Capacitive Anion Intercalation Enables High-power Graphite Cathodes

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Energy storage mechanism differences

### Li-ion batteries

- **Cathode:** LiCoO$_2$, LiFePO$_4$, LiMn$_2$O$_4$...
- **Anode:** graphite, hard carbon, Li$_4$Ti$_5$O$_{12}$...

**Ion transport:** cation (Li$^+$)

Limited rate capability

### Dual-ion/Al-ion batteries

- **Cathode:** graphite, graphene...
- **Anode:** graphite, Al, Li$_4$Ti$_5$O$_{12}$...

**Ion transport:** cation (Li$^+$) and anion (PF$_6^-$)

High power performance
Progress of graphitic carbon cathodes

**Anion intercalation mechanism:**

Charge → Discharge

**Advantages of graphitic carbon cathodes:**
- High electrical conductivity
- Excellent electrochemical stability
- Tailorable porous structure
- Redox-amphoteric intercalation: cation/anion
- Various anions in option: PF$_6^-$, TFSI$^-$, AlCl$_4^-$...

**Reported high-power graphitic carbon cathodes: porous structures**

<table>
<thead>
<tr>
<th>Graphene foam</th>
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<th>Porous Graphene film</th>
<th>Graphite in porous matrix</th>
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*Graphene foam: Nature 2015, 520, 324.*
Benefits and Problems of porous graphitic carbon cathodes

- Alleviate volume change during anion intercalation

- High cost and low volumetric energy of porous carbon
- Fundamental missing: high power originates from porous structure/graphene?

Our strategy:
- Commercial graphite powder: low cost, high tap density (2.2 g/cm³), excellent compatibility
- Strong binder: Alg-Na, CMC, PAA, PVDF.
Role of Alg binder:

- Suppressing the disintegration of electrode
- Stable platform to investigate the anion intercalation behavior of graphite and energy storage kinetics.
Electrochemical performance of graphite cathodes:

Half cell:

Staging anion intercalation behavior.

5 pairs of intercalation/de-intercalation peaks appear.
Excellent rate capability (Peak power density ~ 43 kW/kg at 334 Wh/kg): never discovered before.
Cycling performance:

Long-term cycling stability: >10000 cycles.
Scale-up ability: graphite loading 2-12.6 mg/cm²
Kinetics analysis: electrochemical impedance spectra (EIS)

EIS at 0-2000\(^{th}\) cycle

Sloping line: 45°\(\rightarrow\)90°

- Mass transfer enhancing

\(R_{ct}\) decreased!

- Charge transfer enhancing

\(\tau_0\) shortened!

- Response accelerating

Anion intercalation into graphite is a self-activating process.
Kinetics analysis: galvanostatic intermittent titration technique (GITT)

The PF$_6^-$ diffusion coefficient (D) also showed an activating process.
Anion (PF$_6^-$) intercalation into graphite is a fast (pseudo)capacitive process, leading to high power performance of graphite cathodes.

**Kinetics analysis: CV measurements**

O1-O4: anion intercalation  
R1-R4: anion deintercalation

Power law: $i = av^b$; $b \approx 1$.  
Capacitive contribution: 93%

All redox peaks contain substantial capacitive contribution.
Comparison with cation intercalation

The same graphite electrode; 0.01-1.5V; 1M LiPF₆ in EC/EMC

Cation (Li⁺) intercalation into graphite is a slow diffusion-controlled process.

Power law: \( i = a v^b \); \( b << 1 \).
Diffusion-limited intercalation process.

Cation (Li⁺) intercalation into graphite is a slow diffusion-controlled process.
Rate performance of graphite anode

The same graphite electrode; 0.01-1.5V; 1M LiPF$_6$ in EC/EMC

Inferior rate performance of graphite anode.
Structure and composition analysis of graphite cathode after cycling

Graphite cathodes remained stable after long-term cycling.
Conclusions:

- Graphite is an **intercalation-pseudocapacitive cathode** material;
- Ultrahigh power capability and long cycling life can be achieved on commercial graphite powders.
- Anion intercalation is a self-activating, pseudocapacitive process;
- Anion intercalation (PF$_6^-$) is much faster than diffusion-limited cation (Li$^+$) intercalation;
- The high power feature of graphitic carbon cathodes mainly derives from the fast anion intercalation, rather than porous structure.

## Perspective and challenges

### Graphitic carbon cathodes
- In-situ characterizations on anion intercalation process.
- Detailed investigation on different intercalation stages.
- Further increase graphite capacity

### Electrolytes
- Stable electrolyte working at >5 V is highly desired.
- Enhance compatibility with conventional anode materials.
- Improve stability of Na, K, Mg and Al-ion electrolytes...

### Energy storage devices
- New high-energy and high-power devices
- Multifunctional batteries
- Solid state dual-ion batteries...

### High-capacity dual-ion batteries
- Demonstration of high-capacity dual-ion batteries (>3000 mAh)...

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