Graphene 2018

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Capacitive Anion Intercalation Enables High-power Graphite Cathodes

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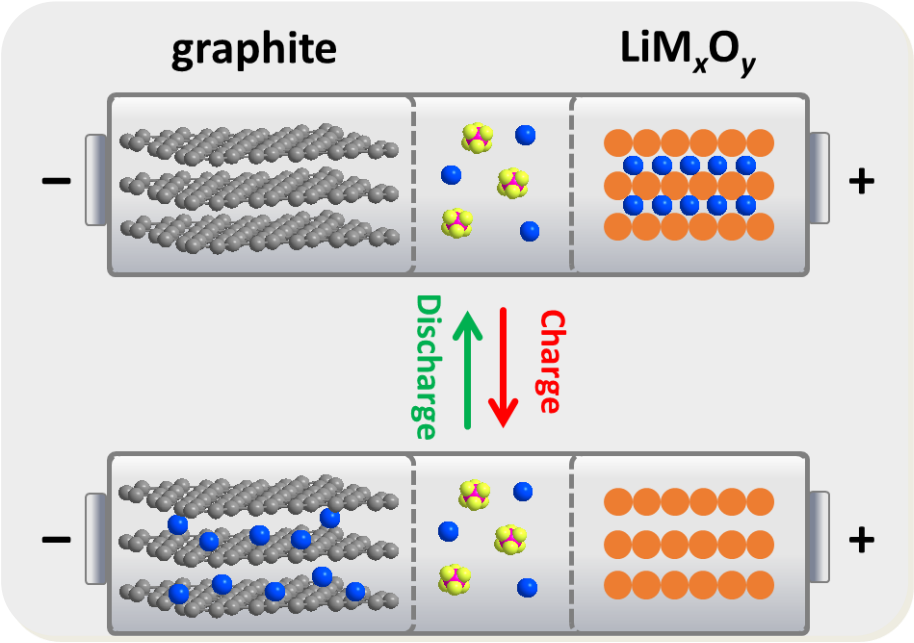
Energy storage mechanism differences

Li-ion batteries

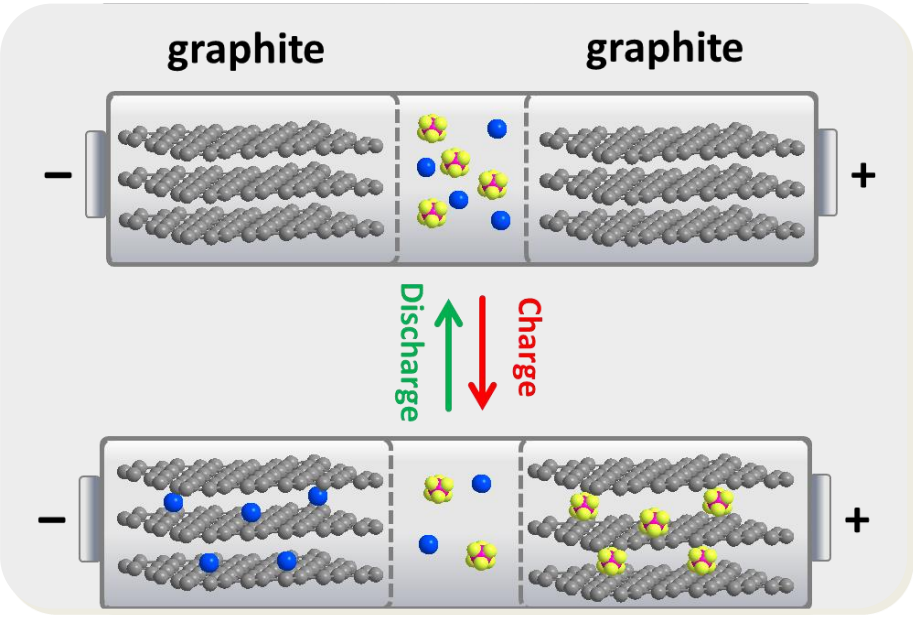


Ion transport: cation (Li^+)

Cathode: $LiCoO_2$, $LiFePO_4$, $LiMn_2O_4$…
Anode: graphite, hard carbon, $Li_4Ti_5O_{12}$ …

Limited rate capability

Dual-ion/Al-ion batteries



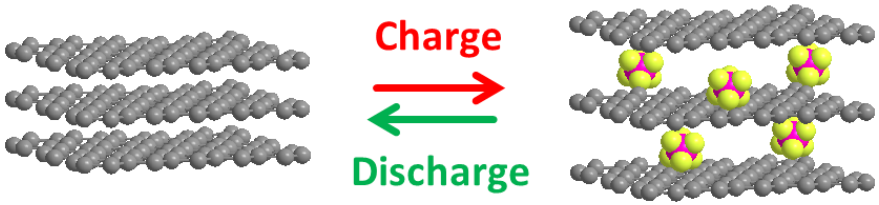
Ion transport: cation (Li^+) and anion (PF_6^-)

Cathode: graphite, graphene…
Anode: graphite, Al, $Li_4Ti_5O_{12}$…

High power performance

Progress of graphitic carbon cathodes

Anion intercalation mechanism:

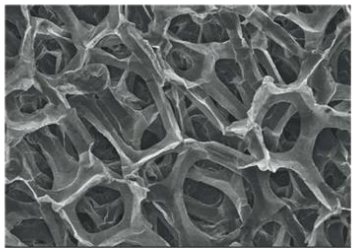


Advantages of graphitic carbon cathodes:

- High electrical conductivity
- Excellent electrochemcial 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

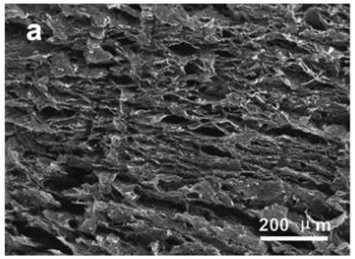
Graphene foam



Nature **2015**, *520*, 324.

$AlCl_4^-$ intercalation

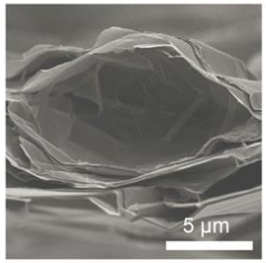
Porous Graphite foam



Adv. Mater. **2016**, *28*, 9218.

$AlCl_4^-$ intercalation

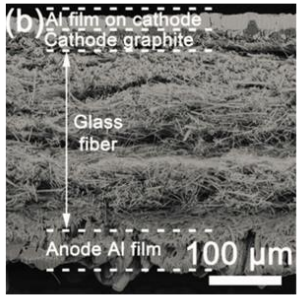
Porous Graphene film



Sci Adv **2017**, *3*, eaao7233.

$AlCl_4^-$ intercalation

Graphite in porous matrix



Adv. Energy Mater. **2017**, 1700913.

PF_6^- intercalation

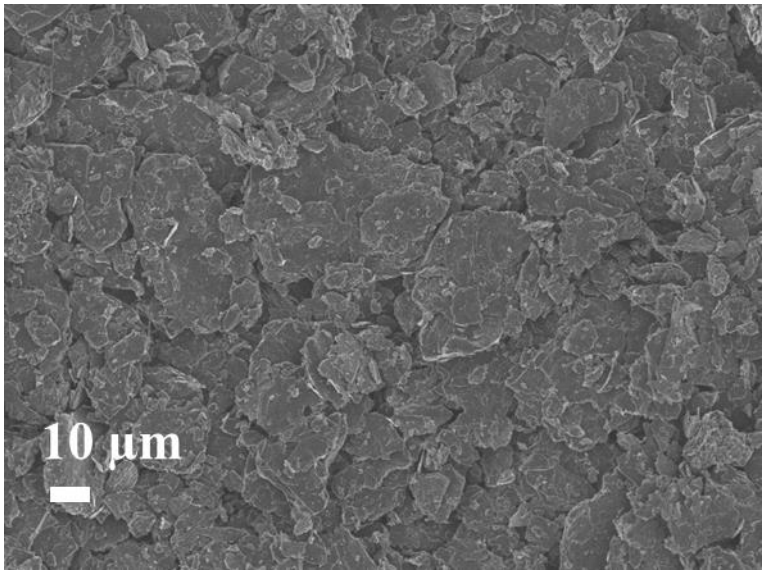
Benefits and Problems of porous graphitic carbon cathodes

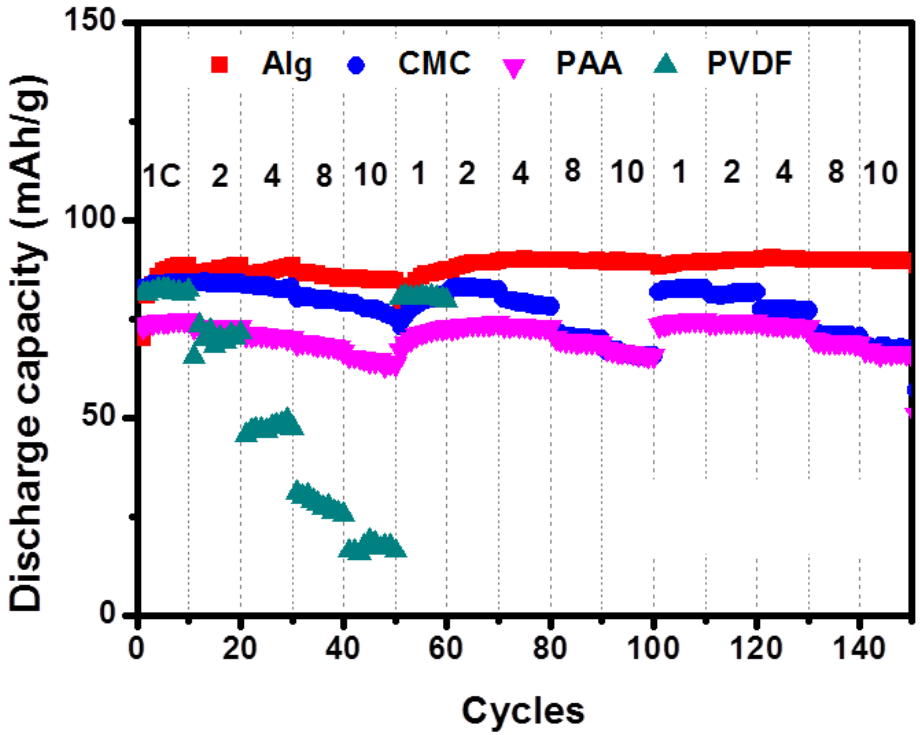
- Alleviate volume change during anion intercalation

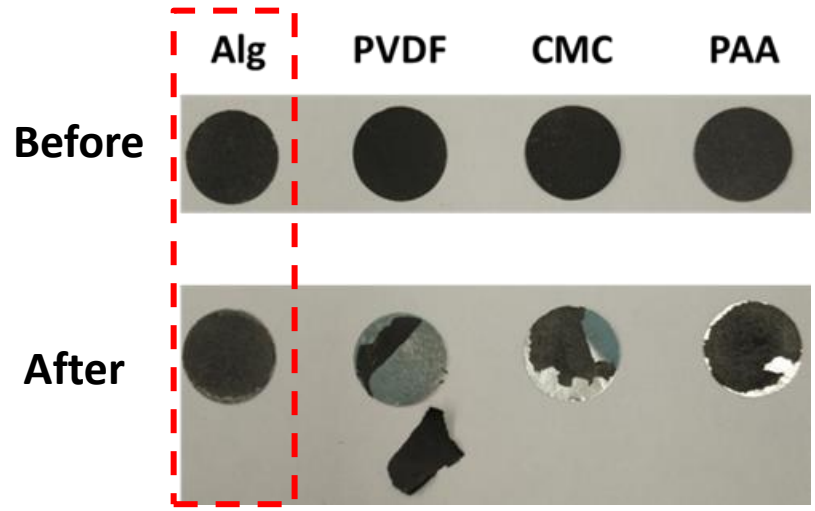
- **High cost** and **low volumetric energy** of porous carbon
- **Fundamental missing**: **high power originates from porous structure/graphene?**

Our strategy:

- **Commercial graphite powder:** low cost, high tap density (2.2 g/cm^3), excellent compatibility
- **Strong binder:** Alg-Na**,** CMC, PAA, PVDF.





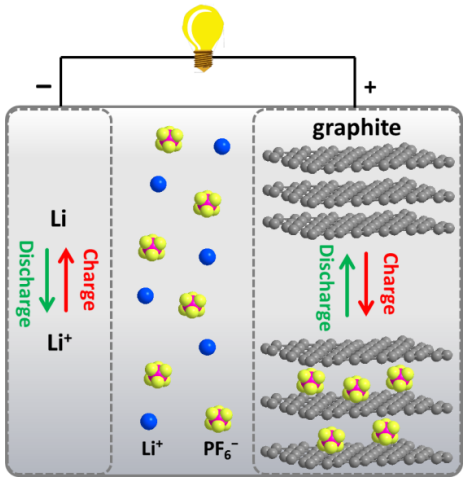


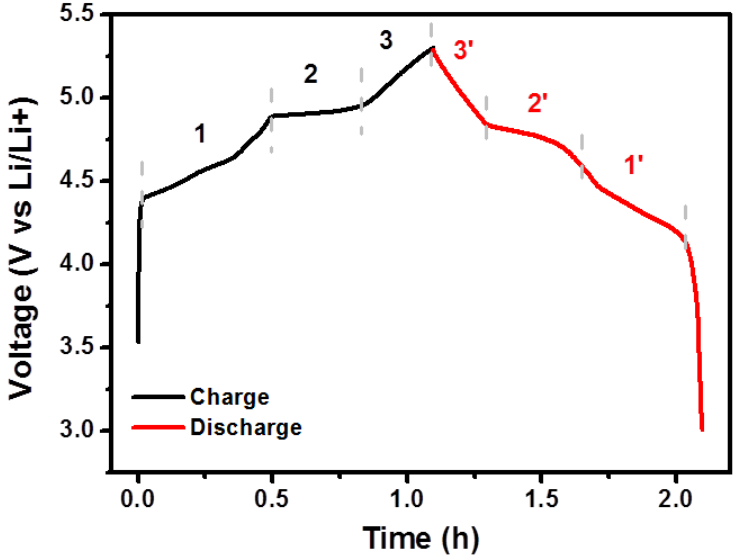
Role of Alg binder:

- ✓ **Suppressing the disintegration** of electrode
- ✓ Stable platform to investigate the **anion intercalation bahavior** of graphite and **energy storage kinetics**.

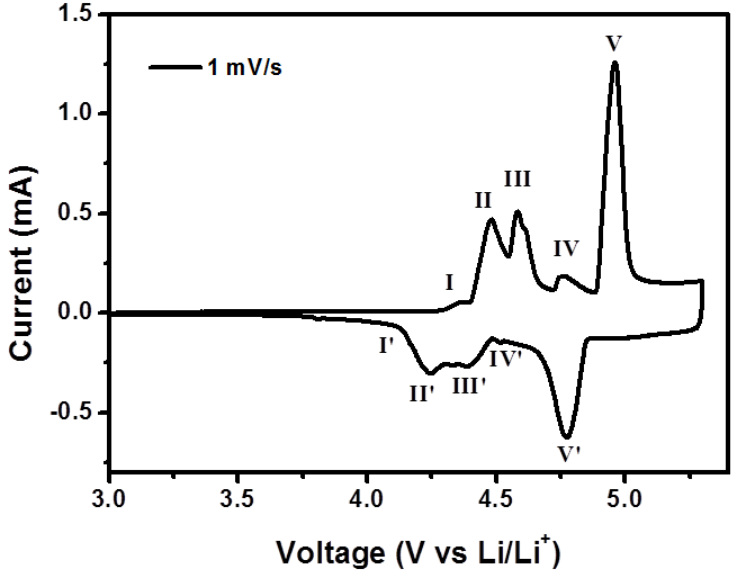
Electrochemical performance of graphite cathodes:

Half cell:



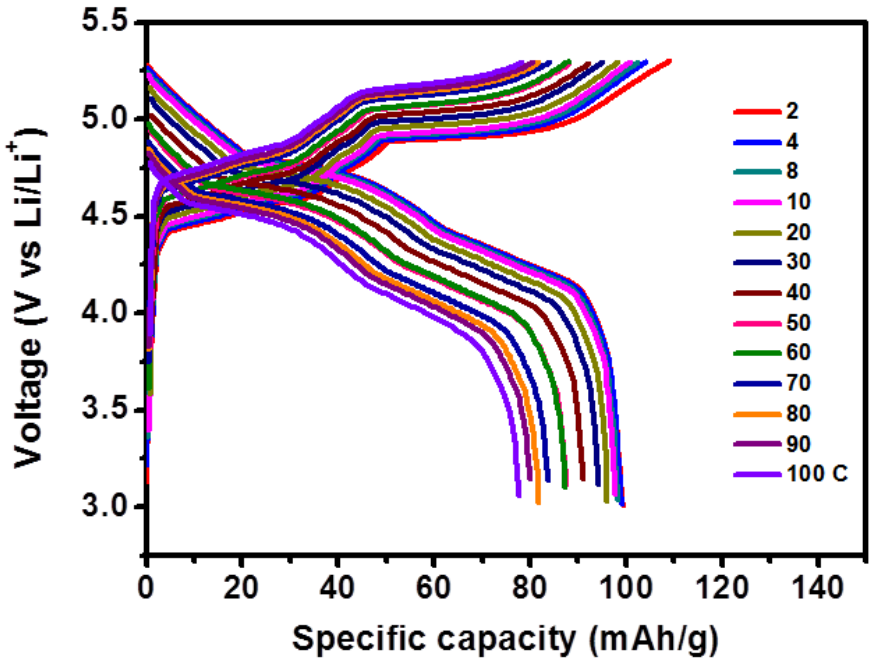


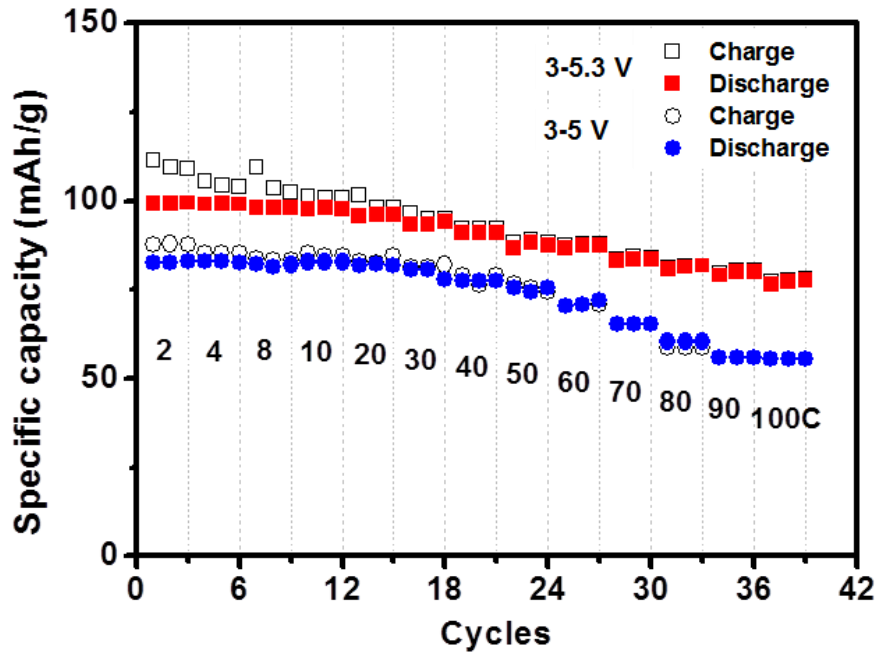
Staging anion intercalation behavior.



5 pairs of intercalation/de-intercalation peaks appear.

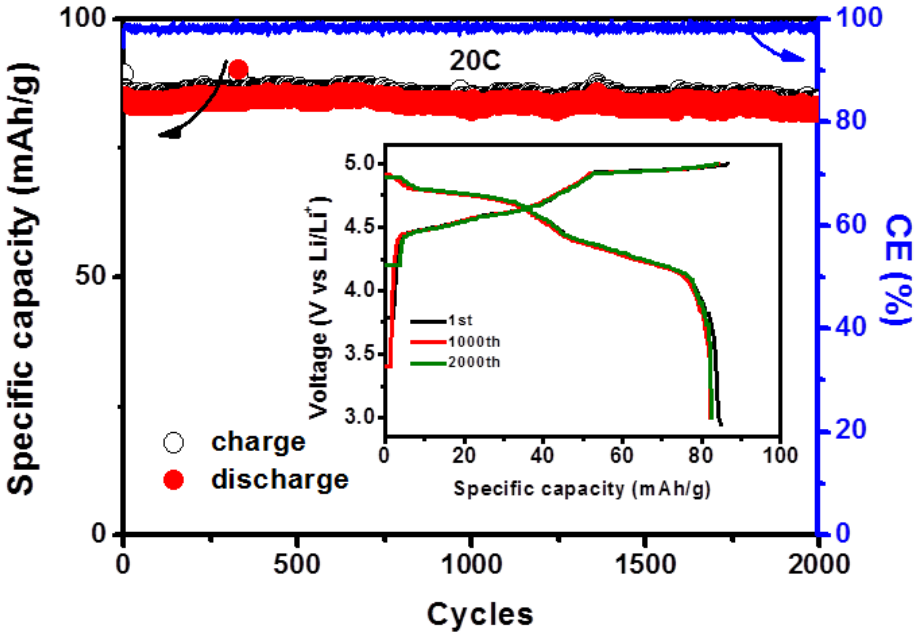
Rate performance:

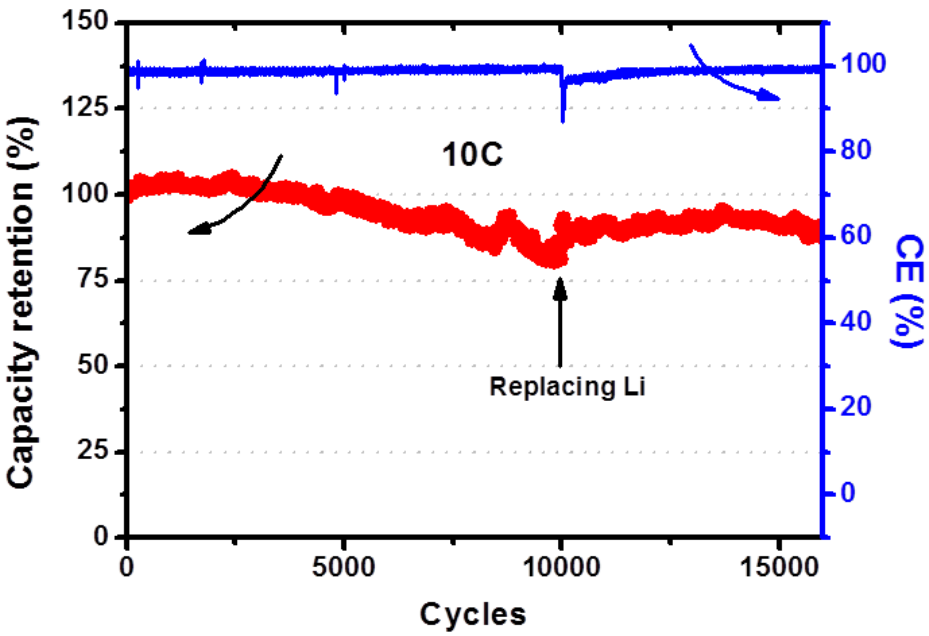




Excellent rate capability (Peak power density ~ **43 kW/kg** at 334 Wh/kg): never discovered before.

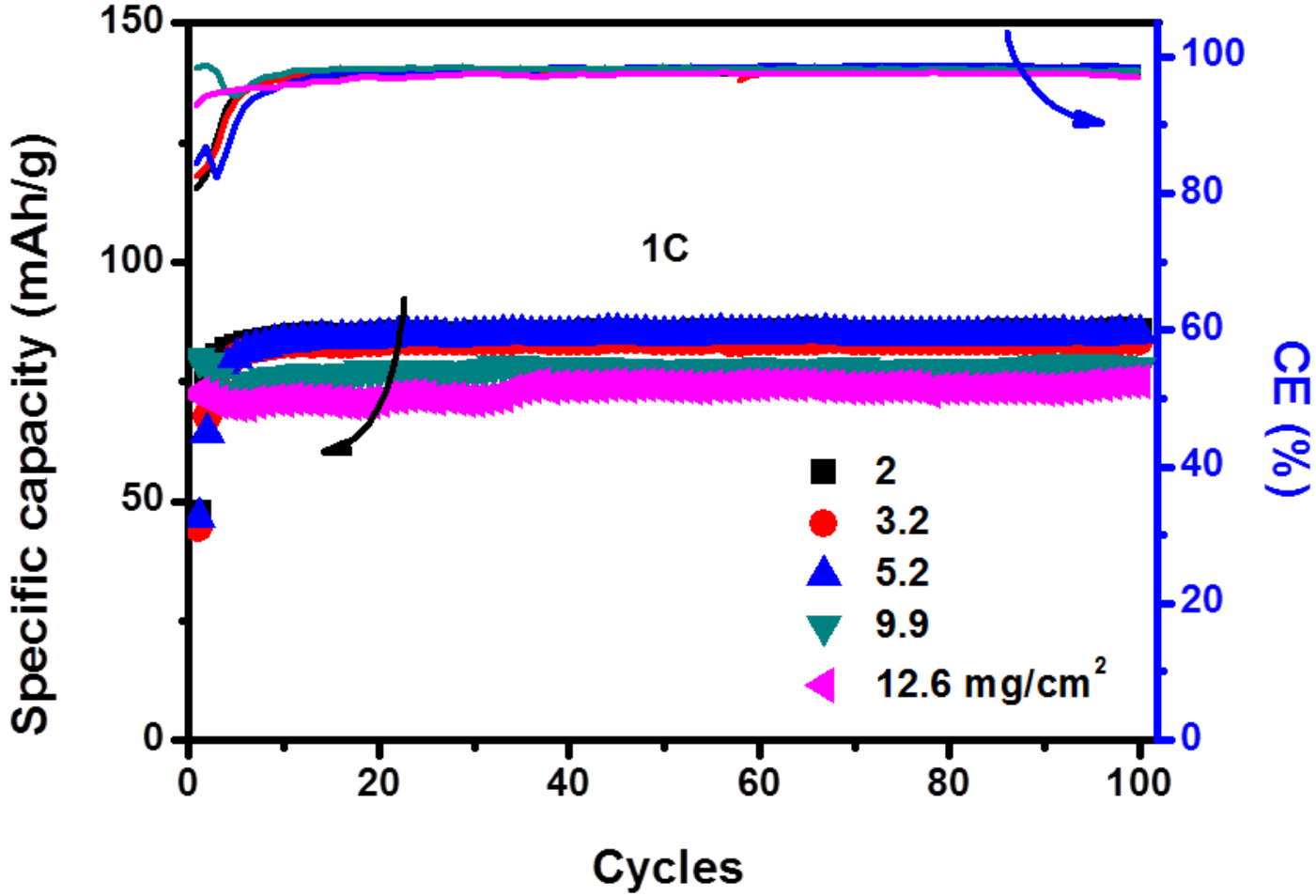
Cycling performance:





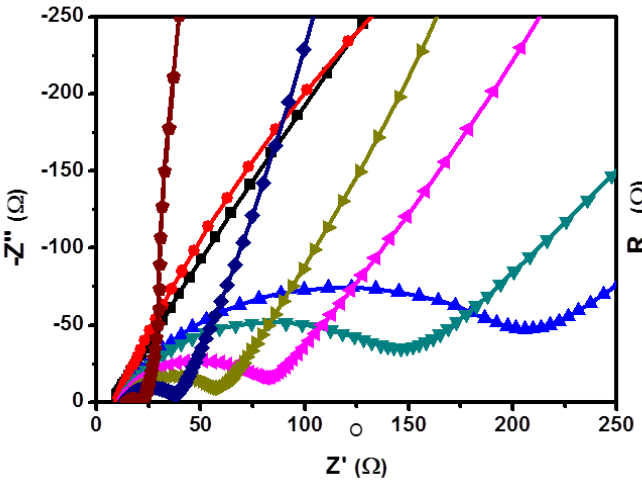
Long-term cycling stability: >10000 cycles.

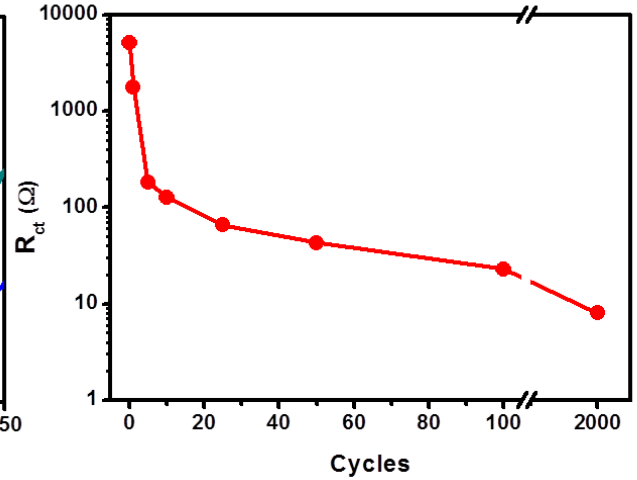
Scale-up ability: graphite loading 2-12.6 mg/cm^2

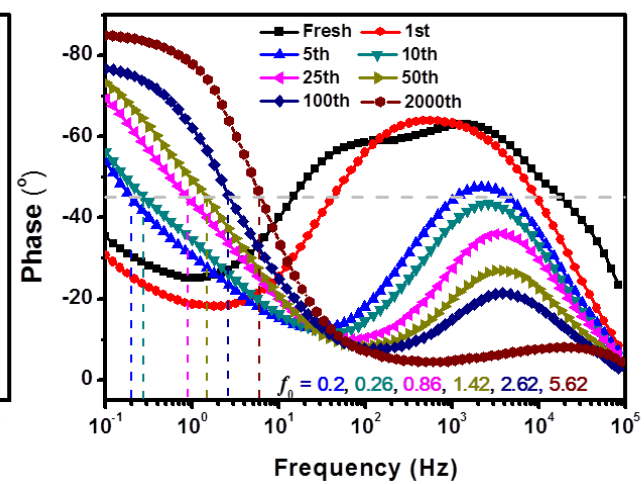


Kinetics analysis: electrochemical impedance spectra (EIS)

EIS at 0-2000th cycle







Sloping line: 45°→90°

R_{ct} decreased!

τ_0 shortened!

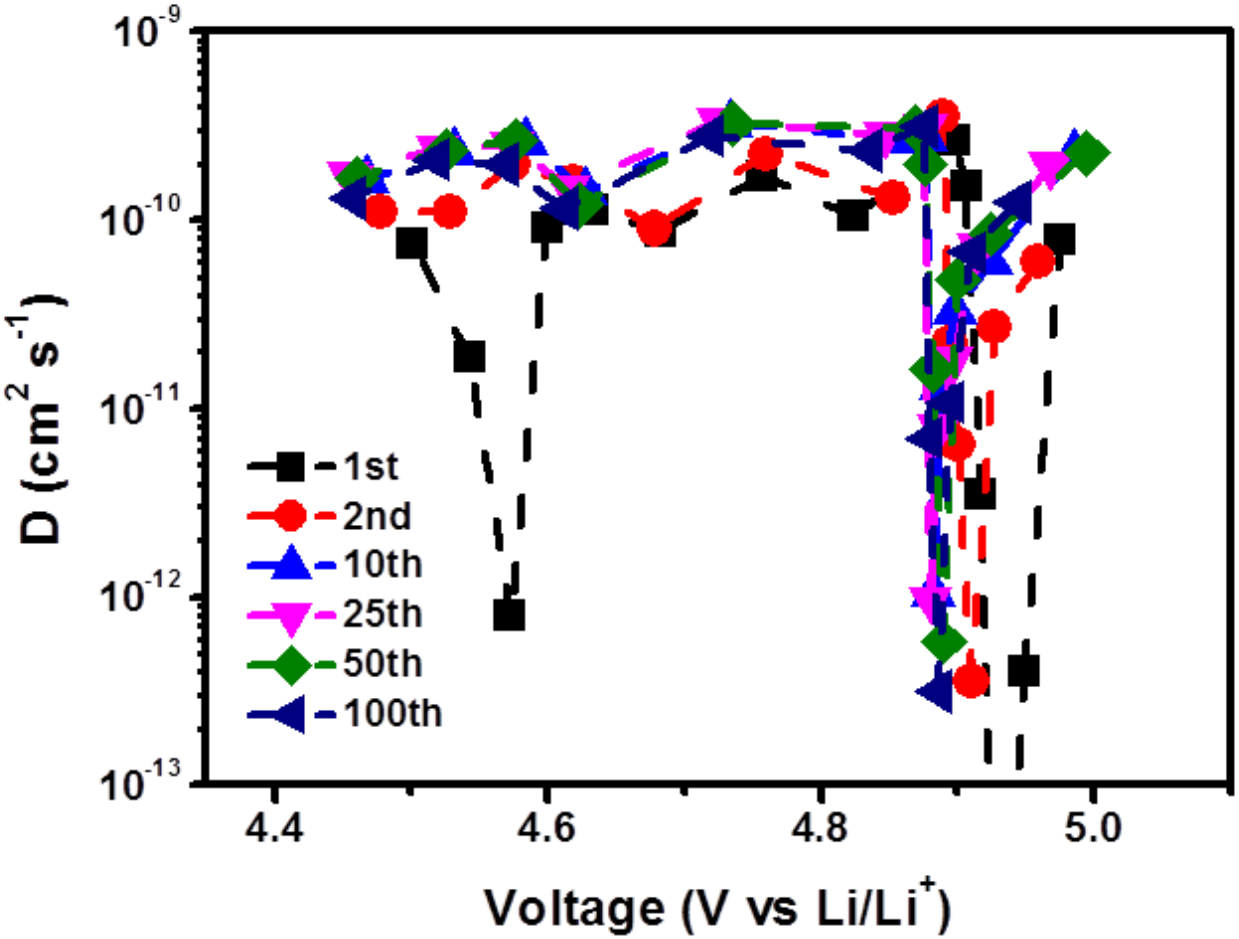
Mass transfer enhancing

Charge transfer enhancing

Response accelerating

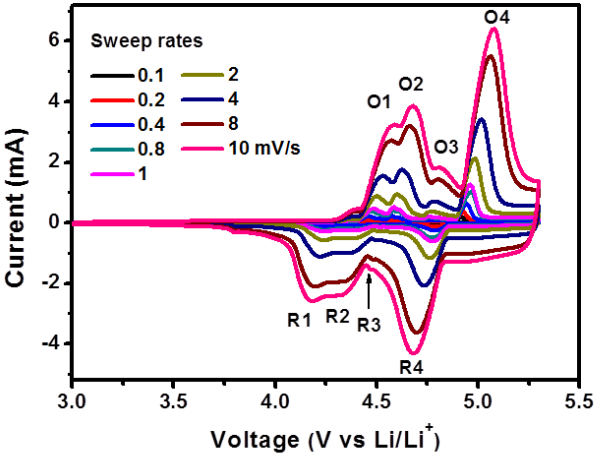
Anion intercalation into graphite is a self-activating process.

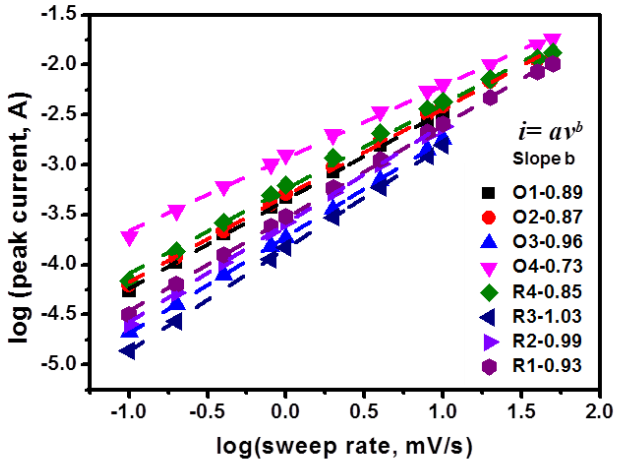
Kinetics analysis:
galvanostatic intermittent titration technique (GITT)

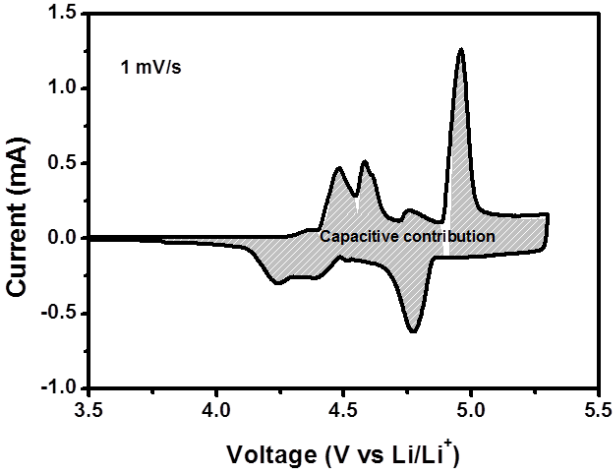


The $PF6^-$ diffusion coefficient (D) also showed an activating process.

Kinetics analysis: CV measurements







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

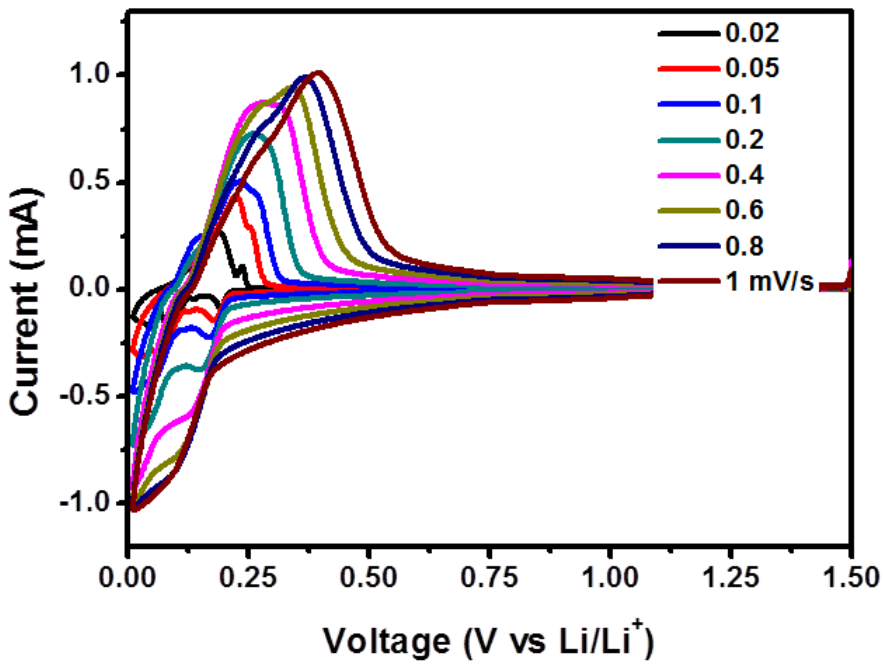
Power law: $i = av^b$; b≈1.
All redox peaks contain substantial capacitive contribution.

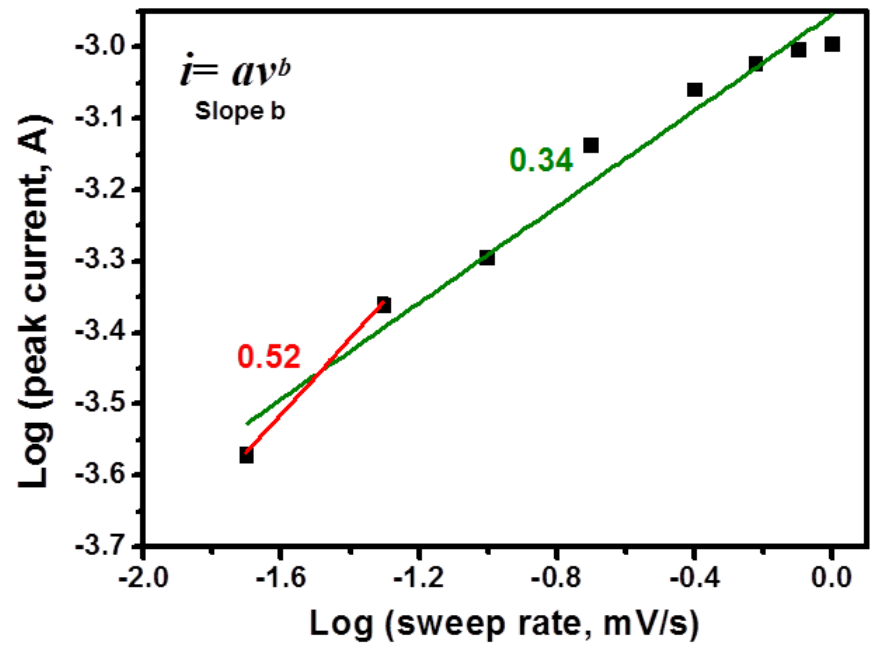
Capacitive contribution: 93%

Anion (PF_6^-) intercalation into graphite is a fast (pseudo)capacitive process, leading to high power performance of graphite cathodes.

Comparison with cation intercaltion

The same graphite electrode;
0.01-1.5V;
1M $LiPF_6$ in EC/EMC





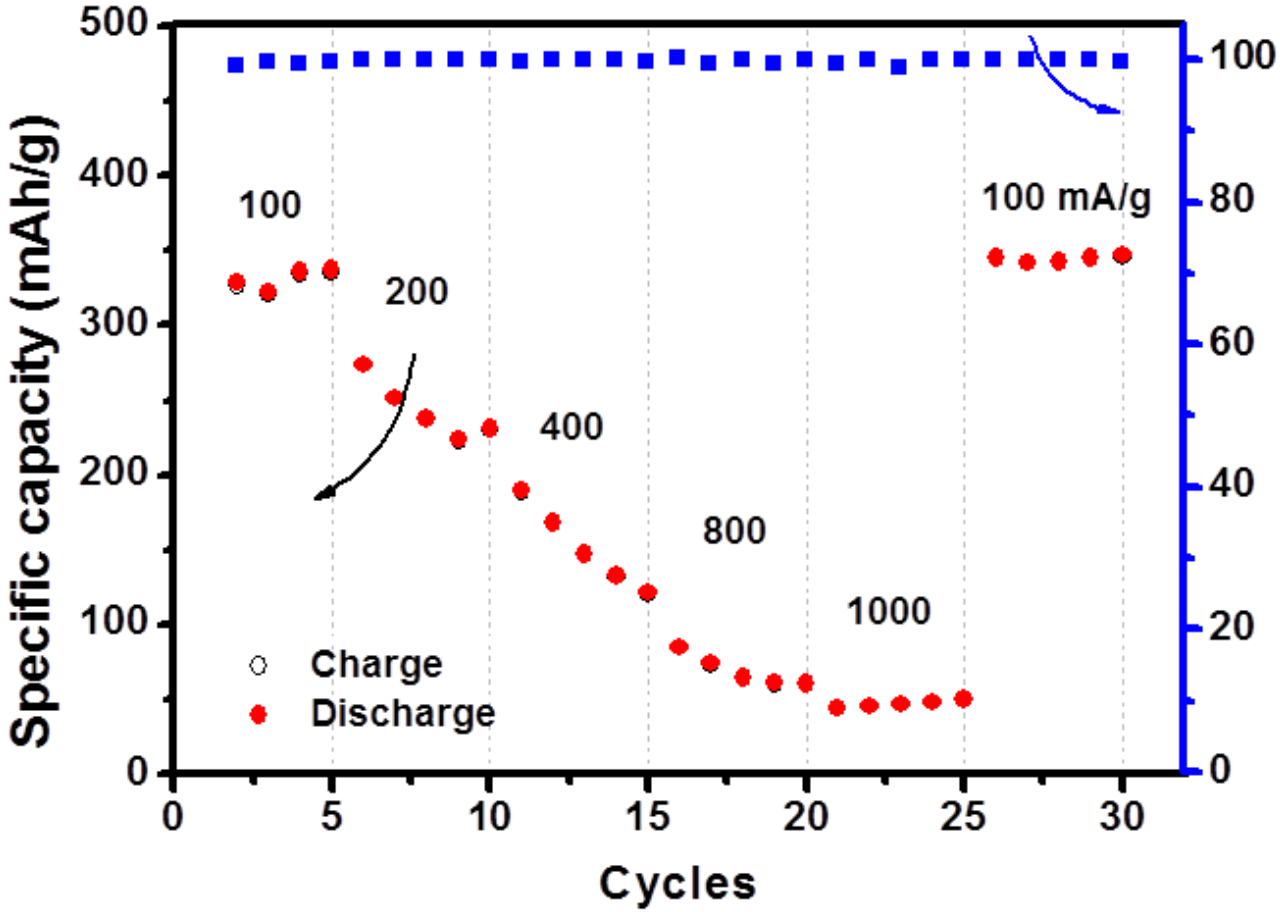
Power law: $i = av^b$; b<<1.

Diffusion-limited intercalation process.

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

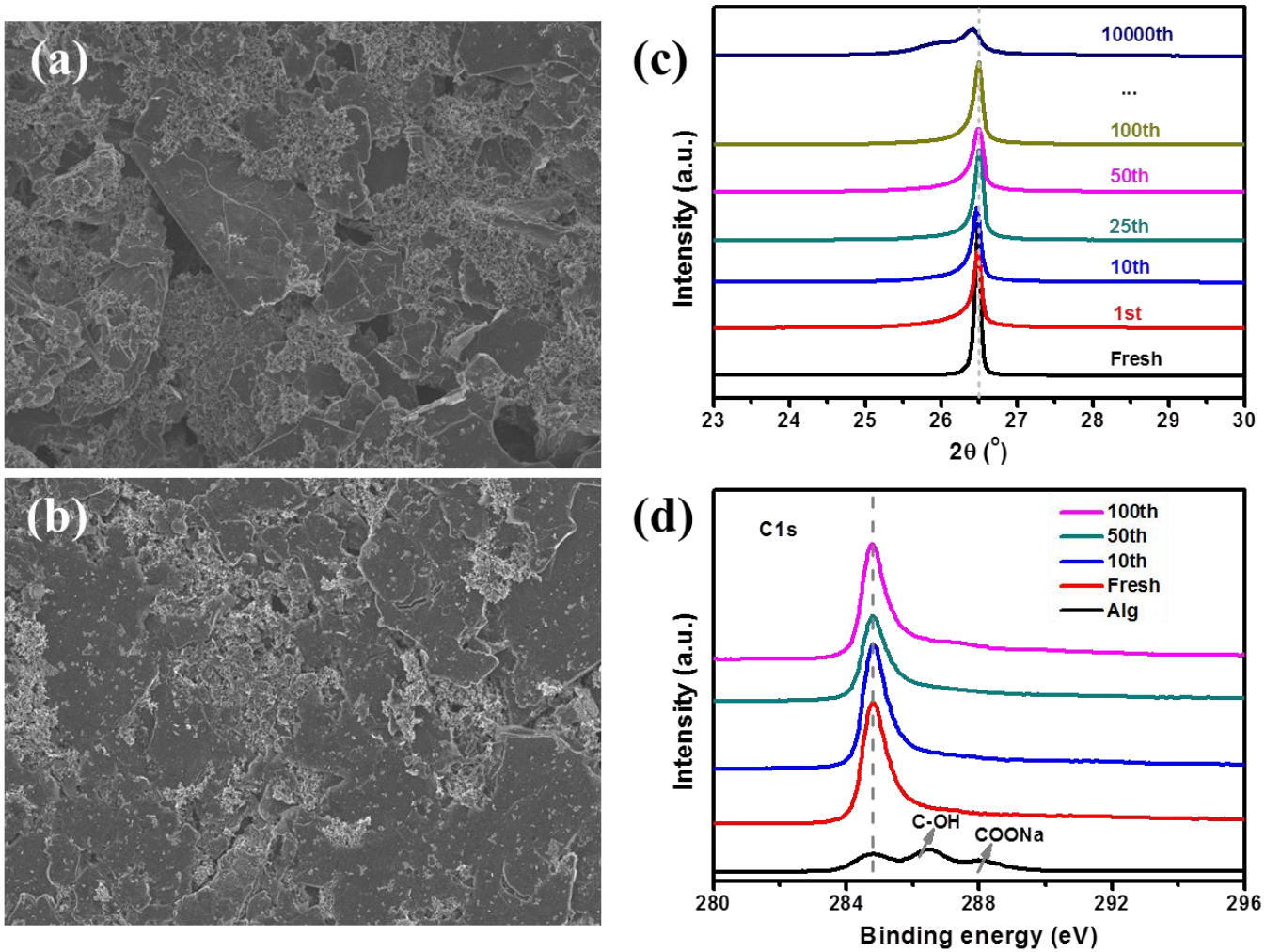
Rate performance of graphite anode

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.

G. Wang, M. Yu, J. Wang, D. Li, D. Tan, M. Loffler, X. Zhuang, K. Mullen, X. Feng, ***Adv. Mater.*** **2018**, *30*, e1800533.

Perspective and challenges

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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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