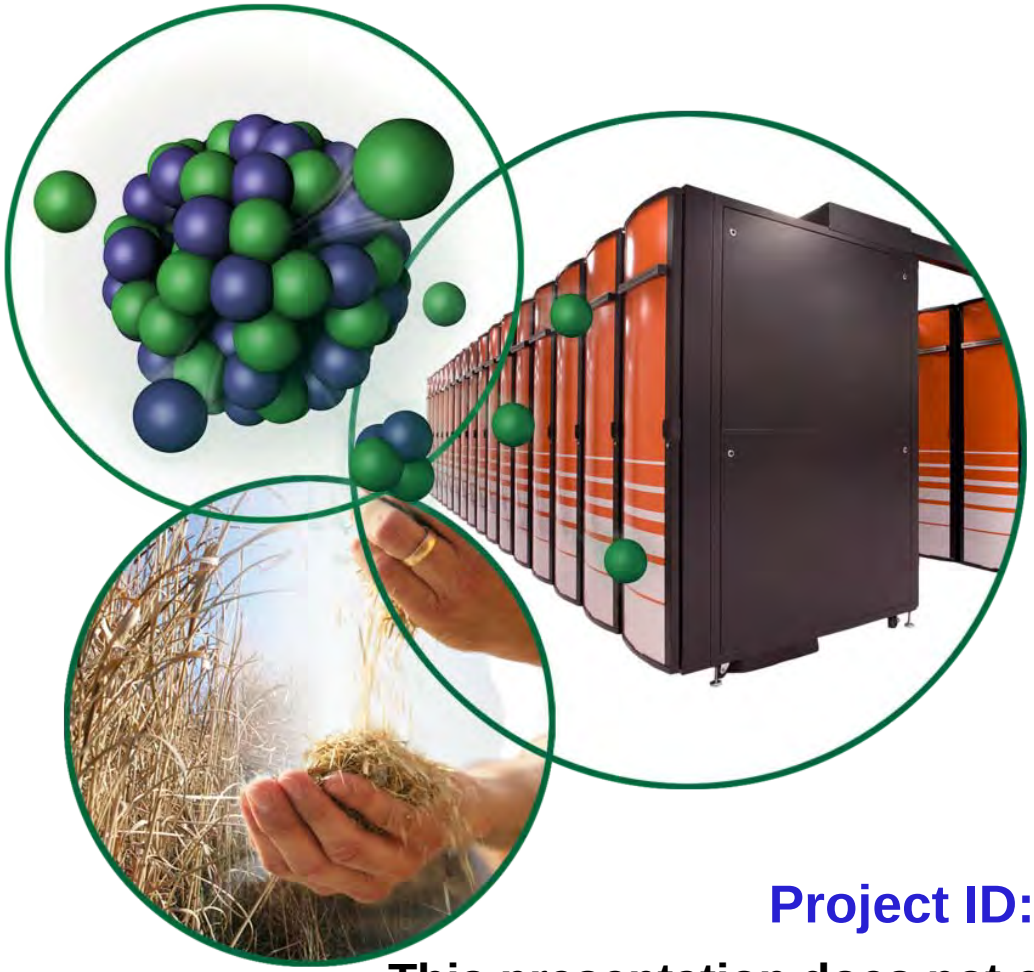
# Hard Carbon Materials for High-Capacity Li-ion Battery Anodes

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## Project ID: ES104

**This presentation does not contain any proprietary, confidential, or otherwise restricted information**

# Overview

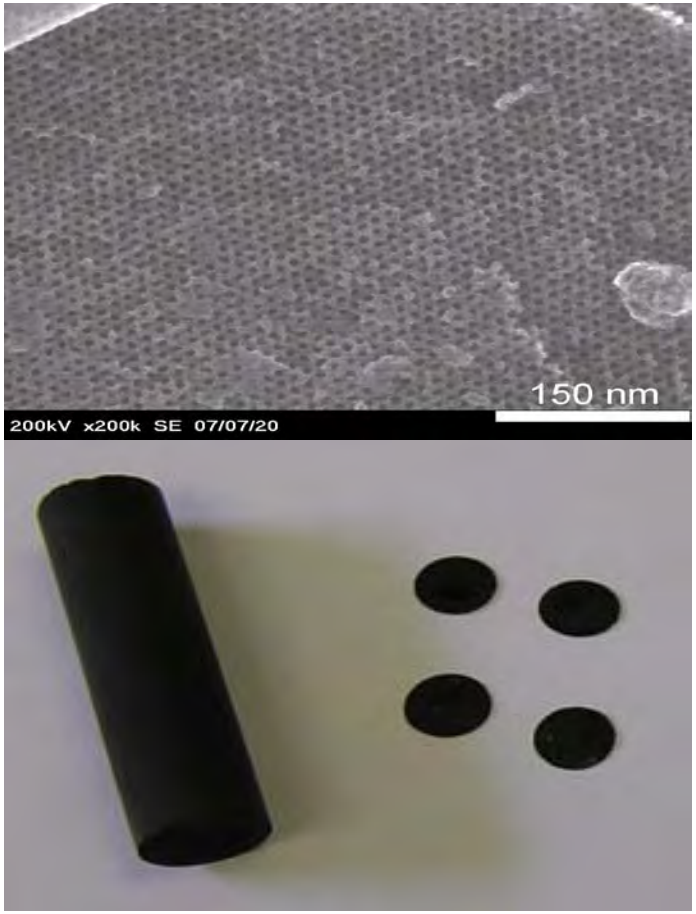
- **Start date:**
  - **June, 2010**
- **Budget:**
  - **-Funding received in FY 10: $120K**
  - **-Funding for FY 11: $300K**

## Barriers

- **Barriers addressed**
  - **Low energy density**
  - **Poor cycle performance**
  - **Cost**

# Outline

- **Background**
  - Why hard Carbon?
  - Why is hard carbon more suitable for vehicle application?
  - Why mesoporous carbon?
- **Progress report**
  - Objective
  - Challenges and Approaches
  - Milestones
  - Progress towards milestones
- **Future work**
- **Summary**




Li, Dai*, et. al, *J. Am. Chem. Soc.* 2004, *126*, 12782; Li, Dai*, et. al, *Chem. Mater.* 2005, *17*, 1717
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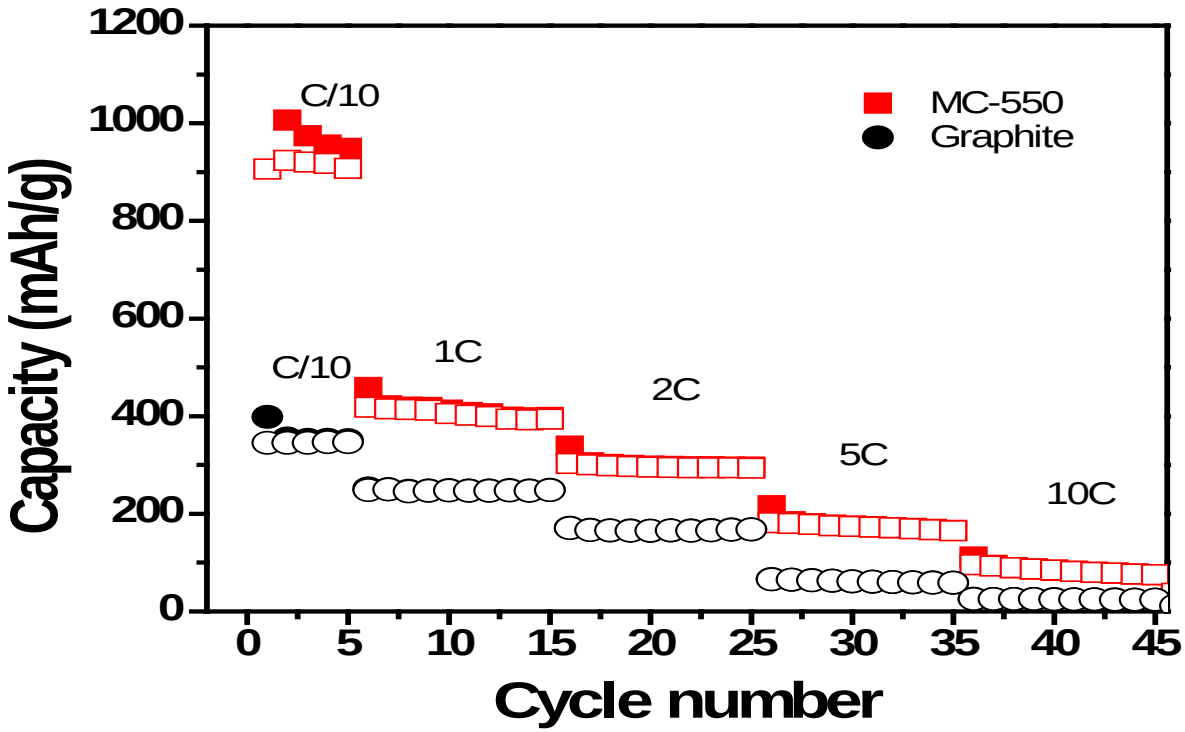
Wang, Dai*, et. al., *Chem. Mater.* 2008, *20*, 4800; Lee, Dai*, et. al., *J. Am. Chem. Soc.* 2009, *131*, 4596
Wang, Dai*, *Angew. Chem. Int. Ed.* 2010, *49*, 6664; Wang, Dai*, et. al., *Chem. Mater.* 2010, *22*, 2178

# Why hard carbon?



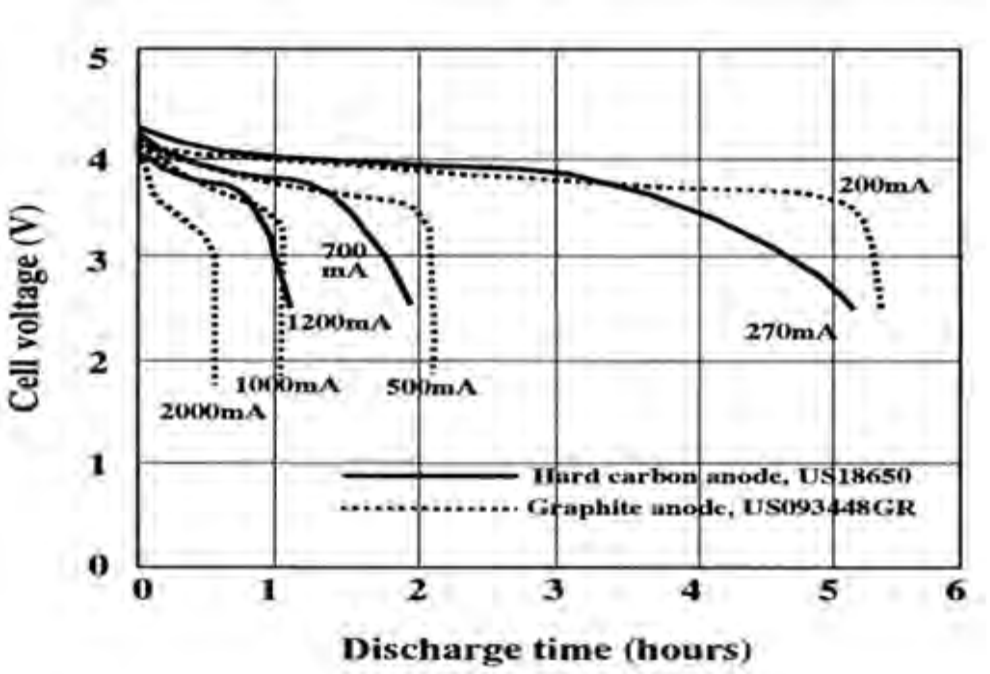

## Disadvantages of Graphite

- Limited Capacity: 372 mAh/g
- Susceptibility to exfoliation by electrolytes
- Poor rate performance
- Difficulty to form composites and molecularly doped anodes

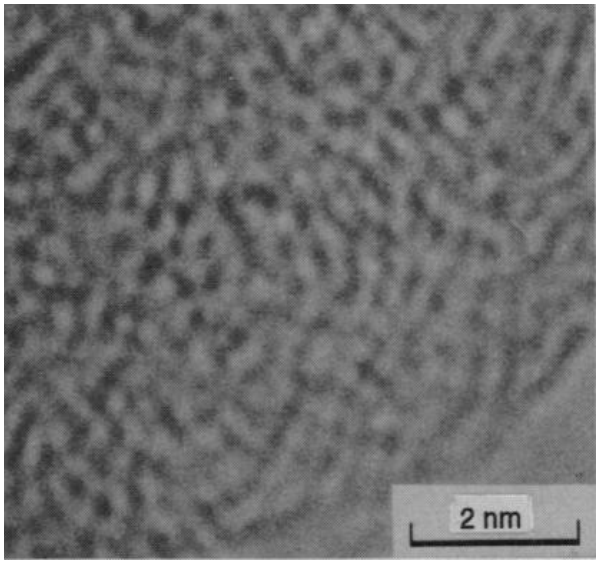
## Advantages of Hard Carbon

- High Capacity
- No intercalation-induced exfoliation
- Fast rate capability
- Easy to form composites and molecularly doped anodes

# Why is hard carbon more suitable for Vehicle applications?



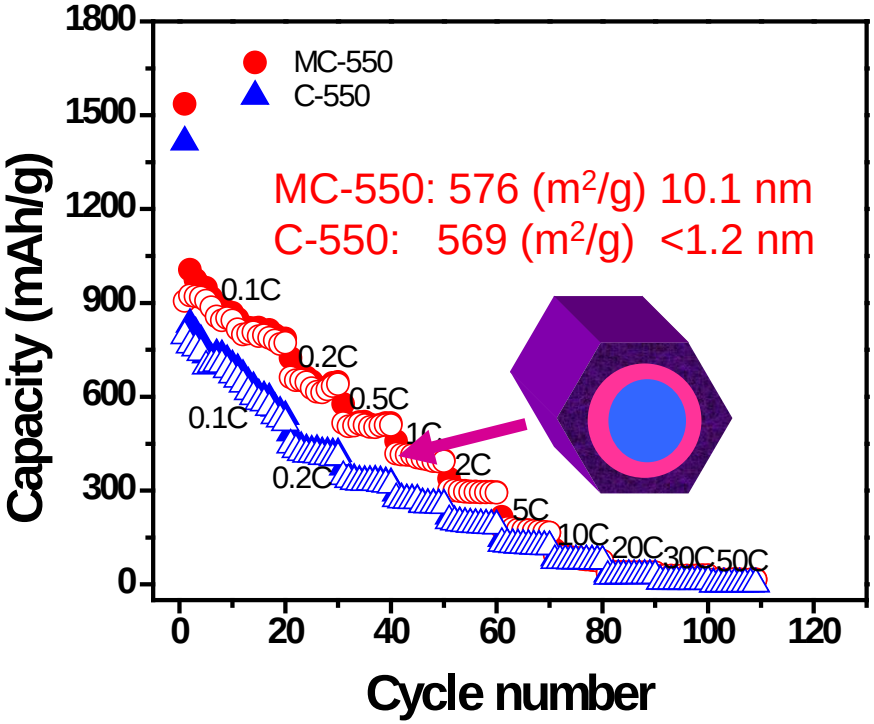

Endo et al, Carbon, *38*, 183 (2000).

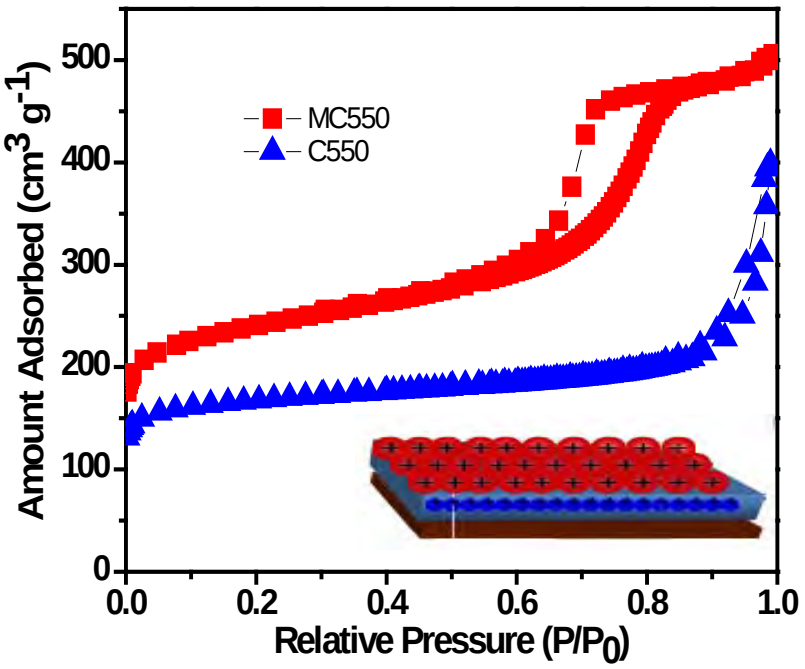



Endo et al, SCIENCE, *264*, 6556 (1994).

- **The I/V curve of hard carbon based battery can be used as a gauge for power management**
- **The I/V curve of graphite based battery can't be used as a gauge for power management unless sophisticated power management system is in place!**

# Why mesoporous hard carbon?




1. Li can be stored in the nanopores of the carbon via interfacial and surface charging!
2. The mesoporous structure provides fast Li transport channel and also reduces the solid-state diffusion length for Li and thus render high rate capability.
3. The mesoporous structure can buffer well against the local volume change during the Li insertion/extraction reactions and thus enhance the structural stability.

# Objectives

**To develop low-cost hard carbon materials with capacity higher than 372 mAh $g^{-1}$ and offering good cycle performance for uses in lithium ion batteries targeted on EV applications.**

# Challenges and Approaches

## Challenges

- Capacity fade with cycling
- Low initial coulombic efficiency
- Low density (low volumetric capacity)

## Approaches

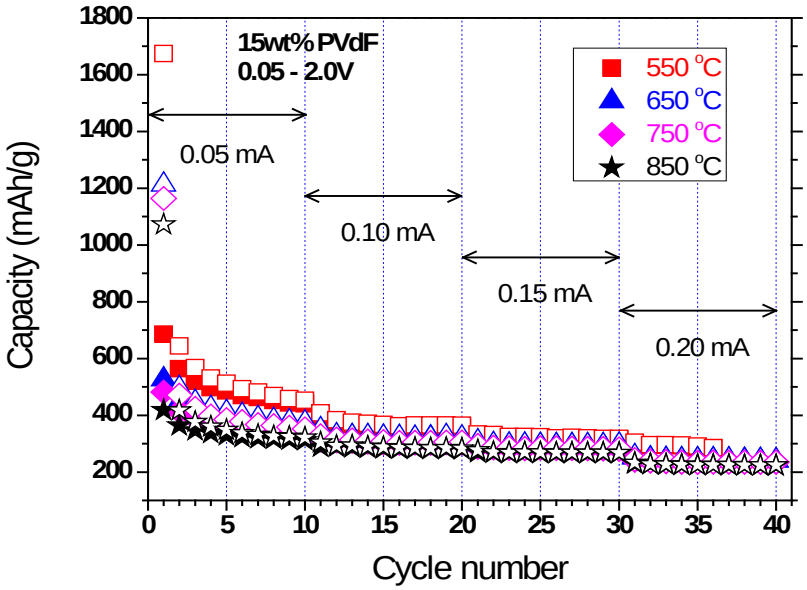
1. Improve cycle performance by surface coating or doping
2. Improve initial coulombic efficiency (CE) by surface coating with single ion conductors
3. Improve volumetric capacity by forming carbon composite with metal oxide

# Milestones

- **Finish investigation on the effect of carbonization temperature on physical and electrochemical properties of carbon materials. (03/30/2010)**
- **Improve long cycle performance of the carbon half cells. (9/30/2011)**
- **Optimize carbon || Li half cells and reduce the initial irreversible capacity. (09/30/2011)**
- **Identify the structural and surface changes of the carbon electrode after cycling. (09/30/2011)**

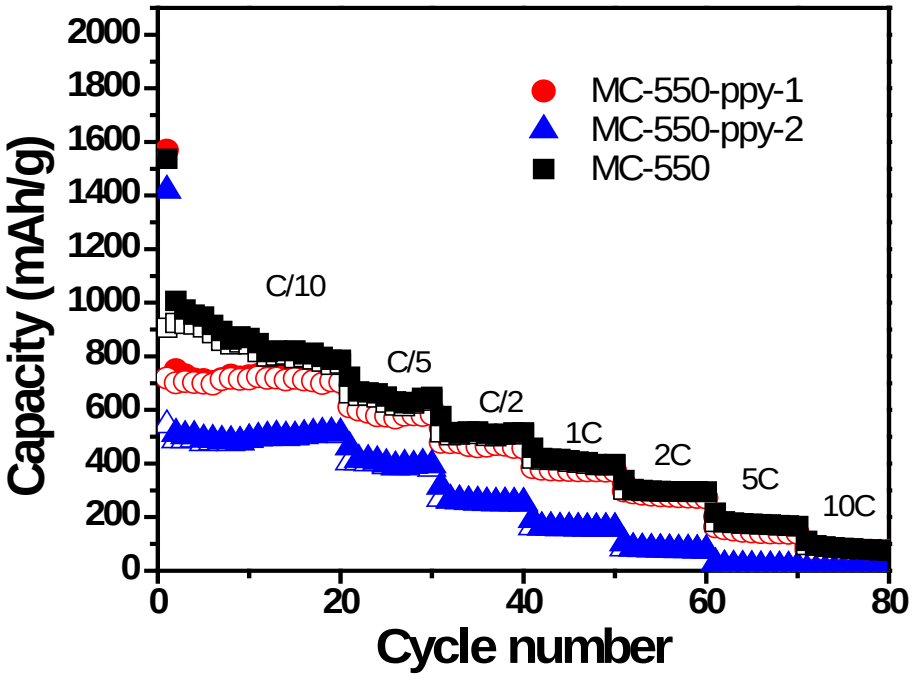
# Effect of Carbonization Temperature on cell performance

| T / °C | C % | H % | N % | O % | BET ($m^2/g$) | Pore Size (nm) | 1st intercalation capacity (mAh $g^{-1}$) | 1st de-intercalation capacity (mAh $g^{-1}$) | Coulombic efficiency (%) |
|---|---|---|---|---|---|---|---|---|---|
| 550 | 82.90 | 2.55 | 0.98 | 10.08 | 517.6 | 9.0 | 1674.5 | 685.3 | 40.9 |
| 650 | 88.05 | 2.13 | 0.53 | 5.86 | 517.4 | 5.9 | 1212.5 | 526.2 | 43.4 |
| 750 | 88.17 | 1.38 | 0.52 | 3.09 | 505.1 | 7.5 | 1164.1 | 481.5 | 41.3 |
| 850 | 91.30 | 1.29 | <0.5 | 3.64 | 530.1 | 6.2 | 1072.6 | 418.1 | 39.0 |




- Increasing temp. results in H, O reduction
- Surface area remains almost same
- Li stores in defects (Nanopores, Cavities)
- Unstable defects result in the reduction of the capacity with cycling.
- Low initial capacity and coulombic efficiency are partially related to the low cut off voltage of 2.0V; use 3.0V instead will increase capacity 200-300mAh $g^{-1}$ and coulombic efficiency 15%-20%.

# Approach 1: Improve Cycle Performance by surface coating




•Enhance electronic conductivity

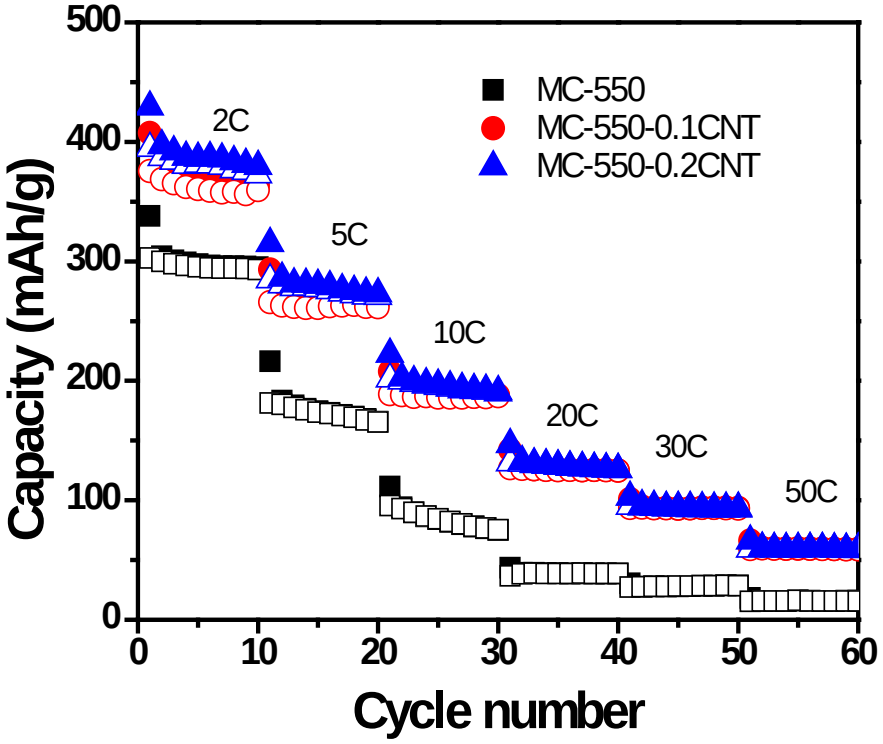
| | BET ($m^2/g$) | Pore Size (nm) |
|---|---|---|
| MC-550 | 497 | 10.1 |
| MC-550-PPy-1 | 292.2 | 8.2 |
| MC-550-Ppy-2 | 232.5 | 7.5 |

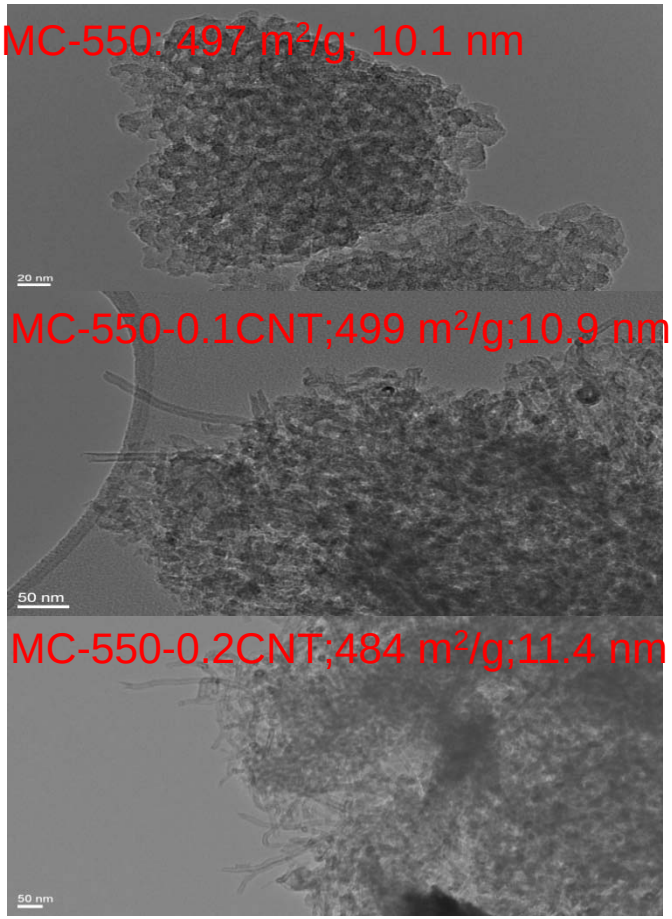
- **The surface coating of Polypyrrole (ppy) reduces unstable defects of mesoporous carbon and improves its cycle performance.**

- **The less contribution from surface charging due to the reduced surface area after Ppy coating is the cause of capacity reduction.**

# Approach 1: Improve Cycle Performance by surface coating (con't)

•Enhance electronic conductivity




- **The distribution of CNT in the carbon matrix enhances the electronic conductivity of mesoporous carbon.**
- **The mesoporous structure of the composite provides fast $Li^+$ transport channels.**

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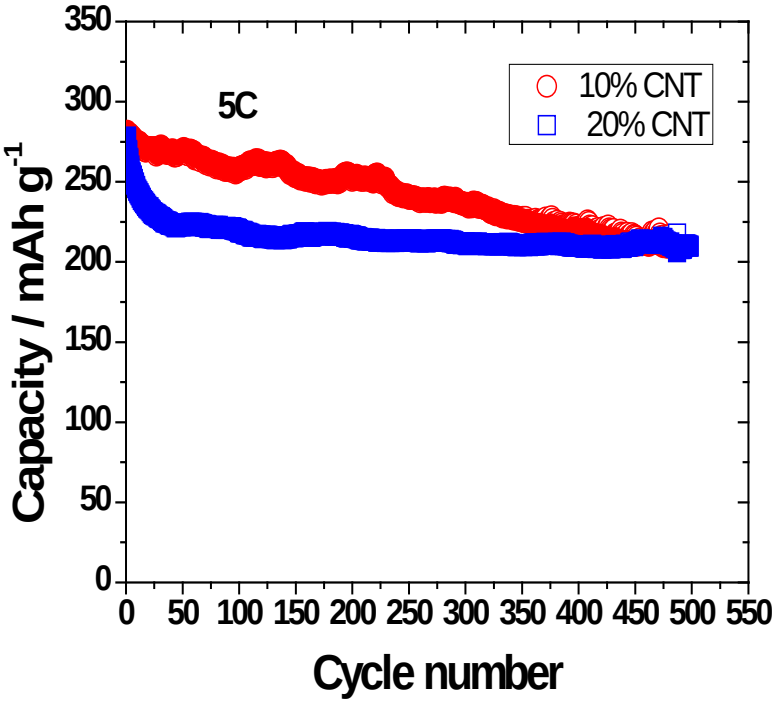
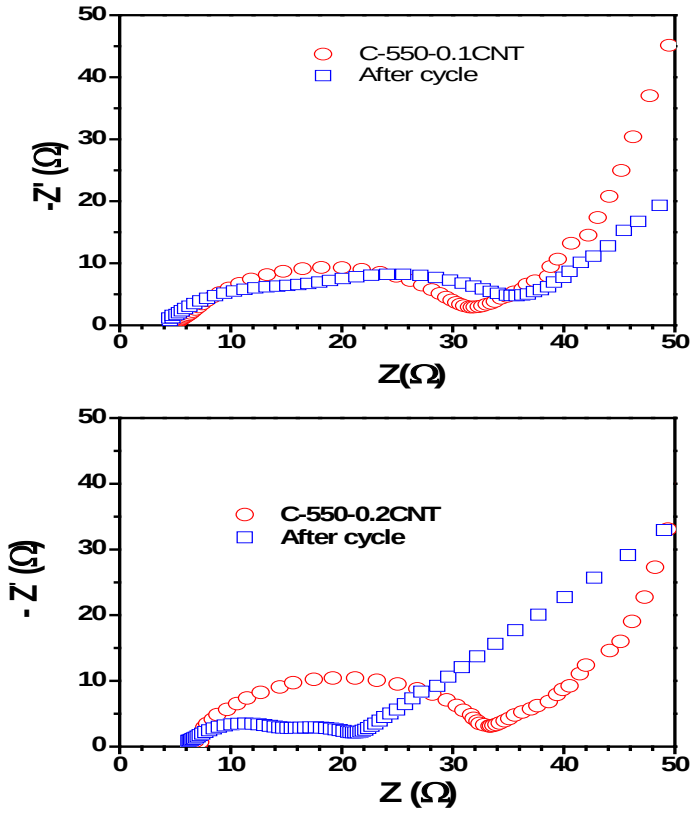
# Approach 1: Improve Cycle Performance by surface coating (con't)

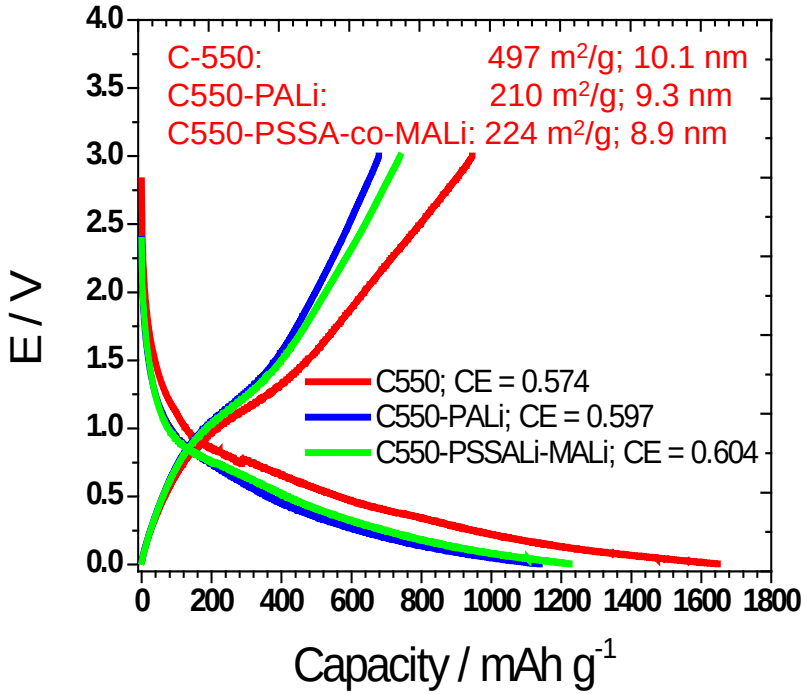


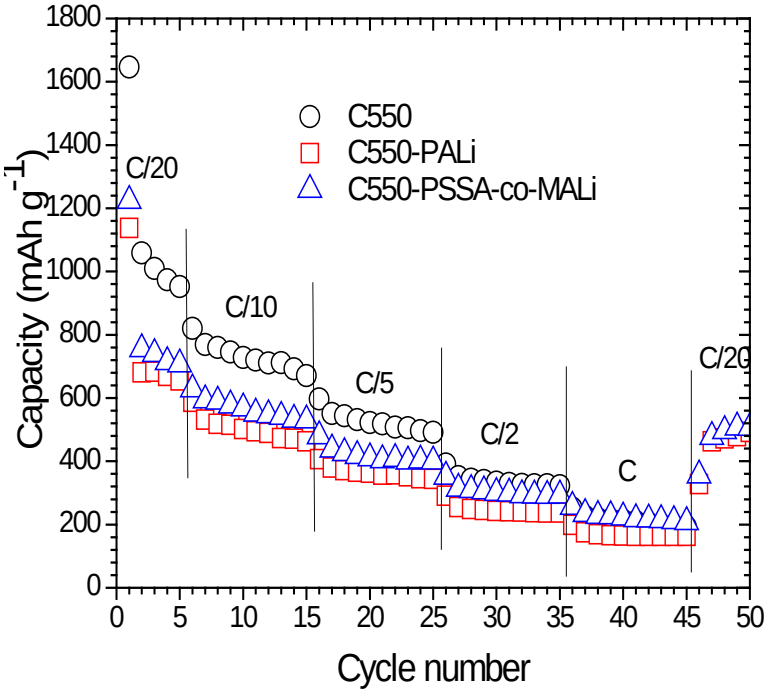




- **Under the current rate of 5C, the cell with 20wt% CNT reaches stable cycling quickly!**
- **Cell with 20wt% CNT has a lower charge transfer resistance that facilitates faster charge/discharge.**

# Approach 2: Improve coulombic efficiency by surface coating with single ion conductors

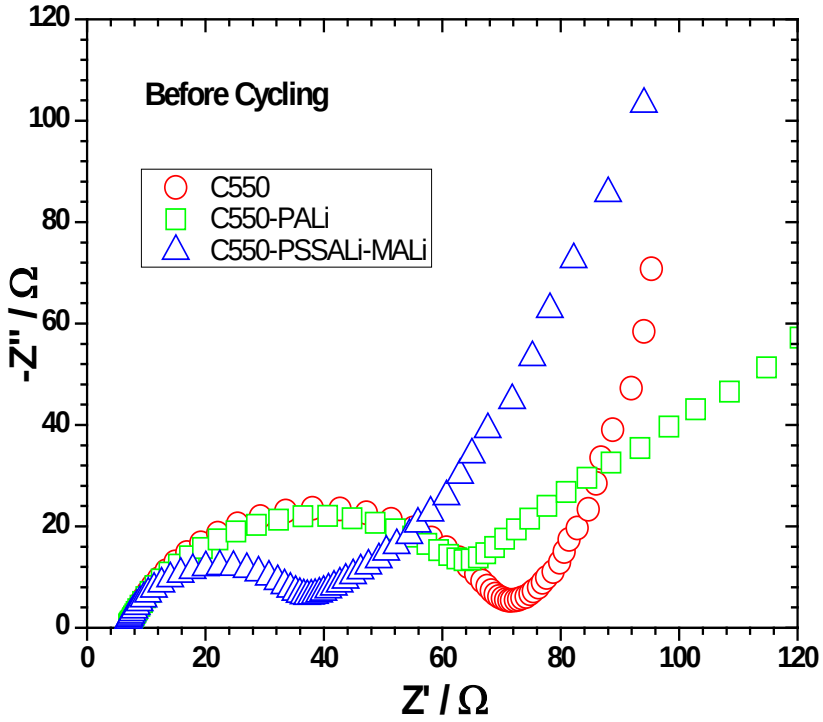
- Use Single ion conductors as artificial SEI layer on carbon surface to improve initial coulombic effciency

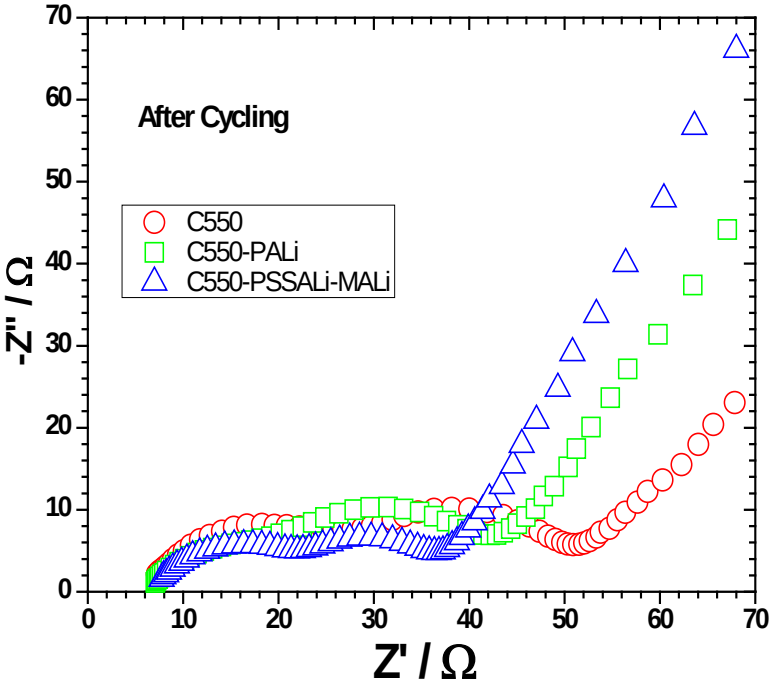



- **The improvement in the initial coulombic efficiency by surface coating with single ion conductors is very limited.**
- **Surface coating with single ion conductors indeed improved the cycling stability.**

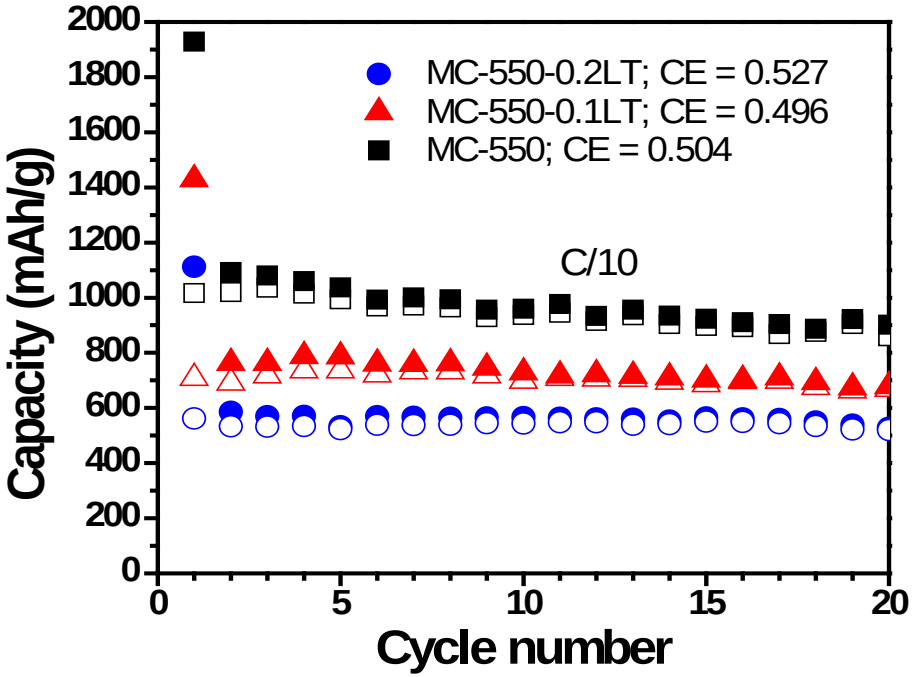
# Approach 2: Improve coulombic efficiency by surface coating with single ion conductors (con't)




- **Surface coating with single ion conductors reduces both SEI and charge transfer resistance, either before cycling and after cycling.**
- **PSSA-MALi is more effective than PALi in reducing the charge transfer resistance.**

# Approach 2: Improve coulombic efficiency by surface coating with single ion conductors (con't)



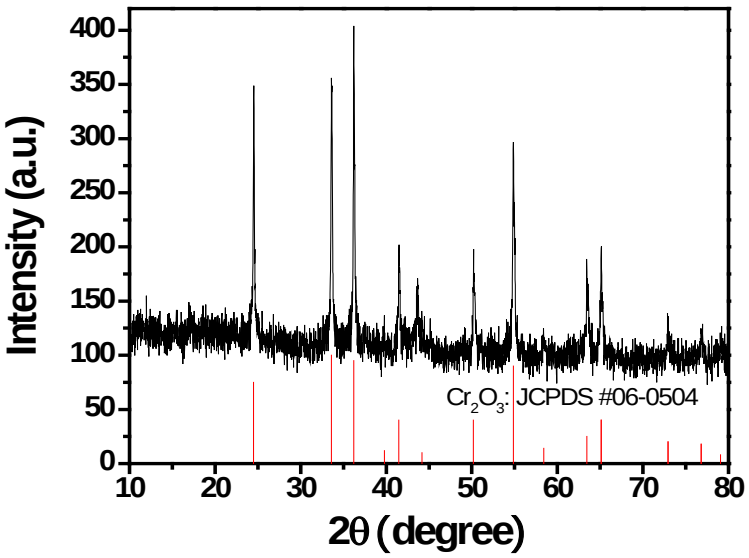

| | BET ($m^2/g$) | Pore Size (nm) |
|---|---|---|
| MC-550 | 497 | 10.1 |
| MC-550-0.1LT | 344 | 9.4 |
| MC-550-0.2LT | 329 | 8.9 |

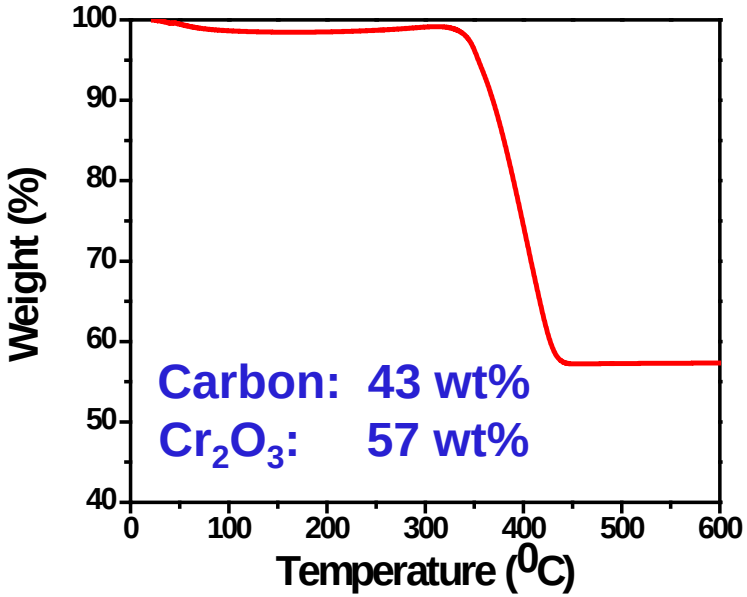
- **Coating is a suitable method to reduce unstable defects of mesoporous carbons and improve their cycle performance.**

- **Needs new approaches, new coating technique or combination of both to improve initial coulombic efficiency.**

# Approach 3: Improve volumetric capacity by forming carbon composite with metal oxide

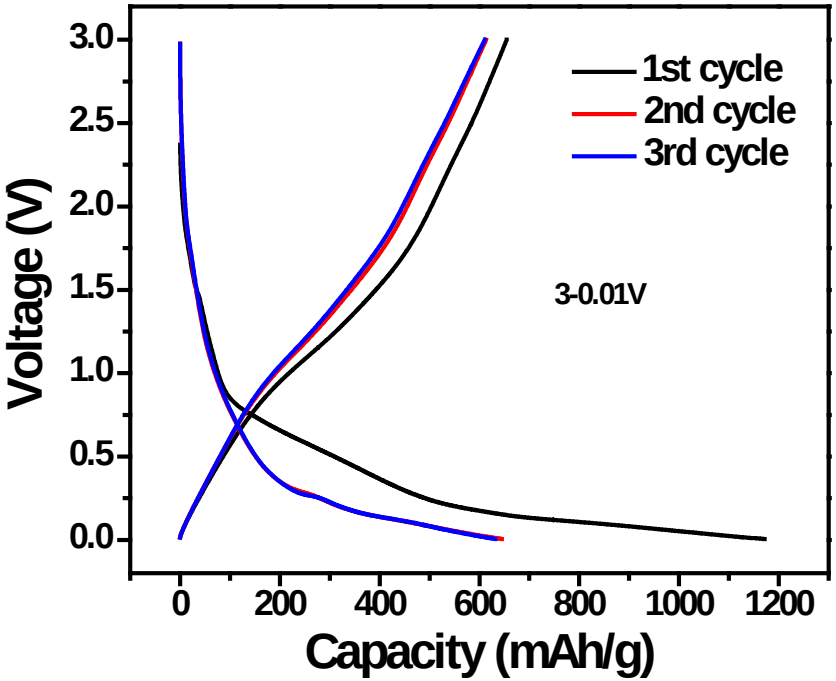
- **Form composite with metal oxide that have comparable capacity within the same discharge voltage range as mesoporous carbon but having poor reversibility.**
- **Mesoporus carbon matrix provide electron conductivity and confinement effect to improve the overall performance.**

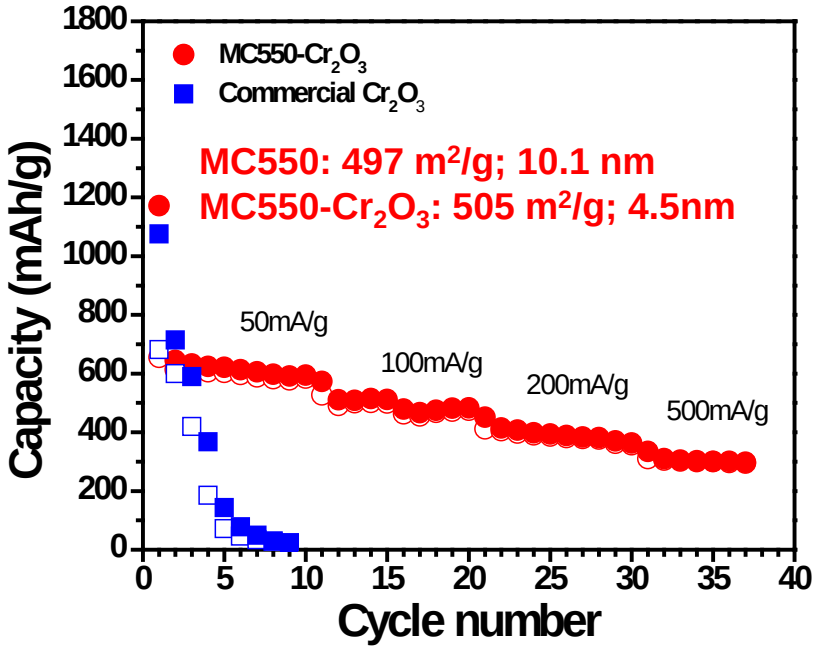



**Densities:$Cr_2O_3$ : 5.22 g/cm$^3$; C550: 1.90 g/cm$^3$; Composite: 3.0g/cm$^3$**
**The density is increased by 58%!**

# **Approach 3:** Improve volumetric capacity by forming carbon composite with metal oxide (con't)

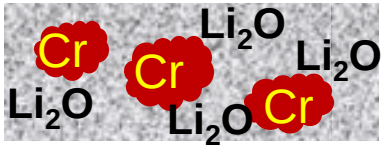



**The cycling stability was greatly improved as a result of composite.**

**Conversion (displacement)**

**$6Li + Cr_2O_3 \leftrightarrow 3Li_2O + 2Cr$**




Fulvio, Dai*, et. al., *Adv. Funct. Mater.*, 2011, in press

# Future Work

- **Continue to seek suitable candidates and new methods in modifying the surface of mesoporous carbons to increase the initial coulombic efficiency and improve the cycle performance.**

- **Seek other high density or high capacity active materials to increase the volumetric capacity density of mesoporous carbons.**

- **Focus on characterization and diagnostic studies using XPS, XRD, EIS, SEM/TEM, Neutron etc.**

# Summary

- **Hard carbons with high capacity (1000mAh $g^{-1}$) have been made and their cycle stability has been improved by surface coating with polypyrrole and doping with carbon nanotube.**
- **Different single ion conductors have been used to improve the initial coulombic efficiency, however, only limited success is achieved.**
  - **-- Further improvement in initial coulombic efficiency is pending upon characterization of the modified electrodes after first cycle to understand morphology, composition and their effects on coulombic efficiency.**
  - **-- Needs new approaches, new coating technique or combination of both to improve initial coulombic efficiency.**
- **The volumetric density of mesoporous carbon has been increased by forming composite with $Cr_2O_3$.**