



# **ELECTROCHEMICAL REDUCTIVE DEHALOGENATION OF BROMINATED AND CHLORINATED ORGANIC COMPOUNDS IN WATER-METHANOL MEDIA ON A BORON - DOPED DIAMOND ELECTRODE: A VOLTAMMETRIC STUDY**

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## **ABSTRACT**

Electrochemical reduction of the 1,2-dibromoethane, chloroform, and bromobenzene on the Boron Doped Diamond Electrode (BDDE) was studied in aqueous methanol media. The reaction was studied at room temperature in the potential region between 0.0 and - 2.2 V vs. SHE by the linear sweep voltammetry method. In the presence of halogen-organic compounds, the cathodic current at a given potential was significantly higher than the background current.

**Key words :** Halogen-organic compounds, BDD electrode, Electrochemical reduction.

## **INTRODUCTION**

Electrochemical reductive dehalogenation is one of the promising methods of detoxification of halogen organic compounds<sup>1,2</sup>. The choice of electrode material is very important for successful reduction because of the necessity to carry out electrolysis at very negative potentials, sometimes close to - 2V and even less than - 2V vs. SHE<sup>1,2</sup>. Carbon-based electrodes (Carbon Cloth, Glassy Carbon) were considered to be most suitable for this purpose<sup>2,3</sup>. The recently discovered Boron Doped Diamond Electrode (BDDE) has a wide potential window as it is very stable at oxidative conditions and has been widely investigated for the purpose of oxidation. However, possible use of BDDE as a cathode was not investigated on the same scale. Reduction of 1, 4-benzoquinone in acetonitrile on BDDE has been reported<sup>4</sup>, Reduction of Ni<sup>2+</sup> and nitrate in aqueous solution on fluorinated

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BDDE was studied by Sine et al.<sup>5</sup> The hydrogen evolution in acidified aqueous solution has been studied<sup>6</sup>. According to them in 1M HClO<sub>4</sub> and 0.5M sulfuric acid, significant evolution of hydrogen starts at - 0.5 V and - 0.75 V, respectively<sup>5,6</sup>. Modification of BDDE with fluorine shifts evolution of hydrogen to - 1.25V, which allows the reduction of Ni<sup>2+</sup> and nitrate<sup>5</sup>, but is not enough for the reduction of majority of halogen organic compounds. In neutral aqueous solutions, potential can be shifted as far as -1.8 V<sup>7</sup>, which would be enough for the reduction of aliphatic halogen organic compounds<sup>1,2</sup>. However, solubility of halogen organic compounds in water is usually very small and needs to be increased. One of the possible ways is use of alcohol<sup>2</sup>, or a water-alcohol mixture<sup>3</sup>. In this study, we used a 60 : 40 and 30 : 70 mixture of methanol and water as a solvent; 1,2-dibromoethane, chloroform and bromobenzene were used as examples of aliphatic and aromatic halogen organic compounds.

## EXPERIMENTAL

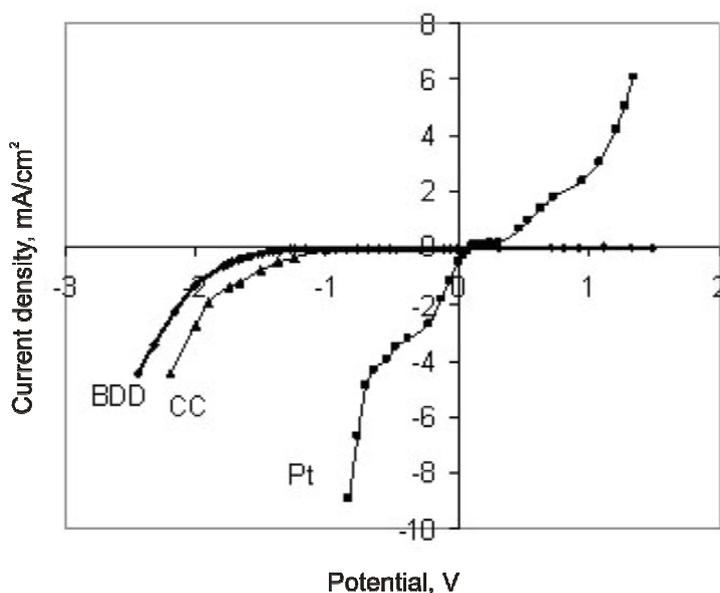
In this work, a polycrystalline thin-film Boron-Doped Diamond electrode (5 micrometer thickness), prepared by hot filament chemical vapour deposition on niobium substrate, was used. Boron content was 3000 ppm, apparent electrode area was 1.6 cm<sup>2</sup>. (The Boron-Doped Diamond Electrode used in this work was provided by Fraunhofer Institut fuer Schicht- und Oberflächentechnik, IST Braunschweig/Germany).

Electrochemical measurements were made in a conventional three-electrode glass cell at room temperature. An Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> (sat) electrode served as the reference electrode, and Pt (1 cm<sup>2</sup>) as counter electrode. For comparison, measurements were also performed on Pt, and Carbon Cloth "Busofit"<sup>2</sup> electrodes. As a supporting electrolyte, Na<sub>2</sub>SO<sub>4</sub> (0.04M) was used. All chemicals used were of analytical grade (> 99%), except 1,2-dibromoethane (98%, Aldrich). All solutions were prepared with bi-distilled water, and deoxygenated by purging with N<sub>2</sub>. Stock solutions of 1, 2-dibromoethane (0.116 M), chloroform (0.123 M) and bromobenzene (0.095 M in methanol) were kept in the dark, and aliquots of these solutions were used to prepare working solutions of different concentrations. A computer-controlled Zahner IM6 electrochemical workstation (Zahner-elektric GmbH & Co., Germany) was used for the voltammetry measurements.

## RESULTS AND DISCUSSION

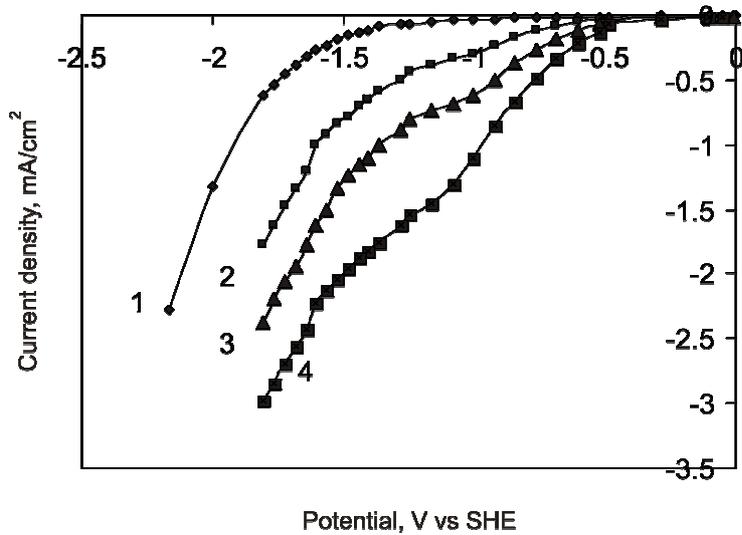
Fig. 1 shows the voltammograms corresponding to BDDE, Carbon Cloth and Pt electrodes obtained in 60% methanol aqueous solution, in neutral media. In agreement with Becker et al.<sup>7</sup>, BDDE showed a wide negative potential window from 0.0 V to - 2 V vs.

SHE without significant water decomposition. Pt, and even Carbon Cloth electrodes, recorded for comparison at the same conditions, showed significant hydrogen evolution at much less negative potentials (Fig. 1). BDDE has practically zero background current until -1.7 V, and even at -2.2 V the current was only approximately 2 mA/cm<sup>2</sup>. According to the literature<sup>1</sup>, aliphatic Br-organic compounds can be relatively dehalogenated easily when compared to Cl-organic compounds, and/or aromatic halogenorganic compounds<sup>1</sup>. The overall electrochemical reaction is –

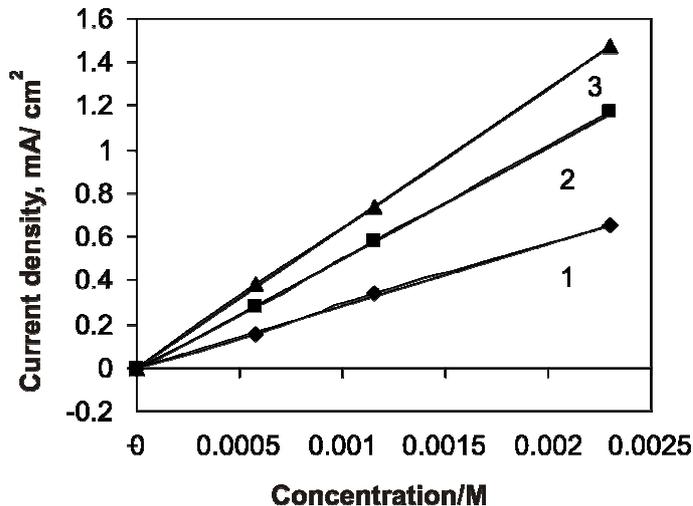


**Fig. 1. Linear potential sweep voltammetry of BDDE, Carbon Cloth (CC) and Pt. Recorded in 60:40 MeOH: Water (volume), 0.04M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte, scan rate 100 mV/s.**

Fig. 2 shows typical cathodic polarization curves for BDDE in 60% volume methanol solutions with different concentrations of 1,2-dibromoethane. The first electrochemical step is transition of one electron to an adsorbed molecule of 1,2-dibromoethane. Cathodic current increases at potentials between -0.5 V and -1.2 V, and reaches an intermediate current limit at approximately -1.2V. Upon further shift into the negative potential region, current starts to increase rapidly. This can be attributed to the transition of the second electron to the substrate – the partially reduced molecule of 1,2-dibromoethane, which is adsorbed on the surface.

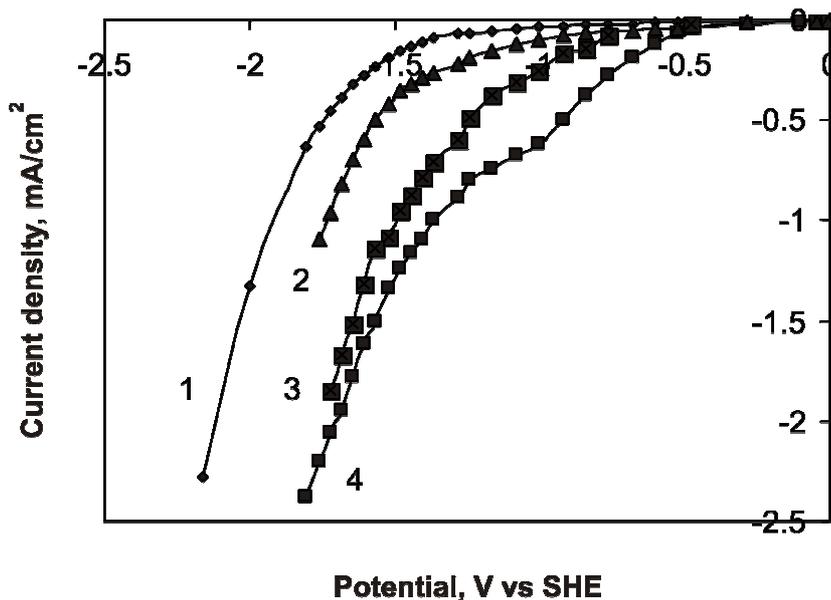


**Fig. 2.** Linear potential sweep voltammetry of BDDE with different dibromoethane concentrations. 1- solvent, 2 – 0.58 mM, 3 – 1.16 mM, 4 – 2.32 mM. Recorded in 60 : 40 MeOH: Water (volume), 0.04M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte, scan rate 100 mV/s.



**Fig.3.** Dependence of current density (absolute values) on the concentration of 1,2-dibromoethane at different potentials. -0.84V (1), -1.0V (2), -1.24V (3). Recorded in 60:40 MeOH: Water (volume), 0.04M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte, scan rate 100 mV/s

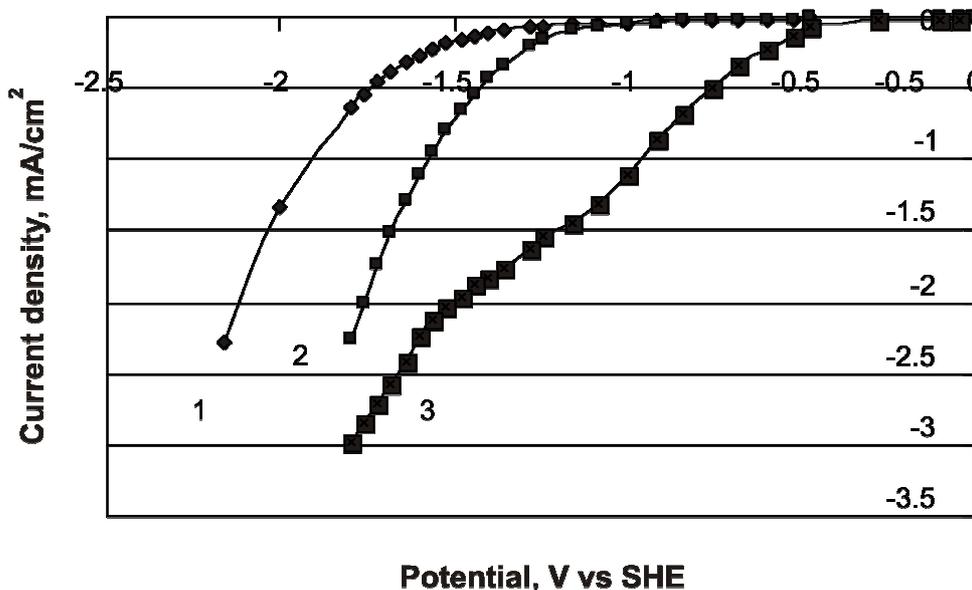
Current density at potentials between -0.5V and -1.25V is directly proportional to the concentration of 1,2-dibromoethane (Fig.3). According to results presented in Fig.2 and Fig.3, the optimal potential for reduction of dibromoethane lies between -1.5V and -1.6V.



**Fig. 4. Linear potential sweep voltammetry of BDDE with different water concentrations. 1 – solvent, 4 – 1.16 mM dibromomethane in 60:40 MeOH: Water (volume), 2 – solvent, 3 – 1.16 mM dibromomethane in 30:70 MeOH:Water (volume), 0.04M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte, scan rate 100 mV/s.**

At more negative potentials, hydrogen evolution will reduce current efficiency. Fig. 4 illustrates the influence of water on electrochemical behaviour of BDDE at negative potentials. A switch from 60% MeOH to 30% MeOH causes a negative influence on current density of 1,2-dibromoethane reduction, especially in the region between -0.5 V and -1.2 V. However, at potentials around -1.5 V current density in 30% MeOH is close to that in 60% MeOH. Thus, practical electrolysis can be done at relatively small alcohol concentration, if solubility of substrate is still high enough. Fig. 5 illustrates the comparison between aliphatic Cl-organic (chloroform) and Br-organic (1,2-dibromoethane) compounds. Reduction of chloroform is more difficult and this is consistent with previous findings<sup>1</sup>; significant current density is reached at potentials more negative than -1.75 V, where hydrogen evolution certainly decreases current efficiency. Electrochemical reductive dehalogenation of aromatic halogenorganic compounds is more

difficult compared to aliphatic ones. Electrochemical reductive dechlorination of polychlorinated benzenes start at  $-1.8\text{ V}^{1,2}$ . Removal of the last Cl atom from chlorobenzene requires a potential as low as  $-2.44\text{ V}^{1,2}$ . Successful dehalogenation at such potentials has been achieved only in relatively non-polar organic solvents, like acetonitrile and DMSO by electrocatalytic reduction<sup>1,2</sup>. In MeOH, such reaction was unsuccessful<sup>2</sup>. Brominated organic compounds can be dehalogenated more easily compared to chlorinated compounds<sup>1</sup> (Fig. 4).



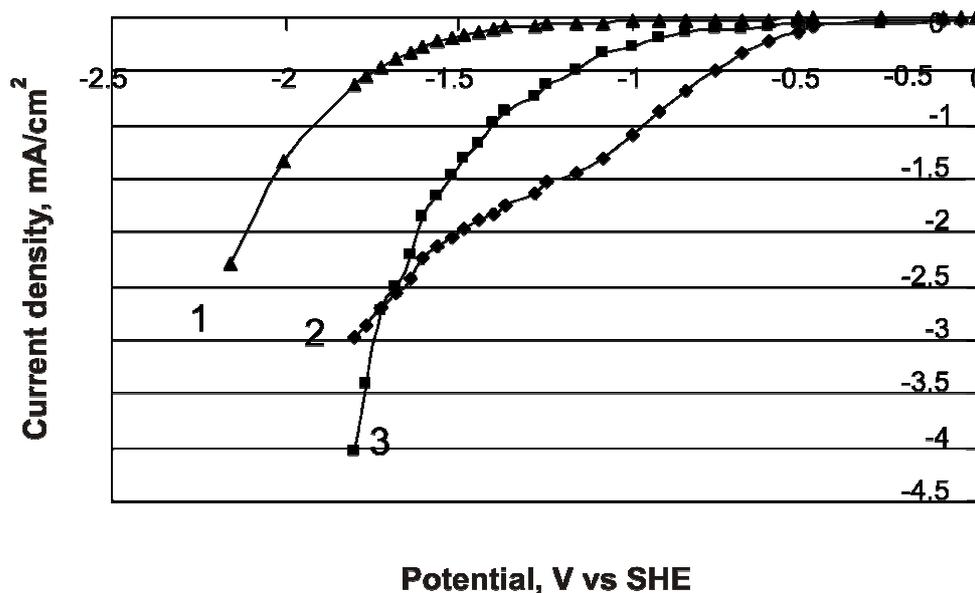
**Fig. 5. Linear potential sweep voltammetry of BDDE in 60 : 40 MeOH : Water (volume), 0.04M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte, scan rate 100 mV/s. 1 – solvent, 2 – chloroform (3 mM), 3- dibromomethane (2.32 mM)**

Data in Fig. 6 show a cathodic polarization curve in the presence of bromobenzene. Starting from a potential of  $-1.5\text{ V}$ , the cathodic current was significantly higher than the background current. This can be attributed to reduction of bromobenzene (Eq.1). However, bromobenzene could also be hydrated into bromocyclohexadiene, without debromination (Eq. 2)



Partial electrochemical hydration of the aromatic ring has been described<sup>8</sup>.

Electrochemical hydration of phthalic acid into dihydrophthalic acid in a dioxane/water mixture is actually an industrial process carried out with high current efficiency<sup>8</sup>. Thus, without product analysis we can not be sure, whether debromination or hydration, or a combination of both is reflected by the polarization curve (Fig. 6).



**Fig. 6. Linear potential sweep voltammetry of BDDE in 60 : 40 MeOH : Water (volume), 0.04M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte, scan rate 100 mV/s. 1 – solvent, 2 – dibromomethane (2.32 mM), 3- brombenzene (4.3 mM).**

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