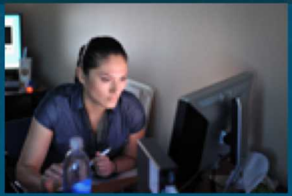
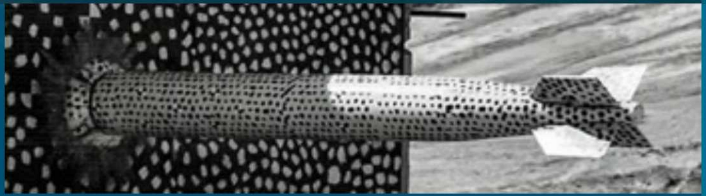
SAND2019-3790C

Correlating Nanoporous-Carbon Structure with Li-Ion Anode Energy Storage Properties





International Battery Seminar & Exhibit
Ft. Lauderdale, FL
Mar. 25 - 28, 2019

PRESENTED BY **Michael P. Siegal**, Katherine Harrison, Matthaeus Wolak, Subrahmanyam Goriparti, and Paul Cuillier

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories.

Outline

1. **Background for nanoporous-carbon (NPC)**
    a. **Tailoring NPC nanostructural properties**
    b. Chemical sensor coatings
2. Coin cell testing
    a. Li-ion anode intercalation materials
    b. Comparisons with other nanocarbon materials
3. NPC scaffold for Si?
4. Can NPC be used for Na-ion intercalation?
5. Summary

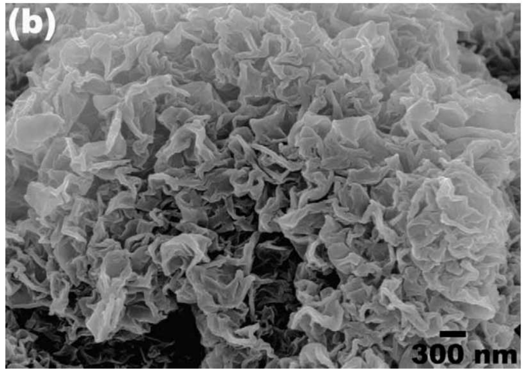
Disordered Graphitic Carbons

Graphitic Carbon

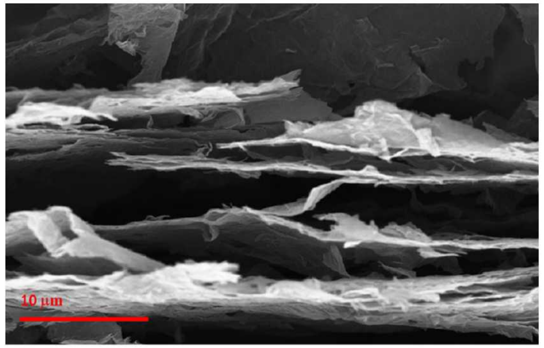
fine, loosely-packed graphitic particles

Requires using a polymeric binder material

Graphene Clusters



Wang et al, *Carbon* (2009)

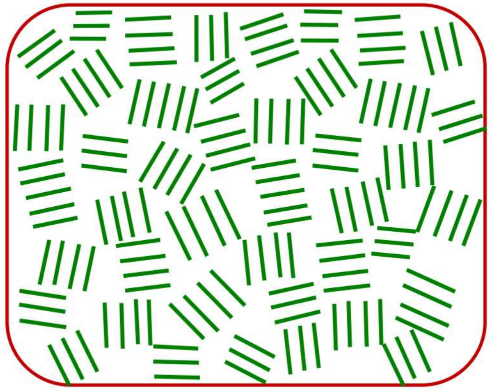


Mukherjee et al, *ACS Nano* (2012)

Sheets several to 10's of µm wide, requires binders

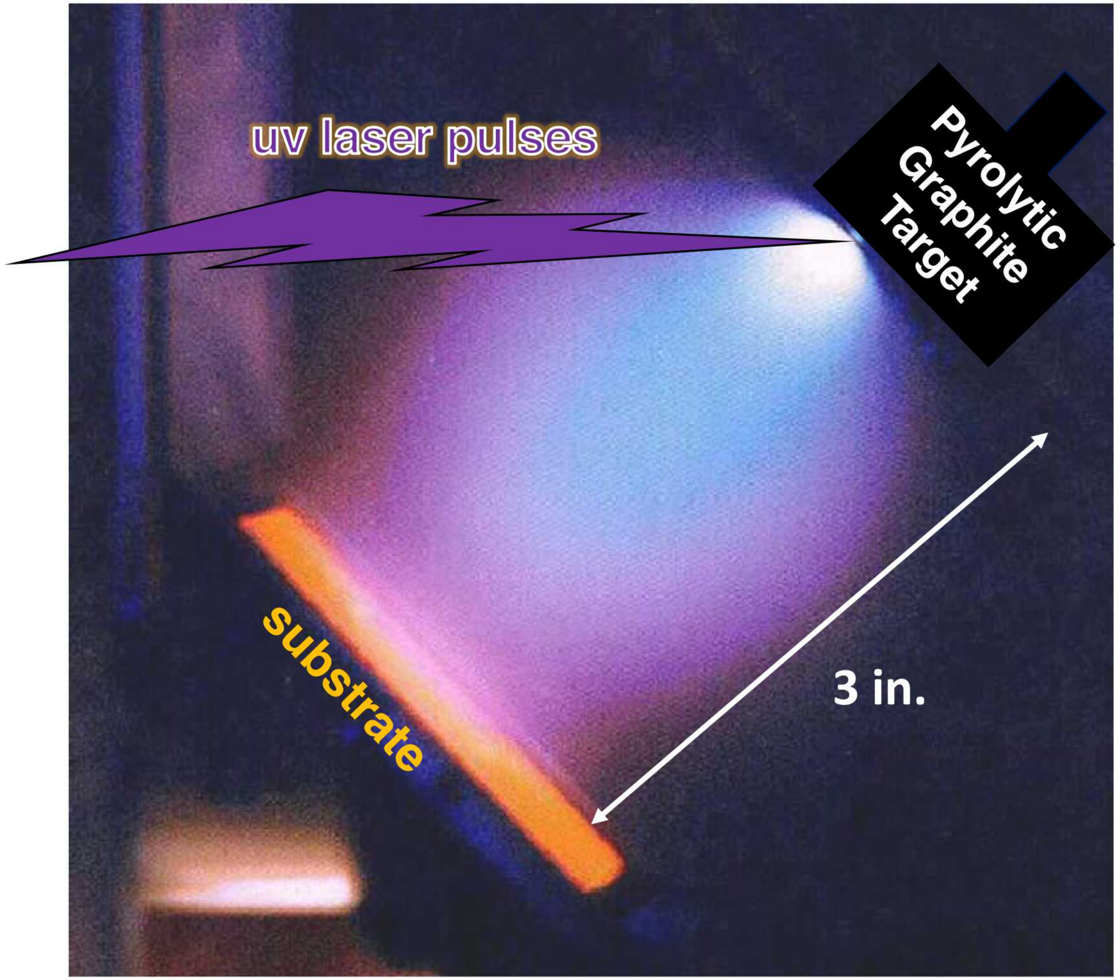
Nanoporous Carbon (NPC)

randomly-stacked 1 – 2 nm-sized platelets of 3 – 5 layer thick graphene with lots of grain boundaries



Controllable density and surface area to tailor structure for chemical intercalation. Requires NO binders!

Pulsed Laser Deposition (PLD) Growth of NPC

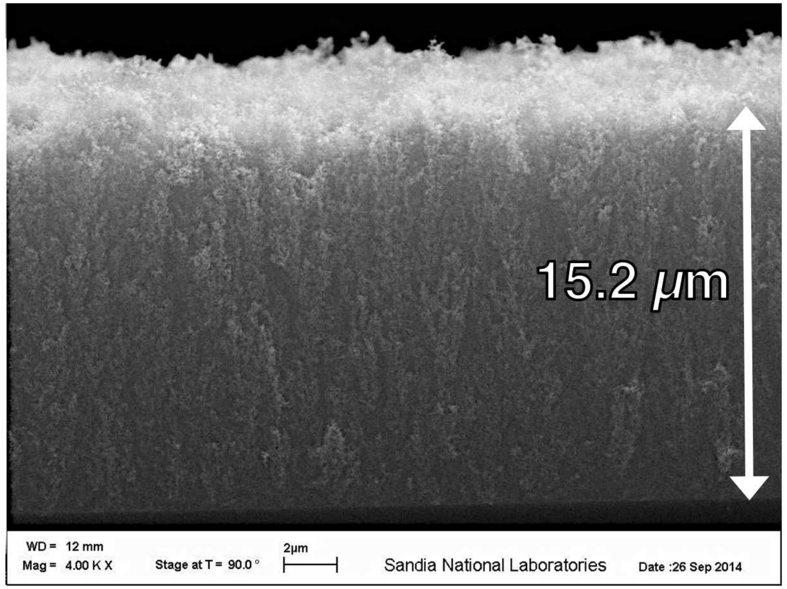


- **Room temperature deposition** of low kinetic energy few carbon atom clusters yields high surface-area graphitic films onto <u>any</u> substrate!
- Deposit C (from pyrolytic graphite) using 248 nm (UV) laser light at ~ 1.3 J/cm^2, slightly above the carbon ablation limit.
- **P(Ar) used to control the deposition energy.**
- ***Controlling the deposition energy enables control of mass density and surface area!***

Controlling NPC Mass Density

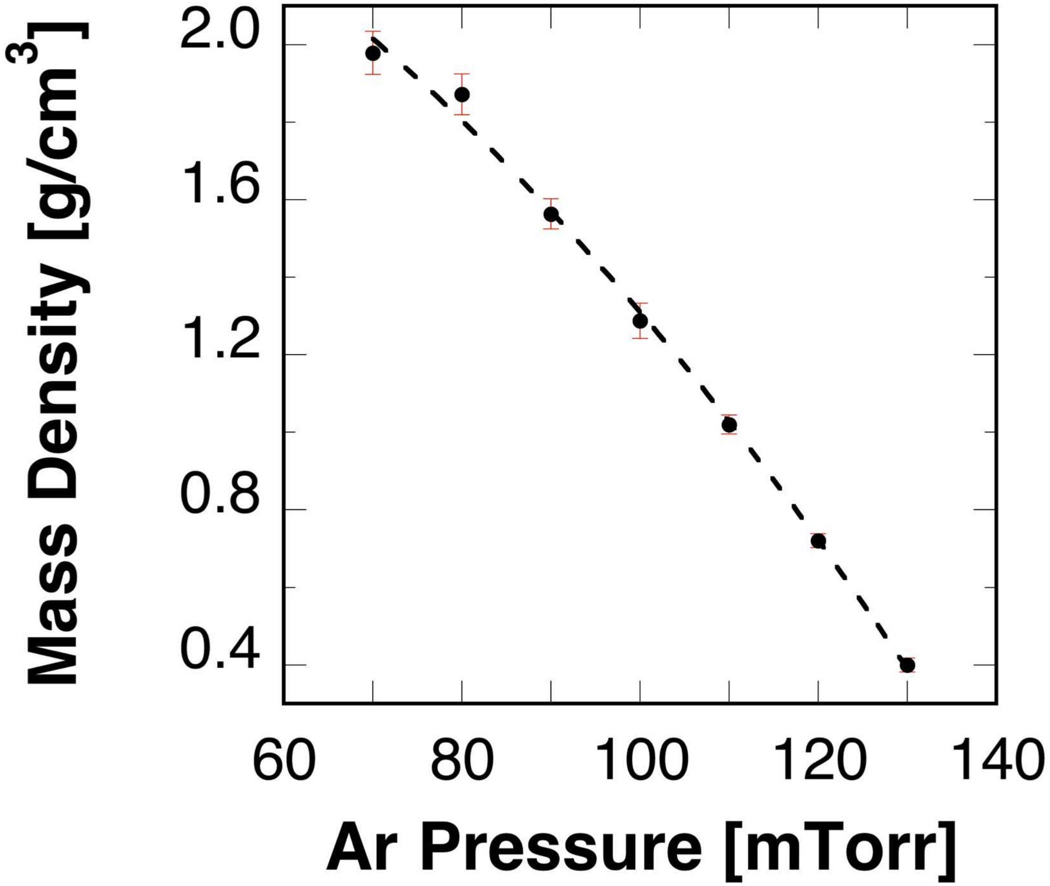
density = weight/volume

1. grow film onto 1 cm^2 Si substrates
2. weigh sample before and after deposition (using a microbalance)
3. measure film thickness via SEM



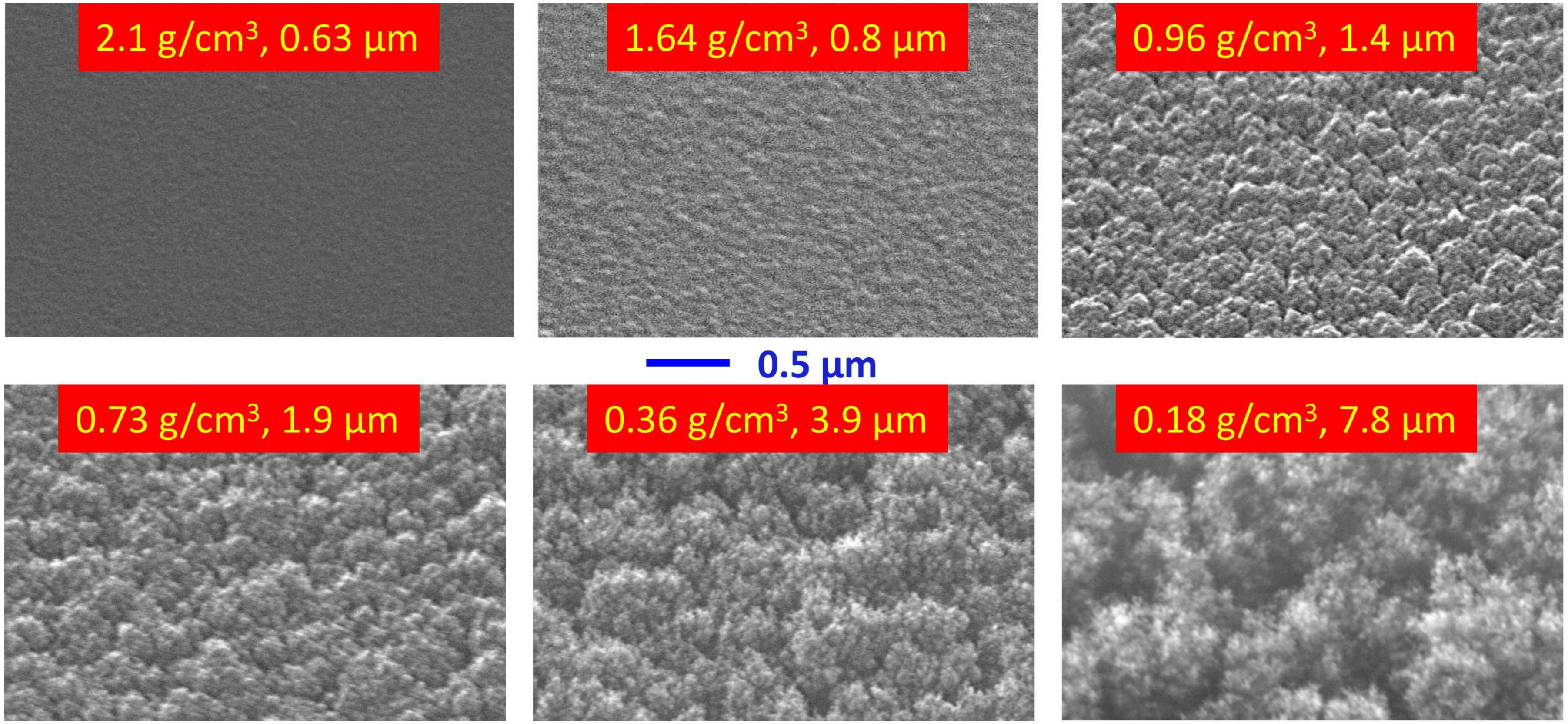
This NPC film has density = 0.26 g/cm^3

NPC Mass Density vs. PLD Growth Condition



NPC Morphology vs. Density

all films have constant mass areal density ~ 0.13 (± 0.02) mg/cm^2
equivalent to 0.58 μm of high-density graphite (2.27 g/cm^3)



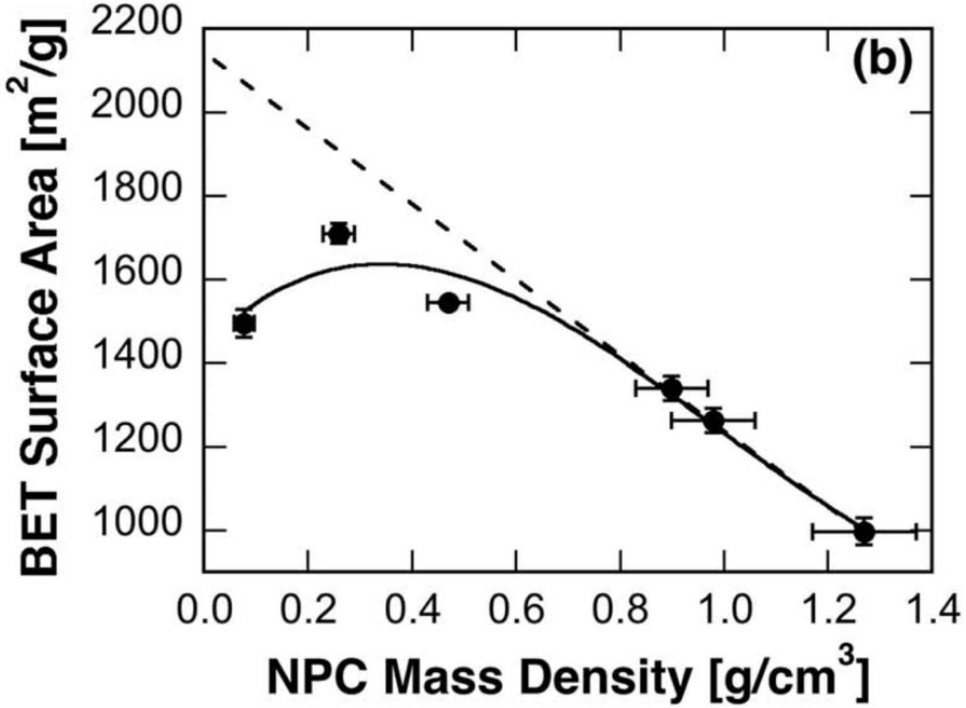
Siegal et al, *Appl. Phys. Lett.* (2002).

NPC Surface Area

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 77K.



Typical surface area values of other reported carbon materials

single graphene sheet:	2630 m^2/g (theoretical)
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

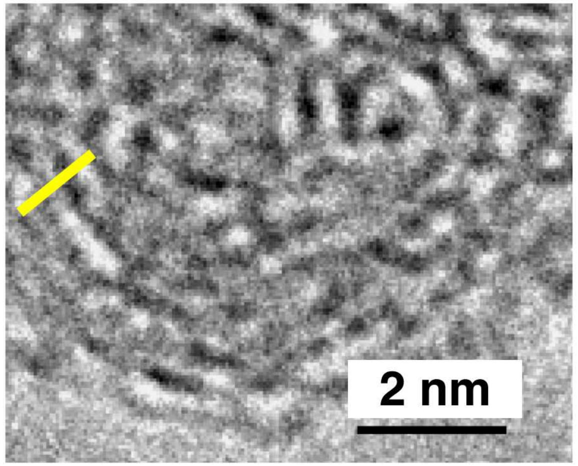
All these materials have mass densities 10 – 100x less than NPC!

Siegal et al, *J. Electrochem. Soc.* **163**, A1030 (2016).

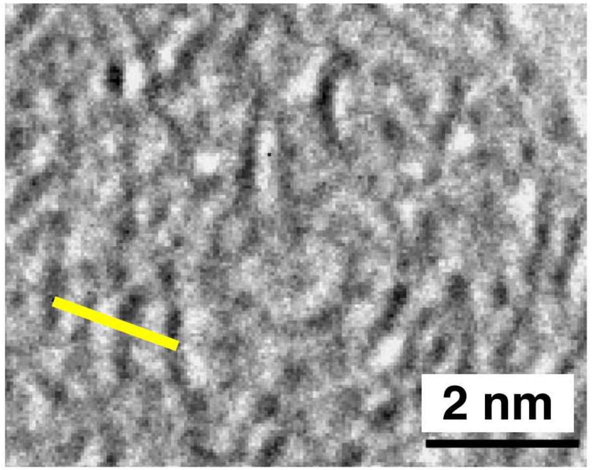
NPC ≠ Ordinary Graphitic Carbon

NPC consists of randomly oriented sheets of graphene fragments
i.e. "3D nanocrystalline graphene"

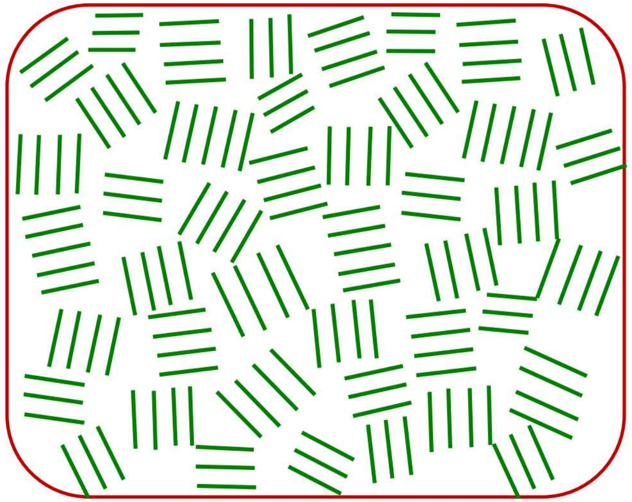
density = 1.0 g/cm^3
~1200 m^2/g (BET)



density = 0.25 g/cm^3
~1600 m^2/g (BET)



What is Nanoporous-Carbon?



typical interplanar spacings *(graphite = 3.35 Å)*

4.4 - 4.8 Å **enhanced diffusion channels** 5.1 - 5.4 Å

- **Randomly stacked 1 – 2 nm platelets of 3 – 5 layer thick graphene**
- **Copious grain boundaries**
- **Enhanced interplanar spacings**

Siegal et al, *Langmuir* (2004).

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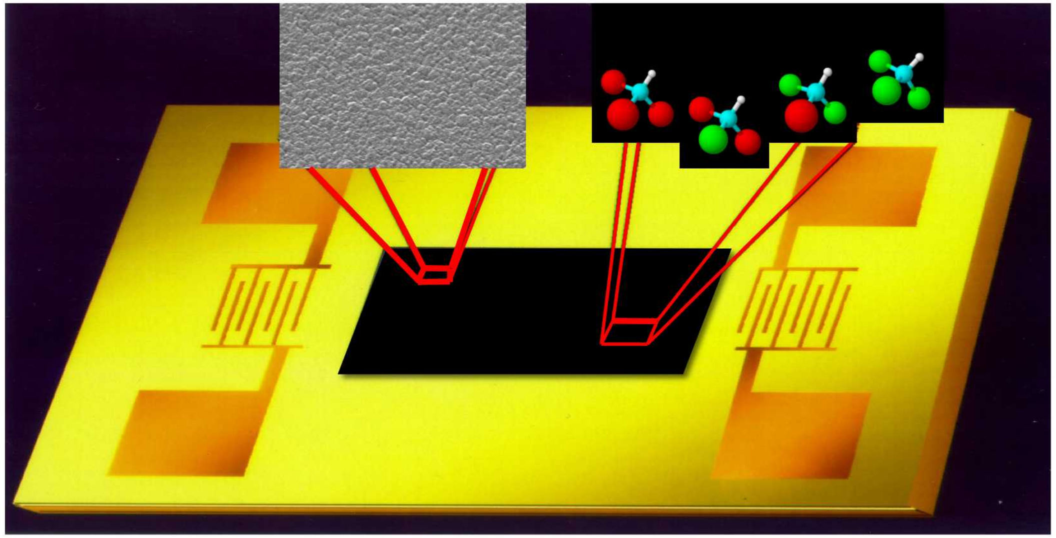
Surface Acoustic Wave (SAW) Sensor

97 MHz SAW sensor device



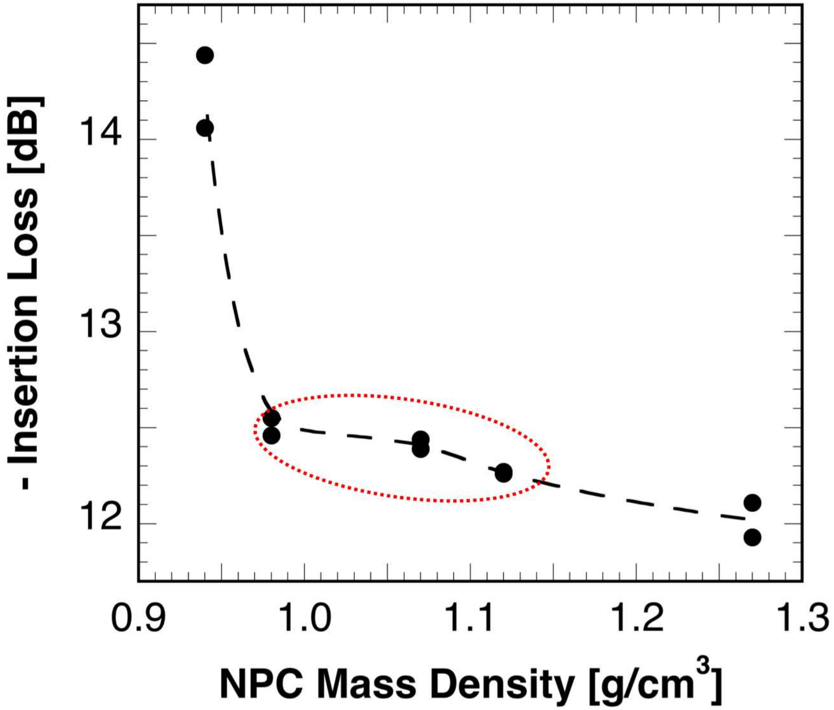
- **ST-cut quartz is coated with NPC**
- **expose device to analyte**
- **measure change in vibrational frequency or phase angle**

$$\frac{\Delta\phi}{\phi_o} = -k_m \frac{\Delta m}{m_o}$$

oscillator phase shift

surface mass density

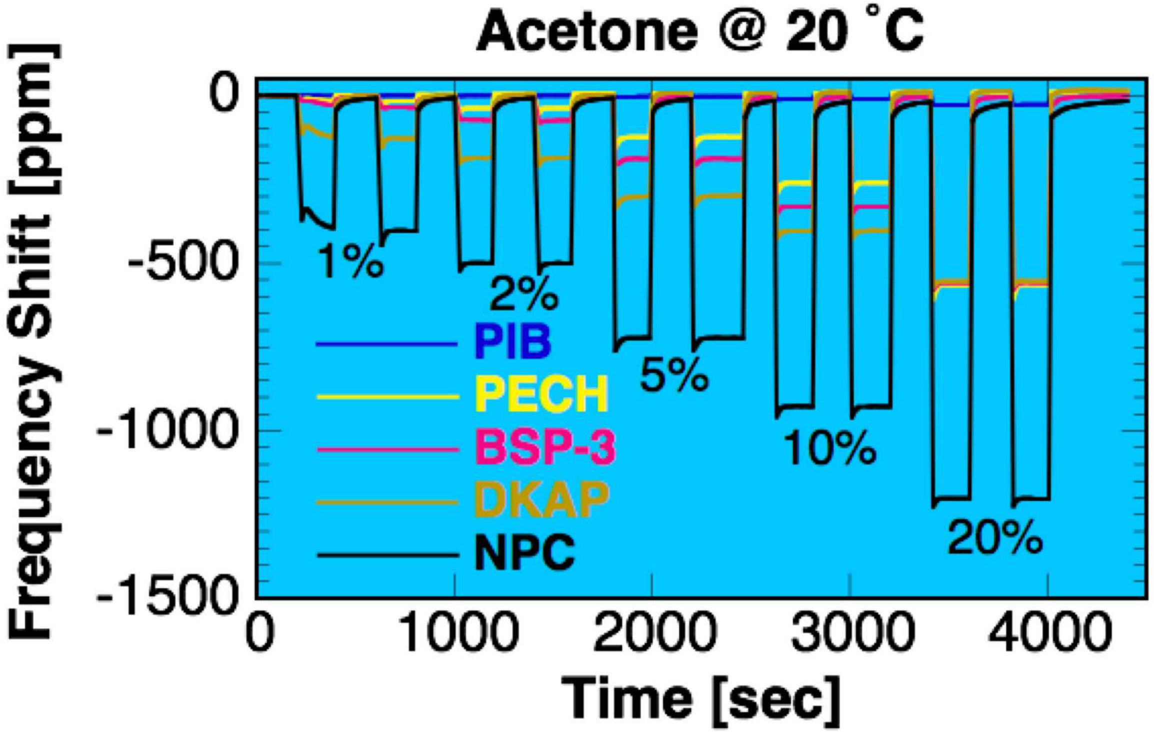
Minimizing Acoustic Dampening



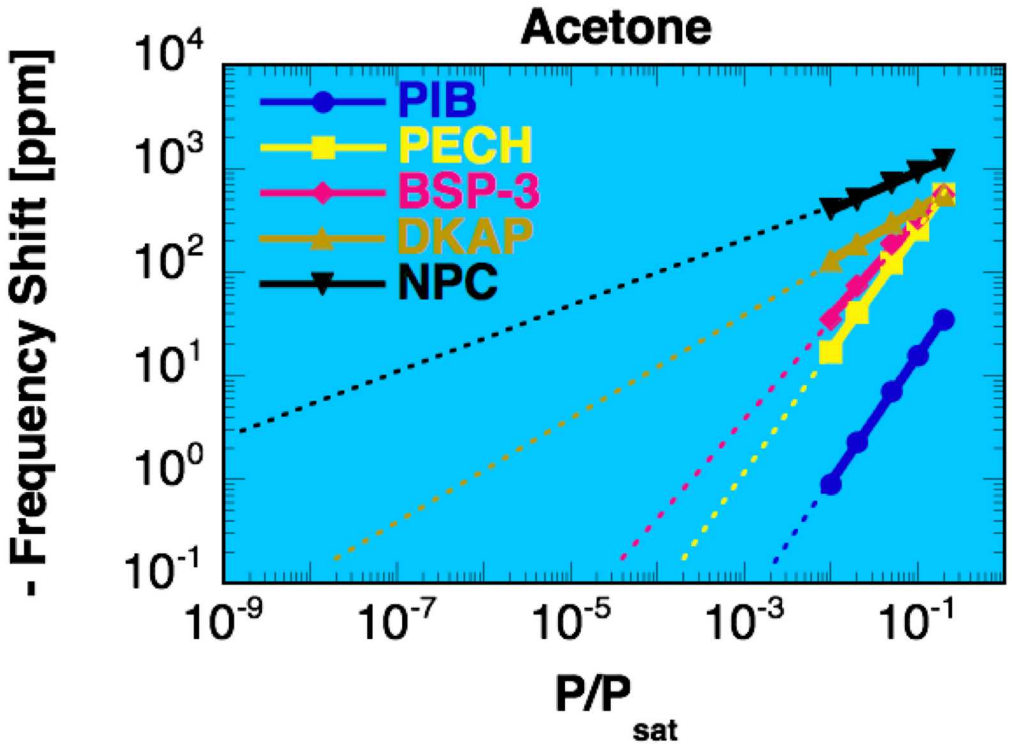
- **desire highest possible surface area**
- **sufficient stiffness to pass an acoustic wave w/minimal insertion loss**
- **sweet spot just above 1 g/cm^3.**

Acetone Sorption Isotherms

NPC vs. commonly-used SAW coatings



Extrapolations to frequency detection limit



Orders-of-magnitude higher responses than other coating materials.
Similar results for numerous other volatile organic compounds.

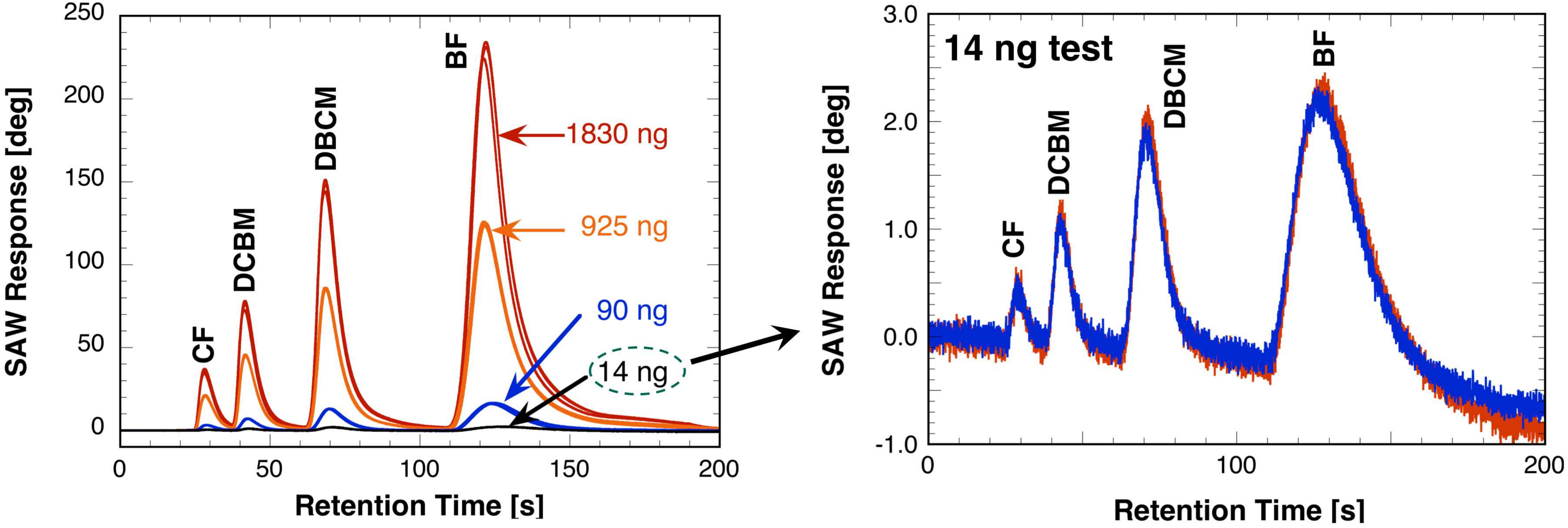
Siegal et al, *Adv. Sci. & Technol.* (2006).

Detecting EPA-Regulated Chemicals in Treated Water

Trihalomethanes (THMs) are disinfection byproduct chemicals resulting from the (necessary) chlorination of drinking water by utilities to reduce diseases.

THMS: chloroform, dichlorobromoform, dibromochloroform, bromoform

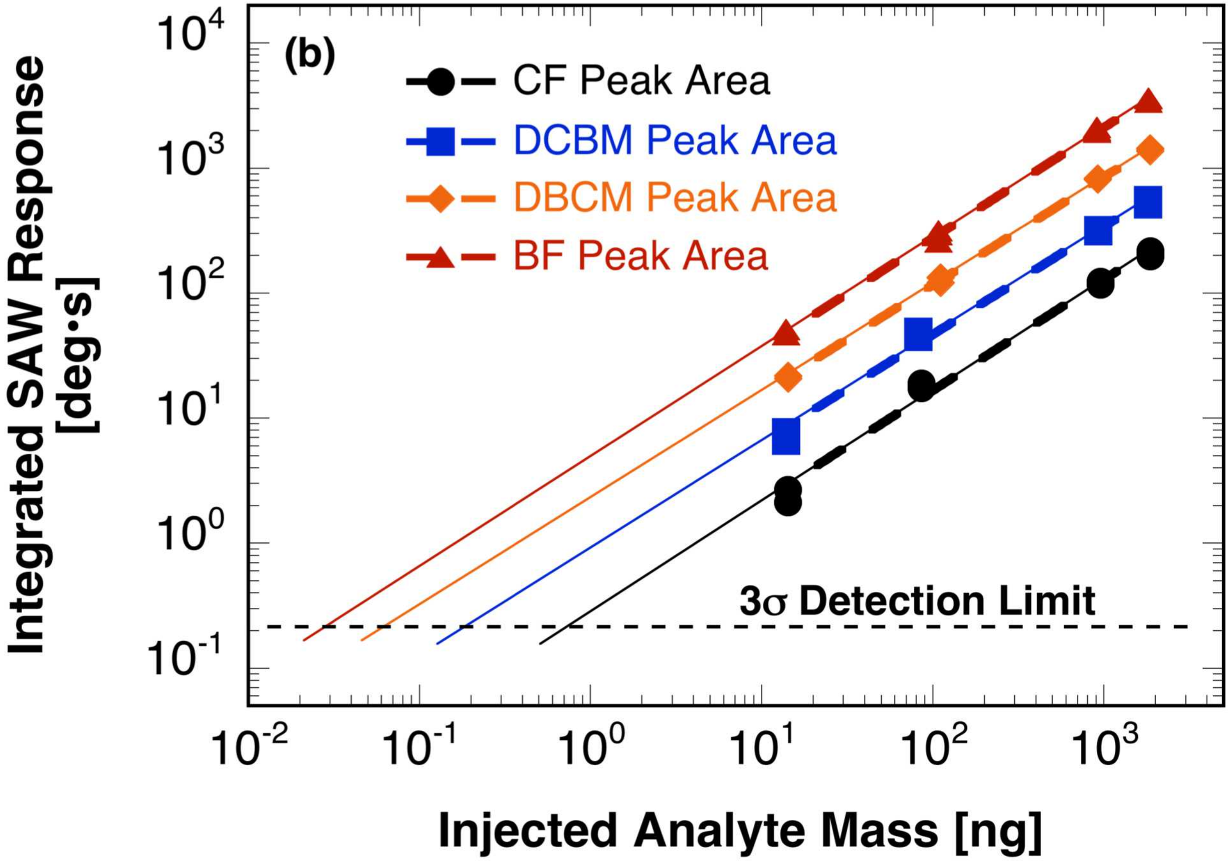
Inject known THM quantities into GC for separation and use NPC-coated SAW for detection.



(Note: 10 ng is equivalent to 1 ppb.)

Siegal et al, *J. Electrochem. Soc.* (2015).

NPC-Coated SAW Response to Trihalomethanes

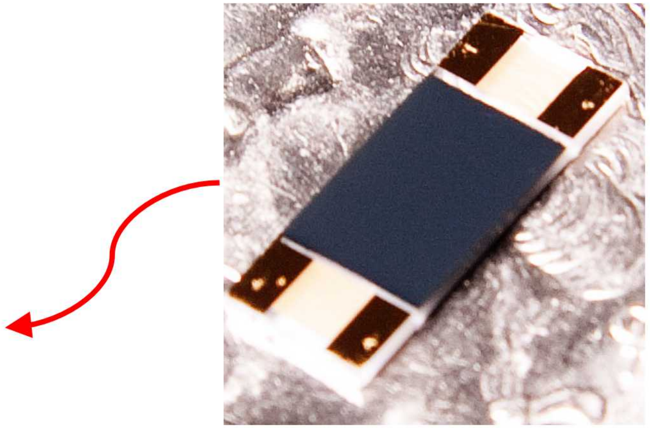


THM	LOD [ng]	LOD [ppb]	LOD [ppt]
Chloroform	**0.73**	**.073**	**73**
DCBM	**0.18**	**.018**	**18**
DBCM	**0.06**	**.006**	**6**
Bromoform	**0.03**	**.003**	**3**

Siegal et al, *J. Electrochem. Soc.* (2015).

Parker THM Analyzer (making your drinking water safer!)

Purge and Trap, Gas Chromatography using a NPC-coated SAW detector



- **SAW devices have been used for 1000’s of THM tests by utilities.**
- **Each test involves sorbing large molecules in and out of NPC.**
- **No NPC-coated SAW device has yet failed!**

NPC Background Summary

- NPC is a unique form of graphitic carbon with controllable:
  - mass density,
  - interplanar graphene sheet spacings,
  - total surface area.
- Other graphitic carbons with similar total surface areas typically have > 10x lower mass densities than NPC.
- NPC with density ~ 1 g/cm^3 provides unparalleled performance for SAW device chemical microsensors.
- Commercial sensor products using NPC-coated SAWs have experienced 1000’s of chemical sorption cycles without failures.

Can NPC be used as an insertion anode material for Li-ions?

Can NPC act as an appropriate spacing scaffold for Si?

Can NPC be used for Na-ion intercalation?

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1. Background for nanoporous-carbon (NPC)
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Procedures

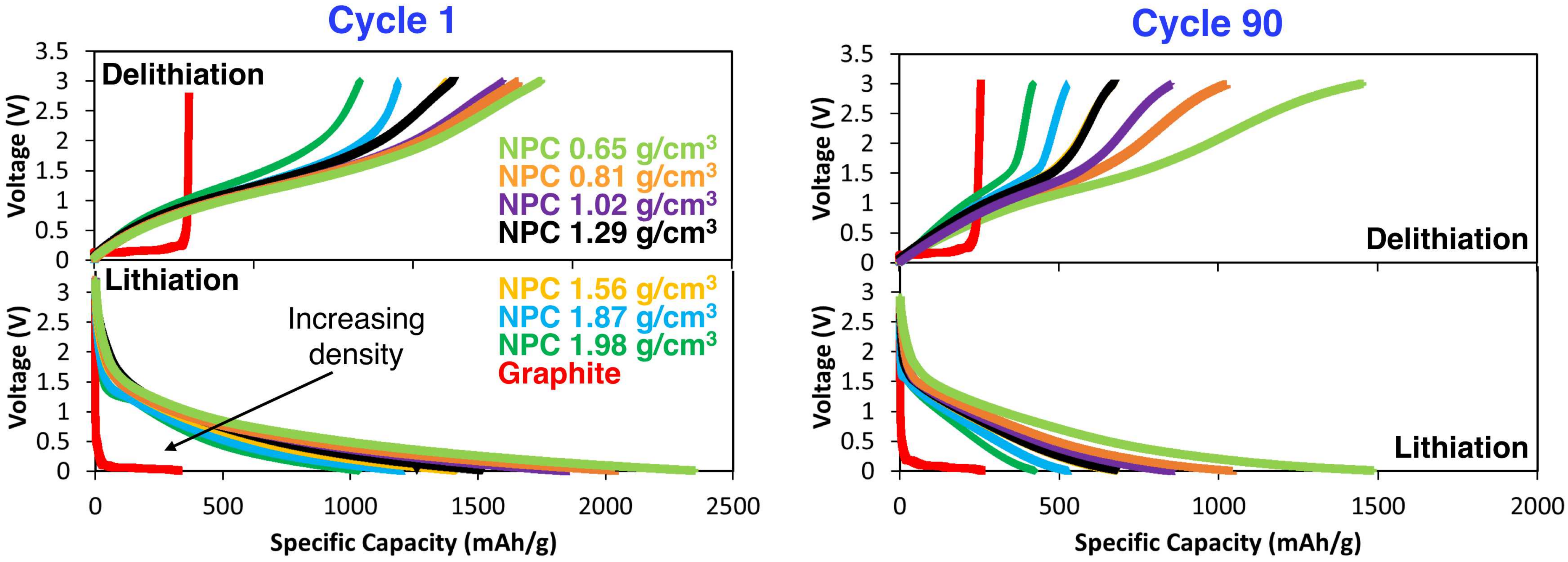
NPC film depositions for coin cells

1. Deposit NPC via PLD on stainless steel disc current collectors (working electrode)
   - each disc coated with 0.05 ± 0.01 mg/cm^2 NPC
   - only NPC mass density is varied – ranging from 0.2 to 2.0 g/cm^3.
2. Assemble coin cells
   a. Every NPC film dried and outgassed in Ar glove box for 48 hrs prior to assembly
   b. All coin cells assembled in dry Ar glove box

Electrochemical Testing

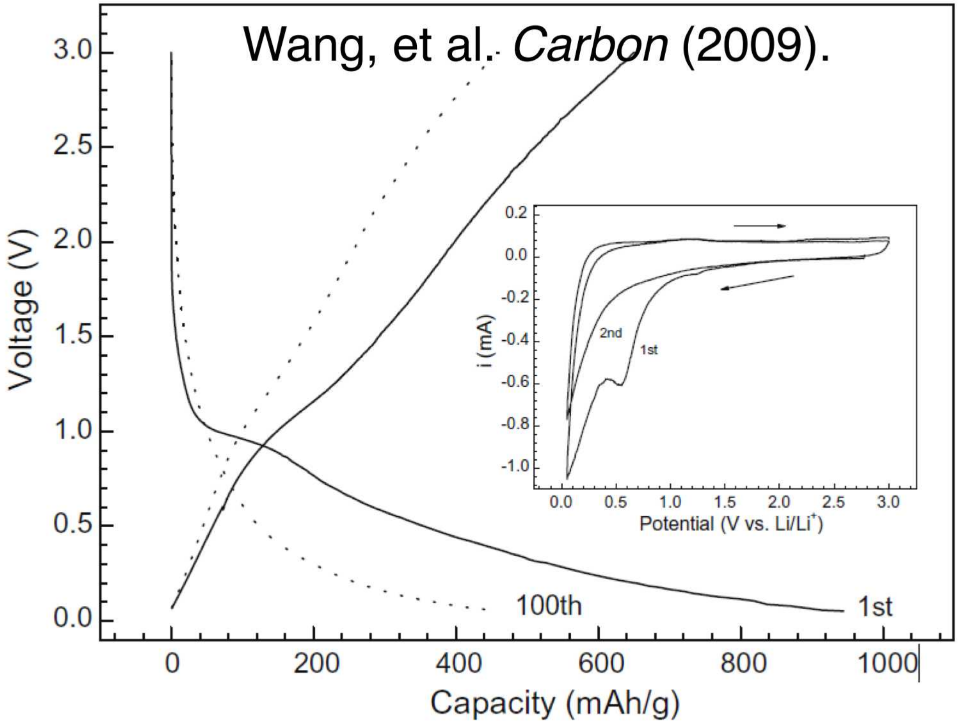
1. 2032 half cells vs. Li
2. 1 M $LiPF_6$ in 1:1 ethylene carbonate:diethyl carbonate
3. Testing performed using Arbin battery cyclers
4. C-rates based on the theoretical capacity of graphene, i.e. assume that Li is absorbed on both sides of every graphene sheet rather than only 1 Li-ion intercalated between 2 sheets.

Charge – Discharge Performance

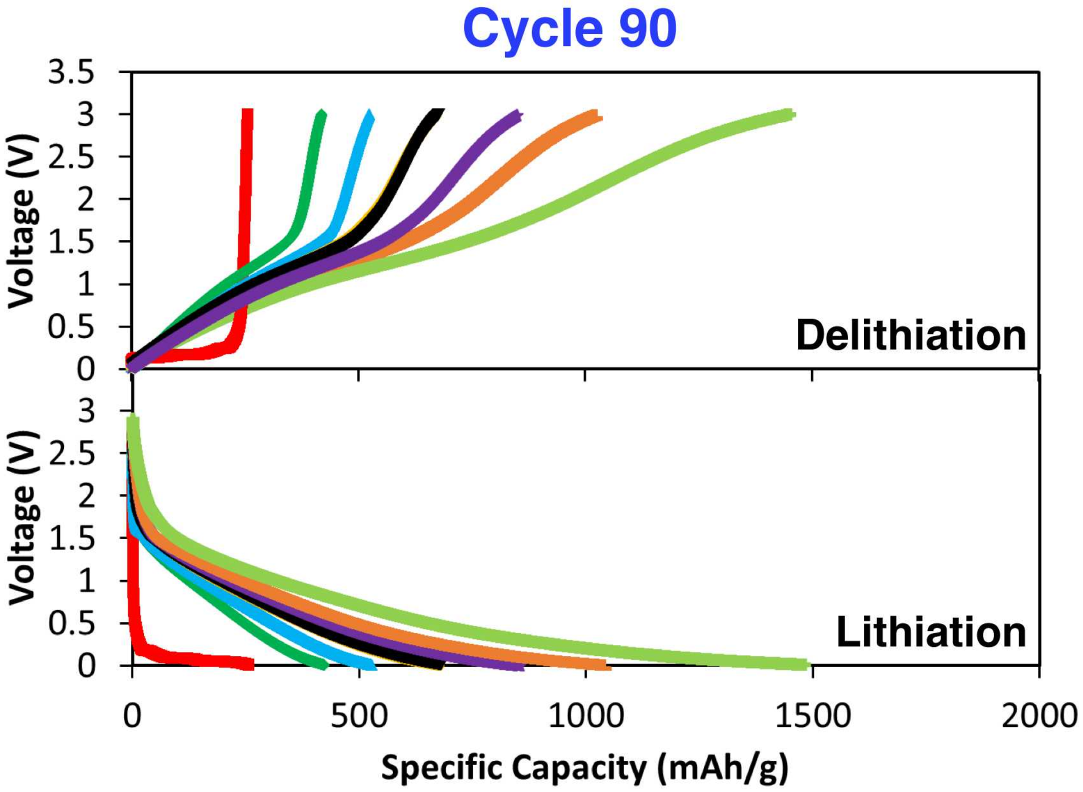


- **Li$^+$ ions reversibly insert into NPC!**
- Capacity increases with decreasing NPC mass density.
- Sloped curve shapes typical of nanocarbon materials.
- Capacity fade with increased cycling is more typical of graphene than graphite.
- Very high capacities compared to other graphene-like materials.

Comparison to Graphene



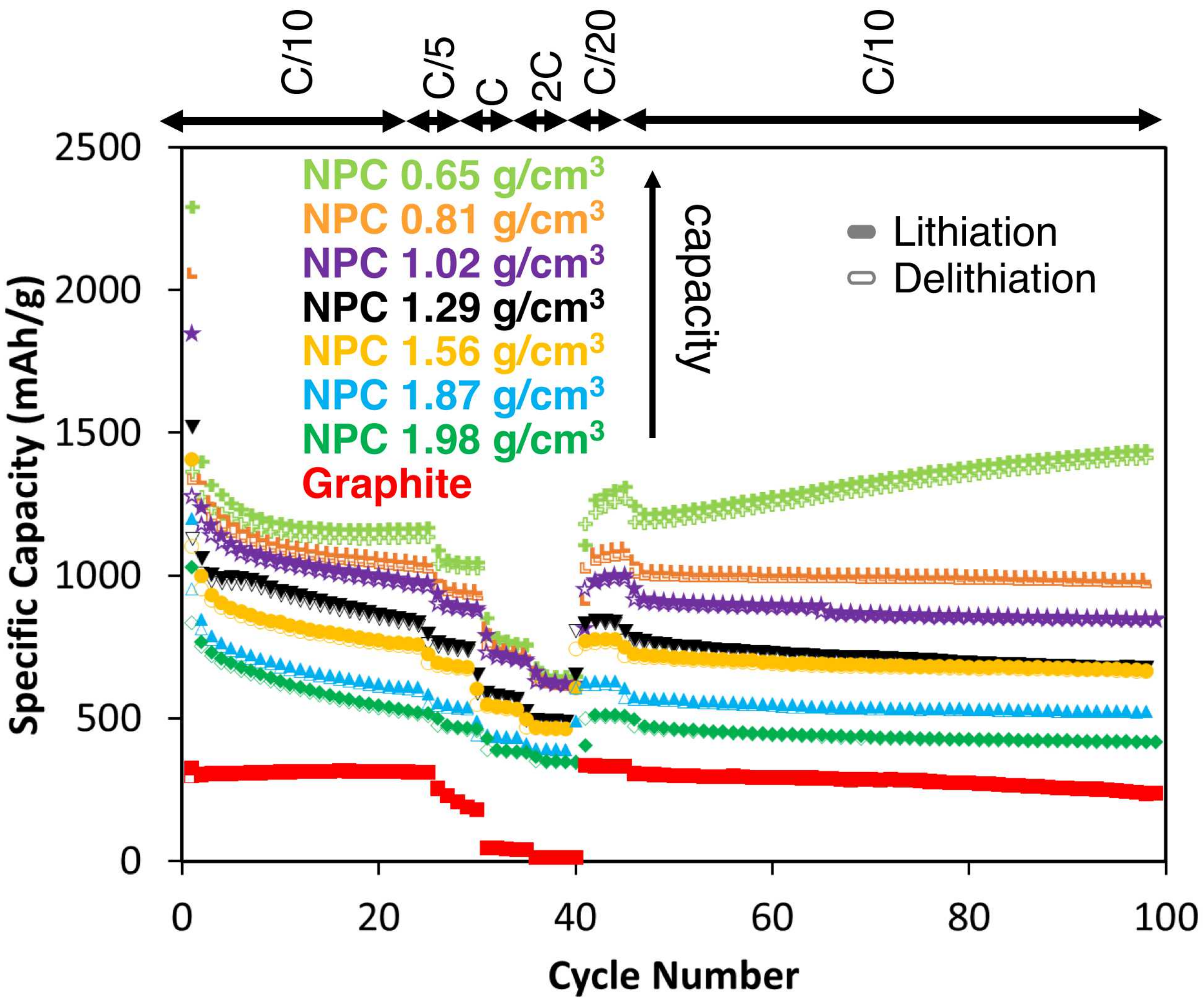
Wang, et al. *Carbon* (2009).



Cycle 90

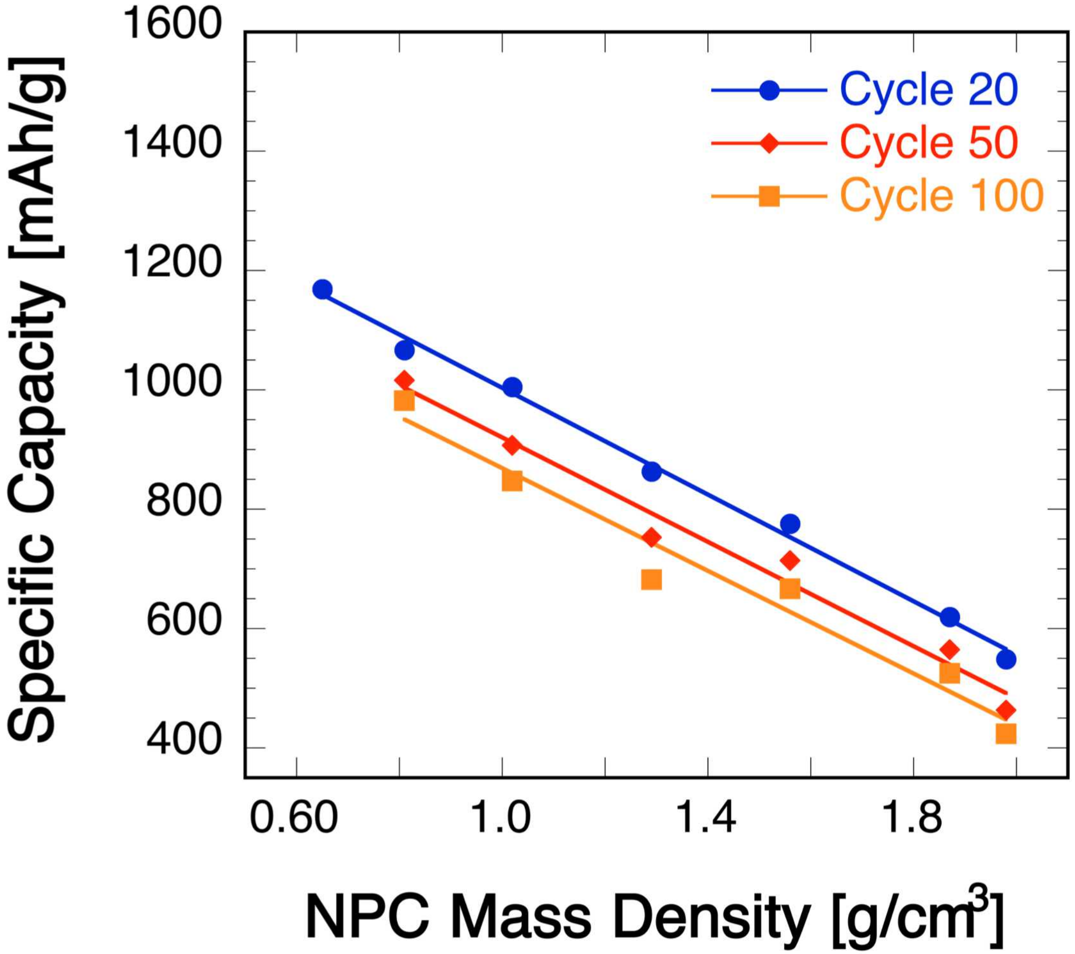
- **NPC behaves similar to graphene, not graphite.**
- **However, with the ability to control mass density and interplanar graphene sheet spacings, NPC achieves higher capacities for many mass densities.**

Cycle Life vs. Density



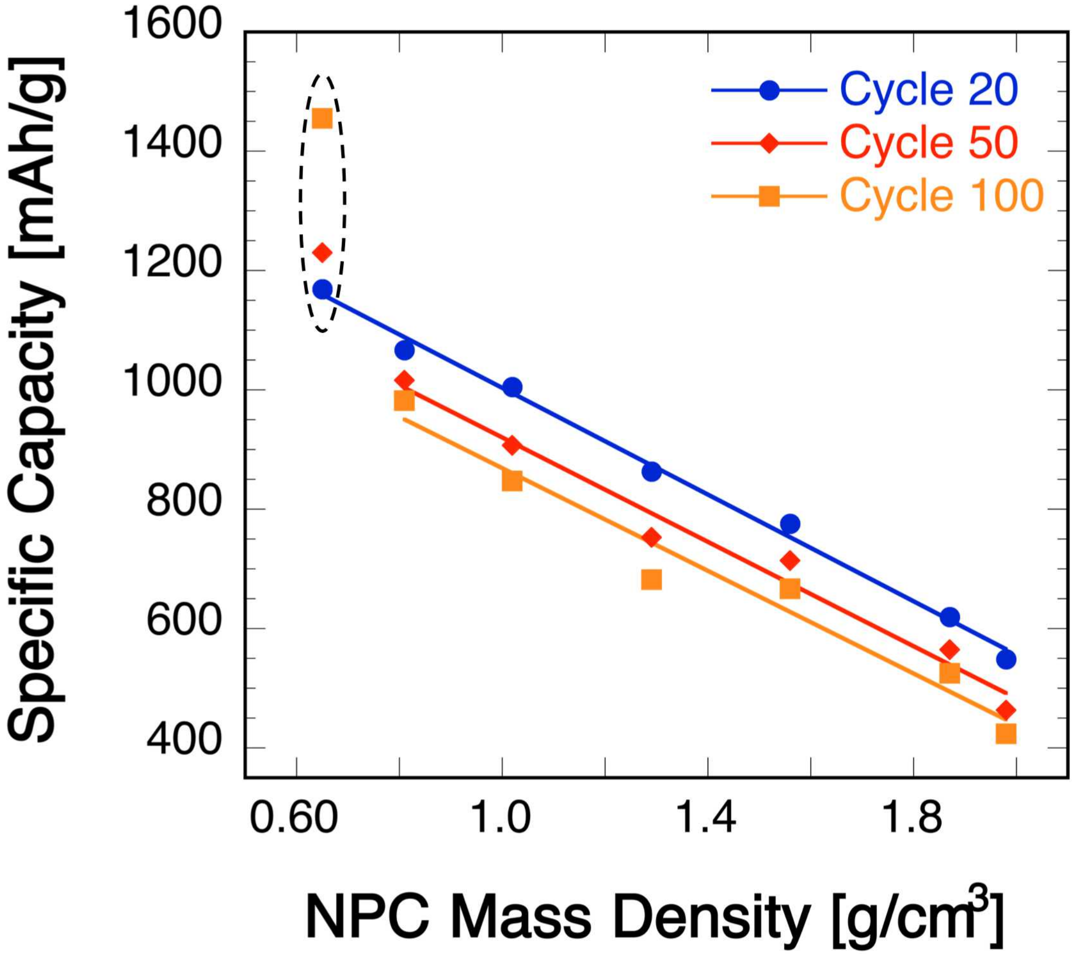
- Capacity increases with decreasing density.
- Large decrease after 1st cycle hints at start of solid-electrolyte interphase (SEI) formation. ***More later.***
- Increasing discharge rate reduces charging efficiency.
- Decreasing discharge rate recovers CE.
- Capacity for 0.65 g/cm³ sample increases beyond cycle 24! ***More later.***

Capacity vs. Density



- Capacity is inversely proportional to NPC mass density
- Capacities very high for lowest densities!
- Perhaps a result of excess Li storage in NPC grain boundaries?

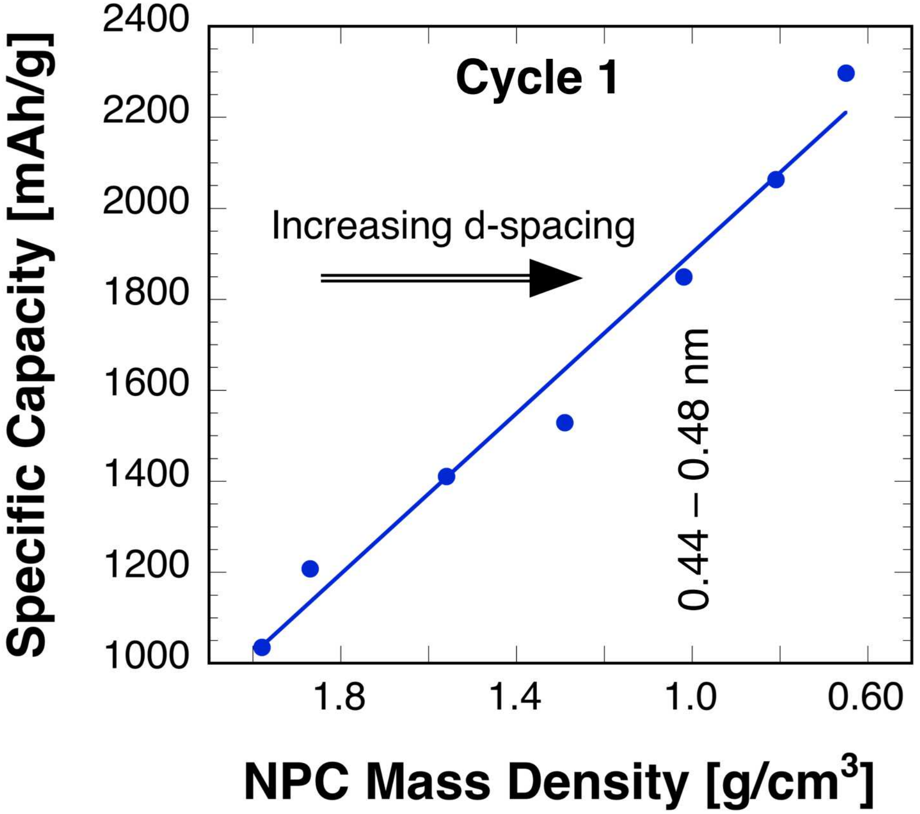
Capacity vs. Density

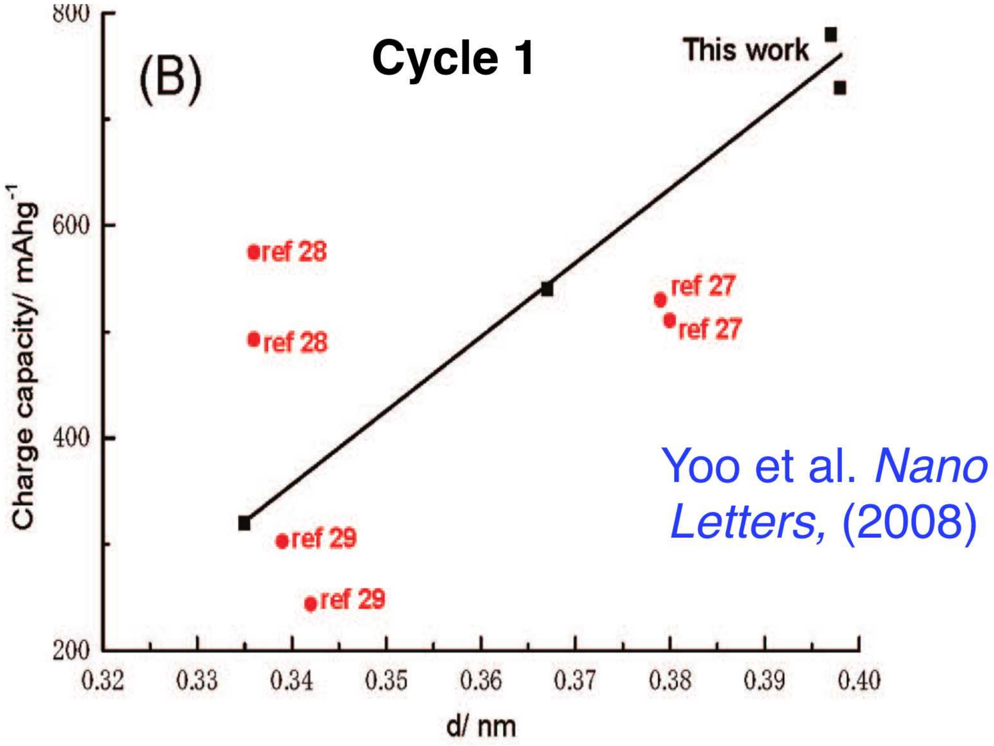


- Capacity is inversely proportional to NPC mass density
- Capacities very high for lowest densities!
- Perhaps a result of excess Li storage in NPC grain boundaries?
- *Note that capacity greatly increases with continued cycling for lowest NPC density – **more later.***

Capacity vs. Interplanar Spacing

NPC consists of tightly-packed 1 – 2 nm wide graphene platelets only a few layers thick, and has a plethora of grain boundaries for ready diffusion.

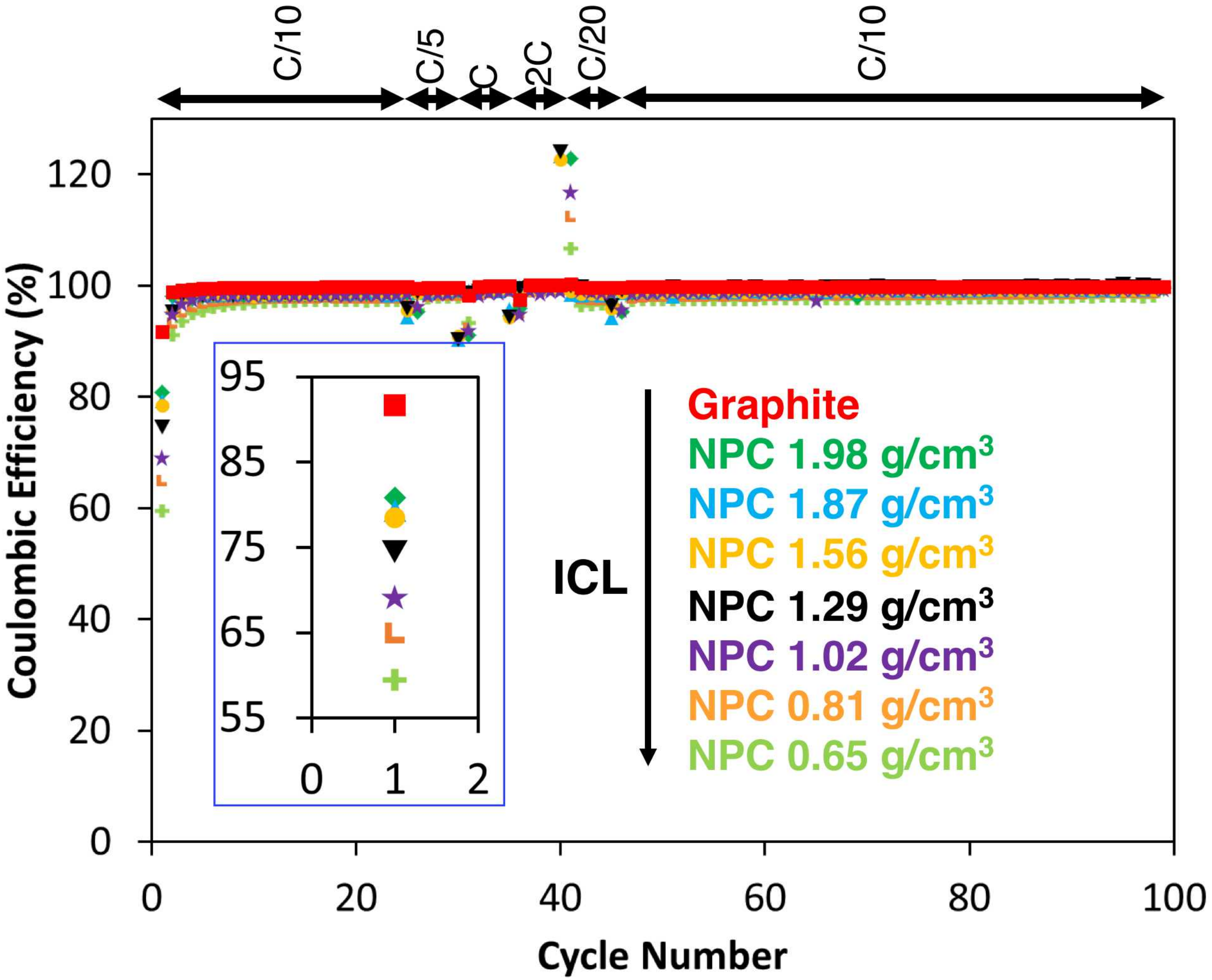




Yoo et al. *Nano Letters*, (2008)

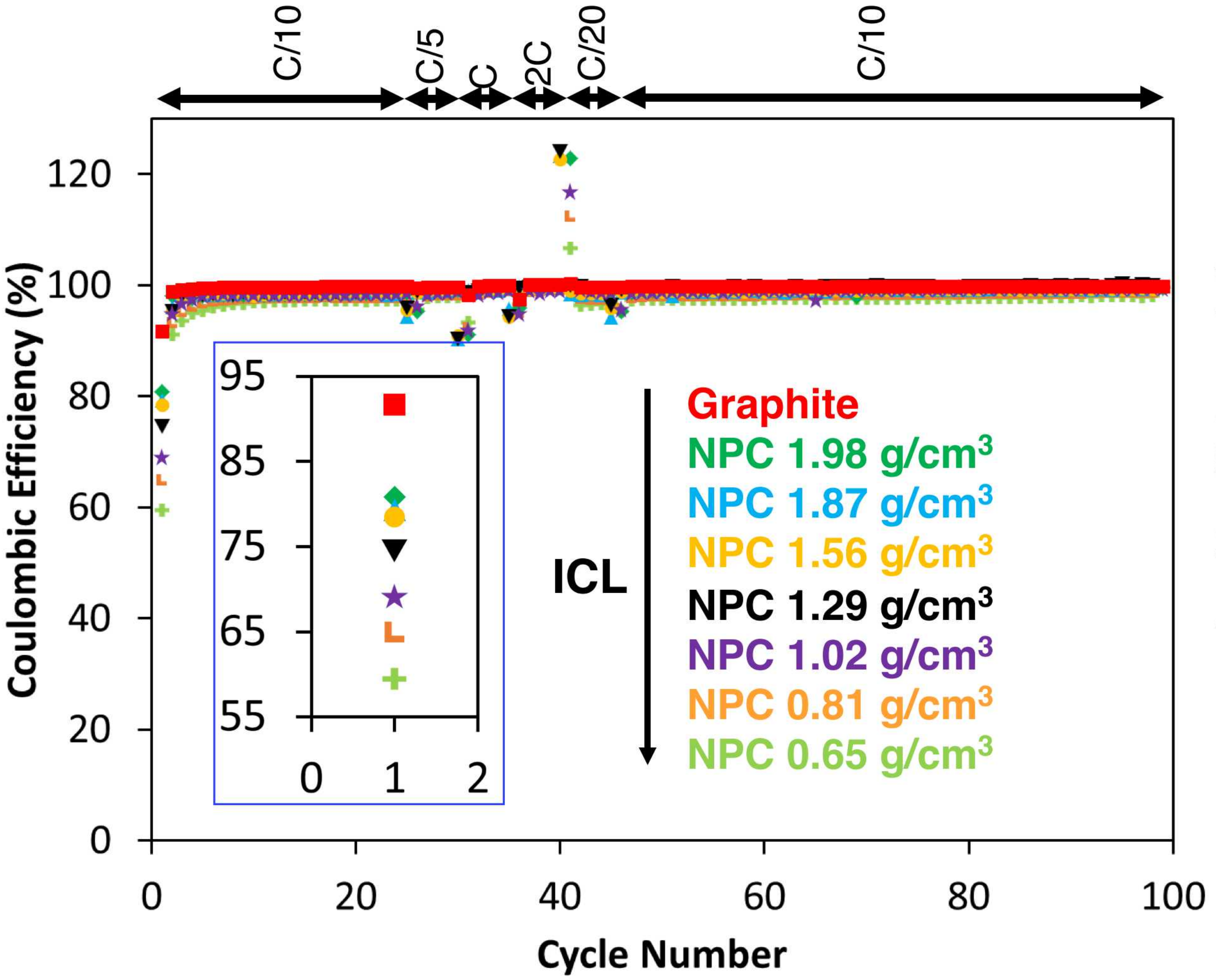
Achieved enhanced d-spacing by incorporating CNTs and fullerenes into graphene sheet stacks.

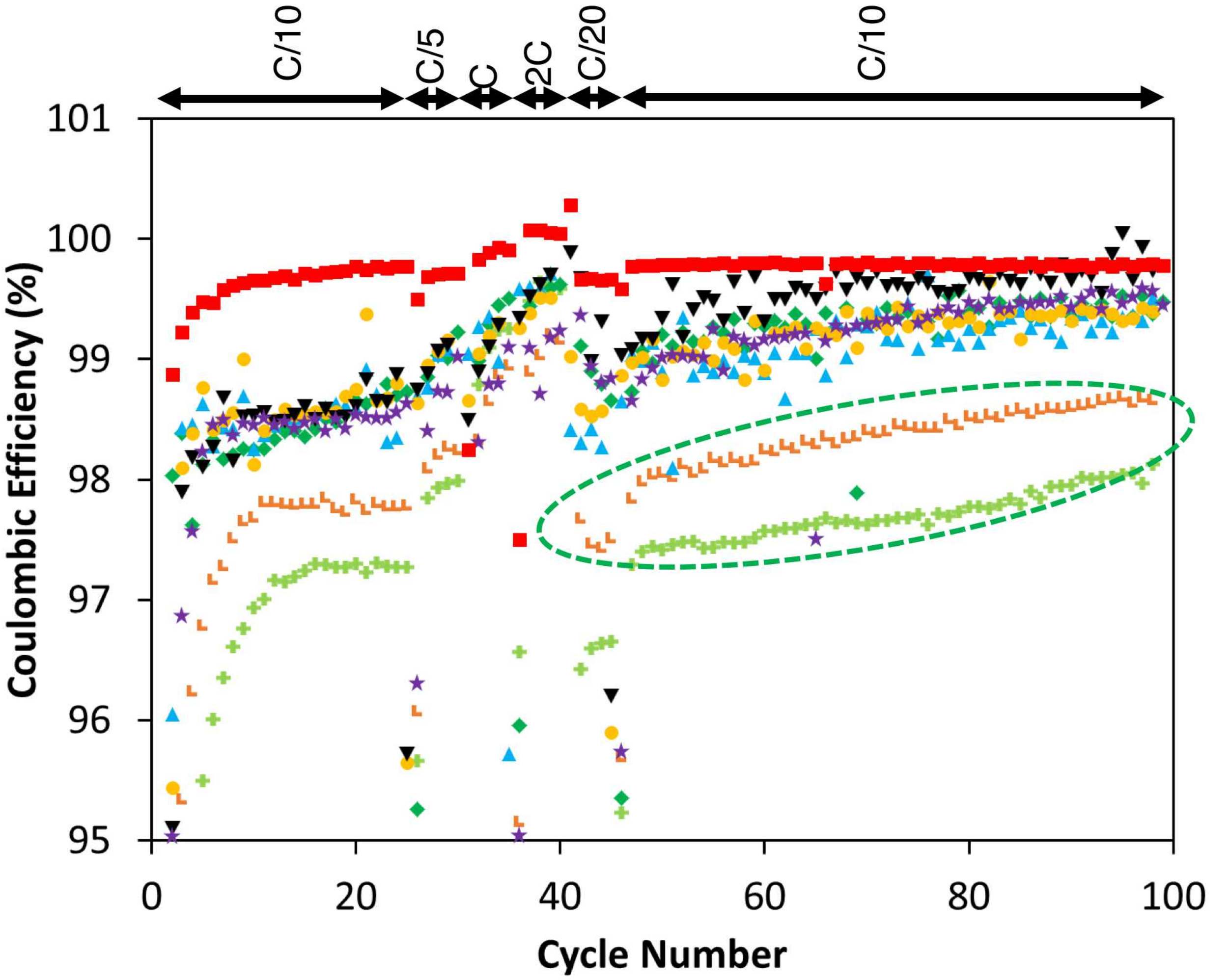
Coulombic Efficiency vs. Density



- **Cycle 1: irreversible capacity loss (ICL) ↑ with ↓ density.**
- **CE drops after increasing C-rate suggests either (a) additional SEI formation, or (b) Li is harder to remove than to insert.**

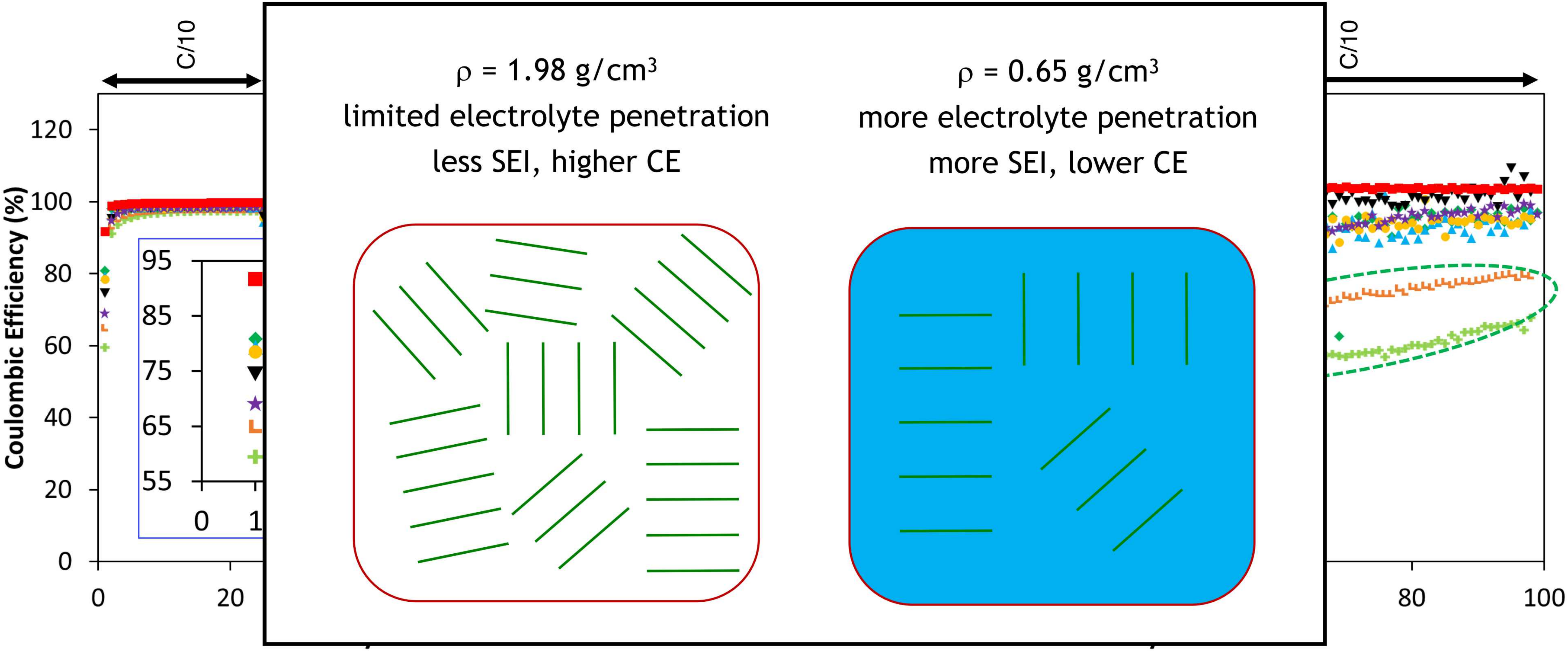
Coulombic Efficiency vs. Density





- Cycle 1: irreversible capacity loss (ICL) ↑ with ↓ density.
- CE drops after increasing C-rate suggests either (a) additional SEI formation, or (b) Li is harder to remove than to insert.
- NPC CE < graphite CE – similar by 100 cycles.
- However, CE is lower for densities ≤ 1 g/cm³. WHY?

Coulombic Efficiency vs. Density



ρ = 1.98 g/cm³
limited electrolyte penetration
less SEI, higher CE

ρ = 0.65 g/cm³
more electrolyte penetration
more SEI, lower CE

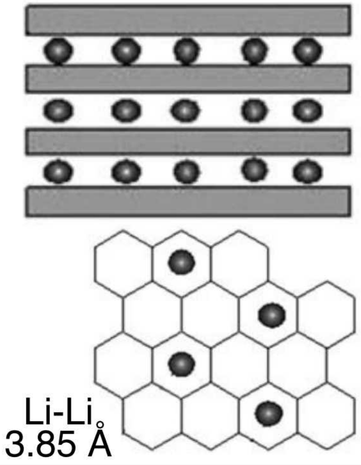
- Cycle 1: irreversible capacity loss (ICL) ↑ with ↓ density.
- CE drops after increasing C-rate suggests either (a) additional SEI formation, or (b) Li is harder to remove than to insert.
- NPC CE < graphite CE – similar by 100 cycles.
- However, CE is lower for densities ≤ 1 g/cm³. WHY?
- Electrolyte penetrates for densities ≤ 1 g/cm³.

Mechanisms for Li Storage in Graphite and Graphene

Graphite

LiC_6 (372 mAh/g)

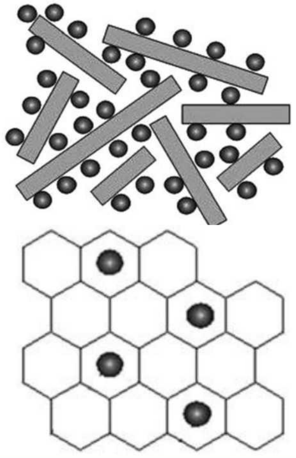
Li^+ intercalated in alternating C rings[a]



Graphene and Other Carbons

Li_2C_6 (744 mAh/g)

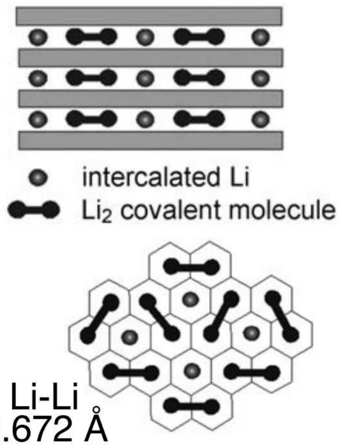
Li^+ adsorbed both sides of sheets in hard carbon[b,c]



Li_3C_6 (1157 mAh/g)

Li^+ intercalated

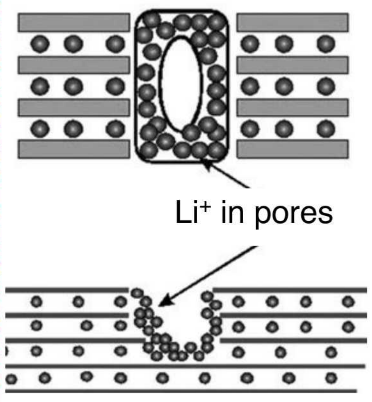
Li_2 other C rings[d]



LiC_6 + pores (? mAh/g)

Li^+ intercalated

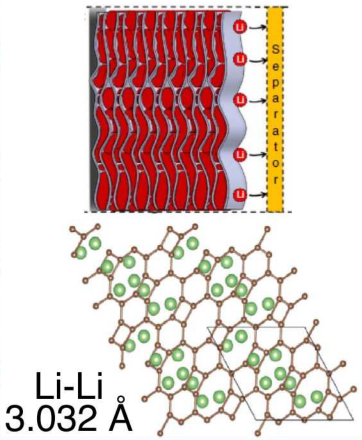
Li^+ adsorbed pores[e,f]



$Li_3C_8 + Li^0$ (? mAh/g)

defects adsorb Li^+

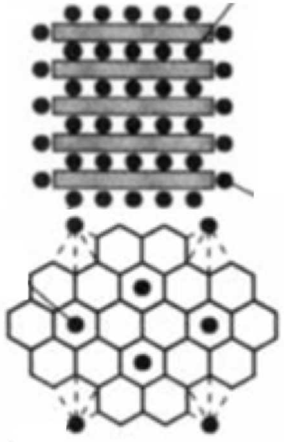
Li^0 between sheets[g]



LiC_6 + edges (? mAh/g)

Li^+ intercalated

Li^+ store on edge groups[h]



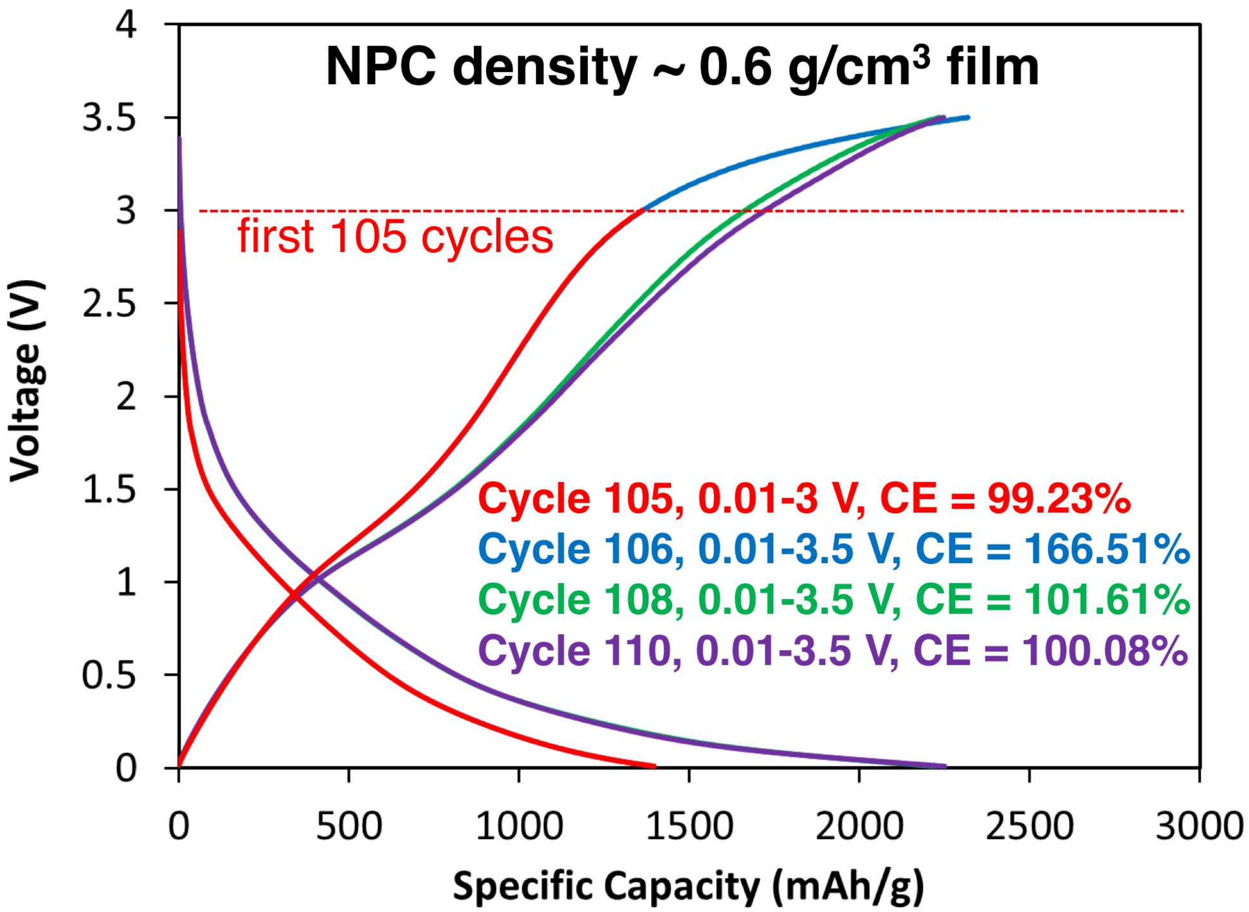
NPC exhibits increased interplanar spacing, and has both edge and pore sites.

Therefore, NPC likely has numerous potential Li storage mechanisms.

Li removal may be inhibited by being trapped in certain sites (e.g. nanopores). ***Indeed, NMR finds that quasimetallic Li clusters form in nanopores < 1 nm and removal requires higher voltages.***[i,j]

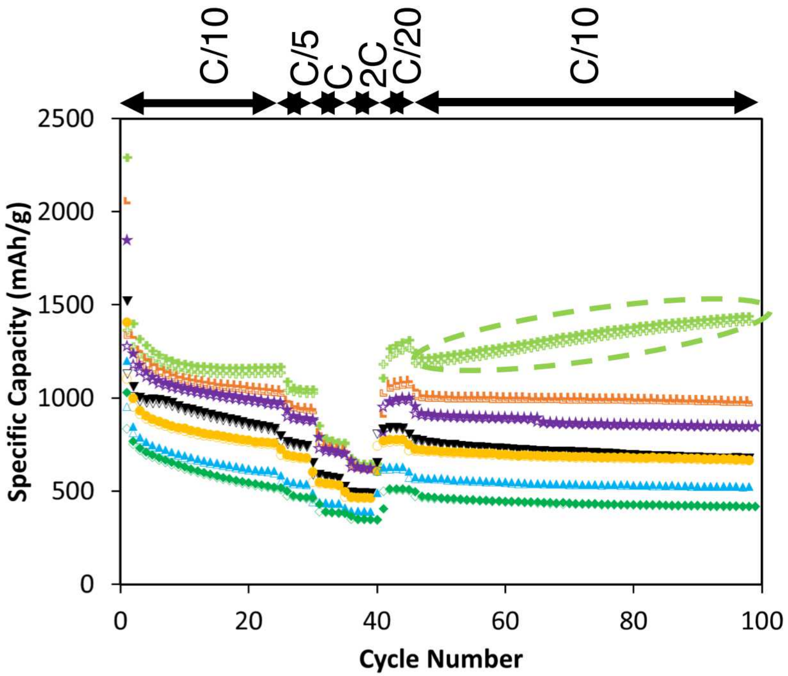
[a] Su et al. Chem. Sus. Chem. (2010). [b] Winter et al. *Li-ion Battery: Fundamentals and Performance* (1998). [c] Zheng et al. Carbon (1996). [d] Sato et al. *Science* (1994). [e] Mabuchi et al., *Tanso* (1994). [f] Tokumitsu et al., J. Electrochem. Soc. (1996). [g] Mukhergee et al. *Nature Comm.* (2014). [h] Larcher et al. Electrochim. Acta. (1999). [i] Letellier et al. J. Chem. Phys. (2003). [j] Tatsumi et al. J. Electrochem. Soc. (1996).

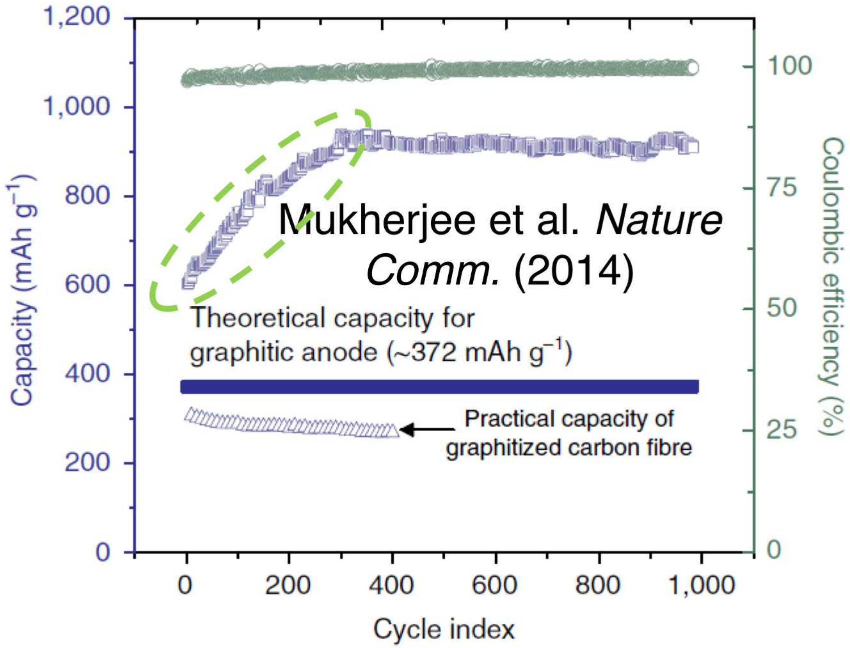
Restoring Capacity with Higher Voltage Charging



- This cell was cycled 105 times between 0.01 – 3 V, followed by extending the voltage range to 3.5 V.
- **CE increases well above 100%,** indicating significant capacity exists above 3 V, *i.e. Li was trapped rather than electrolyte parasitic losses.*
- Li^+ ions likely trapped at graphene edge groups and/or as Li^0 clusters in nanopores
- **Note,** while routine high voltage charging may not be practical, it may be possible to perform occasional high V charges to restore capacity every few cycles.

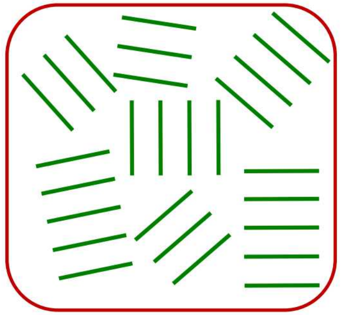
Mechanism for Capacity Increase with Cycling



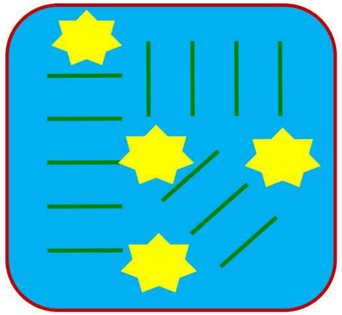


Mukherjee et al. *Nature Comm.* (2014)

NPC density = 1.98 g/cm^3.
Limited electrolyte penetration.
Minimal Li^0 metal.



NPC density = 0.65 g/cm^3.
Electrolyte penetration.
✸ = Li^0 metal.



- **Increasing capacity with cycling suggests underpotential Li deposition.**
- **Li can plate at graphene defect sites where Li_3C_8 is present.**
- **Cycling can lead to further volume expansion, resulting in deeper electrolyte penetration each cycle until saturation.**

NPC Li-ion Coin Cell Summary

- Specific capacity and coulombic efficiency behavior is similar in nature to other graphene-like nanocarbons.
- Capacity increases with decreasing NPC density:
  - appears to be a function of increasing interplanar spacings,
  - for < 1 g/cm^3 NPC, capacities are very high, perhaps due to lithiation of edge groups and/or Li metal plating in ~ 1 nm sized void regions between graphene platelets.
- Irreversible capacity loss (ICL) increases with decreasing density perhaps due to:
  - greater electrolyte penetration and SEI formation,
  - Li-ions trapped at graphene sheet edges.
- Higher voltages can be used to recover 'trapped' Li and restore CE.

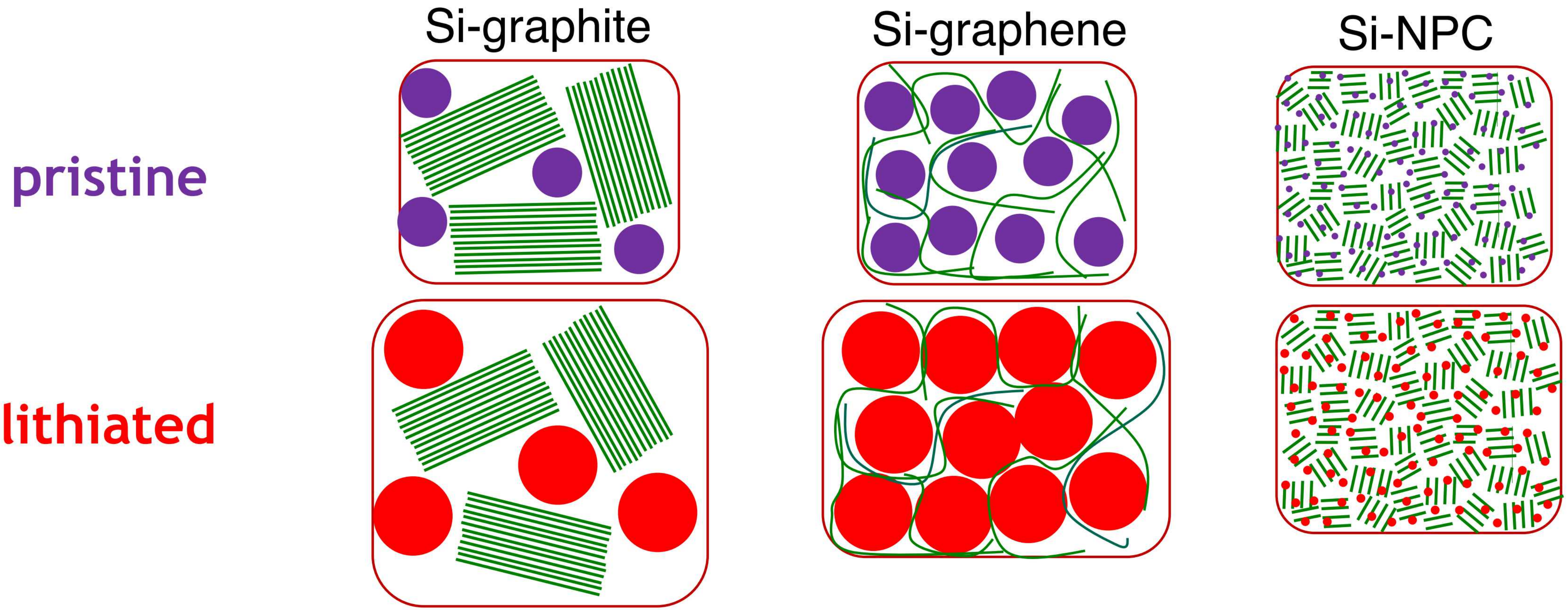
Due to a unique ability to control nanostructure, NPC may provide an opportunity to study, understand, and design a bulk carbon material for Li-ion energy storage.

Outline

1. Background for nanoporous-carbon (NPC)
   a. Tailoring NPC nanostructural properties
   b. Chemical sensor coatings
2. Coin cell testing
   a. Li-ion anode intercalation materials
   b. Comparisons with other nanocarbon materials
3. **NPC scaffold for Si?**
4. Can NPC be used for Na-ion intercalation?
5. Summary

Nanoarchitectured Si-NPC – Design for Volume Expansion

I.e. Can Si self-pulverization be avoided?



RF-sputter co-deposit Si during PLD, *resulting in Si atoms and/or small clusters within NPC.*

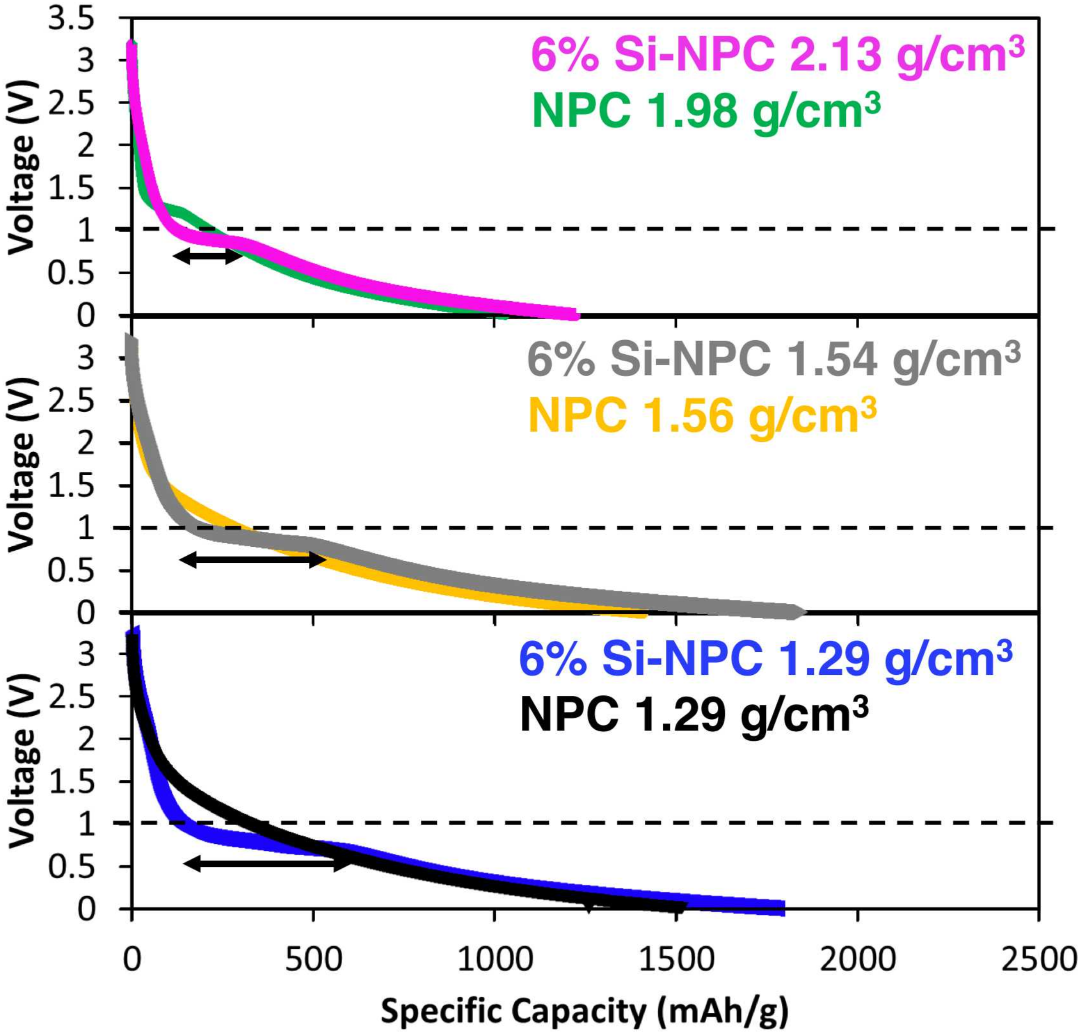
Prepared 6 atomic % Si-NPC films with densities = 2.13, 1.54, and 1.29 g/cm^3.

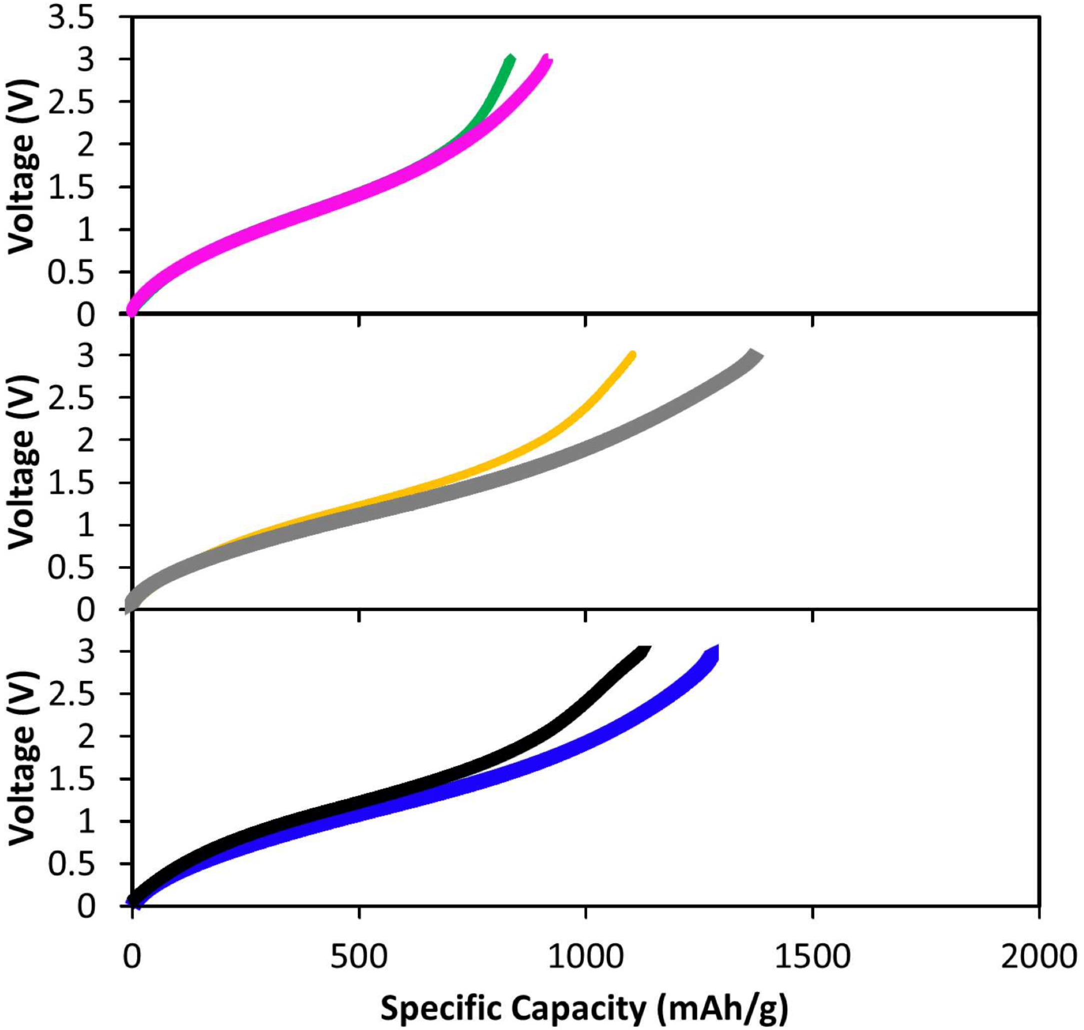
Hypothesis: NPC may allow space for small Si atom cluster volume expansion.

Preliminary 6% Si-NPC Cycle 1

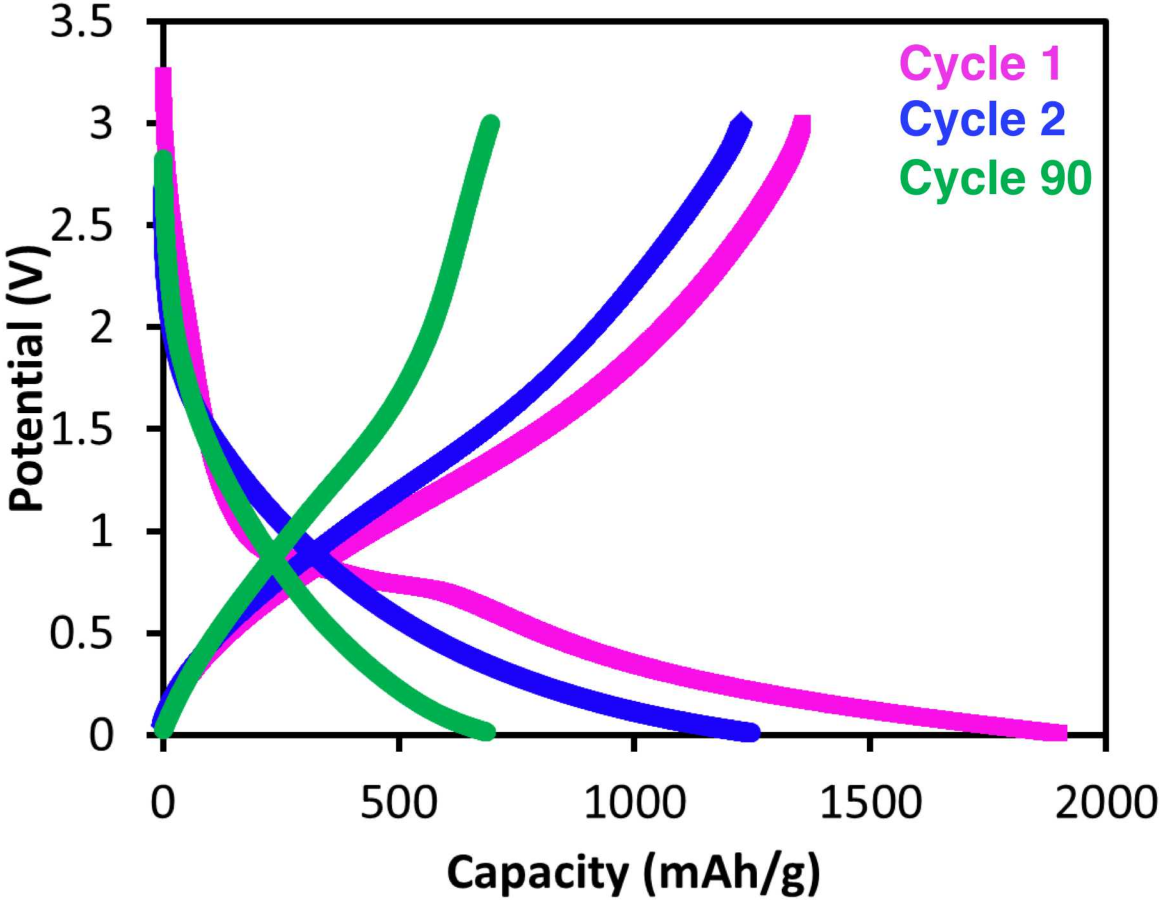
- Capacity ↑ as density ↓
- Plateau around 0.7 V ↑ as ρ ↓
- Distinctly different curve shape with Si

- Si-NPC higher capacity than NPC with similar ρ
- No plateau upon delithiation
- Excess delithiation capacity at high voltage



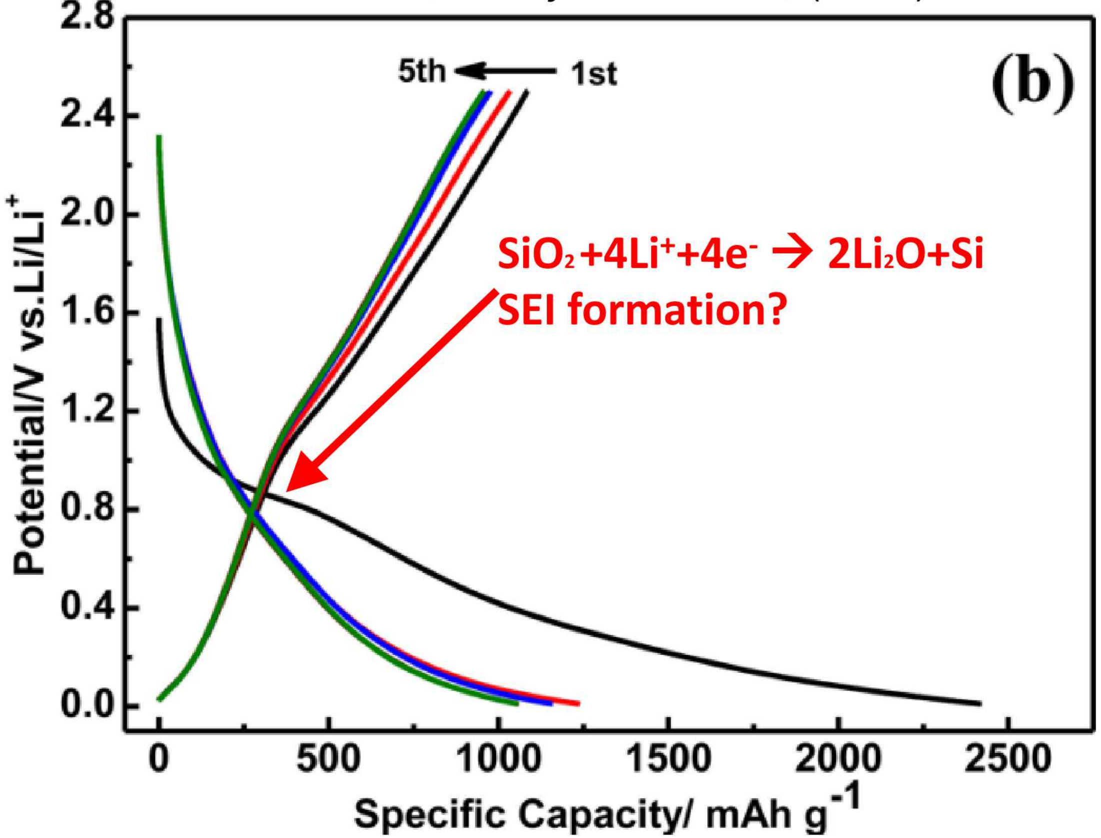


Preliminary Comparison of 6% Si-NPC 1.29 g/cm^3 to SiO_2



- **Plateau only present on first cycle**

Tu et al., *J. Phys. Chem C.*, (2014).

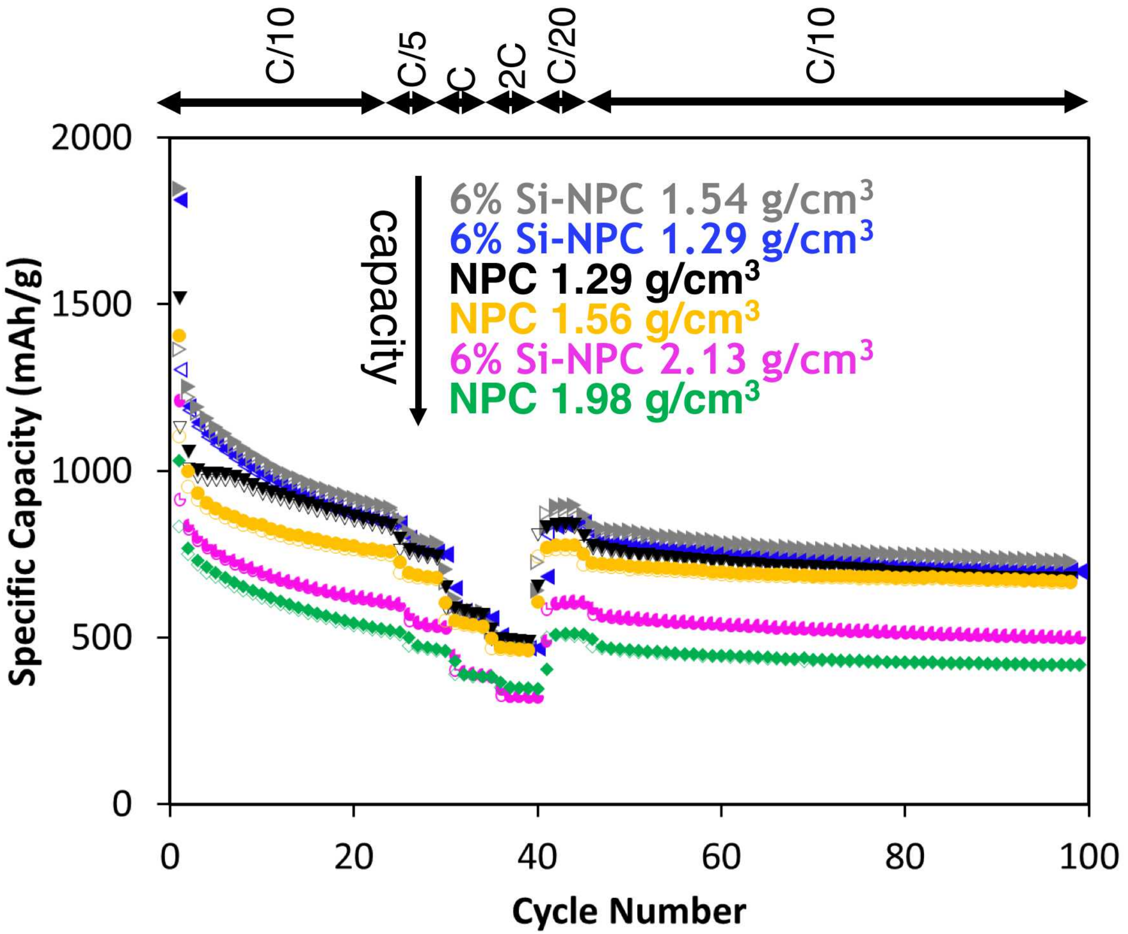


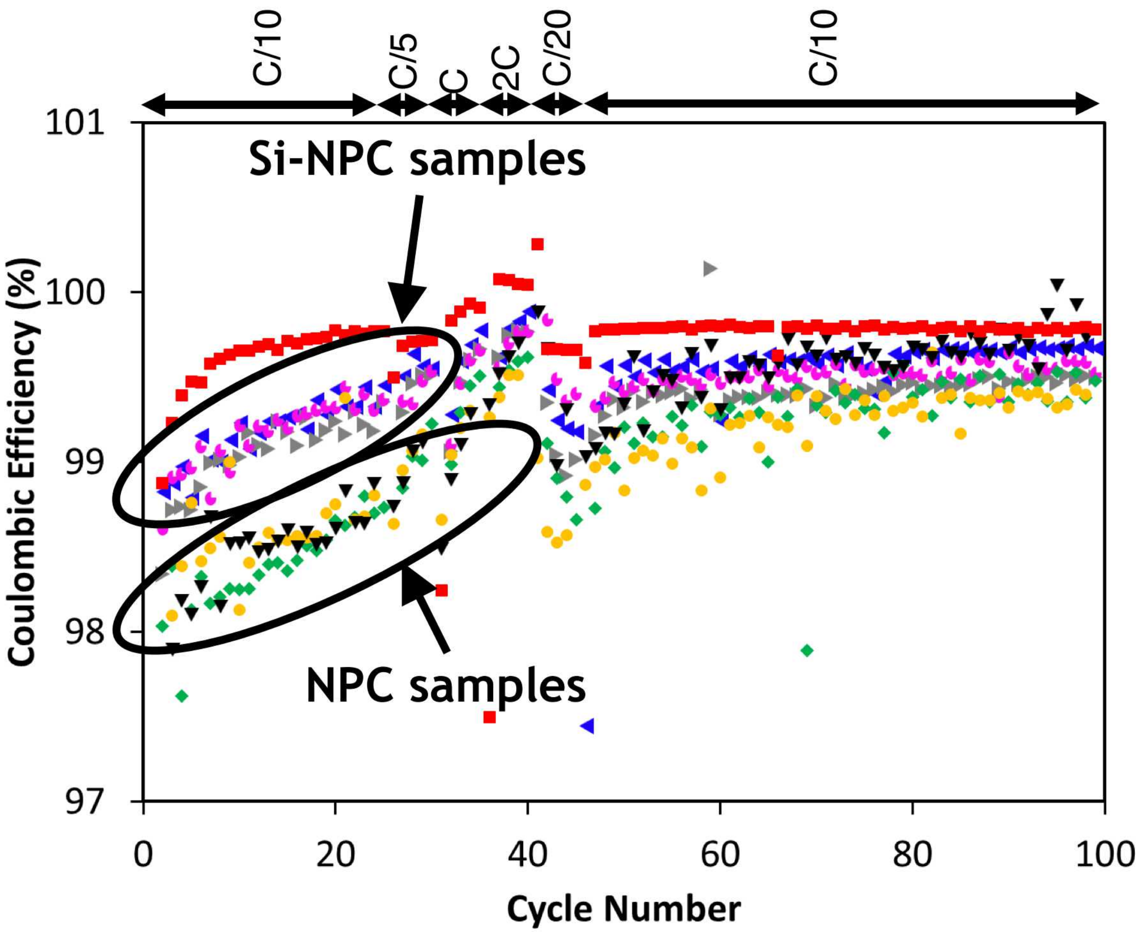
$SiO_2 + 4Li^+ + 4e^- \rightarrow 2Li_2O + Si$

SEI formation?

- **Plateau and cycling behavior similar to SiO_2**
- **Evidence for small Si clusters likely dominated by oxide formation?**

Preliminary 6% Si-NPC Cycle Life





- Si-NPC has slightly higher capacity than NPC with same density.

- Like NPC with densities ≥ 1 g/cm³, Si-NPC samples have similar CE.
- However CE higher for Si-NPC.

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Why Sodium (Vs. Li) Ion Intercalation?

Advantages:

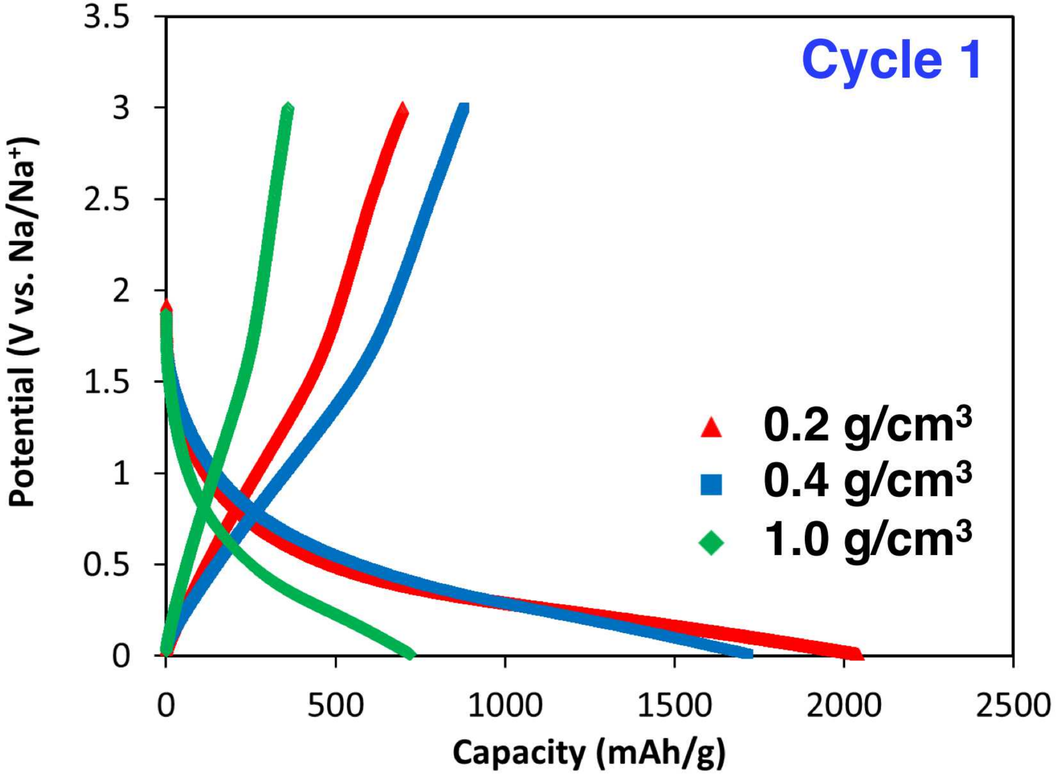
- Li availability and cost are projected to eventually become problematic.
- Na is abundant and inexpensive.
- Na batteries can be completely discharged w/out safety issues.

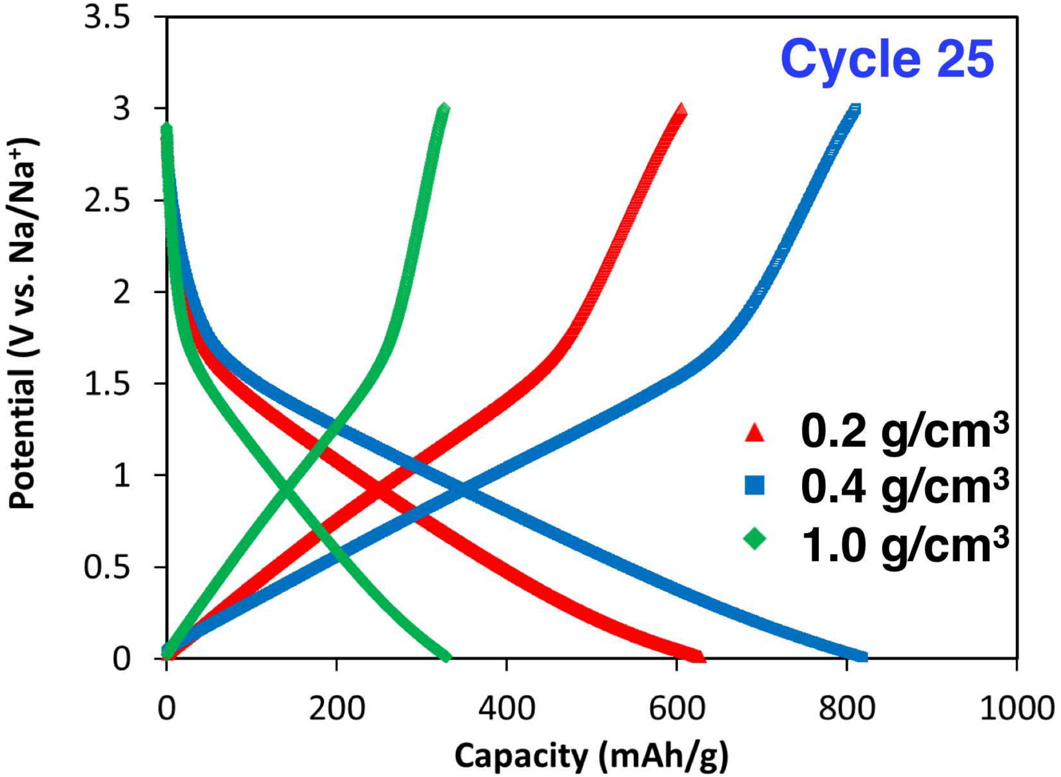
Disadvantages:

- Na has a higher standard potential and is heavier than Li, both leading to lower energy densities than Li-ion batteries.
- Na^+ ions are too large to insert between graphite sheets like Li ions, so interest exists in alternative forms of carbon for anode materials.

- **2032 Half-Cells vs. Na**:
- Electrolyte = 1 M $NaPF_6$ in 1:1 ethylene carbonate:diethyl carbonate (EC:DEC).
- Na metal counter electrode.

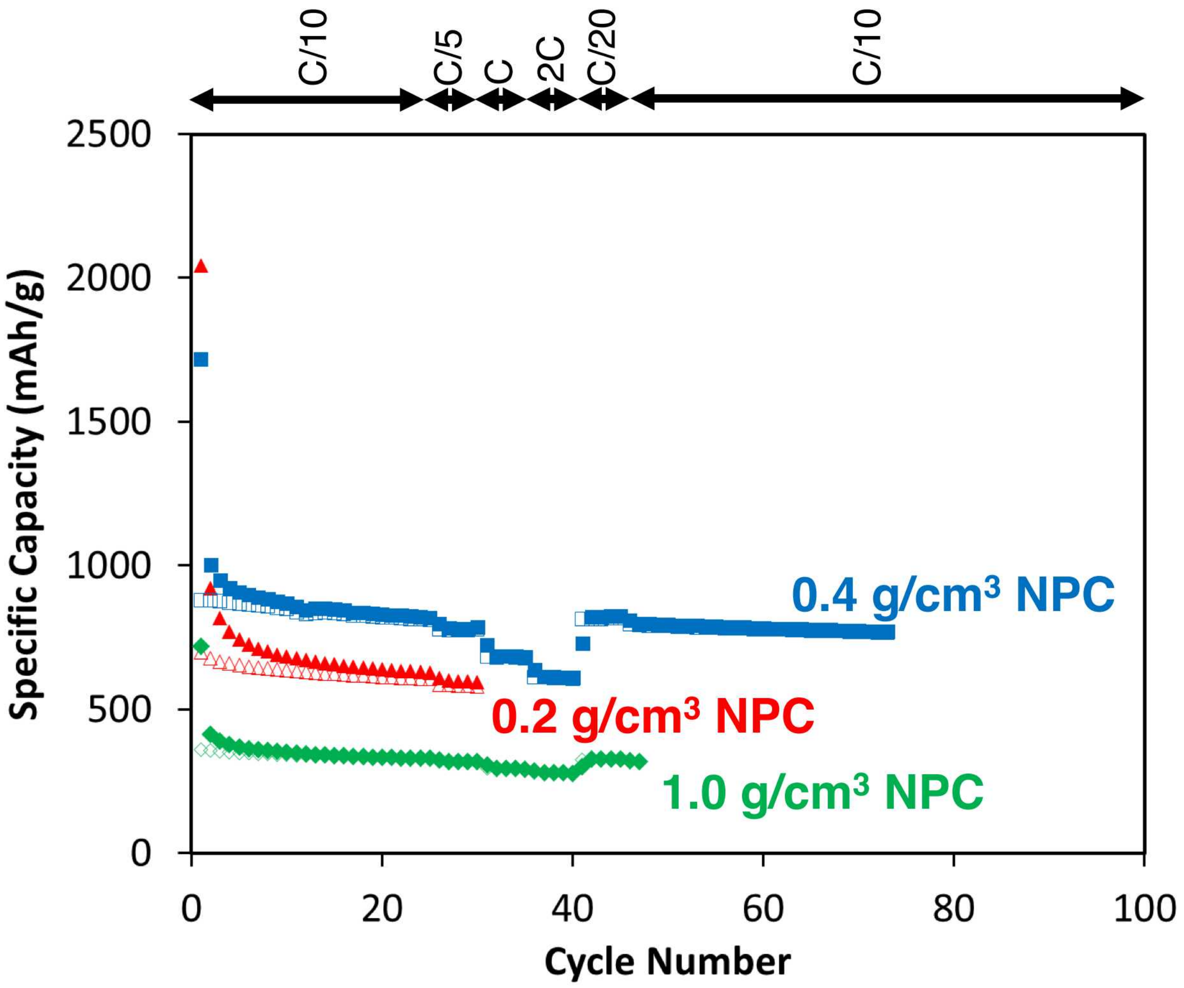
Preliminary Na Charge – Discharge Performance in NPC





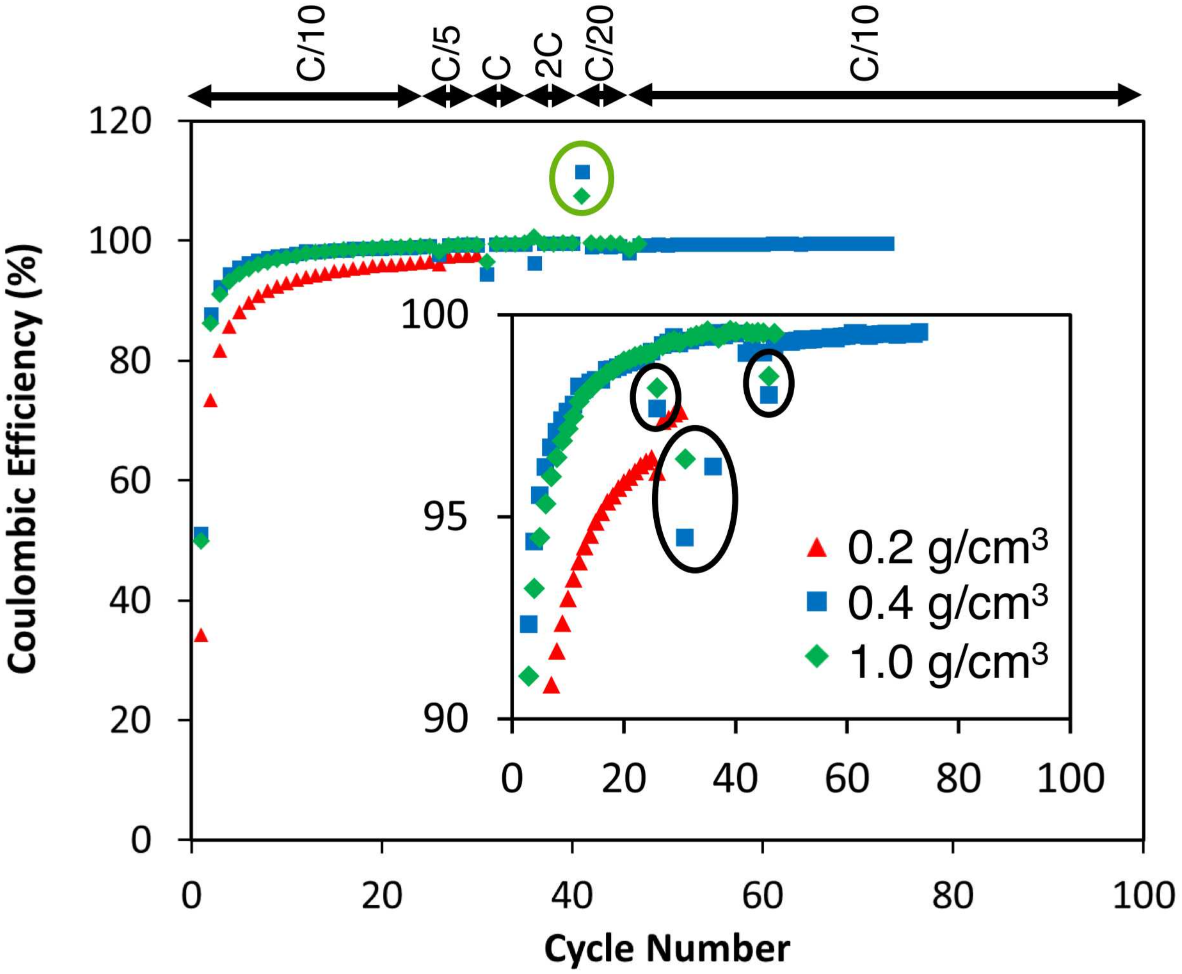
- **Na$^+$ successfully inserts reversibly into NPC!**
- The large irreversible capacity loss in 1st cycle can indicate (a) SEI layer formation, (b) Na being trapped in pores, or (c) Na irreversibly reacting with graphene sheet edge groups.
- Sloping behavior (similar to Li$^+$ intercalation) has been observed for graphene-like carbons.
- Capacity fade decreases in later cycles, such as cycle 25.

Preliminary Cycle Life vs. NPC Density for Na Intercalation



- Typical capacity values for graphene-like materials are similar to the 1.0 g/cm^3 NPC. (e.g. Wan et al, *Chem. Mater.* 2016)
- Highest capacities > 750 mAh/g associated with NPC density ~ 0.4 g/cm^3.
- Differences in NPC performance most likely related to different interplanar spacings.
- Reduced capacity for 0.2 g/cm^3 NPC most likely due to its weak mechanical integrity.
- ***Perhaps there exists an optimal NPC density between 0.4 – 1.0 g/cm^3?***

Preliminary Na-Ion Coulombic Efficiency vs. NPC Density



- CE is similar for 0.4 and 1.0 g/cm^3 NPC samples, reaching > 99% after extended cycling, typical of graphene-like materials.
- The initial low CE suggests
  - SEI formation in early cycles and/or
  - some Na is trapped in NPC and cannot be removed below 3.0 V, similar to Li.
- The lower CE for the 0.2 g/cm^3 NPC likely due to weak mechanical integrity, leading to additional SEI growth where NPC is newly exposed to electrolyte solution.
- CE drops when charge rate is increased, but recovers when it drops again, inferring that Na removal is more difficult than insertion.

Summary

NPC (Li-ion anode)

- NPC capacity increases with decreasing density.
- Best specific capacity > 1400 mAh/g after 100 cycles.
- Li-plating in NPC likely occurs at lower densities.
- *Additional capacity available at higher voltages.*

Preliminary 6% Si-NPC (Li-ion anode)

- Capacity and CE both increase relative to NPC.
- *Si may be incorporated as SiO_2.*

Preliminary NPC (Na-ion anode)

- NPC can serve as an insertion material for Na^+ ions.
- *Capacities much higher than previous graphene reports.*

The ability to control the density, surface area, and interplanar spacing in NPC uniquely enables optimizing anode intercalation performance that is unavailable in graphitic carbon materials.