High performance phosphorous based carbon composites anodes for lithium batteries and soft X-ray near edge structure studies

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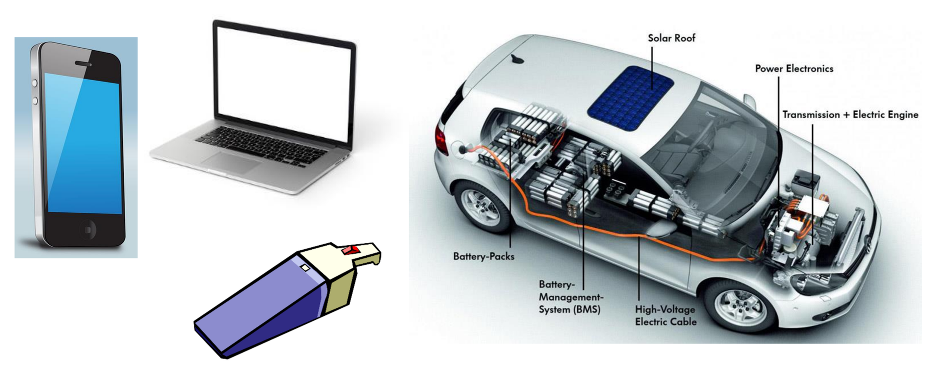
I. Introduction

Lithium batteries

ENERGY STORAGE DEVICES



~ 2/3 weight coming from battery !

one charging < 300 miles (Tesla M3)

Why Phosphorous

Table 1 The comparison of anode materials

anode materials	theoretic capacity /mAh·g^{-1}	material cost/ ×10^4 ¥·t^{-1}	cost/ ¥·Ah^{-1}
C (graphite)	372 (LiC_6)	0.3~0.5	0.01
Si	4200 ($Li_{4.4}Si$)	1.68	0.004
Sn	900 ($Li_{4.4}Sn$)	14.25	0.158
P	2594 (Li_3P)	0.25	<0.001

Nature 2001, 414, 359 Progress in Chemistry, 2016, 28 193.
http://www.alternative-energy-news.info/technology/transportation/electric-cars/

Low cost and high capacity!

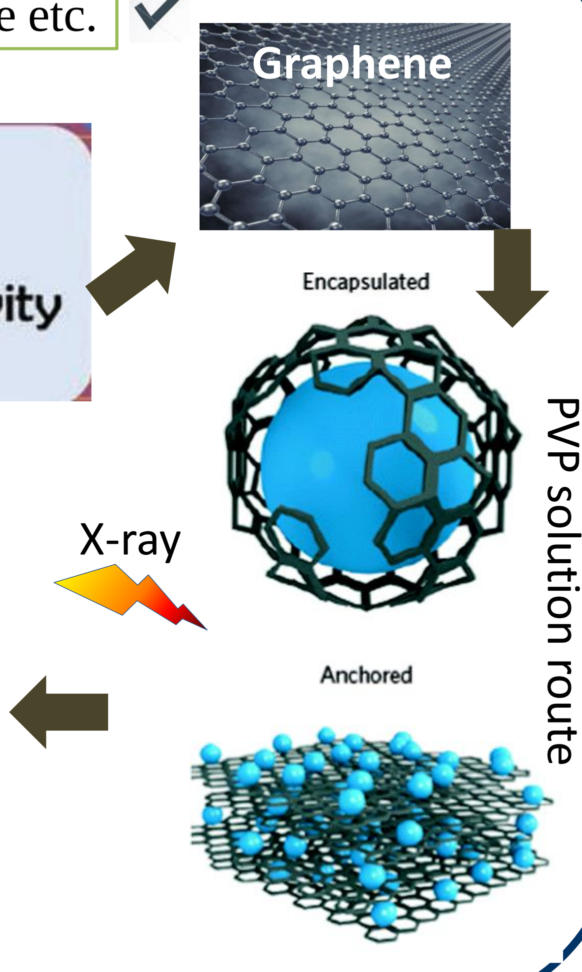
II. Experimental

Study Object

White phosphorous
Violet phosphorous
Black phosphorous
Red phosphorous ✓

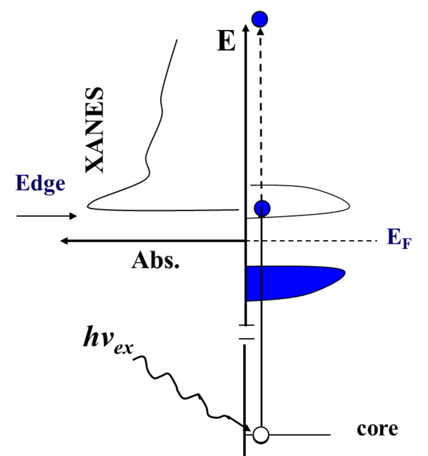
Conductive/Flexible/Stable etc. ✓

Abundant, low-cost
High chemical stability
Poor electrical conductivity
Large volume change



Technique

X-ray Absorption Fine Structure
Li K (47.5-75 eV)
P L (125-155 eV)
Cu K (8920-9060 eV)

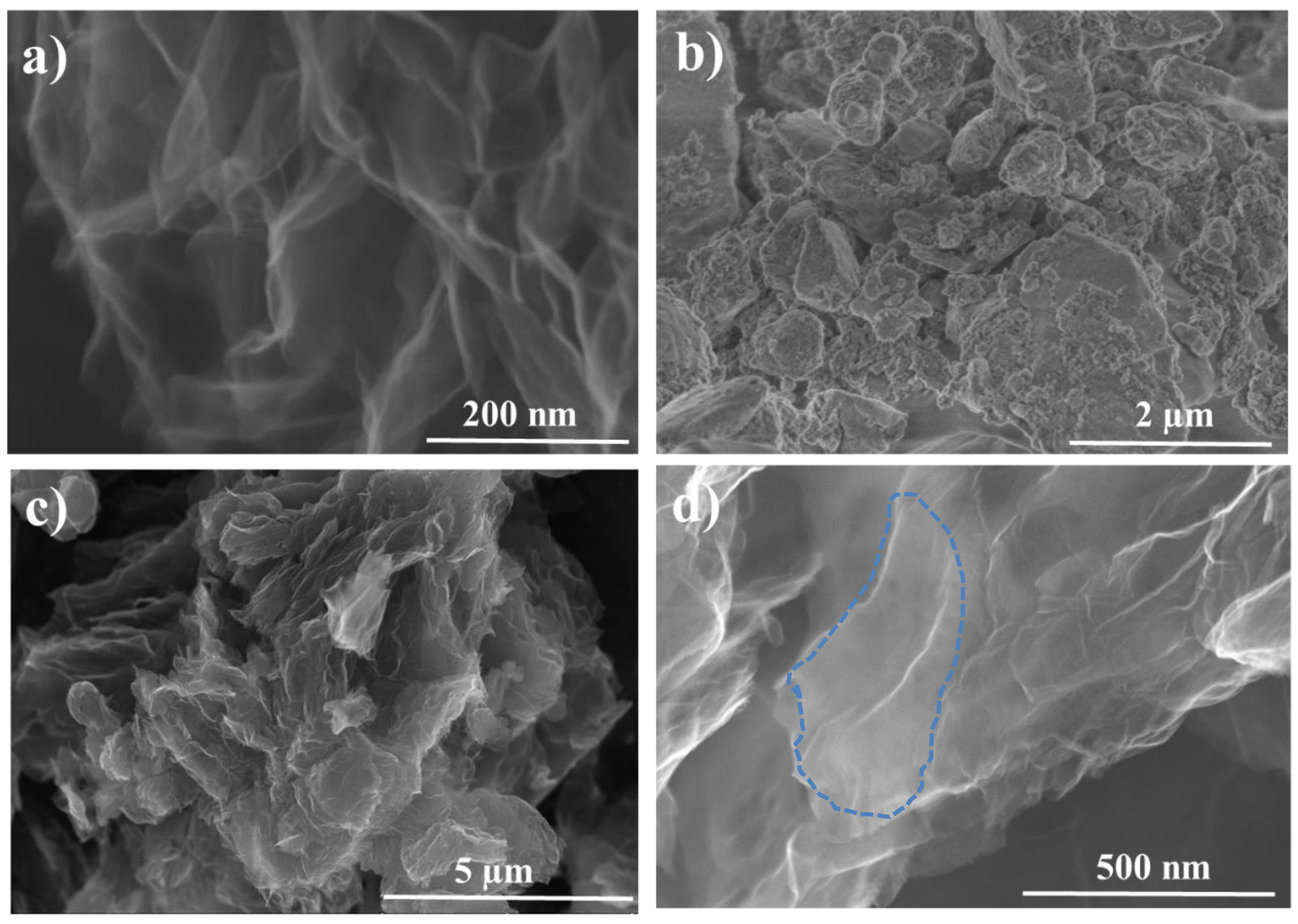


Reaction Mechanism, interphase and more!

J. Mater. Chem. A, 2014,2, 2306. Adv. Energy Mater. 2018, 1702849. Chem. Soc. Rev., 2015, 44, 6230

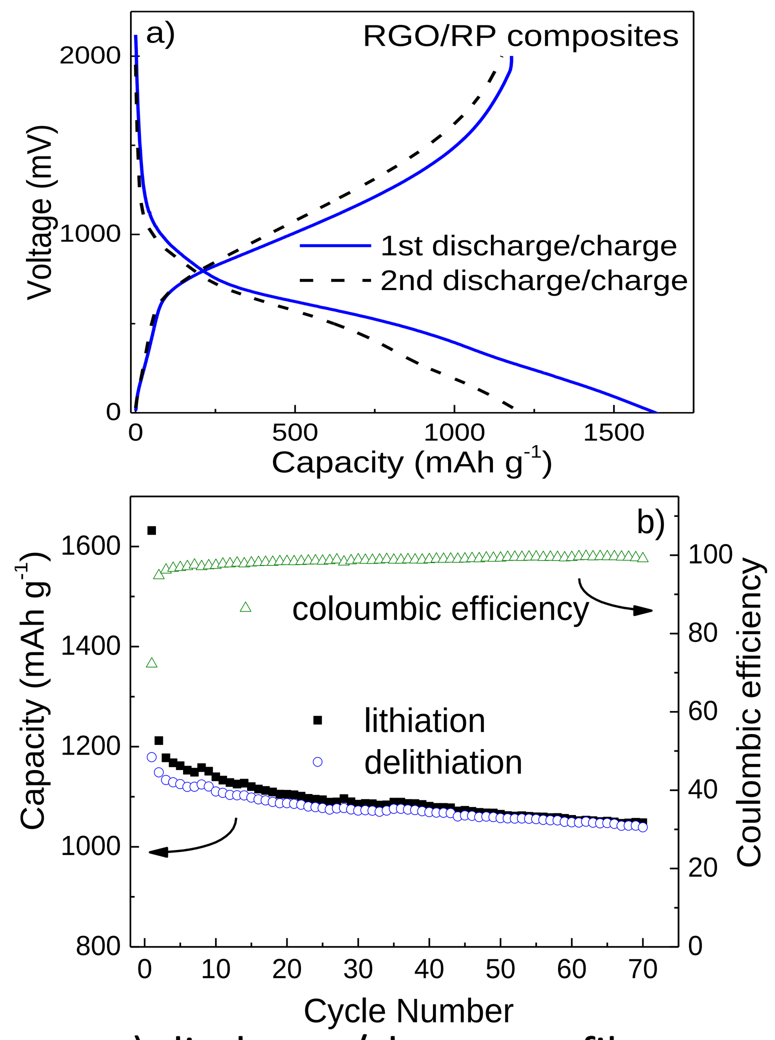
III. Results

SEM images

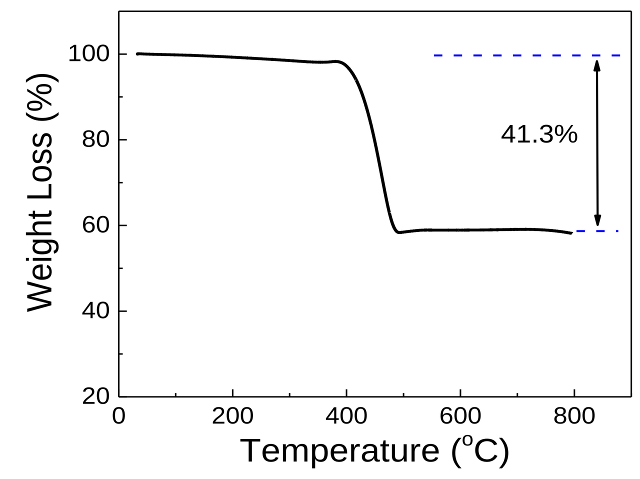


(a) graphene(RGO), (b) Red P (RP), (c) and (d) RGO/RP composites.

Battery performances

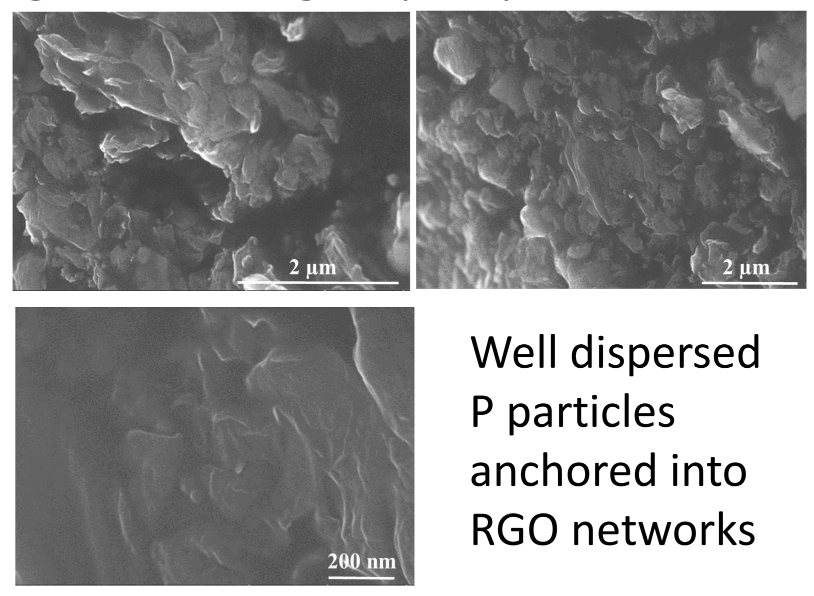


a) discharge/charge profiles;
b) cyclic performances



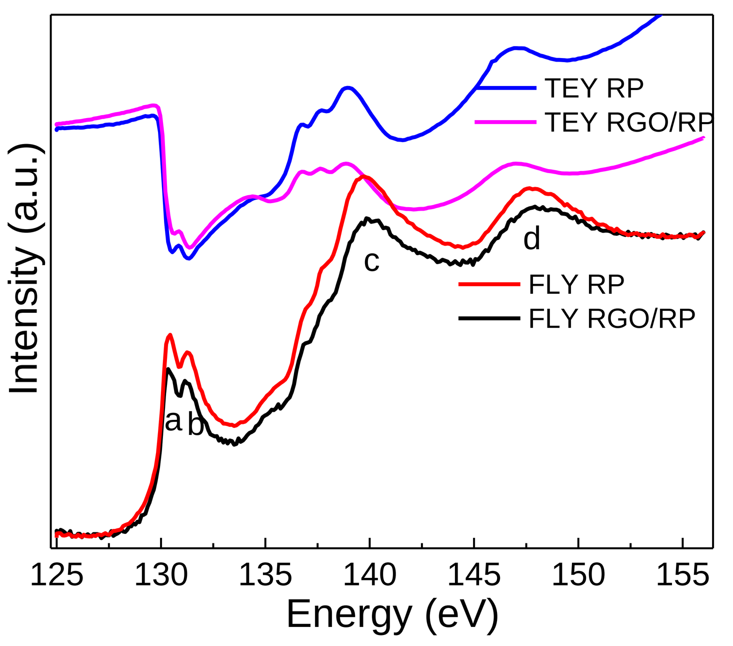
RGO/RP under Nitrogen

Thermal analysis reveals high P content: guarantees high capacity



Well dispersed P particles anchored into RGO networks

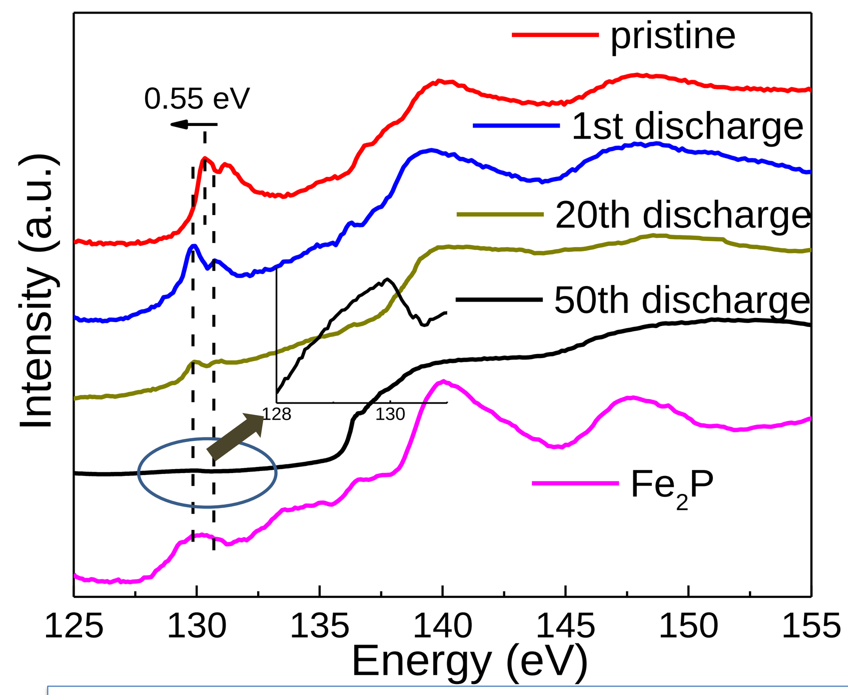
P L-edge XANES



TEY and FLY XANES spectra of RP and RGO/RP composites

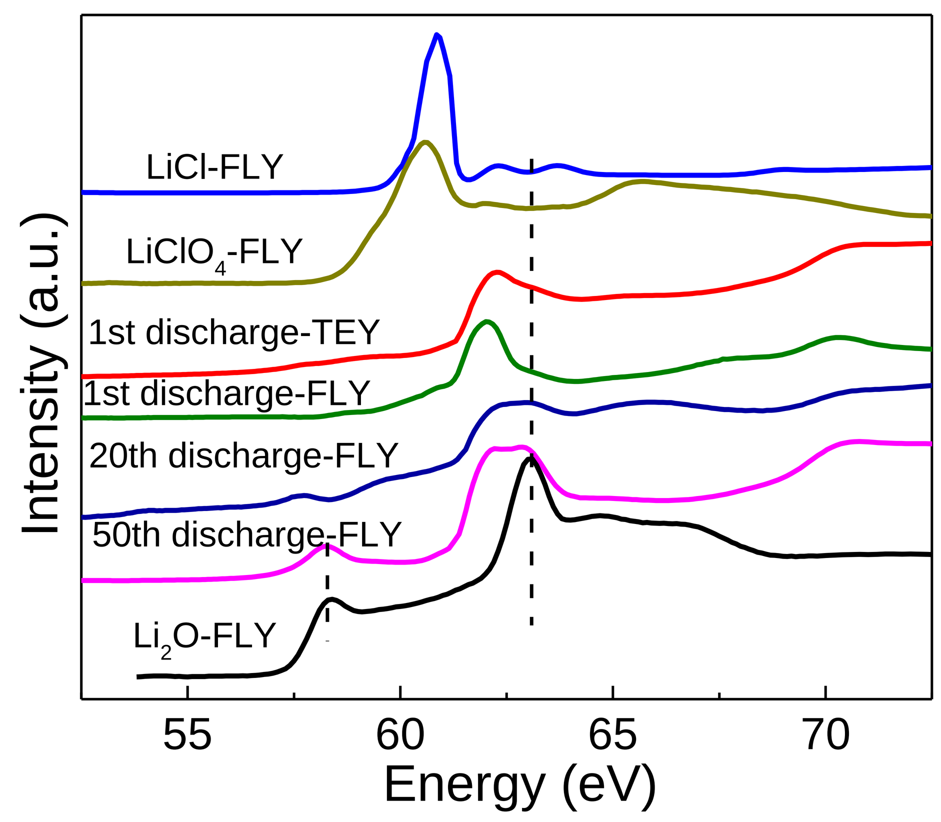
2p electrons to unoccupied states; Surrounding RGO networks are donating electrons to phosphorous

Reaction mechanism



Low valence P(Phosphide) formed after lithiation; resonances become weaker upon cycling due to more and more deposited solid electrolyte interphase. (limited P-L XANES detection depth)

Solid electrolyte interphase investigation



Switch to Li K-edge XANES, Li_2O is demonstrated to accumulate in surface of electrode. Residue oxygen in RGO would facilitate formation of Li_2O.

Future P K-edge XAS is planned for in-situ/operando study to conduct dynamic analysis.

IV. Conclusions

1. RGO/RP anodes for LIB were successfully synthesized by a convenient solution route. The 3D conductive RGO networks effectively anchor RP particles.
2. XANES investigations reveal that charge redistribution happened in between RP and RGO, facilitating their intimate contact by potential chemical bonding.
3. P L- and Li K-edge XANES results further demonstrate lithium phosphide as discharging product and lithium oxide as the main SEI component, respectively.

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