical properties in aqueous electrolytes such as the large potential window and low capacitive background currents doped-diamond is especially well suited to serve as such a substrate.

Examples for nanoparticles deposited on a doped diamond substrate are IrO_2 [91, 92], RuO_2 [93], gold [91], platinum [91, 94], platinum/ruthenium [91], platinum/tin [95], copper [96] or cobalt [97]. Iridium oxide and platinum nanoparticles can be deposited onto doped-diamond by thermal decomposition of corresponding precursor solutions (e.g. H_2IrCl_6 or H_2PtCl_6 in isopropanol at 350^oC) [91, 92]. Goal of the modification of doped-diamond with IrO_2 or Pt nanoparticles is to produce electrodes with the well known properties of iridium oxide or platinum electrodes by using only very low amounts of these precious metals. It could be shown that this is possible. However, long term stability is not sufficient at the current state of development.

Another example for the advantage of the use of nanoparticle modified diamond electrodes will be explained for the case of gold modified doped-diamond [91]: Gold is often used as an electrode material for the reduction of dissolved oxygen in water for the amperometric determination of oxygen concentration. If a diamond electrode modified with gold nanoparticles is used instead of a macroscopic gold electrode an anodic shift of the reduction peak and a 4-fold increase in peak current have been measured [91]. Such an electrode would be very advantageous compared to a conventional gold electrode. Unmodified diamond electrodes have a very large overvoltage for oxygen reduction.

3.4.6. Deposition of thin films

Modification of diamond electrodes has also been performed by the deposition of thin films. This concerned mainly metal oxide films such as SnO_2 [98], cobalt oxide [99], nanocrystalline ZnO [100] and TiO_2 films [101]. Cobalt oxide has a good catalytical activity for oxygen evolution and reduction [99]. Cobalt oxide electrodeposited on doped diamond substrates resulted in electrodes with stable and high electrocatalytic performance for oxygen evolution. The deposition of very thin films is possible.

Another material which has been deposited as a thin film on diamond electrodes is cellulose [102]. This has been performed by anodic electrodeposition from alkaline aqueous solution. Electrodeposited cellulose and cellulose composite films may be of interest in sensor development and for the protection of sensor electrodes against interferences [102].

3.4.7. Ion implantation

Another possibility for modification of doped-diamond is metal ion implantation [103-105]. Conducting diamond thin films were implanted with 750 keV Ni^{2+} and Cu^{2+} ions (dose: 5×10^{14} cm^{-2}) [103], 750 keV Pt^{2+}-ions (dose: 5×10^{14} cm^{-2}) [104] or 800 keV Ir^{+}-ions (dose: 10^{15} cm^{-2}) [105]. It is reported that ion-implanted diamond electrodes are useful especially for electroanalytical applications (see parargraph 4.4.). Nickel and copper implanted diamond electrodes were tested for the amperometric determination of glucose [103], whereas platinum implanted electrodes were used for hydrogen peroxide analysis [104] and iridium implanted electrodes for As(III) determination [105].

4. USE OF DIAMOND ELECTRODES

Because of their unique electrochemical properties doped diamond electrodes can be used for a multitude of applications. Since their properties largely differ from that of conventional electrode materials in most cases they will not replace these materials but will make electrochemical processes possible that were not before.

4.1. Water treatment

Currently, water treatment is the most intensively investigated diamond electrode application area. The high overvoltage for oxygen evolution and the possibility to anodically produce hydroxyl radicals with high current efficiency (see paragraph 3.2.2.) makes diamond electrodes especially interesting for the destruction of organic pollutants in water. No modification (see paragraph 3.4.) of diamond electrodes is necessary for this purpose.

4.1.1. Destruction of organic pollutants in water

Because of their high redox potential of 2.8 V_{NHE} OH· radicals are a very strong oxidizing agent. This is used in group of water treatment processes called advanced oxidation processes or AOP [106]. They are used for the destruction of organic contaminants in water. The Fenton process (addition of H_2O_2 to Fe^{2+} in water), photocatalytic oxidation using TiO_2 and UV radiation, the combination of ozone and hydrogen peroxide and photolysis of H_2O_2 with UV radiation are all AOP's [106].

The electrochemical production of $OH^{\cdot}$ radicals directly from polluted water is an alternative AOP process which is sometimes called electrochemical advanced oxidation process or EAOP [4, 13, 107-109]. With this process it is also possible to completely mineralize organic compounds dissolved in water to CO_2 and water [4, 8, 10, 13, 107-167]. Current efficiencies approaching 100 % are found as long as mass transfer of the organic compound to the diamond electrode surface is not the rate determining step. This means, for a high current efficiency always enough molecules of organic substances have to be in the vicinity of the diamond anode surface so that all electrogenerated hydroxyl radicals can react with them. Otherwise hydroxyl radicals could combine to form hydrogen peroxide which would decay to water and oxygen. This side process would lower the current efficiency for the destruction of organic compounds.

To guarantee mineralization of organic compounds a sufficiently high anodic potential at which hydroxyl radicals are formed has to be applied. If lower potentials are used, reactions involving simple electron transfer can occur. Polymeric materials, which lead to electrode fouling, can also be formed in this potential region. Some organic substances but not all give fouling films under such conditions. Comparison of electrochemical oxidation of methanol and benzyl alcohol on diamond electrodes at relatively low potentials showed that methanol gave no fouling whereas benzyl alcohol did [168]. Electrolysis at potentials at which hydroxyl radicals are produced quickly remove fouling films.

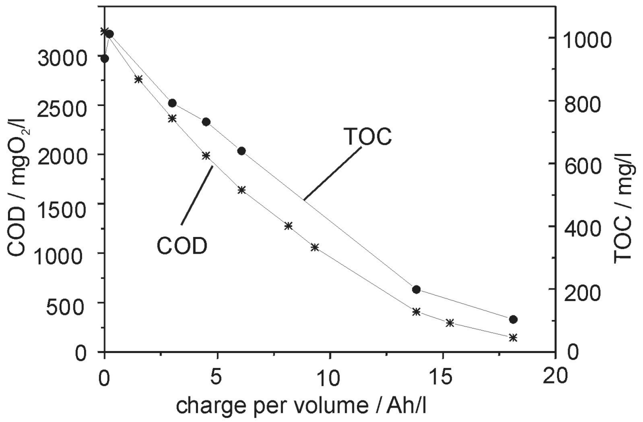

Figure 7. COD and TOC removal from an aqueous solution of benzyl alcohol (initial concentration 1.5 g/l) during constant current electrolysis with diamond electrodes, volume 100 l, current 150 A, diamond anode area 0.5 m^2

In the last years a multitude experimental results have been published in which the application of anodic oxidation of organic substances in water with diamond anodes have been investigated [4, 8, 10, 13, 107-167]. This concerned both the treatment of real waste waters [128, 138, 145, 163] as well as treatment of model substances. In table 1 some of the model substances which have been treated so far are listed.

In each test it could be shown that organic compounds dissolved in water can be completely mineralized to CO_2 and water with current efficiencies approaching 100 % in the absence of mass transfer limitations independent on doping level of the diamond electrode, on the current density, on the temperature and on the waste water used be it an artifically produced one or a real wastewater. The most popular test substances were carboxylic acids, phenol and dyes. Figure 7 shows an example for the anodic destruction of benzyl alcohol in water. In this test 100 l sample volume was treated with a diamond anode area of 0.5 m^2. This is the largest test this has been reported so far [7].

100 % current efficiency equals a COD removal rate of 298.5 mg O_2/ Ah. COD (chemical oxygen demand) and TOC (total organic carbon) are sum parameters in water treatment chemistry. COD equals the amount of oxygen which is necessary to oxidize all substances in a contaminated water. Even dissolved polymers (polyacrylates) could successfully be destroyed in aqueous solution [121].

Table 1: Examples for organic substances treated by anodic oxidation with diamond anodes in aqueous solution

Pollutant	References
carboxylic acids	4, 13, 101, 102, 104, 106, 117, 120, 125, 134, 136, 156
EDTA	99, 101, 102, 118, 120, 147
phenol(s)	4, 107, 110, 111, 119, 120, 123, 129, 133, 137, 146, 148
chlorophenols	115, 116, 130, 131
nitrophenols	142, 147
hydroquinone	110, 146, 152
alcohols	111, 112, 113, 145, 153
amines	128
water soluble polymers	121
aromatic sulphonated acids	156
dyes	125, 128, 138, 141, 148, 158, 159, 161, 162
lubricants	127
surfactants	132, 149
herbicides	151, 154
biocides	140
drugs and their metabolites	150, 157, 161

If organic compounds in water with very low conductivity shall be destroyed a combination of the solid polymer electrolyte technology with perforated diamond anodes is necessary [153, 167].

Problems with anodic oxidation of organic pollutants can arise if they are not dissolved in water but present as a oil-water emulsion or in similar form. This has been shown for the case of water contaminated by lubricants [127]. Here insufficient contact of between oil droplets and the oxidizing species formed at the electrode in the aqueous phase resulted in very low COD removal rates [127].

In some cases unwanted by-products can be formed. The oxidation of amines by electrogenerated $OH^{\cdot}$ radical results in the formation of nitrite and nitrate parallel to COD removal. This has been shown for treatment of triethanolamine dissolved in water [128]. During electrochemical COD removal first ammonium and nitrite are formed. In the later part of the oxidation process the concentration of ammonium and nitrite are decreasing whereas the nitrate concentration increases. This is due to the fact that first the carbon atoms of triethanolamine are oxidized by hydroxyl radicals leaving behind ammonium ions. Subsequently they are oxidized to form nitrite and later the end product nitrate [128].

Another example is anodic oxidation of organic substances in water in the presence of chloride ions [128]. COD removal can be achieved with high current efficiency. But with chloride ions present in the electrolyzed solution, AOX (a sum parameter for chlorinated organic compounds) is formed during the initial stages of COD removal. This can be seen in a decrease of chloride concentration and a rise in the AOX level [128]. However, eventually the chlorinated organic compounds are also destroyed by electrogenerated hydroxyl radicals. Thus, in the end range of the COD destruction, the AOX value is also lowered. But the chloride ion concentration was decreased during the whole electrolysis process leaving behind a very low end concentration. This could only be explained by the formation of chlorine-oxygen compounds such as chlorate and perchlorate [128]. Thus, unwanted by-products can be formed during anodic oxidation of organic waste compounds in water. This together with economical considerations [128] has seriously taken into account when designing electrochemical waste treatment processes with diamond anodes.

4.1.2. Destruction of inorganic pollutants in water

Electrochemical processes with diamond electrodes can also be useful for the treatment of water contaminated with inorganic pollutants such as nitrate [128, 170-172], nitrite [128, 171] or cyanide [107, 111, 173].

In the case of nitrite and nitrate removal from aqueous solutions cathodic reactions with diamond electrodes are employed. Depending on the pH of the solution different products are formed during the reduction of nitrate. This can be nitrite, ammonia and nitrogen gas [170-172]. Hydrogen evolution is a competing side reaction. Current efficiencies between 10 and 30% [172] are not so high as for the anodic destruction of organic compounds.

For the treatment of cyanide contaminated water again diamond anodes are used to oxidize cyanide ions [110, 111, 173]. The oxidation of cyanides leads to the formation of cyanate in a first step, and later to the formation of carbon dioxide and nitrogen [173].

Diamond anodes can also be used for direct conversion of sulfide, an important contaminant in geothermal brines, to sulfate, whose discharge limits are much less stringent than those for sulfide with current efficiency of 90% [174].

4.1.3. Water disinfection

Electrochemical water disinfection is a rarely used but highly efficient water treatment technology [175]. It is based on the electrochemical production of disinfecting substances directly from the water to be disinfected or from substances dissolved in the water. No addition of chemicals is necessary. Usually DSA® type anodes based on mixed metal oxides of Ir and/or Ru are used in electrochemical water disinfection. Often hypochlorite produced from the natural chloride content of the water is the main disinfecting agent in electrochemical water disinfection. For electrochemical hypochlorite production from very dilute chloride solutions DSA® type anodes are much better suited than diamond anodes [175, 176]. This can also be seen from figure 8 in which the electrochemical prodution rate of free chlorine is compared for DSA®, platinum and boron-doped diamond anodes. Nevertheless, in some reports [177-181] diamond electrodes are proposed for this type of electrochemical water disinfection probably because the authors did only compare diamond with platinum not with DSA® mixed metal oxide anodes.

But in cases in which water with a very low or no chloride ion content shall be disinfected by electrochemical means diamond anodes could play an important role. This is because other oxidants could be produced such as ozone directly from the water [37, 182], peroxycarbonate from the bicarbonate dissolved in the electrolysed water [183] or persulfate from sulfate ions [184]. However, a complete disinfection is apparently not possible with only peroxodicarbonate as electrogenerated disinfectant because it leads only to a partial deactivation of bacteria [183]. Some companies are already selling electrochemical disinfection equipment based on diamond electrodes: Condiapure by Condias GmbH, Germany, Esazon® Systems by Esau & Hueber, Germany and Oxineo® by Adamant SA, Switzerland.

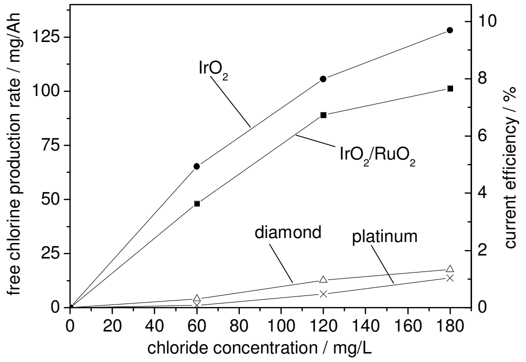

Figure 8. Dependence of the free chlorine production rate on chloride concentration for 4 different electrode materials

4.1.4. Metal finishing industry

The use of diamond electrodes in metal finishing industry concerns on one hand of course the water treatment techniques described in paragraph 4.1.1. and 4.1.2. on the other hand the replacement of currently used DSA® type, platinum or lead dioxide anodes in several electrodeposition technologies.

In water treatment especially the cyanide destruction by anodic oxidation with diamond anodes is interesting for the metal finishing industry because of the still frequent use of cyanide salts in electrodeposition formulations for noble metals [185].

The use of diamond-coated niobium anodes has been tested for high current applications in zinc, nickel and chromium electrodeposition baths [185]. In zinc plating baths without additives, electrolysis tests showed a lifetime much longer than that of currently used mixed metal oxide coated anodes. The chemical inertness of diamond-coated anodes to complex-forming agents in zinc and nickel baths lead to longer anode lifetimes. In hexavalent chromium baths, the diamond-coated anode allows the use of mixed metal oxide coated titanium as the working anode and the diamond coated anode as the oxidation anode in replacement of lead dioxide anodes [185]. With diamond anodes a high current efficiency for the oxidation of Cr(III) to Cr(VI) can be achieved [186]. Additionally, doped-diamond coated niobium anodes could be used as inert anodes in fluoride containing electrodeposition baths [185].

4.2. Inorganic electrosynthesis: Production of strong oxidizing substances

Because of their high oxygen overvoltage in aqueous electrolytes doped-diamond electrodes should be well suited for the electrochemical production of strongly oxidizing agents. Indeed it has been shown for several of these substances that electrochemical production with diamond anodes is superior to the electrosynthesis with other electrode materials. However, although otherwise stated [39, 177] this is not the case for chlorine production. In table 2 strongly oxidizing inorganic substances which can be produced with diamond anodes with higher efficiencies than with conventional electrode materials are listed. Some of them have not been produced electrochemically before in aqueous media.

The highest technical importance may be the production of persulfate and ozone by use of diamond anodes. Electrochemical production was the first preparation method for ozone. Today, however, most ozone is produced by corona discharge. Only a minor amount of ozone is produced by electrolysis with lead dioxide anodes in solid polymer electrolyte (SPE) reactor with current efficiencies around 15%. In conventional electrochemical reactors ozone is produced on diamond anodes with a current efficiency of about 5% [37, 182]. But combining diamond anodes and the SPE technology [169] leads to electrochemical ozone production efficiencies of more than 20% [187, 188].

A current production method for persulfate is the anodic oxidation of sulfate with polished platinum electrodes at high sulfate concentrations and very high current densities in the presence of NH_4SCN. It could be shown [189-191] that by the use of diamond electrodes generally higher current efficiencies compared to platinum electrodes are possible. High current efficiencies are retained even at low sulfate concentrations. Additionally, NH_4SCN additives are not necessary and lower current densities are possible without loss in current efficiency.

Table 2: Examples for inorganic substances produced by anodic oxidation with diamond anodes in aqueous solution

substance	reaction	E_0 / V vs. NHE	references
ozone	$3\ H_2O \rightarrow O_3 + 6\ e^- + 6\ H^+$ (2)	2,07	37, 182, 187, 188
cerium (IV)	$Ce^{3+} \rightarrow Ce^{4+} + e^-$ (3)	1,71	53
peroxodisulfate	$2\ HSO_4^- \rightarrow S_2O_8^{2-} + 2\ H^+ + 2\ e^-$ (4)	2,12	189-191
silver (II)	$Ag^+ \rightarrow Ag^{2+} + e^-$ (5)	1,98	192
ferrate	$Fe^{3+} + 4\ H_2O \rightarrow FeO_4^{2-} + 8\ H^+ + 3\ e^-$ (6)	2,20	193
peroxycarbonate	$2\ HCO_3^- \rightarrow C_2O_6^{2-} + 2\ H^+ + 2\ e^-$ (7)	1,80	194
periodate	$IO_3^- + H_2O \rightarrow IO_4^- + 2\ H^+ + 2\ e^-$ (8)	1,60	195
peroxodiphosphate	$2\ PO_4^{3-} \rightarrow P_2O_8^{4-} + 2\ e^-$ (9)	2,07	196
permanganate	$Mn^{2+} + 4\ H_2O \rightarrow MnO_4^- + 8\ H^+ + 5e^-$ (10)	1,51	197

The oxidation of Mn^{2+} to MnO_4^- has also been investigated with boron-doped diamond electrodes [197]. Current efficiencies as high as 37% were obtained. The formation of a MnO_2 film, which shows a blocking effect on the production of MnO_4^-, reduced the current efficiency of permangante production. Higher Mn^{2+} concentrations led to thicker MnO_2 films, which further reduced MnO_4^- production [197].

4.3.Organic electrosynthesis

In electroorganic synthesis often graphite electrodes are used because they are the most cost effective ones. However, they do have some drawbacks such as mechanical and chemical instability. Therefore, in the last years some investigations on the use of diamond electrodes in organic electrosynthesis have been performed [62-65, 117, 198-200].

In general, it has been shown that diamond electrodes behave similar to graphite electrodes in organic electrolytes such as in methanol, acetonitrile, tetrahydrofurane or *N*,*N*-dimethylformamide [199]. Because they are mechanically, thermally and chemically more stable, the use of diamond anodes in organic media should have some advantages. One possible use is the regeneration of oxidation mediator systems for oxidative reactions with organic compounds such as the regeneration of Cer(IV) which is e.g. used for the oxidation p-methoxytoluene to p-methoxybenzaldehyde [200].

But also direct electrochemical reactions of organic compounds on diamond electrodes are of interest. Examples are the methoxylation of p-tert-butyltoluene [64], the electrochemical cleavage of 1,2-diphenylethanes [65] and the anodic conversion of 2,4-dimethylphenol under solvent-free conditions to 2,2′-biphenol [198].

4.4. Electroanalytical applications

In electroanalytical applications both bare and modified diamond electrodes can be used depending on the specific analytic task. A lot of work has been done in the last years concerning electroanalytical applications of diamond electrodes [6, 9, 201-251].

What are the reasons for this intensive work? They lie of course in the special properties of doped diamond electrodes that makes them especially well suited for electroanalytical applications. The large potential window between oxygen and hydrogen evolution in aqueous electrolytes offers a large potential range for electroanalytical measurements [6]. Additionally, the absence of the formation and reduction of surface oxides characteristically found on gold or platinum electrodes is advantageous. Low capacitive currents lead to enhanced signal-to-background ratios [6, 201]. Among these properties are also excellent response stability [201] and a high degree of electrochemical activity without surface pretreatment [201]. Low adsorption of contaminants lead to better long term stability [6]. The on-line reactivation of the diamond electrode surface was shown to be possible by an anodic treatment of the electrode at about 3 V in case of electrode fouling, which may occur after a prolonged use [217].

The electroanalytical techniques for which diamond electrodes have been applied are amperometric detection [88, 91, 103-105, 203, 206, 208, 213, 214, 217, 218, 221, 225, 227, 231, 237-

241, 244, 248, 250], anodic stripping voltammetry (ASV) [6, 209, 219, 224, 228, 229, 235, 243], cathodic stripping voltammetry (CSV) [6, 204, 209, 227], abrasive stripping voltammetry (AbrSV) [6, 220] and square wave voltammetry [216]. Amperometric detection was connected with flow injection analysis [105, 202, 203, 206, 213, 214, 218, 225, 230, 231, 240, 244] or HPLC [206, 208, 237, 250]. It has been shown that doped diamond electrodes present a viable alternate electrode to Hg for ASV [226, 243].

Organic substances which have been determined so far with diamond electrodes are adenosine [231, 247], ascorbic acid [206], caffeine [222], carbamate pesticides [217], catecholamines [206], cephalexin [213], chlorophenols [211, 216, 248], chlorpromazine [206], *p*-cresol [248], cysteine [212], dopamine [205], formaldehyde [241], flavonoids [241], glucose [103], glutathione [213, 223], guanosine [231], histamine [210], indoles [233], NADH [205], nitrophenol [226, 245], nucleic acids [221], oxalic acid [240], penicillamine [218], phenol [248], polyamines [207, 214], purine [250], pyrimidine [250], serotonin [210, 246], sulfa drugs [208], tetracycline antibiotics [230, 237], theobromine [222], theophylline [211, 222], tiopronin [225] and xanthine [222] among others.

Inorganics include azide anion [203, 206, 251], hydrazine [236], hydrogen peroxide [104], iodide [231], nitrate [96], nitrite [206], dissolved oxygen [91], dissolved ozone [239], peroxodisulfate [88], sulfate [88], sulfide [245] as well as the metal ions Ag^+ [220, 228, 235, 243], As(III) [108, 249], Cd^{2+} [228, 229, 243], Cu^{2+} [219, 228, 243], Hg^+ [233, 237], Mn^{2+} [204, 245], Ni^{2+} [227] Pb^{2+} [209, 219, 224, 228, 235, 243], Sn^{4+} [220] and Zn^{2+} [228, 243].

In most cases unmodified diamond electrodes have been used. But also diamond electrodes modified by nanoparticles [6, 91, 96, 223, 236, 238, 249] or ion-implanted [103-105, 237] ones have been used for electroanalytical applications. The application of diamond microelectrodes and microelectrode arrays [88, 89, 236, 245] is also possible.

4.5. Optical transparent electrodes

Diamond electrodes can also be used as optically transparent electrodes (OTE) for spectroelectrochemical measurements over a wide wavelength range [252-255]. In principle, two diamond electrode forms are possible for OTE. One form is a polished thin doped diamond film on a nondiamond substrate such as undoped Si for IR or quartz for UV-Vis spectroelectrochemical measurements [253, 255]. The other form is a free-standing diamond electrode also mechanically polished [252, 254]. Such an electrode can be produced by growing a thicker film of doped diamond on a suitable metal substrate, like Mo. If the sample is cooled rapidly from the growth temperature, then the film will separate from the substrate due to stress resulting from the difference in thermal expansion coefficients for diamond and the substrate material. The polycrystalline free-standing doped diamond electrode is then mechanically polished smooth to reduce the surface roughness which would lead to light scattering.

Conventional OTE use ITO (tin doped indium oxide) coated glass electrodes. Due to the lower band gap of indium oxide spectroelectrochemical measurements in the UV below 300 nm are not possible. A diamond OTE has a short-wavelength cutoff of ~225 nm, which is the indirect band gap of the material [252]. In theory, the electrode has an optical window from 225 nm well out into the far-infrared, except for the boron acceptor band and the intrinsic multiphonon absorptions [252].

Electrochemical measurements with some model redox systems have been performed combined with simultaneous spectroscopic measurements [252-254]. This concerned $Fe(CN)_6^{3-/4-}$ [251, 253], methyl viologen [252], $Ru(NH_3)_6^{3+/2+}$ [253] and ferrocene/ ferricinium [254].

4.6. Electrochemical energy technology

There is also some research going on towards the use of diamond electrode materials in electrochemical energy storage or energy conversion systems. Energy storage systems concerns supercapacitors and lithium ion batteries, whereas energy conversion systems concerns fuel cells.

The possibility to use doped diamond as an electrode material in double layer capacitors has been explored [256, 257]. Commercial double capacitors are advanced energy storage devices which are suited for the fast exchange of electrical energy. They use an electrode material with a very large surface area, usually activated carbon with surface area of 1.000 m^2/g or more. A high voltage is also necessary for high storage capacity. This voltage has to be lower than the breakdown of the electrolyte. Therefore, often acetonitrile is used in commercial double layer capacitors. Because of cost and environmental concerns the use of aqueous electrolytes for double layer capacitors is desirable. The special properties of diamond electrodes, mainly the high overvoltage for oxygen and hydrogen evolution, could be useful at this point. However, a large electrode surface area has also to be realised. For this purpose so-called nano-honeycomb structured diamond electrodes have been produced (see paragraph 3.4.4.). This lead to 200-fold increase in surface area [256]. However, not enough to compete with commercial capacitors based on activated carbon and acetonitrile electrolytes.

Recently, it has been tested to use doped diamond as an intercalation electrode for lithium ion batteries [258]. For this purpose doped diamond thin films have been deposited onto carbon fibre material. First results did show that a relevant lithium ion intercalation corresponding to capacities up to 370 mAh/g could be measured [258]. However, earlier measurements with diamond electrodes in solvent-free lithium ion-conducting polymer electrolytes gave no evidence of intercalation of Li^+ into the diamond [67].

Another possibility to realize a lithium ion intercalation material with doped diamond electrodes is the combination of nano-honeycomb doped diamond with carbon nanotubes introduced into the pores of nano-honeycomb diamond [259]. Lithium ions can be inserted into the carbon nanotubes with capacities up to 894 mAh/g. A combination with double layer capacitor behaviour was found. Therefore, the authors believe that the combination of supercapacitor and Li-ion battery that work simultaneously supporting each other in one electrochemical cell is possible leading to the realization of a hybrid electrode material with high energy density and high specific power [259].

Fuel cells could also profit from the use of doped diamond. A special conducting diamond powder has been produced by coating undoped diamond particles (8 – 12 μm diameter) with a boron-doped diamond thin film [260]. Because of their much higher chemical and mechanical stability, these diamond particles shall substitute the currently used graphite based material as the substrate for electrocatalytically active nanoparticles.

The deposition of electrocatalysts onto doped diamond for the use in fuel cells is also a research topic [261-264]. This concerned Pt–RuO_2/C [261] Pt, Pt-RuO_2, Pt-RuO_2-RhO_2 [262] and Pt/Ru/Sn [264] catalysts onto diamond film electrodes and Pt–RuO_x onto diamond powder [263] including measurements of their catalytical activity towards ethanol and methanol oxidation. Pt–RuO_x/diamond powder had higher catalytical activity for methanol oxidation than commercial available Pt–Ru/C [263]. Next step will be the incorporation of such materials in real fuel cells.

4.7. Bioelectrochemical applications

Doped diamond electrodes are also useful for several bioelectrochemical applications. Some examples are discussed.

Martin and coworkers [246, 247] are using diamond electrodes for the study of neurodynamics in an animal model. Implantable diamond microelectrodes provide a unique opportunity to integrate neural stimulation and amperometric sensing (e.g. of dopamine, adenosine and serotonin) in the same implantable device.

Biosensors are another bioelectrochemical application area of diamond electrodes [248, 264]. They make use of biomolecules which can be attached covalently to doped diamond thin films via a surface layer of amino groups [85, 265, 266]. Biomolecules immobilized at the doped diamond surface are often still fully functional and active. Example are an amperometric biosensor based on covalent immobilization of tyrosinase on a boron-doped diamond electrode [248] or catalase modified diamond electrode [265]. These biosensors could be used to detect phenolic compounds [248] or hydrogen peroxide [265], respectively. Also diamond electrodes modified with DNA oligonucleotides have been produced with the aim to create field-effect biological sensors [266].

It has also been found that boron-doped diamond activated by anodic oxidation is a highly active material providing appropriate contact of laccase enzyme molecules with the electrode surface and leading to direct bioelectrocatalysis of the dioxygen reduction which could be useful in biofuel cells [267].

5. SUMMARY AND OUTLOOK

Since their introduction into electrochemical reasearch in 1987 doped diamond electrodes have become more and more popular. This is based on their unique properties which distinguishes them from conventional electrode materials und which makes many electrochemical processes more attractive or even possible. Meanwhile, several companies are producing and distributing diamond electrodes on a commercial basis from microelectrodes and microelectrode arrays up to electrodes with areas of 0.5 m^2. Therefore, in the future we will see a broad introduction of diamond electrodes in several different practical technical application areas.

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