Boron Doped Diamond Electrodes for Trace Metal Detection

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Highly boron doped diamond (BDD) electrode films grown on silicon substrates were used to detect mercury, lead and cadmium in laboratory made as well as coal power plant flue gas samples (Hg only). We have successfully detected ppb levels of mercury, lead and cadmium metal ions in standard solutions. Anodic differential pulse voltammetric technique has been used for detecting Pb, Cd, and Hg concentrations up to (10^{-9} M). Further, the presence of ionic species such as chloride and nitrate also influence the sensitivity especially for mercury. Presence of chloride ions improves the sensitivity than nitrates indicating the formation of mercurous chloride which affects the reproducibility. We have found the sensitivity and reproducibility can be improved by gold co-deposition method. Feasibility of BDD electrodes for trace mercury detection and calibration plots will be reported.

BDD films were deposited on conductive silicon substrates by use of microwave-assisted plasma-enhanced chemical vapor deposition. A specially designed O-ring-type three-electrode electrochemical cell was used. The metal solutions were prepared with analytical grade reagents. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and counter electrodes, respectively. A Hokuto-Denko Model HZ-3000 potentiostat was used for all of the electrochemical measurements.

Cyclic voltammetric scans for millimolar concentrations of Hg at a BDD electrode revealed significant anodic oxidation and cathodic reduction peaks at 0.4V vs. SCE and 0.32V vs. SCE respectively in high pure nitrate electrolyte. Figure 1a and 1b show the CVs for the high-purity mercuric nitrate as well as the effect of the addition of 0.14% chloride. As you can see the addition of chloride significantly shifts the anodic peak to 0.18V vs. SCE and as well as the peak current. Figure 1. Cyclic voltammetry for $Hg(NO_3)_2$ solution (2 ×10^{-5} M) in 0.1 M KNO_3 (pH = 1) electrolyte a) without b) with the addition of 0.14% KCl. The mercury stripping peak appeared at 0.4 V vs. SCE (a) is shifted to 0.18V vs. SCE (b). This clearly explains the effect of chloride addition. The peak appearing at 0.18V vs. SCE is due to the calomel formation.

However for example, if an anion, e.g., chloride, that forms an insoluble mercury compound is present, the reversible potential will be shifted substantially in the negative direction:

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$$
$$E^0 = +0.27 \text{ V vs. SHE}, +0.03 \text{ V vs. SCE} \quad (1)$$
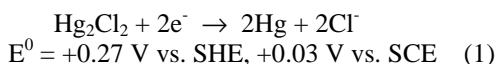
For comparison with glassy carbon (GC), we have carried DPASV on both BDD and GC electrodes. Figure 2 shows clear evidence for the observation of the mercury stripping peak at BDD electrode surface whereas no peak was observed for the GC.

It should be noted that the important observation is the oxidation process that involves the formation of highly insoluble product Hg_2Cl_2 (calomel) which can affect the reproducibility of the experiment unless the calomel is cleaned from the surface. In order to avoid this problem, we followed a new approach in which 1-3 ppm amount of gold was co-deposited on the BDD electrode surface simultaneously.

We have shown successfully, the feasibility of BDD electrodes as electrochemical sensors for the analysis of mercury and other trace metals. The effect of nitrate and chloride ions is very clearly evident from the cyclic voltammetric analysis. The presence of chloride enhances the stripping peak currents and on the other hand it forms insoluble calomel at the surface of the electrode. In this regard, we have successfully utilized a gold co-deposition method. Figure 3 shows the calibration plot for 2-10 ppb of mercury in the presence of 3 ppm of gold standard solution. All these results will be discussed.
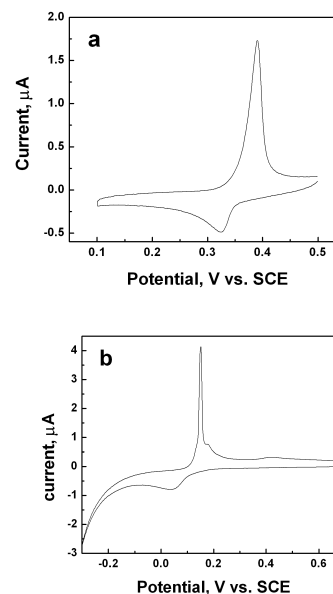

Figure 1. Cyclic voltammetry for $Hg(NO_3)_2$ solution (2 ×10^{-5} M) in 0.1 M KNO_3 (pH=1) a) without b) with the addition of 0.14% KCl. The mercury stripping peak at 0.4 V vs. SCE (a) is shifted to 0.18V vs. SCE (b).
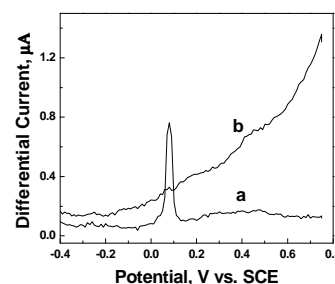

Figure 2. DPV for curves for $Hg(NO_3)_2$ solution (6.4 ×10^{-7} M) in 0.1 M KNO_3 (pH=1) electrolyte for a) diamond b) glassy carbon electrodes.
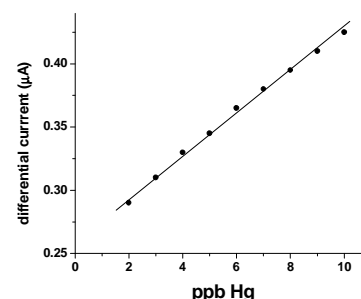

Figure 3. Calibration plot for mercury with 3 ppm gold co-deposition.