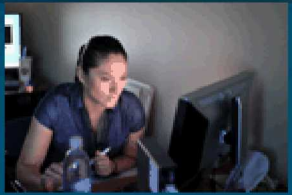
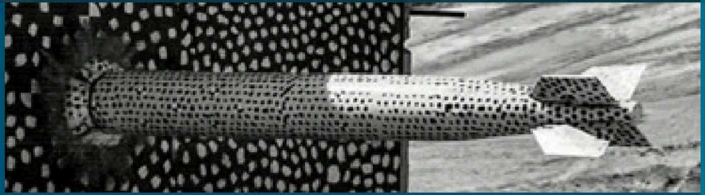
SAND2019-12672C

Pulsed Laser Deposited Nanoporous Carbon As a Lithium Ion Battery Anode





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PRESENTED BY **S. Goriparti**, M. A. Wolak, T.E. Beechem, P. Cuillier, M. P. Siegal and K. L. Harrison

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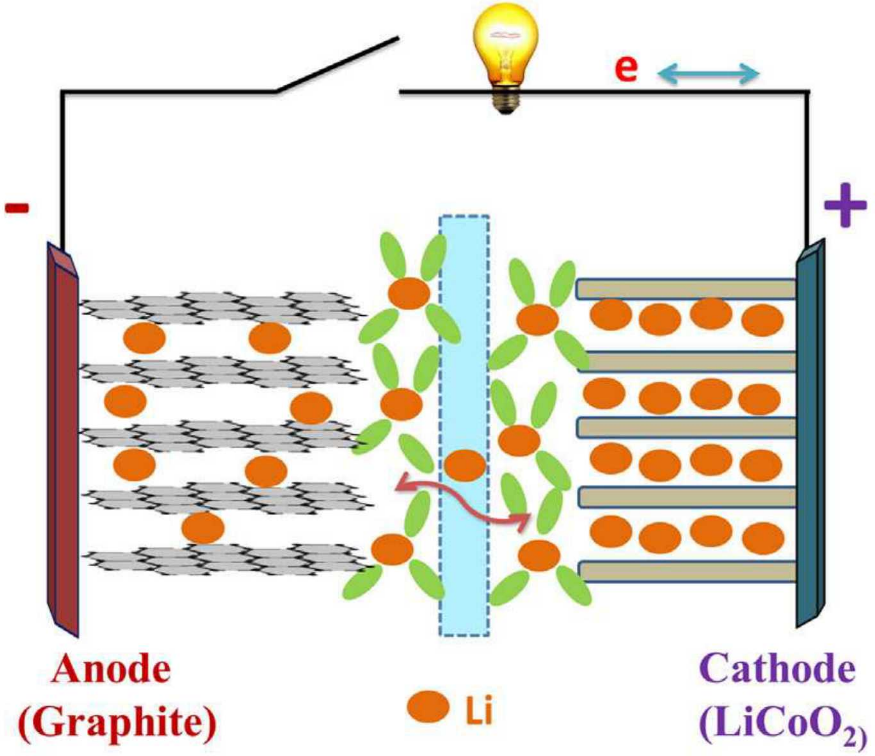
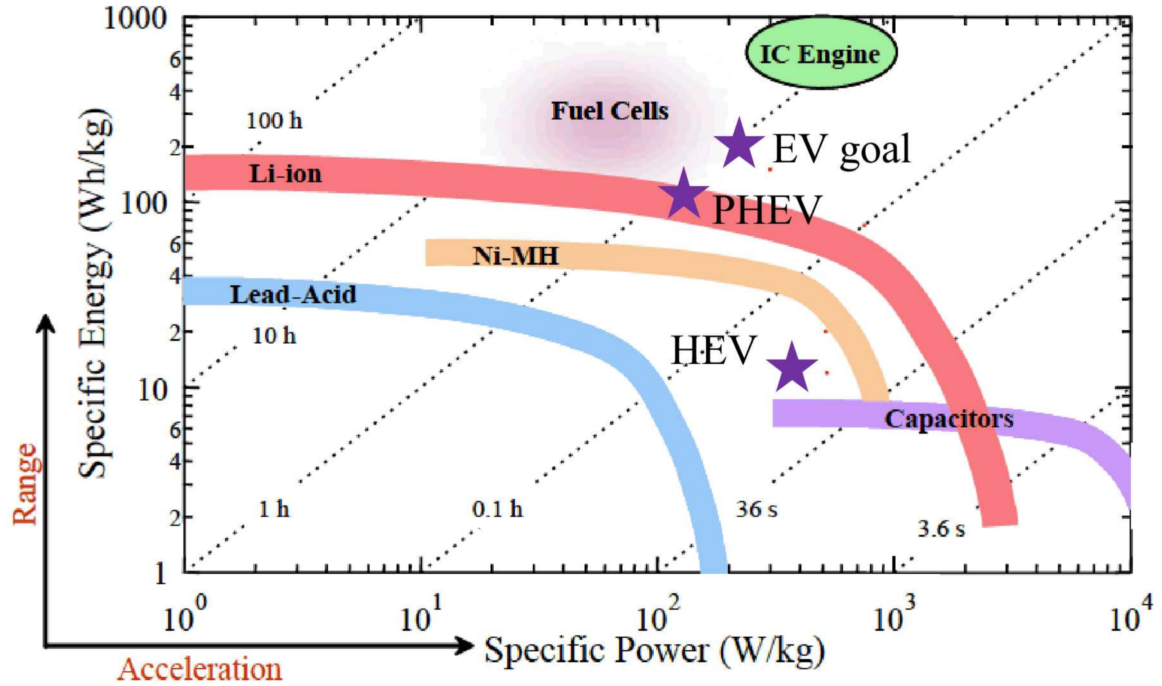
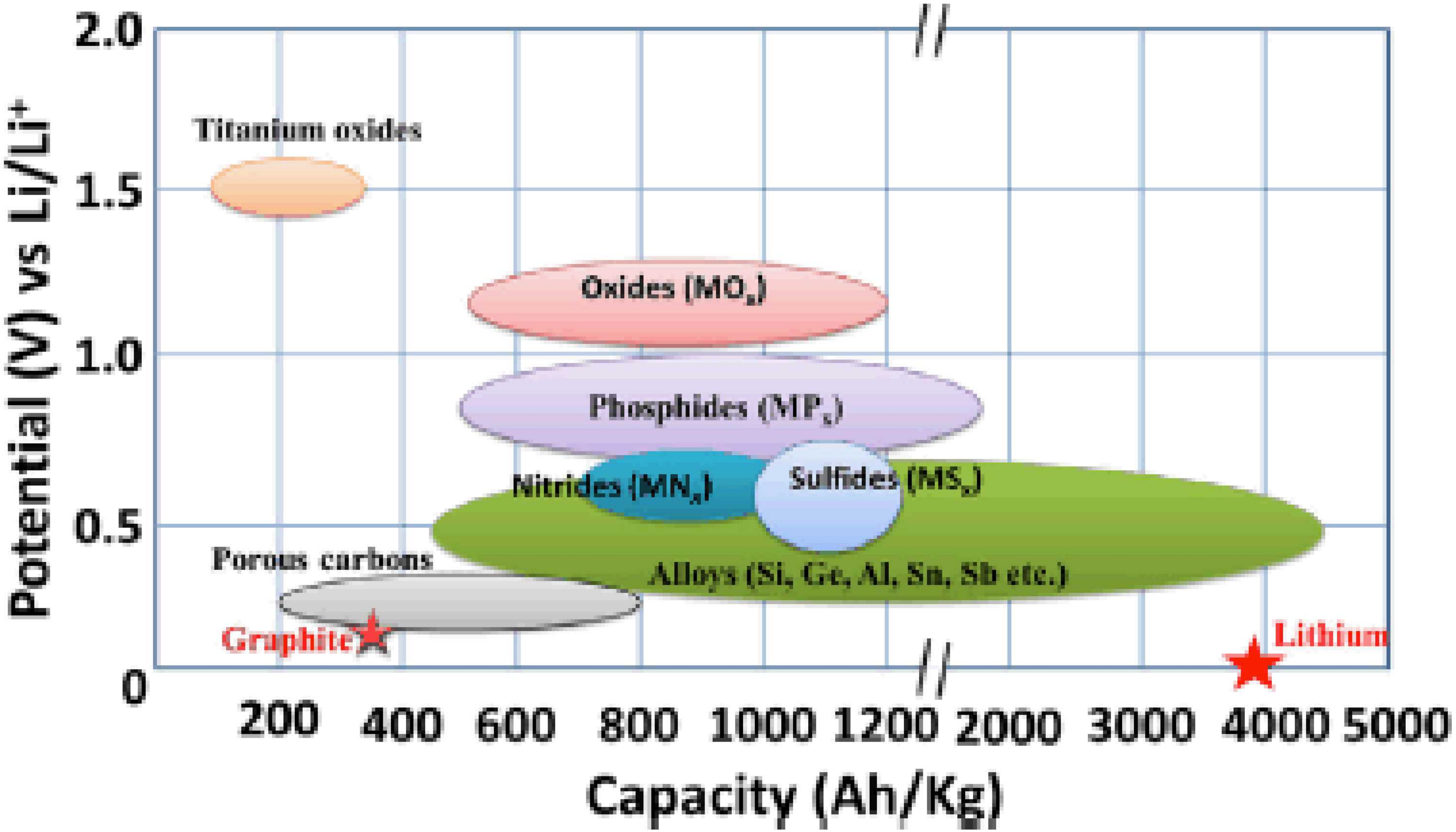
Lithium Ion Batteries





Goripart et al., Journal Power Sorces (2014)

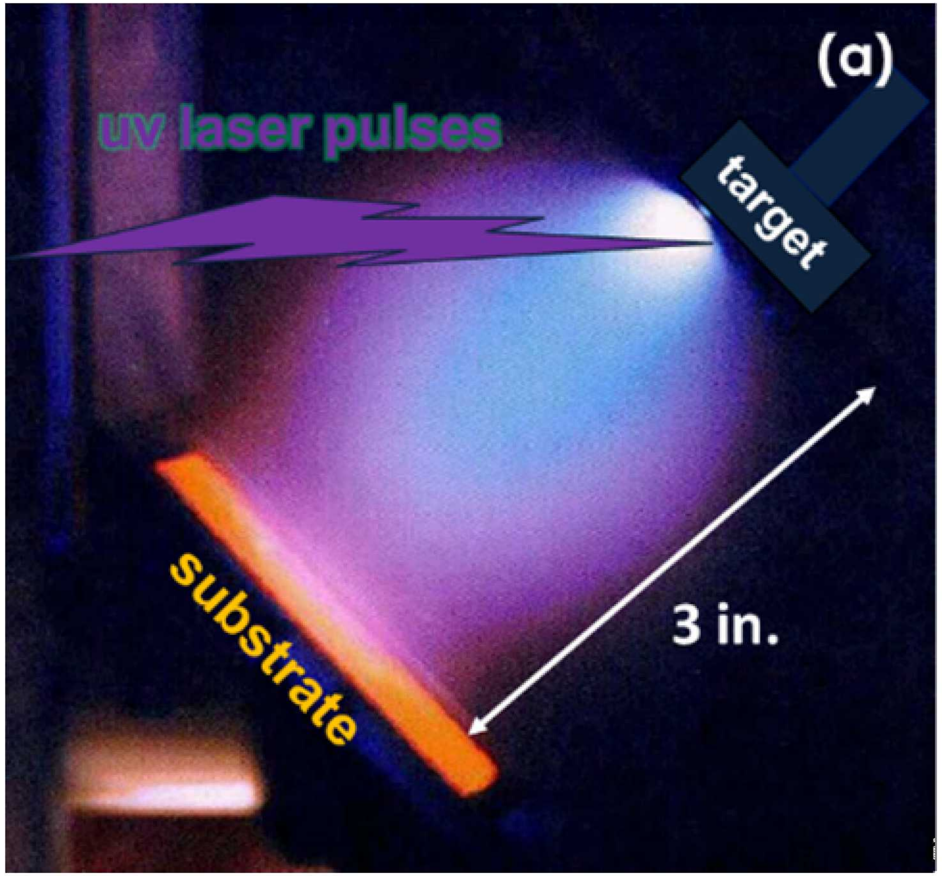


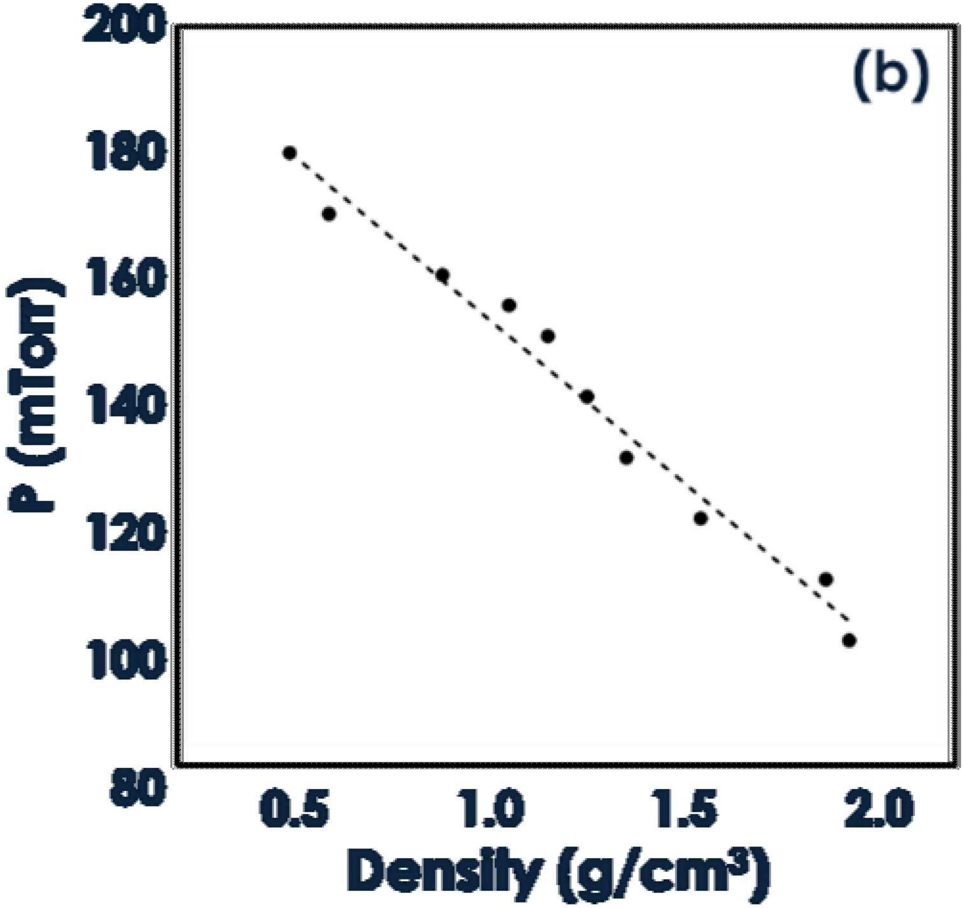
Most used Graphite has a limitation of charge storage capacity (372 mAh/g), Hence, alternative anodes are needed for next generation lithium ion batteries

Goripart et al., Journal Power Sorces (2014)

Nanoporous Carbon Pulsed Laser Deposition (PLD)

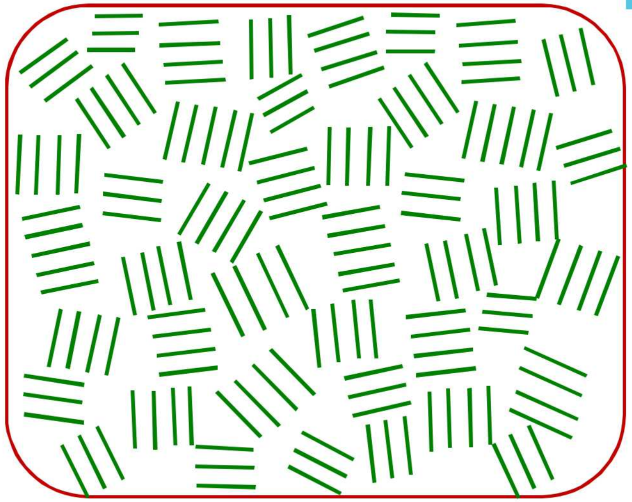
- **PLD C deposition using background Ar gas to attenuate energy of ablated C**
- **Result: 3D graphene-like, zero-residual-stress C films**
- **Control density and surface area by tuning laser energy, target-to-substrate distance, and Ar pressure**

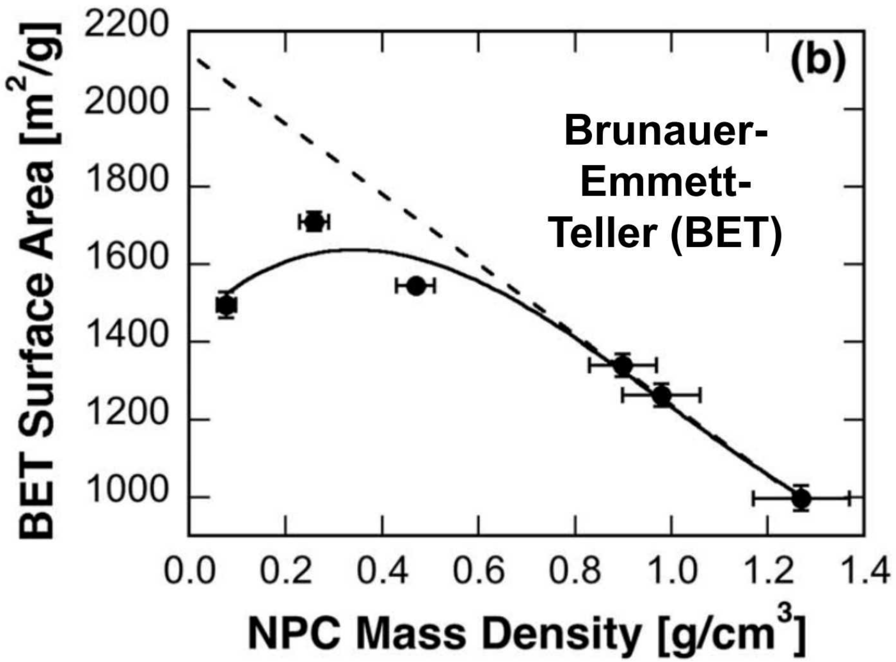




NPC = 3D Nanocrystalline Graphene

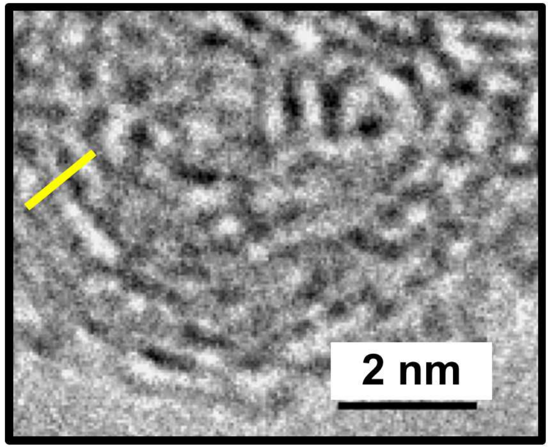
- **Nanoporous carbon**
  - **Randomly-stacked 1–2 nm-sized platelets of 3–5 layer thick graphene**
  - **Interlayer spacing up to 5.4 Å (compare to 3.35 Å for graphite)**
  - **Density: 0.2 - 2.0 g/cm^3**
  - ***Clean, binderless, tunable 3D form of graphene!***



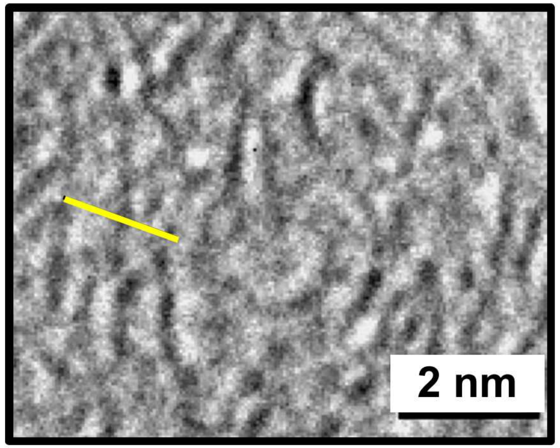


Siegal et al, *J. Electrochem. Soc.* (2016).

1.0 g/cm^3
4.4-4.8 Å
~1200 m^2/g (BET)

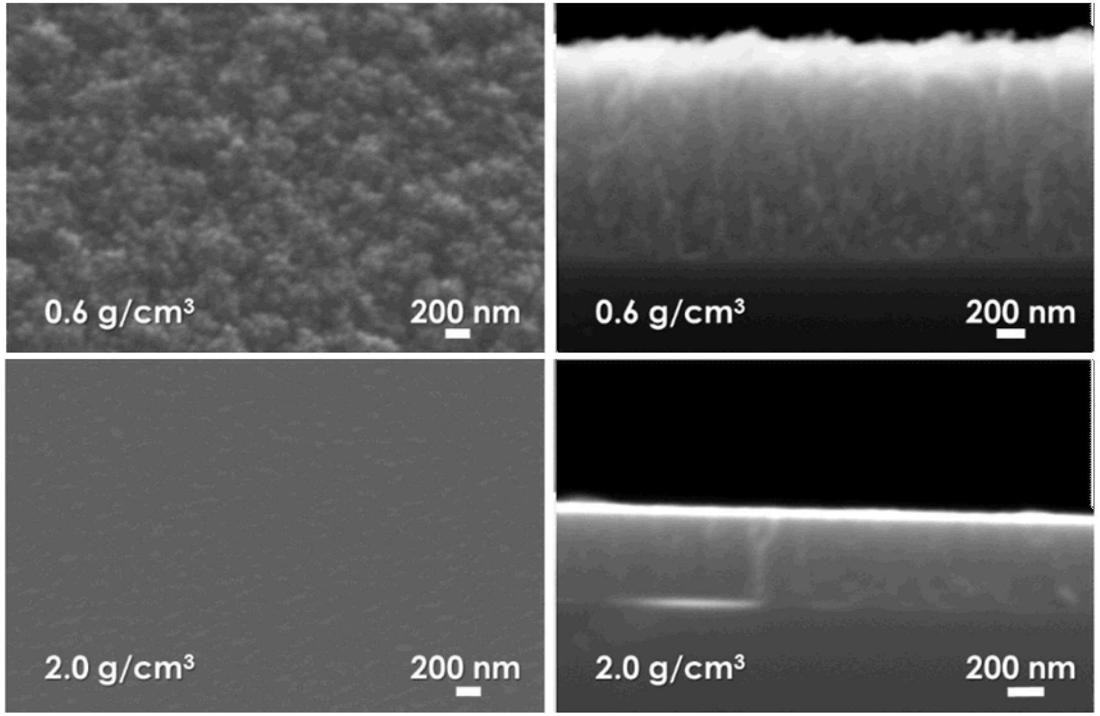


0.25 g/cm^3
5.1-5.4 Å
~1600 m^2/g (BET)



Siegal et al, *Langmuir* (2004).

Procedures



Deposition

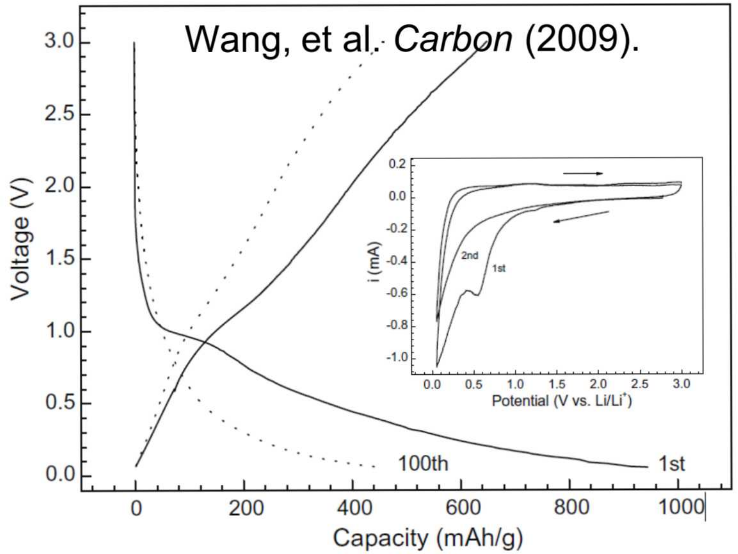
1. Grow NPC on SS current collectors
2. Simultaneously grow NPC on Si witness samples
3. Weigh witness sample before and after deposition (microbalance)
4. Measure film thickness via SEM and calculate density
5. Determine mass of NPC on SS (mass = density*thickness*area)

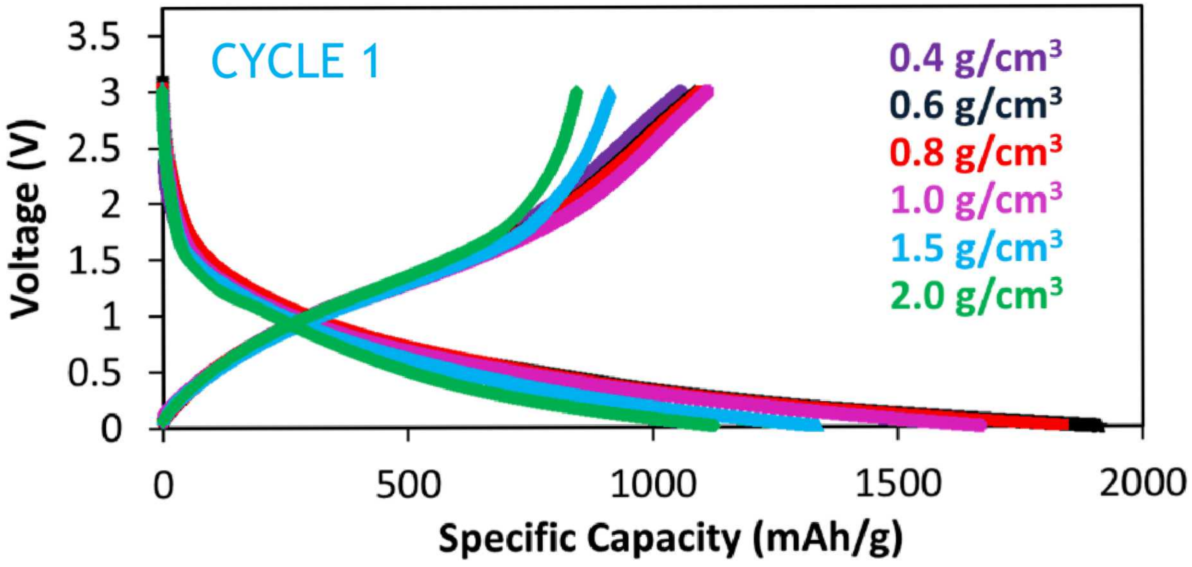
Electrochemical Testing

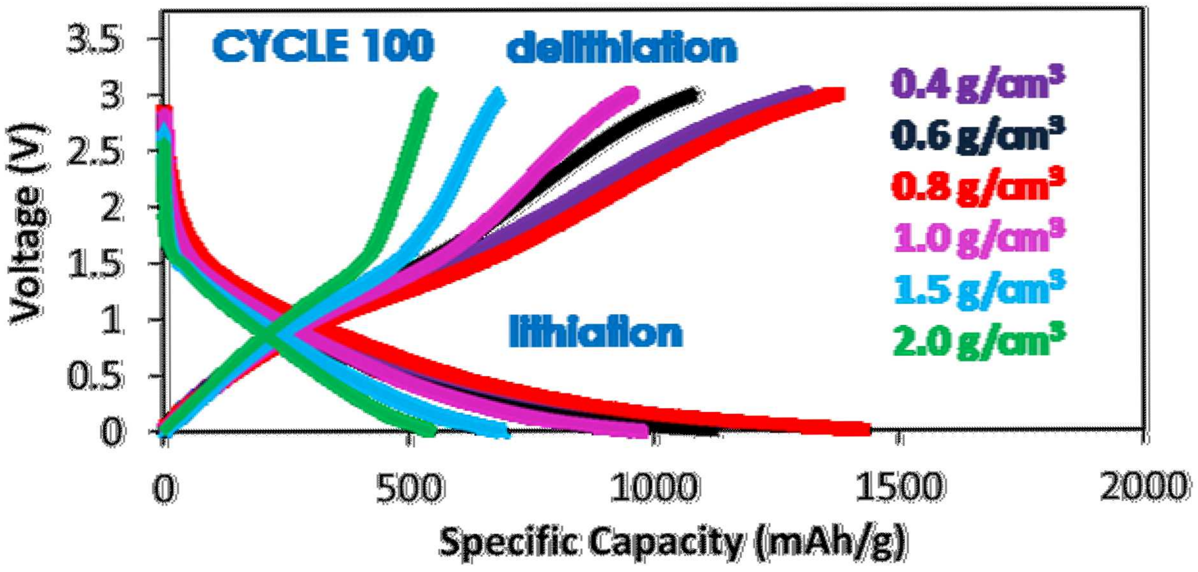
- 2032 half cells versus Li
- 1 M $LiPF_6$ in 1:1 ethylene carbonate:diethyl carbonate
- Constant areal loading = 0.05±0.01 mg/cm^2 (~0.22 um graphite equivalent)

Charge – Discharge Performance

- ❖ NPC behaves like graphene
- ❖ Capacity increases with decreasing the
- ❖ Higher capacity with 0.8 g/cm3 compare to other densities



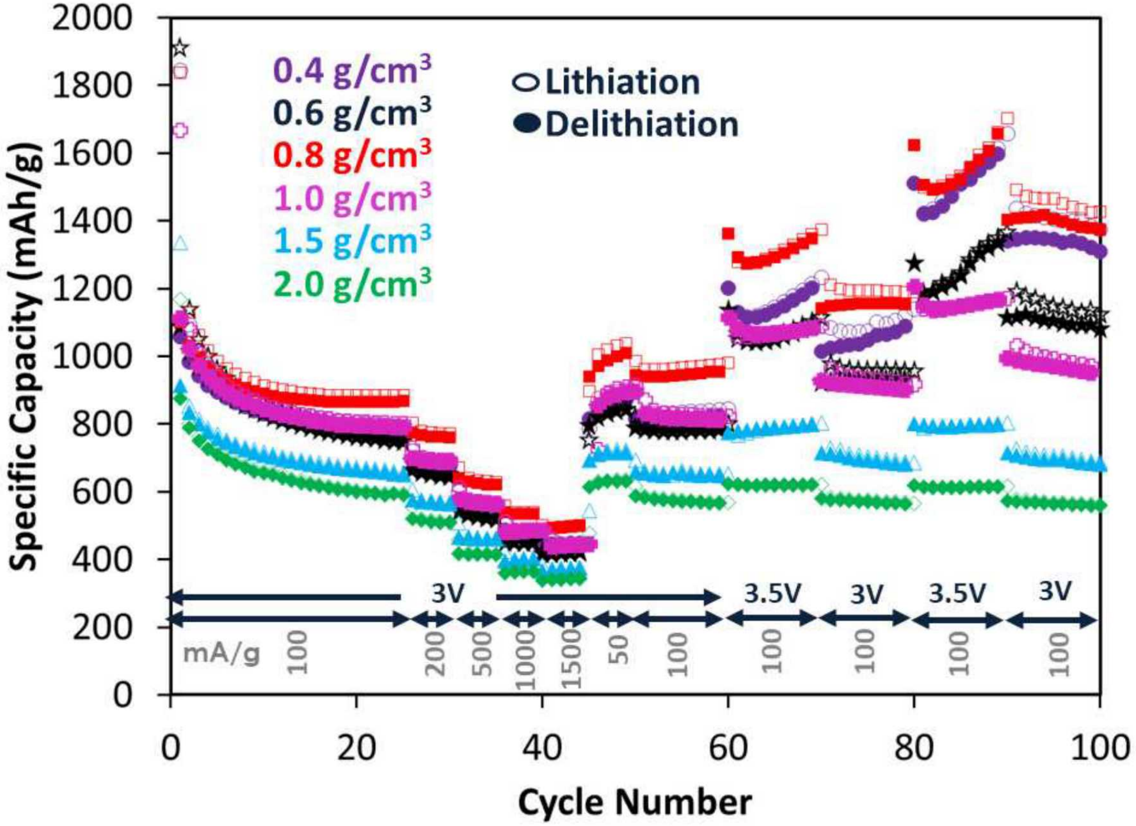


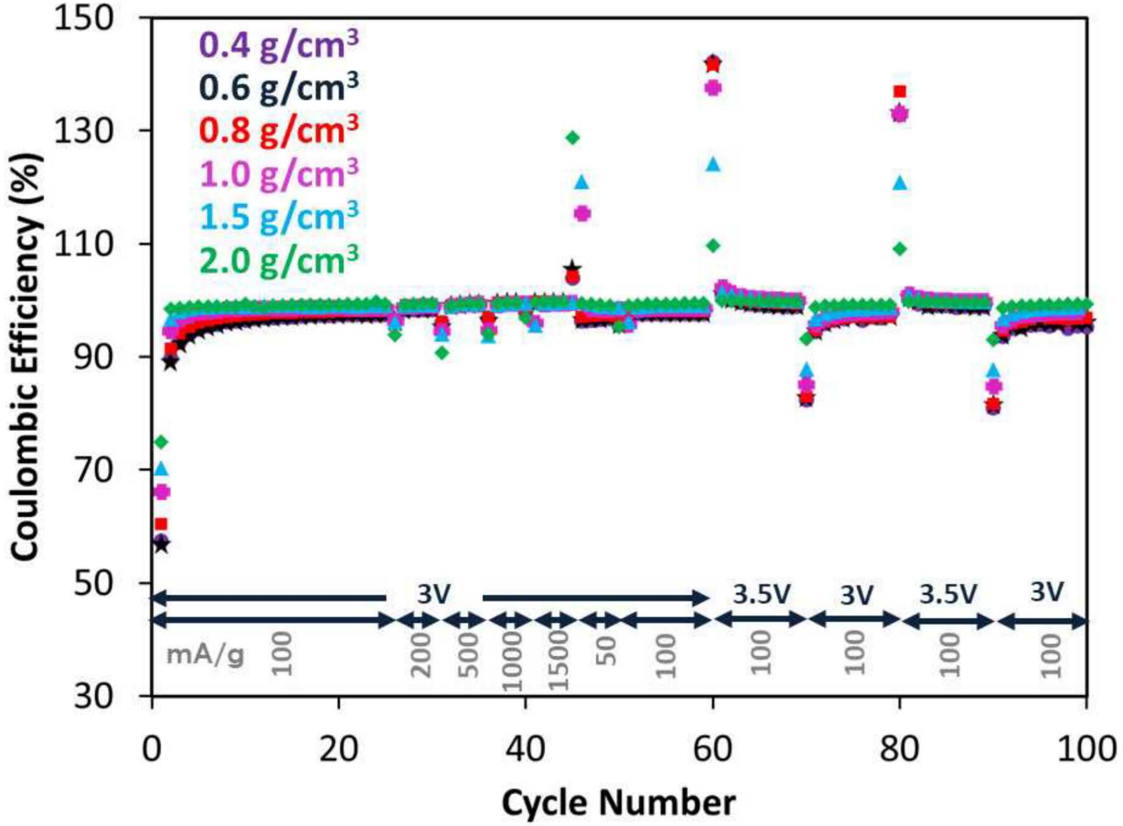


Cycle Life and Coulombic Efficiency *vs* Density

- ❖ Capacity ↑ with ↓ density between 2 and 0.8 g/cm^3
- ❖ 0.4-0.6 g/cm^3 lower capacity than 0.8 g/cm^3
- ❖ Capacity much higher if ↑ cutoff voltage to 3.5 V

- Cycle 1: ↑ irreversible capacity loss (ICL) when ρ ↓
- CE ↓ when ↑ C-rate and CE ↑ when ↓ C-rate
- CE ↑ when delithiation potential to 3.5V

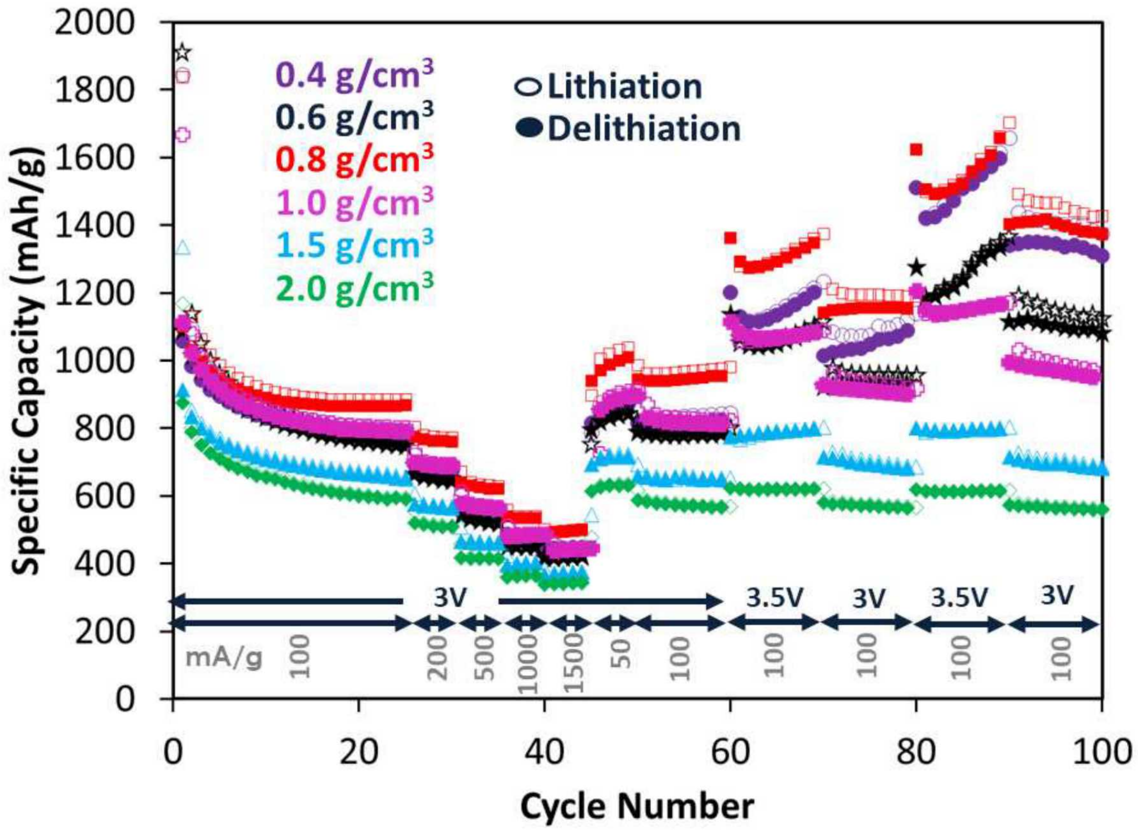




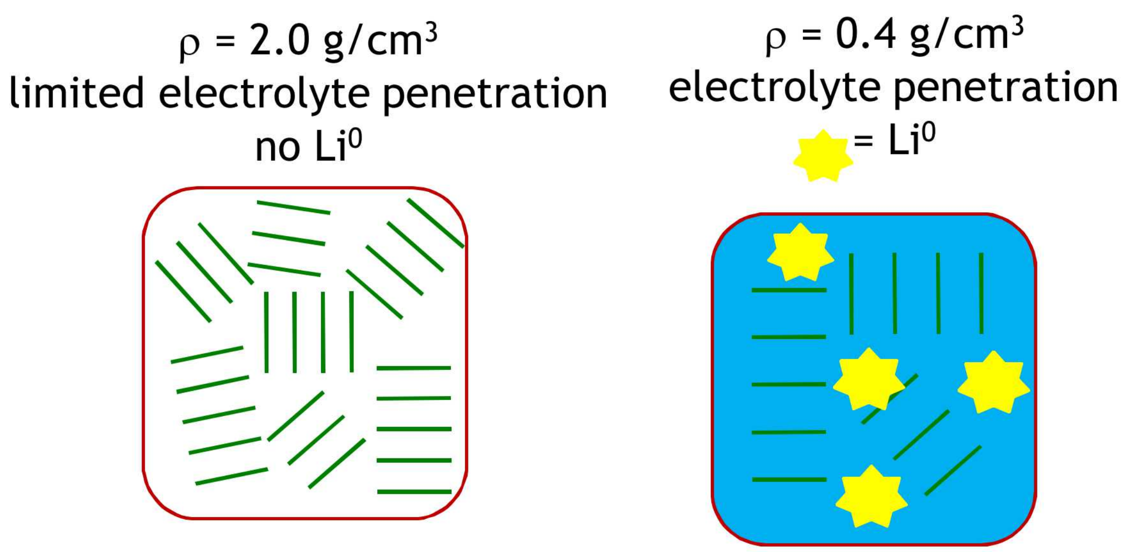
Cycle Life and Coulombic Efficiency *vs* Density

- Capacity per unit weight or atom C ↑ with ↓ ρ
- Capacity for 0.8 g/cm³ sample increases with cycling
- Capacity per unit volume maximized at 0.8 g/c
- With ↓ ρ, high voltage delithiation capacity ↑

- Cycle 1: ↑ irreversible capacity loss (ICL) when ρ ↓
- CE ↓ when ↑ C-rate and CE ↑ when ↓ C-rate
- CE ↑ when delithiation potential to 3.5V



Mechanism for Capacity Increase with Cycling



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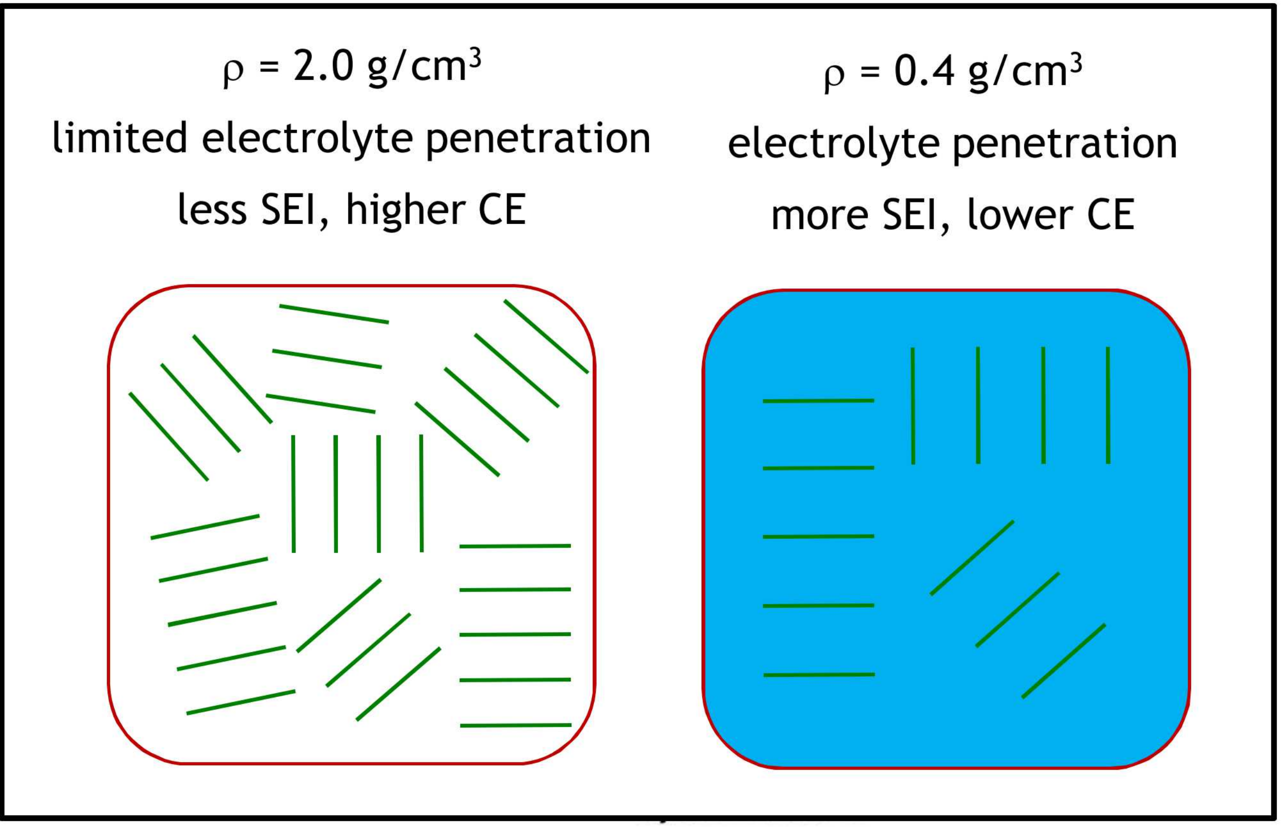
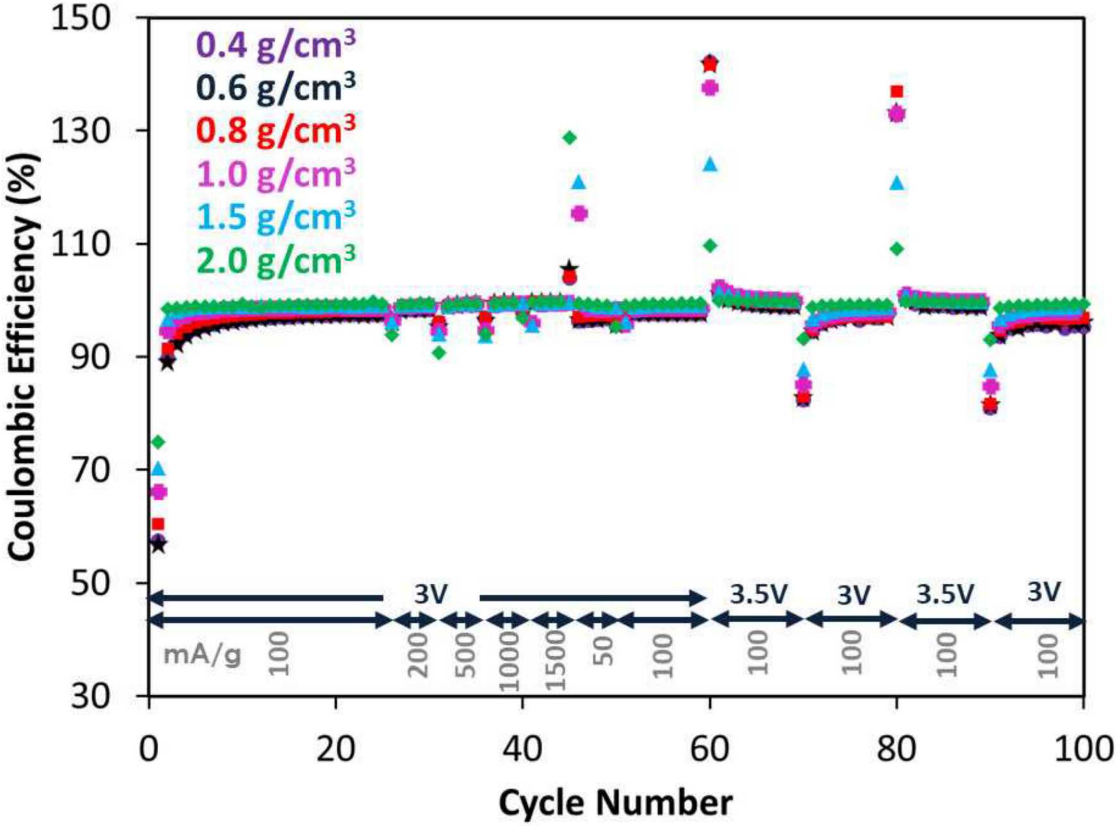
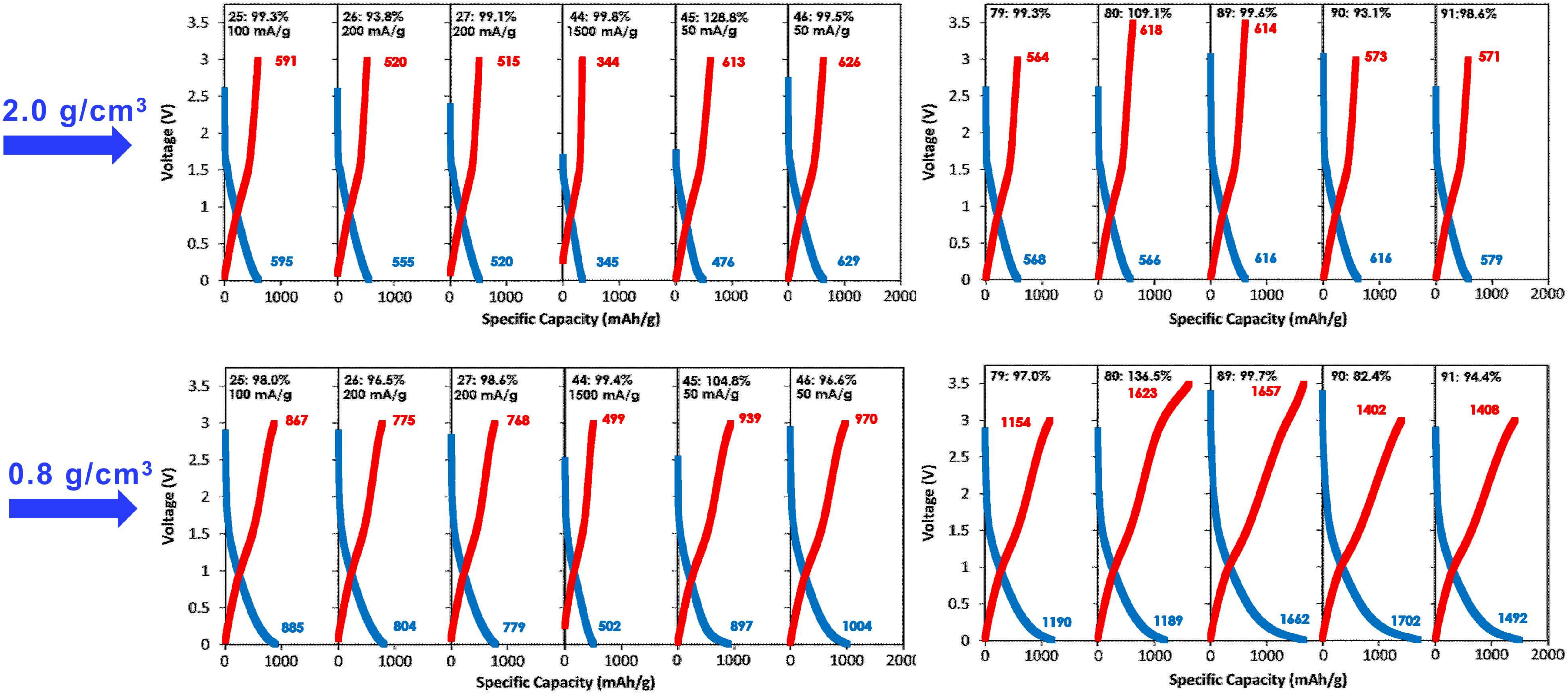


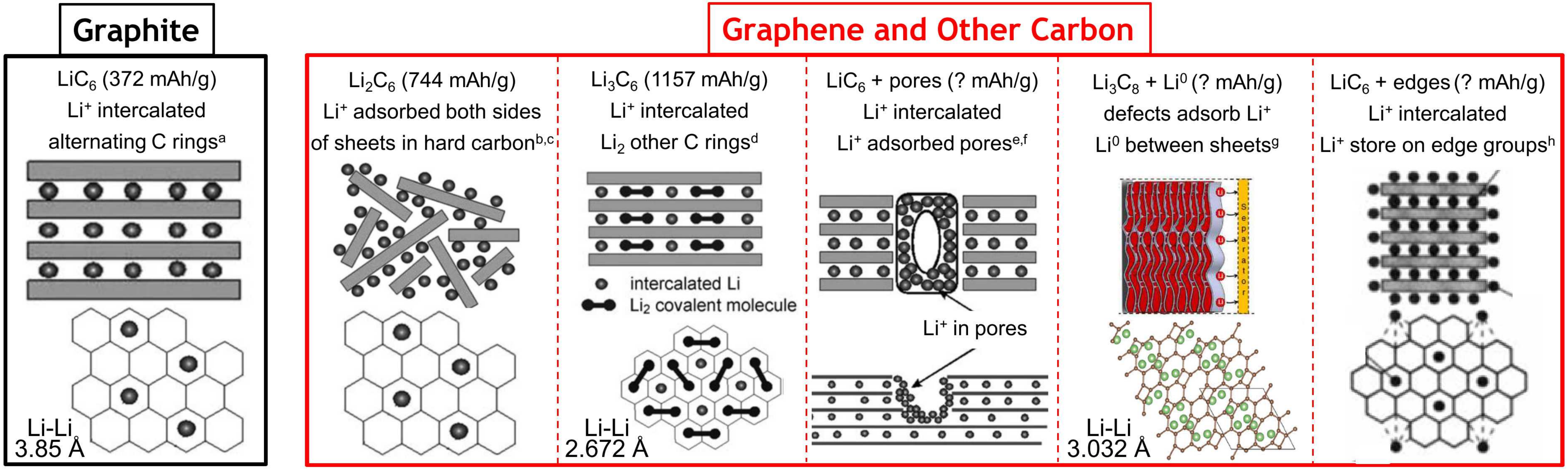


Capacity and Coulombic Efficiency *vs* Delithiation Potential



With ↓ ρ, high voltage delithiation capacity ↑

Mechanisms for Li storage in graphite and graphene



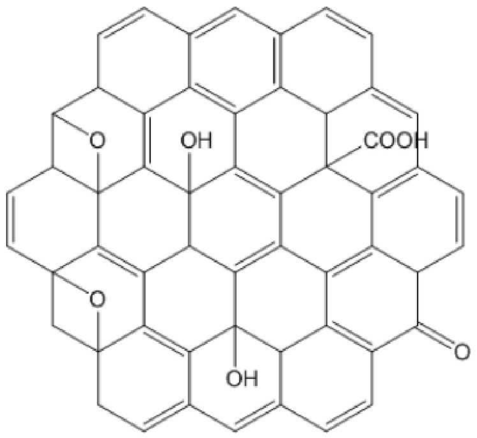
- **Ab Initio: Li can only be adsorbed at defect sites (no pristine graphene)[g]**
- **Capacity ↑ with H content[i] increased d spacing[j]**
- **NMR: quasimetallic Li clusters form in nanopores (<1 nm) and removed at high voltage[k,l]**

[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]Yata et al., Synthetic Metals (1990). [j]Yoo et al. *Nano Letters,* (2008). [k]Letellier et al. J. Chem. Phys. (2003). [l]Tatsumi et al. J. Electrochem. Soc. (1996).

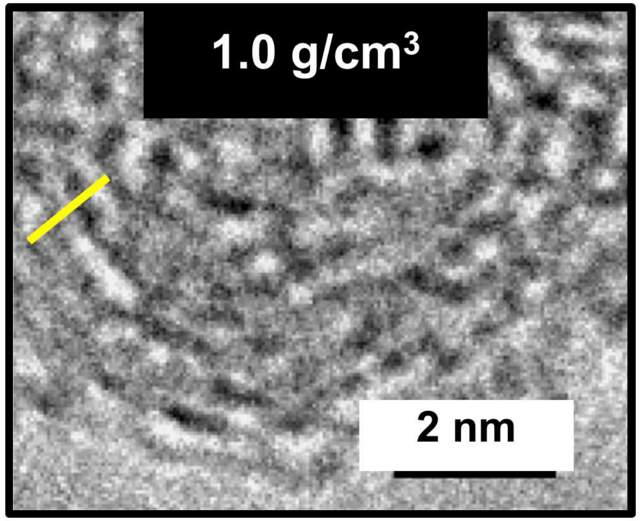
Mechanism for Lithium Storage and Irreversible Capacity Loss (ICL)

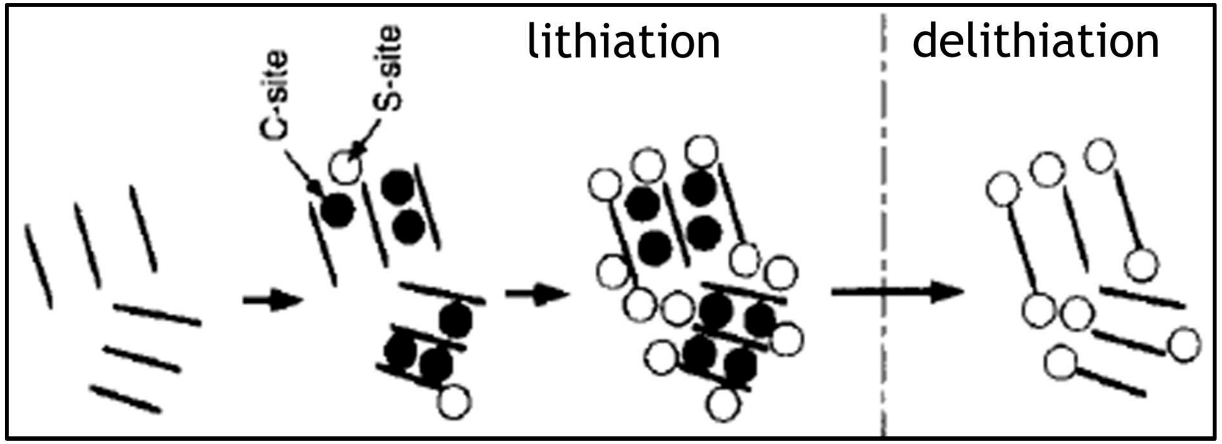
- **NPC: ↑ ICL with ρ ↓**
- **Li^+ can be trapped at edges[1]**
- **Li → Li_2O at oxygen edge groups[2]**
- **NPC → lots of edges to trap Li**
- **NPC ICL: trapped Li + SEI**

[1]Mori et al. J. Power Sources (1995).
[2]Larcher et al. Electrochim. Acta. (1999).

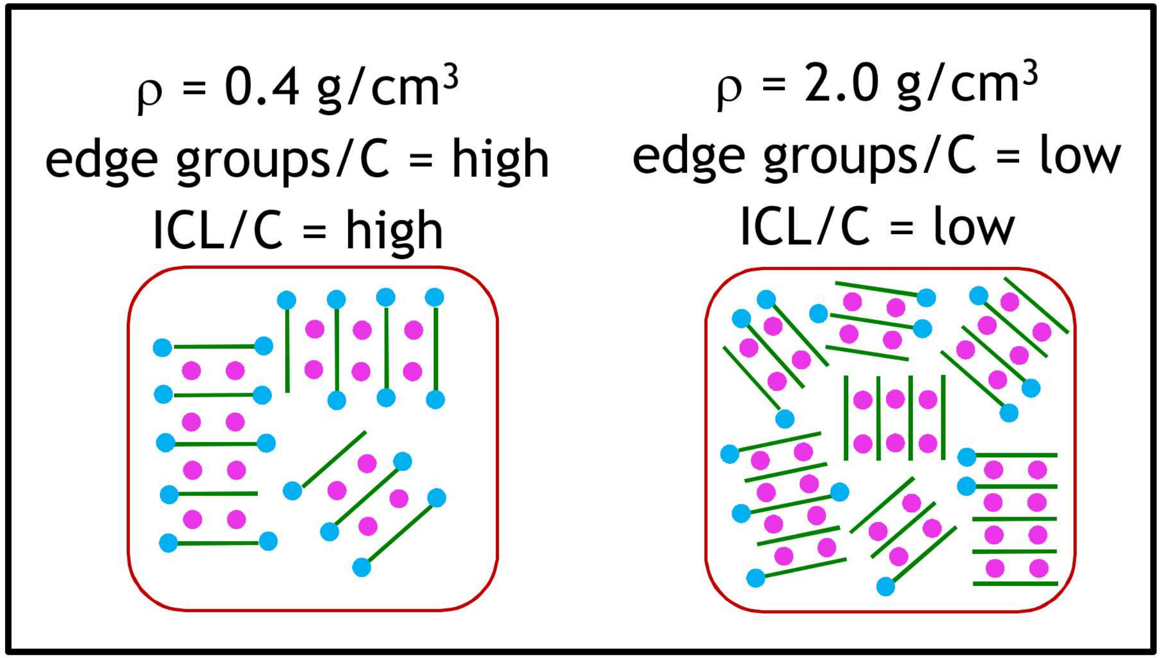


Schedy et al., *J. Chem. Educ.* (2018).

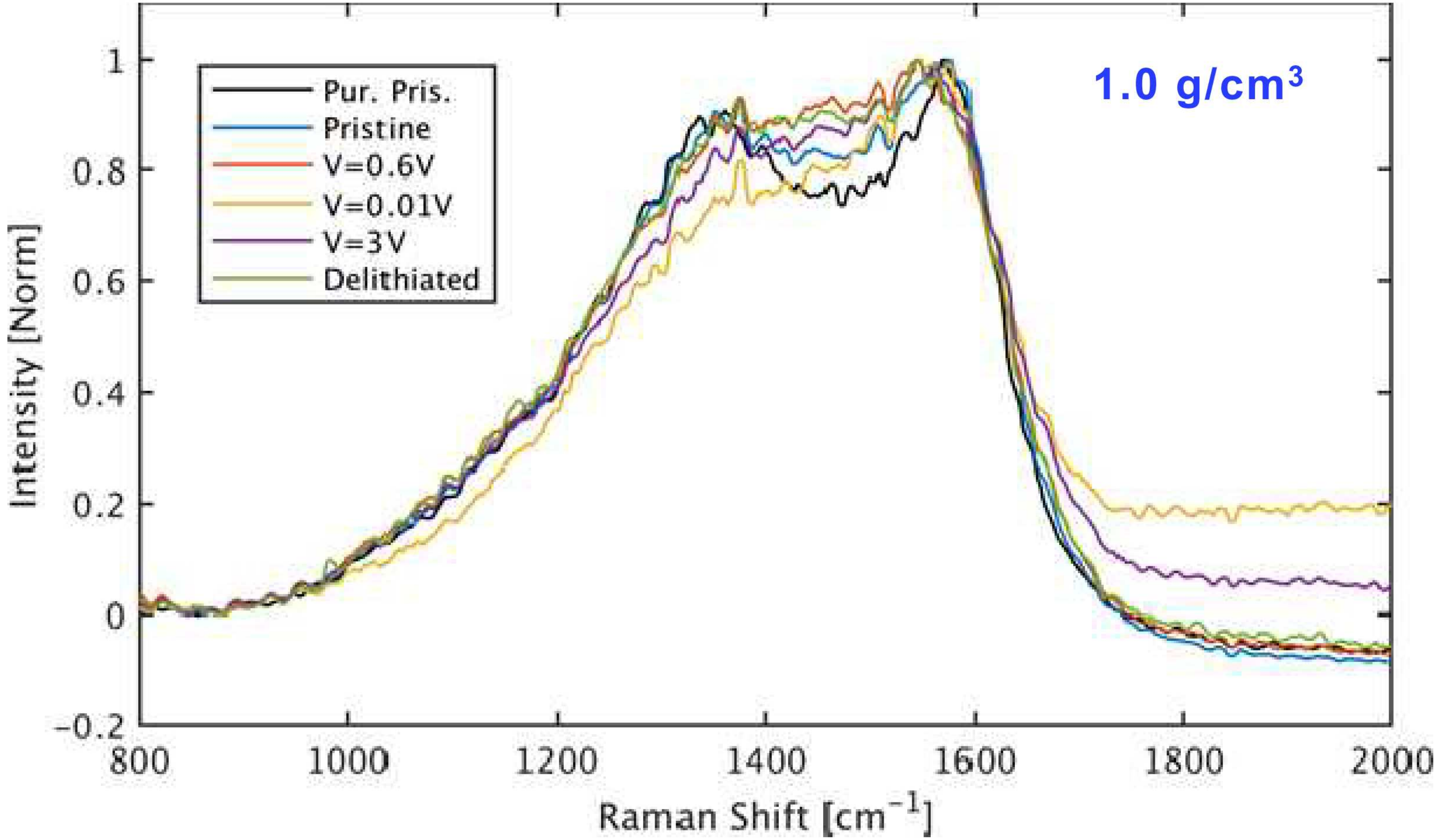




[1]Mori et al. J. Power Sources (1995).



Ex-Situ Raman Analysis of NPC



- ➢ Lithiate to 0.01 V → D peak decrease → more disordered NPC
- ➢ Delithiate to 3V → D peak increase → less disordered NPC
- ➢ Delithiate to 3.5 V → D peak increase more → similar to 0. V sample
- ➢ Demonstrates there is a change in the sp^2 NPC structure between 3 and 3.5 V

Summary

- NPC capacity increases with decreasing the density between 2.0 g/cm^3 and 0.8 g/cm^3
- 0.4-0.6 g/cm^3 lower capacity than 0.8 g/cm^3 (mechanical integrity)
- Capacity increases with higher cut off delithiation potential 3.5 V, particularly for low density samples
- Best specific capacity >1400 mAh/g after 100 cycles

Thank you

Questions?

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525