Boron-doped Graphene/Silicon Composite as Anodes of Lithium-ion Batteries

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Abstract

Silicon attracts extensive attention as the promising anode material for lithium-ion batteries (LIB) owing to ultrahigh capacity and appropriate voltage plateau. However, the main problems including volume expansion, poor electrical, and Li⁺ conductivity cause the poor cycle and c-rate performance. In this study, one-pot synthesis process produces boron-doped graphene-silicon through high energy ball milling, solving the poor conductivity by boron-doping silicon and preventing silicon particle expansion via graphene. The modified resulting silicon with boron-doping and graphene shielding (BG-1) can provide improved stability (70% retention after 80 cycles). Owing to the synergistic effect, the resultant Boron doped graphene Si-graphite composite (BG-1@G) shows a high capacity of 850 mAh g⁻¹ at 0.3C and excellent cycle retention of 76.5% over 180 cycles.

Experimental Procedure

FTIR analysis

- The −OH bonding at about 3425 cm⁻¹ becomes −BOH bonding in the BG sample.
- C=O and C–C bonds react to B−O and B–C bonds after boron-doping.
- FTIR demonstrates boron doping in BG structure successfully.

ICP

<table>
<thead>
<tr>
<th>Sample/%</th>
<th>B</th>
<th>Si</th>
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<tbody>
<tr>
<td>BG-1</td>
<td>0.27</td>
<td>98.72</td>
</tr>
<tr>
<td>BG-2</td>
<td>0.27</td>
<td>98.69</td>
</tr>
<tr>
<td>BG-3</td>
<td>0.28</td>
<td>98.71</td>
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EIS analysis

- The EIS measurement shows that the BG-1 illustrates lower charge transfer resistance as compared to pristine.
- Boron doping not only enhances conductivity, but also offers a better path for Li-ions diffusion.

Electrochemical performance

- BG-1 with an huge area between 0.01 and 1.5 V indicates that Li-ion is favorable for adsorbing/desorbing on BG-1 as shown in Fig.(a).
- BG-1 can still recover to 2435 mAh/g when the current density returns to 100 mA/g; further illustrating the superior rate capability as shown in Fig.(b).
- BG-1 has high capacity with initial coulombic efficiency of 82.5%, indicating rare irreversible reaction in first cycle, as shown in Fig.(c).
- BG-1@G still shows better cycling performance than other, with the capacity retention 80% after 150 cycles, as shown in Fig.(d).

XRD analysis

- The powder displays high crystallinity and purification.
- The peak shift caused by the boron-doped effects on lattice constant.

Raman spectrum

- The ratios of I_p/I_g were calculated as 1.73, 1.55, indicating more defects in BG.

Conclusion

- Boron doped silicon increase the conductivity of silicon due to charge carrier concentration increasing.
- Boron doped graphene not only support volume variation of silicon but also offer tunnel for Li-ion transport.
- BG-1 shows heteroatom boron doping into graphene framework and silicon particle decoration in a simple process.

Acknowledgement

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