

The Electrochemistry of Boron-Doped Diamond Films on Single Crystal Diamond in Li⁺-Based Solid Polymer Electrolyte in Ultrahigh Vacuum

Lin-Feng Li,[†] Dana Totir,[†] Barry Miller,[†] Gary Chottiner,[‡] Alberto Argoitia,[§] John C. Angus,[§] and Daniel Scherson^{*,†}

Departments of Chemistry, Physics, and Chemical Engineering, Case Western Reserve University Cleveland, Ohio 44106

Received April 28, 1997

Hydrogen-terminated boron-doped diamond (BDD) has emerged as a unique electrode material displaying, among other properties, extraordinary low reactivity in aqueous electrolytes^{1,2} over a wide potential range.² Electrochemical studies of BDD in nonaqueous solvents would offer an even larger voltage window and, thereby, the possibility of investigating an expanded array of reactions without interference from processes derived from electrolyte decomposition.

This paper presents cyclic voltammetry of hydrogen-terminated BDD films, grown on diamond macles,³ in LiClO₄-poly(ethyleneoxide)(PEO) and LiI/PEO solid polymer electrolytes. Diamond is an ideal substrate material as its lack of chemical reactivity may avoid ambiguities in the interpretation of the electrochemical data derived from reactions involving other supports, which either form alloys, such as silicon,⁴ or promote lithium underpotential deposition.⁵ These experiments were conducted at temperatures of ca. 60 °C in ultrahigh vacuum (UHV)⁶ with *in situ* pre-electrolysis to minimize problems with impurities. As will be shown, the voltammetry in the first and subsequent cycles is characteristic of only Li bulk deposition and stripping, with very small featureless negative background currents attributable to the kinetically hindered reduction of perchlorate ion and/or PEO in the LiClO₄/PEO electrolyte.

Boron-doped diamond (BDD) films (ca. 10²⁰ B atom/cm³) were grown on clean, unpolished diamond macles by the hot filament method, using a source gas mixture of overall composition 0.5% CH₄ and 2 × 10⁻³% trimethyl boron in H₂. Additional details of the growth method are given elsewhere.^{7,8}

[†] Department of Chemistry.

[‡] Department of Physics.

[§] Department of Chemical Engineering.

(1) (a) Pleskov, Y.; Sakharova, A.; Krotova, M.; Bouilov, L.; Spitsyn, B. *J. Electroanal. Chem.* **1987**, *228*, 19. (b) Sakharova, A.; Sevast'yanov, A.; Pleskov, Y.; Templitskaya, G.; Surikov, V.; Voloshin, A. *Electrokhimiya*, **1991**, *27*, 239. (c) Swain, G. M.; Ramesham, R. *Anal. Chem.* **1993**, *65*, 345. (d) Alehashem, S.; Chambers, F.; Strojek, J. W.; Swain, G. M. *Anal. Chem.* **1995**, *67*, 2812. (e) Sakharova, A.; Pleskov, Y.; Quarto, F. D.; Piazza, S.; Sunseri, C.; Teremetskaya, I. G.; Varnin, V. *J. Electrochem. Soc.* **1995**, *142*, 2704. (f) Pleskov, Y.; Varnin, V. P.; Teremetskaya, I. G.; Churikov, A. V. *J. Electrochem. Soc.* **1997**, *144*, 175.

(2) (a) Tenne, R.; Patel, K.; Hashimoto, K.; Fujishima, A. *J. Electroanal. Chem.* **1993**, *347*, 409. (b) Martin, H. B.; Argoitia, A.; Angus, J. C.; Anderson, A. B.; Landau, U. In *Applications of Diamond Films and Related Materials: Third International Conference*; Feldman, A., Tzeng, Y., Yarbrough, W. A., Yoshikawa, M., Murakawa, M., Eds.; NIST Special Publication 885, 91, National Bureau of Standards and Technology: Gaithersburg, MD, 1995. (c) Martin, H. B.; Argoitia, A.; Landau, U.; Anderson, A. B.; Angus, J. C. *J. Electrochem. Soc.* **1996**, *143*, L133. (d) Vinokur, N.; Miller, B.; Avyigal, Y.; Kalish, R. *J. Electrochem. Soc.* **1996**, *143*, L238.

(3) Macles are twinned, flat triangular diamond platelets, with the twin plane parallel to the two triangular (111) faces.

(4) Holmes, R. W. In *Proceedings of the ECS Symposium on Lithium Batteries*; Dey, A. N., Ed.; Pennington, NJ, 1994; 323.

(5) (a) Aurbach, D.; Daroux, M.; Faguy, P.; Yeager, E. *J. Electroanal. Chem.* **1991**, *297*, 225. (b) Mo, Y.; Gofar, Y.; Hwang, E.; Scherson, D. A. *J. Electroanal. Chem.* **1996**, *409*, 87.

(6) Gofar, Y.; Barbour, R.; Luo, Y.; Tryk, D. A.; Scherson, D. A.; Jayne, J.; Chottiner, G. *J. Phys. Chem.* **1995**, *99*, 11739; **1995**, *99*, 11797.

(7) Argoitia, A.; Angus, J. C.; Wang, L.; Ning, X. I.; Pirouz, P. *J. Appl. Phys.* **1993**, *73*, 4305.

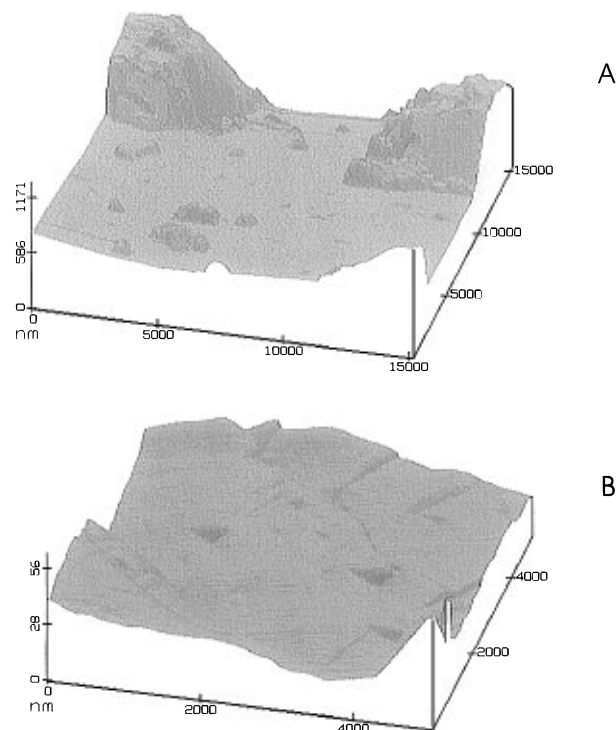


Figure 1. Atomic force microscopy (AFM) images of boron-doped diamond on diamond (BDD/D) in two different magnifications: panel A. 15 μm × 15 μm, panel B. 5 μm × 5 μm.

During deposition, macles were kept at a temperature of 800 °C, placed 0.5 cm away from four hot (2000 °C) tungsten filaments, and rotated at 1/3 rpm to improve homogeneity. Films obtained after 7–24 h deposition displayed a sharp Raman scattering peak at 1332 cm⁻¹,⁹ characteristic of diamond, with no evidence of graphitic, sp² carbon (ca. 1580 cm⁻¹). Atomic force microscopy (AFM) images of BDD films recorded in air (Nanoscope II, Digital Instruments) using Si₃N₄ microfabricated cantilevers with a force constant of 0.58 N/m revealed rather large protrusions evenly distributed on a fairly smooth background (see panels A (15 μm × 15 μm) and B (5 μm × 5 μm)) in Figure 1. These prominent features are believed to arise from penetration twins, which are a common occurrence when growing diamond on (111) surfaces.¹⁰

A large Ni foil (1 cm × 1.5 cm, Alfa, 99.995% purity) with a triangular opening slightly smaller than the dimensions of the triangle-shaped macle (2.5 mm per side, see Figure 2) was used to mount the BDD on diamond (BDD/D) specimens onto a specially designed stainless steel holder.¹¹ This holder is used to transfer samples in and out of a UHV chamber equipped with both preparation (thermal annealing) and characterization (Auger electron spectroscopy, AES) capabilities.⁶ The AES spectra of BDD/D, (*i*_{beam} = 10 μA, electron beam diameter = 1 mm) showed, after annealing in UHV at 700 °C for 1 h, a pre-edge carbon AES peak at 268 eV, characteristic of diamond,¹² with only a very small trace of oxygen (see Figure 3) and as expected no traces of B, for which the bulk concentration would be less than 0.1%.

(8) Argoitia, A.; Martin, H.; Rozak, E. J.; Landau, U.; Angus, J. C. In *Diamond for Electronic Applications*; Dreifus, D. L., Collins, A., Humphrey, T., Das, S. K., Pehrsson, P., Eds. *Mat. Res. Soc. Symp. Proc.* **416**, 349, MRS, Pittsburgh, PA, 1996.

(9) Knight, D. S.; White, W. B. *J. Mater. Res.* **1988**, *4*, 385.

(10) Angus, J. C.; Cassidy, W. D.; Wang, L.; Wang, Y.; Evans, E.; Kovach, C.; Tamor, M. A. *Mat. Res. Soc. Symp. Proc.* **383**, 45, MRS, Pittsburgh, PA, 1995.

(11) Chottiner, G. S.; Jennings, W. D.; Pandya, K. I. *J. Vac. Sci. Technol.* **1987**, *5A*, 2970.

(12) Pepper, S. V. *Appl. Phys. Lett.* **1981**, *38*, 344.

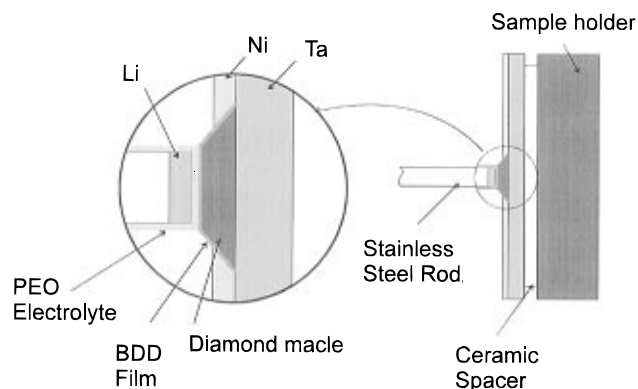


Figure 2. Schematic diagram of the experimental arrangement for electrochemical measurements of hydrogen terminated boron-doped diamond (BDD) films in a Li^+ -based solid polymer electrolyte in ultrahigh vacuum (UHV).

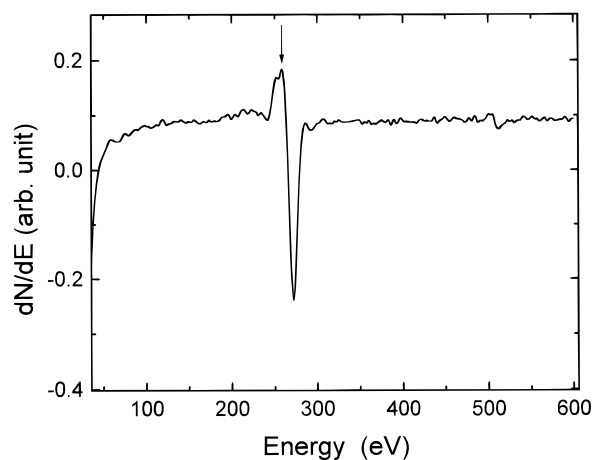


Figure 3. Auger electron spectra (AES) of a hydrogen terminated boron-doped diamond film supported on a diamond macle (see text for details).

The PEO/LiClO₄ (or LiI) electrolyte films were prepared from ultrapurified materials according to procedures specified elsewhere.⁶ A description of the Li/Li⁺-counter-reference [C/R] electrode/PEO electrolyte assembly, the methodology involved in the transfer and formation of the electrochemical cell in UHV as well as other experimental details are given in the original literature.⁶ The PEO/LiClO₄ (or LiI) electrolyte films were pre-electrolyzed *in situ* (in UHV), prior to placing the assembly in contact with the AES-characterized BDD/D films. To this end, the assembly (cross-sectional area: 0.9 mm²) was first pressed against the Ni foil, and the temperature then raised to ca. 55 °C. Subsequently, a series of linear potential scans was performed between 1.8 and 0.0 V vs Li/Li⁺[C/R] followed by constant polarization at 50 mV vs Li/Li⁺[C/R] for 40 min. The residual currents found toward the end of this last cleaning stage were found to be much higher for LiClO₄ (1.7 μA/cm²) compared to LiI-based electrolytes (negligible), suggesting that perchlorate ion undergoes reduction at these very negative potentials.

The cell was dislodged from the Ni foil at about room temperature and placed in contact with the substrate in question. The first cyclic voltammogram of BDD/D in PEO/LiClO₄ recorded at 60 °C and 5 mV/s showed a virtually featureless trace in the region 0.05–2.1 V vs Li[C/R], down to the most negative end (see dotted line, in Figure 4). Although the current during the negative-going scan appears larger than that observed during the positive counterpart, especially at the more negative limits, the overall shapes of these curves are consistent with an increase in the interfacial capacity as the potential becomes more

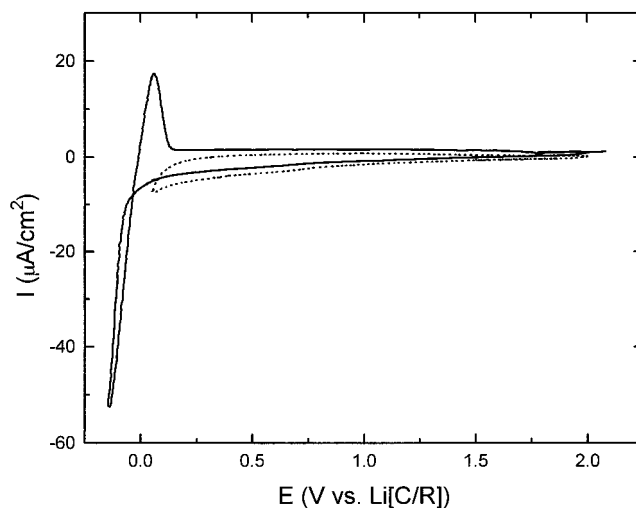


Figure 4. First (dotted line) and a subsequent (solid line) cyclic voltammograms of hydrogen terminated boron-doped diamond film supported on a diamond macle in PEO/LiClO₄ acquired in ultrahigh vacuum (UHV) at ca. 60 °C. Scan rate: 5 mV/s (see text for details).

negative, to the extent that faradaic contributions can be excluded. For BDD films grown on Si, the interfacial capacity in aqueous media, in a much more positive potential range, decreases monotonically as the potential becomes more negative.¹³ Taken together, these results suggest that the interfacial capacity of BDD may exhibit a minimum at a potential between 2.5 and 3.5 V vs Li/Li⁺. The same qualitative behavior has been found for the basal plane of graphite both in aqueous¹⁴ and nonaqueous electrolytes,¹⁵ where the minimum has been ascribed to the minimum in the density of states near the Fermi level.¹⁵ It must be stressed, however, that a quantitative determination of actual interfacial capacities can be made most reliably employing impedance spectroscopy techniques in a suitable cell configuration. These measurements are in progress in this laboratory and will be reported in due course.

During a subsequent cycle, the negative potential limit was extended to −0.3 V vs Li[C/R] (see solid line, Figure 4), yielding features characteristic of those expected for the deposition and stripping of bulk Li with only very minor contributions due to the kinetically hindered reduction of PEO and perchlorate ion.

The results presented in this work identify BDD as the only electrode material examined to date which does not form alloys with Li or promote Li underpotential deposition. Furthermore, the experimental conditions under which these measurements were performed have made it possible for the first time to electrodeposit and strip metallic lithium directly from the electrolyte under conditions which minimize the formation of films due to interfacial reactions involving the salt, solvent, and/or adventitious impurities. Such a strategy is expected to open new prospects for the study of a wide variety of reduction reactions at very negative potentials in the absence of significant contributions due to other parasitic processes.

Acknowledgment. This work was supported by the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.

JA971322E

(13) Swain, G. M. Private communication.

(14) (a) Randin, J. P.; Yeager, E. *J. Electrochem. Soc.* **1971**, *118*, 712 (b) Randin, J. P.; Yeager, E. *J. Electroanal. Chem.* **1972**, *36*, 257; **1975**, *58*, 313.

(15) Gerischer, H.; McIntyre, R.; Scherson, D.; Storck, W. *J. Phys. Chem.* **1987**, *91*, 1930 and references therein.