Applications of DIACHEM® Electrodes in Electrolytic Water Treatment

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Diamond coated electrodes have been investigated worldwide over the past number of years with notable results. It is possible to vary electrical properties of diamond from semiconductor (very wide band gap) to close to metallically conductive by varying the boron doping level (10^{19}-10^{21} cm^{-3}).[1] The most important electrochemical properties are the very high corrosion stability in electrochemical applications and the extremely high overvoltage for water electrolysis.[2-6] This large working potential window in aqueous electrolytes provides the possibility of producing strong oxidizing solutions with extremely high efficiency. As reported by Comninellis,[7] compared to other electrode materials, hydroxyl radicals are produced with higher current efficiency on the diamond surface. These hydroxyl radicals completely mineralize organic impurities in water, such as oil, cooling fluid, toxic compounds.[8,9] As diamond electrodes are both stable as anodes and cathodes, it is possible to reverse polarity in order to prevent calcium build-up on the electrode surface. Through the use of diamond electrodes, it is possible to obtain an electrochemical process which, without the addition of further chemicals, results in an environmentally friendly and relatively maintenance-free method for the treatment of waste water. Additional industrial applications in which diamond electrodes have been tested include, electrochemical synthesis—especially in the production of strong oxidizing solutions, such as persulfate,[10] hydrogen peroxide, ozone or chlorine,[11] and technical galvanic applications, such as lead free chroming bath or recycling processes.[12]

Despite the numerous advantages of diamond electrodes, it is a material which, in the past, has not achieved its full potential due to the fact that large area production was not possible. The Fraunhofer IST, in cooperation with CSEM in Switzerland, has developed a technology for large area production of diamond coatings with sizes up to 50 cm x 100 cm. Apart from the aforementioned facilities, CONDIAS GmbH also uses this technology so that DIACHEM® electrodes may be produced on a variety of base materials and geometries for industrial applications (see Fig. 1).

Fabrication and Properties of DIACHEM® Electrodes

The fabrication of DIACHEM® electrodes consists of substrate pretreatment, deposition of the diamond coating, and preconditioning of the prepared electrode.[13] The pretreatment of technical electrode materials for the preparation of metal based DIACHEM® electrodes includes sandblasting for cleaning and increasing of surface roughness to promote diamond adhesion. This is followed by a wet cleaning process which is used to remove residual sandblasting material. Ultrasonic seeding is then performed in a suspension of diamond powder in alcohol, followed by cleaning with ultrapure water, before diamond deposition.

After pre-treatment, the various substrates with different geometries undergo a hot-filament activated chemical vapor deposition (HFCVD) process in which they are coated with a boron-doped diamond layer. The process consists of heating, diamond deposition, and substrate cooling—a process controlled and monitored automatically using a programmable process control unit. Figure 2 shows the newest and largest diamond coating system, HFCVD XXL[2], which contains an automated substrate exchange for continuous coating without interruption. This HFCVD machine consists of two deposition chambers, both of which are connected to a load lock chamber. The substrates to be coated are automatically divided between both coating chambers so that up to 1 m^2 of DIACHEM® electrodes may be produced per day.

The typical temperature for thermal activation at the filaments is in the 2200-2600 °C range (measured with an optical pyrometer). The substrate temperatures range between 700-925°C (measured using a thermocouple fixed into a dummy substrate). Total pressures of 10-50 mbar are applied in gas phase compositions of 0.5-2.5 % methane and 10-200 ppm diborane in hydrogen (96-99%). Carrying out HFCVD processes under these deposition conditions, leads to growth rates of 0.2-1.0 µm/h. Metal electrode substrates are thus coated with 1-5 µm thick conductive diamond films. All deposited diamond films (examples of the variety of DIACHEM® electrodes can be seen in Fig. 1) contain boron concentrations of 500-8000 ppm in the film.
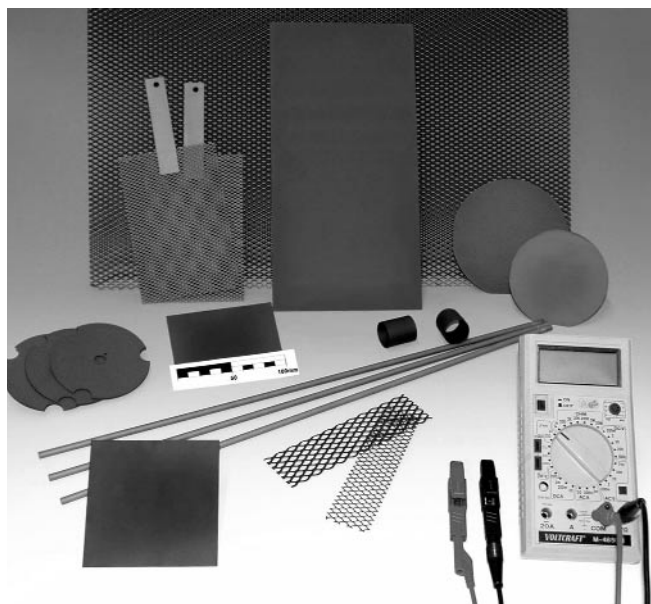

FIG. 1. Boron-doped diamond mesh, plate, tube, and cylinder electrodes on tantalum, niobium, and graphite base materials.

Following diamond deposition, the electrodes pass through the various stages of quality control. Each electrode is examined optically for damage to the diamond layer. The diamond electrode surface is initially inspected with a magnifying glass or, if a problem area has been identified, then with a light microscope. If there are no visible signs of damage to the diamond layer, then the electrical conductivity at various positions on the electrode is measured with a two-point measurement device. Such measurements provide an indication of macroscopic electrical properties, together with the doping concentration of the DIACHEM® electrodes. In Fig. 3, the dependence of film resistivity on the doping concentration is shown, as measured using SIMS analysis. Electrochemical testing then follows if the expected electrical properties are exhibited. Test samples are used at this stage of the quality control; samples are coated with each batch of electrodes and if these samples do not pass our standard testing procedure then further detailed examination takes place.

Characterization is performed using scanning electron microscopy (SEM) (JEOL JSM 6300 F), Raman spectroscopy (Instruments S. A. EXPLORER at 514.5 nm), and secondary ion mass spectrometry (CAMECA ims 5f SIMS with Cs+ ion cluster method). Typical SEM images of a metal-based DIACHEM® electrode are shown in Fig. 4. Various magnifica-tions of the mesh type electrode demonstrate that even for critical substrate areas, such as edges, a high quality diamond coating exists. A surface roughness of several μm is a result of the roughening pretreatment. This roughness is superimposed on the diamond film roughness which depends on the film thickness and the boron concentration in the film. With ever increasing boron-doping levels, smaller diamond grain sizes and higher grain densities are observed. For high boron doping levels the diamond grain size is below 1 μm even if the film is several μm thick due to secondary nucleation promoted by boron incorporation.

Raman spectra of these diamond films exhibit the sharp peak characteristic of polycrystalline diamond in the range from 1332 cm^{-1} to 1340 cm^{-1}. In the region of non-diamond carbon (1140 cm^{-1} to 1600 cm^{-1}), no Raman features are visible. Secondary ion mass spectrometry (SIMS) characterization reveals negligible amounts (below 1 ppm) of filament material in the diamond coatings. Hydrogen incorporations of about 1% are typical for CVD diamond films. Boron concentrations in the film vary between 500-8000 ppm resulting in electrical resistances between 0.1 and 0.05 Ωcm. The boron doping as well as impurity levels are constant through the whole diamond film, demonstrating the uniformity of the deposition process.

FIG. 2. Largest machine for the production of diamond electrodes (500mm x 1000mm) by hot filament chemical vapour deposition.
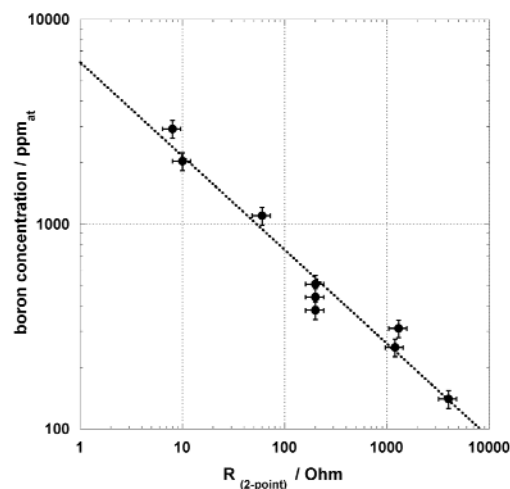

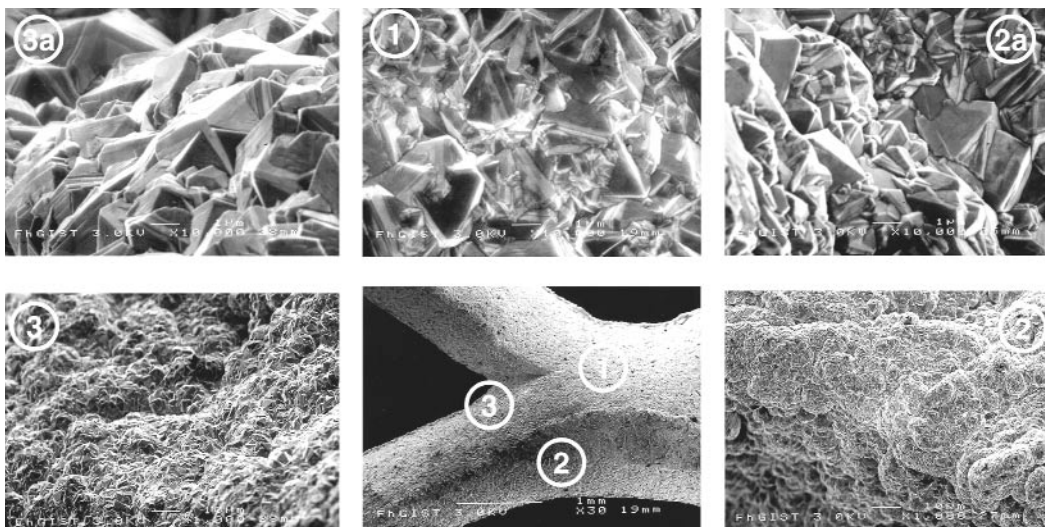FIG. 3. Resistivity as a function of the boron concentration in the diamond coating.

FIG. 4. SEM photographs of diamond film morphology from different areas of a grid electrode.
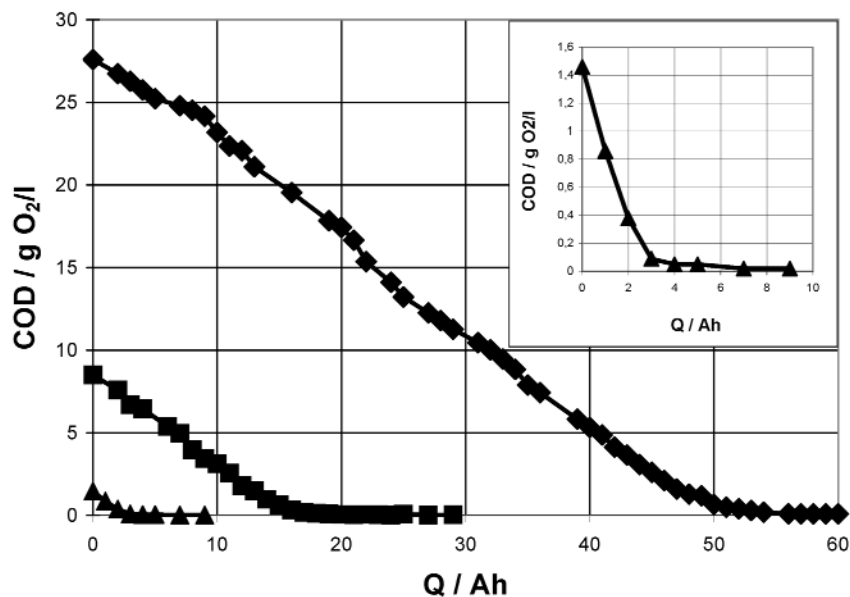
FIG. 5. *Decomposition of acetic acid model waste water with different initial concentrations.*

The final step in DIACHEM® electrode production is the preconditioning of the electrodes by anodic polarization in 1 M sulphuric acid with current densities of 50 mA/cm² for at least 30 min in order to ensure stable and reproducible operating conditions. During polarization the as-deposited hydrogen-terminated sites at the diamond surface are changed to oxygen terminated functionalities.[14-16] Anodically preconditioned DIACHEM® electrodes exhibit stable electrochemical behavior for several months.

Application of DIACHEM® Electrodes

In order to identify potential industrially relevant areas of application, laboratory scale model systems are set up. Typically, on the basis of results form these tests, a pilot system is set up so that the real technical operating conditions can be determined.

Water Treatment

With a rapidly growing world population and increasing levels of pollution, protection of the environment and the preservation of resources have become major issues for future technological progress. The most important method for the removal of organic load—characterized by COD (chemical oxygen demand)—from polluted waters is biological treatment, which is well established and relatively inexpensive with regard to operating costs. Having said this, biological treatment techniques are relatively slow and not suitable for all pollutants.

Over the last several years, Advanced Oxidation Processes (AOP) have been used for the total mineralization or the decomposition to harmless or biological degradable products of organic pollutants.[17-20] A common feature of all AOPs is the utilization of hydroxyl radicals with the highest oxidation potential for an effective oxidation process.

Due to their easy handling and reliable operating conditions, electrochemical generation of oxidants, used for the recovery or treatment of wastewater from industrial plants by electrochemical oxidation processes, play an ever increasing role.[21-23] Economical and efficient oxidation rates for industrial water treatment, however, require appropriate anode materials. Recent investigations with diamond electrodes have demonstrated the unique chemical and physical advantages of this electrode material for such applications.[24]

Efficient production of hydroxyl radicals takes place only under conditions of simultaneous oxygen evolution, which yields a non-selective but efficient oxidation of organic compounds.[25] Figure 5 shows the decomposition of waste water containing three initial levels of acetic acid.

It can be seen that the COD is independent of the initial concentration of organic load and then increases linearly with increasing load. In this region, the current efficiency for decomposition is almost 100%. It is at COD values under 0.5 g O_2l^{-1} that the decomposition curve deviates from linearity (see insert, Fig. 5) and the current efficiency is reduced due to mass transportation limitations. As a result of these mass transportation limitations, electrochemical systems must be adapted to the concentration range in terms of hydrodynamic conditions. In principle, the organic load could, however, be reduced with close to 100% current efficiency which has been proven in many decomposition tests with real waste waters.

In Fig. 6, the decomposition curve for cooling fluid in water can be seen. The concentration of the cooling fluid is 2 gl^{-1}. In addition to the COD, the carbon parameters (TOC, TIC and TC) are shown. What is clearly seen is that within the boundary of measurement accuracy the organic carbon is completely mineralized (CO_2 formation) without the production of by-products. The total carbon concentration was measured to show that, in the experiment, no carbon was lost through outgassing out of volatile organic compounds. At the end of the test, the temperature of the electrolyte increased and there was outgassing of CO_2, which explains the low measured TIC and TC values. This proves that even long chain, organic molecules, such as cooling fluid, can be mineralised by hydroxyl radicals without the development of intermediate products.

In addition to the examples cited above, we have successfully treated waste waters from the automotive, chemical, paper, and pigment industries without mass transport limitations and with very low operating costs. As a common feature of these investigations, it turns out that the electrochemically-assisted AOP is a very efficient process for COD reduction. It is also, in most cases, independent of the class of organic pollutants. It therefore should be highly suitable for waste water treatment processes in the specific COD region shown in Fig. 7 (shaded black region), which compares different treatments. The EAOP process may be applied over the complete range (shaded grey region) as shown, however it is most
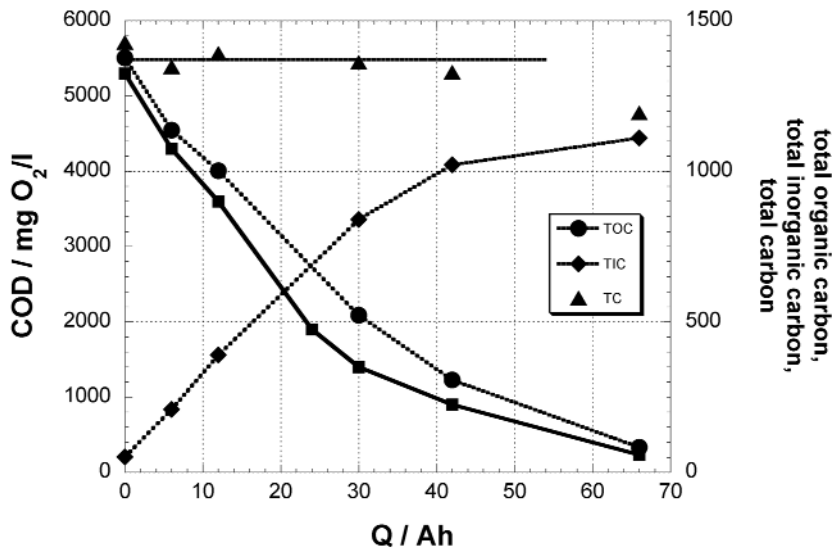
FIG. 6. COD reduction and transfer of organic carbon into inorganic carbon at pH = 10.
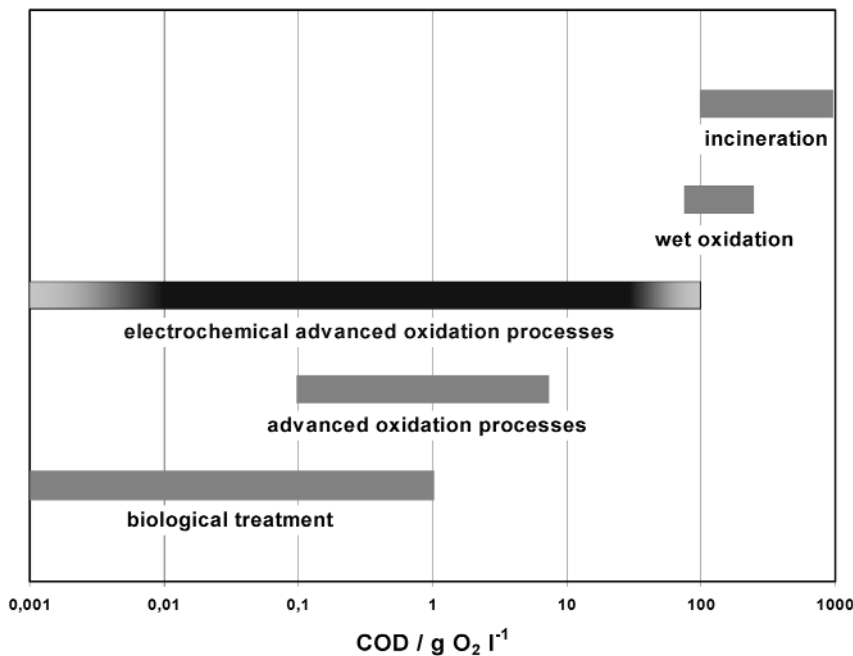

FIG. 7. Applicability of water treatment technologies according to the amount of organic load (chemical oxygen demand, COD).

cost effective and efficient when applied in the range from 100mg/l to 25g/l.

Conclusions

The technology for depositing polycrystalline diamond has considerably improved in recent years. Using large-area hot-filament activated CVD processes with *in-situ* boron doping via gas phase precursors, it is possible to deposit conductive diamond films on areas of up to 0.5 m^2 and also on three dimensional structures. Reproducible coating of electrodes for electrochemistry is possible through automated process control and highly automated deposition systems.

Laboratory and field testing has proven conductive diamond to be a useful anode and cathode material for a variety of electrochemical processes. Promising results with respect to effectiveness and energy efficiency have been demonstrated for waste water treatment, electrosynthesis, and electroplating. In particular, electrochemical advanced oxidation process with DIACHEM® electrodes is highly promising for water treatment, supplementing or complementing current methods. ∎

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