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THE EFFECT OF BORON DOPING ON THE STRUCTURE AND PROPERTIES OF CARBONIZED HYDROTHERMAL CARBON

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ABSTRACT

Structural and surface characterization of pristine and boron doped carbonized hydrothermal carbons (CHTC) is reported. Boron was introduced into glucose precursor solution with concentration of 0.2% and 1%. Following hydrothermal treatment, samples were carbonized to 1000°C and examined by Raman spectroscopy and temperature programmed desorption. Characterization of obtained samples as material for carbon paste electrode was performed by cyclic voltammetry measurements of the Fe (CN)₆^{3-/4-} redox couple. Structural analysis showed that lower boron content in precursor solution induced structure ordering, while higher amount of boron caused structural disorder of CHTC sample. Boron presence in CHTC samples reduced number of surface active sites for oxygen adsorption and consequently improved their electrochemical response as electrode material for carbon paste electrode.

INTRODUCTION

In recent years hydrothermal carbonization has demonstrated its capability of converting carbohydrate into highly functionalized carbon materials under mild processing conditions [1]. After additional carbonization, hydrothermal carbons (HTC) with various shape size, chemical compositions, and surface functional groups have shown novel and interesting intrinsic properties which allow widespread use of these materials [2].

Incorporation of heteroatoms into carbon materials affects their surface properties and oxidation resistance. Boron is by far the most widely used doping element in carbon. It enters the graphite lattice by substituting for carbon at the trigonal sites and consequently alters the electronic properties of the material [3].

The aim of this study was to investigate the effect of boron incorporation on the structural and surface characteristics of carbonized HTC. Additionally,

electrochemical characterization of carbonized boron doped HTC as material for carbon paste electrode was examined.

EXPERIMENTAL

To produce HTC, 2M water solution of D(+)-Glucose was prepared. Boric acid was used as source of boron and it was added in the starting solution to obtained boron concentration of 0.2% and 1%. After sealing, the autoclave was heated in programmable oven for 24 h at 180°C. All HTC samples were additionally carbonized in nitrogen to 1000°C. Obtained samples were marked as CHTC (undoped carbonized hydrothermal carbon) and boron doped samples as CHTCB_{0.2} and CHTCB₁.

Raman spectra were taken with an Advantage 532 Raman spectrometer (DeltaNu Inc.).

Temperature programmed desorption (TPD) in combination with mass spectrometry was used to investigate the quantity of surface oxygen groups. Evolution of CO and CO₂ to 1000°C was monitored with a quadrupole mass spectrometer (Extorr).

Carbon paste was made by intimate hand-mixing of carbonized HTC powders with the paraffin oil as a liquid binder. All pastes, homogenized at the same ratio of 1.2 g of material and 0.4 cm³ paraffin oil, were packed into a piston-driven Teflon holder.

A 797 VA Computrace analyzer (Metrohm) controlled by 797 VA Computrace software ver. 1.2 was applied for all voltammetric measurements.

RESULTS AND DISCUSSION

Table 1. Raman spectra parameters for CHTC, CHTCB_{0.2} and CHTCB₁

Sample	Peak	Peak position (cm ⁻¹)	Bandwidth (cm ⁻¹)	I _D /I _G
CHTC	D	1347	205	2.22
	G	1579	106	
CHTCB _{0.2}	D	1345	200	1.95
	G	1575	90	
CHTCB ₁	D	1345	215	2.6
	G	1580	103	

Table 1 shows Raman spectra parameters. The main features of these spectra are two broad peaks at 1350 cm⁻¹ (D band) and at 1590 cm⁻¹ (G band), commonly observed in mixture of graphitic and disordered sp²-bonded carbon. There are no significant changes in G and D peak positions

for CHTCH and CHTCB₁. However, the D peak bandwidth increased because of higher amount of B atoms, which occupy the lattice points to a greater extent and behave as defects for Raman scattering (higher values for I_D/I_G). For CHTCB_{0.2} sample all Raman parameters indicate increasing of structure ordering.

Table 2. Amounts of evolved CO, CO₂ and CO+CO₂ for CHTC, CHTCB_{0.2} and CHTCB₁

Sample	Q _{CO} (μmol/g)	Q _{CO₂} (μmol/g)	Q _{CO₂+CO} (μmol/g)
CHTC	195.9	115.9	311.8
CHTCB _{0.2}	24.6	15.9	40.5
CHTCB ₁	73.6	21.5	95.1

Amounts of evolved CO₂, CO obtained by TPD are summarized in Table 2. It can be noted that amounts of released CO₂ and CO for B doped samples are several times less compared to CHTC. This indicates that boron incorporation induced changes in electronic structure by reducing number of surface active sites for oxygen adsorption.

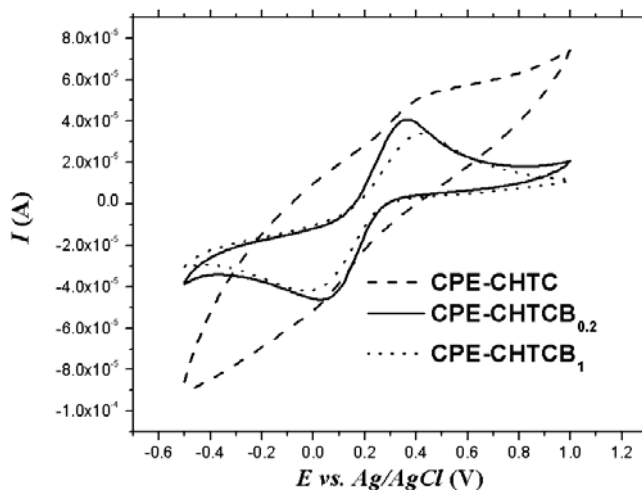


Figure 1. Cyclic voltammograms (50 mVs^{-1}) for $1 \text{ mmol K}_3\text{Fe}(\text{CN})_6 / \text{K}_4\text{Fe}(\text{CN})_6$ for electrode made from CHTC, CHTCB_{0.2} and CHTCB₁

Figure 1. shows cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ for carbon paste electrodes made from carbonized HTC samples (CPE-CHTC, CPE-

CHTCB_{0.2}, and CPE-CHTCB₁). It can be noted that on CPE-CHTC Fe (CN)₆^{3-/4-} exhibited a poor electrochemical behavior with broadened wave shape and high capacitive background current. Granger et al. [4] previously reported that several factors are known to influence redox-reaction kinetics at sp² carbon electrode: surface cleanliness, presence of adsorbed layers and fraction of edge plane exposed. According TPD results, the highest amount of surface oxygen groups was obtained for CHTC sample (Table 2), which caused the poor electrochemical behavior. Contrary to this, for boron doped samples drastically improved electrochemical responses were obtained and results are in compliance with TPD results. However, boron fraction of 1% worsens peaks intensity as well as the peak to peak potential separation compare to fraction of 0.2%.

CONCLUSION

Results showed that the different amount of boron allows obtaining carbonized hydrothermal carbons with modified structural, chemical and electrochemical characteristics compared to the pristine sample. It was shown that boron concentration of 0.2% in precursor solution generates structure ordering of carbonized sample, which induced a greater extent of surface active sites reduction for oxygen adsorption compared with sample with higher boron concentration. Modification of hydrothermal carbon with boron and its additional carbonization facilitate preparation of the material with good surface properties, which are important for the development and application of this material as a carbon paste electrode.

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