Carbon Materials for Cathode in Lithium-O_2 Battery

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Motivation

O_2 reduction reaction (aqueous system)*

Graphite:

$O_2 \rightarrow O_2(ads)$

$O_2(ads) + e^- \rightarrow O_2^-(ads)$

$2O_2^-(ads) + H_2O \rightarrow O_2 + HO_2^- + OH^-$

Carbon Black:

$O_2 \rightarrow O_2^-$

$O_2^- + H_2O \rightarrow HO_2^- + OH$

$OH + e^- \rightarrow OH^-$

The reaction is site-sensitive on carbon materials. *

Hypothesis: "Similar" site-sensitive behavior is expected on O_2 reduction and the insoluble-Li_2O_2 oxidation for non-aqueous Li-O_2 battery system. More complex nature of the structure-activity correlation is expected.

*Kinoshita, K. in *Handbook of Battery Materials*, Wiley –VCH, 1999.

Methodology

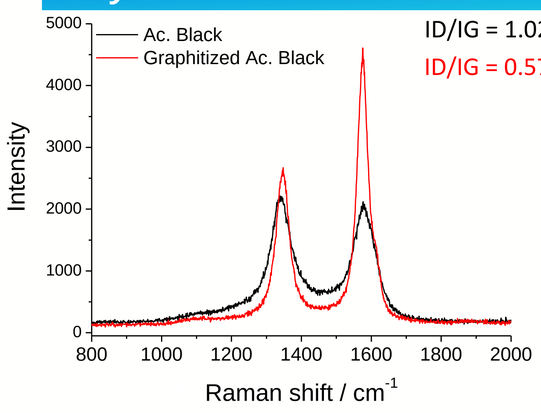
Carbon Materials used in this study

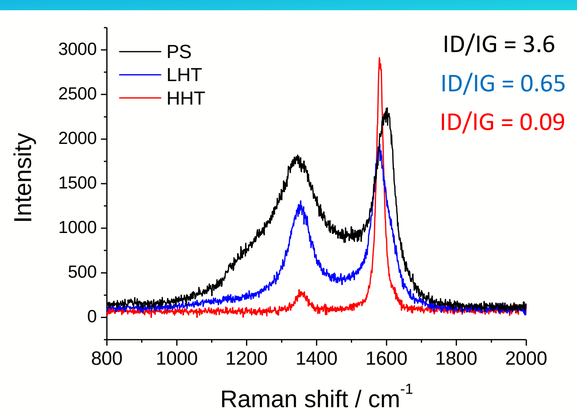
1. **Acetylene** black & **Graphitized** acetylene black (annealed at 2500°C)
   - Chain-like with meso-macroporous texture
2. PR24-**PS**, **LHT**, and **HHT** (annealed at 700, 1500 and 2700° C).**
   - Vapor-grown Nanofibers with hollow open channels, highly entangled forming meso-macroporous texture.

- Cyclic Voltammetry (CV)
- Impedance spectroscopy

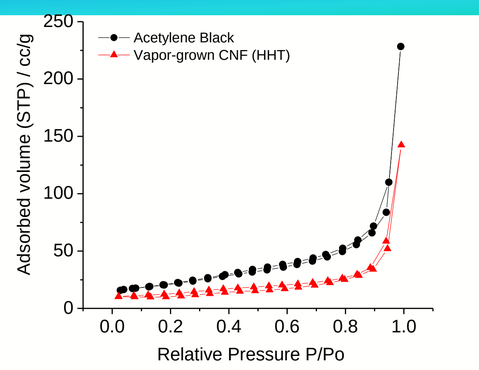
**J.P. Tessonnier et al. *Carbon*, 2009, 47, 1779.

Physical characterization of carbon

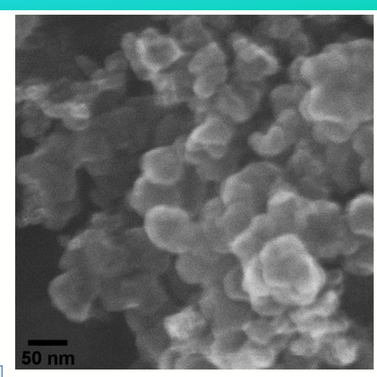




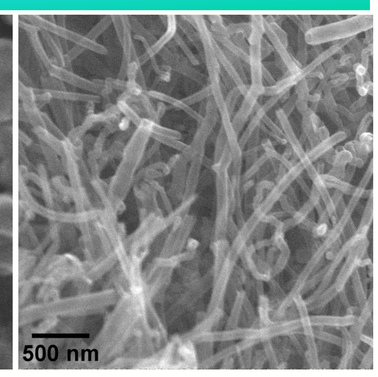
Increase of annealing temperature decrease the defect density



Sample	BET SA m^2/g	Pore volume* mL/g
Acetylene black	75.4	0.3
Vapor-grown CNF	37.5	0.2



Acetylene Black

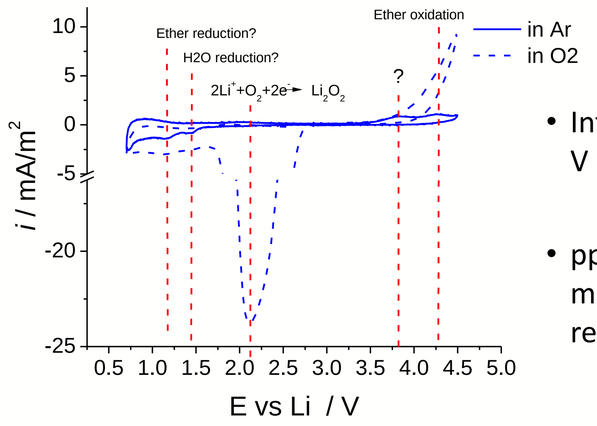


Vapor-grown CNF

*Up to ~100nm (at P/P_0 0.99).

Cyclic Voltammetry

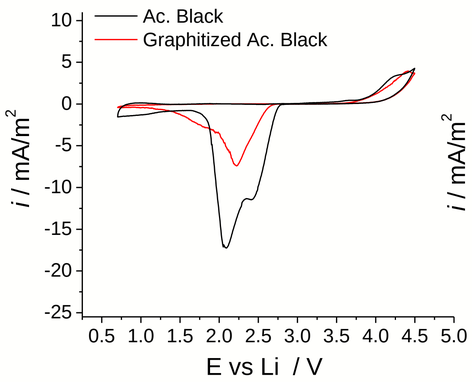
Cathode: Carbon of ~ 30um, 20wt% PVDF binder. Anode: Lithium. Separator: Celgard .Electrolyte: 150uL of 0.1M $LiClO_4$ in DME (1,2 dimethoxyethane), under 0.05ml/min O2, CV:0.1 mV/sec

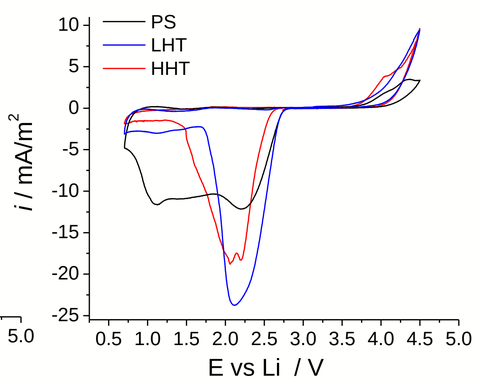


- Intense peak at ~2.1 V is O_2 reduction.
- ppm level of H_2O may alter the reaction profiles.

The solvent reduction & oxidation seem to be influenced by the presence of O_2 and/or by O_2–reduction reaction and/or the discharge products.

Under Oxygen (Cycle 1)

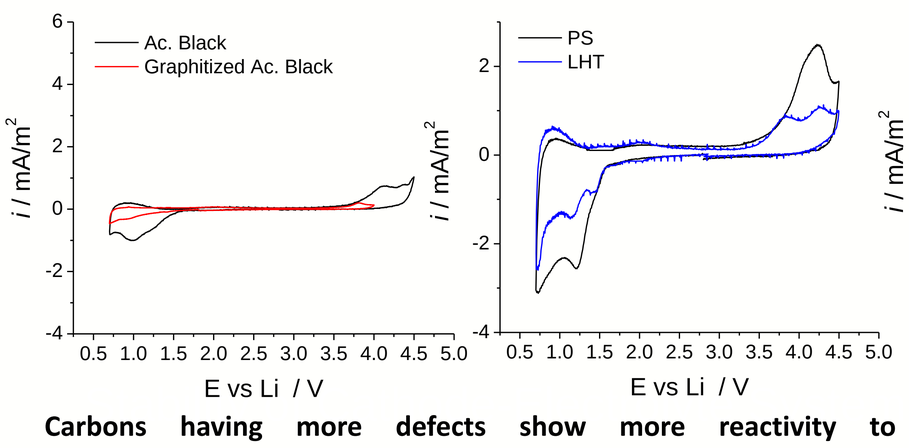




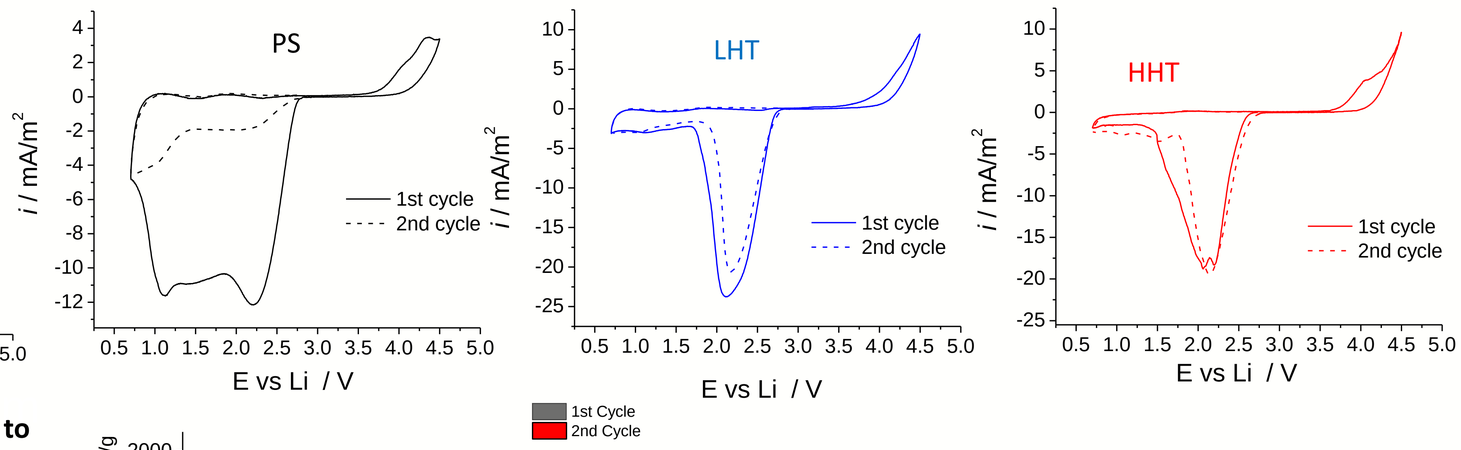
- O_2 reduction reaction is influenced by *amount of defects*, indicating an *optimum ratio* between graphitic & defects sites available on carbon surface.
- The ether & H_2O reduction is *still* observed under O_2 exposure, with defective carbons showing higher activity.

The nanofiber samples (LHT & HHT) seem to have more active sites per area as compared to acetylene black samples

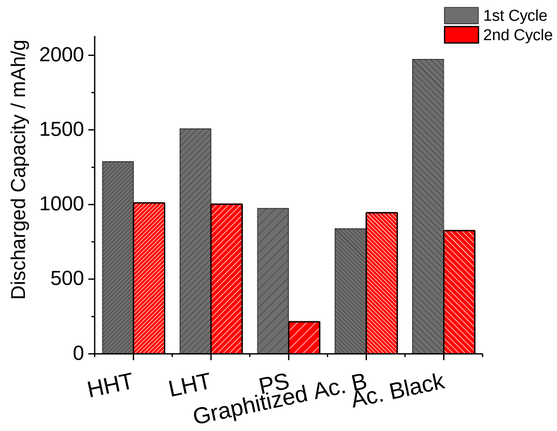
Under Argon (Cycle 1)



Under Oxygen (Cycle 1 & 2)

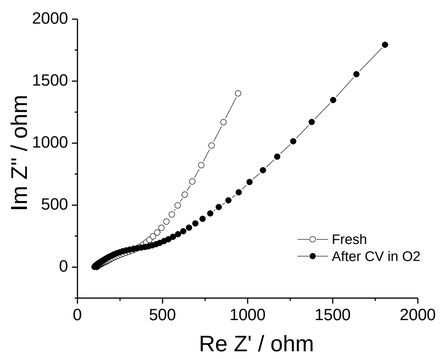


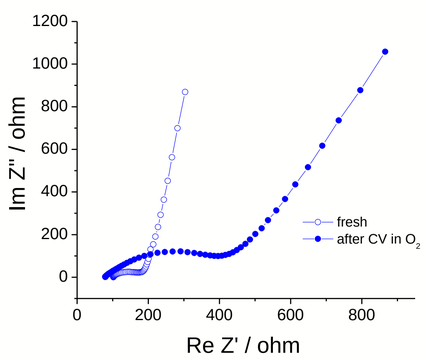
Carbons having more defects show more reactivity to electrochemically reduce and oxidize the ether solvent.

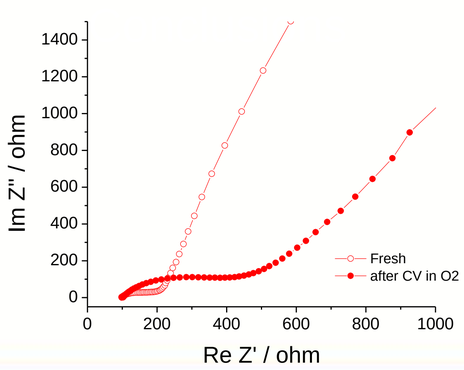


- Graphitic carbons have higher O_2 reduction activity in second cycle
- There maybe microstructural & chemical differences of the discharge products formed on carbon of different defect density.
- Different rate of active sites regeneration?

Impedance Measurement







- Higher impedance after CV → formation of insoluble & non-conducting Li_2O_2 and other discharge products deposits.
- Poor charge-transfer & site blocking contribute to the activity loss of electrochemical reduction of O_2 .
- Different deactivation mechanism for the highly defective carbon cathode (PS) is possible.

Conclusion

- Carbons of similar texture and porosity having different surface microstructure (different defect density) were shown to give different reactivity for electrochemical reduction of O_2 , regeneration, and other side reactions in non-aqueous Li-O_2 battery system.
- Our preliminary results suggest an optimum ratio of defects on the graphitic matrix for the efficient electro-catalyst.
- Further investigation are in progress!

Feel free to ask, comment & discuss…

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