Electroanalytical Applications of Bare and Modified Diamond Electrodes

Akira Fujishima

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Boron-doped diamond (BDD) has been realized as the outstanding electrode material for several electrochemical applications, including electrochemical waste treatment (1) and electroanalysis (2-4). The high overpotential for oxygen evolution in aqueous solution allows diamond to detect electroactive species (e.g., histamine) which react at highly positive potentials. The same property of diamond is exploited for the generation of hydroxyl radicals by applying much higher potentials, thus enabling electrochemical incineration reactions to be carried out. Another well-known property of diamond is its relative inertness in terms of adsorption of polar and neutral chemical species. This property makes diamond a stable material for electroanalysis. Although diamond is prone to fouling in exceptional cases such as phenol oxidation, its wide potential window allows electrochemical cleaning of the electrode surface by applying high anodic potentials (5).

We have recently demonstrated the use of diamond electrodes for the detection of chlorophenols in wastewater from municipal incineration plants. Detection of chlorophenols in drinking water and wastewater is important as they are carcinogenic and are known to be precursors for dioxins. Diamond in this case exhibits excellent stability and sensitivity, especially at low chlorophenol concentrations. For example, after 100 repetitive injections of 5 mM 2,4-dichlorophenol, the current response at diamond electrodes decreased only 10% while the decrease was about 70% for a glassy carbon (GC) electrode. Another interesting observation is that applying highly positive potentials for a short time can restore the response of diamond. In another study, we have demonstrated the use of the diamond electrode for the detection of the oxidized form of glutathione (GSSG) which could not be detected on GC electrode due to the high oxidation potential. Similar is the case with xanthine derivatives such as caffeine and theophylline. Detection of these compounds in rabbit serum samples was successfully carried out.

While the above unique features of diamond are being exploited by several electrochemists for various applications, interesting findings on diamond electrodes modified with various electrocatalyst materials have also been reported. For example IrO_2 clusters deposited on diamond electrodes were found to show excellent electrocatalytic properties (6). We have modified diamond electrodes with metal catalysts such as Pt, Cu and Ni in view of electroanalytical applications. For example, electrochemically deposited Cu nonoparticles on diamond surfaces exhibited excellent electrocatalytical properties for the oxidation of glucose and other carbohydrates in alkaline medium (7). Diamond, being an inert and stable material, acts as an excellent support for metal catalysts. However, oxidative electrochemical pretreatment is necessary to improve the adherence of the metal particles to the electrode. These Cu-modified electrodes are useful as detectors for carbohydrate detection in food products after HPLC separation. Modification of diamond with several other metals is in progress. We have also modified nano-structured honeycomb diamond electrodes with Pt clusters. In this case, the Pt particles were deposited in the pores. These Pt-modified honeycomb electrodes were found to be selective for methanol compared to several other alcohols, probably due to size selectivity (8).

References

1. G. Foti, D. Gandini, W. Haenni, A. Perret, and Ch. Comninellis, Electrochem. Solid State Lett., **3**, 77 (2000).
2. J. Xu and G. M. Swain, Anal. Chem., **70**, 1502 (1998).
3. T. N. Rao and A. Fujishima, Diamond Relat. Mater., **9**, 384 (2000).
4. N. Spataru, B. V. Sarada, E. Popa, D. A. Tryk and A. Fujishima, Anal. Chem. 73, 514 (2001).
5. M. Panizza, I. Duo, P. A. Michaud, G. Cerisola, and C. Comninellis, Electrochem. Solid State Lett., **3**, 429 (2000).
6. I. Duo, P. A. Michaud, W. Haenni, A. Perret, and C. Comninellis, Electrochem. Solid State Lett., **3**, 325 (2000).
7. R. Uchikado, T. N. Rao, D. A. Tryk and A. Fujishima, Chem. Lett., 144 (2001).
8. K. Honda, M. Yoshimura, T. N. Rao, D. A. Tryk, A. Fujishima, K. Yasui, Y. Sakamoto, K. Nishio and H. Masuda, J. Electroanal. Chem., submitted.