Curtin-UQ Workshop on Nanostructured Electromaterials for Energy
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Carbon-metal interaction in hybrid graphene-based electrocatalysts
A case study of graphene oxide/Mn$_3$O$_4$ composite

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Our road map

Carbon materials

Carbon forms a great variety of crystalline and disordered structures because it can exist in three different hybridizations: sp3, sp2 and sp1.

Non-metal Heteroatoms: Functionalization/Substitution/Doping

Carbon materials

G Centi, S Perathoner, ChemSusChem 4 (7), 913-925

Functional Oxygen Groups

Cation electrosorption:
Charge storage

The examination of graphene oxide for rechargeable lithium storage as a novel cathode material

J. Mater. Chem. A, 2013, 1, 3607-3612

Specific Capacity (mAh g⁻¹)

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Specific Capacity (mAh g⁻¹)
Functional Oxygen Groups

- Interface locking
- Interface catalysis
- Interface charge storage

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**History of electrochemical energy technologies**

Ragone Plot with Current and Next-generation Battery technologies

- 1859: Lead-acid
- 1891: Sony
- 1989: NiCd, NiMH
- 1991: Lithium-ion
- Internal combustion engine

Over 130 years No Moore’s law!! Sorry...

theoretical estimation for post-Li-ion batteries

Sources: Journal of Power Sources, IM Energy
Metal-Air Battery – Oxygen reduction

That is...

- Large capacity
- Stable $\epsilon$ output
- Portable
- Rechargeable/refuel-able

* from a weightless O$_2$ source

Fuel Cells

Metal-air batteries

Precious Metals
- Pt, Co alloy
- Pt-Co core-shell
- Pt on carbon

Non-precious Metals
- Non-precious metal based
- N-doped carbon
- N-doped graphene
- Metal-free materials
- Metal-free carbons

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Metal-Air Battery

Oxygen Reduction Reaction (ORR)

High Specific Capacity Cathode Reaction

High capacity energy devices

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**N-doped carbons vs. oxidized carbons**

**N-doped Carbons**
- N – deliberately introduced into carbon
- Not always highly conductive
- Highly asymmetric charge density
- Possible sp² bonding configuration
  - $R_xC=N-R_y$
- Directs 4e ORR (basic)
- Low reaction overpotential

**Oxidized Carbons**
- (or O-doped carbons)
- O – the most common impurity in carbon
- Usually less conductive
- Highly asymmetric charge density
- Possible sp² bonding configuration
  - $R_xC=O$
- Directs predominantly 2e ORR
- High reaction overpotential

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**So, the question is...**

*Why cannot the “doped” oxygen offer superior ORR activity?*

- Is O-groups on carbons really ORR active and is there a particularly active O-group?

- The aim is to elucidate:
  - the ORR activity of oxidized carbons.
  - the way to activate oxidized carbons for 4e ORR.
Phase 1

- The ORR activity of oxidized carbons

Garten and Weiss mechanism for O₂ electroreduction on carbon surfaces

Elemental analysis of OCNTs – XPS

**XPS Quantitative Analysis**
- Oxygen content varies from 4.0 at% up to 28 at%. (stabilized at ~31 at% at a CNT:KMnO₄ ratio of 1:10)

Typical XPS survey spectra
- No other elemental impurities.

Is the oxygen active in some way?

**Upon oxidation:**
- A higher $E_{onset}$ was commonly observed.
- An improved reaction current for peroxide production.
What if the oxygen is removed…?

- The onset dropped to the level of CNT or worse.
- The reaction currents were reduced.

Only 2.9 at.% oxygen remained for both samples. (with O-deficient/defect-rich surface)

- The $E_{\text{onset}}$ dropped to the level of CNT or worse.
- The reaction currents were reduced.

Clearly, the oxygen presence improves the ORR onset potential & reaction current for peroxide production.

A quick summary

Oxidized CNTs exhibit improved ORR activity compared to unmodified CNTs.

- Onset potentials at +50 mV versus CNT & higher reaction current.

Still, oxidized carbons are not competitive against N-doped carbons and only allow peroxide production.
Phase 2

The way to activate oxidized carbons for 4e ORR

4e pathway:

\[ \text{O}_2 + \text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

[2+2]e pathway

Peroxide decomposition

\[ 2\text{HO}_2^- \rightarrow 2\text{OH}^- + \text{O}_2 \]

* In alkaline solution

Structural Origin of the Activity in Mn₃O₄–Graphene Oxide Hybrid Electrocatalysts for the Oxygen Reduction Reaction

Methodology

(a)

(b)
Does the Mn$_3$O$_4$-GONR hybrid mimics the enzyme functions?

Is there an interface?

E, F: Mn(III)
G: Mn(II)
The role of the interface in ORR

The role of the interface in $\text{H}_2\text{O}_2$ reduction
Summary

\[ \text{Mn}_3\text{O}_4 \text{ particles grown on the surface of oxidized carbons create new interface structures and activate the reduction of oxygen molecules via a 2e}^+\text{2e pathway.} \]

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Thanks for your attention!