

Abrasive Stripping Voltammetry at Polycrystalline Diamond Electrodes

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We present a new approach for the electrochemical fingerprinting of a wide range of materials using abrasive differential pulse stripping voltammetry (AbrDPSV) at boron-doped diamond electrodes. In this study, the abrasive stripping voltammetry of metallic Pb and Fe samples and of a brass alloy sample at diamond electrodes was carried out. The results obtained with brass indicate that the differential pulse voltammogram is an electrochemical fingerprint of the material and can be used to characterize possible interactions between the constituent metals as well as to reveal information on the chemical composition.

The extreme hardness, low coefficient of friction and unmatched mechanical strength of diamond render it highly effective for cutting and abrasion.^{1,2} In this Letter, we demonstrate the superior qualities of diamond as an electrode material for electroanalytical techniques involving abrasive sampling. Abrasive stripping analysis is a relatively new technique developed for the qualitative and quantitative analysis of solid materials. Previous studies have employed carbon-based electrodes, for example, wax-impregnated graphite electrodes, for the analysis of soft alloys, minerals and synthetic inorganic compounds.³⁻⁵ The range of materials that can be sampled is limited by the hardness and friction properties of carbon-based electrodes. The present approach, employing conductive, boron-doped polycrystalline diamond film electrodes, can be used with practically any type of metal, alloy, mineral or compound.

The principle behind abrasive stripping voltammetry (AbrSV) and abrasive differential pulse voltammetry (AbrDPV) involves the mechanical transfer of extremely small amounts of solid materials, by abrasion, from the bulk material to the electrode surface. The deposited material can be simply analyzed by choosing an appropriate voltammetric technique and electrolyte. Polycrystalline diamond, whose deposited surface is rough, consisting of microcrystallites of the order of 1-10 μm , is well-suited for this type of analysis, not only due to its superior abrasive properties but also due to its wide potential window, low background current, and extreme chemical stability. The latter characteristic also enables diamond to be able to withstand large-amplitude potential pulses.⁶

For the present experiments, highly boron-doped polycrystalline diamond thin films were deposited on conductive silicon wafers using microwave-assisted plasma chemical vapor deposition. The deposited films were highly crystalline, as determined by Raman. A specially designed O-ring-type three-electrode electrochemical cell was used for the electrochemical measurements. The electrolyte (0.1 M KCl, adjusted to pH 1 with HCl) was prepared from analytical reagent grade chemicals. A Hokuto Denko Model HZ 3000 potentiostat was used to carry out the electrochemical measurements. Our present preliminary experiments were carried out with pure Pb (99%) and Fe (99.3%) metal samples and a brass alloy sample (65% Cu, 35% Zn, Nilaco). Prior to the abrasive stripping measurements, the diamond film sample ($\sim 1\text{ cm} \times 1\text{ cm}$) was simply rubbed against

the metal sample two or three times by hand.

Figure 1 represents the anodic stripping peak for Pb trapped on the diamond electrode in 0.1 M KCl (pH 1) after simple abrasion of the metal sample. The stripping peak for Pb appeared at -0.48 V vs. SCE. Similar measurements were carried out for Fe and brass (Figures 2 and 3, respectively). In Figure 2, the stripping peak at $+0.8\text{ V}$ is clear. The peak width for Fe in this figure ($\sim 0.3\text{ V}$ at half-height) is much greater than that for Pb in Figure 1 ($\sim 0.1\text{ V}$). Such variations of peak width have also been observed by Scholz et al.; narrower peaks are most likely due to facile dissolution in the particular electrolyte.³ As long as the conditions are the same for repeated experiments, i.e., fresh diamond surface, same pulsing conditions and electrolyte, the stripping voltammograms are highly reproducible.

The stripping behavior for brass particles trapped on the diamond film is shown in Figure 3. Three peaks are observed, at -0.85 V , -0.02 V and $+0.42\text{ V}$ vs. SCE. Based on the stripping behavior of the individual metals, the peak at -0.85 V vs. SCE can be assigned to the oxidation of Zn, while the peaks at -0.02 V and 0.42 V vs. SCE can be assigned to the two sequential one-electron oxidation steps for Cu, which occur due to stabilization of Cu^+ by chloride.⁷ In this case, the peak potentials for the alloy are relatively close to those for the individual metals, e.g., $\pm 70\text{ mV}$ in the case of the Cu peaks. For other alloys, this is not always the case.^{8,9}

Thus, the stripping behavior can represent a fingerprint

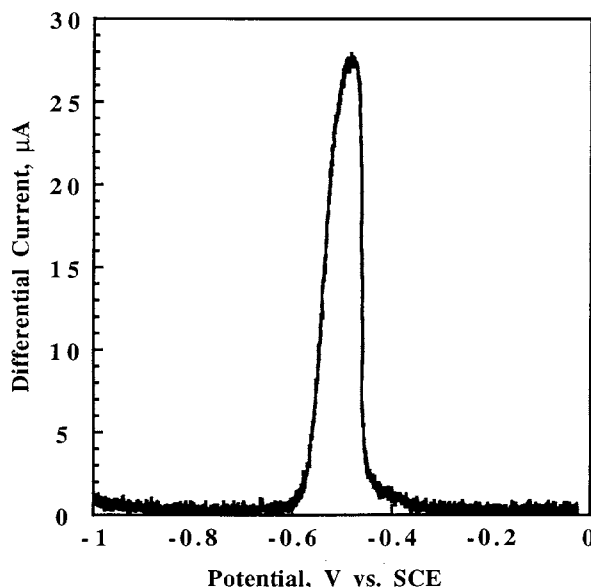


Figure 1. Abrasive differential pulse anodic stripping voltammogram (AbrDPASV) for Pb metal, carried out in 0.1 M KCl (pH 1). Potential sweep rate, 20 mV s^{-1} ; pulse amplitude, 25 mV ; electrode area exposed to the solution, 0.4 cm^2 .

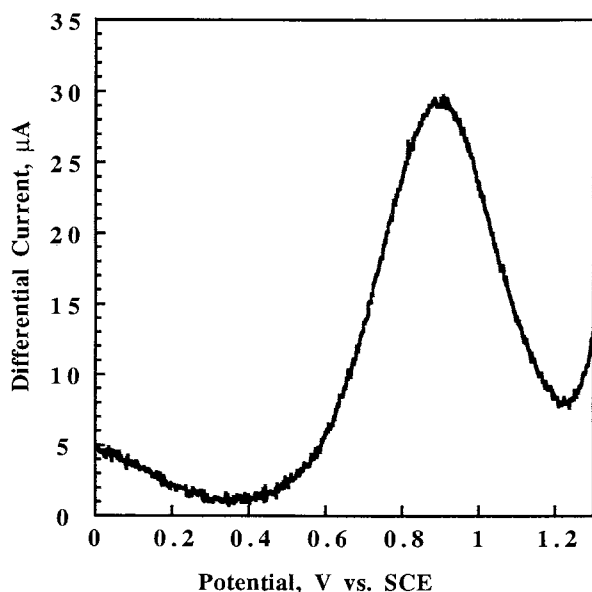


Figure 2. AbrDPASV for Fe metal, carried out under the same conditions as in Figure 1.

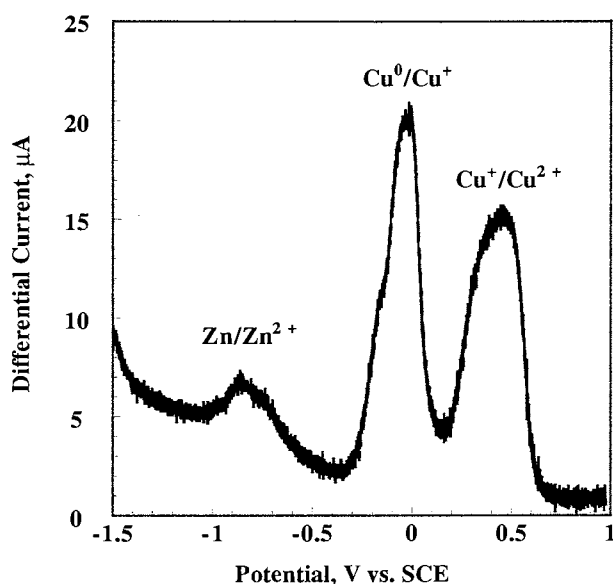


Figure 3. AbrDPASV for brass (65% Cu, 35% Zn), carried out under the same conditions as in Figure 1.

for the particular alloy, providing information on the types of interactions between the constituent metals. However, as long as the interactions are not too strong, this method can be used to obtain a semiquantitative analysis for the alloy composition. For example, using wax-impregnated carbon electrodes, Scholz et al.

examined a series of Pb-Sb alloys, finding monotonic increases in the stripping peak heights with increasing metal concentration.^{10,11} This fingerprint technique can be highly useful in identifying various types of alloys, for example in industrial or forensic applications. In addition, it is attractive in terms of rapid identification (less than one minute after mounting the electrode). Preliminary results for the abrasive stripping of stainless steels, superalloys, and minerals are also encouraging.¹² Experiments dealing with the identification of various types of alloys and compounds are now in progress.

The aim of this Letter is to demonstrate for the first time the use of polycrystalline diamond electrodes in abrasive stripping analysis. Polycrystalline diamond is perhaps the only material that can be used for the abrasion of very hard materials but is also well suited for sampling all types of solids. Thus, the abrasive stripping technique with diamond can be applied widely in the rapid identification of materials and compounds in a number of different fields, including environmental pollution, metallurgy, semiconductors, pharmaceuticals, forensics and agriculture.

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