

WASTEWATER TREATMENT WITH DIAMOND ELECTRODES

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Abstract

Boron doped diamond films have been deposited by large area hot-filament CVD (HFCVD) on silicon, siliconcarbide and different industrial electrode materials, like niobium, tantalum, titanium, tungsten, zirconium and graphite on areas up to 40 cm x 60 cm (Fig. 1). These diamond electrodes have been characterized with regard to their material and electrochemical properties.

The oxidation of organic compounds has been studied using alcohols, organic acids and halogenated aromatic molecules. These organic model molecules are oxidized to CO₂ without major amounts of other detectable byproducts even at very low concentrations («3ppm). Concentrated (1 M) and diluted (3.1×10^{-4} M) cyanide solutions have been oxidized on diamond electrodes both in the presence and in the absence of chloride ions. At low concentrations, the oxidation process is strongly catalysed by the presence of Cl⁻.

These experimental data demonstrate the applicability of diamond electrodes for industrial processes of wastewater treatment and purification.

INTRODUCTION

With a rapidly growing world population and increasing levels of pollution, the protection of the environment and the preservation of resources have become a major issue for future technological progress. Strategies for ecological protection generally include the development of new or improved industrial processes that have no or minor effects on nature, and of processes for the treatment of inevitable waste.

Due to the fact, that water is a limited and vital resource, it should not end as inevitable waste after having been used e. g. in industrial processes. Therefore, one of the main common R&D tasks in the future is the provision of high quality water in sufficient quantity

and at an affordable price. These R&D tasks aim at the treatment of wastewater for reuse. In this context electrochemical processes used for the recovery or treatment of wastewater from industrial plants play an important role (1, 2). Oxidative processes have a continuously increasing importance in the reduction of toxic pollutants or at least in their conversion to biocompatible species (3). Economical and efficient oxidation rates for industrial water recycling, however, require appropriate anode materials. Recent investigations with diamond coated electrodes have demonstrated the superb chemical and physical properties.

However until now, diamond has not been introduced in electrochemical applications because of the limited availability of diamond for large-area electrodes. In the last years large-area chemical vapour deposition (CVD) of polycrystalline diamond films has been developed, yielding deposition areas of up to 0.3 m² on metallic and ceramic substrates. These boron doped conductive diamond electrodes are semiconductor electrodes with a microcrystalline structure and comparatively rough surfaces. Diamond-coated electrodes are chemically, mechanically and thermally very resistant (4) and show no significant corrosion even under high electrochemical load (5, 6). Galvanostatic investigations show no detectable changes of the electrodes for example after several hours in a solution of NaF in concentrated nitric acid at 50 °C (6) or in sulphuric acid (7). Over several weeks at 2 to 10 A cm⁻² and thousands of Ah cm⁻² the electrochemical activity of these diamond electrodes remains also constant in contrast to other conventional carbon electrodes (8).

Additionally, diamond electrodes show high overpotentials for water electrolysis (hydrogen - as well as oxygen evolution) (9) and present no surface redox processes as known from other carbon electrodes (for example glassy carbon (10)). This electrochemical window is large enough to produce hydroxyl radicals with high efficiency, which oxidise organics completely to carbon dioxide. Depending on the presence of other reactants in aqueous solutions different species with a high oxidising potential could also be produced. All of these reactants contribute to the complete, indirect oxidation of pollutants in used water. These properties of diamond electrodes meet the requirements for an efficient electrochemical wastewater treatment.

EXPERIMENTAL

We produced diamond coated electrodes on metallic (for example Ta, Ti, Mo, W, Zr), silicon, ceramic and graphitic substrates by a large-area HFCVD (hot filament CVD) process (Fig. 1) (11).



Fig. 1. 40 cm x 60 cm large-area boron-doped diamond electrode of expanded niobium base material

Metallic substrates were pretreated by sand blasting, a technical cleaning process followed by ultrasonic seeding in an alcoholic diamond powder suspension and an end cleaning step with ultrapure water. Graphite substrates were electroplated with a thin (10 – 50 nm) Au or Pt interlayer and afterwards seeded and cleaned like the metallic substrates. These technical electrode substrates were coated with 2 – 10 μm thick diamond films. Conducting 4 inch Si substrates (0.1 Ωcm and 1 $\text{m}\Omega\text{cm}$, Siltronix) were seeded, cleaned and coated with a less than 1 μm thick diamond film.

Before starting a process the chamber with a volume of 0.4 m^3 was evacuated to a pressure of less than 0.1 mbar. In the following deposition steps (heating, deposition and cooling) filament temperature (2200 $^{\circ}\text{C}$ – 2600 $^{\circ}\text{C}$), pressure (10 – 50 mbar), gas flow (flow rates of 1000 – 5000 sccm of 0.8% - 2.3% CH_4 in H_2 containing 1 – 100 ppm $\text{B}(\text{OCH}_3)_3$) and substrate temperature (700 $^{\circ}\text{C}$ – 925 $^{\circ}\text{C}$) were reproducibly and reliably adjusted and automatically controlled using a programmable process control unit. After the growth step the diamond electrodes were slowly cooled to room temperature under pure hydrogen gas flow.

SEM investigations were performed using a JEOL JSM 6300 F scanning microscope. The Raman spectra were obtained with an Instruments S.A. EXPLORER spectrometer using the green 514.5 nm line of an Ar^+ ion laser. Analysis of elemental composition, especially the boron content, has been performed by a CAMECA ims 5f SIMS with the Cs^+ ion cluster method.

For electrochemical characterisation all diamond electrodes were anodically polarised in 1 M NaOH or 1 M H_2SO_4 by current densities of 100 mA for at least 30 min to ensure stable and reproducible conditions. Characterisation was made in a conventional EG&G Parc three electrode flat cell using a ZAHNER electric IM5d potentiostat, where the diamond electrode

was used as working electrode, Pt or Zr as counter and Ag/AgCl (sat. NaCl) as reference electrode.

The electrochemical oxidation and decomposition of organic model substances has been carried out in 1M H₂SO₄ at 30 mA/cm². A model of the experimental setup is shown in Fig. 2.

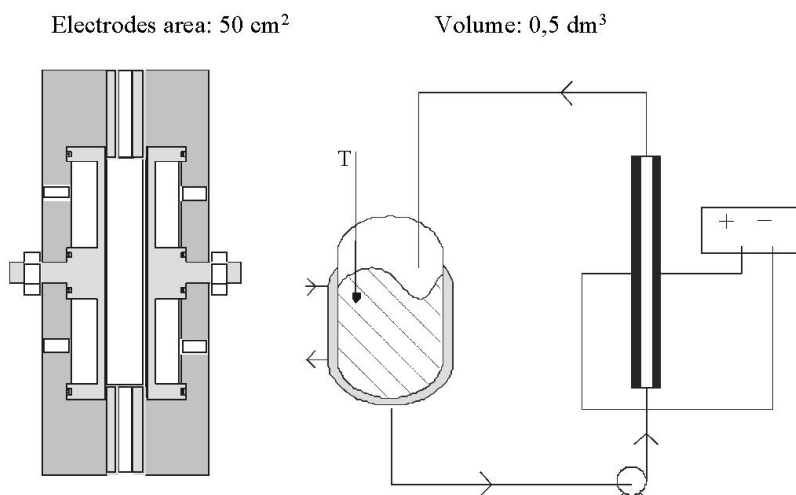


Fig. 2. Model of the experimental setup used for electrochemical oxidation and decomposition of organic model substances

The degradation of these products, the formation of new by-products as well as TOC (total organic carbon) and DCO (demand of chemical oxygen) was continuously controlled. The organics were analysed by HPLC (high performance liquid chromatography). In case of cyanides the electrolytical oxidation has been carried out in 1M KOH at 36 mA/cm² with and without addition of 1 to 100 mM KCl. The decomposition of cyanides has been controlled either by titration or by the pyridine pyrazolon method.

RESULTS AND DISCUSSION

Preparation of diamond electrodes

On the metals Nb, Ta and W conductive doped diamond layers (resistivities down to 0.005 Ω cm) were deposited directly with sufficient adhesion for electrochemical applications. For diamond deposition on Ti, a widely used anode material in industrial electrochemistry, special adaptations need to be made in order to get sufficient adhesion. On one hand the embrittlement and phase transformation of the titanium by hydrogen diffusion must be prevented. On the other hand stresses at the interface originating from the different thermal expansion coefficients have to be compensated (12, 13).. By a defined surface roughening

and the formation of a conducting carbide layer at the interface, a sufficient adhesion improvement could be achieved.

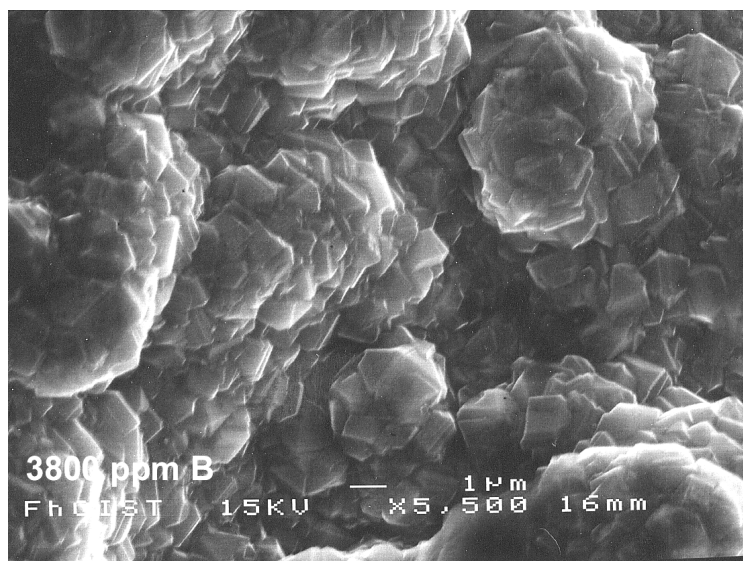


Fig. 3. SEM image of diamond deposited on Ta with different boron content

In Fig. 3 typical SEM images of produced metal / diamond electrode surfaces are shown. The visible roughness of several μm is a result of surface roughening pretreatment of the metallic substrate surfaces. The grain size is in the order of $1 \mu\text{m}$ and the surface morphology changes with increasing boron content in the diamond films. The Raman spectra of these diamond films (Fig. 4) exhibit a sharp peak in the range from 1332 cm^{-1} to 1340 cm^{-1} , which is characteristic for crystalline diamond.

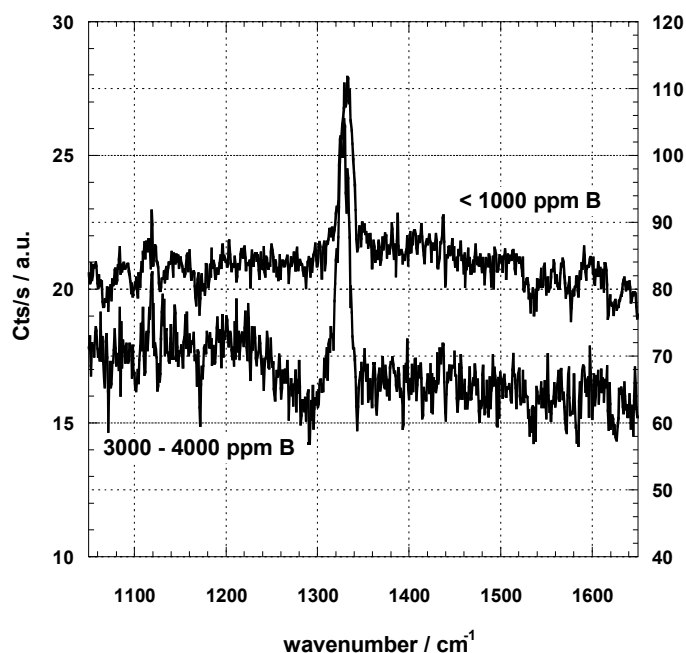


Fig. 4. Raman spectra of diamond electrodes with different boron content

The non-appearance of other graphitic or amorphous carbon peaks usually ranging from 1450 cm^{-1} to 1600 cm^{-1} rates these diamond films as relatively phase-pure high quality material. The weak peak at 1140 cm^{-1} is usually observed for smaller diamond grain sizes. In addition a broad peak at approximately 1200 cm^{-1} could be observed especially for high boron content. This peak has been extensively reported in the literature (14, 15, 16, 17, 18). It has been observed that this peak, compared to the 1332 cm^{-1} diamond peak, increases with increasing boron content in heavily doped films, because of increasing disorder in the diamond crystallite structure by the incorporation of boron.

Properties of diamond anodes

Due to the fact that for industrial applications the stability of technical anodes is often limiting the lifetime, the main interests are the anodic properties of diamond electrodes. Fig. 5 shows a cyclic voltammogram for Ta/diamond electrodes in $0.5\text{ M H}_2\text{SO}_4$, which are representative for other metal/diamond electrodes, too.

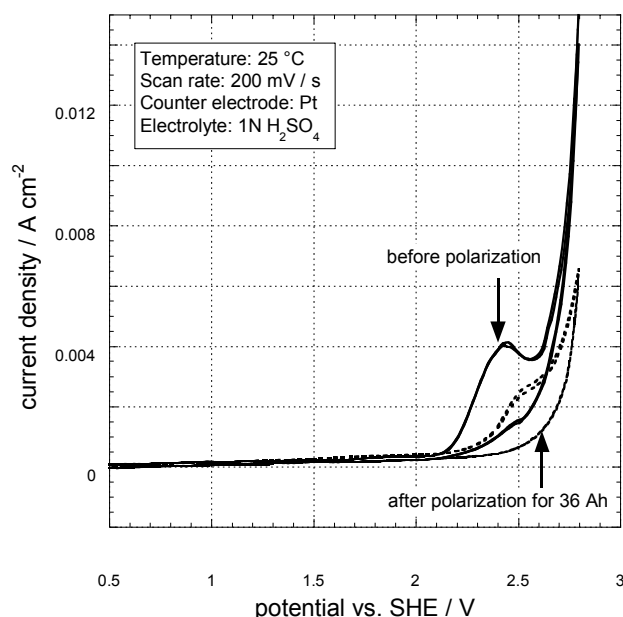


Fig. 5. Cyclic voltammograms for a diamond anode at high current densities before and after polarisation.

It is clearly visible, that there seems to be a surface chemical factor. Possibly the density of redox active carbon oxygen functionalities on the diamond surface also influences electrochemical response of these electrodes (19). For current densities up to 5 mA cm^{-2} there is an increase of current, but with increasing potential there is a peak clearly visible before oxygen evolution takes place with higher current densities. In sulphuric acid solutions the sulphate ion will be efficiently oxidized to peroxodisulphate on diamond electrodes. Therefore the electrochemical investigations at low current densities do not show the evolution of oxygen by water decomposition, but the oxidation of sulphate ion. This reaction depends strongly on the anodic pretreatment. By polarisation with potentials lower than 2.3 V it remains unaffected while at higher potentials it decreases strongly as visible in Fig. 5b in the CV curve after polarization with 36 Ah cm^{-2} .

Electrodes pretreated at a high potential remain stable in their electrochemical behaviour for several weeks or thousands of Ah cm^{-2} . Nb / diamond electrodes for example were anodically stable in the course of an electrolysis in 1 M H_2SO_4 at 10 A/cm^2 for more than 750 h.

Diamond electrodes for wastewater treatment

Another great advantage of diamond electrodes is the described widest known electrochemical window before water decomposition in aqueous electrolytes takes place as shown in Tab. 1. On one hand in this large potential range anodic and cathodic electrochemical synthesis could be carried out with higher energy efficiency, because of the smaller amount of by-products (hydrogen or oxygen evolution). On the other hand oxidation of organic compounds in aqueous electrolytes is very efficient. In the case of oxidative degradation of organics in wastewater treatment, the aim is the conversion of toxic organic compounds to biocompatible materials.

Tab. 1: Overpotentials of diamond electrodes for different gas evolution reactions

Electrolyte	Boron concentration (ppm)	Overpotential (for 100 mA/cm^2)
0.5 m H_2SO_4 ($+\Rightarrow \text{O}_2 / - \Rightarrow \text{H}_2$)	100 – 500	$\eta_+ = 2.0 - 2.8$ $\eta_- = 1.1 - 1.8$
	1000 – 5000	$\eta_+ = 1.7 - 2.3$
1.0 m NaOH ($+\Rightarrow \text{O}_2 / - \Rightarrow \text{H}_2$)	100 – 500	$\eta_+ = 0.9 - 2.3$ $\eta_- = 1.8 - 2.5$
	1000 – 5000	$\eta_+ = 0.8 - 0.9$
1.0 m NaCl ($+\Rightarrow \text{Cl}_2 / - \Rightarrow \text{H}_2$)	100 – 500	$\eta_+ = 1.3 - 1.7$ $\eta_- = 2.0 - 2.5$
	1000 – 5000	$\eta_+ = 1.2 - 1.3$

Only reactions involving simple electron transfer are active on diamond electrodes (20). More complex reactions can take place only under conditions of simultaneous oxygen evolution, which yields a non selective oxidation of organic compounds. On diamond electrodes the organic compounds are often completely oxidized to CO_2 with a current efficiency higher than 85% (20, 21). In Fig. 6 the oxidation of phenol as a model for aromatic pollutants and in Fig. 7 the oxidation of acetic acid as a model aliphatic compound for wastewater treatment are shown.

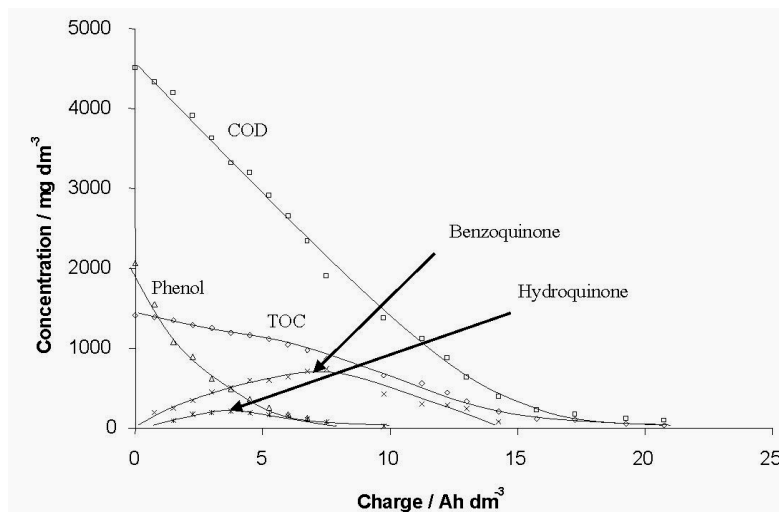


Fig. 6. Oxidation of phenol on diamond electrodes. Oxidation has been performed from a 2 mM aqueous solution at pH 2 and 60 °C under galvanostatic conditions (0.03 A cm^{-2}). Also indicated are the chemical oxygen demand (COD) and total organic carbon (TOC) during electrolysis with diamond electrodes.

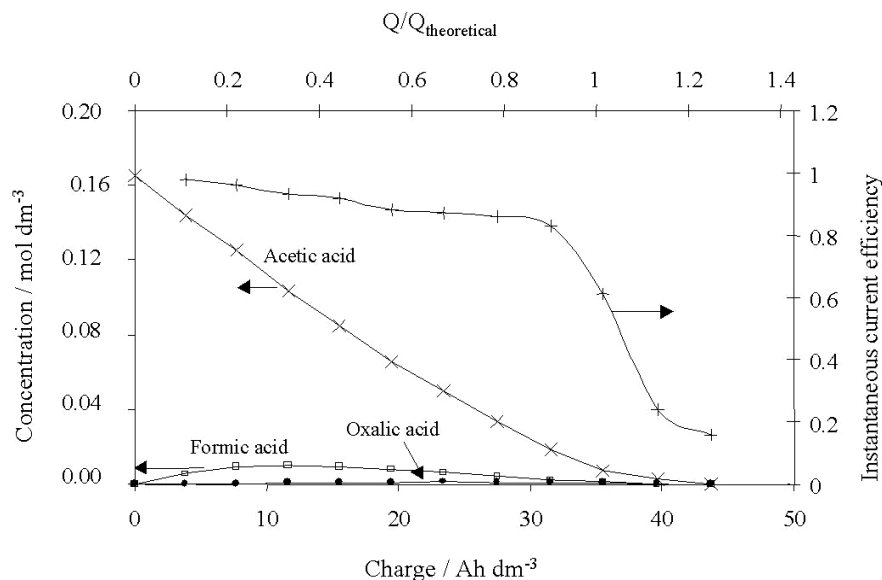


Fig. 7. Oxidation of acetic acid in 1M H_2SO_4 on diamond electrodes under galvanostatic conditions (0.03 A cm^{-2}). The instantaneous current efficiency is near 100% and decreases for the case that the concentration of organic substance is limited by the mass transfer.

The quantitative HPLC analysis of organic compounds during electrolysis yields a final phenol concentration lower than 3 ppm. The low concentration of intermediates in both oxidation reactions indicates that the organic molecules are directly oxidized to CO_2 on the diamond electrode. This fact is confirmed by comparing the rates of phenol elimination with those of TOC (*Total Organic Carbon*) and COD (*Chemical Oxygen Demand*) during electrolysis. During several weeks of oxidation the properties of these electrodes have not been affected and poisoning of the surface is not detectable.

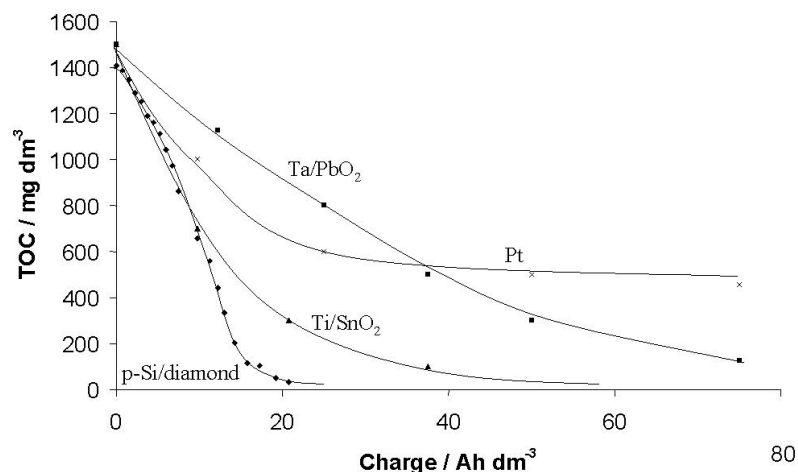


Fig. 8. Anodic oxidation of phenol in 1M sulfuric acid on 4 types of electrodes.

In Fig. 8 a comparison of 4 different electrode materials for the oxidation of phenol in terms of current efficiency is shown. On the platinum electrode there is not a complete oxidation of the organic compound, because of the effect that oxidation of acetic acid did not take place with platinum electrodes. The lead oxide and tin oxide electrode allows a complete elimination of phenol with different charge input. With the diamond electrode a complete elimination of organics with nearly the theoretical necessary charge, in our case 16 Ah/l, is possible. The reason for the final difference of the theoretical and real charge is the limitation in mass transfer at low concentrations due to the simplicity of the electrochemical cell.

In addition to the organic model systems above, also decompositions of inorganic pollutants have been investigated with diamond electrodes. As model system concentrated (1 M) and diluted (0.0003 M) cyanide solutions have been oxidized with and without an assisting redox system (Fig. 9) of chloride ions.

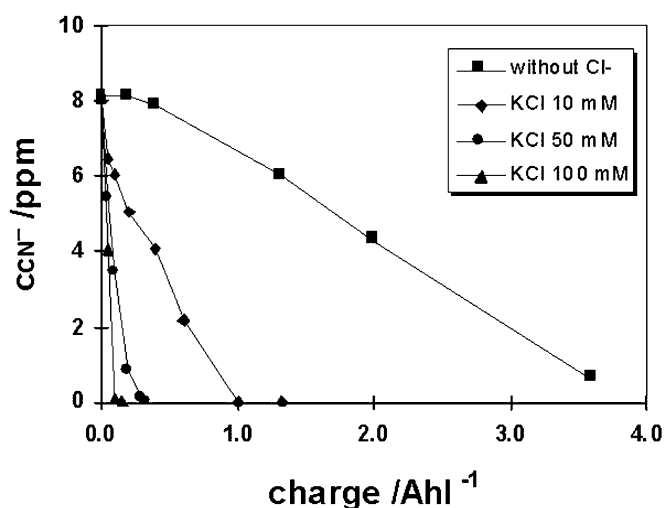


Fig. 9. Indirect oxidation of cyanide on diamond electrodes in presence of KCl. The composition of the electrolyte was 8.1 mg l⁻¹ CN⁻ in 0.1M KOH with different amounts of KCl.

With conventional electrodes these electrochemical treatments were unsuitable because of the low stability of the anodes and the poor current efficiency whereas diamond electrodes remains stable under these conditions. The direct electrochemical oxidation of cyanide on diamond electrodes yields an exponential decrease in cyanide concentration with increasing electrical charge. Therefore direct decomposition of low cyanide concentrations could not be achieved under efficient electrical conditions by direct oxidation. However, the presence of chloride ions at low cyanide concentrations increased the current efficiency strongly. In Fig. 9 this influence of chloride concentration on the rate of cyanide elimination is demonstrated for different KCl concentrations. It is clearly demonstrated that even a small amount of Cl^- ions increases the efficiency of the reaction, especially for low cyanide concentrations.

CONCLUSIONS

Metal/diamond electrodes with large areas up to $50 \times 60 \text{ cm}^2$ has recently become available by HFCVD process technology. Heavy doping yields diamond layers with resistivities down to $0.005 \text{ }\Omega\text{cm}$ and unaffected mechanical and chemical properties. Due to their extreme properties - chemical inertness, temperature-stability up to 600°C , even under oxidizing conditions, and high current efficiency for oxidation of anorganic as well as organic molecules- metal / diamond electrodes are very promising for industrial electrochemical water and wastewater treatment.

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