Boric acid assisted reduction of graphene oxide: A promising material for sodium ion batteries

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Abstract
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Boric Acid Assisted Reduction of Graphene Oxide: A Promising Material for Sodium-ion Batteries

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KEYWORDS: Sodium-ion batteries; Anode materials; Graphene oxide; Expended interlayer; Boron; Boric acid

ABSTRACT: Reduced graphene oxide, an intensively investigated material for Li-ion batteries, has shown mostly unsatisfactory performance in Na-ion batteries, since its $d$-spacing is believed
to be too small for effective insertion/de-insertion of Na\textsuperscript{+} ions. Herein, a facile method has been developed to produce boron-functionalized reduced graphene oxide (BF-rGO), with an enlarged interlayer spacing and defect-rich structure, which effectively accommodates the sodiation/desodiation and provides more active sites. The Na/BF-rGO half cells exhibit unprecedented long cycling stability, with about 89.4 % capacity retained after 5000 cycles (0.002 % capacity decay per cycle) at 1000 mA·g\textsuperscript{−1} current density. High specific capacity (280 mAh·g\textsuperscript{−1}) and great rate capability were also delivered in the Na/BF-rGO half cells.

1. INTRODUCTION

Successful development of Li-ion batteries (LIBs) has promoted its application in load-leveling.\textsuperscript{1-5} The high demand for LIBs, however, has led to increasing concern about the limited resources and high cost of lithium. Consequently, great efforts have been spent on finding alternatives to LIBs.\textsuperscript{6-11} Amongst all the candidates, Na-ion batteries (NIBs) have attracted much attention due to the high deposit and low cost of sodium. The radius of Na\textsuperscript{+} is about 55 % larger than that of Li\textsuperscript{+}, so that it requires larger channels (minimum space of 0.37 nm)\textsuperscript{12} for its diffusion.\textsuperscript{13-14} This is why reduced graphene oxide (rGO, $d$-spacing: 0.34 nm), which is widely used in LIBs, fails to deliver a decent performance in NIBs.

The use of carbon-based materials in NIBs, however, is still highly advantageous due to their high abundance and low cost. To date, studies on carbon materials for Na\textsuperscript{+} storage are focused mainly on poorly or non-graphitized hard carbon. Various sources, such as glucose, banana peels, and polyaniline, have been used to produce hard carbon, which delivers high capacities (100 to 200 mAh·g\textsuperscript{−1}) and good rate capability.\textsuperscript{15-17} Hard carbon, however, often features poor cycling stability, and degraded Coulombic efficiency (CE).\textsuperscript{18}
rGO has demonstrated excellent cycling stability and high capacity in LIBs, but has not received comparable attention in NIBs. This is likely because its d-spacing is smaller than 0.37 nm. In 2014, Wang et al. synthesized rGO with an expanded d-spacing of 0.42 nm by controlling the reduction temperature, and the larger interlayer spacing was reported to improve Na-ion storage capability (184 mAh·g⁻¹ at a current density of 100 mA·g⁻¹ for 2000 cycles). Another strategy to enhance the electrochemical properties of rGO is chemical decoration by heteroatoms (N, P, B, etc.). The introduced heteroatoms create more defects and change the electronic conductivity of rGO so as to promote Na-ion storage. For example, N-doped rGO foam delivered a high capacity of 594 mAh·g⁻¹, which outperformed pure rGO. Inspired by the above-mentioned methods, finding a suitable way to simultaneously expand the interlayer spacing and to chemically modify rGO with heteroatoms would be highly desirable for enhancing its Na-ion storage performance.

Boron is an ideal candidate to functionalize rGO, due to its lower electronegativity and similar atomic radius to carbon. In addition, the strong chemical bonds between boron and oxygen (–B–O–) can serve as pillars to enlarge the interlayer spacing of rGO. First-principles calculations predicted the superior sodiation of boron doped rGO, which outperformed other hard carbon and pure graphene materials. Experimental results on the sodiation/desodiation performance of boron functionalized rGO (BF-rGO) are rarely available. Normally, methods used to incorporate B into the rGO lattice require high temperatures, long time, or toxic precursors. Herein, we report a gentle method to fabricate BF-rGO, which features expanded interlayer spaces and defect-rich structure. The Na/BF-rGO half cells deliver a high reversible capacity of 280 mAh·g⁻¹ and great rate capability. More importantly, ultra-long cycling stability was achieved, with high capacity retention of 89.4 % after 5000 cycles (corresponding to 0.002 % capacity
decay per cycle) at a current density of 1000 mA·g⁻¹. The continuous insertion/de-insertion of Na⁺ between BF-rGO layers was also confirmed.

2. EXPERIMENTAL METHODS

Graphene oxide (GO) was synthesized according to our previous work.²⁸ Typically, the BF-rGO was prepared via a one-pot hydrothermal procedure: 100 mg GO was dispersed in 70 ml aqueous solution and then ultrasonic for 0.5 h. Then, boric acid (3 g) was added into the GO suspension and stirred for another half an hour. The well dispersed boric acid and GO mixture were kept inside an autoclave, and maintained at 180 °C for 12 h. Finally, the samples were washed 5 times with distilled water. To obtain a porous structure, freeze-drying was employed to remove water from the BF-rGO powder. Sufficient washing was crucial for removing the extra boric acid and other potential by-products. For comparison, pure rGO was synthesized without the addition of boric acid. The final powders turned from yellow-brown to black, indicating the reduction of GO.

The details of characterization and electrochemical tests are given in the “Supporting Information”. To optimize the electrochemical performance, electrolytes consisting of 1 M NaClO₄ in three different solvents were used: (1) 1,2-dimethoxyethane (DME); (2) ethylene carbonate (EC) and diethyl carbonate (DEC) (EC:DEC, 1:1, v:v); (3) EC:DEC with the addition of 5 % fluorinated ethylene carbonate (FEC) (EC:DEC:FEC).

3. RESULTS AND DISCUSSION

The synthesize procedure of the BF-rGO is illustrated in Figure 1. Typically, when boric acid is added to the GO suspension, strong intermolecular hydrogen bonding takes place between the hydroxyl groups in boric acid and the hydroxyl and carboxyl groups in GO. The extended hydrogen network is reflected in Figure S1 (Supporting Information), which shows red-shifted
B–O–H out-of-plane bending (from 816 to 725 cm\(^{-1}\)) and O–B–O ring bending (from 652 to 632 cm\(^{-1}\)).\(^{29}\) When GO was reduced to rGO, the B-containing functional groups (–B–O–C/–B–C–O–) survived in the resultant BF-rGO (shown in Figure S2).

Figure 1. Synthesis of BF-rGO: (a) Dispersion of boric acid in rGO suspension, (b) formation of the BF-rGO via a hydrothermal process.

The structure of the resultant samples was further characterized (Figure 2). Compared with GO, the (002) reflection for the rGO and BF-rGO in the X-ray powder diffraction patterns (XRD, Figure 2a) shifts to a higher angle, indicating the removal of large amounts of functional groups during the hydrothermal process. The (002) reflection of rGO at 26.7° is associated with an interlayer spacing of ~0.34 nm. The (002) reflection of the BF-rGO is located at 24.3°, indicating a larger interlayer space of ~0.37 nm, which has been predicted large enough to facilitate Na\(^+\) ion insertion/de-insertion.

Raman spectroscopy further reveals the differences between rGO and BF-rGO (Figure 2b). The prominent peak at 1320-1338 cm\(^{-1}\) is assigned to the D bond, and the prominent peak at 1580-1590 cm\(^{-1}\) is assigned to the G bands in carbon. The D band is associated with disorder, and the G band relates to the stretching of \(sp^2\) atoms. GO and rGO both display their D and G bands around 1335 and 1548 cm\(^{-1}\), respectively. For BF-rGO, obvious peak shifts are observed. The blue shift in the G band (1589 cm\(^{-1}\)) is due to the different bond distances between C–C and
C–B, indicating the incorporation of B into the two-dimensional (2D) structure of rGO.\textsuperscript{19, 22} Compared with rGO, the red shift in the D band indicates different ordering of the BF-rGO. The intensity ratio of the D to the G band ($I_D/I_G$) in the GO, rGO, and BF-rGO is 1.03, 1.07, and 1.27, respectively. In general, $I_D/I_G$ varies inversely with crystallization. The highest value of $I_D/I_G$ in the BF-rGO indicates a defect-rich structure. This defect-rich structure facilitates sufficient contact between the electrode and electrolyte, and is favorable for ion diffusion.\textsuperscript{30-31}

X-ray photoelectron spectroscopy (XPS, Figure 2c) confirmed the high purity of resultant samples, as only C, O, and B were observed. The oxygen content (Figure 2d) in BF-rGO is higher than that of rGO, but lower than for GO. The oxygen−containing groups are necessary for enlarging the interlayer spacing, but excess groups decrease the electronic conductivity.\textsuperscript{17} Since the B−O bond (125 kJ mol$^{-1}$) is stronger than the C−O bond (85.5 kJ mol$^{-1}$), it could survive this reduction reaction and therefore help to enlarge the interlayer spacing. The atomic content of boron is 2.4 at.% in the BF-rGO. The C 1s high resolution spectrum of the BF-rGO reveals that most of the carbon exists in the $sp^2$ state, located at 284.65 eV (Figure 2e). Two peaks associated with the B−C and B−O−C bonds at 283.31 and 289.10 eV,\textsuperscript{19} respectively, are also observed. The B 1s peak (Figure 2f) can be divided into three peaks at 190.15, 191.28, and 192.28 eV, corresponding to the BC$_3$, BC$_2$O, and BCO$_2$ entities, respectively.\textsuperscript{26} Taking all the above findings into consideration, the schematic structure of the BF-rGO is given in Figure 2g and h. Boron is likely to be present in three forms: (1) substituting into the six-ring C to form BC$_3$ (structure A); (2) co-doping with O to form BC$_2$O, introducing nanovoids into the layer (structure B); and (3) forming functional groups such as BCO$_2$ (structure C). The presence of these groups not only helps to expand the interlayer spacing, but also introduces defects, both of which are believed to be beneficial for sodiation/desodiation.
The Brunauer-Emmett-Teller (BET) surface areas of rGO and BF-rGO were analyzed by N\textsubscript{2} adsorption-desorption isotherms (Figure S3). Typical type-IV hysteresis loops are observed in both samples, indicating their mesoporous nature. The specific surface area is calculated to be 634 and 281 m\textsuperscript{2}\cdot g\textsuperscript{-1} for rGO and BF-rGO, respectively. The decreased specific surface area of BF-rGO is likely caused by the incorporation of B and the preservation of oxygen-containing groups in its structure.

**Figure 2** (a) XRD plots, (b) Raman spectra, (c) XPS analysis, and (d) atomic contents of C, O, and B in the GO, rGO, and BF-rGO. Inset in (a) is the XRD pattern of GO. High-resolution XPS spectra of (e) C 1s and (f) B 1s in the BF-rGO. Schematic illustrations of the BF-rGO: (g) top and (h) side views.

The electrochemical performance of the BF-rGO was investigated. To optimize the electrochemical performance, three types of electrolytes were used (Figure 3). Compared with the first cycle profiles (shown in Figure S4), all the batteries show capacity decline in the second cycle (Figure 3a-c). The initial capacity loss can be attributed to the reactions between the electrolyte and the BF-rGO, and the irreversible insertion of Na\textsuperscript{+} ions into the BF-rGO structure.\textsuperscript{12,16} This is commonly observed in carbon-based anode for Na-ion batteries, where the first cycle
experiences high irreversible capacity (Table 1). In addition to the high-energy defects, the oxygen-containing functional groups in BF-rGO may also lead to irreversible Na\(^+\) ion storage.\(^{32-33}\) Although the Na/BF-rGO half cells in EC:DEC show higher initial discharge capacity (640 mAh\(\cdot\)g\(^{-1}\)) than in DME (601 mAh\(\cdot\)g\(^{-1}\)), their CE is only 28.3 % (about 5.2 % lower than that in DME). Inspired by the LIBs where FEC was added into the electrolyte to improve the cycling stability and capacity,\(^{34-37}\) the electrochemical performance of Na/BF-rGO half cells with EC: DEC: FEC was also investigated. A comparison of the Na/BF-rGO half cells in those electrolytes is given in Table S1. Compared with the half cells with EC: DEC electrolyte, the half cells with FEC showed a higher capacity and better capacity retention over 115 cycles (Table S1). A higher CE of 99.6 % for the half cell in EC: DEC: FEC was maintained from the 10\(^{th}\) cycle onwards, compared to 98.3 % for the half cells in EC: DEC. At the 115\(^{th}\) cycle, the cells with EC: DEC: FEC delivered a stable discharge capacity of 180 mAh\(\cdot\)g\(^{-1}\), compared to 128 mAh\(\cdot\)g\(^{-1}\) for cells with EC: DEC. These results indicate that FEC may play a role in maintaining the Na-ion storage performance in Na/BF-rGO that is similar to that reported in LIBs. The stabilizing effect of FEC has also been observed in other reports.\(^{37}\) For comparison, the electrochemical performance of pure rGO in these electrolytes was also studied, and a similar trend was observed (Figure S5). Therefore, the electrochemical performance was investigated using 1 M NaClO\(_4\) in EC:DEC:FEC as electrolyte.

To evaluate the rate capability of the BF-rGO electrode, we discharged and charged the NIBs at different current densities, from 20 to 1000 mA\(\cdot\)g\(^{-1}\) (Figure 4a). The discharge-charge profiles for the BF-rGO electrode at various current densities are given in Figure S6, which show good capacity retention when the current density increases. The electrochemical performance of pure rGO was also investigated for comparison (Figure S7). Clearly, the BF-rGO showed a high
capacity of 280 mAh·g⁻¹ at 20 mA·g⁻¹, about 1.6 times higher than that of pure rGO. When increasing the current density to 80, 200, and 400 mA·g⁻¹, the BF-rGO electrode can still deliver 212, 176, and 153 mAh·g⁻¹, respectively. More importantly, even at 1000 mA·g⁻¹ current density, the BF-rGO still showed a high capacity of 123 mAh·g⁻¹. When the current was returned to 20 mA·g⁻¹, the capacity of the BF-rGO recovered to 253 mAh·g⁻¹, which indicates high cell integrity during the Na⁺ insertion/de-insertion.

**Figure 3** Electrolyte optimization for the Na/BF-rGO half-cells. (a, b, c) Discharge-charge profiles at 100 mA·g⁻¹ with electrolyte consisting of 1 M NaClO₄ in DME, EC: DEC, and EC: DEC: FEC, respectively. (d) Cycling stability in different electrolytes.

The kinetic properties were investigated by electrochemical impedance spectroscopy (Figure 4b). The depressed semicircle and the sloping line in the Nyquist plots are related to the resistance and Warburg impedance, respectively. To study the solution resistance related to electrolyte ($R_s$), charge-transfer resistance ($R_{ct}$), constant phase element (CPE), and Warburg impedance ($W$, corresponding to Na⁺ diffusion), an equivalent electric circuit was constructed.
Parameters used to fit the Nyquist plots are given in Table S2. For the BF-rGO, $R_{ct}$ is calculated to be 586 $\Omega$, in sharp contrast to that of the pure rGO electrode (1509 $\Omega$). The decreased $R_{ct}$ offers a lower energy barrier for sodium insertion/de-insertion, and therefore contributes to the good rate capability of the BF-rGO electrode.

**Figure 4** Electrochemical performance of BF-rGO. (a) Rate performance; (b) Nyquist plots and the fitting results. (c, d) Long-life cycling stability at 400 and 1000 mA·g$^{-1}$. The results of rGO are shown for comparison, and inset (b) shows the equivalent electrical circuit.
Table 1 Performance comparison of carbon-based anode materials for NIBs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Current (mA·g⁻¹)</th>
<th>Capacity (mAh·g⁻¹)</th>
<th>Capacity Retention</th>
<th>1st cycle Capacity Loss (%)</th>
<th>Year/Ref.</th>
</tr>
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<tr>
<td>aHCNW</td>
<td>50</td>
<td>251</td>
<td>82.5% after 400 cycles</td>
<td>49 %</td>
<td>2012/12</td>
</tr>
<tr>
<td>bHCNS</td>
<td>100</td>
<td>160</td>
<td>66.6% after 100 cycles</td>
<td>58 %</td>
<td>2012/38</td>
</tr>
<tr>
<td>rGO</td>
<td>40</td>
<td>141</td>
<td>45.0% after 1000 cycles</td>
<td>77 %</td>
<td>2013/39</td>
</tr>
<tr>
<td>cN-CS</td>
<td>50</td>
<td>155</td>
<td>44.4% after 50 cycles</td>
<td>65 %</td>
<td>2013/32</td>
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<tr>
<td>dFN-CNF</td>
<td>200</td>
<td>134</td>
<td>88.7% after 200 cycles</td>
<td>58 %</td>
<td>2013/40</td>
</tr>
<tr>
<td>eEG</td>
<td>100</td>
<td>184</td>
<td>73.9% after 2000 cycles</td>
<td>50 %</td>
<td>2014/18</td>
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<tr>
<td>fG-HC</td>
<td>20</td>
<td>274</td>
<td>94.8% after 195 cycles</td>
<td>17 %</td>
<td>2015/41</td>
</tr>
<tr>
<td>gNSHC</td>
<td>20</td>
<td>289</td>
<td>89.1% after 100 cycles</td>
<td>28 %</td>
<td>2015/42</td>
</tr>
<tr>
<td>hPCNF</td>
<td>50</td>
<td>196</td>
<td>81.4% after 100 cycles</td>
<td>30 %</td>
<td>2015/43</td>
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<tr>
<td>iGF</td>
<td>200</td>
<td>16</td>
<td>55.5% after 200 cycles</td>
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<tr>
<td>rGO/Juglone</td>
<td>100</td>
<td>212</td>
<td>69.5% after 300 cycles</td>
<td>56 %</td>
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<tr>
<td>jCNTs</td>
<td>100</td>
<td>75</td>
<td>80% after 300 cycles</td>
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<td>2015/46</td>
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<tr>
<td>kF-CP</td>
<td>200</td>
<td>228</td>
<td>99.4% after 200 cycles</td>
<td>47 %</td>
<td>2015/44</td>
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<tr>
<td>lCM</td>
<td>40</td>
<td>270</td>
<td>90.1% after 200 cycles</td>
<td>26 %</td>
<td>2016/47</td>
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<tr>
<td>Porous-C</td>
<td>20</td>
<td>253</td>
<td>96.5% after 100 cycles</td>
<td>45 %</td>
<td>2016/48</td>
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<tr>
<td>mN-HCS</td>
<td>200</td>
<td>136</td>
<td>90.0% after 2500 cycles</td>
<td>77 %</td>
<td>2016/49</td>
</tr>
<tr>
<td>nNOC</td>
<td>2000</td>
<td>240</td>
<td>~87.0% after 2000 cycles</td>
<td>~18 %</td>
<td>2016/50</td>
</tr>
<tr>
<td>BF-GO</td>
<td>1000</td>
<td>117</td>
<td>89.4% after 5000 cycles</td>
<td>63 %</td>
<td>This work</td>
</tr>
</tbody>
</table>

aHCNWs: hollow carbon nanowires, bHCNSs: hollow carbon nanospheres, cN-CSs: nitrogen-doped carbon sheets, dFN-CNF: functionalized nitrogen-doped carbon nanofibers, eEG:

Long-life stability of the Na/BF-rGO half cells was first investigated at 400 mA·g$^{-1}$ (Figure 4c). The BF-rGO anode shows little capacity fading during the following 1100 cycles (~130 mAh·g$^{-1}$), and a high CE of nearly 100 %. More importantly, at a higher specific current of 1000 mA·g$^{-1}$, a capacity of 117 mAh·g$^{-1}$ was delivered at the end of 5000 cycles, corresponding to 89.4 % capacity retention (0.002 % capacity decay per cycle, Figure 4d). The discharge-charge plot of the BF-rGO electrode after 5000 cycles is shown in Figure S8, which is similar to those of the first few cycles (Figure 3c). Such excellent cycling stability is rarely reported for carbon-based anode in NIBs under equal or even low specific currents (Table 1). The reversible capacity of 280 mAh·g$^{-1}$ at 20 mA·g$^{-1}$ is much higher than for other reported carbon-based anode materials in NIBs.$^{38,51-54}$ These significant improvements highlight the potential of the BF-rGO as anode material for NIBs.

Morphology, interlayer spacing, and structural defects all play important roles in the electrochemical performance. Both the rGO and the BF-rGO show a layered structure with some overlapping wrinkles (Figure S9). The wrinkles create some interconnected pores, which minimizes diffusive resistance and enhances the surface area for active site dispersion.$^{39}$ The TEM and HR-TEM images reveal the structural changes during cycling (Figure 5). Clear lattice fringes can be observed in rGO, with an average interlayer spacing of 0.34 nm. The as-obtained BF-rGO shows a slightly disordered structure with an enlarged interlayer distance (~0.37 nm), which was caused by formation of pillars during the reaction between boric acid and the functional groups in GO. The after-cycled BF-rGO maintained the layered structure, with some wrinkles on the surface. Importantly, the interlayer distance of the after-cycled BF-rGO was
further expanded into 0.42 nm, which is likely caused by the continuous insertion/de-insertion of Na$^+$ ions between the layers.

**Figure 5** TEM and HR-TEM images of (a, d) rGO, (b, e) as-obtained BF-rGO, and (c, f) long-term cycled BF-rGO. Insets (d, e, f) are the contrast profiles. All the samples are in fully charged state.

The excellent performance of the BF-rGO can be attributed to the following reasons. First, enlarged interlayer distance is beneficial for Na$^+$ insertion/de-insertion. The strong B–O bond in comparison to C–O contributes to the formation of sturdy pillars that prevent the coalescence of graphitic layers, and the resultant expanded spacing is crucial for Na$^+$ storage. Second, the incorporation of B and O into the rGO basal planes introduces more active sites (e.g., voids in structure B in Figure 2g) that help to trap more Na$^+$ ions, leading to a higher capacity compared to rGO. In addition, the resultant 2D structure effectively shorten the Na$^+$ diffusion distance, and enable better contact between electrode and electrolyte.

4. CONCLUSIONS

In summary, BF-rGO was obtained through a one-pot hydrothermal reaction and displayed great potential as anode for NIBs. The resultant BF–rGO features a large amount of active
defects, and an enlarged interlayer spacing. The Na/BF–rGO half cells demonstrated excellent electrochemical performance with high reversible capacity and superior cycling stability. The strategy used in this work to simultaneously expand the interlayer spacing and introduce heteroatoms into rGO is low-cost and easy to accomplish, which makes it feasible for scaling up. This work sheds light on how to prepare rGO with expanded interlayer space by using heteroatoms such as N and P, and the resultant rGO can be explored as high-performance NIB anode materials.

ASSOCIATED CONTENT

Supporting Information. Characterization, cells assembling, FTIR spectra, nitrogen sorption isotherms, electrochemical performance curves, SEM images, and parameters of the fitted Nyquist plots are available free of charge via the Internet at: http://pubs.acs.org.

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