Na-ion Anode Development

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Sodium-ion batteries could be cheaper than Li-ion batteries, and use a much more abundant resource.

Li$_2$CO$_3$ (Li precursor) price, 1990-2010

Known global supply (tons):
Li$_2$CO$_3$: ~135 million
Na$_2$CO$_3$: ~47 billion

Na$_2$CO$_3$ price today:
~$200/ton

Plot from http://www.lithiumsite.com/market.html
Phosphorus is a promising material for sodium-ion batteries thanks to its high capacity and low cost.

Dahbi et al., *Phys. Chem. Chem. Phys.*, 16 (29), 2014, 15007-15028
Issues

- Low electrical conductivity \((1 \times 10^{-14} \text{ S/cm})\)

- Large volume expansion

  Particle pulverization

  Loss of electrical contract

  Unstable SEI

<table>
<thead>
<tr>
<th>Element</th>
<th>Max. Na content in (\text{Na}_x\text{X})</th>
<th>Vol. ratio of (\text{Na}_x\text{X}/\text{X})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C</td>
<td>&lt; (\text{NaC}_6)</td>
<td>&lt; 2%</td>
</tr>
<tr>
<td>Si</td>
<td>(\text{NaSi})</td>
<td>130%</td>
</tr>
<tr>
<td>Sn</td>
<td>(\text{Na}_{3.75}\text{Sn})</td>
<td>525%</td>
</tr>
<tr>
<td>Sb</td>
<td>(\text{Na}_3\text{Sb})</td>
<td>390%</td>
</tr>
<tr>
<td>Pb</td>
<td>(\text{Na}_{3.75}\text{Pb})</td>
<td>487%</td>
</tr>
<tr>
<td>P</td>
<td>(\text{Na}_3\text{P})</td>
<td>491%</td>
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</table>
Graphene-nanosheet-wrapped Phosphorous Composite Anode

(1) a facile, low-energy ball milling technique was adopted (400 rpm for 1000 min).

(2) Low cost commercial red phosphorus and graphene stacks as raw materials.
Characterization

(1) Amorphous structure structure of the P/G composite.
(2) Graphenen stacks were exfoliated to graphene nanosheets driven by mechanical shearing upon ball-milling.
Morphology

(1) The graphene nanosheets can form a conductive matrix within the composite. 
(2) The large bulk phosphorus were grinded into microscale or nanoscale particles.
Chemical Interaction between Phosphorous and Graphene Sheets

The graphene nanosheets can chemically bind with phosphorus during milling process, which facilitates the intimate contact of graphene nanosheets with phosphorus particles.

Formation of P-O-C bond between phosphours and graphene nanosheets via ball-milling
Chemical Interaction between Phosphorous and Graphene Sheets
Cyclic voltammetry and voltage profiles indicate stable electrochemical behavior with cycling.

I) SEI formation

II) Na$_x$P formation upon sodiation

III-V) Na$_2$P, NaP, and NaP$_7$ formation upon desodiation
A high capacity and coulombic efficiency are achieved using graphene-wrapped phosphorous.

<table>
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<tr>
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<th>Value</th>
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<tbody>
<tr>
<td>Initial Capacity</td>
<td>2077 mAh/g</td>
</tr>
<tr>
<td>Initial Columbic Efficiency</td>
<td>83%</td>
</tr>
<tr>
<td>60th Cycle Capacity</td>
<td>1706 mAh/g</td>
</tr>
</tbody>
</table>
The rate performance for graphene-wrapped phosphorous was also exceptional.
Effect of different graphene content and chemical bonding in the P/graphene composite

(1) With the increasing Graphene content, the electrochemical performance are significantly improved.
(2) Chemical bonding also plays an important role on the battery performance.
Fluoroethylene carbonate (FEC) can help form a stable SEI layer to improve cycling stability.

Stable SEI with FEC

FEC-Free

FEC-Containing
Optimization of Electrolyte (1M NaClO₄ in EC/DEC+ 10wt% FEC)

Significant Na deposition
Particles Un-observable

No Na metal deposition
Particles Observable
Using FTIR, more robust SEI species were found to form with FEC.

Both have some $\text{ROCO}_2\text{Na}, \text{RCO}_2\text{Na}$

**FEC-containing has more:**
- $\text{RCO}_2\text{Na}$
- Polycarbonates

**FEC-free has more:**
- $\text{RONa}$
- Monocarbonate $\text{ROCO}_2\text{Na}$ (possible)
- Ester or alkyl carbonate

More robust species with FEC
(1) The almost overlapped EIS spectra indicate a good maintenance of conducting electrical contact and relatively stable SEI.

(2) The graphene still have a uniform distribution in the composite and provides a good conducting matrix upon cycling.
Summary

1) Graphene-nanosheet-wrapped phosphorus composite anode for sodium-ion batteries via a simple ball-milling approach with low-cost precursors of red phosphorous and graphene stacks

2) The featured structure and chemical bonding (P-O-C) between P and G play an important role on the electrochemical performance of P-Based anode for SIB.

3) More stable SEI formation using FEC

Progress toward sodium-ion batteries
For stationary energy storage
Acknowledgements

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