Published in final edited form as:

J Chromatogr A. 2008 November 14; 1210(2): 154–159. doi:10.1016/j.chroma.2008.09.069.

Electrochemically modulated liquid chromatography using a boron-doped diamond particle stationary phase

Grace W. Muna^a, Vernon M. Swope^b, Greg M. Swain^b, and Marc D. Porter^{a,*}

^a Departments of Chemistry, Chemical Engineering and Bioengineering, University of Utah, 383 Colorow Road, Salt Lake City, UT 84108, USA

^b Department of Chemistry and the Fraunhofer Center for Coatings and Laser Applications, Michigan State University, 320 Chemistry Building, East Lansing, MI 48824, USA

Abstract

This paper reports on preliminary tests of the performance of boron-doped diamond powder (BDDP) as a stationary phase in electrochemically modulated liquid chromatography (EMLC). EMLC manipulates retention through changes in the potential applied (E_{appl}) to a conductive packing. Porous graphitic carbon (PGC) has routinely been utilized as a material in EMLC separations. Herein the utility of BDDP as a stationary phase in EMLC was investigated and its stability, both compositionally and microstructurally, relative to PGC was compared. The results show that BDDP is stable over a wide range of E_{appl} values (i.e., -1.2 to $+1.2$ V vs. Ag/AgCl, sat'd NaCl). The data also reveal that electrostatics play a key role in the adsorption of the aromatic sulfonates on the BDDP stationary phase, and that these analytes are more weakly retained in comparison to the PGC support. The potential for this methodology to provide a means to advance the understanding of molecular adsorption and retention mechanisms on carbonaceous materials is briefly discussed.

Keywords

Electrochemically modulated liquid; chromatography (EMLC); Boron-doped diamond powder (BDDP); Porous graphitic carbon (PGC); Applied potential (E_{appl}); Stationary phase

1. Introduction

Carbonaceous packings (e.g., porous graphitic carbon, PGC) have been used in a wide variety of liquid chromatography separations [1–9]. Carbon-based materials differ microstructurally and chemically from commonly used reversed-phases. From a retention perspective, carbonaceous packings have a π -electron selectivity that is superimposed on classical reversed-phase characteristics [1–9].

Electrochemically modulated liquid chromatography (EMLC) is a separation technique that manipulates retention by changes in the potential applied (E_{appl}) to a conductive stationary phase. In other words, the packing functions as both a stationary phase and a working electrode in a chromatographic column designed to function as a three-electrode electrochemical cell [8,10–23]. Past work has shown that carbon materials, like PGC and glassy carbon (GC) [13], are viable stationary phases for EMLC and there are several

intriguing examples in which these packings have been coated with conductive polymers, like polyvinylferrocene and polypyrrole [24–26]. Recent work has also demonstrated that, by monitoring the influence of E_{appl} on the capacity factor (k') for analyte retention, a chromatographic tool for the examination of electrosorption phenomenon can be devised [10,11,21].

Stationary phases in EMLC must possess several properties: high surface area, compositional and microstructural stability, and high electrical conductivity. Note that stability must also include the inertness of the packing material over a wide range of E_{appl} . To date, the greatest degree of success in EMLC has been achieved using PGC. This material has a high surface area (120 m²/g) [9,10] and a high inherent electrical conductivity (≥ 100 S/cm) [22], which is requisite for functioning as a working electrode. PGC is also available as micron-sized particles with a narrow dispersity. However, the tendency of this material to slowly oxidize at high anodic potentials ($> +0.5$ V) over a few days of continuous use can prove problematic with respect to compositional stability and, therefore, retention reproducibility [27,28]. This oxidation not only alters the surface chemistry of the packing but also can change its microstructure and electronic properties (i.e., density of states), both of which can have a significant influence on retention.

This paper describes initial tests of an alternative carbonaceous packing for EMLC: boron-doped diamond powder (BDDP). The conducting powder was formed by overcoating insulating diamond powder with a layer of boron-doped diamond [29,30]. In this core-shell approach, a boron-doped microcrystalline diamond layer is deposited on 8–12 μm diamond powder particles using microwave chemical vapor deposition (CVD) and a conventional CH_4/H_2 source gas mixture. The electrical conductivity is controlled by the doped-diamond layer (carrier concentration and mobility) rather than by an adventitious non-diamond sp^2 carbon impurity phase. With respect to GC-based materials, BDDP is more hydrophobic, is much more compositionally and morphologically stable, exhibits a wider potential window before the onset of solvent-electrolyte electrolysis in conventional aqueous media, and is less prone to surface fouling [27–35].

At a more detailed level, electrically conducting diamond thin films can be formed with a resistivity as low as 0.01 $\Omega\text{-cm}$ by introducing dopants, such as boron, into the source gas mixture. Doping produces a highly conductive material that functions effectively as a working electrode. When deposited on a suitable substrate, these coatings are chemically inert and dimensionally stable in aggressive chemical (e.g., high temperature and extremes in pH) and electrochemical (e.g., large anodic and cathodic potentials and high current densities) environments [36–38]. Indeed, reports over the past decade have established the superior morphological and microstructural stability of diamond thin films with respect to several sp^2 carbon materials, including GC and highly oriented pyrolytic graphite [38–43]. Recent work has also investigated the electrochemical stability of BDDP [29]. In that report, BDDP was anodically polarized at +1.6 V (vs. Ag/AgCl sat'd NaCl) at room temperature for 1 h with no apparent changes in microstructure, as determined with scanning electron microscopy (SEM), or in electrical conductivity, as measured by a four-point conductivity probe. By contrast, SEM images for GC particles were diagnostic of marked morphological changes (e.g., pitting) [29].

The goal of this preliminary work was to prepare columns packed with BDDP and to examine the possibility of probing molecular interactions at this material via retention changes with respect to E_{appl} . Experiments with BDDP were carried out to: (1) characterize its microstructure and electrical conductivity; (2) assess its utility in the reproducible manipulation of separations by using a mixture of aromatic sulfonates (ASFs) via changes in

E_{app} ; and (3) to compare its retention properties with respect to that of PGC. This paper reports these initial findings.

2. Experimental

2.1. Boron-doped diamond growth and characterization

Prior to deposition of the boron-doped diamond coating, 8–12 μm diameter diamond powder (8–12 μm RVM, Diamond Innovations, Worthington, OH) was cleaned in aqua regia (concentrated hydrochloric and nitric acids, 3:1) for 30 min, and then in 30% hydrogen peroxide for 30 min. The particles were subsequently rinsed with ultrapure water, isopropyl alcohol, and acetone. The boron-doped diamond overlayer was formed by microwave plasma-assisted CVD (1.5 kW, 2.45 GHz, Seki-ASTeX, Tokyo Japan). The specific surface area, measured by the Brunauer-Emmett-Teller (BET) method, was 1.0 m^2/g . Procedurally, a 50-mg sample of diamond powder was spread out on a silicon wafer and mounted in the reactor. The deposition was carried out using a source gas mixture of 1% CH_4/H_2 and 10 ppm B_2H_6 at a microwave power of 1.0 kW, a pressure of 45 Torr, and deposition time of 4 h.

The crystallinity of the coated diamond particles was evaluated using powder X-ray diffraction analysis (XRD, 1.54 $\text{\AA}$, Rigaku Rotaflex RTP300 RC) by scanning 2θ from 30° to 100° . The microstructure of the particles was examined by Raman spectroscopy. Raman spectra were recorded in a backscattering collection geometry using a 100-mW, Melles Griot CW argon ion laser at 514.5 nm, an Olympus BH-2 microscope assembly, and a Spex 1250 spectrograph (600 grooves/mm holographic grating). The detector was a Horiba Jobin Yvon Symphony 2000 $\times$ 800 CCD with a pixel size of 15 μm . Spectra were collected with an incident power density of 1.4 kW/cm^2 . The spectrometer was calibrated using the first-order phonon peak of cubic diamond at 1332.6 cm^{-1} . The powder morphology of the particles was probed by field-emission scanning electron microscopy (FE-SEM, JSM-6300F, JEOL, Ltd., Tokyo, Japan).

Electrical resistance measurements of the particles were made before and after overcoating with conducting diamond using an in-house fabricated test fixture. The measurements were carried out by placing a fixed quantity ($\sim 30\text{ mg}$) of the powder between two metal plates and measuring the contact-to-contact resistance with an ohmmeter. The top metal plate was attached to a copper rod (0.114 cm^2), which fit inside the glass tube used to contain the powder sample between the two plates. A 240-g weight was placed on the top metal plate to ensure that a constant force was applied during the measurement. The powder resistance was calculated by using Ohm's law as a function of three different dc currents (± 6 , ± 10 , and $\pm 20\text{ mA}$). All powder resistances prior to doped diamond growth were $>40\text{ M}\Omega$. Ohmic behavior was observed after coating. The electrical conductivity of the BDDP was $2.4\text{ S}/\text{cm}$.

2.2. Chromatographic column construction

The design of the EMLC column has been described elsewhere[11]. Briefly, the column consists of a Nafion cationic-exchange membrane in a tubular form (Perma Pure) that is placed inside a porous stainless steel cylinder. The Nafion membrane serves as a container for the stationary phase. The stainless steel cylinder prevents the deformation of the Nafion tubing under the high pressure of chromatographic flow and acts as the auxiliary electrode in a three-electrode electrochemical cell. BDDP was dispersed in a dibromomethane/acetonitrile (1:1, v/v) slurry and then packed in an EMLC column at 6000 psi using methanol for $\sim 30\text{ min}$. The same column and packing procedures were used to prepare a PGC (5- μm particles) column. The length and the inner diameter of the column were 7.8 and 0.3 cm, respectively. The actual surface area of the BDDP and PGC stationary phase is 1.0 and 18 m^2 , respectively. These values were calculated based on the BET adsorption

measurements ($1.0 \text{ m}^2/\text{g}$ for BDDP and $120 \text{ m}^2/\text{g}$ for PGC), and the amount of material loaded into the column (1.0 g for BDDP and 0.15 g for PGC).

2.3. Instrumentation

Chromatographic experiments were performed using an Agilent 1200 Series system, equipped with solvent cabinet, autosampler, quaternary pumping system, and UV/Vis diode array detector. This unit was interfaced to a Pentium IV 600 MHz computer, equipped with Chemstation software for control of injection sequences, data acquisition, and flow rate parameters. The potential of the working electrode/chromatographic packing was controlled using an AMEL Instruments Model 2055 high power potentiostat (Milan, Italy).

2.4. Mode of operation

After packing, both EMLC columns were equilibrated with degassed mobile phase (0.10 M LiClO_4) at a flow rate of 0.40 mL/min until a stable detector response was obtained ($\sim 30 \text{ min}$). After each change in E_{appl} , the system was allowed to achieve a stable baseline, which typically required $\sim 10 \text{ min}$ for a BDDP-packed column and $\sim 30 \text{ min}$ for a PGC-packed column.

Injection volumes were set at $5 \mu\text{L}$, and injections of the analyte mixtures were repeated four times at each value of E_{appl} . Individual injections of each analyte were performed in triplicate for peak identification and for retention time determination when elution bands overlapped. Injections of water ($5 \mu\text{L}$) were used to determine the void volume of the column for calculation of k' . The void volume represents the interstitial (both interparticle and intraparticle) volume of the column [44]. The void volume was 0.28 and 0.41 mL for the BDDP- and PGC-packed column, respectively. The absorbance of all analytes was monitored at 210 nm . All experiments were performed at room temperature.

2.5. Chemicals and reagents

Sodium 4-toluenesulfonate (TS), disodium 1,3-benzenedisulfonate (BDS), sodium benzenesulfonate (BS), dibromomethane, lithium perchlorate, and acetonitrile were purchased from Aldrich. Disodium 1,5-naphthalenedisulfonate (NDS) was acquired from Eastman Kodak. All chemicals were used as received. All aqueous solutions were prepared with HPLC grade water.

3. Results and discussion

3.1. Material characterization

Fig. 1 presents an SEM image of BDDP. Though clearly not ideal from a separation perspective, the image reveals that the particles are irregularly shaped, with sizes ranging between ~ 8 and $12 \mu\text{m}$. The particles possess sharp jagged edges, which hinder efficient packing. The small spots observed on some particles are probably due to the secondary nucleation of diamond on the much larger particles.

The crystal structure of the BDDP was investigated by XRD. Fig. 2 shows an XRD spectrum for the powder sample. Three reflections are observed at 2θ values of 43.9° , 75.5° , and 91.5° , and are assigned to the $(1\ 1\ 1)$, $(2\ 2\ 2)$, and $(3\ 1\ 1)$ crystallographic planes of cubic diamond, respectively. This conclusion is based on a comparison with a reference diamond material: ASTM 6-0675 [34]. The diffraction data reveal that the bulk film structure is sp^3 -bonded carbon.

Raman spectroscopy was used to examine this material because of its sensitivity to the microstructure (sp^2 and sp^3 carbon bonding), boron-doping level, and residual stress

(intrinsic and thermal) [45–48]. Fig. 3 presents a Raman spectrum for the BDDP. The spectrum shows the distinctive first-order diamond phonon peak at 1330 cm^{-1} . The diamond particles are free of detectable sp^2 non-diamond carbon impurities, as indicated by the absence of scattering between 1350 and 1580 cm^{-1} . The basis of this conclusion can be qualified by recognizing that the scattering cross-section for graphite is ~ 50 times larger than that for diamond at visible excitation wavelengths [45,46].

3.2. Retention as a function of E_{appl}

The influence of E_{appl} on the retention of ASFs has previously been examined on both GC and PGC [10–14]. The change in retention generally follows predictions based on electrostatic forces but varies slightly between solutes. These differences reflect a complex mixing of donor-acceptor, dispersive, and solvophobic interactions between the solute and the solid phase [49]. Past work has also found that, if present, the small amounts of oxygen-containing surface groups (e.g., carboxylic acids, quinones, and phenols) can contribute to retention through dipole and hydrogen bonding interactions [50–55].

The importance of the above interactions is likely to differ at BDDP, which is devoid of an extended π -bonding system, and has a hydrogen-terminated surface. Termination renders the surface nonpolar and, therefore, highly hydrophobic [56–59]. In other words, chemisorbed hydrogen replaces carbon-oxygen functionalities on the surface during hydrogenation [60,61]. Oxygen-containing groups can form at surface sites (both diamond and non-diamond carbon), and are usually present at low levels in high-quality hydrogen-terminated diamond thin films [29].

The effect of E_{appl} on the separation of a four-component ASF mixture (BDS, BS, TS, and NDS) is presented in Fig. 4 for values ranging from -1.2 to $+1.2\text{ V}$ (vs. Ag/AgCl , sat'd NaCl) on a BDDP-packed EMLC column. This span in E_{appl} is much larger than the usable range for PGC, which is roughly from -1.0 to $+0.5\text{ V}$. Above $+0.5\text{ V}$, the PGC surface can slowly oxidize over a few days of continuous use at edge planes and defects sites to form carbon–oxygen surface groups that may be redox-active and/or ionizable [60,61]. These changes lower the reproducibility of retention and the overall effectiveness of the separation.

As is evident, the retention of all four analytes is strongly dependent on E_{appl} . At -1.2 V , the ASFs co-elute with the void volume. However, as E_{appl} becomes more positive, the retention of some of the analytes begins to extend beyond that of the void volume. At -0.9 V , the k' values for TS ($k' = 0.34$) and NDS ($k' = 0.32$) are smaller than those at -0.15 V by factors of 1.7 and 3.6, respectively. The application of more positive values of E_{appl} results in further increases in retention. At $+0.45\text{ V}$, the k' values for BDS/BS (BDS and BS were not resolved at any value of E_{appl} , which we ascribe to the low surface area for the BDDP packing), TS, and NDS are 0.28, 0.84, and 4.57, respectively. These values represent an increase by a factor of 1.3 or more over those at 0 V .

The modulation of ASF retention is summarized in Fig. 5 through $\ln k' - E_{\text{appl}}$ curves. The error bars for $\ln k'$ are roughly the size of the data points and represent the average of four replicate separations. The plots of TS and NDS extend from $+1.2$ to -0.9 V . The curves for BDS/BS cover $+1.2\text{ V}$ to 0 V because BS and BDS eluted with the void volume ($k' \approx 0$) at more negative values of E_{appl} . Each compound follows a linear dependence, which is consistent with our past findings, and reflects the role of electrostatics on the EMLC-based manipulation of adsorption [10]. Though not yet understood, the slope of the plots in Fig. 5 do not all follow the observed dependence found when using PGC as a packing in EMLC [11]. In particular, the slopes for BDS and BS are indistinguishable from each other despite the difference in ionic charge. This observation, which suggests a possible mechanistic difference in electrosorption phenomenon at the two materials, merits further investigation.

Together, these data demonstrate the ability of EMLC to alter molecular adsorption over a wide potential range when using BDDP as a stationary phase. This ability is highlighted by the retention of NDS, which undergoes an increase in k' by a factor of ~53 between -1.2 and +1.2 V. The next subsection briefly details the findings from a study of retention reproducibility and packing stability.

3.3. BDDP stability

The stability of BDDP was examined by checking the day-to-day reproducibility of retention times of the four ASFs at several values of E_{appl} , especially above +0.5 V. This study was accomplished by calculating the relative standard deviation (%RSD) of eight runs obtained in 2 days (four consecutive injections of the mixture on each day) at different E_{appl} values. Retention times typically exhibited less than a 5% RSD for ASFs from day-to-day comparison. For example, the RSDs of TS and NDS at +0.8 V for 2 consecutive days were 3.6 and 1.6%, respectively. This finding demonstrates that BDDP microstructure remains comparatively stable over a wide range of E_{appl} values. The basis for this conclusion arises from our earlier experiments using PGC. Excursions to values of E_{appl} in excess of +0.5 V often led to decreases in retention. This situation proved particularly problematic when carrying out EMLC separations at elevated temperatures in order to measure thermodynamic parameters (e.g., enthalpy and entropy) of adsorption. In these cases, the retention times of the ASFs decreased as much as 20% [62]; characterization by X-ray photoelectron spectroscopy revealed that these decreases (both in room and elevated temperature studies) corresponded to an increase in the amount of oxygen-containing surface functional groups, which, at least quantitatively render the carbon surface less hydrophobic. Thus, the morphological and microstructural stability of BDDP point to its potential use as a model material to study the thermodynamics of electrosorption phenomenon (e.g., enthalpy and entropy of adsorption) by examining the dependence of retention with respect to temperature and pressure.

3.4. Comparison of BDDP to PGC

To develop a very brief comparison of the molecular adsorption characteristics of BDDP, a separation of a mixture of BDS, BS, TS, and NDS using 0.10 M LiClO₄ (aq) was carried out at different values of E_{appl} (+0.3, +0.1, and 0.0 V) using a PGC-packed column. As reported previously [10,14], the time for all compounds to elute increased with E_{appl} . Fig. 6 shows a chromatogram of the ASFs using the PGC-packed column at +0.3 V. The analysis took ~65 min for BDS, BS, and TS to elute from the PGC-packed column, but only ~3 min from the BDDP-packed column (Fig. 4). NDS did not detectably elute from the PGC-packed column after ~80 min at any value of E_{appl} ; longer times were not tested. The long elution times in the aqueous mobile phase are consistent with stronger interactions of the π -system of the analytes with PGC, which in nearly all cases dictates the use of a mixed (e.g., acetonitrile/water) mobile phase in order to decrease retention [1].

Table 1 compares the electrosorption of TS on BDDP- and PGC-packed columns at the three values of E_{appl} after accounting for the difference in the absolute surface area of the packings and void volume of the two different columns. This approach develops via Eq. (1), which defines the partition coefficient, K , for a chromatographic column as

$$K = k' \frac{V_{\text{mp}}}{A_{\text{sp}}} \quad (1)$$

where V_{mp} is the volume of the mobile phase and A_{sp} is the surface area of the column packing. Thus, by dividing K_P by K_B , the impact of V_P , V_B , A_P , and A_B can be taken into consideration to give K_{ratio} :

$$K_{ratio} = \frac{K_P}{K_B} \quad (2)$$

where the subscripts B and P link the appropriate variables to either BDDP or PGC, respectively. Based on this treatment, the data in Table 1 show that TS is retained more strongly on a PGC-packed column by at least a factor of five when compared to BDDP. While much more in-depth investigation is needed and planned, we presently attribute the differences in retention strength, at least in part, to the importance of π -system interactions in the retention at PGC.

4. Conclusions

In this paper, we presented initial findings on the performance of BDDP as a stationary phase in EMLC separations. The work herein demonstrates the utility of EMLC for fine-tuning separations with BDDP. Due to the inert nature and a wide potential window of conductive diamond, EMLC separations were carried out at high positive and negative potentials without observable limitations due to surface oxidation and the microstructural changes associated with it, or solvent electrolysis common with other carbon-based materials. These data also argue that the morphological and microstructural stability of BDDP support its potential use as a model material to study the thermodynamics of electrosorption phenomenon (e.g., enthalpy and entropy of adsorption) by examining the dependence of retention as a function of temperature and pressure.

We are presently pursuing the creation of conductive diamond coated particles with higher surface area, and the results from EMLC experiments using these particles will be reported on in future work [30]. These studies will focus particularly on measurements of interfacial excesses and the potential of zero charges, both of which are central to engineering insights into the many chemical factors of importance to molecular adsorption.

Acknowledgments

This work was supported by the University of Utah USTAR Initiative, the Biodesign Institute of Arizona State University, and the Ames Laboratory-USDOE at Iowa State University (contract DE-AC 02-02H11358). V.M.S. acknowledges financial support provided by the Fraunhofer Center for Coatings and Laser Applications at MSU.

References

1. Knox JH, Wan QH. *Chromatographia*. 1996; 42:83.
2. Maxime D, Maiete B, Jerome D, Nicole G, Martine PG. *J Chromatogr A*. 2006; 1114:34. [PubMed: 16494887]
3. Mazan S, Cretier G, Gilon N, Mermet JM, Rocca JL. *Anal Chem*. 2002; 74:1281. [PubMed: 11922295]
4. Shibukawa M, Terashima H, Nakajima H, Saitoh K. *Analyst*. 2004; 129:623. [PubMed: 15213830]
5. Shibukawa M, Unno A, Miura T, Nagoya A, Oguma K. *Anal Chem*. 2003; 75:2775. [PubMed: 12948149]
6. Anders K, Mattias B, Christine CJ. *J Chromatogr A*. 1998; 797:75.
7. Kaur B. *LC-GC*. 1990; 8:472.
8. Hern JL, Strohl JH. *Anal Chem*. 1978; 50:1954.

9. Jackson PT, Schure MR, Weber TP, Carr PW. *Anal Chem.* 1997; 69:416. [PubMed: 9030054]
10. Keller DW, Porter MD. *Anal Chem.* 2005; 77:7399. [PubMed: 16285692]
11. Keller DW, Ponton LM, Porter MD. *J Chromatogr A.* 2005; 1089:72. [PubMed: 16130774]
12. Ting EY, Porter MD. *Anal Chem.* 1998; 70:94.
13. Deinhammer RS, Ting EY, Porter MD. *J Electroanal Chem.* 1993; 362:295.
14. Deinhammer RS, Ting EY, Porter MD. *Anal Chem.* 1995; 67:237.
15. Deinhammer RS, Porter MD, Shimazu K. *J Electroanal Chem.* 1995; 387:35.
16. Deng H, Berkel GJV, Takano H, Gazda D, Porter MD. *Anal Chem.* 2000; 72:2641. [PubMed: 10857648]
17. Ting EY, Porter MD. *J Chromatogr A.* 1998; 793:204.
18. Ting EY, Porter MD. *Anal Chem.* 1997; 69:675.
19. Wang S, Porter MD. *J Chromatogr A.* 1998; 828:157.
20. Ho M, Wang S, Porter MD. *Anal Chem.* 1998; 70:4314.
21. Ponton LM, Porter MD. *Anal Chem.* 2004; 76:5823. [PubMed: 15456303]
22. Harnisch JA, Porter MD. *Analyst.* 2001; 126:1841. [PubMed: 11763053]
23. Harnish JA, Gazda DB, Anderegg JW, Porter MD. *Anal Chem.* 2001; 73:3954. [PubMed: 11534722]
24. Antrim RF, Scherrer RA, Yacynych AM. *Anal Chim Acta.* 1984; 164:283.
25. Ghatak-Roy AR, Martin CR. *Anal Chem.* 1986; 58:1574.
26. Nagaoka T, Fujimoto M, Nakao H, Kakuno K, Yano J, Ogura K. *J Electroanal Chem.* 1994; 364:179.
27. Engstrom RC. *Anal Chem.* 1982; 54:2310.
28. McCreery, RL. *Electroanalytical Chemistry*. Bard, AJ., editor. Vol. 17. Marcel Dekker; New York: 1991. p. 221
29. Fischer AE, Swain GM. *J Electrochem Soc.* 2005; 152:B369.
30. Ay A, Swope VM, Swain GM. *J Electrochem Soc.* 2008; 155:B1013.
31. Nishimura K, Das K, Glass JT. *J Appl Phys.* 1991; 69:3142.
32. Granger MC, Witek MA, Xu J, Wang J, Hupert M, Hanks A, Koppang MD, Butler JE, Lucazeau G, Mermoux M, Strojek JW, Swain GM. *Anal Chem.* 2000; 72:3793. [PubMed: 10959965]
33. Fischer AE, Show Y, Swain GM. *Anal Chem.* 2004; 76:2553. [PubMed: 15117197]
34. Show Y, Witek MA, Sonthalia P, Swain GM. *Chem Mater.* 2003; 15:879.
35. Lowe MA, Fischer AE, Swain GM. *J Electrochem Soc.* 2006; 153:B506.
36. Chen X, Chen G. *J Electrochem Soc.* 2004; 151:B214.
37. Wang J, Swain GM. *Electrochem Solid-State Lett.* 2002; 5:E4.
38. Fischer AE, Lowe MA, Swain GM. *J Electrochem Soc.* 2007; 154:K61.
39. Swain GM. *J Electrochem Soc.* 1994; 141:3382.
40. Cruickshank BJ, Gewirth AA, Reynolds RM, Alkire RC. *J Electrochem Soc.* 1992; 139:2829.
41. Bowling R, Packard RT, McCreery RL. *Langmuir.* 1989; 5:683.
42. Goss CA, Brumfield JC, Irene EA, Murray RW. *Anal Chem.* 1993; 65:1378.
43. Chen Q, Granger MC, Lister TE, Swain GM. *J Electrochem Soc.* 1997; 144:3806.
44. Yun KS, Zhu C, Parcher JF. *Anal Chem.* 1995; 67:613.
45. Knight DS, White WB. *J Mater Res.* 1989; 4:385.
46. Dennison JR, Holtz M, Swain GM. *Spectroscopy (Eugene Or).* 1996; 11:38.
47. Nemanich RJ, Glass JT, Lucovsky G, Shroder RE. *J Vac Sci Technol A.* 1988; 6:1783.
48. Wang Y, Alsmeyer DC, McCreery RL. *Chem Mater.* 1990; 2:557.
49. Nikitas P. *J Electroanal Chem.* 2000; 484:137.
50. Bassler BJ, Kaliszan R, Hartwick RA. *J Chromatogr Sci.* 1989; 27:162.
51. Bassler BJ, Kaliszan R, Hartwick RA. *J Chromatogr.* 1989; 461:139.
52. Tanaka N, Tanigawa T, Kimata K, Hosoya K, Araki T. *J Chromatogr.* 1991; 549:29.

53. Chiantore O, Novak I, Berek D. *Anal Chem.* 1988; 60:638.
54. Weinberg NL, Reddy TB. *J Appl Electrochem.* 1973; 3:73.
55. Hafkenscheid TL, Tomlinson E. *Adv Chromatogr.* 1986; 25:1.
56. Swain GM, Anderson AB, Angus JC. *MRS Bull.* Sept.1998 :56.
57. Haenni, W.; Rychen, P.; Fryda, M.; Comninellis, C. *Thin-Film Diamond Part B Semiconductors and Semimetals series.* Nebel, Ch, editor. Academic Press Elsevier; 2004. p. 149
58. Martin HB, Argoitia A, Angus JC, Landau U. *J Electrochem Soc.* 1999; 146:2959.
59. Martin HB, Argoitia A, Landau U, Anderson AB, Angus JC. *J Electrochem Soc.* 1996; 143:L133.
60. DeClements R, Swain GM. *Langmuir.* 1996; 12:6578.
61. Xu J, Chen Q, Swain GM. *Anal Chem.* 1998; 70:3146.
62. Ponton, LM. *Dissertation.* Iowa State University; 2004.

Fig. 1.
SEM image of BDDP.

Fig. 2.
XRD pattern of BDDP.

Fig. 3.
Raman spectrum of BDDP.

Fig. 4. Chromatograms illustrating the effect of E_{appl} (V vs. Ag/AgCl sat'd NaCl) on the retention of a mixture of BDS (1, 5 μM), BS (2, 5 μM), TS (3, 10 μM) and NDS (4, 2 μM) on a BDDP-packed EMLC column. The mobile phase consisted of 0.10 M LiClO_4 (aq). The flow rate is 0.4 mL/min.

Fig. 5.

Plots of $\ln k'$ vs. E_{appl} for BDS (5 μM), BS (5 μM), TS (10 μM) and NDS (2 μM). Four replicate injections were made at each E_{appl} , and the data points are roughly the size of the error bars.

Fig. 6. Chromatogram showing the retention of a 20 μ M mixture of BDS (1), BS (2), and TS (3) on a PGC-packed EMLC column. The E_{appl} was +0.3 V (vs. Ag/AgCl sat'd NaCl). The mobile consisted of 0.10 M LiClO₄ (aq). The flow rate is 0.4 mL/min.

Table 1Comparison of retention of 4-toluenesulfonate at BDDP and PGC-packed columns^{a,b}

E_{appl} (V) ^b	k'_P	k'_B	K_{ratio}
+0.30	54.83	0.79	5.6
+0.15	46.66	0.70	5.4
0	37.49	0.60	5.1

^a Average values from four replicate injections. The values for k' have less than a 2% RSD.

^b E_{appl} given with respect to Ag/AgCl (sat'd NaCl). Data for benzene sulfonate and 1,3-benzene disulfonate also showed a comparable qualitative trend, but are not included in the tabulation because of the small changes in their k' values.