Research Experience for Undergraduates

Section 1

Support for the REU program is provided by the NSF MRSEC program (DMR-1120296) and the REU Site program (DMR-1460428).
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Functionalizing Hierarchical Porous Carbon For Supercapacitor
Abdulrahman Alfaraidi\textsuperscript{1}, Turki Baroud\textsuperscript{2} and Emmanuel P.Giannelis\textsuperscript{3}

Introduction:
Renewable Energy systems - such as Photovoltaic modules and Wind turbines- are developing rapidly and soon -hopefully- to replace the finite fossils fuels. However, one major issue facing those new emerging energy sources is their natural intermittency. One proposed way to solve this challenge is to develop a composite Energy Storage system that utilizes the high-power density supercapacitors backed up by batteries\textsuperscript{1}. Moreover, Supercapacitors are also becoming investigated in various application such as hybrid vehicles, fuel cell vehicles and in energy and power industrial management\textsuperscript{2}. Hence, developing high performance electrodes material that increase the energy density and decrease internal resistance of supercapacitors has become essential. Porous carbon is promising electrode material because of their high surface area, controllable pore size, adjustable surface structure, availability, low cost, conductivity and electrochemical stability\textsuperscript{3}. Tailoring these properties towards improving the performance of supercapacitors has been a goal for energy storage scientists. For example, a new structure called “Hierarchical Porous Carbon” (HPC) was developed to create more active site at the interface between electrode surface and ions\textsuperscript{4}. The three-dimensional structure consisting of Micropores (diameter < 2nm), Mesopores (diameter: 2-50nm) and Macropores (diameter >50nm) enables a smooth pathway for electrolyte ions to access active sites on electrode’s surface for adsorption\textsuperscript{5}.

Functionalizing the surface of porous carbon with heteroatoms or metal oxide is another possible method to enhance supercapacitor performance. For instance, introducing little amount of nitrogen and boron into the carbon matrix can improve surface wettability and enhance electric conductivity while maintaining electrochemical stability\textsuperscript{6,7}. Having approximately similar atomic size, nitrogen and boron can strongly bond with carbon without distorting the general structure of the carbon material\textsuperscript{8}. Electron deficient boron with its three outer-shell electrons and smaller electronegativity (than carbon) can act as p-type dopant, and thus, allows neighboring carriers to roam more freely leading to conductivity enhancement\textsuperscript{9}. Moreover, boron doping can enhance chemisorption of oxygen on the surface of carbon electrode, which introduces pseudocapacitance mechanism of storing charges\textsuperscript{10}. Nitrogen, on the other hand, can act as n-type dopant with its five outer electrons, enhancing the number of carrier and hence increase conductivity. Moreover, Nitrogen can enter the carbon structure with different functionalities, like pyridinic, graphitic and pyrrolic nitrogen, that improve charge storage by pseudocapacitance. Due to these special properties of boron and nitrogen, it would be interesting to see their effects combined on the performance of Supercapacitor.

Here, we report a successful co-doping of nitrogen and boron into porous carbon structure. The co-doped sample improved the capacitance of porous carbon electrode by 100% and, also, outperformed the singly doped nitrogen and boron electrodes.

Experimental:
Primarily, four types of electrodes were compared: bare carbon electrode (HPC), boron doped carbon electrodes (HPC-B), nitrogen doped carbon electrode (HPC-N), and boron-nitrogen co-doped carbon electrode (HPC-N-B).
We synthesized hierarchical porous carbon following the facile recipe developed by professor Giannelis’s group\textsuperscript{11}.

**HPC-N-B synthesis:**

Sucrose (carbon precursor), boric acid (boron source), cyanimide (nitrogen source) and colloidal silica (4nm in diameter) were mixed and swirled well. The mixture solution was plunged in a liquid nitrogen bath until ice crystal completely grow to the center of the solution. Then, the frozen sample was subjected to freeze-drying for three days. The freeze-dried composite was calcined at 1000 °C for 3 h dwelling time and at ramp of 3 °C/min. The sample then was placed overnight in 3M NaOH to etch the silica template. Finally, the sample was washed with boiling DI water (to achieve pH of 7 and to remove bi-product boron oxide) and placed in a vacuum oven overnight before use.

The other three samples were synthesized in same procedure except for initial precursors. For example, to synthesize HPC, boric acid and cyanimide were not added in the beginning.

All electrochemical tests were performed in 6M KOH in a three-electrode set-up. The working electrode consisted of active material mixed with carbon black and a binder before it was coated on graphite piece. Galvanostatic charge/discharge (CC) and cyclic voltammetry (CV) tests were done in a potential window between 0 and 0.9 mV.

**Results and discussion:**

As shown in figure 1, HPC-N-B sample outperformed other samples at 2,5,10,20 and 50 mV/s scan rates by having the largest area under CV plot. The specific capacitance was calculated at those scan rates and plotted in figure 2 for each of the four samples. HPC-N-B sample reached a specific capacitance of 225 F/g at 2 mV/s that is almost double the capacitance of HPC sample (114 F/g) at 2 mV/s. Moreover, HPC-N-B maintained a high capacitance of 186.5 F/g and 165 F/g at 20 mV/s and 50 mV/s respectively. Moreover, charge/discharge measurement were performed for all samples and iR drop or resistance were calculated. From figure 4, it is clear that boron is decreasing the resistance of electrolyte ions in our porous carbon, and that might be a result of the hole boron created in the carbon structure, leading to a lower band gap.

![Scheme 1: steps of synthesis and creating different sizes of pores in HPC.](image)

![Figure 1: CV test at 2mV/s for all four samples.](image)
Figure 2: specific capacitance of all four samples at different scan rates.

Figure 3: charge/discharge measurement for HPC-N-B at different currents.

Figure 4: iR drop or Ohmic resistance of all four samples obtained from charge/dischage measurement at 2mA.

Furthermore, we wanted to know how nitrogen and boron affected the surface area compared to bare carbon sample (HPC). Table one shows that the BET surface area for both HPC and HPC-N-B were between 800-900 m²/g, which indicates a successful doping without diminishing the surface area and blocking the pores. Pore size distributions in figure 5 for both HPC and HPC-N-B show a very close similarity with majority of pores with diameter around 6nm, which is expected from the 4nm diameter silica template we used.

<table>
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<th>Sample</th>
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<th>HPC-N-B</th>
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<tr>
<td>BET Surface Area (m²/g)</td>
<td>800 - 900</td>
<td>800 - 900</td>
</tr>
<tr>
<td>Micropores Volume (cm³/g)</td>
<td>0.0208</td>
<td>0.0217</td>
</tr>
<tr>
<td>Mesopores Volume (cm³/g)</td>
<td>1.5476</td>
<td>1.5609</td>
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Table 1: BET surface area and pores volume for HPC and HPC-N-B samples.

Figure 5: Pore size distribution for a)HPC and b)HPC-N-B
Figure 6) HPC-N-B sample exhibit excellent symmetry and cyclic stability with over 600 cycles at 2mA.

XPS analysis was performed to understand the surface properties, types of functionalities exist and contents of our samples. Table 2 shows element contents in HPC, HPC-N and HPC-N-B. It is interesting to see that the addition of boron in HPC-N-B increases the dopant of oxygen and nitrogen even though a fixed amount of cyanimide (nitrogen source) was added in both HPC-N and HPC-N-B.

Furthermore, XPS peaks of nitrogen and boron existed clearly, confirming a successful doping of both nitrogen and boron into the carbon structure. As shown in figure 7a, Boron peak was fitted into four smaller peaks, indicating the existence of four types of boron compounds in the surface of carbon. We believe that BCO$_2$, BN and BC$_2$O enhanced the chemisorption of oxygen and thus improved charge storage. However, boron oxide or B$_2$O$_3$ is just a by-product that we aimed to minimize in the synthesis procedure.

As shown in figure 7b, nitrogen also existed in four types. However, we believe that all four types contributed to a greater performance by introducing pseudo-capacitance, especially those highly stable aromatic structure with their delocalized electrons, such as Pyridinic-N and Pyrrolic-N.

![Graph showing voltage and time](image)

**Figure 7: XPS spectra of a) boron and b) nitrogen in HPC-N-B sample**

**Conclusion:**

Nitrogen & Boron were successfully co-doped and integrated in a facile method of synthesizing 3D ordered porous carbon. Functionalities of Boron and Nitrogen enhanced supercapacitor performance by introducing Pseudo-capacitance. Moreover, due to synergistic effect of the heteroatoms doping, we were able to double the capacitance of bare carbon sample and decrease Ohmic resistance while maintaining high surface area and electrochemical stability.

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