# Na-ion Anode Development

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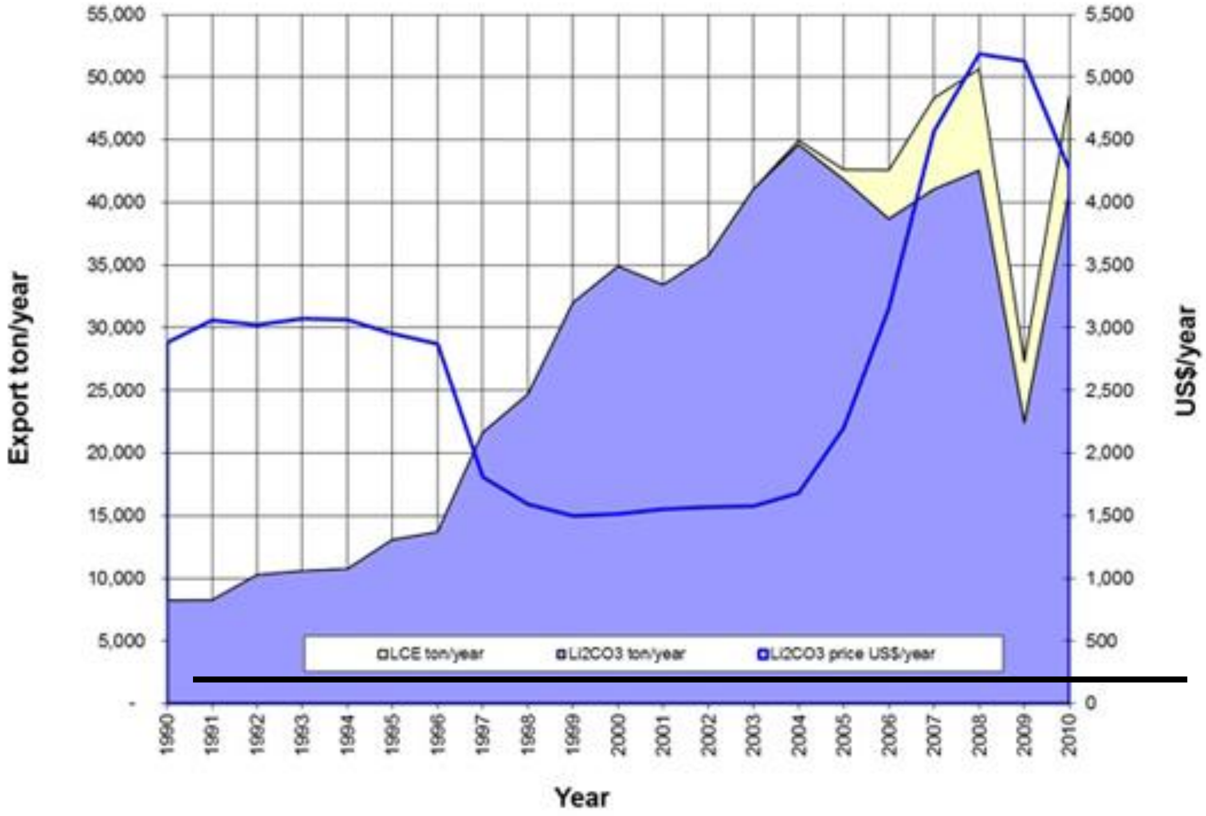
# Sodium-ion batteries could be cheaper than Li-ion batteries, and use a much more abundant resource.

**$Li_2CO_3$ (Li precursor) price, 1990-2010**

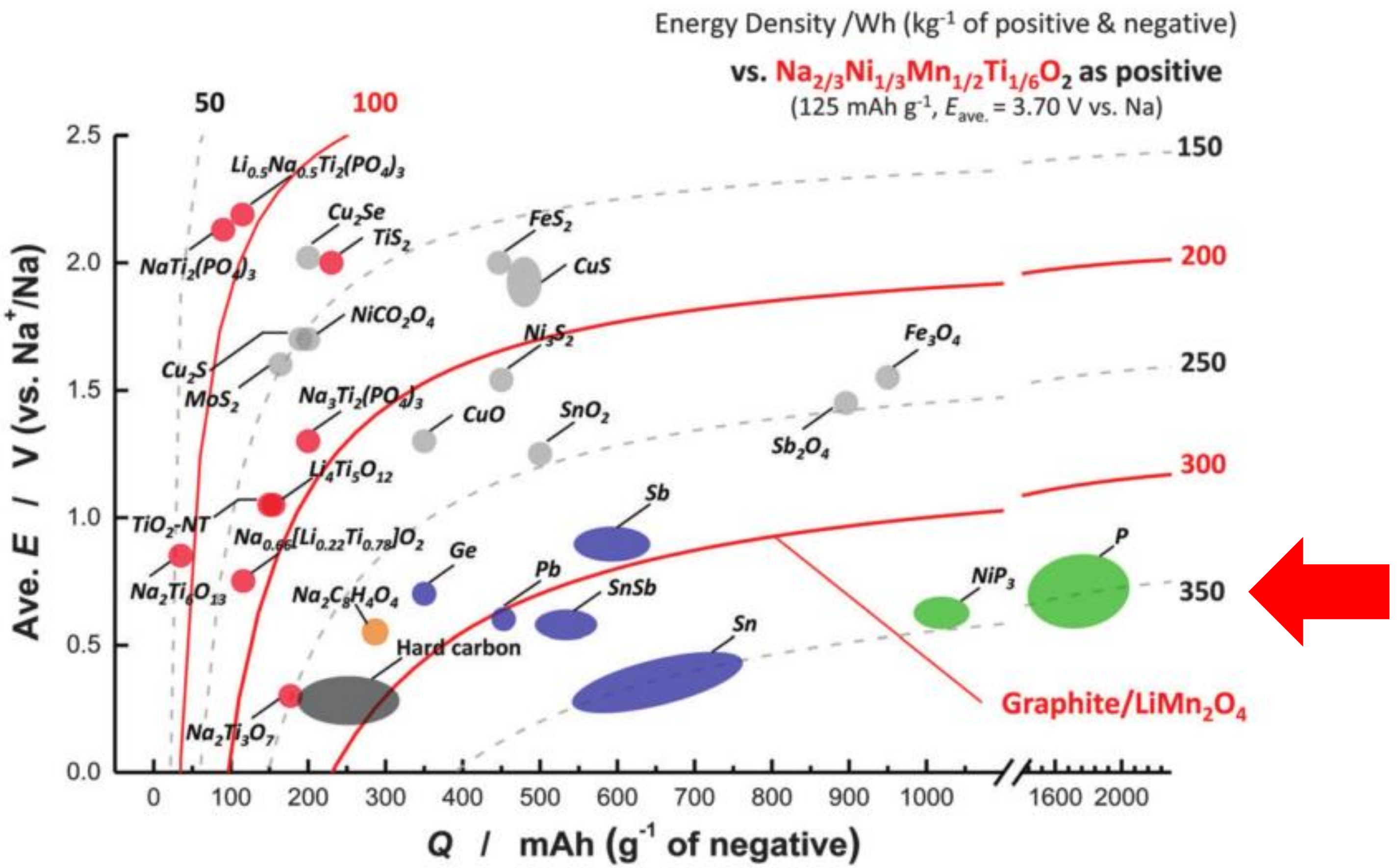



**Known global supply (tons):**
$Li_2CO_3$: ~135 million
$Na_2CO_3$: ~47 billion

**$Na_2CO_3$ price today:**
~$200/ton

Plot from http://www.lithiumsite.com/market.html
Values from Evans, An Abundance of Lithium, 2008; Dolley, Soda Ash, U.S. Geological Survey Mineral Commodity Summaries, 2014; alibaba.com, http://www.alibaba.com/showroom/sodium-carbonate-price-per-ton.html, accessed August 24, 2014

# Phosphorus is a promising material for sodium-ion batteries thanks to its high capacity and low cost.

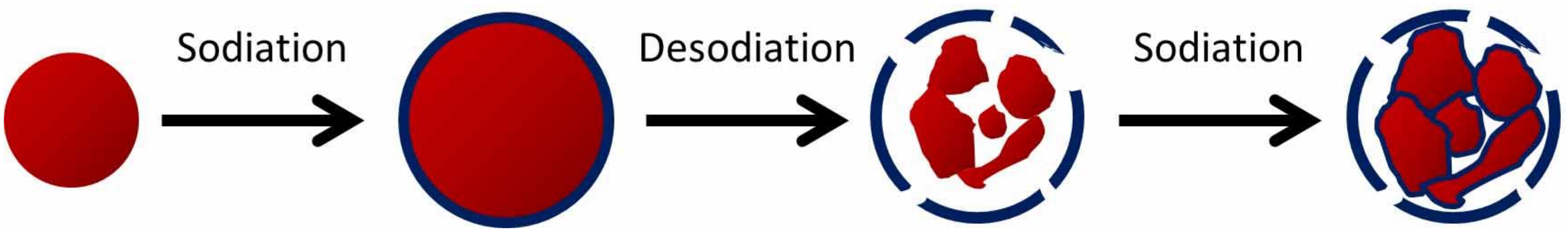



Dahbi *et al.*, *Phys. Chem. Chem. Phys.*, 16 (29), 2014, 15007-15028

# Issues

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

- Large volume expansion




Particle pulverization

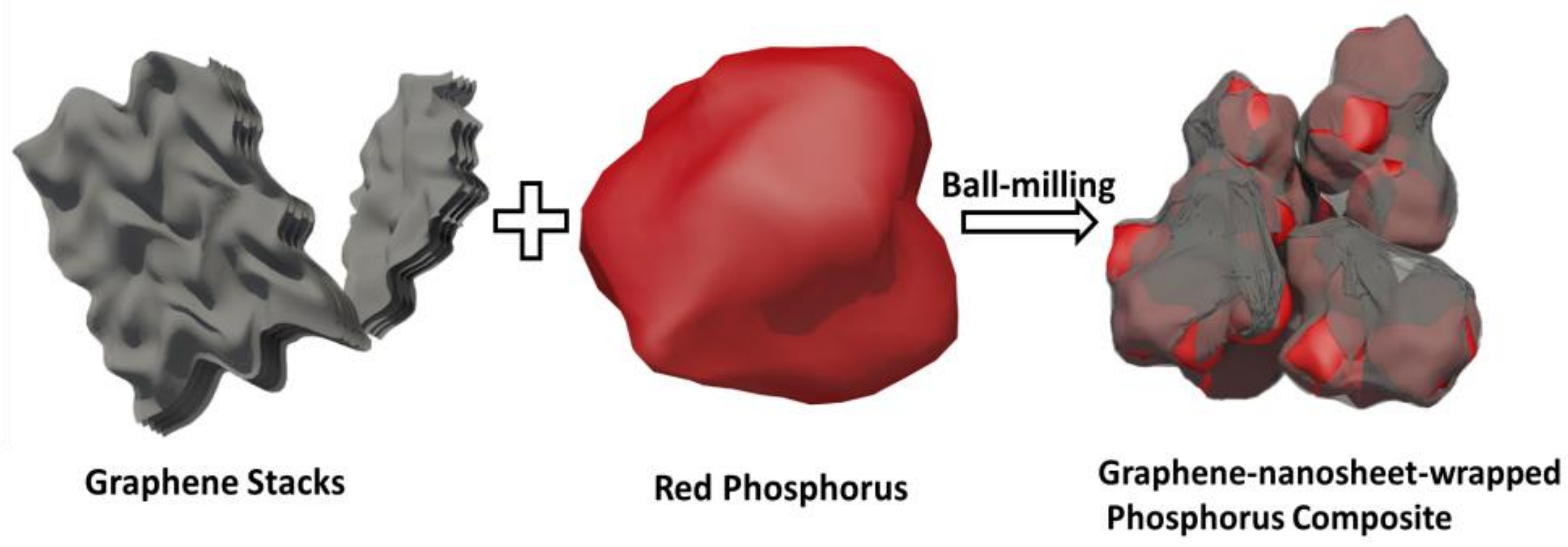
Loss of electrical contract

Unstable SEI

……..

| Element | Max. Na content in $Na_xX$ | Vol. ratio of $Na_xX/X$ |
|---|---|---|
| Na | – | – |
| C | $< NaC_6$ | < 2 % |
| Si | NaSi | 130 % |
| Sn | $Na_{3.75}Sn$ | 525 % |
| Sb | $Na_3Sb$ | 390 % |
| Pb | $Na_{3.75}Pb$ | 487 % |
| P | $Na_3P$ | 491 % |

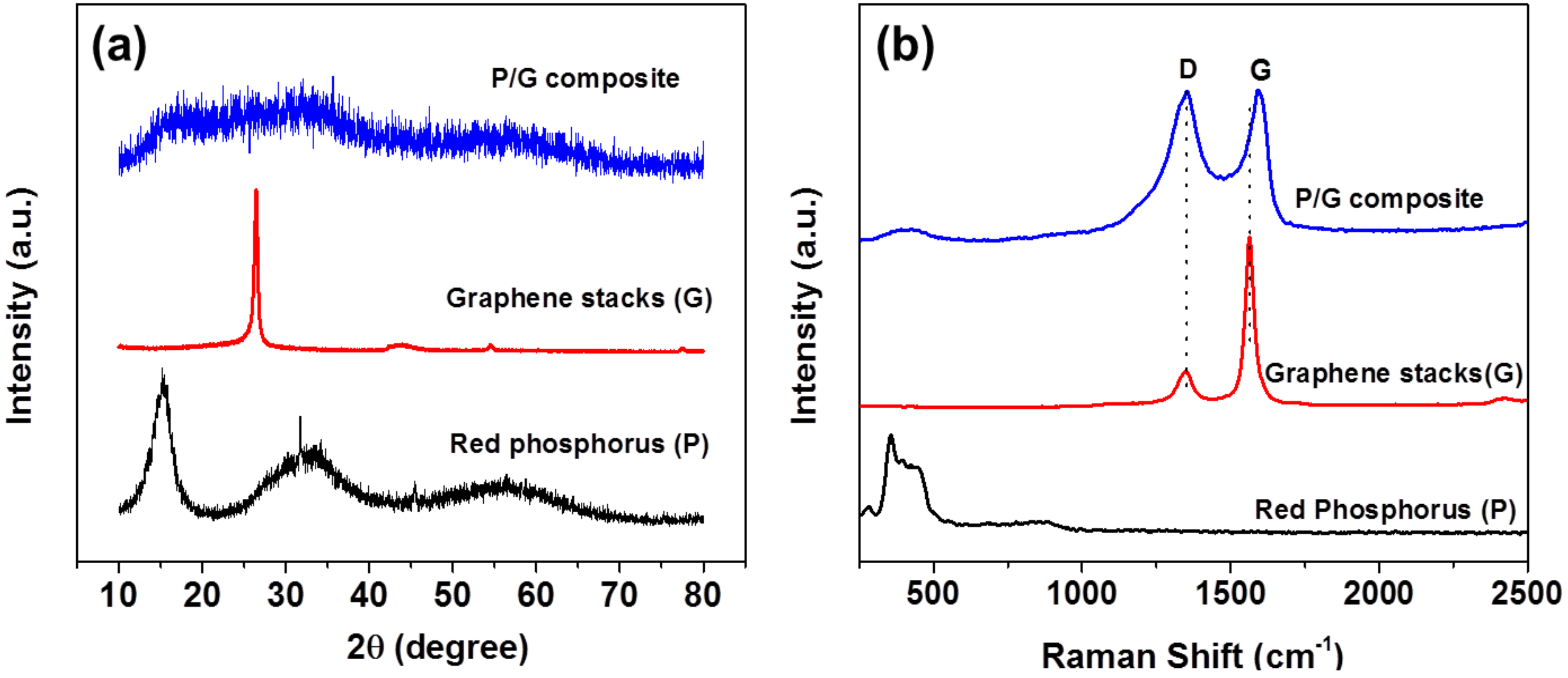
# Graphene-nanosheet-wrapped Phosphorous Composite Anode




(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.

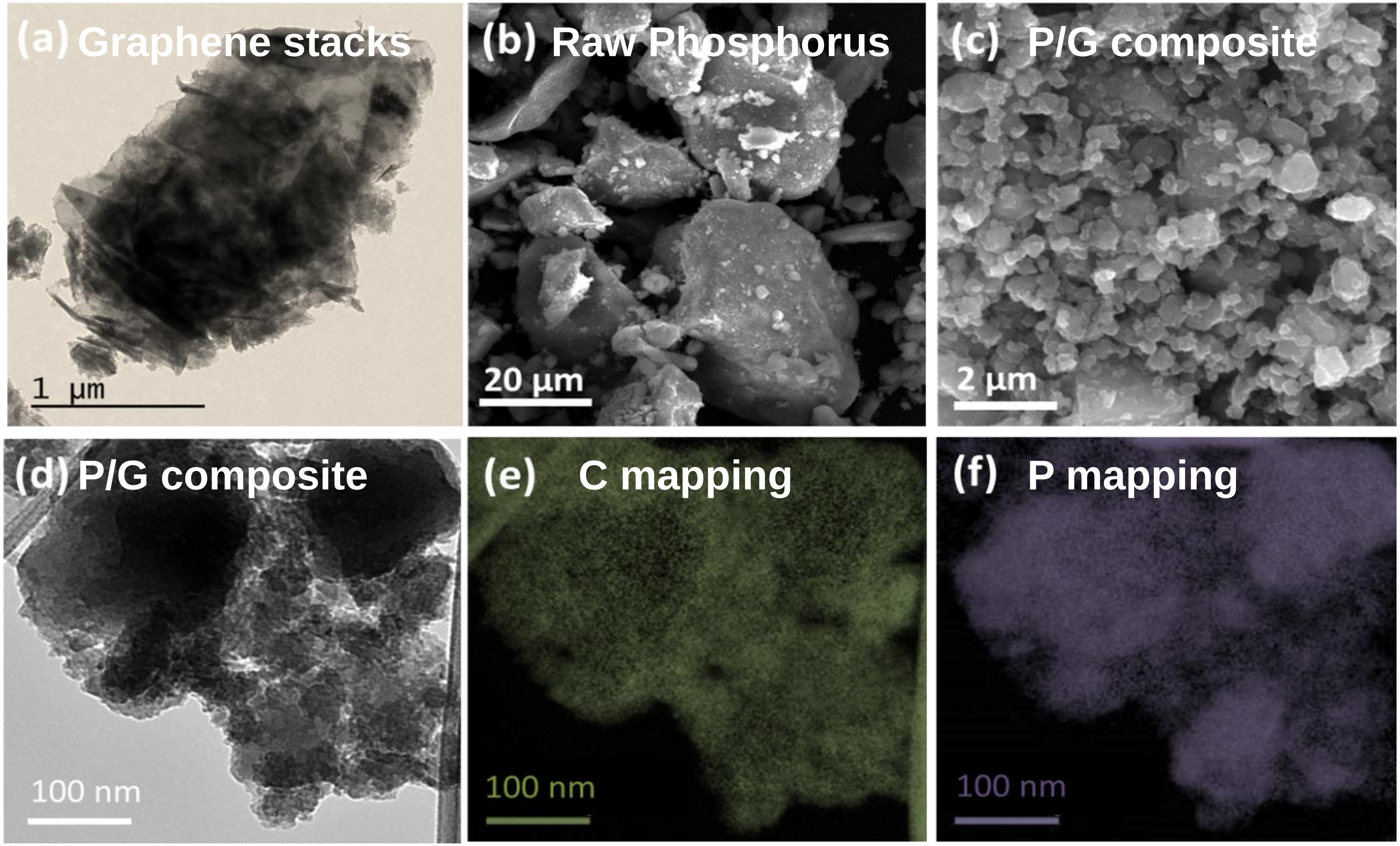
# Characterization




(1) Amorphous structure structure of the P/G composite.

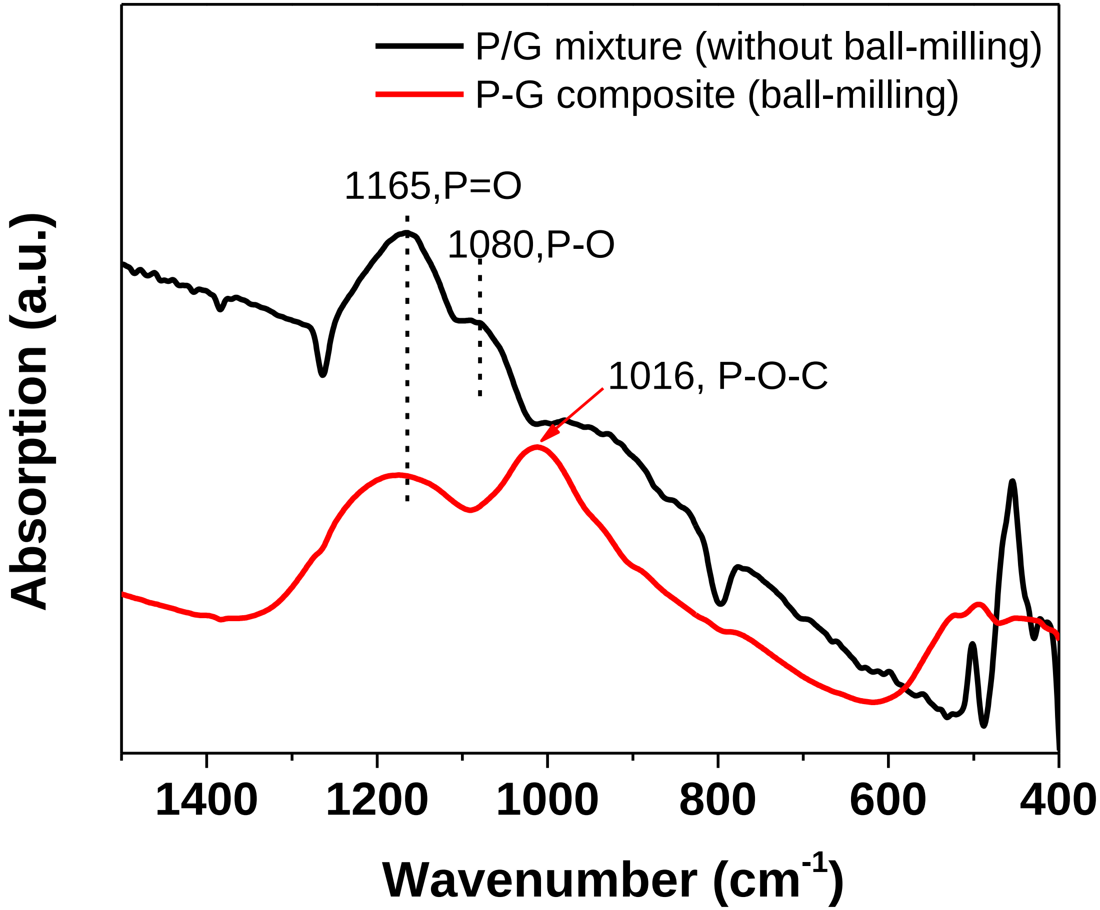
(2) Graphenen stacks were exfoliated to graphene nanosheets driven by mechanical shearing upon ball-milling.

# 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.

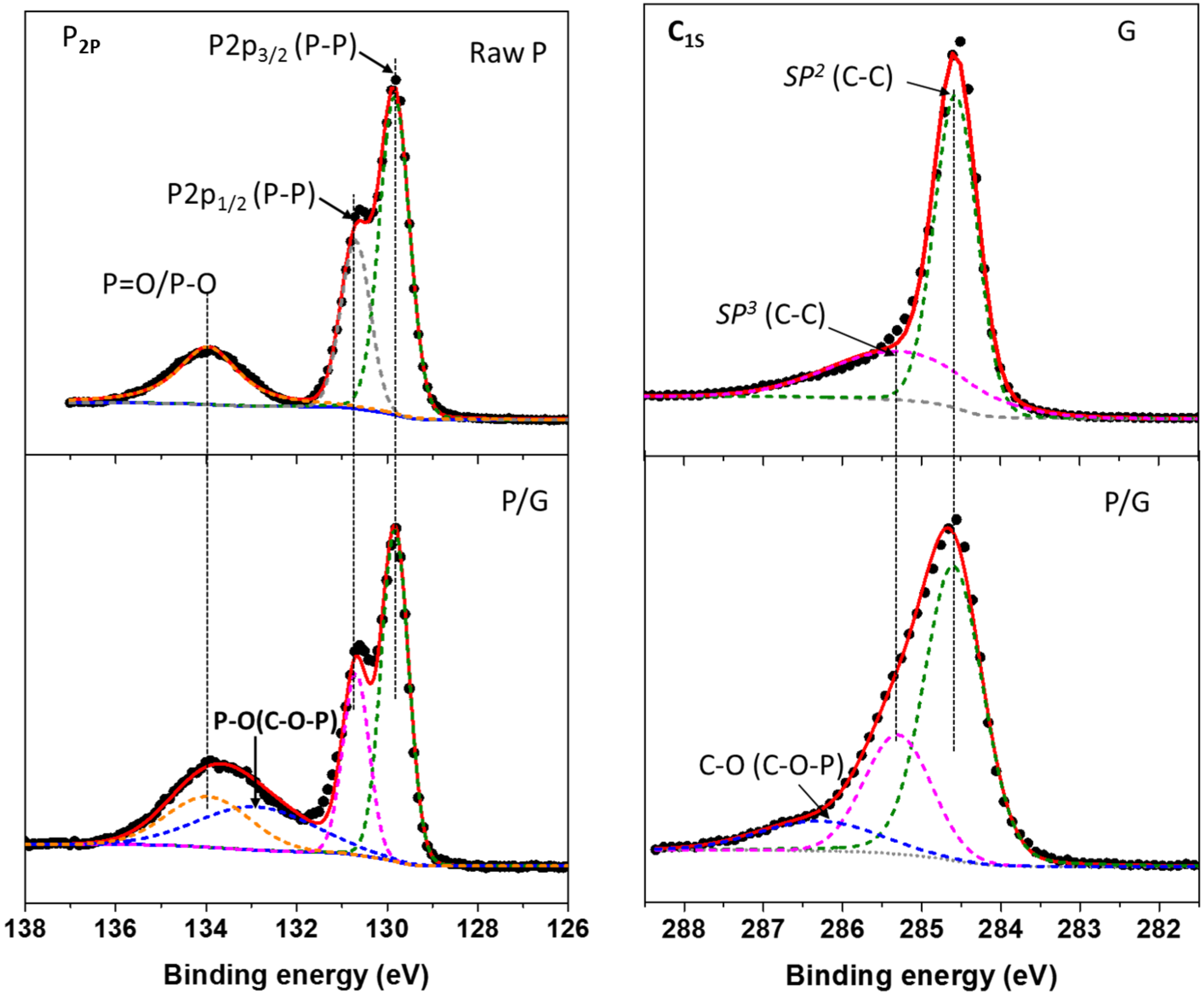
# Chemical Interaction between Phosphorous and Graphene Sheets



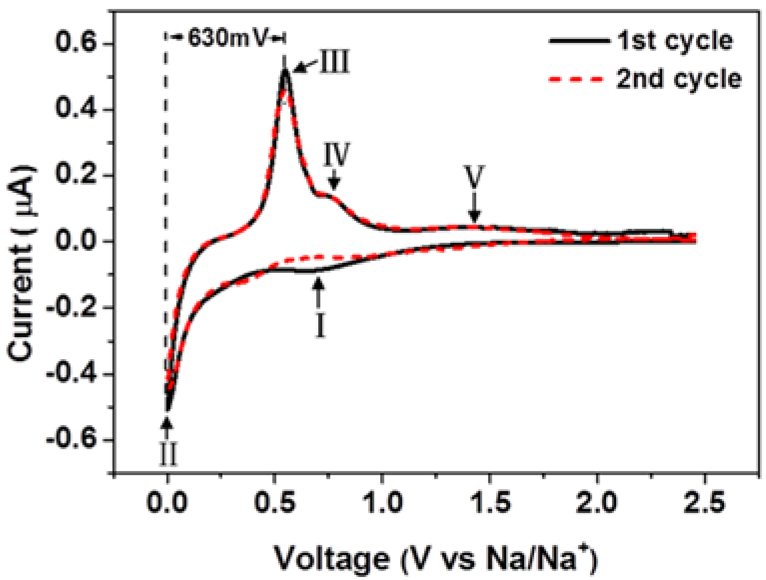

**Formation of P-O-C bond between phosphours and graphene nanosheets via ball-milling**

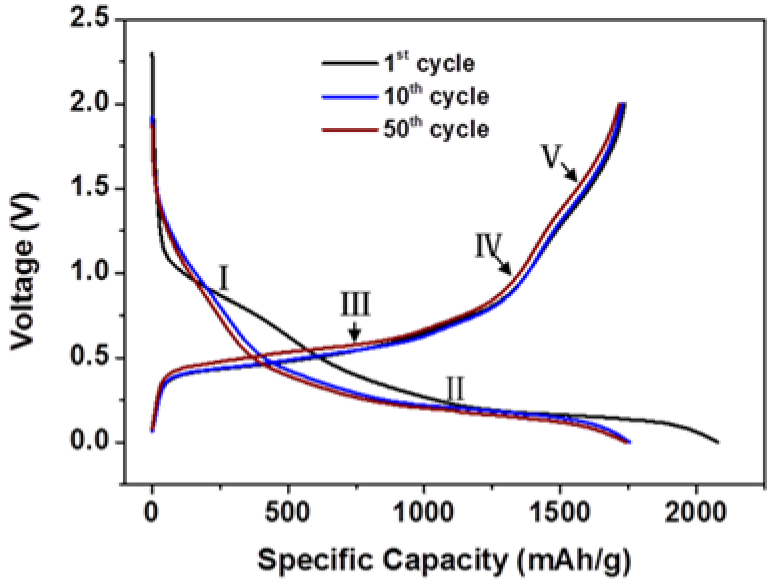
**The graphene nanosheets can chemically bind with phosphorus during milling process, which facilitates the intimate contact of graphene nanosheets with phosphorus particles.**

# Chemical Interaction between Phosphorous and Graphene Sheets



# Cyclic voltammetry and voltage profiles indicate stable electrochemical behavior with cycling.



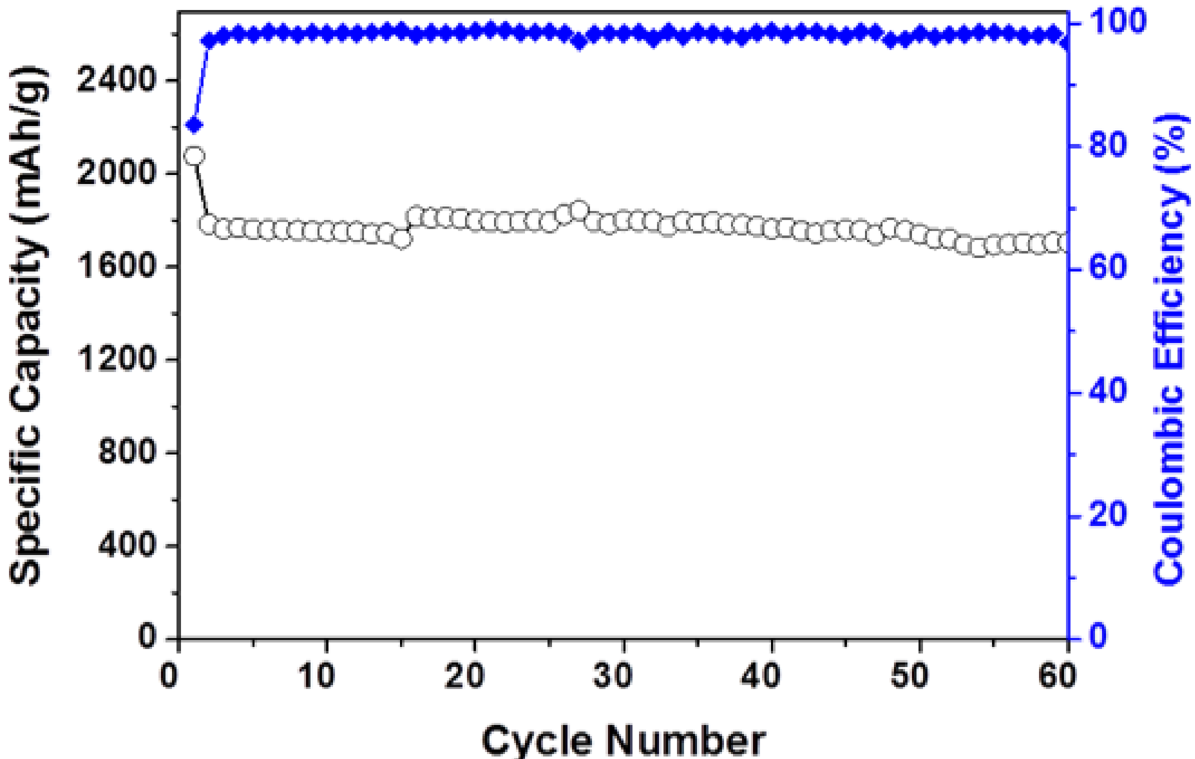




**I) SEI formation**

**II) $Na_xP$ formation upon sodiation**

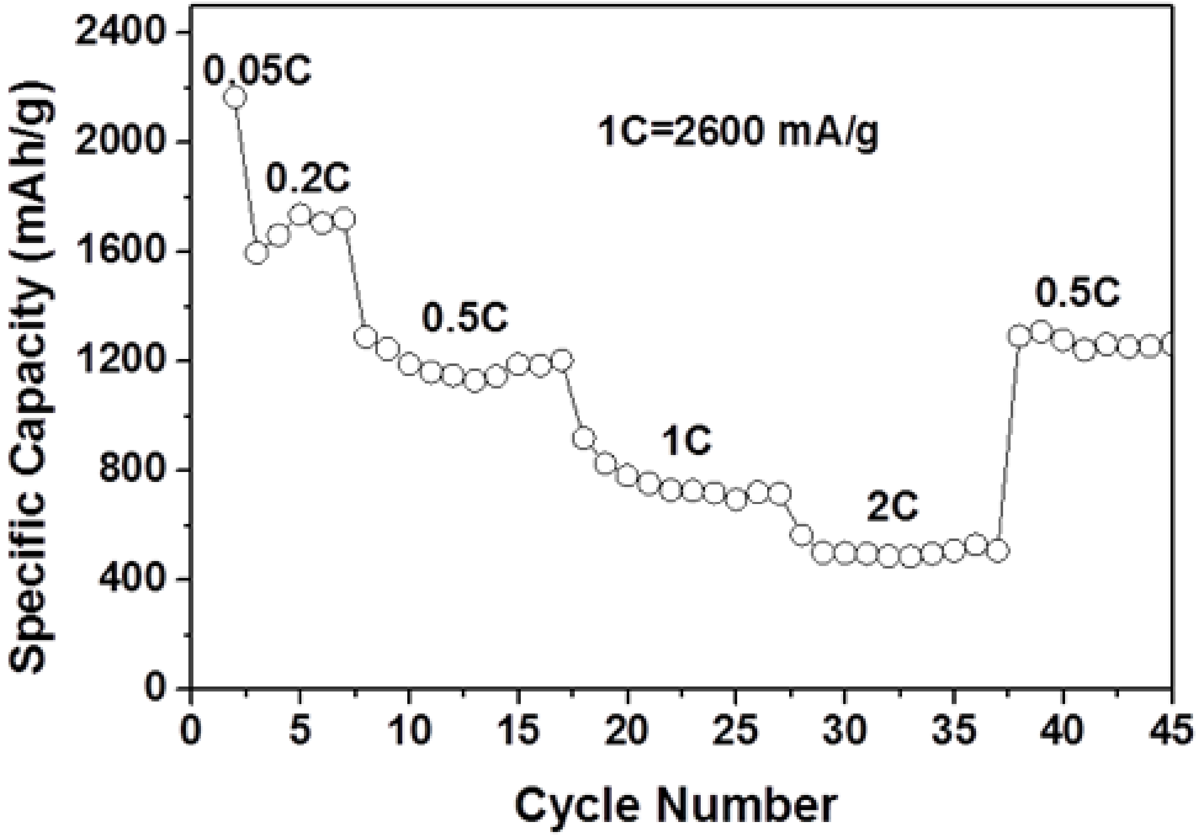
**III-V) $Na_2P$, NaP, and $NaP_7$ formation upon desodiation**

# A high capacity and coulombic efficiency are achieved using graphene-wrapped phosphorous.

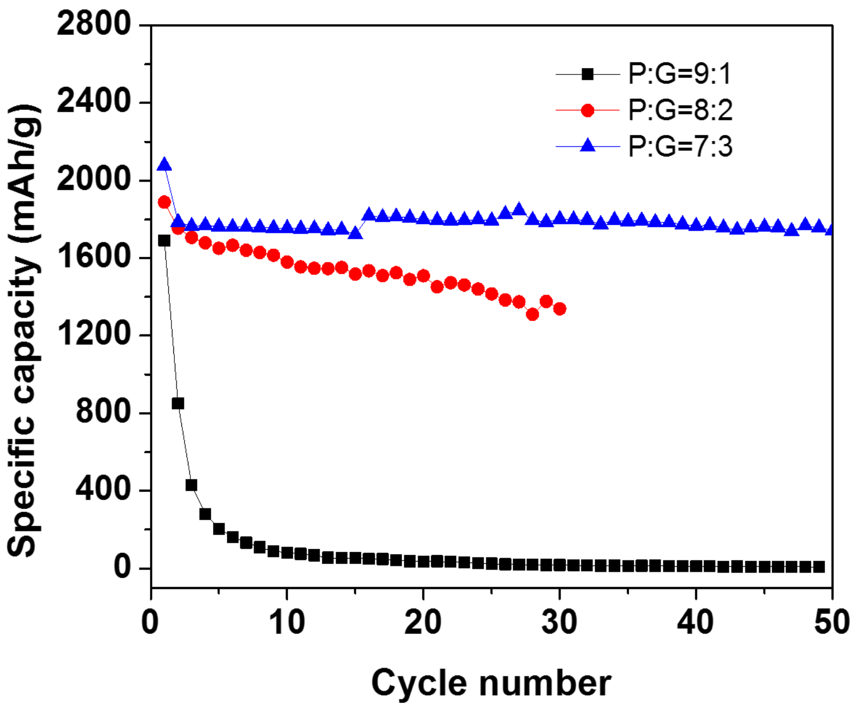


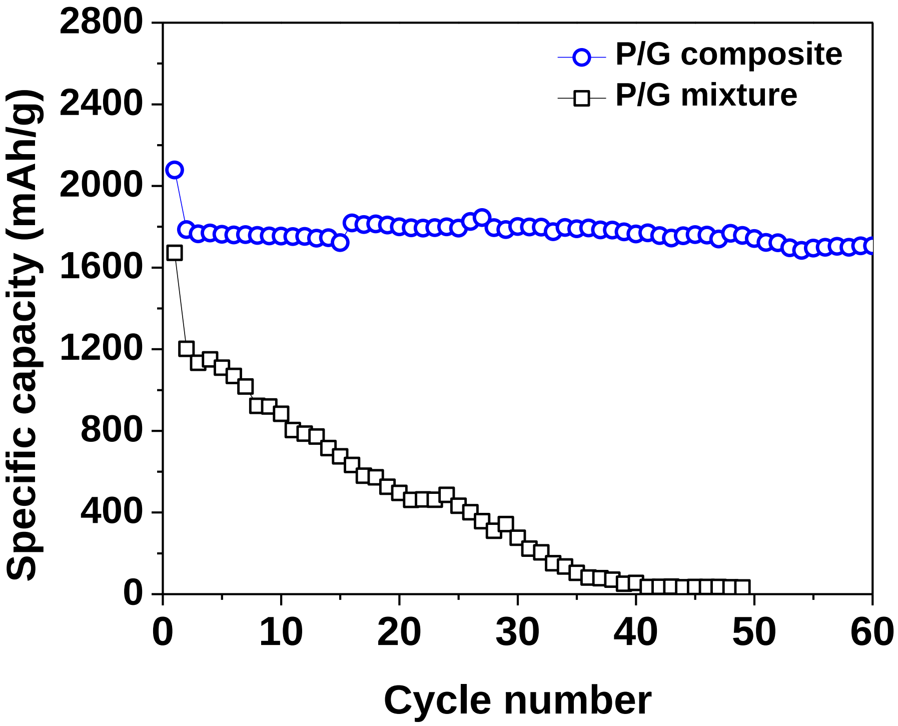

| Initial Capacity | 2077 mAh/g |
|---|---|
| Initial Columbic Efficiency | 83% |
| 60th Cycle Capacity | 1706 mAh/g |

The rate performance for graphene-wrapped phosphorous was also exceptional.



# Effect of different graphene content and chemical bonding in the P/graphene composite

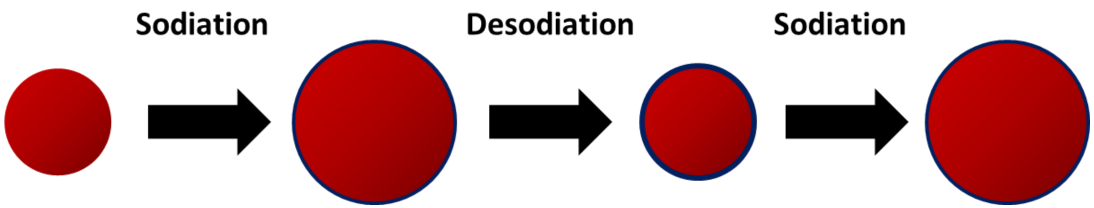


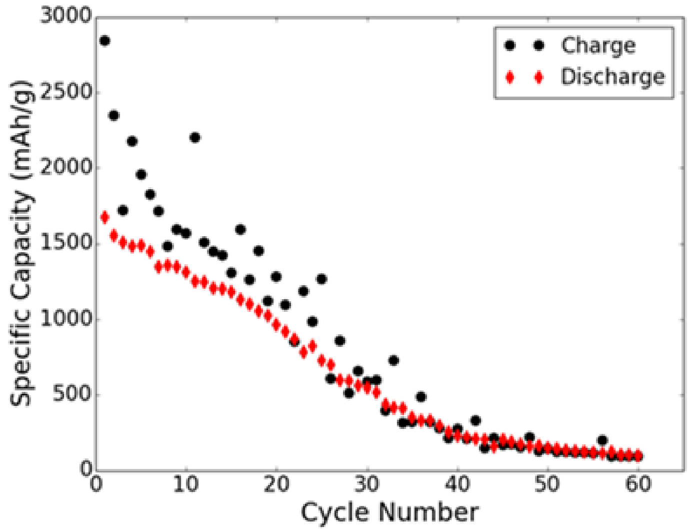

(1) With the increasing Graphene content, the electrochemical performance are significantly improved.

(2) Chemical bonding also plays an important role on the battery performance.

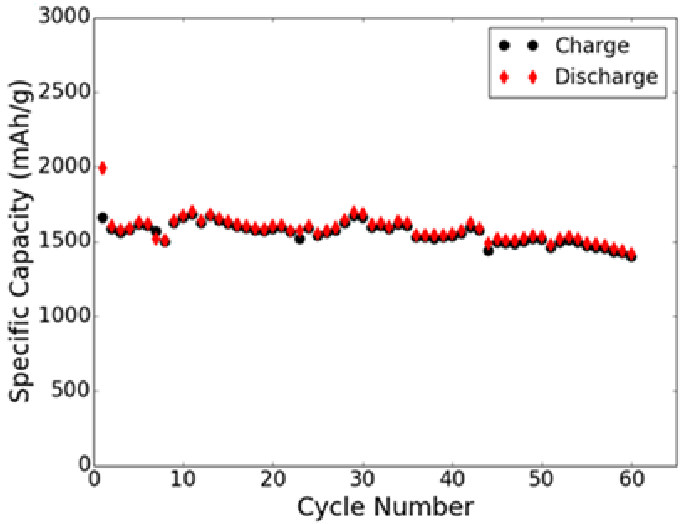
# Fluoroethylene carbonate (FEC) can help form a stable SEI layer to improve cycling stability




Stable SEI with FEC

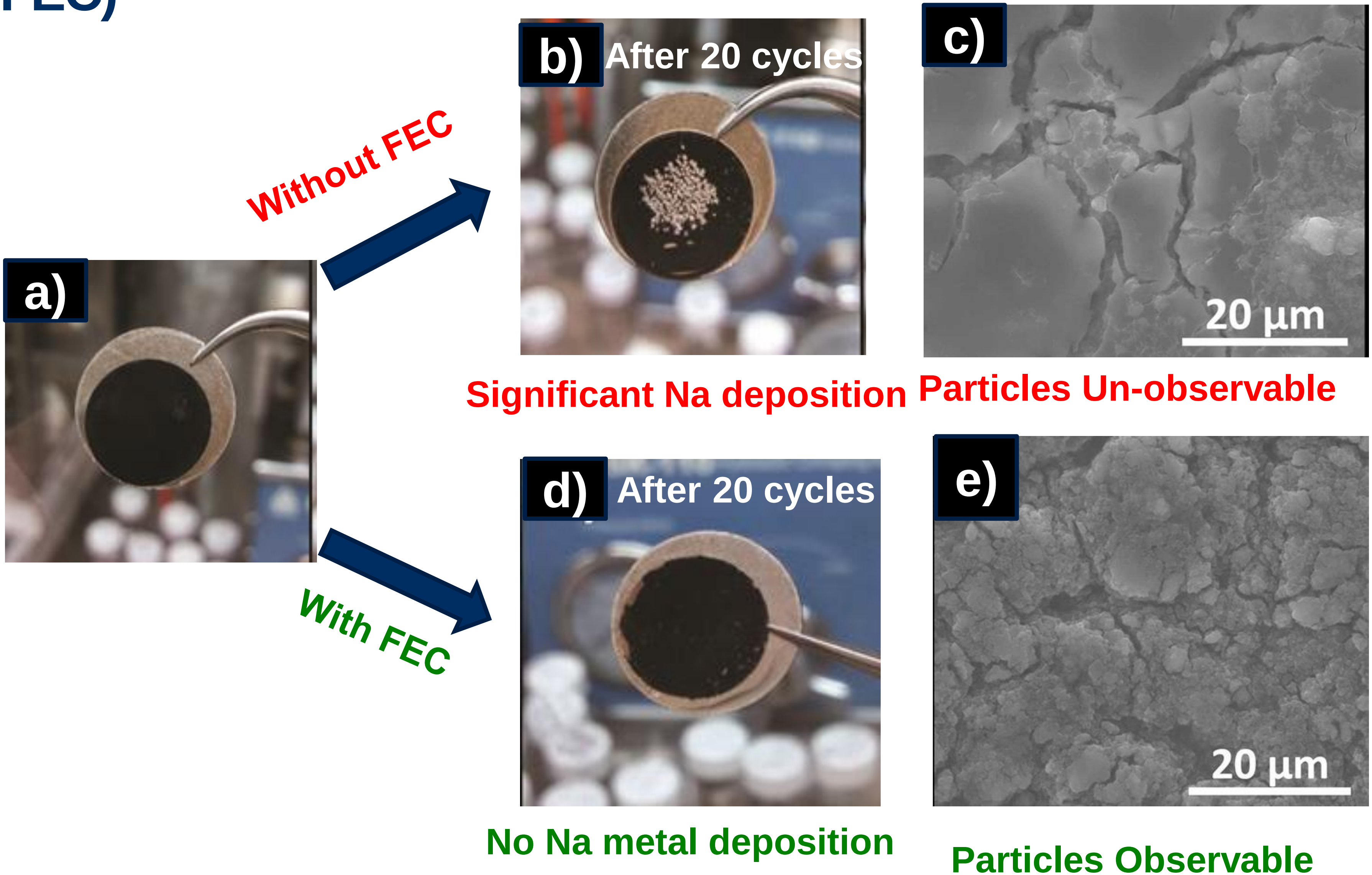



**FEC-Free**

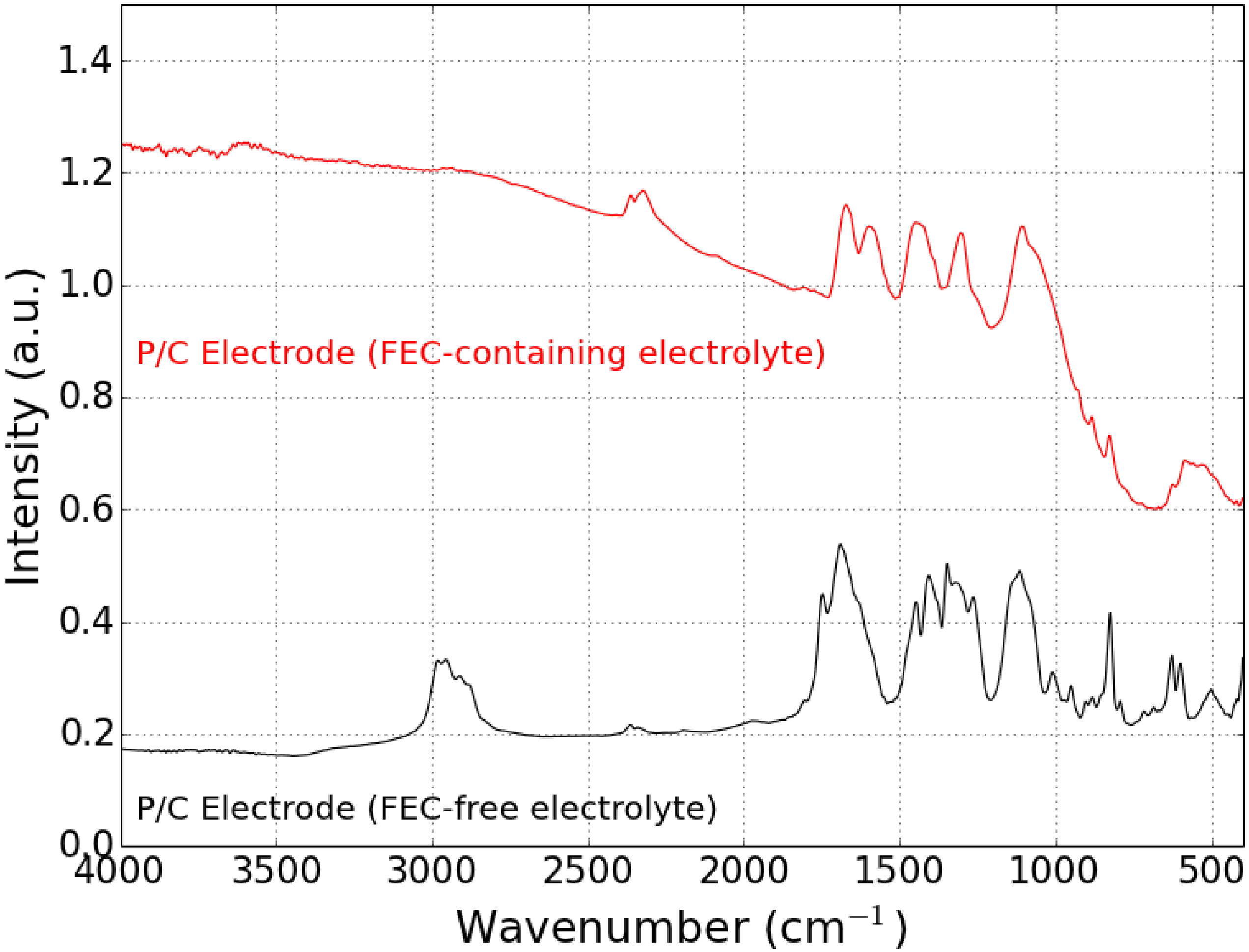



**FEC-Containing**

# Optimization of Electrolyte (1M $NaClO_4$ in EC/DEC+ 10wt% FEC)



# Using FTIR, more robust SEI species were found to form with FEC.




Both have some $ROCO_2Na$, $RCO_2Na$

**FEC-containing has more:**

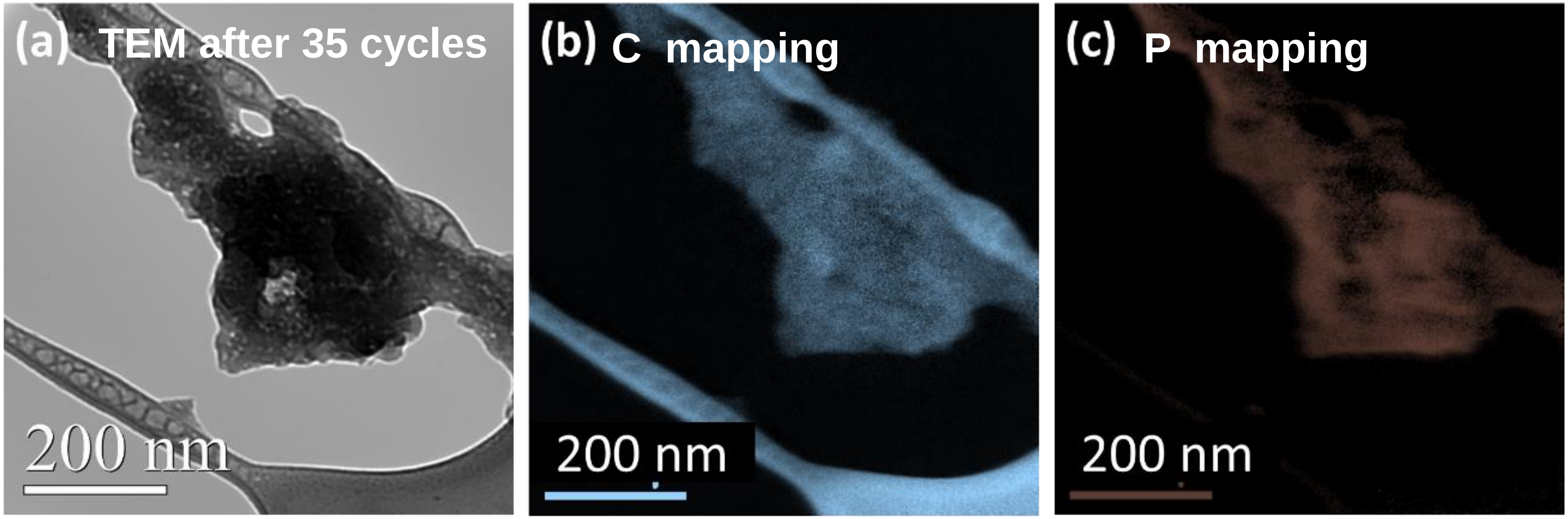
- $RCO_2Na$
- Polycarbonates

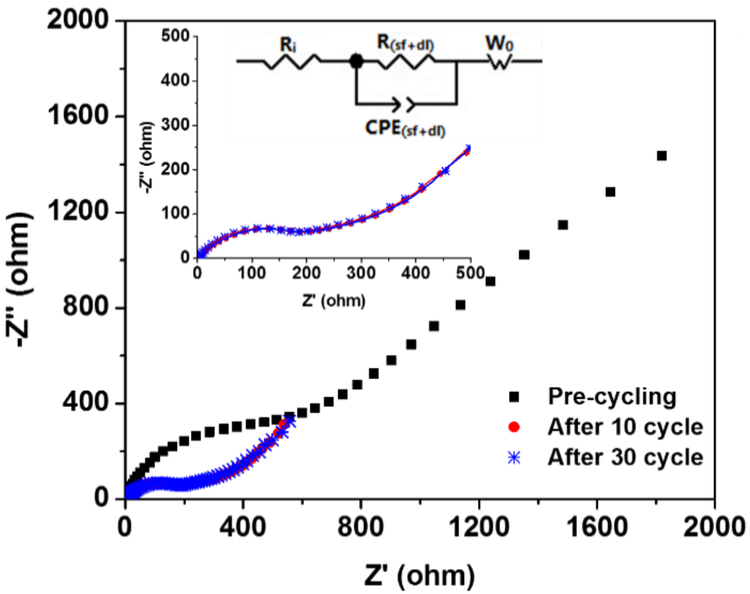
**FEC-free has more:**

- RONa
- Monocarbonate $ROCO_2Na$ (possible)
- Ester or alkyl carbonate

More robust species with FEC

# Post-cycling characterization




(1) The almost overlapped EIS spectra indicate a good manitance 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**

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