On the Use of Diamond Anodes to Electrochemically Purify Photoprocessing Effluent

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Abstract

Several techniques have been applied to photoprocessing effluents to reduce chemical oxygen demand and destroy organic components. Electrochemical destruction of photoeffluent has received attention in the past, but the method has suffered from slow kinetics and deleterious effects as a result of electrode corrosion. Anodes constructed of thin-film microcrystalline diamond deposits can overcome both of these obstacles. In model experiments, oxidation of phenol is seen to be about ten times faster with diamond anodes than with platinum or other metal/metal oxide anodes. These higher rates of oxidation carry over to the treatment of photoprocessing solutions such as developers or solutions containing chelating agents such as EDTA. Chemical and biological oxygen demand can be lowered by several orders of magnitude with this treatment technique. The major product of electrolysis is carbon dioxide. Another advantage of diamond anodes is that the corrosion process does not result in the release of heavy metals into solution as is the case with electrodes based on platinum or other heavy metals.

Introduction

Effluents from photoprocessing contain chemical oxygen demand and have organic substituents. After silver recovery, the residual solutions can be treated by a number of methods to lower COD and decompose the organic substituents. These methods include biological treatment, chemical oxidative treatments with ozone, peroxide, and other oxidants, and high temperature incineration.[1]

One form of oxidative treatment is electrochemical oxidation (electro-oxidation). One of the main impediments to the use of electro-oxidation on photoprocessing effluents is the corrosive nature of these solutions. Typical metal/metal oxide electrodes such as platinum, ruthenium, lead, and their oxides are not sufficiently resistant to corrosion. This results in short electrode lifetime and an unacceptable release of metals into the treated solution. Some of these electrodes also suffer from slow electrode kinetics or passivation when used to treat photographic effluent.

We have identified boron-doped diamond, in the form of a polycrystalline conductive film, as a superior anode for use in electro-oxidation of photographic effluents. This electrode material is more resistant to corrosion than metal-based electrodes, and any corrosion of diamond that does occur will not result in release of heavy metal into the treated solution. In addition, the electrode kinetics with some materials of interest in photographic effluents are much faster at diamond anodes, and the increased stability of diamond allows a higher current density to be used. These attributes result in shorter treatment time with diamond anodes compared with conventional metal-based electrodes.

Characterization of Diamond Electrodes

Diamond films used in this work were prepared by the hot filament chemical vapor deposition technique by Advanced Technology Materials, Inc. The support used for these films was a silicon wafer. The films contain polycrystalline deposits with predominant <111> orientation. Conductivity is conferred by boron doping during the deposition process.

Scanning electron micrographs show the diamond crystallites to range from 1-7 μ in diameter. The Raman spectrum shows a moderate band at 520 cm^{-1} from the silicon support, a strong band at 1333 cm^{-1} (sp^3 carbon from the diamond structure), and a weak band at 1525 cm^{-1} (sp^2 carbon indicating graphite-like character). The weakness of this band combined with the greater scattering cross-section for this band (about 50 times that of the 1333 cm^{-1} band) indicates that a minimal amount of graphite-like impurity exists within the sample.

Estimates of the surface roughness can be obtained from atomic force microscopy (AFM). These measurements indicate that the surface area is about 16% greater than one would calculate for a flat plane of the same dimensions.

The diamond structure is generally C-H terminated. Use of a diamond film as an anode in aqueous oxidations results in formation of C-O and O-H species on the diamond surface. This is supported by high-resolution electron energy loss spectroscopy (HREELS) measurements, which show a growth of bands at about 1500 cm^{-1} and 3400 cm^{-1} attributed to O-H modes. Applying a negative potential to the diamond film to create a reductive environment resulted in diminution of these bands, suggesting a reversion to C-H termination on the diamond surface.

Electroactivity of the diamond film was demonstrated by performing cyclic voltammetry (CV) on a solution of ferrocene-dimethanol in an aqueous solution containing 0.5 M $NaNO_3$. Reversible electrochemistry was demonstrated by a peak splitting of 60 mV in the CV scan. Following use of this diamond film as an anode (2.5 V vs SCE) in oxidation of an $NaNO_3$ electrolyte solution, the CV peak splitting broadened slightly to ~75 mV. This suggests the surface is modified in some fashion during the oxidation of water, which is consistent with the HREELS data discussed above.

Electro-oxidation Studies

Initial electro-oxidation studies were performed on solutions of phenol in aqueous 0.5 M sodium sulfate. Typical results are displayed in Figure 1. The rate of destruction as measured by decrease in chemical oxygen demand (COD) shows phenomenological first-order behavior with both anode materials, but the rate of destruction is ten times faster with a diamond anode than with a platinum-titanium (Pt-Ti) anode. Trapping experiments with barium hydroxide indicated that 86 ± 8% of the carbonaceous product of oxidation was carbon dioxide.

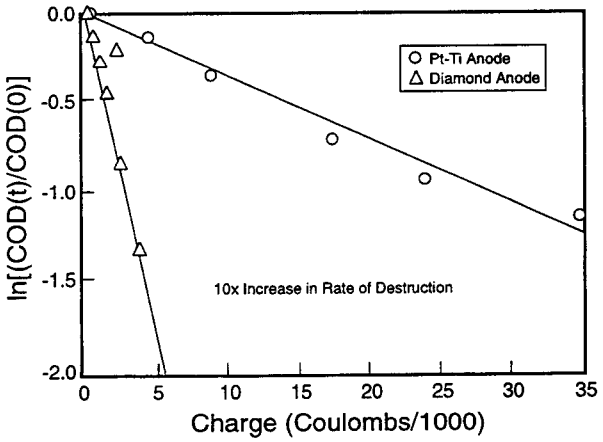

Figure 1.

This increased rate of oxidation is also observed with effluents from photoprocessing. For example, the oxidation of a mixture of process C-41 color film developer and RA-4 color paper developer proceeded eight times faster with diamond anodes than with Pt-Ti. Measurements of treated solutions following use of Pt-Ti as an anode showed up to 2 ppm Pt in these solutions. The oxidation proceeded even slower with an RuO_2 anode, and this anode fouled after a short time. We have also observed that the rate of oxidation with diamond anodes is insensitive to current density over a range of 300-1200 mA/cm^2. This allows the passage of higher currents resulting in shorter treatment times with diamond anodes.

The rate coefficients for oxidation of various chelating agents are shown in Table I. The rate of oxidation with the diamond electrodes is always significantly faster than with the Pt-Ti anode. In some cases, particularly with the phosphonic acid chelating agents NMPA and HEPA, the rate is effectively zero with Pt-Ti. The rate of oxidation with the diamond anode is much less sensitive to the nature of the chelating agent.

Table I. Rate Coefficients for Chelating Agent Oxidations[a]

Chelating Agent[b]	Pt-Ti Anode (normalized)	Diamond Anode (normalized)	Rate Factor[c]
EDTA	1	3.3	3.3
PDTA	0.83	3.1	3.7
2-OH-1,3-PDTA	1.3	3.8	0.9
DTPA	1.1	4.2	3.8
NTA	1	2.6	2.6
glycolate	0.3	4.4	14.6
citrate	0.05	1.8	36
NMPA	0	2.7	-
HEPA	0	2	-

[a]All rate coefficients are normalized to EDTA/Pt-Ti. [b]EDTA: ethylenediamine-tetraacetic acid; PDTA: 1,3-propylenediaminetetraacetic acid; 2-OH-1,3-PDTA: 2-hydroxy-1,3-propylene-diaminetetraacetic acid; DTPA: diethylenetriaminepentaacetic acid; NTA: nitrilotriacetic acid; NMPA: nitrilotris (methylene-phosphonic) acid; HEPA: hydroxyethylidenediphosphonic acid. [c]The rate factor is the rate using diamond anodes divided by the rate using Pt-Ti.

Summary

Microcrystalline diamond films show several advantages over metal-based anodes for electro-oxidation of photoprocessing effluents. They yield faster rates of oxidation and can withstand higher current densities, both of which allow for faster treatment of the effluent. Some organic compounds that are not oxidizable at a Pt-Ti anode are readily oxidized at diamond film anodes. Diamond films do not release metals into solution, thereby avoiding the need for a secondary treatment step.

References

1. T. W. Bober, T. J. Dagon, and H. E. Fowler, **Treatment of Photographic Processing Wastes,** in *Handbook of Industrial Waste Treatment*, L. K. Wang and M. H. S. Wang, Eds., Marcel Dekker, New York, Vol. 1, 173-227 (1992).