New Territories of Sustainable Batteries by Carbon-Based Materials

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- Hydronium ion storage
- Energetics of ion insertion in carbons: anions and cations
Production Scale of Purified Minerals

Vesborg and Jaramillo RSC. Adv. 2012, 2, 7933-7947
Molecular Solids: Hosts for $\text{H}_3\text{O}^+$

Xing, Ji et al. Energy Storage Materials, 2016, 2, 63-68
Structural and Computational Studies Confirm Reversible Hydronium Storage

• Hydronium is a meaningful charge carrier for batteries
• Grotthuss mechanism may be applicable
- Hydronium ion batteries
- Energetics of ion insertion in carbons
Dual-Ion Batteries/Dual-Graphite Batteries

The Challenge of DIBs: Cathode Operation Potential Is Simply Too High!
Thermodynamics of Inserting One Anion to Graphite in a Graphite/Metal Cell

If we do not consider the entropy change of desolvation and ohmic IR drop

\[ \Delta G = -eV \approx \Delta H = \]
\[ (E_{(C+A^-)} + E_{(n+1)M} + \Delta H_{\text{desolv. of } M^+} + \Delta H_{\text{desolv. of } A^-}) - (E_C + E_{nM}) \]

\[ \Delta G = -eV \approx \Delta H = \]
\[ E_{(C+A^-)} - E_C + E_M + \Delta H_{\text{desolv. of } M^+} + \Delta H_{\text{desolv. of } A^-} \]
Less Dense Hydrocarbons As Anion-Insertion Cathode

Density: 1.47 g cm⁻³ vs 2.23 g cm⁻³ (graphite)

Rodríguez-Pérez, Lerner, Carter, Ji et al. ACS Energy Letters 2016, 1, 719
• Graphite is not uniquely redox amphoteric

• Oxidative insertion can be generic

• The operation potentials correlate more to the solid structures than to the molecules themselves
Na Does Not Intercalate Graphite

LiC$_6$ GIC: 372 mAh/g

NaC$_{64}$ GIC: 35 mAh/g

Ion Size: The Decisive Factor?

Li⁺  Na⁺  K⁺

Stage III  Stage II  Stage I

Reversible Electrochemical Insertion of K in Graphite

Jian, Ji et al. J. Am. Chem. Soc., 2015, 137, 11566
Luo, Hu et al. Nano Lett. 2015, 15, 7671-7677-175
Reversible Electrochemical Staging of K-GICs

Hard-Soft Composite Carbon: Optimal for Cycling and Rate

Non-Aqueous KIBs: An Emerging Field of Energy Storage

Nazar ACS Energy Lett. 2017, 2, 1122-1127

Ji, Chem. Mater. 2017 In press An invited Perspective

Until June 25, 2017
Why Non-Aqueous K-Ion Batteries?

Favorable potentials

<table>
<thead>
<tr>
<th>Redox Potentials</th>
<th>In Water vs. SHE (V)</th>
<th>In PC vs. SHE (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺/Li</td>
<td>-3.04</td>
<td>-2.79</td>
</tr>
<tr>
<td>Na⁺/Na</td>
<td>-2.71</td>
<td>-2.56</td>
</tr>
<tr>
<td>K⁺/K</td>
<td>-2.94</td>
<td>-2.88</td>
</tr>
<tr>
<td>Rb⁺/Rb</td>
<td>-3.03</td>
<td>-2.95</td>
</tr>
</tbody>
</table>

Compatible with the LIB carbon anode infrastructure

Similar specific energy as NIBs

Komaba et al. Electrochim. Commun. 2015, 60, 172-175
Debated Mechanisms of Na-Ion Storage in Hard Carbon

**Slope capacity:** Na intercalates turbostratic nanodomains

**Plateau Capacity:** Na-sorption (nanoplasting) in nanopores


**Slope capacity:** Na-defects binding

**Plateau Capacity:** Na intercalates turbostratic nanodomains

Bommier, Ji et al. *Nano Lett.*, 2015, 15, 5888

Hard Carbon and Soft Carbon

Franklin, R. E. Acta Cryst. 1951
If we do not consider the entropy change of desolvation and ohmic IR drop

\[ \Delta G = -eV \approx \Delta H = (E_{(C-M^+)} + E_{(n-1)M} + \Delta H_{\text{desolv. of } M^+} + \Delta H_{\text{solv. of } M^+}) - (E_C + E_{nM}) \]

\[ \Delta G = -eV \approx \Delta H = (E_{(C-M^+)} - E_M) - E_C \]
Vacancy Defects Lead to High Sloping Potentials

Monovacancy

Divacancy

Large-vacancy

0.529 eV

-1.1 eV

-0.81 eV

-3.00 eV

Decrease Vacancy Defects ➔ Less Sloping Capacity

\[ G(r) = \frac{2}{\pi} \int Q(S(Q) - 1) \sin(Qr) \, dQ = 4\pi \rho_0 r (g(r) - 1) \]

Bommier, Ji *Nano Lett.*, 2015, 15, 5888
Increase Vacancy or Heteroatom Defects ➔ More Sloping Capacity

Electrodes | HC | P-HC | B-HC | S-HC
--- | --- | --- | --- | ---
Sodiation | 178 | 245 | 304 | 195
Desodiation | 134 | 157 | 70 | 151

Correlation: sloping capacity and defects

A Design Principle

More defective Expanded Structure

Li, Ji et al. under preparation

Conclusions

- Hydronium ion storage: a promising new area
- Anion insertion into carbon: energetics
- Non-aqueous KIBs competitive to NIBs
- An alternative mechanism for Na-ion storage in hard carbon
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Chongmin Wang (Pacific Northwest National Laboratory)

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Questions?