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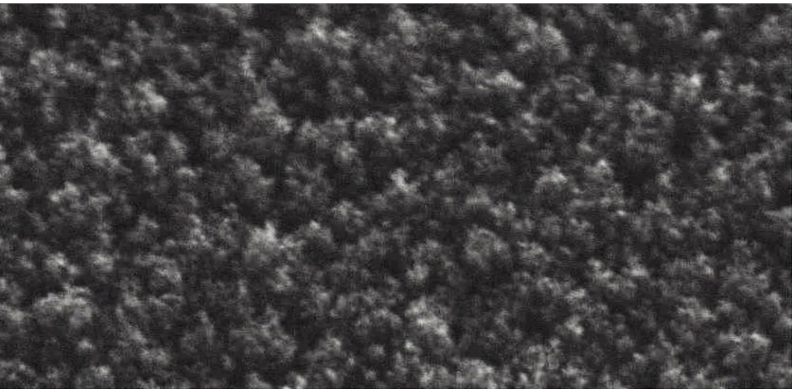

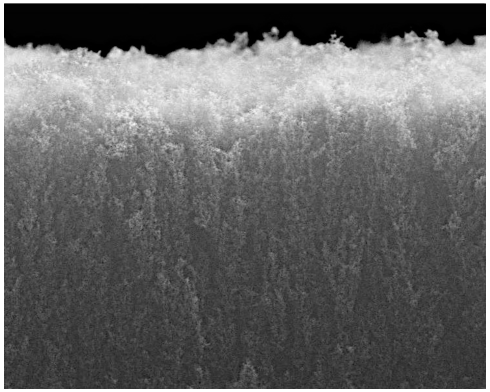

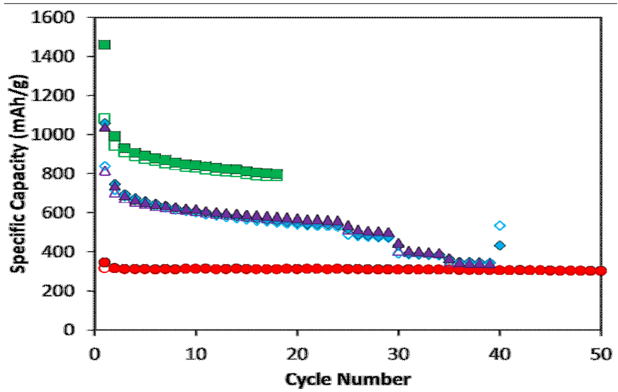

Nanoporous-Carbon as Host Material for High-Performance Li-Ion Energy Storage

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Nanocarbons for Energy and Catalysis I

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Outline

- Motivation for carbon host materials for Li ion energy storage
  - Growth by pulsed-laser deposition (PLD)
  - Controlling physical properties: Morphology, mass density, and surface area
- Li coin cell fabrication and cyclic voltammetry measurements
  - Charge-discharge behavior as a function of NPC mass density
  - Capacity vs. NPC density
  - Coulombic efficiency vs. NPC density
- Summary

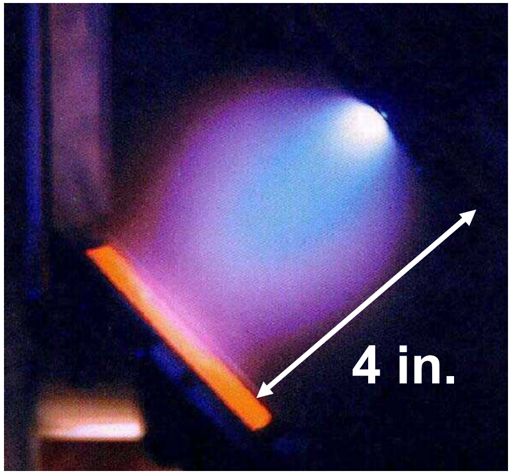
Carbon based Li ion energy storage

- Li-ion energy storage is near optimal performance, limited by the single electron valence.

Electrode materials	Specific Energy Density (mAh/g)	Volumetric Energy Density (mAh/cm^3)
Li metal	3861	2061
Graphite (LiC_6)	372	841
Graphene (assuming Li_2C_6)	744	1927

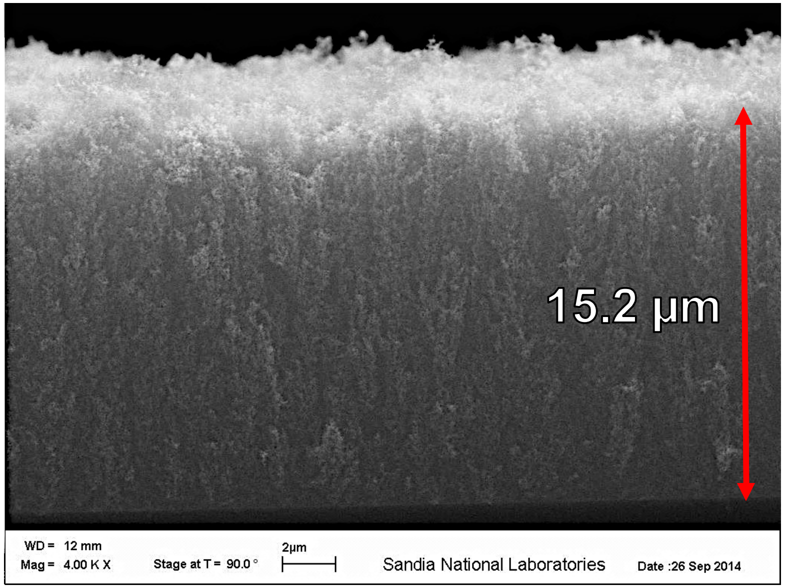
- Despite high theoretical energy capacity, Li has limited effectiveness due to the formation of solid electrolyte interphase (SEI), uncontrolled morphology issues (dendrite formation), and low coulombic efficiency.
- Metal alloys experience large irreversible capacity losses due to stress-induced cracking resulting.
- Graphite intercalation hosts have small 3.35 Å interplanar spacings between graphene layers, impeding full Li intercalation.
- Graphene offers higher theoretical capacitance but suffers from low coulombic effieciency and capacity fade.
- ***Nanoporous-carbon (NPC) offers an opportunity for a controlled study of a 3D scaffold of graphene!***

NPC Growth by Pulsed Laser Deposition (PLD)



- We grow NPC via pulsed laser deposition via 248-nm ultraviolet pulsed excimer radiation in a controlled argon atmosphere.
- Choice of argon atmosphere dictates density of the resulting NPC film, allowing for fine tuning of the material property based on device application

- NPC is a pure sp^2-bonded carbon material with negligible residual stress enabling multi-µm thick film growth.
- NPC film with density of 0.26g/cm^3 shown here



Nanoporous-Carbon ≠ ordinary graphitic material!

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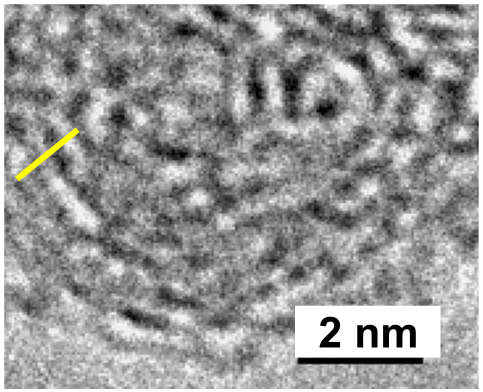
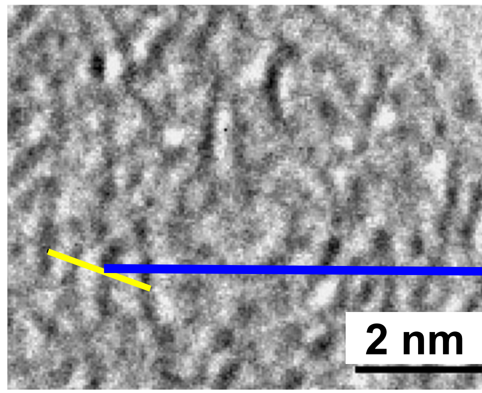
- NPC consists of randomly oriented sheets of graphene → “3D graphene”

density = 1.0 g/cm^3

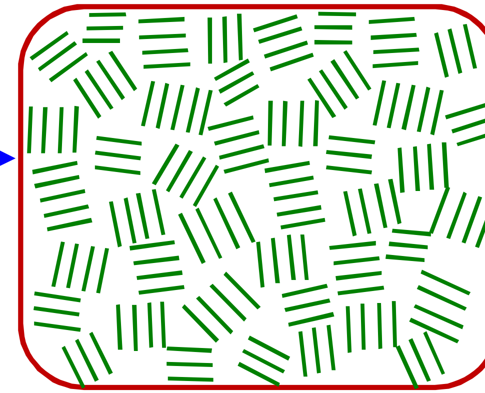


density = 0.25 g/cm^3



4.4 - 4.8 Å interplanar spacing 5.1 - 5.4 Å

lots of grain boundaries between nm-sized grains/domains with enhanced interplanar spacings

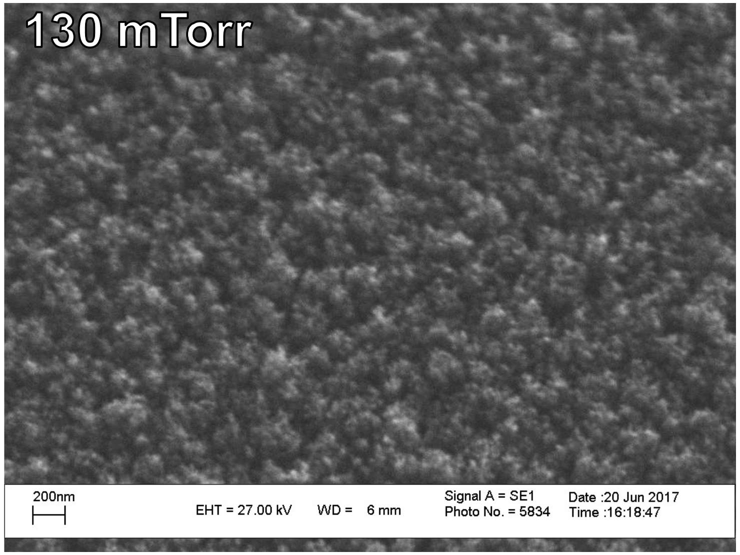


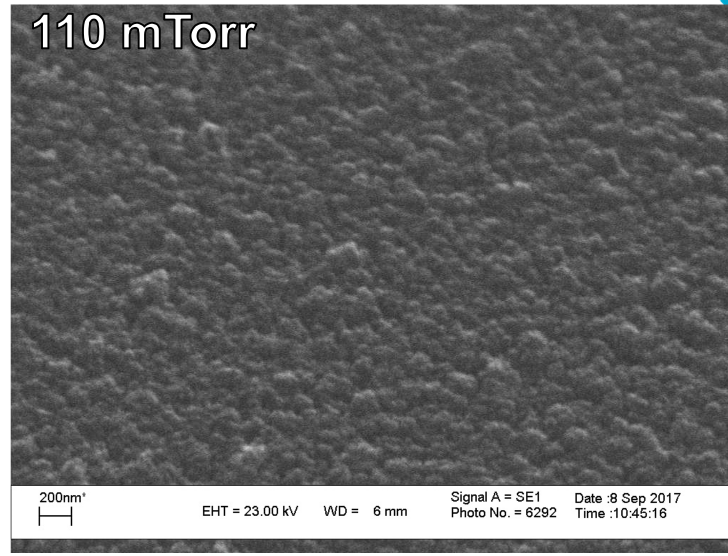
- typical interplanar spacings of graphite: 3.35 Å
- enhanced Li transport through larger channels
- can every carbon atom be accessible to cations?

Siegal et al., *Langmuir,* **20**, 1194 (2004)

NPC Surface Morphology vs. Pressure (Ar)

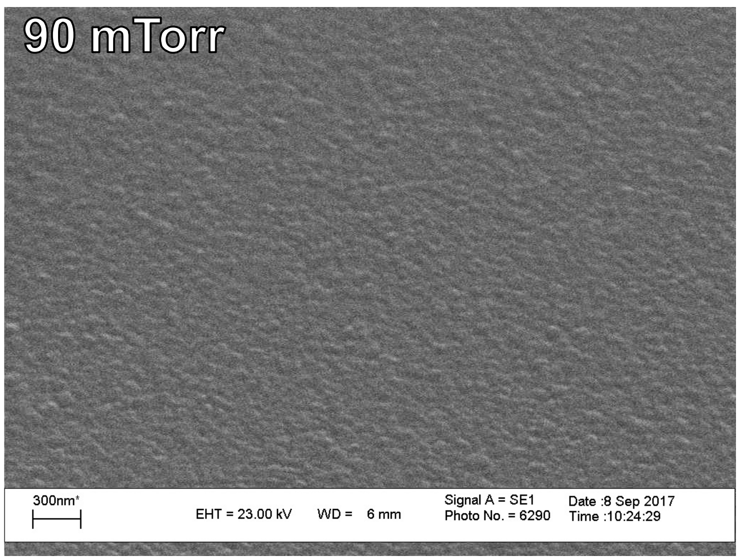
0.42 g/cm^3

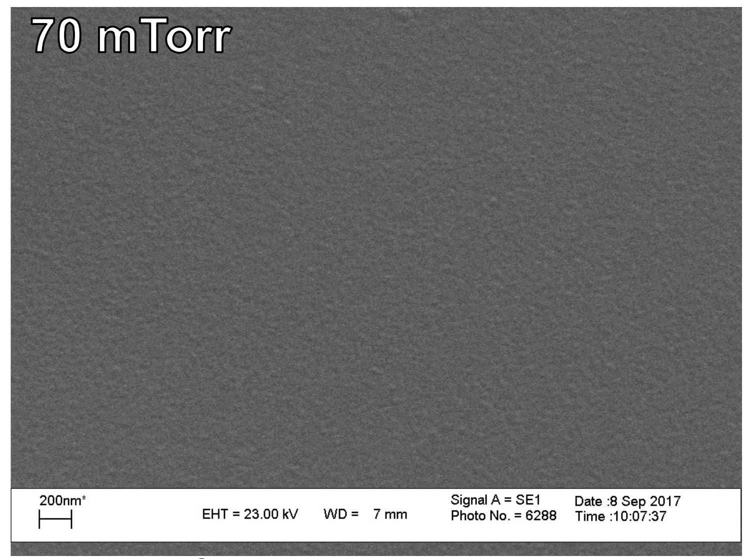




1.19 g/cm^3

1.64 g/cm^3

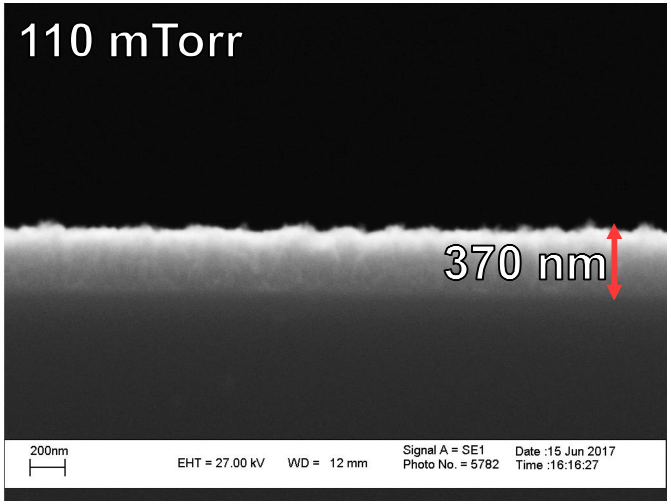


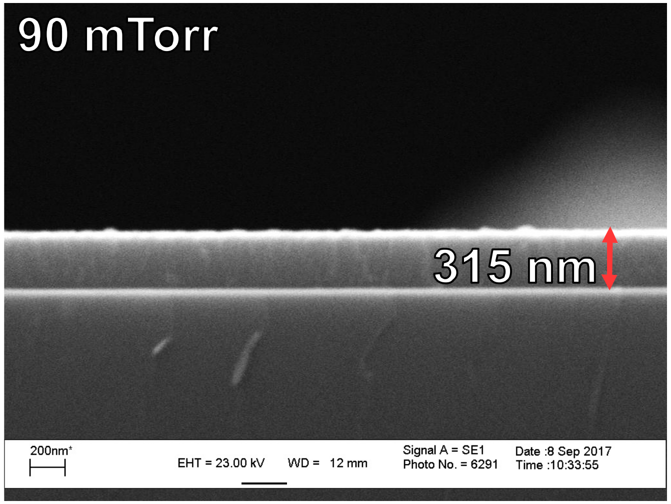


2.1 g/cm^3

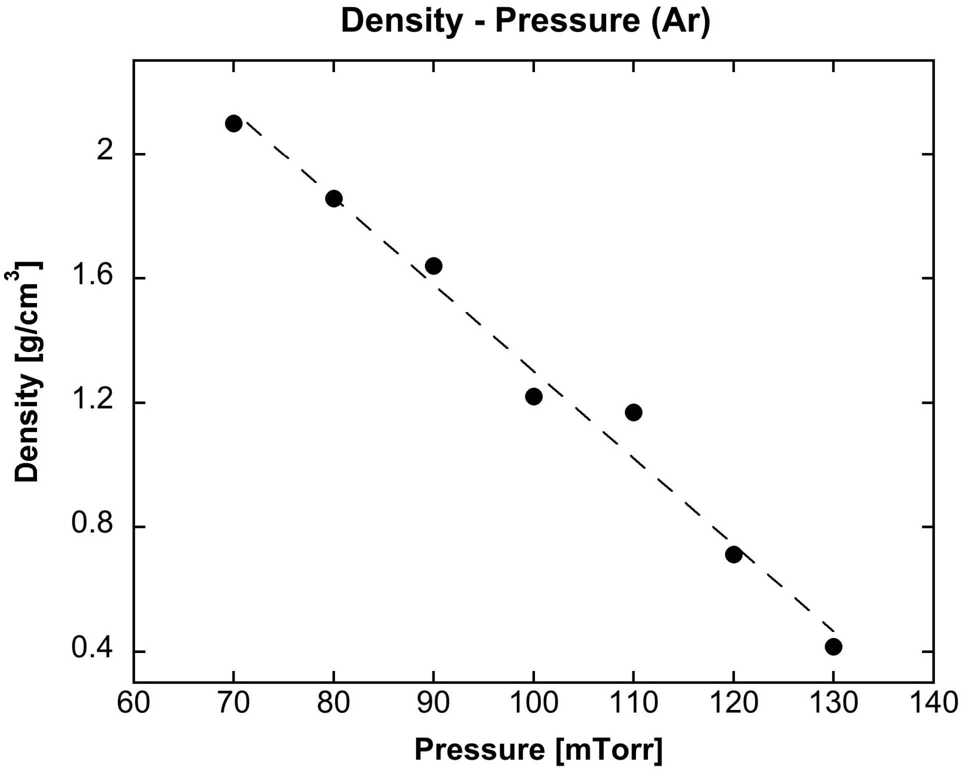
- films have carbon areal mass = 0.05 ± 0.01 mg/cm^2
- electrochemical testing as a function of volumetric mass density

Mass Density vs. Pressure (Ar)





- substrates are being weighed before and after NPC deposition using a microbalance, allowing for an accurate calculation of the density
- difference in film thickness is evident despite all films having a similar carbon areal mass of 0.05 ± 0.01 mg/cm^2



Surface Area Characterization

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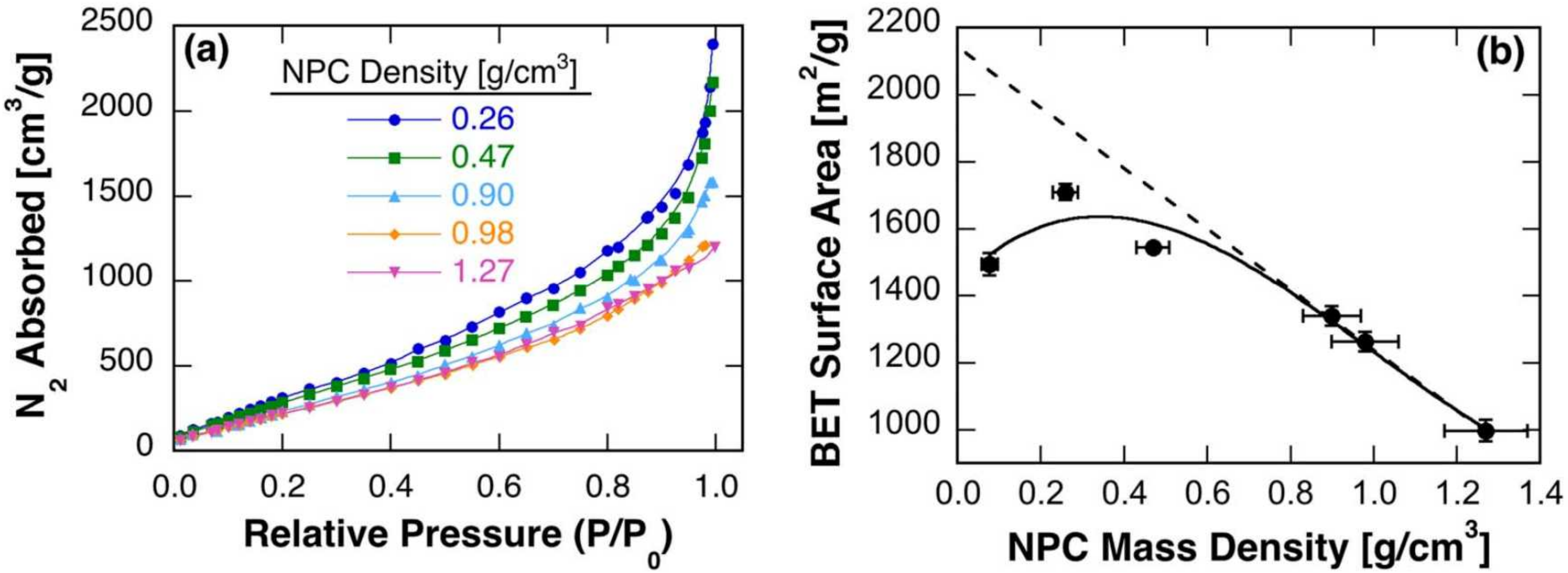
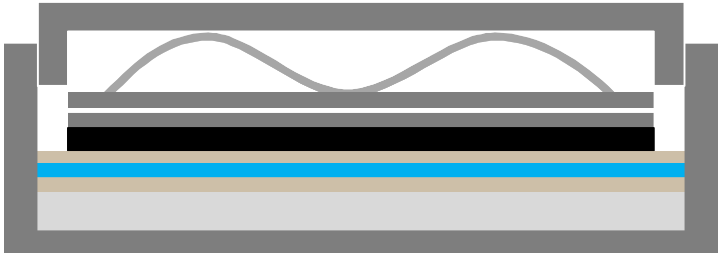
- Brunauer-Emmett-Teller (BET) method
- Samples outgassed under vacuum at 373 K for 6 hours.
- Full adsorption and desorption N_2 isotherms up to 0.995 relative pressure (P/P_0) were measured at 77 K.



- Surface area values reported for other carbon materials:

- *single graphene sheet: 2630 m^2/g*
- *graphene agglomerates: 705 m^2/g*
- *carbon blacks: 500 – 850 m^2/g*
- *ordered mesoporous carbons: 1500 – 1800 m^2/g*
- *CNT bundles: 200 – 600 m^2/g*

Coin Cell Fabrication



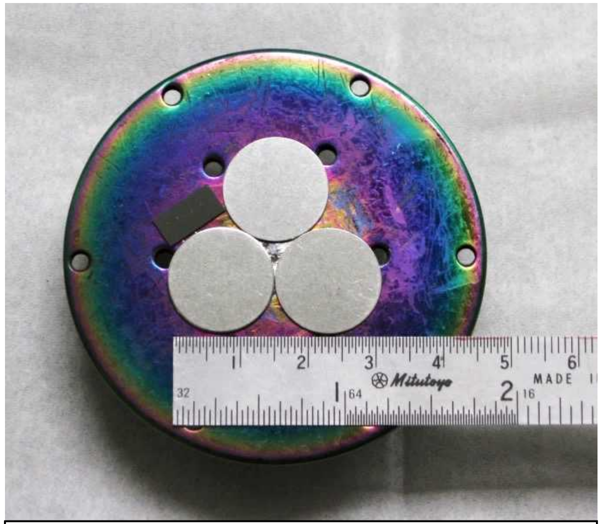
- Anode consists of:
  - anode cap
  - stainless steel flat spring
  - stainless steel disk #1
  - stainless steel disk #2 (CR2032 (20 mm diameter, 3.2 mm height) coated with NPC, acting as the working anode for the battery.
- Cathode consists of:
  - polypropylene seal #1 (Celgard 2400)
  - Electrolyte solution:
    1 M LiPF6 in 1:1 ethylene carbonate:diethyl carbonate (EC:DEC)
  - polypropylene seal #2 (Celgard 2400)
  - Li metal disc
  - cathode cap
- All NPC films were dried and outgassed for over 48 hours in glove box prior to assembly.
- Assembled in a dry Ar purged glove box

Electrochemical Testing

- Films deposited onto Si for structural characterizations and stainless steel disks for electrochemical coin cell evaluation.

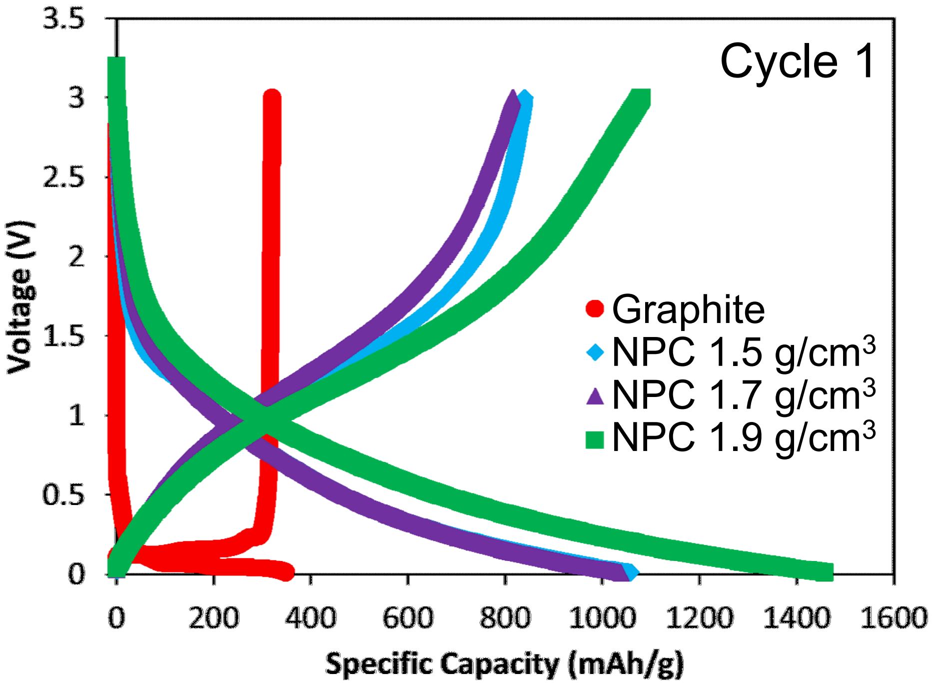
- C-rates are based on theoretical capacity of graphene where Li is assumed to adsorb on both sides of each graphene sheets (744 mAh/g) rather than one Li intercalated between two sheets in graphite

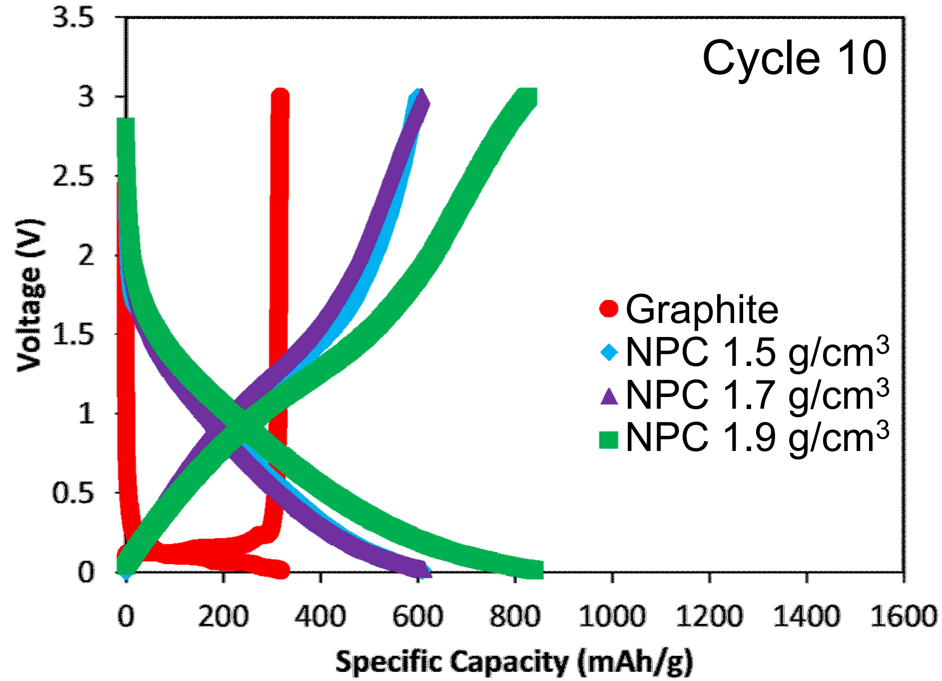
- scans collected with Arbin battery cyclers



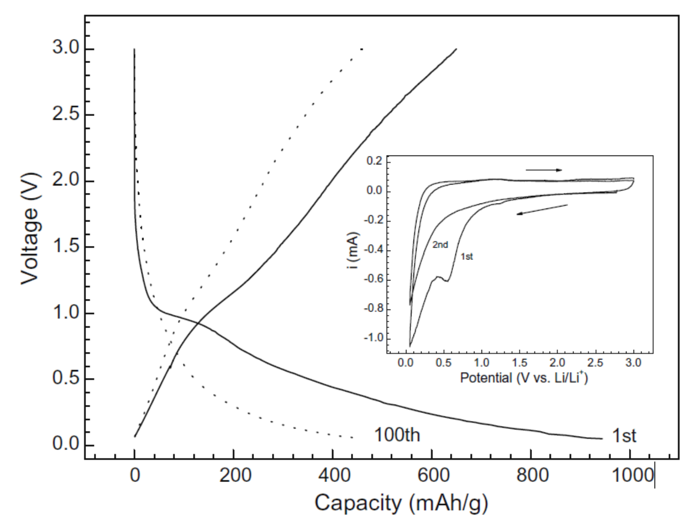
Sample stage with 3 stainless steel disks and one witness sample

Charge - Discharge Performance



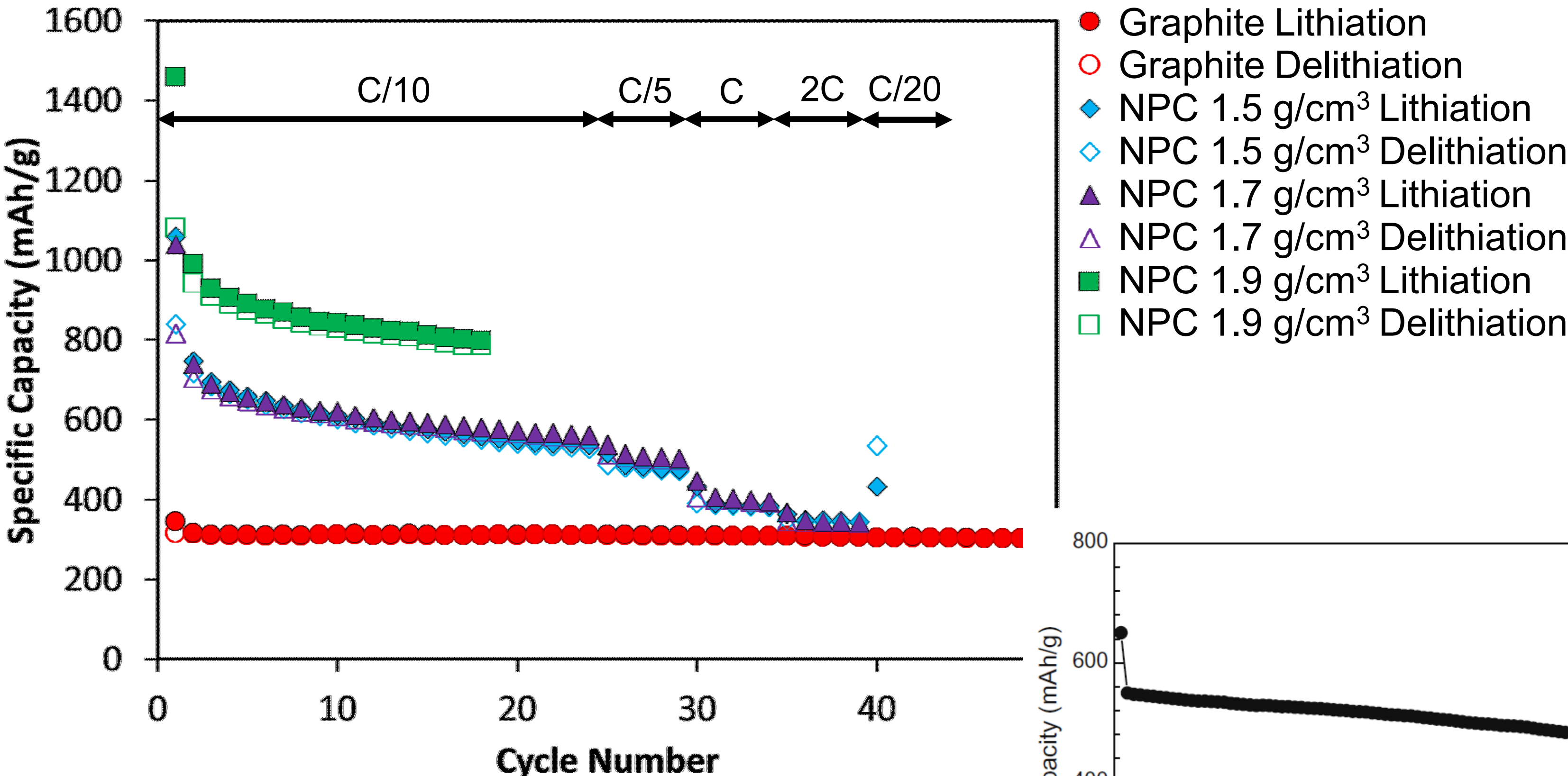


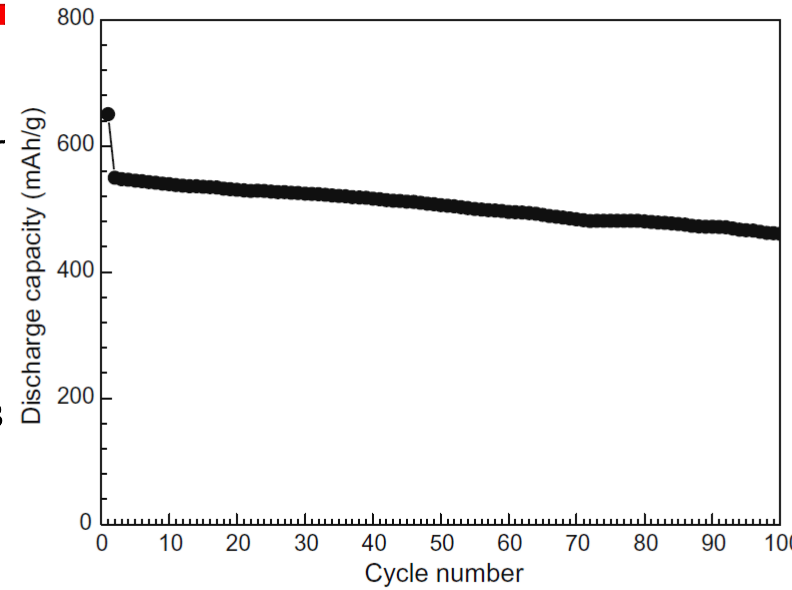
- Li can be successfully inserted into NPC
  - NPC behaves like graphene rather than graphite
  - This is in correlation to the expanded interplanar spacing of NPC as compared to graphite



Wang, Guoxiu, et al. *Carbon* 47.8 (2009): 2049-2053.

Capacity

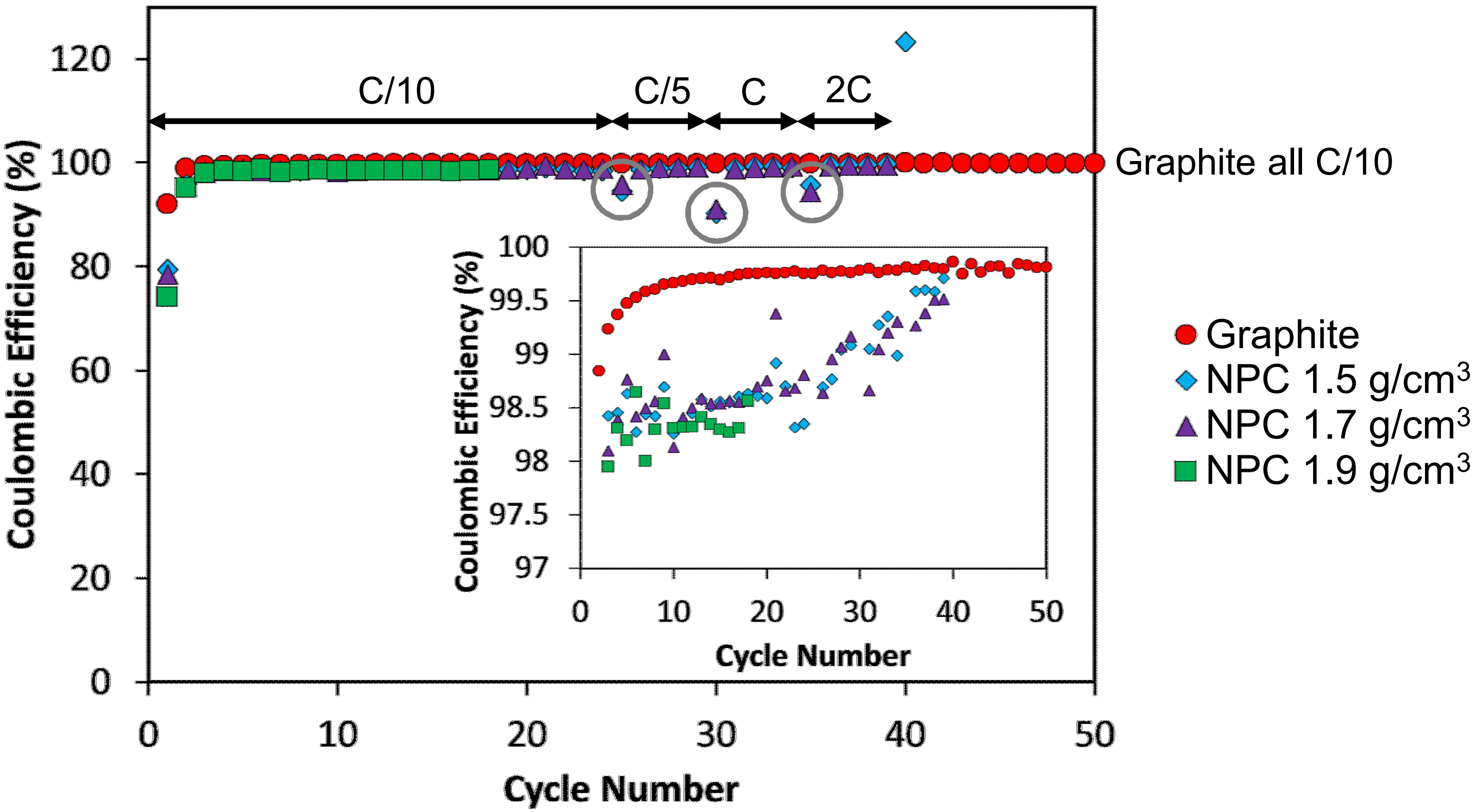




- 25 cycles at C/10, 5 at C/5, 5 at C, 5 and 2C, and 5 at C/20
- 1.5 and 1.7 g/cm^3 are very similar but 1.9 g/cm^3 shows higher capacity
- Fast drop and difference in charge and discharge at beginning hints at SEI formation

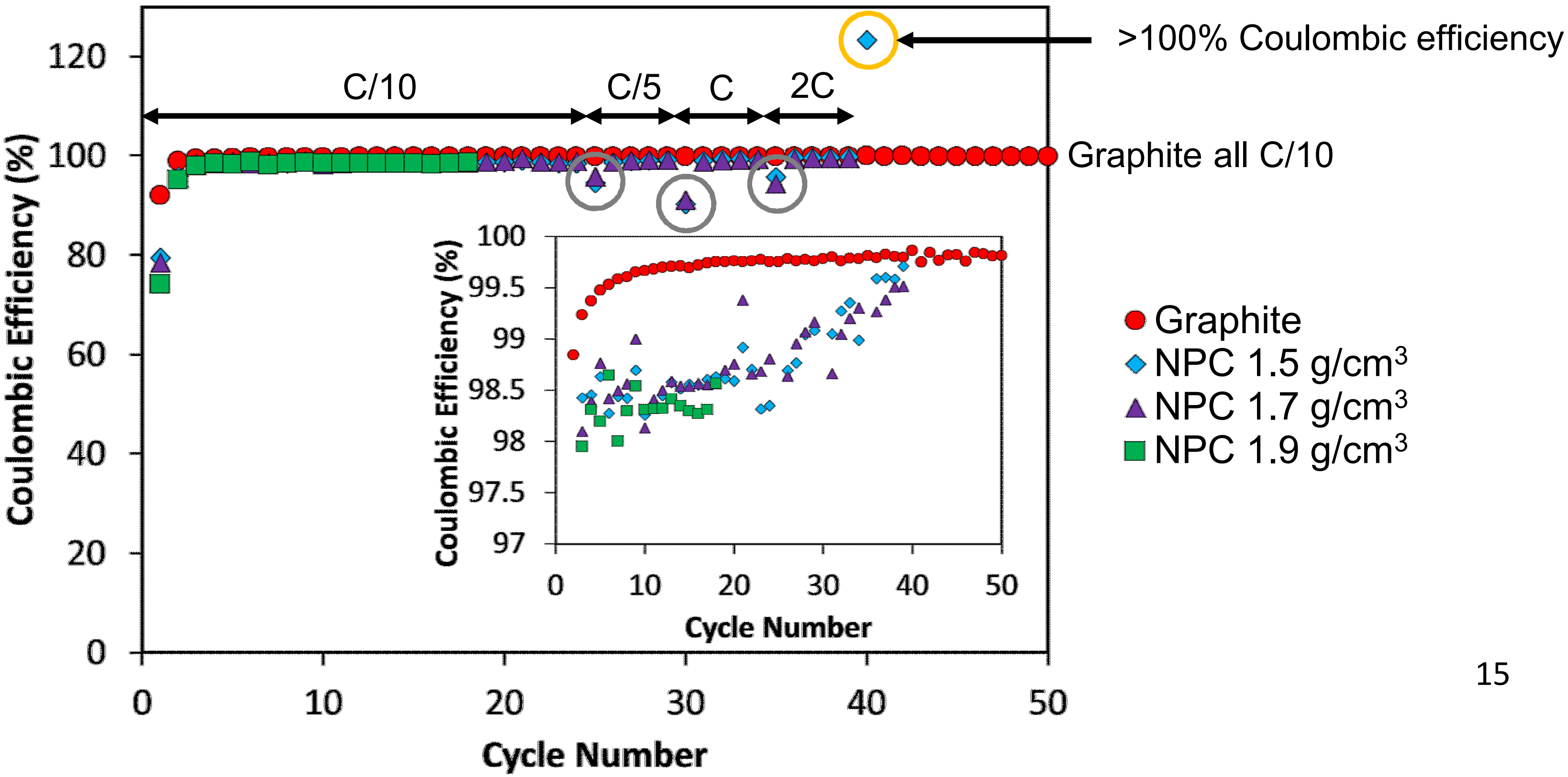
Wang, Guoxiu, et al. *Carbon* 47.8 (2009): 2049-2053.

Coulombic Efficiency



- Coulombic efficiency is not very dependent on density
- Coulombic efficiency lower than graphite, but still increasing with cycling
- Coulombic efficiency drops for the first cycle after increasing C-rate from C/10 to C/5 to C to 2C (gray circles), suggesting additional SEI formation with higher rates or that Li removal is more difficult than insertion at high rates

Coulombic Efficiency



- Initial data suggests that Coulombic efficiency increases when increase C rate from 2C to C/20 indicating that some Li cannot be removed from NPC during cycling at high rates, but can be recovered at a slower rate
- Note that the amount of lost capacity when increasing the rate (gray circles) is approximately the same as the amount of increased capacity (orange circle), indicating trapped Li in NPC

Summary

- Nanoporous carbon coatings on a battery anode can be used to study the reversible lithiation in a host material.
- The ability of NPC to serve as a lithium host is directly related to its controllable mass density and surface area.
- NPC displays an electrochemical behavior similar to graphene, but allows for a systematic study of performance based on density.
- Initial testing of the NPC films shows that films with higher densities (closer to graphite) exhibit higher capacity.
- NPC could be an interesting material for supercapacitors (due to large surface area), or Na ion and LS batteries (due to large interplanar spacing)

Thank you for your attention!

- The SNL team:
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