Reduced graphene oxide as an efficient platform for rechargeable lithium batteries

2016.09.26
Korea-U.S. Forum on Nanotechnology
Contents

- Introduction
  Reduced graphene oxide (rGO) as a conducting support for rechargeable lithium batteries
- Recent result of our group
  I. rGO as a electrical conducting platform for high power lithium ion battery
  II. rGO as an efficient catalyst support for Li-air cells: Study on the catalytic activity of noble metal-RGO hybrids in Li-air cell
- Summary
rGO as a conducting support for lithium batteries

- Reduced graphene oxide (rGO)
  - A derivative of graphene. Reduced from graphene oxide
  - The reduction cannot completely recover graphitic structure in graphene.
  - Thus rGO is a defective graphene with some oxygen functionalities.
  - Though not conductive as perfect graphene, rGO is conducting.

Graphene oxide : oxidized graphene

Reduction to restore graphitic structures (chemically or thermally)

ACS Nano (2010), 4(7), 3845-3852
rGO as a conducting support for lithium batteries

- Oxygen functional groups can be utilized as anchoring sites for particle growth leading nanoparticle growth in 2-D conducting rGO.

Co$_3$O$_4$-rGO, SnO$_2$-rGO, MnO$_2$-rGO hybrid anode showed superior rate capability and cycling stability due to nanosizing and facile electron transport through 2 D sheets.

ACS Nano (2010), 4(3), 1587-1595

ACS Nano (2010), 4(6), 3187-3194
I. rGO as an electrical conducting platform for high power lithium ion battery
Synthesis of Core-Shell LiFePO$_4$/C-rGO (LFP/C-rGO)

- **FeCl$_3$·6H$_2$O** + **GO**
- Mixing
- GO sheet
- **FePO$_4$**
- **(NH$_4$)$_2$HPO$_4$** → pyrrole
- **CH$_3$COOLi·2H$_2$O** → sucrose
- 650°C Ar annealing
- rGO sheet
- Polypyrrole coating
- **LiFePO$_4$**
- Carbon coating layer

Core-Shell LiFePO$_4$/C on rGO (LFP/C-rGO)
Role of rGO

- RGO provides efficient electrical pathway for electrons
- Active material growth on rGO sheets inherently restrict particle growth: platform for nanoparticle growth

Enable High Power Capability!
Structural Analysis of Core-Shell LiFePO$_4$/C-rGO

- Highly crystalline LiFePO$_4$

XRD

SEM, TEM

- Core-shell carbon coated (~ 3 nm) LiFePO$_4$ nanoparticles (30~40 nm) loaded on rGO

XPS

before anneal: GO

after anneal: rGO

- GO successfully reduced to rGO
High Power Performance of LFP/C-rGO

- LFP/C-rGO showed much higher capacity at high rates:
  Superior high power performance (rate capability)

Superior high power performance due to true nanoscale LFP/C active material-rGO conducting support composite formation
High Power Performance

Cyclic Voltammetry

LFP/C-rGO hybrid
- Potential interval is the smallest
- Current highest

Impedance

LFP/C-rGO hybrid
- Smallest semicircle = lowest Ohmic resistance

Better kinetics and lower resistance resulting from fast electron supply
II. rGO as an efficient catalyst support for Li-air cells
Rechargeable Li-Air Batteries

- Fundamental cathode reaction in aprotic Li-Air Batteries
  \[2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2\]

- High theoretical capacity:
  - 11,420 Wh kg\(^{-1}\) (oxygen only)
  - 3500 mAh g\(^{-1}\) (Li\(_2\)O\(_2\) only)

- Catalyst loaded on rGO support

- Cathode charge overpotential, leading to inefficiency

- Efficient catalyst loading necessary
Noble Metal Nanoparticles Supported on rGO

- Pt, Pd, Ru-rGO: polyol synthesis

1. GO dispersion (EG) + noble metal precursors
2. Vortex
3. Reaction
4. Reflux
5. Filter, wash and dry

GO

Noble metal nanoparticles – rGO hybrid
Structural Analysis(1)

- **Average particles size: ~2.2 nm**

![Image of 50 nm scale](image1.png)

- **Nanocrystalline metallic + rGO by XRD**

![Intensity / A.U. graphs](image2.png)

- **Mass content: ~ 50 wt %**

(Pt 49 wt%, Pd 45 wt%, Ru 46 wt%)
Structural Analysis(2)

- Surface oxidation by XPS

Main peaks corresponds to metallic noble metals: No significant surface oxidation
Catalytic Activity in Li-Air Batteries

OER charge

- All noble metals: showed lower overpotentials

ORR discharge

- Did not change much with the presence of noble metals

Ru-rGO showed lowest charge overpotential:
Avg. ~3.5 V, ending 3.9 V
Catalytic Mechanism of Ru-rGO

- 4.0 V peak shifted to lower: conventional OER electrocatalyst
- 3.2 V peak invariant: Not conventional electrocatalyst?

Points to be noted for Ru-rGO:

1. Higher current densities in both cathodic and anodic scan: enhanced reactions in both forward and backward discharge products.

2. For oxidation peaks:
   ① Onset potential at 3.2 V: identical to rGO
   ② Peak of rGO at 4V was shifted to 3.7 V
Identification of Discharge Products

- No crystalline peak from powder XRD: amorphous
- Discharge products analyzed by Raman and XPS

**Ru induces more LiO_2 formation**
Since the current density test is already quite high (400 µA cm$^{-2}$), discharge particles are not toroids, but feature size is clearly smaller for Ru-rGO!

Upon charging: completely decomposed

Nano Letters, accepted (2015)
Suggested Mechanism of Ru-catalysts

The discharge products are a mixture of stoichiometric Li$_2$O$_2$ and defective or smaller sized Li$_2$O$_2$/or the superoxide LiO$_2$. The amount of LiO$_2$ largely depends on the kinetic parameters during discharge.

Catalysts might have stronger binding with oxygen or superoxide providing more nucleation sites & leading LiO$_2$ or poorly crystalline, small-sized Li$_2$O$_2$ structure.

- Dual role of catalyst
  1. During ORR
     - Control the nature of the discharge products
     - Favor the formation of defective, smaller sized Li$_2$O$_2$
  2. During OER
     - Facilitate the decomposition of stoichiometric Li$_2$O$_2$ that might be present in the discharge product
Summary

- rGO served as efficient electrical pathways to enable high power performances in LIB.

- rGO enabled very uniform, nanosized noble metal catalyst (~2 nm) synthesis on its surface. Resulting catalyst system reduces charge overpotentials in Li-air cells.