# Development of Graphene Batteries for Use in Space Applications

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# Batteries for Space Applications

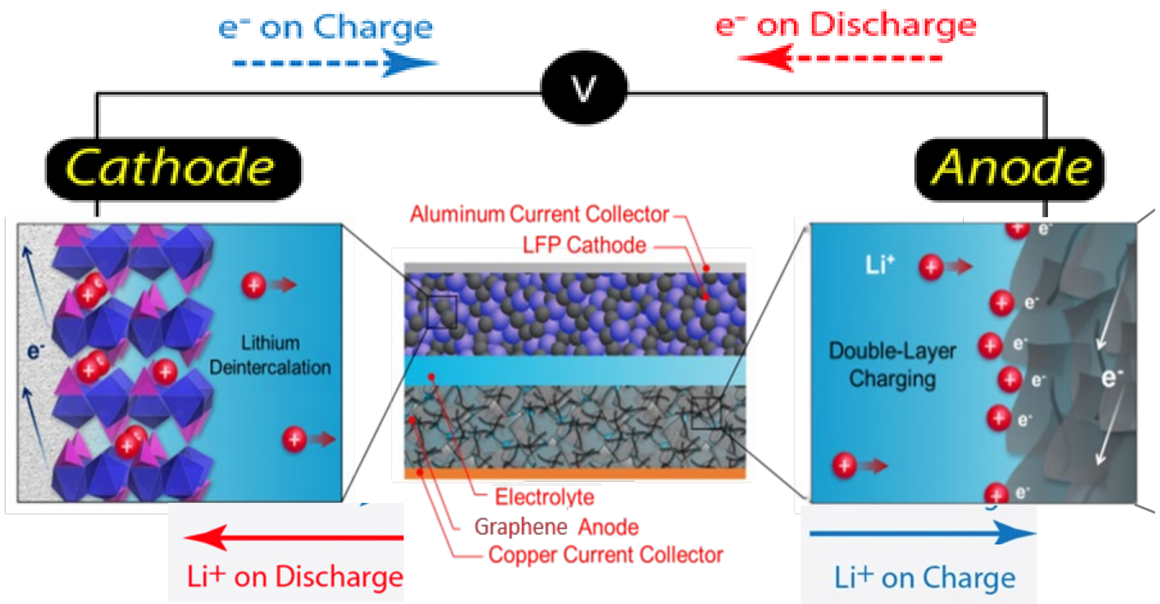
- Batteries play critical role in optimum satellite operation

- Batteries are especially important in low-earth orbit (LEO) satellites: supply power during eclipse

- Space batteries must meet special requirements:
- *Energy density*
- *Charge and discharge rates:* LEO satellites circle the earth in 90 minutes; eclipsed for 35 minutes
- *Depth of Discharge (DOD):* limited to low levels to reduce stress
- *Weight*: Batteries comprise a significant portion of the overall mass, typically 10 to 20%.
- *Lifetime:* Batteries endure about 5,000 cycles per year

- Li-ion batteries (LIBs) are the most popular choice.

Lithium-Ion Batteries
LIBs



# Benefits of Graphene

- Graphite is the main anode material in LIBs
- Graphene adsorb lithium on both sides

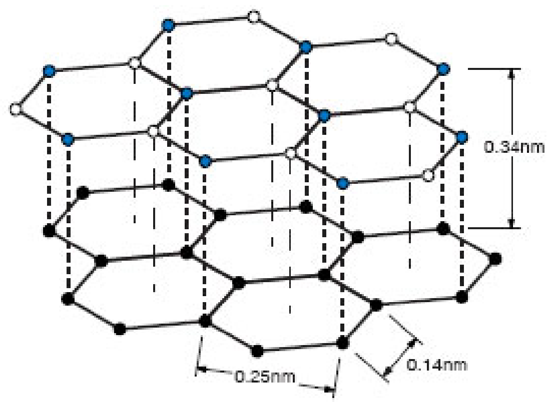
| Anode | Capacity, mAh/g |
|---|---|
| Graphite ($LiC_6$) | 372 |
| Graphene ($LiC_{12}$) | 744 |

- Record in-plane chemical diffusion coefficients for Li at room temperature of up to $7 \times 10^{-5}$ cm$^2$ s$^{-1}$ vs. $10^{-7}$–$10^{-6}$ cm$^2$ s$^{-1}$ in graphite
- Reports of reversible specific capacity as high as 1264 mAh g$^{-1}$ at a current density of 100 mAh g$^{-1}$

Replacing graphite (3D-material) with graphene (2D):

- increased energy
- more power
- fast operation
- reduced weight
- longer battery life

Graphite




Graphene


Tunable interlayer distance
d = 0.335 -0.38 nm

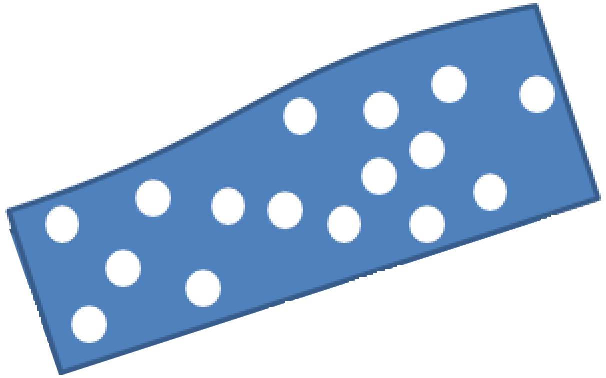
# Technical Challenges

**Graphene**

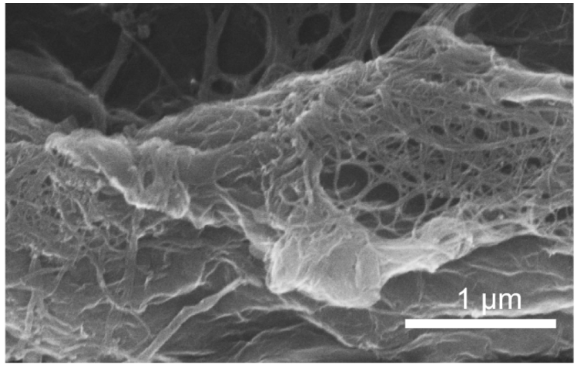

- Graphene re-stacks during electrode preparation and losses advantages over graphite
- Irreversible Li insertion, capacity loss with cycling
- Dendrite growth

## Custom-designed graphene materials for space batteries

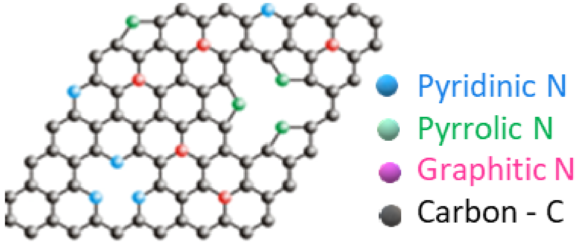
holey graphene



hybrid graphene - carbon nanotubes



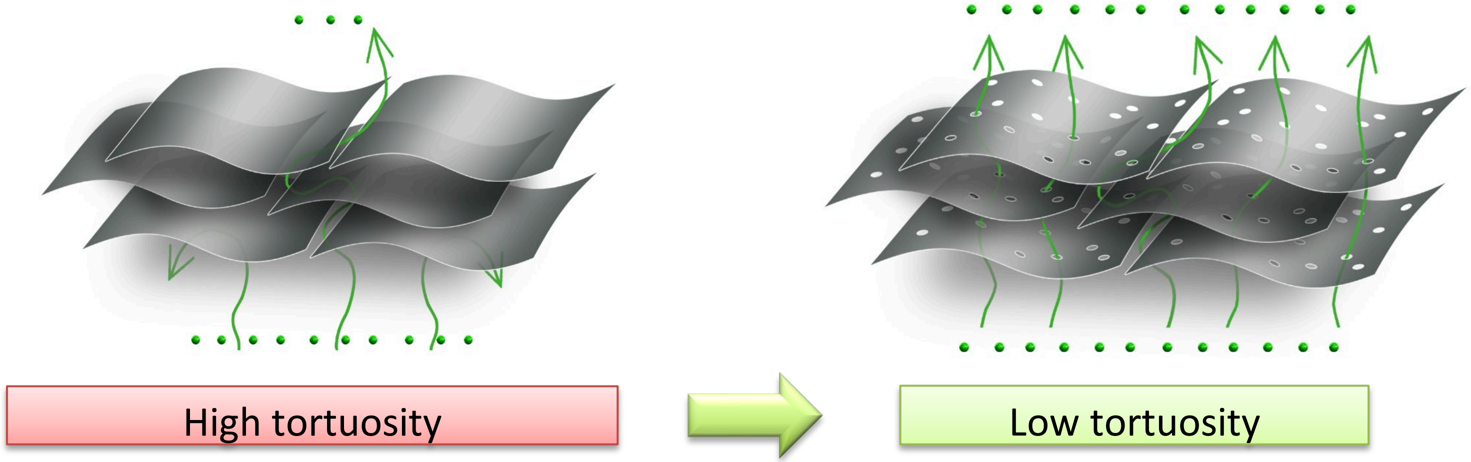

heteroatom doped graphene




added lithiophilic sites

# Holey graphene

- in-plane nano-holes allow fast ion transport
- holey graphene sheets can be densely packed
- in-plane holes allow rapid solvent and air transport to avoid trapped molecules during wet or dry electrode fabrication
- high surface area reduces effective current density and interface fluctuations during cycling, resulting in uniform Li deposition and dendrite suppression
- scalable manufacturing processes



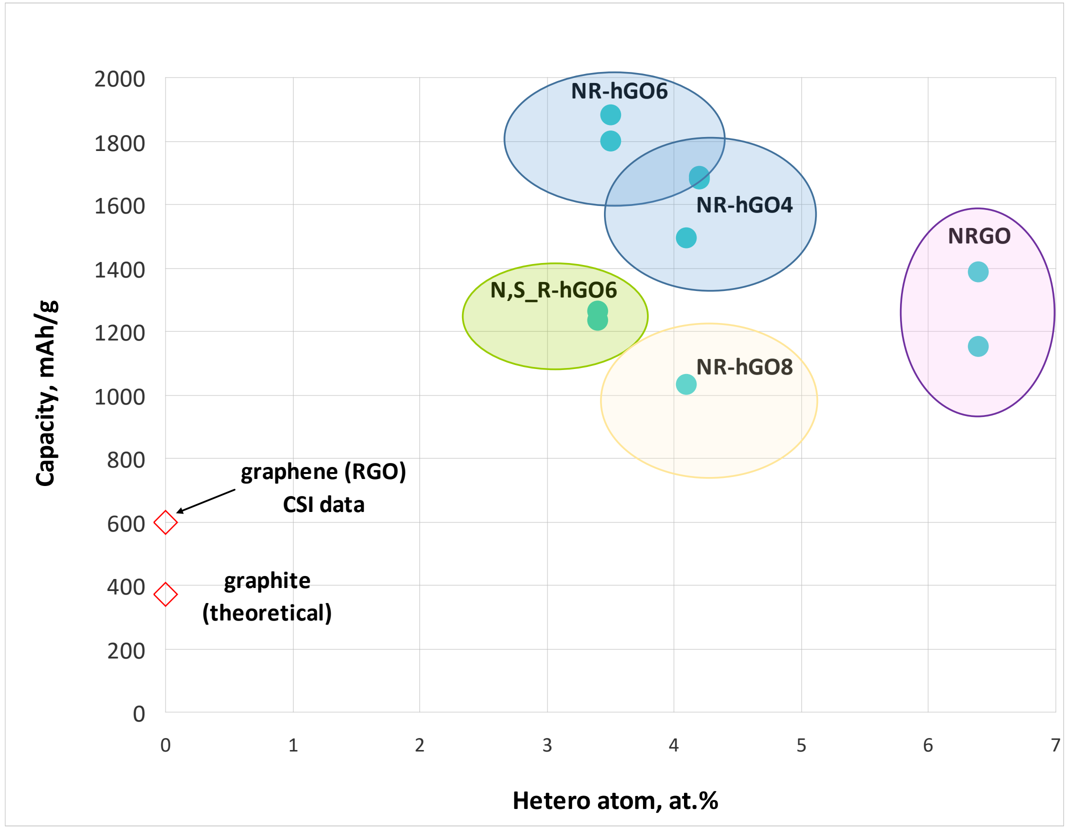

*Liangbing Hu, Nano Lett.* 2015, 15, 7, 4605-4610

# Hetero-atom doped graphene

*Hetero-atoms:*

- improve the interface with electrolyte
- increase the electrical conductivity of graphene
- eliminate dendrite growth: lithiophilic groups such as pyridinic-N, pyrrolic-N and thiophene S act as electron acceptors and facilitate charge transfer with lithium leading to smooth deposition of lithium without formation of dendrites.

Capacity of Graphene Materials as a Function of Hetero-atom Content



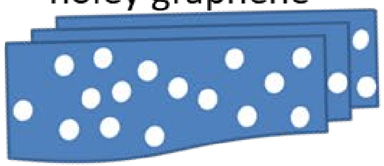

| SAMPLE | Reaction time | N | | | S | |
|---|---|---|---|---|---|---|
| | | pyridinic | pyrrolic | graphitic | C-S-C | $C\text{-}SO_x$ |
| S1: NR-hGO100B | 4 hours | 28 | 63 | 9 | | - |
| S2: NR-hGO96B | 6 hours | 26 | 68 | 6 | | - |
| S3: NR-hGO96C | 8 hours | 28 | 65 | 8 | | - |
| S4: N,S-RhGO-100d | 6 hours | 19 | 72 | 9 | 82 | 18 |

*data from XPS analysis*

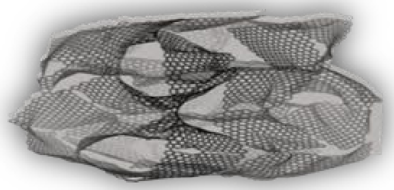
# Technical Approach

## Graphene Materials

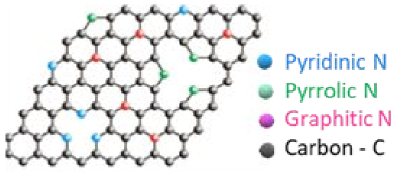
holey graphene



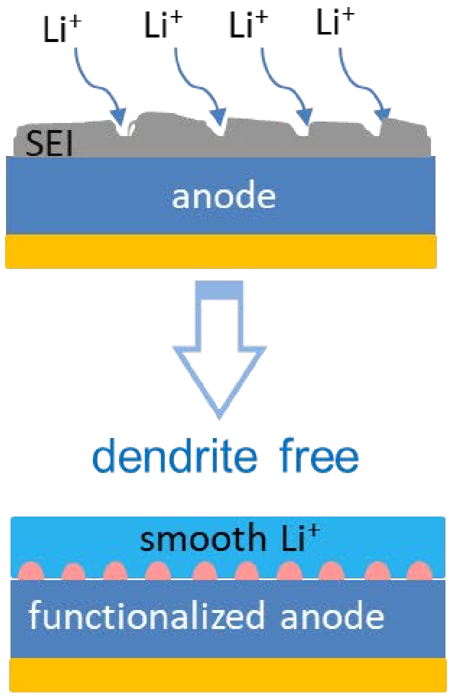
hybrid graphene - carbon nanotube



added lithiophilic sites




## Prelithiation




## Next Generation Lithium Ion Battery

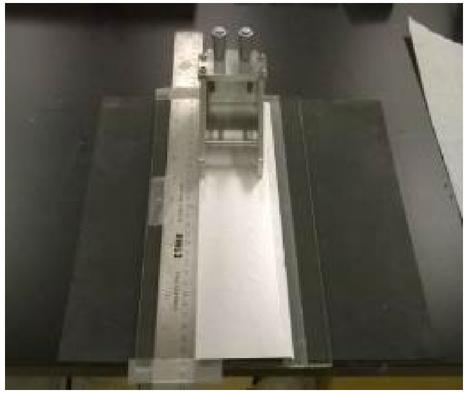

- high energy density
- light weight
- safe dendrite free
- high cycling stability
- long calendar life
- conformal design
- scalable manufacturing

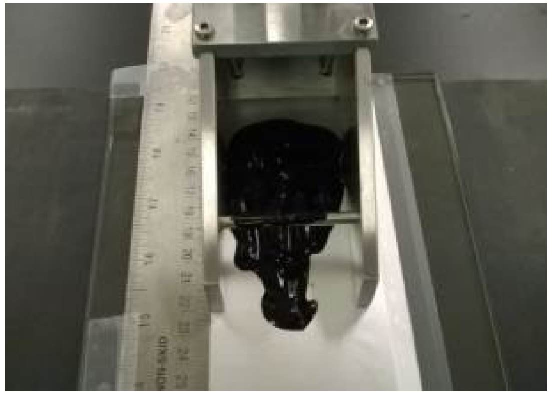
# Preparation of electrodes by doctor blade coating of inks on current collectors

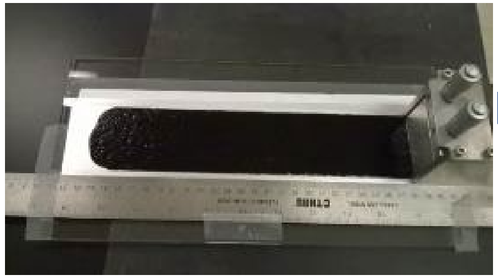

Dry material


Slurry (ink)

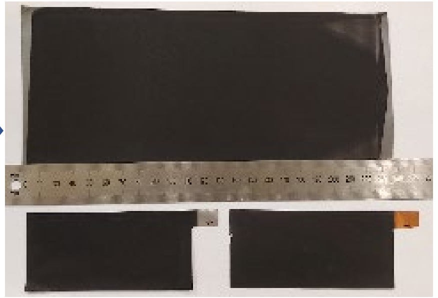

current collectors


Doctor-blade set up


Doctor-blade coating


Coated electrode

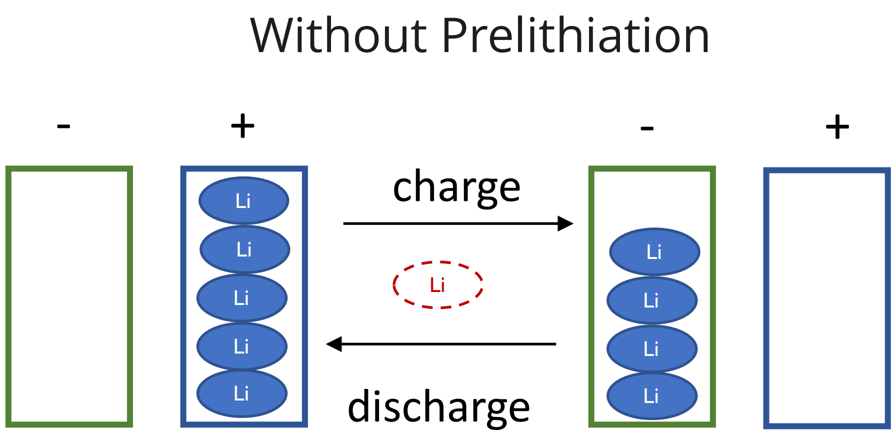

drying

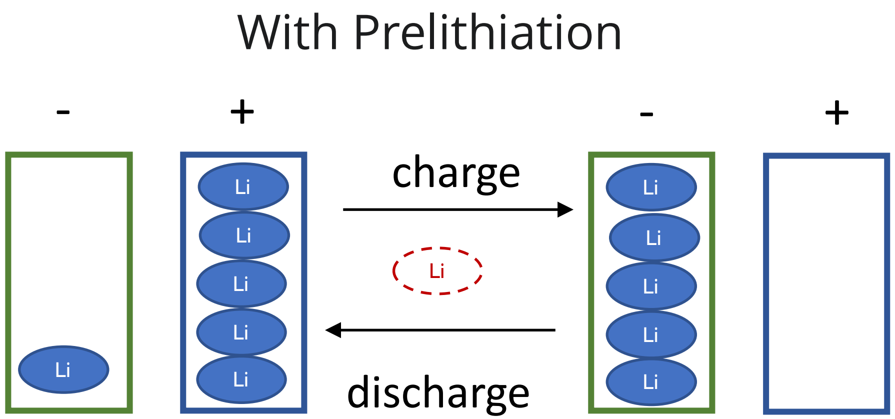

cutting


Anode


Cathode

# Prelithiation of Graphene Anodes

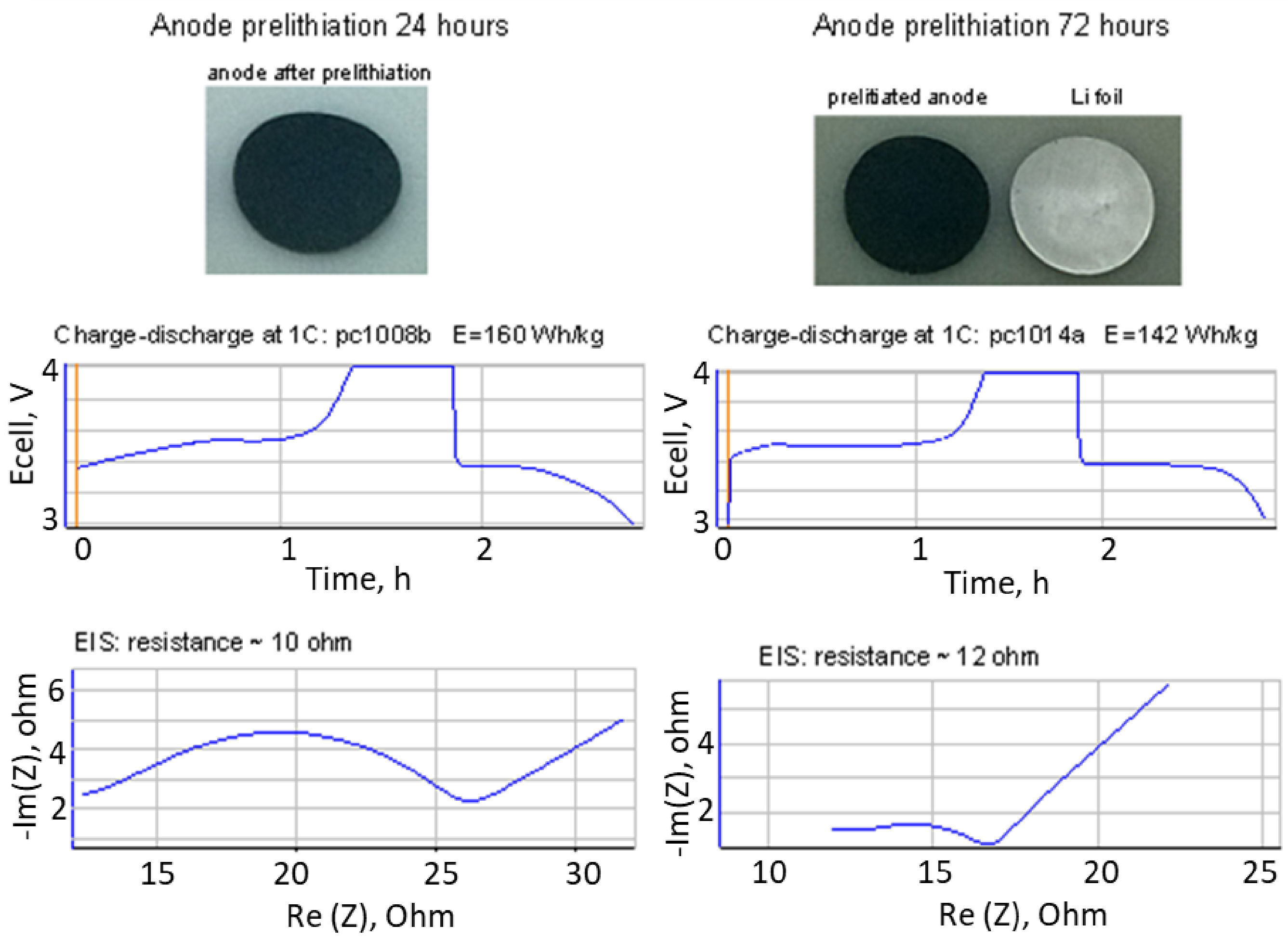



- ❑ Compensates the initial irreversible capacity loss
- ❑ Raises working voltage
- ❑ Decreases electrolyte consumption

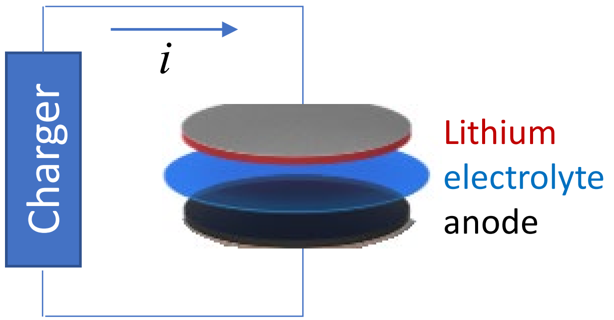
| METHOD | CONCEPT |
| --- | --- |
| **I. Direct contact with lithium** | Li foil in contact with electrode |
| **II. Electrochemical** | Anode assembles with Li metal and electrolyte; low current driven process |
| **III. Additives** | Addition of Li salts to the electrolyte |

# Prelithiation by Direct Contact with Lithium

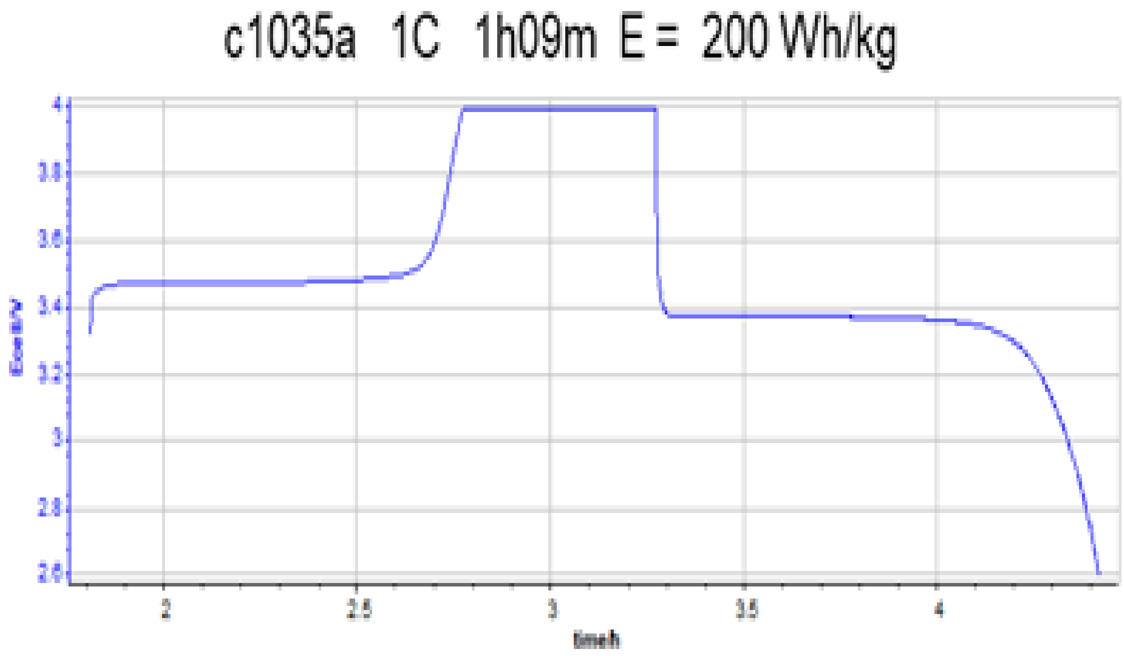



- The anodes prelithiated by direct contact with Li foil resulted in full cells with good energy density (about 150 Wh/kg), but they did not have stable cycling and the cell capacity was continuously decreasing after 5 cycles at 1C.

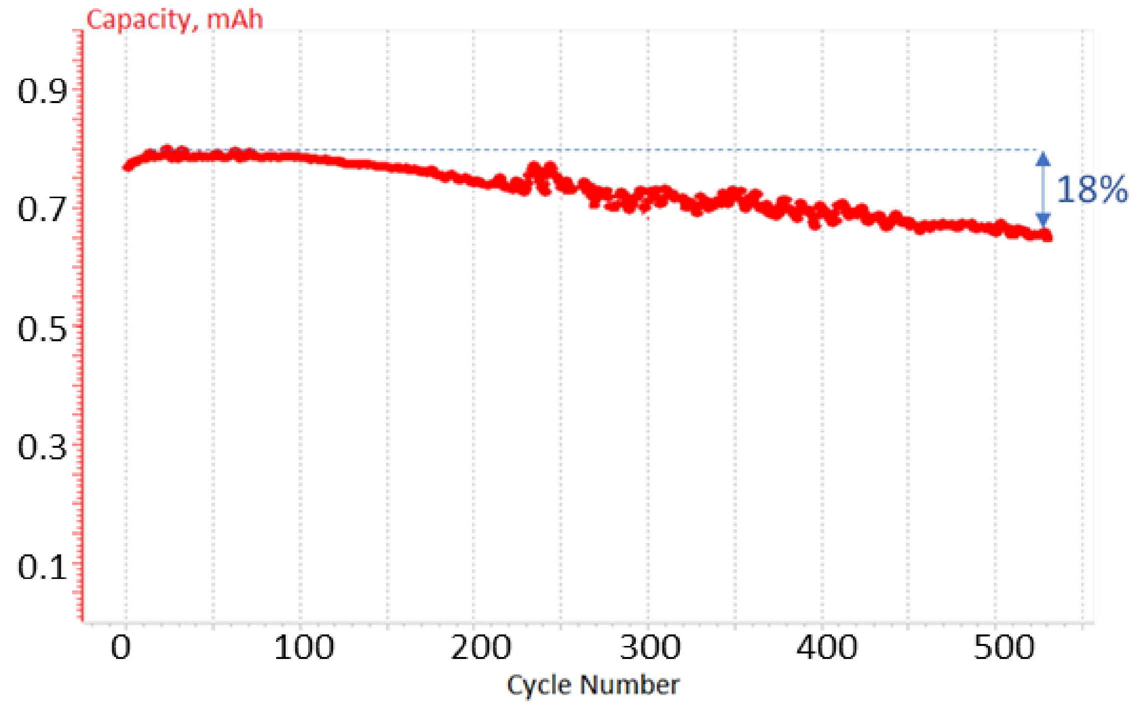
# Electrochemical Prelithiation




**Charge-discharge of a full cell at 1C**



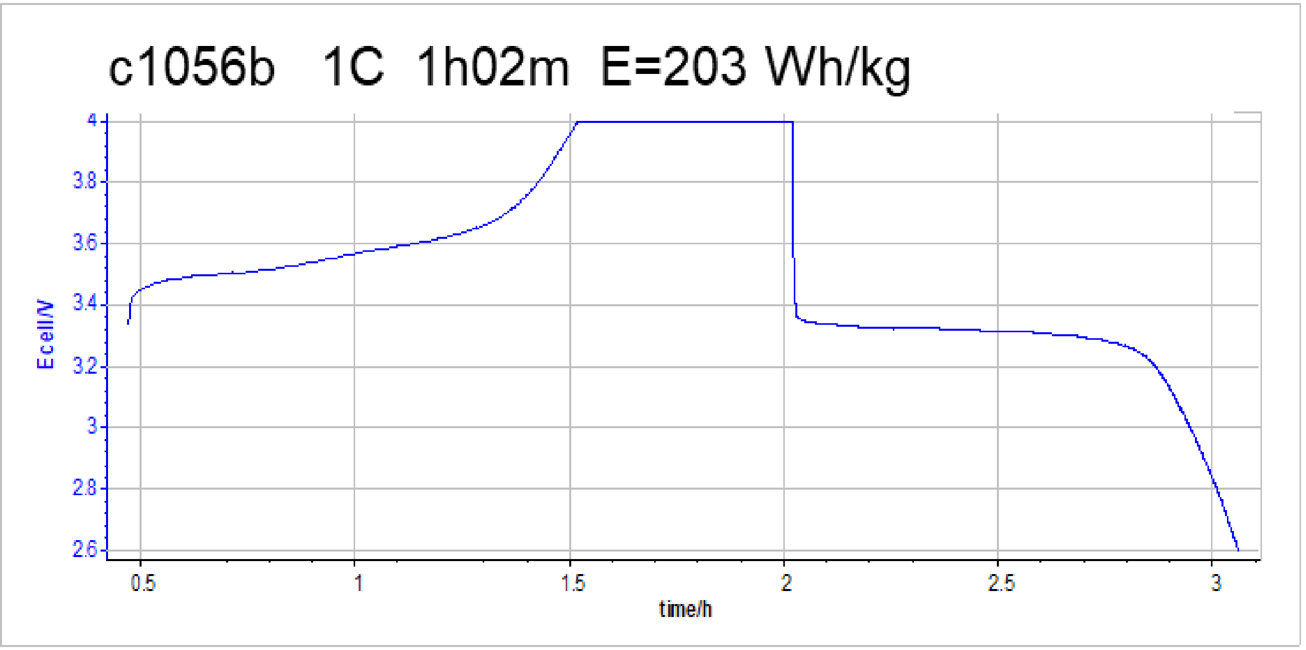

**The cell was cycled at 1C between 2.6 V and 4 V; capacity retention ~82% after 530 cycles**



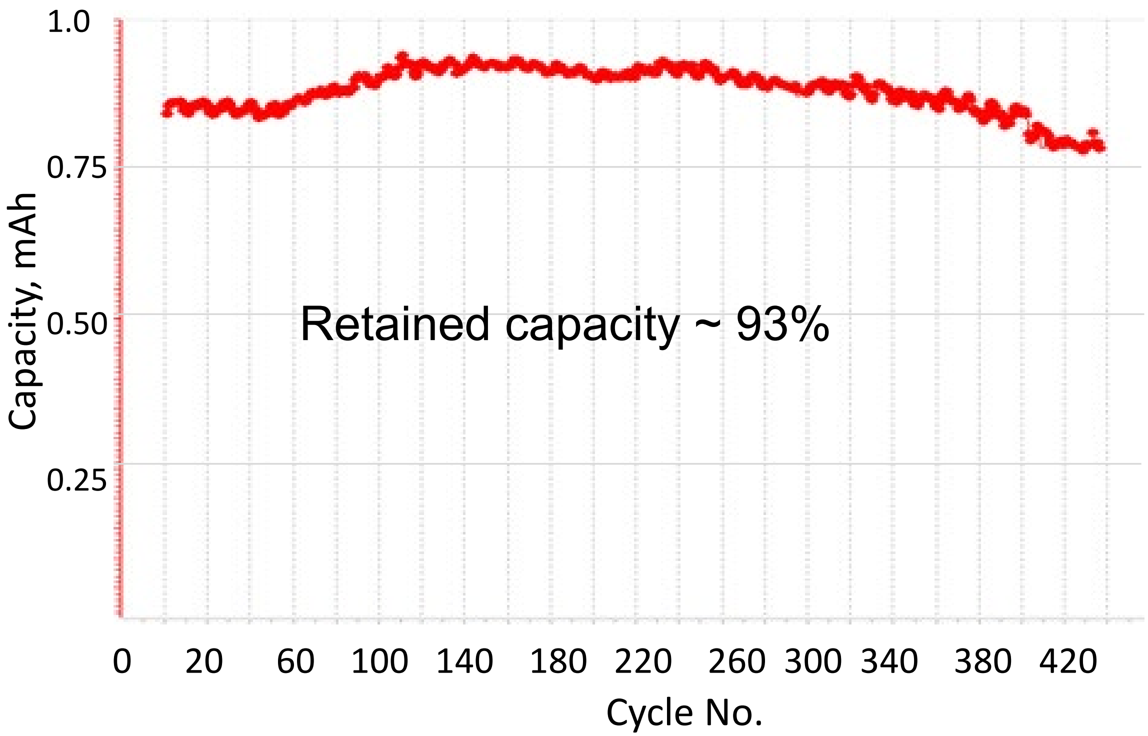
# Optimization of Electrolyte Additives

## Vinylene Carbonate (VC)

**Charge-discharge of Full Cells Built with VC Additive in the Electrolyte**

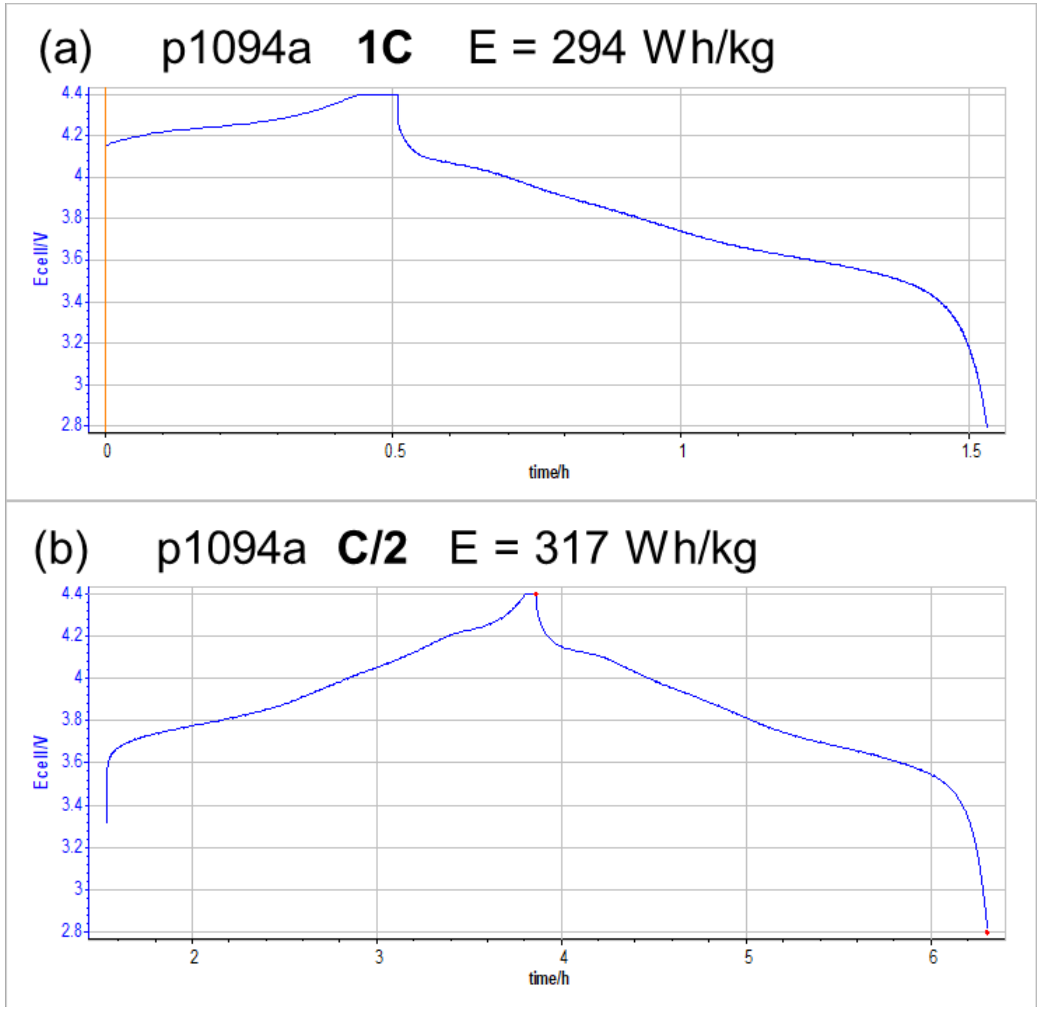



**Capacity vs Cycle Number of a Battery with VC Additive in the Electrolyte**

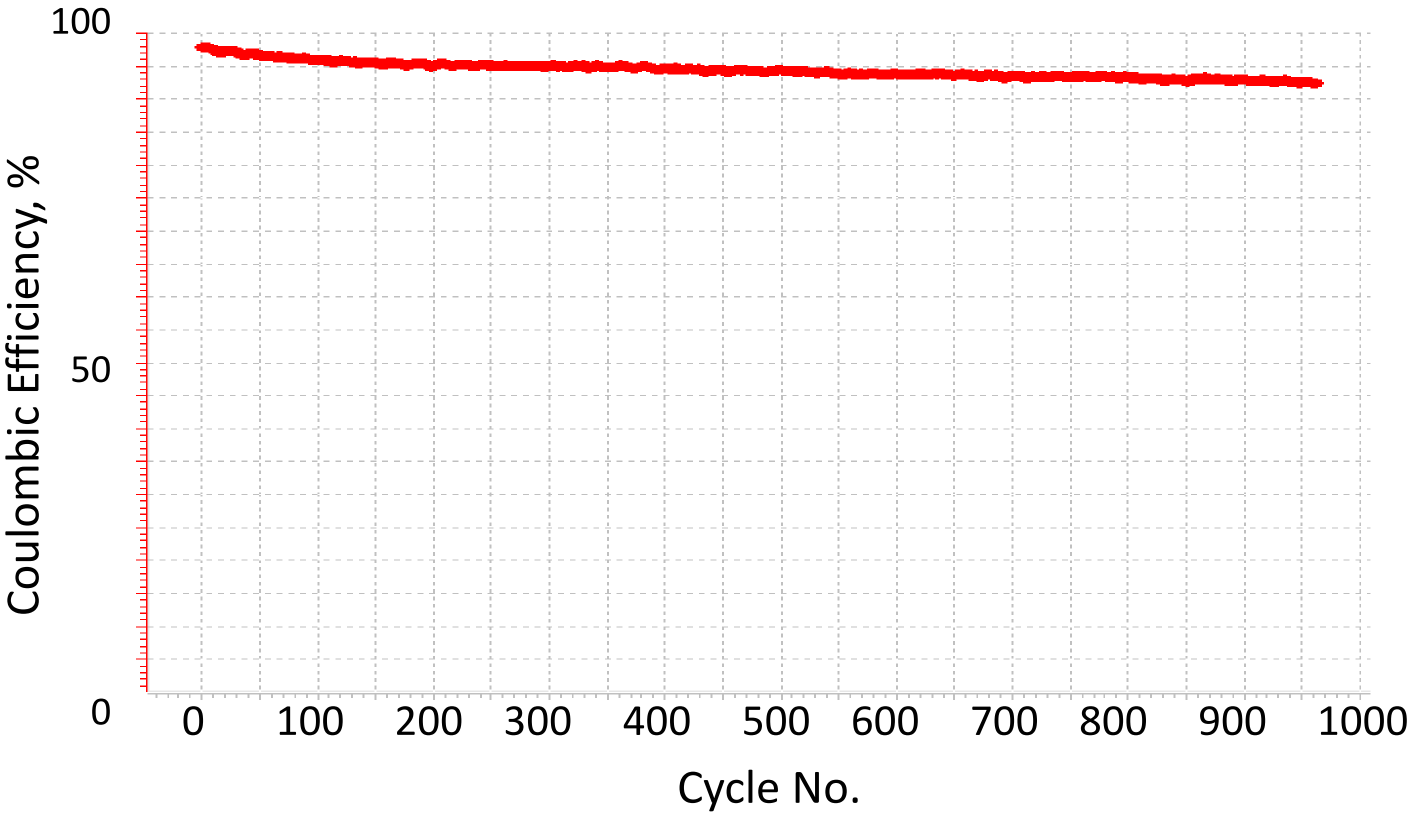


# Pouch Cells with Prelithiated Graphene Anodes

Charge-discharge Profiles of Pouch Cell p1094a
(a) 1C and (b) C/2



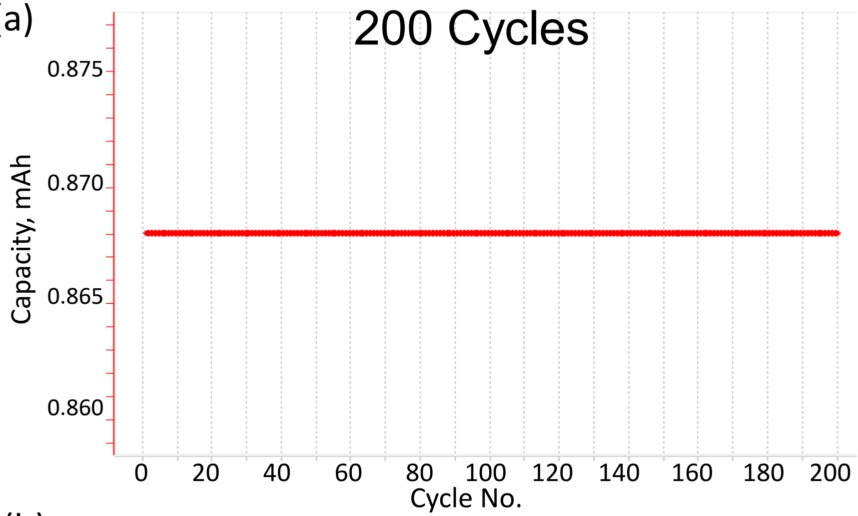

High Coulombic Efficiency



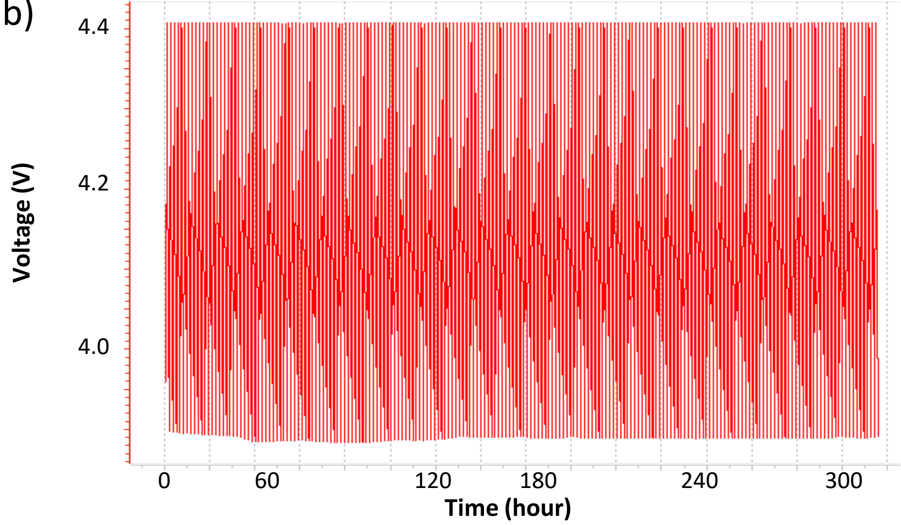
# LEO Cycling of Graphene-based Batteries

Coin cells were cycled continuously at 25 °C with charging rate of C/1.5 and discharge rate of C/2.25 to 40% DOD

(a)

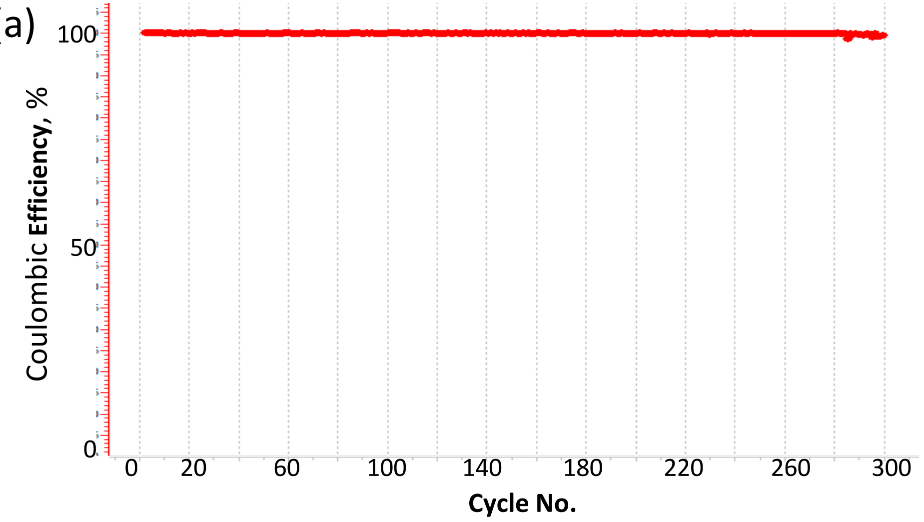



(b)

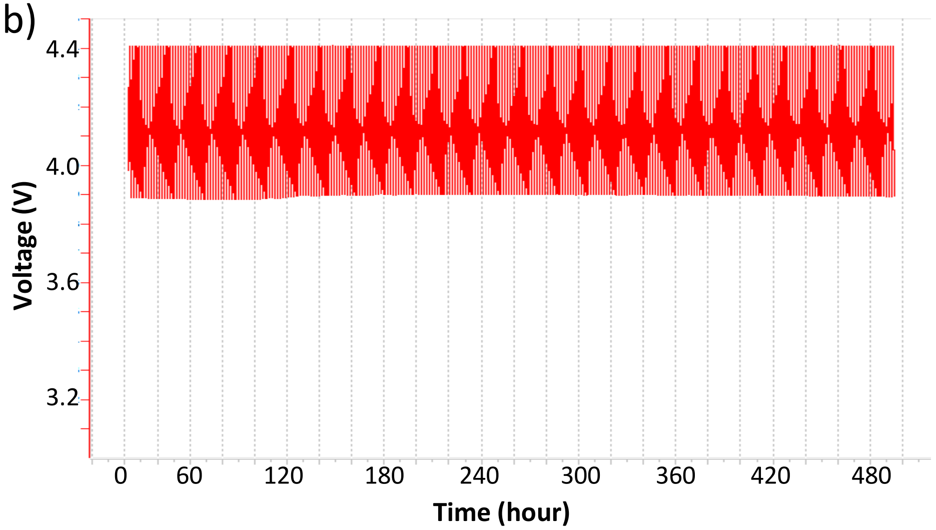



## Additional 300 Cycles

(a)



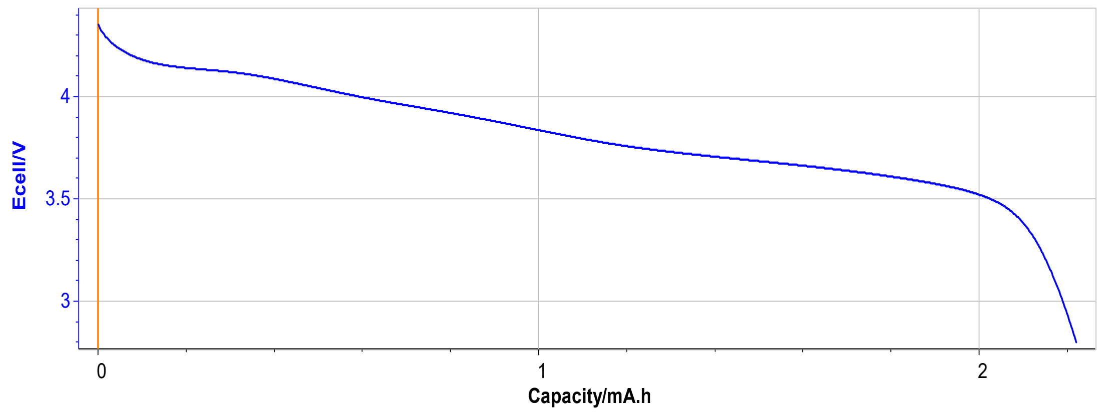

(b)



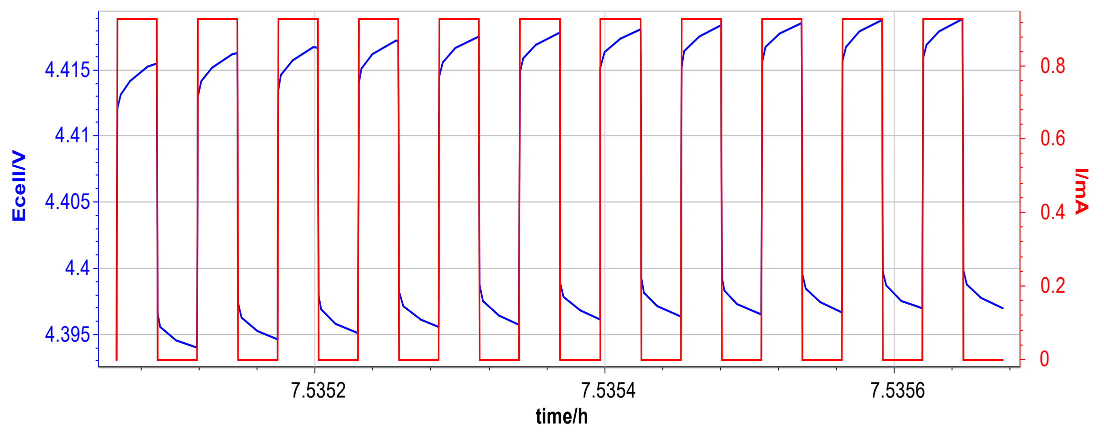
# Battery Characterization: Capacity & Resistance

## Initial Tests

(a) c1089d @C/2.25 E = 319 Wh/kg C = 2.22 mAh

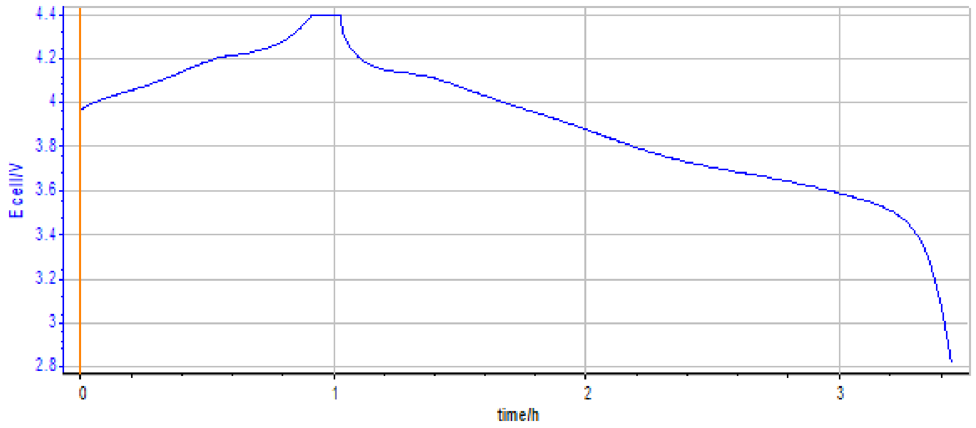



(b) c1089d Rc=16 Ohm

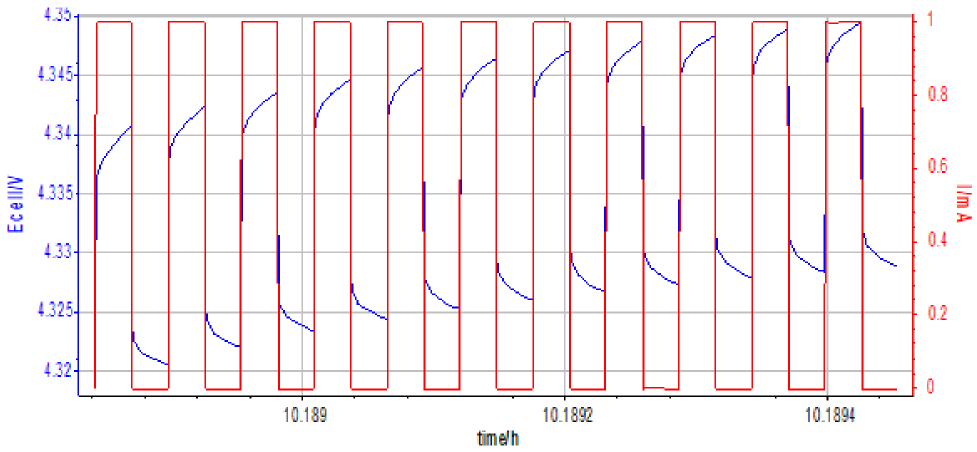



## After 500 LEO cycles

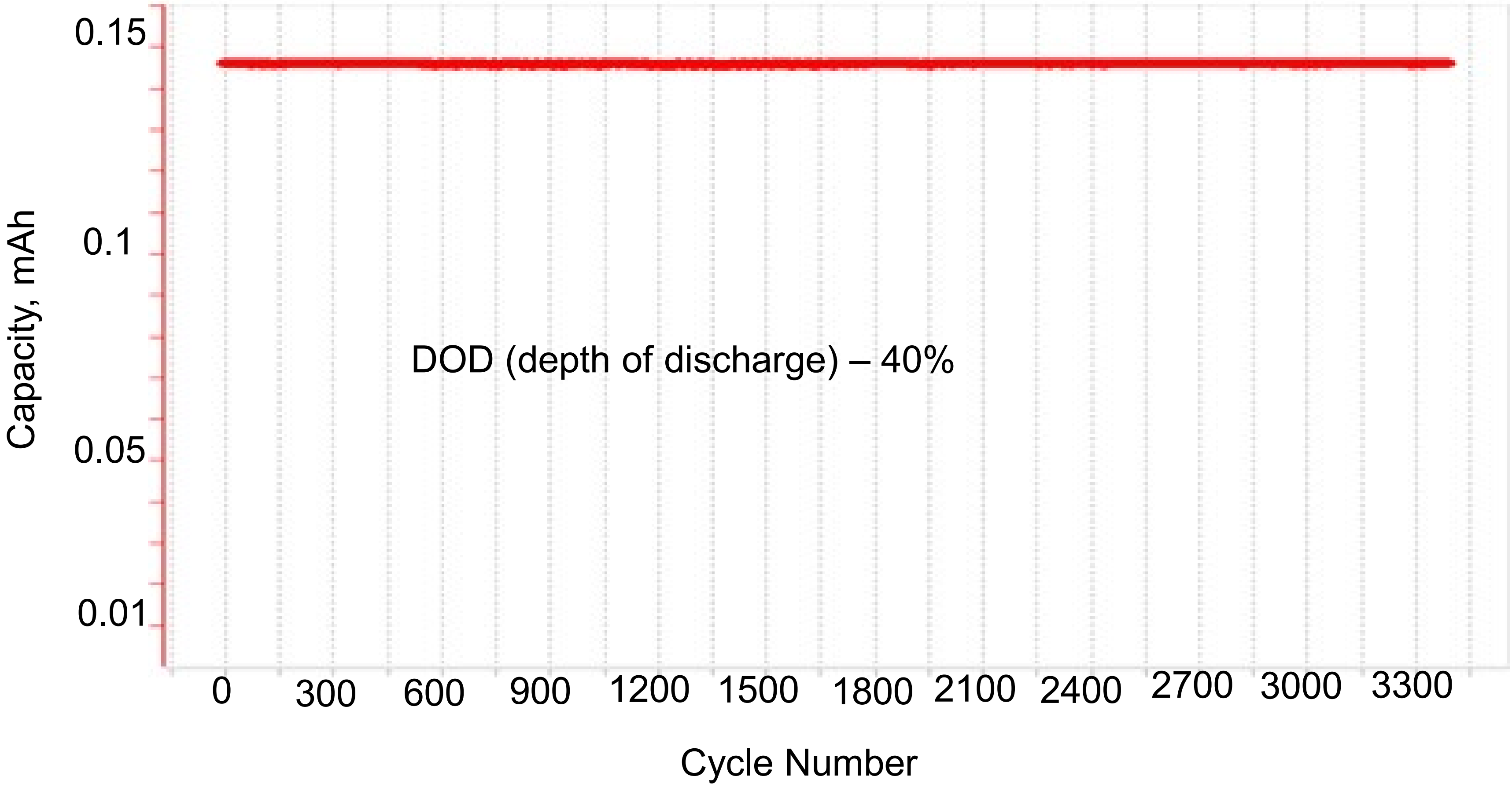
(a) c1089d @C/2.25 E=325Wh/kg C=2.24mAh




(b) c1089d Rc = 13 Ohm



## Stable LEO Cycling of Graphene Battery



## Summary

- Developed graphene-based batteries with energy density in the range of 350 Wh/kg and Coulombic efficiency of >90%
- The optimum graphene materials are comprised of N-doped holey graphene
- The size of the nanoholes in the graphene sheets can be effectively controlled by reaction time
- Heteroaton-doped holey graphene materials exhibit high specific capacity: ~1,500 mAh/g
- The electrochemical prelithiation process produced the highest quality prelithiated anodes.
    - These improvements were critical in achieving graphene batteries with high energy density in the range of 350 Wh/kg and good LEO cycling stability.
- The graphene batteries demonstrated stable performance for 500 cycles at 40% DOD with capacity retention 95 -100 % and stable resistance.
- Graphene batteries show stable LEO cycling for 3,000 cycles (tests continue)

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