The Path Forward for Lithium Metal and Solid State EV Batteries

Lithium Metal Anode Protection:

Enabling Technologies for EV and Battery Industries

Bor Z Jang, Ph.D.

Global Graphene Group (G^3)

Dr. Bor Jang

- G^3 Co-Founder & Chief Scientist
- Pioneer in graphene technology; first to discover graphene in 2002
- Recognized as the world’s No. 1 graphene inventor, a pioneer in graphene-enabled batteries, supercapacitors and fuel cells
- **A total of 580+ US patents & pending applications and numerous foreign patents**

Outline

- A brief introduction to Global Graphene Group (G^3):
- Lithium metal batteries: those rechargeable batteries that contain lithium metal as the primary anode active material, including:
    - Solid-state or quasi-solid state lithium batteries
    - Anode-less lithium batteries (Cells having an initially lithium-free anode or exceptionally low lithium-content anode)
    - Lithium-sulfur battery (sulfur or lithium polysulfide as the cathode material)
    - Lithium-selenium battery (selenium or lithium polyselenide as the cathode material)
    - Lithium-air battery
- Problems associated with lithium metal batteries
    - Continued reactions between liquid electrolyte and lithium metal
    - Lithium dendrites and dead Li particles
    - Solid electrolyte-electrode gap and interfacial impedance
- G^3's lithium metal anode protection technologies
- Summary

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G^3's Li-Metal Anode Protection Technology … Changing the Solid-State Game

- G^3's patented technology **makes solid-state batteries commercially possible** by **decreasing costs** and **dramatically increasing power density**.
- Our elastic polymer anode-protecting layer **prevents dendrite formation**, extending the cycle life of the battery.
- Our graphene protective layer **improves battery performance** and **increases the mileage per charge**.
- Our non-flammable FireShield™ electrolyte offers **unrivaled safety** without sacrificing cycle efficiency.

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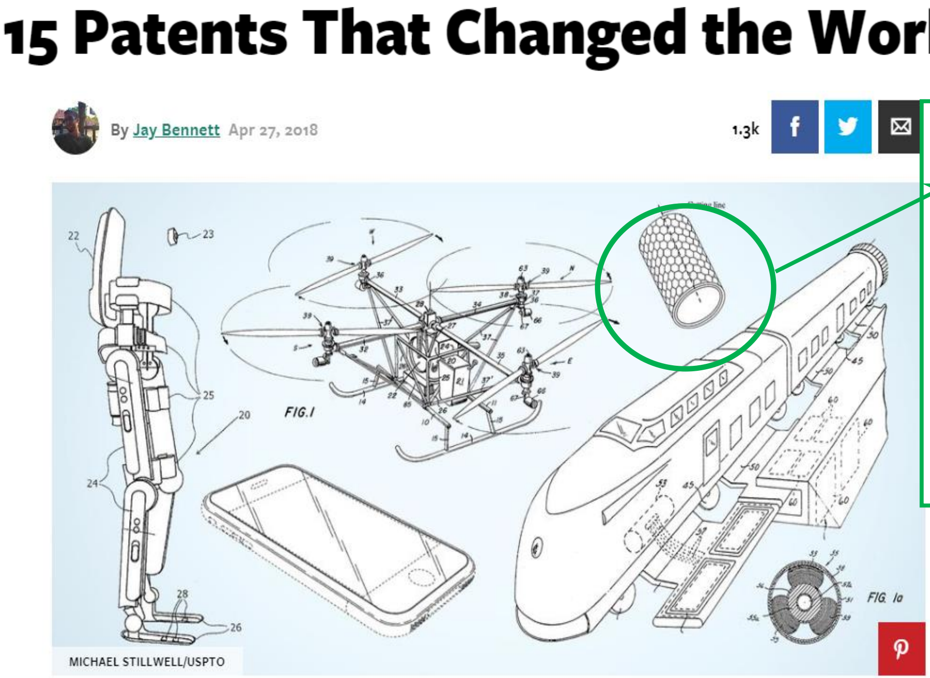
Our IP Noted as One of
"15 Patents that Changed the World"

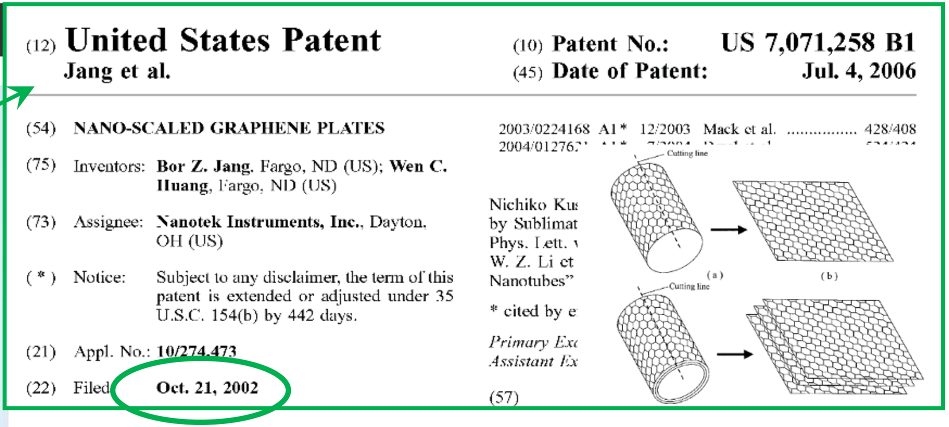


15 Patents That Changed the World

By Jay Bennett Apr 27, 2018

MICHAEL STILLWELL/USPTO

World's first patent on graphene, 10/2002



(12) **United States Patent**
Jang et al.

(10) **Patent No.: US 7,071,258 B1**
(45) **Date of Patent: Jul. 4, 2006**

(54) **NANO-SCALED GRAPHENE PLATES**

(75) Inventors: **Bor Z. Jang**, Fargo, ND (US); **Wen C. Huang**, Fargo, ND (US)

(73) Assignee: **Nanotek Instruments, Inc.**, Dayton, OH (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 442 days.

(21) Appl. No.: **10/274,473**

(22) Filed: **Oct. 21, 2002**

2003/0224168 A1* 12/2003 Mack et al. 428/408
2004/01276

Nichiko Ku
by Sublimat
Phys. Lett.
W. Z. Li et
Nanotubes"

* cited by e

Primary Ex
Assistant Ex

(57)

iPhone, GPS, magnetic levitation, motorized exoskeleton, quadcopter drone, 3D printer, bionic eyes, CRISPR gene editing, brain implant, **graphene**, bluetooth, self-driving car, solar panel, 3G wireless mobile communication, virtual reality

https://www.popularmechanics.com/technology/design/g20051677/patents-changed-the-world/

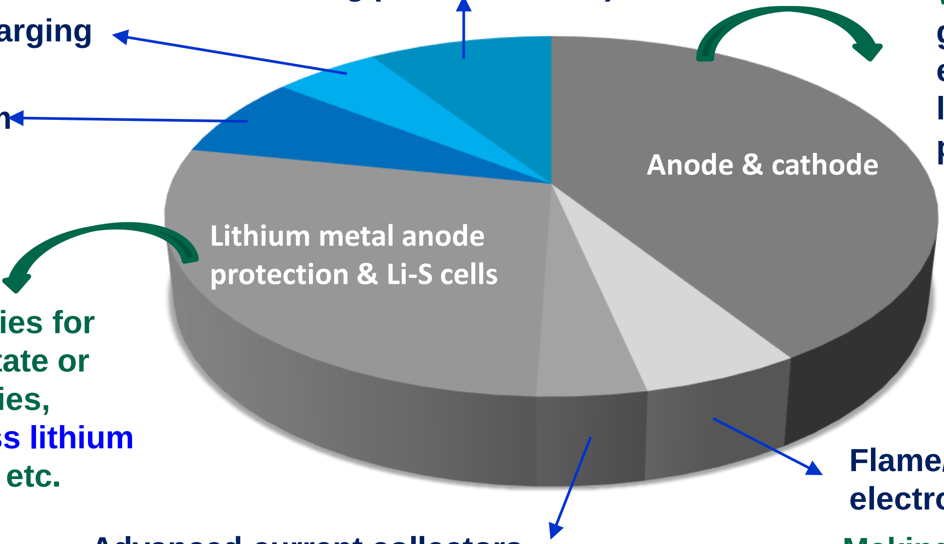
Honeycomb Battery Co. (HBC)

- HBC, a subsidiary of G^3, designs and manufactures next-generation EV battery products
- HBC has 300+ US patents and 100+ foreign patents on next-gen batteries
- 40+ employees in battery business (G^3 currently has 90+ employees)
- Ready to commercialize high-capacity Si anode materials and flame-resistant high-energy lithium batteries for electrified ground, sea, and air transportation

One of the 4 battery-grade dry rooms at HBC/G^3

HBC/G^3's IP Portfolio on Battery Technologies

HBC's critical battery technologies for next-gen EVs are protected by 300+ high-value US patents and 100+ foreign patents



Others (new battery form factors, new manufacturing processes, etc.)

Fast charging

Beyond lithium

Can significantly increase energy density of Li-ion cells from < 250 Wh/kg to 350-400 Wh/kg; including graphene-encapsulated particles, elastomer-coated particles, pre-lithiation and pre-lithiated Si, production of Si nano-wires, etc.

Enabling technologies for next-gen all-solid state or lithium metal batteries, including anode-less lithium cells and Li-S cells, etc. (400-500 Wh/kg)

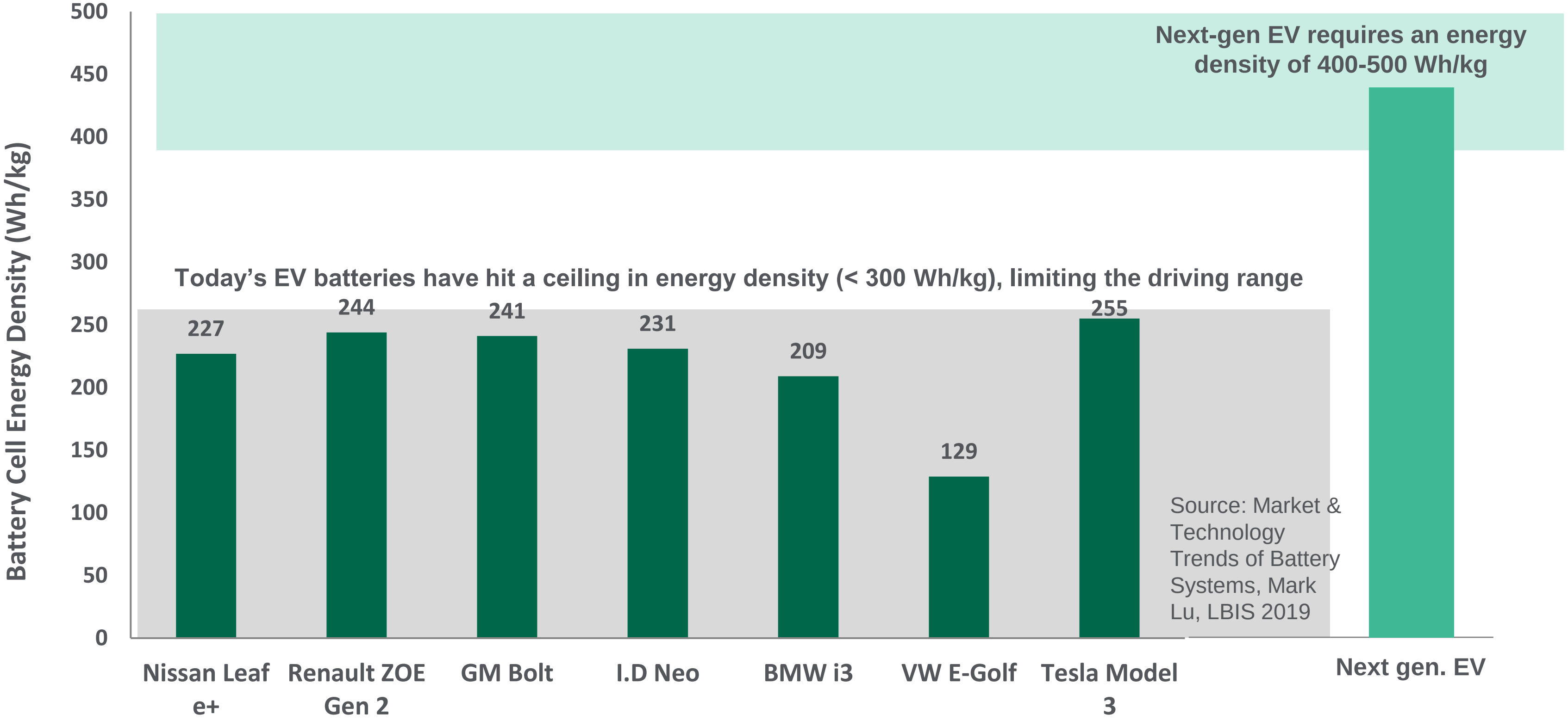
Flame/fire-resistant electrolytes

Making current & next-gen lithium batteries safer

Advanced current collectors
Extending cycle life, operating temperatures & voltages

Conventional Lithium-ion Cells Have Reached Their Performance Limits

The industry needs a revolutionary design for next-gen EV battery



Next-gen EV requires an energy density of 400-500 Wh/kg

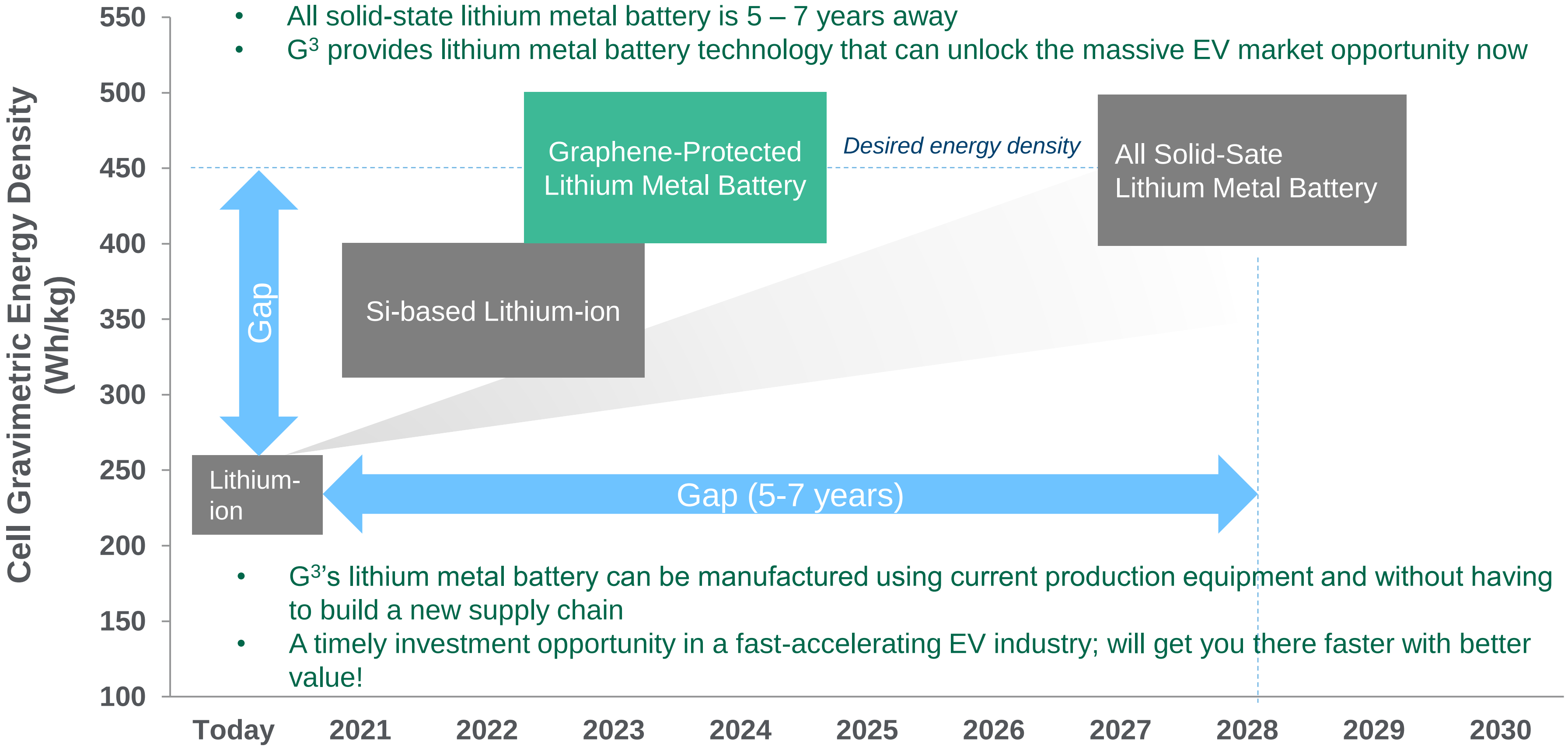
Today's EV batteries have hit a ceiling in energy density (< 300 Wh/kg), limiting the driving range

Source: Market & Technology Trends of Battery Systems, Mark Lu, LBIS 2019

- 400-500 Wh/kg will extend your EV range from 300 miles to 480-600 miles on one battery charge
- Together with a recharge time < 15 minutes, the range anxiety issue can be eliminated

400Wh/kg Lithium Metal Battery Available Today

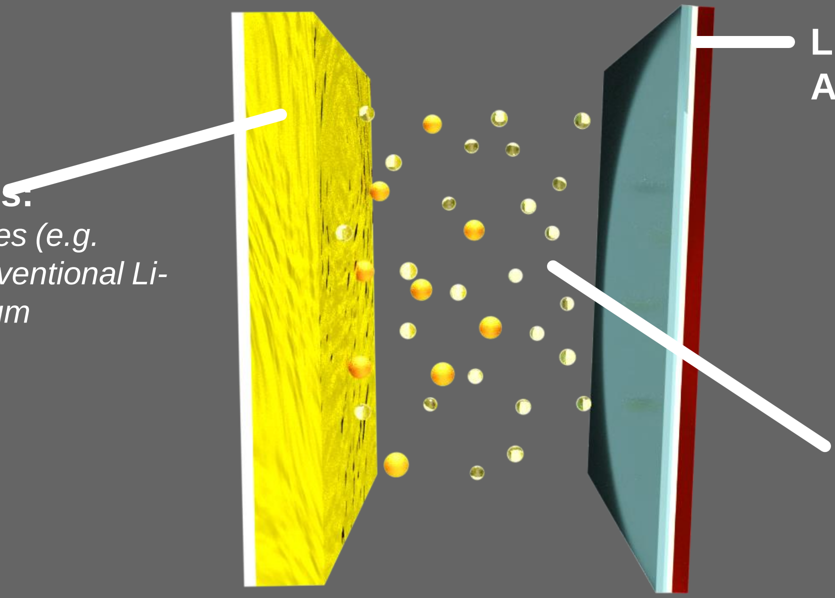
- Li-metal battery has the desired energy density for EV
- All solid-state lithium metal battery is 5 – 7 years away
- G^3 provides lithium metal battery technology that can unlock the massive EV market opportunity now



- G^3's lithium metal battery can be manufactured using current production equipment and without having to build a new supply chain
- A timely investment opportunity in a fast-accelerating EV industry; will get you there faster with better value!

Lithium Metal Batteries (Li Metal as the Anode Active Material)

- Can make use of liquid, polymer gel, quasi-solid, or solid electrolyte (e.g. all solid-state lithium metal batteries)
- Lithium metal film or powder may be implemented at the anode when the cell is made; alternatively, the anode may be initially lithium-free, but receive lithium during a subsequent battery charge ("anode-less" Li metal battery)



Cathode Materials:
high-capacity cathodes (e.g. NCM811 used in conventional Li-ion cells), sulfur, lithium polysulfides, etc.

Li Metal Anode

Electrolyte (Liquid, polymer gel, quasi-solid, or solid)

EV Market Needs: Lithium Metal Batteries

Why?

These batteries can deliver the highest energy densities; providing an EV with the longest driving range on one battery charge (given the same battery weight or volume)

Problems?

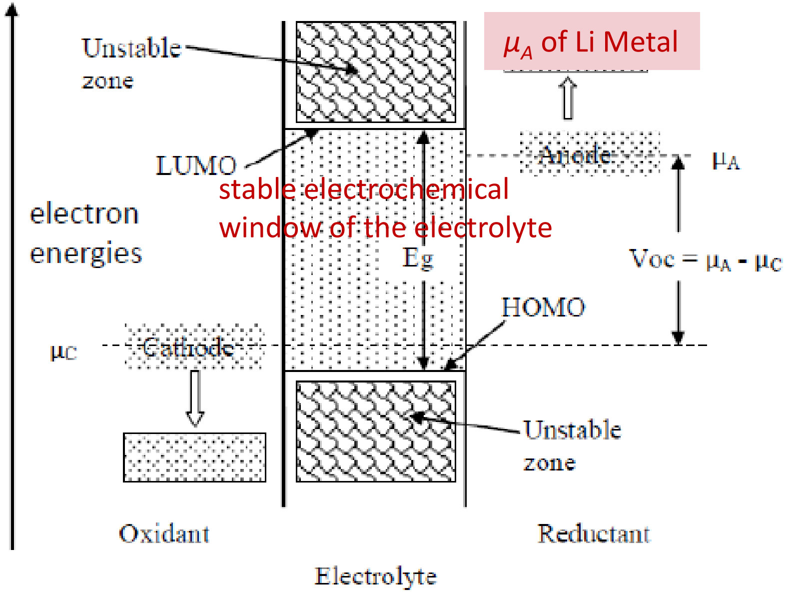
- **Continued reactions between the liquid electrolyte and lithium metal**
  - Electrochemical decomposition of liquid electrolyte and lithium corrosion
  - A major mechanism for Li ion consumption, electrolyte drying, dead lithium particle formation, and gas evolution
- **Lithium dendrites and “dead lithium particles”** (in all types of lithium metal batteries):
  - Can cause internal shorting (fire and explosion hazards)
  - Interfacial instability (e.g. dendrite formation and breakage leads to isolated, inactive lithium particles)
  - Reduced cycle life
- **Large gaps between the lithium metal layer and solid electrolyte and high electrode/electrolyte interfacial resistance** (in all solid-state lithium metal batteries):
  - Reduced power density and poor rate capability (does not perform well under high charge and discharge rates) and reduced cycle life

Three (3) Problems Associated with Lithium Metal Secondary Batteries

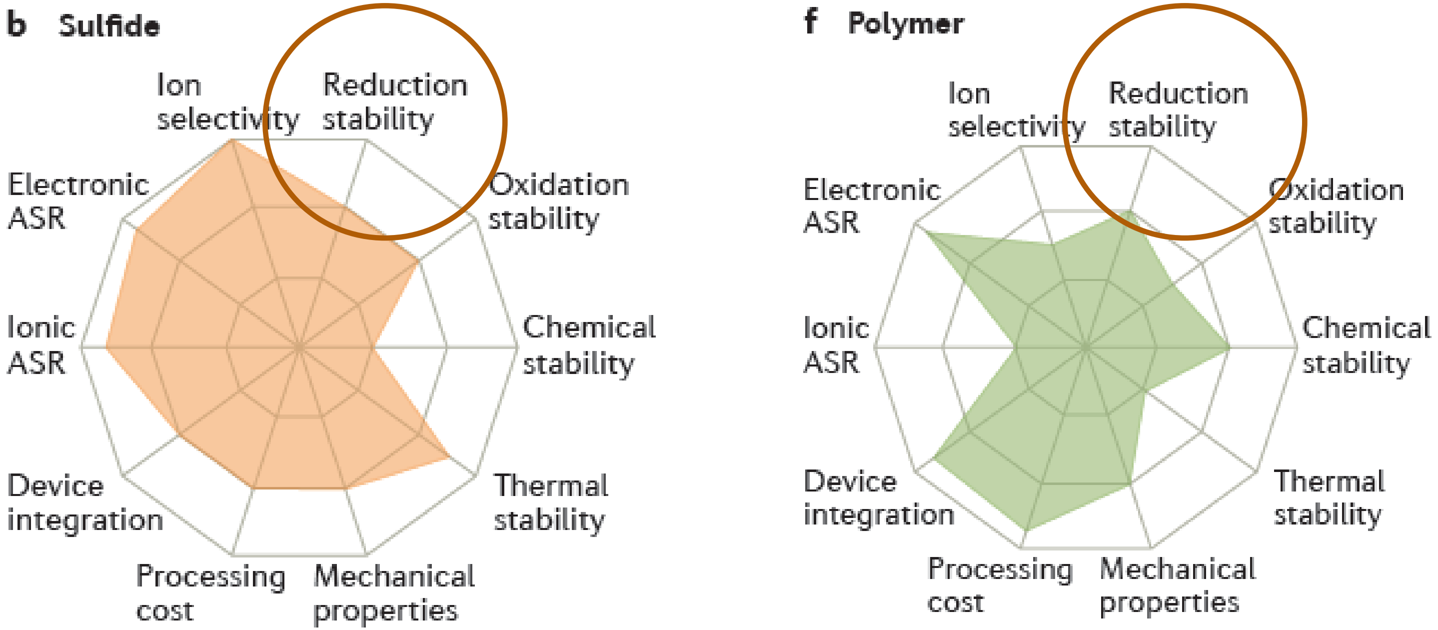
(1) Electrochemical decomposition of liquid electrolyte (e.g. reductive decomposition at the anode)

Why does the electrolyte get decomposed ?

- The thermodynamic stability of the electrolyte is dictated by the relative electron energies (electrochemical potentials) of the two electrodes relative to the energy level of the electrolyte.
- The anode is potentially a reductant, and the cathode an oxidant.
- The energy separation, E_g, between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the electrolyte is the stable electrochemical window.
- In order for the electrolyte to remain stable (i.e. not to decompose), the electrochemical potential of the anode (μ_A) must be maintained below the LUMO and μ_C of the cathode must be above the HOMO.
- An anode with μ_A above the LUMO and a cathode with μ_C below the HOMO will reduce and oxidize the electrolyte, respectively, **unless a passivating film is formed that creates a barrier to electron transfer** between the anode and electrolyte or between the cathode and the electrolyte.
- **Direct and constant contact of liquid electrolyte with lithium metal is a recipe for failure!**



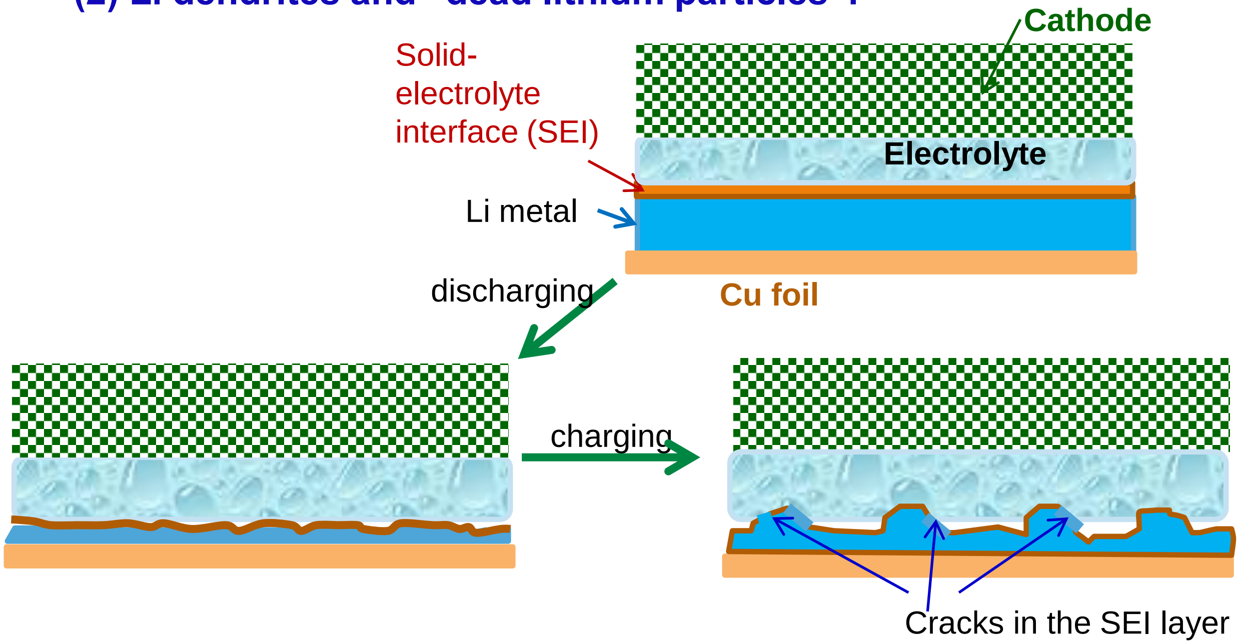
Not just liquid electrolytes, solid electrolytes can react with lithium metal as well



(A. Manthiram, et al. NATURE REVIEWS **MATERIALS, Vol.** 2 | Article No. 16103, 2017.)

Problems Associated with Lithium Metal Secondary Batteries

(2) Li dendrites and "dead lithium particles":


Cathode

Solid-electrolyte interface (SEI)

Electrolyte

Li metal

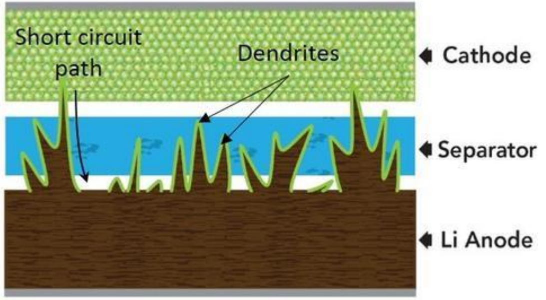
Cu foil

discharging

charging

Cracks in the SEI layer

Li dendrites can shoot out through the cracks



(This image courtesy of SLAC National Laboratory, Stanford University

- **Inhomogeneous flux of incoming Li^+ ions?**
- **Non-uniform electric field?**
- **High local exchange current density?**

Problems Associated with Lithium Metal Secondary Batteries

- Repeated charges/discharges lead to the formation of Li metal dendrites (tree-like features) in the anode
- Dendrites can cause internal shorting (if penetrating through the separator) and inactive "dead" Li particles
- Rapid capacity decay and shortened cycle life

Source: University of Michigan

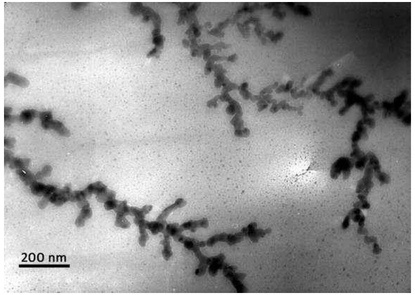
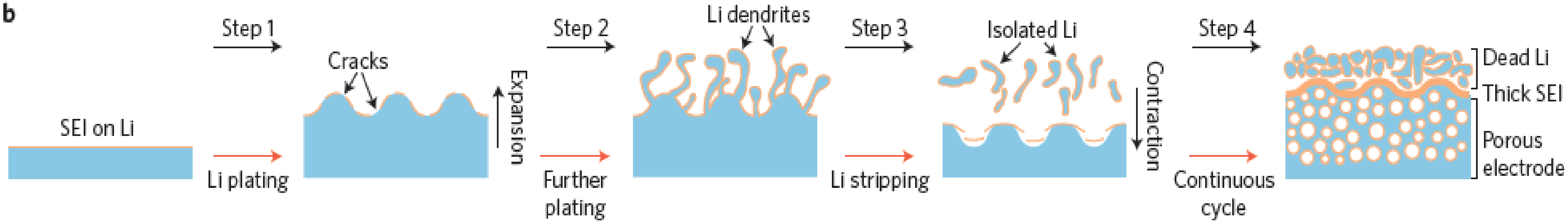


Photo from electronicproducts.com

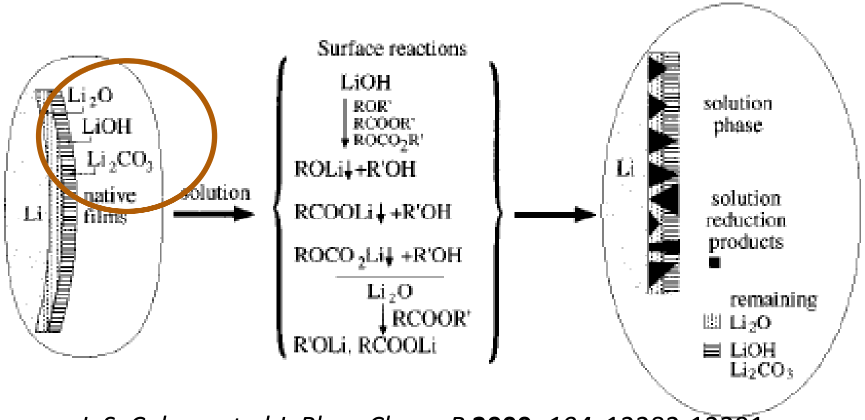


Step 1: Li plating causes volume expansion, which cracks the SEI film. Step 2: further plating causes Li dendrites to shoot out through the cracks. Step 3: Li stripping produces isolated Li which becomes part of the 'dead' Li, while volume contraction results in further SEI fracture. Step 4: Continuous cycling causes steps 1–3 to occur repeatedly, and this finally results in accumulated dead Li, thick SEI and porous Li electrode. (Dingchang Lin, et al. Nature Nanotechnology, March 2017, Vol. 12, 194.)

“The SEI on Li needs to be homogeneous in composition, morphology and ionic conductivity. As there is considerable interface fluctuation during cycling, good flexibility or even an elastic SEI is required.” (D. Lin, et al.)

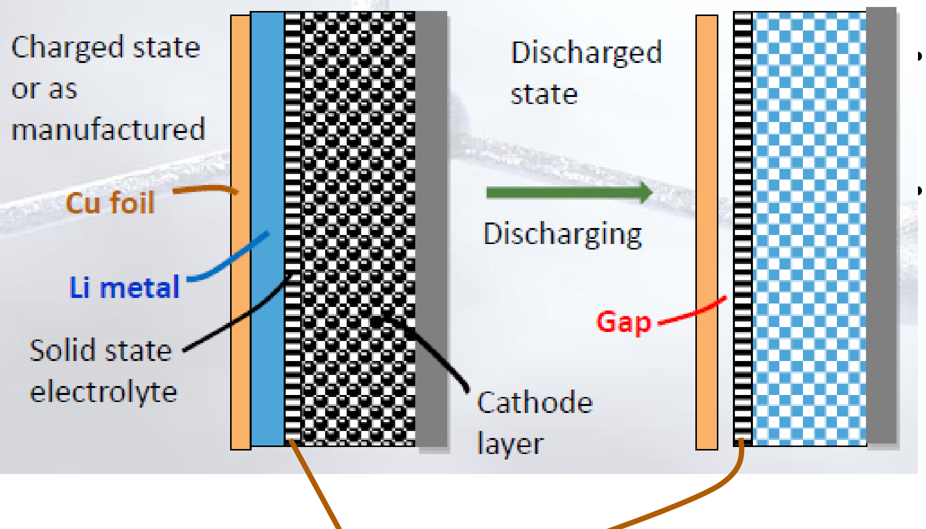
- **SEI must be homogeneous in composition, morphology, and in conductivity**
- **Elastic SEI or flexible interphase on the Li metal surface?**

Natural SEI is not elastic.



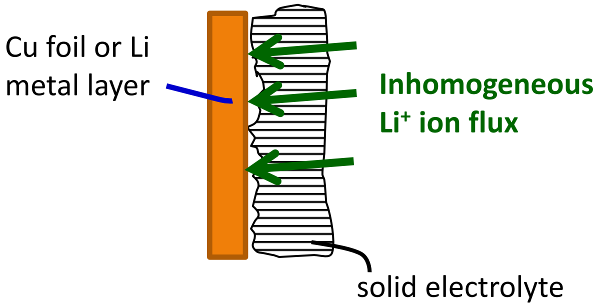
J. S. Cohen, et al J. Phys. Chem. B **2000,** *104,* 12282-12291

(3) Large electrode-electrolyte gaps and interfacial resistance:



Solid-state electrolytes can stop penetration by lithium dendrites, but cannot prevent the formation of dendrites and dead Li particles, which would still lead to a short cycle life.

- This **gap** between a Cu foil and a solid electrolyte makes it challenging to re-deposit lithium metal during subsequent charging
- Even without the gap, the contact between a solid electrolyte and a solid electrode (Cu foil or Li metal layer) is poor, causing a high interfacial impedance



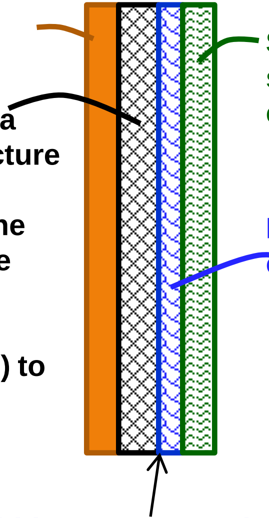
Approaches to Addressing Li Metal-Electrolyte Reactions and Volume Changes

(D. Lin, et al. Nature Nanotechnology, March 2017, Vol. 12, 194)

- Electrolyte engineering for stabilizing Li anodes
    - **Fluorinated compounds**
    - **Self-healing electrostatic shield**
    - **Synergistic effect of Li polysulfide and $LiNO_3$**
    - **High salt concentration**
- Stabilizing Li anode by interface engineering
    - **Artificial SEI**
    - **Nanoscale interfacial engineering**
    - **Homogenizing Li-ion flux**
- Minimizing volume change by using stable hosts
- Guided Li plating and protection
- Preventing dendrite propagation by use of solid electrolyte

Our Differentiating Technologies

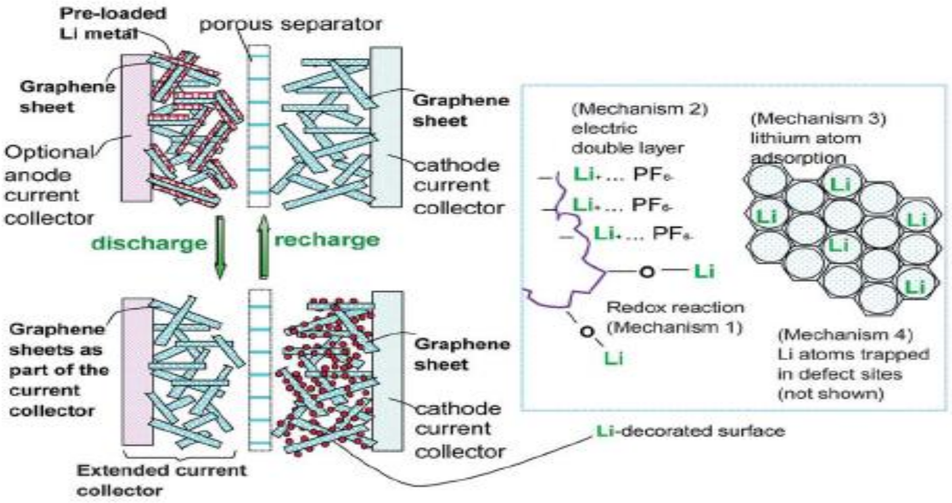
HBC/G3 has 38 US patents (issued or pending) and numerous international patents on an array of **anode-protecting technologies** that are essential to the operation of a long-lasting battery having Li metal as the anode active material (preventing internal shorting, improving solid-liquid interface, eliminating liquid electrolyte-lithium metal interactions, and reducing the formation of dead Li particles near the interface).

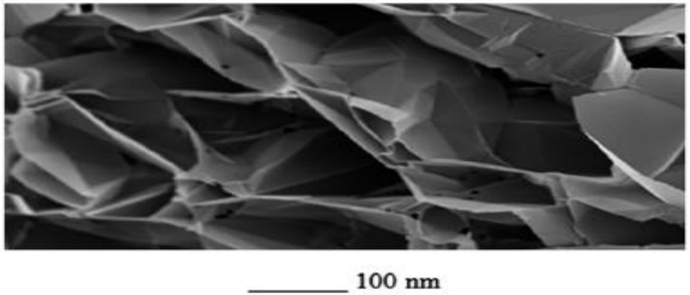


- Graphene-based anode-protecting layer suppresses the initiation and propagation of lithium dendrites (via reducing the local exchange current density and inducing more homogeneous electric current);
- Graphene foam also provide elasticity, enabling close contact between Li metal and solid electrolyte;
- Elastic, ion-conducting polymer layer prevents continued contact between liquid electrolyte and lithium metal;
- Can use either or both protection layers.

Approach 1 (to addressing dendrite issues): Graphene-based Anode-Protecting Layer

- Graphene-based anode-protecting layer, suppressing the initiation and propagation of lithium dendrites (via reducing the local exchange current density & providing a stable host for Li ions)
- Graphene foam provides elasticity, enabling close contact between Li metal and solid-like electrolyte or ceramic separator.





- A. Zhamu, et al. (Bor Z. Jang Group), "Reviving Rechargeable Lithium Metal Batteries: Enabling Next-Generation High-Energy or High-Power Cells," ***Energy & Environment Science***, 2012, **5**, 5701-5707.
- A Zhamu and B. Z. Jang, US Pat. Appl. No. 12/589,999 (11/02/2009); Now US Patent No. 8,236,452 (08/07/2012); US Pat. Appl. No. 12/655,746 (01/07/2010); now US Patent No. 8,962,188 (02/24/2015).

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Dendrite Initiation

Rosso, et al have observed that the dendritic formation is initiated at a time, t_i:

$$t_i = \pi D \left([eCo]/[2J]\right)^2 \left[(\mu_a + \mu_c)/\mu_a\right]^2 \qquad \text{(Eq.1)}$$

J = effective electrode current density,
D = ambipolar diffusion coefficient, e = electronic charge,
Co = initial concentration of ions, and μ_a and μ_c are the anionic and cationic mobilities.
This equation suggests that the dendrite initiation time is proportional to $(1/J)^2$.

(C. Brissot; M. Rosso; J. N. Chazalviel and S. Lascaud, *J. Power Sources* 2001 **97/98,** 804-806.)

- **Cu foil (0.089 m^2/g) replaced by a graphene-based electrode (890 m^2/g);**
- **The effective current density J (unit = mA/cm^2) would be reduced by a factor of 10^5. Hence, the dendrite initiation time would be extended by a factor of 10^{10}.**
- **An original dendrite starting time of 20 hours at 0.1 mA/cm^2 for a conventional Li-polymer cell of Rosso et al would now become 2.0×10^{11} hours.** (22.8 million years)

A. Zhamu, et al. “Reviving Rechargeable Lithium Metal Batteries: Enabling Next-Generation High-Energy or High-Power Cells,” ***Energy & Environment Science***, 2012, **5**, 5701-5707.

Dendrite Propagation

Monroe, et al. develop a comprehensive model to predict the **tip growth rate** (υ_{tip}) of a dendrite, once initiated: (C. Monroe and J. Newman, *J. Electrochem. Soc.* 2003 **150,** A1377-A1384)

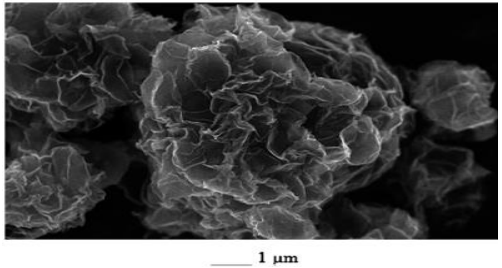
$$\upsilon_{tip} = (J_n V)/F \qquad \textbf{(Eq.2)}$$

J_n = effective current density normal to the dendrite tip,

V = molar volume of lithium, and F = Faraday's constant.

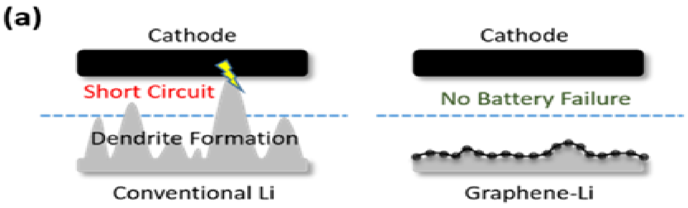
This equation indicates that the dendrite tip growth rate would be slowed down if the current density is reduced.

An original dendrite tip propagation speed of 100 nm/s would now be reduced to 10^{-3} nm/s, requiring 10^{8} seconds (27,777 hours or 31.7 years) to penetrate through a 100 μm thick layer of "electrode + separator" to cause internal short-circuiting.

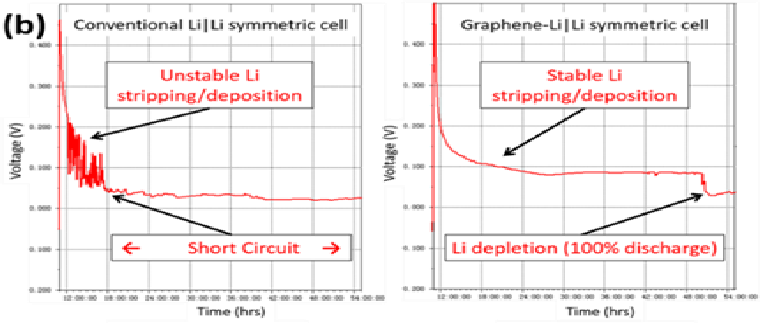


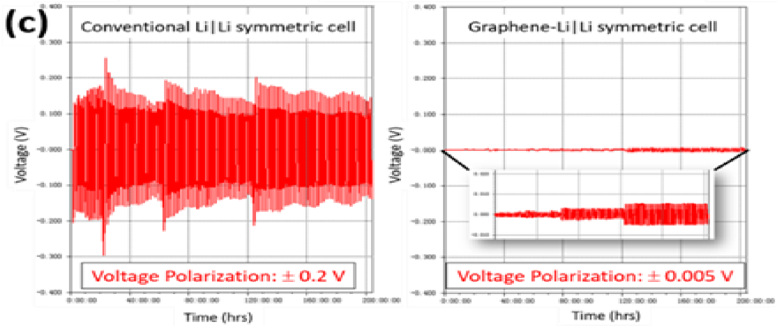
A. Zhamu, et al., "Reviving Rechargeable Lithium Metal Batteries: Enabling Next-Generation High-Energy or High-Power Cells," ***Energy & Environment Science***, 2012, **5**, 5701-5707.

Graphene-Protected Lithium Metal Anode

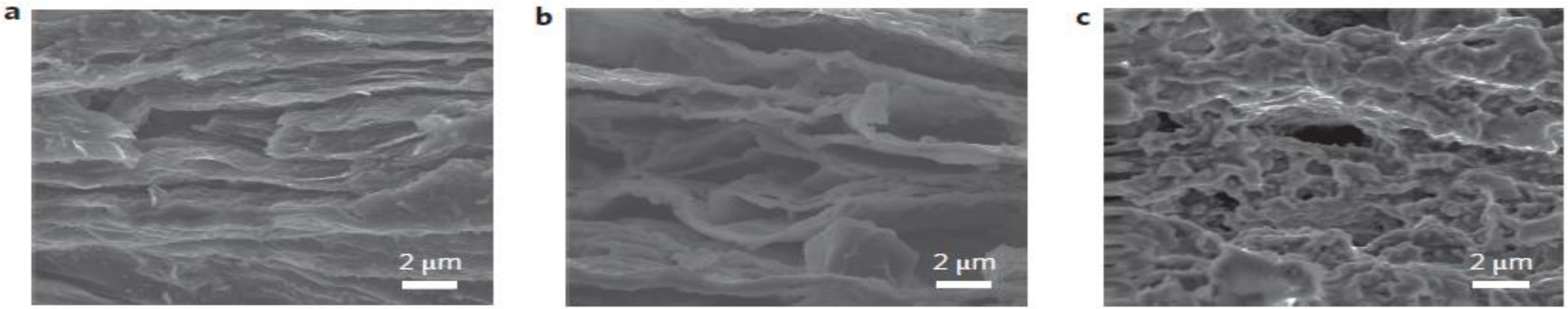


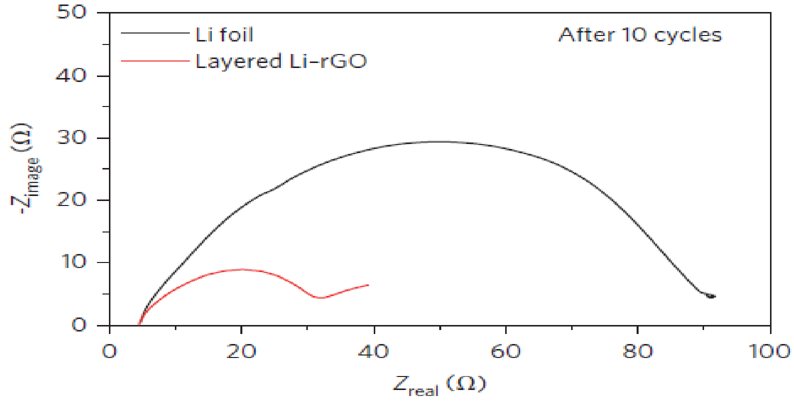
- With graphene, the lithium metal anode forms a much more stable surface during cycling
- Figure (b) shows that graphene-Li anode provides stable Li stripping/deposition, therefore no short circuit occurs before 100% DoD
- Figure (c) suggests that the graphene-Li anode exhibits much less polarization compared to un-protected Li anode



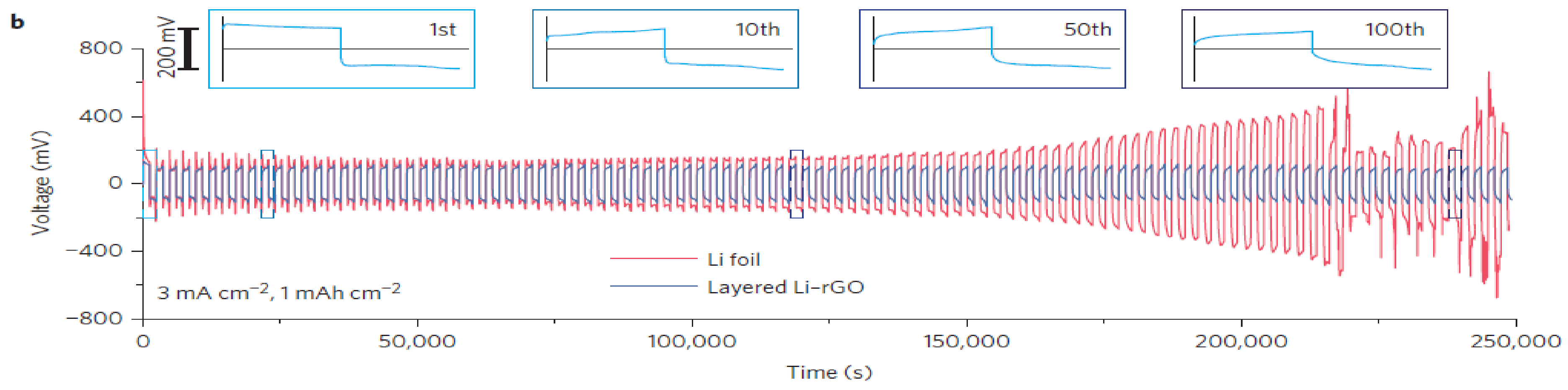


Dendrites: gaps between graphene sheets?

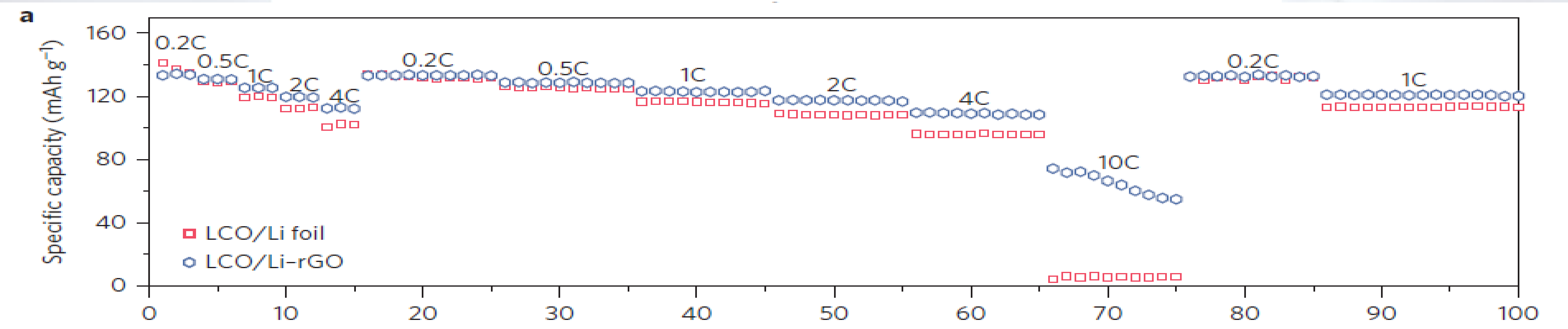




Dingchang Lin (**Yi Cui Group**), "Layered reduced graphene oxide with nanoscale interlayer gaps as a stable host for lithium metal anodes," **Nature Nanotechnology**, PUBLISHED ONLINE: 21 MARCH 2016 | DOI: 10.1038/NNANO.2016.32.



Galvanostatic cycling of a symmetric Li-rGO electrode (blue) and bare Li foil (red)



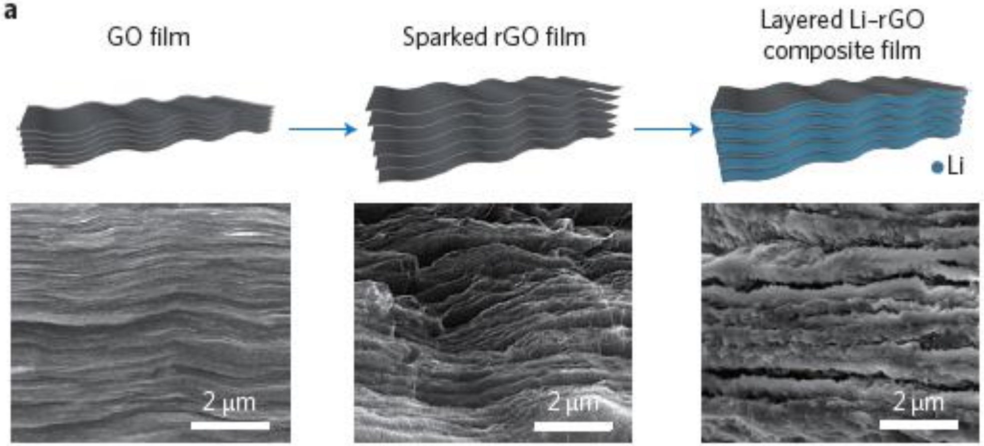
(Lin, D. *et al.*)

Stable Host for Li Metal

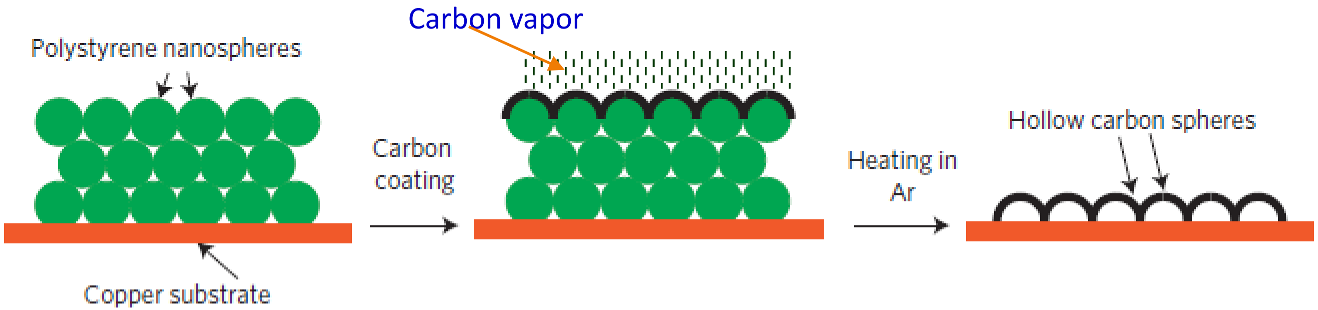
Advantages:

- A stable host minimizes the volume variation by dividing dense Li into smaller domains;
- The increased active Li surface greatly reduces the effective current density, homogenizing the ion flux and further suppressing dendrites;
- Stable volume can be maintained at the electrode level to avoid stress fluctuation within a cell, thus minimizing safety concerns.

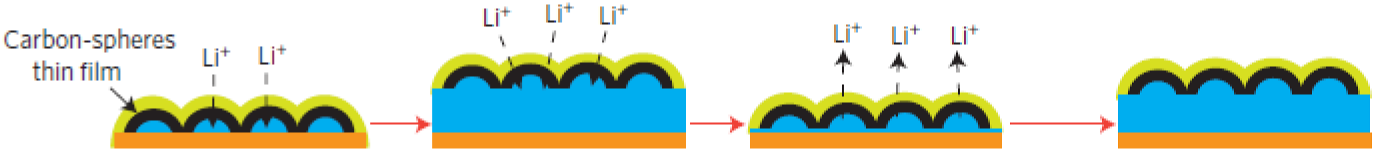
Lin, D. *et al.* Layered reduced graphene oxide with nanoscale interlayer gaps as a stable host for lithium metal anodes. *Nat. Nanotech.* **11,** 626–632 (2016)

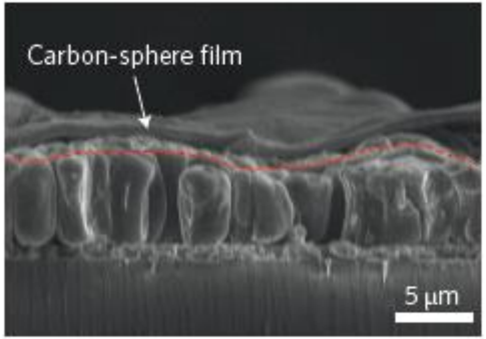


(G. Zheng, et al. *Nat. Nanotech.* **2014**, *9*, 618)



- Polystyrene nanoparticles are first deposited onto the Cu substrate
- A thin film of amorphous carbon is coated on top of the polystyrene array using flash-evaporation of carbon cord
- Thermal decomposition of the polystyrene template results in the formation of interconnected hollow carbon nano-spheres

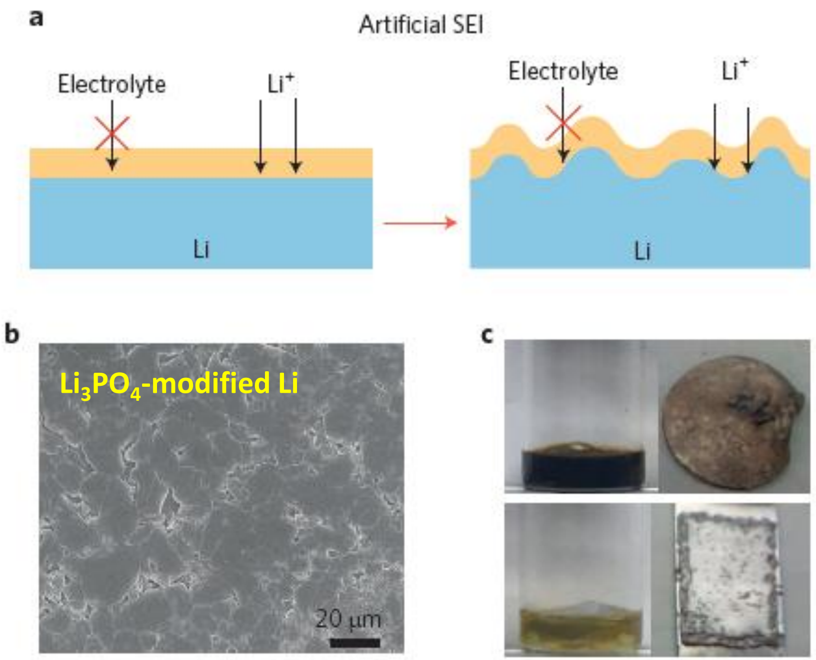




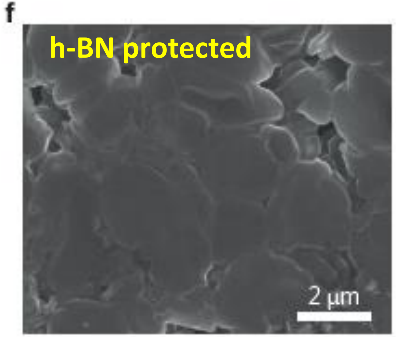
- Schematic showing how interconnected hollow carbon spheres create a scaffold for stabilizing the SEI layer. The volumetric change of the Li deposition process is accommodated by the coating of hollow carbon nano-spheres.
- Cross-section SEM image showing columnar Li deposited underneath carbon nano-sphere layer, with more uniform Li distribution .

This SEI/Carbon layer is really not that flexible; it is fragile.

Artificial SEI and Nanoscale interfacial engineering



- Conventional artificial SEI layers are too brittle, too difficult to make, or too rigid (not elastic);
- Some elastic films are not lithium ion-conducting.



a, design principles and mechanisms of artificial SEI. **b**, Top-view SEM images of **Li_3PO_4-modified Li anode** after 200 cycles. **c**, Optical images of pristine (top) and 14 nm ALD **Al_2O_3-protected** (bottom) Li metal foil soaked in 1 M sulfur/DME solution for 7 days. **f**, Top-view SEM image after the first Li deposition on **a h-BN protected** anode

(D. Lin, et al. Nature Nanotechnology, March 2017, Vol. 12, 194)

Approach 2: High-elasticity polymer-based anode-protecting layer

"Lithium Anode-Protecting Polymer Layer for a Lithium Metal Secondary Battery and Manufacturing Method," US Patent Application No. 15/485,934 (04/12/2017); patent allowed, issue fee paid.
"Lithium Metal Secondary Battery Containing an Anode –Protecting Layer," US Patent No. 10,770,721 (09/08/2020).
"Lithium Metal Secondary Battery Featuring an Anode-Protecting Layer," US Patent No. 10,727,531 (07/28/2020).
"Lithium Metal Secondary Battery Containing Two Anode-Protecting Layers," US Patent No. 10,784,509 (09/24/2020).

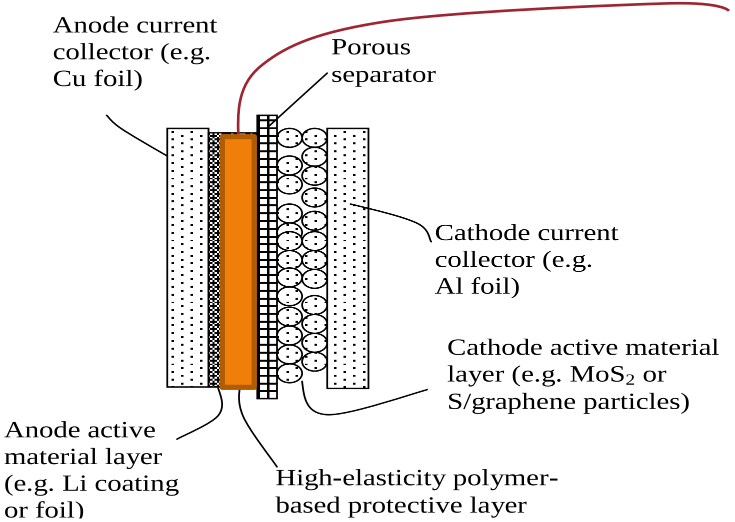
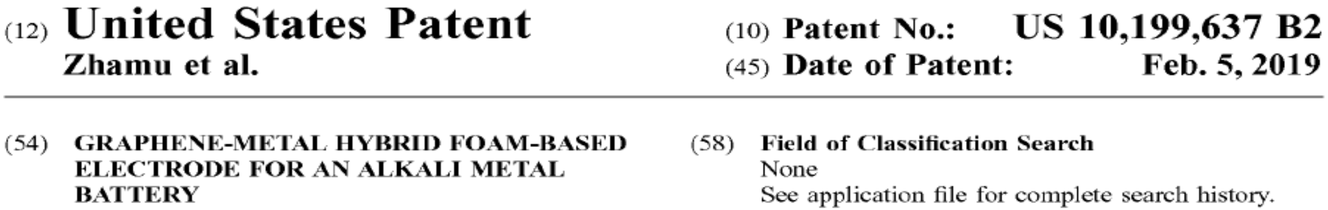


FIG. 2

- A layer of high-elasticity polymer is disposed between the Li metal layer and the separator membrane (or solid electrolyte)
- **This anode-protecting layer expands and shrinks responsive to the shrinkage and expansion of the Li metal layer in a conformal and congruent manner, helping to maintain a good contact between the electrolyte and the electrode (reduced interfacial impedance)**
- The protecting layer may be properly formulated to impart interfacial stability and reduce the propensity to form lithium dendrites and dead lithium particles (e.g. **enabling uniform L^{+} ion flux**)
- Works for liquid, gel, quasi-solid, or solid electrolytes.

Approach 3: Graphene Foam-Supported Transition Metal as an Alternative to Lithium Metal Foil



(12) **United States Patent**
Zhamu et al.

(10) **Patent No.:** **US 10,199,637 B2**
(45) **Date of Patent:** **Feb. 5, 2019**

(54) **GRAPHENE-METAL HYBRID FOAM-BASED ELECTRODE FOR AN ALKALI METAL BATTERY**

(58) **Field of Classification Search**
None
See application file for complete search history.

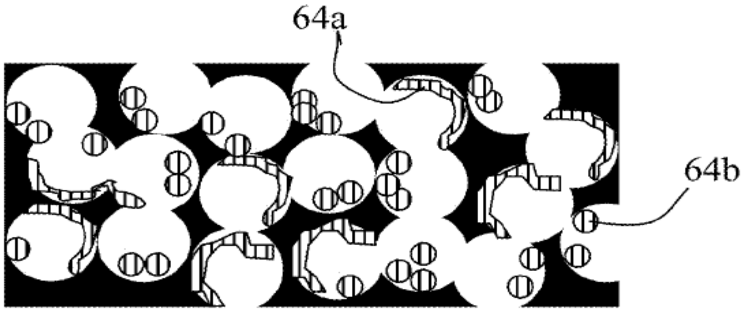


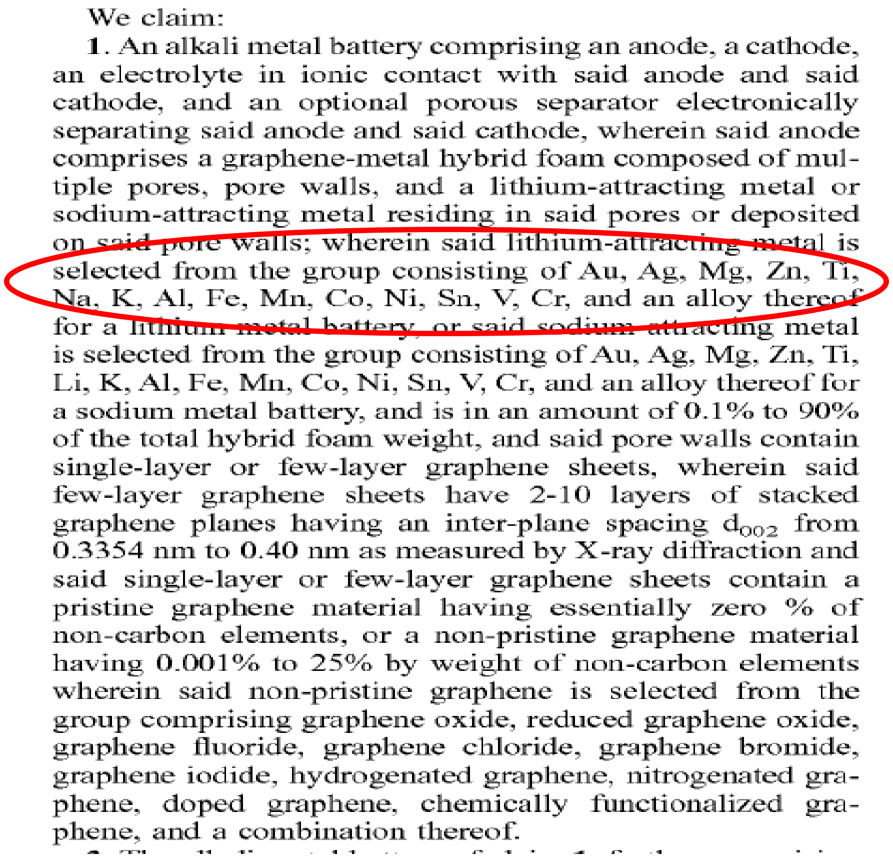
FIG. 3(B)

- “Said lithium-attracting metal (64a, 64b) is selected from **Au, Ag, Mg, Zn, Ti, Na, K, Al, Fe, Mn, Co, Ni, Sn, V, Cr,** or an alloy thereof”
- Certain metal elements have the lowest barrier against nucleation of Li metal for smooth deposition of Li metal on internal graphene surfaces during battery charge
- Graphene foam is highly elastic

Aruna Zhamu and Bor Z. Jang, “Graphene-Metal Hybrid Foam-Based Electrode for an Alkali Metal Battery,” US Patent Application No. 15/175,775 (06/07/2016); now US Patent No. 10,199,637 (02/05/2019).

- Graphene foam is highly elastic, capable of expanding/shrinking in response to lithium metal deposition and dissolution
- Certain metal elements (lithiophilic) promote smooth re-deposition of lithium metal during charging

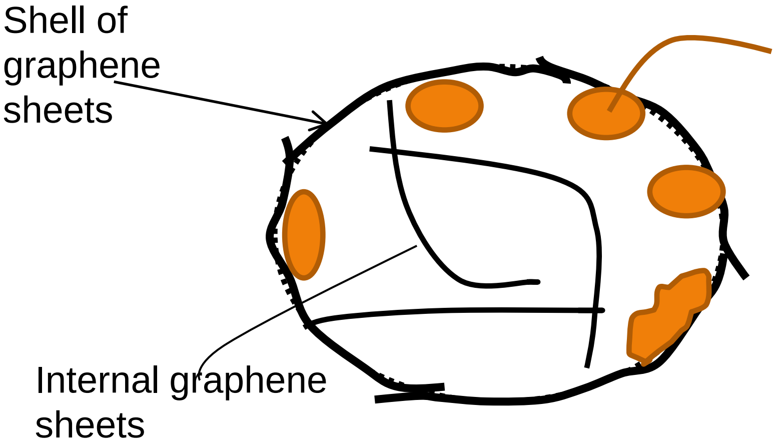
Aruna Zhamu and Bor Z. Jang, “Graphene-Metal Hybrid Foam-Based Electrode for an Alkali Metal Battery,” US Patent Application No. 15/175,775 (06/07/2016); now US Patent No. 10,199,637 (02/05/2019).



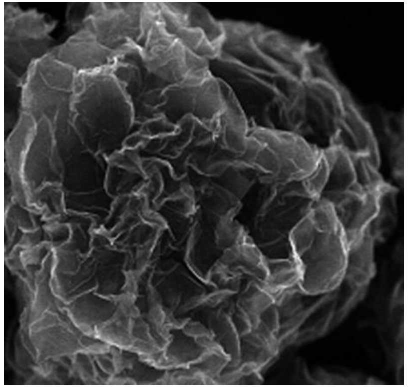
We claim:

1. An alkali metal battery comprising an anode, a cathode, an electrolyte in ionic contact with said anode and said cathode, and an optional porous separator electronically separating said anode and said cathode, wherein said anode comprises a graphene-metal hybrid foam composed of multiple pores, pore walls, and a lithium-attracting metal or sodium-attracting metal residing in said pores or deposited on said pore walls; wherein said lithium-attracting metal is selected from the group consisting of Au, Ag, Mg, Zn, Ti, Na, K, Al, Fe, Mn, Co, Ni, Sn, V, Cr, and an alloy thereof for a lithium metal battery, or said sodium-attracting metal is selected from the group consisting of Au, Ag, Mg, Zn, Ti, Li, K, Al, Fe, Mn, Co, Ni, Sn, V, Cr, and an alloy thereof for a sodium metal battery, and is in an amount of 0.1% to 90% of the total hybrid foam weight, and said pore walls contain single-layer or few-layer graphene sheets, wherein said few-layer graphene sheets have 2-10 layers of stacked graphene planes having an inter-plane spacing d_{002} from 0.3354 nm to 0.40 nm as measured by X-ray diffraction and said single-layer or few-layer graphene sheets contain a pristine graphene material having essentially zero % of non-carbon elements, or a non-pristine graphene material having 0.001% to 25% by weight of non-carbon elements wherein said non-pristine graphene is selected from the group comprising graphene oxide, reduced graphene oxide, graphene fluoride, graphene chloride, graphene bromide, graphene iodide, hydrogenated graphene, nitrogenated graphene, doped graphene, chemically functionalized graphene, and a combination thereof.

Approach 4: Graphene Ball-Protected Metal as an Alternative to Lithium Metal Anode



Particles or coating of a lithium-attracting metal selected from **Au, Ag, Mg, Zn, Ti, Na, K, Al, Fe, Mn, Co, Ni, Sn, V, Cr,** or an alloy thereof”



- Certain metal elements have the lowest barrier against nucleation of Li metal for deposition of Li metal on internal graphene surfaces during battery charge
- Graphene balls are also highly elastic

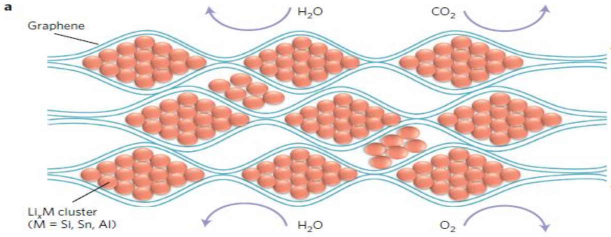
Approach 5: Li ion-conducting composite-based dendrite-stopping layer

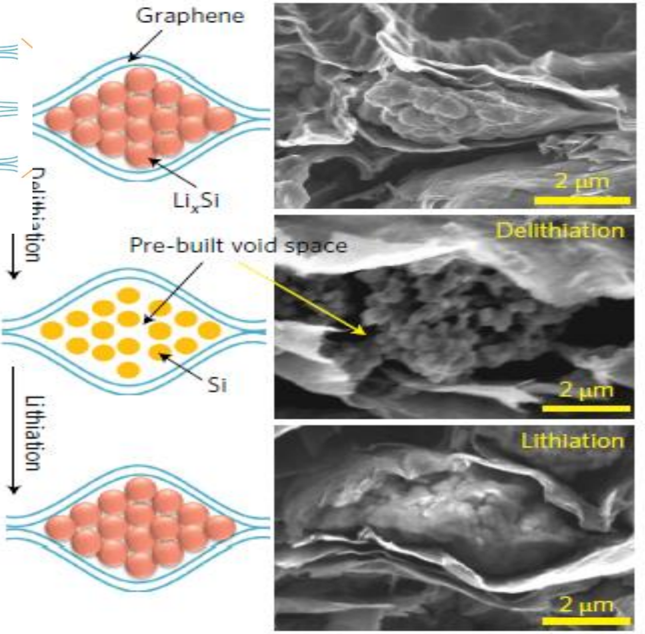
A dendrite penetration-resistant layer:

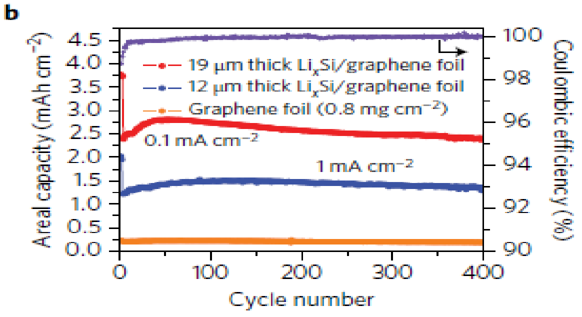
- Comprising multiple graphene sheets or exfoliated graphite flakes that are chemically bonded by a lithium-containing species to form an integral layer that prevents dendrite penetration
- The lithium-containing species is selected from Li_2CO_3, Li_2O, $Li_2C_2O_4$, LiOH, LiX, $ROCO_2Li$, HCOLi, ROLi, $(ROCO_2Li)_2$, $(CH_2OCO_2Li)_2$, Li_2S, Li_xSO_y, Na_2CO_3, Na_2O, $Na_2C_2O_4$, NaOH, NaiX, $ROCO_2Na$, HCONa, RONa, $(ROCO_2Na)_2$, $(CH_2OCO_2Na)_2$, Na_2S, Na_xSO_y, or a combination thereof, wherein X = F, Cl, I, or Br, R = a hydrocarbon group, x = 0-1, y = 1-4.
- These species are commonly found ingredients in solid-electrolyte interfaces (SEI) of lithium-ion batteries.

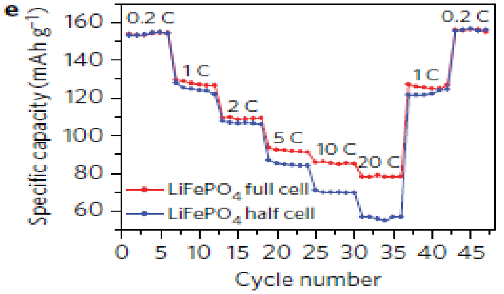
“Alkali Metal Secondary Battery Containing a Dendrite-Intercepting Layer” US Patent No. 9,755,241 (09/05/2017).
“Dendrite-Intercepting Layer for Alkali Metal Secondary Battery” US Patent No. 9,755,236 (09/05/2017).
“Alkali Metal Secondary Battery Containing a Carbon Matrix- or Carbon Matrix Composite-based Dendrite-Intercepting Layer” US Patent No. 9,780,379 (10/03/2017).
“Carbon Matrix- or Carbon Matrix Composite-based Dendrite-Intercepting Layer for Alkali Metal Secondary Battery” US Patent No. 9,780,349 (10/03/2017).

Approach 6: Graphene Foam-Protected Pre-lithiated Si as an Alternative to Lithium Metal Anode







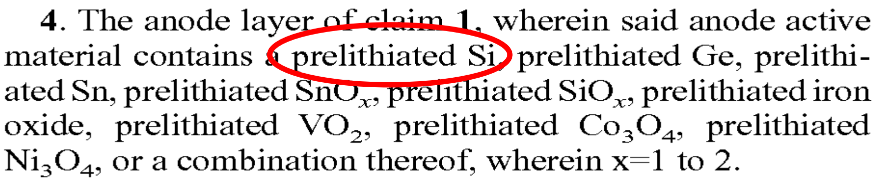


Jie Zhao, et al. (Yi Cui Group), "Air-stable and freestanding lithium alloy/graphene foil as an alternative to lithium metal anodes," published online: 10 JULY 2017 | DOI: 10.1038/NNANO.2017.129

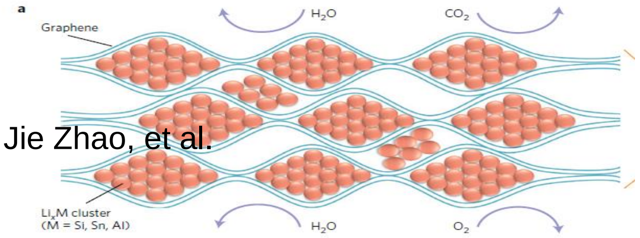
This paper by the Stanford group was published in 2017, but we had already submitted a patent application on identical approach in 2014!

Aruna Zhamu and Bor Z. Jang, "Graphene Foam-Protected Anode Active Materials for Lithium Batteries," US Patent Application No. 14/121,151 (08/07/2014); now US Patent No. 9,742,001 (08/22/2017)

Graphene Foam-Protected Pre-lithiated Si as an Alternative to Lithium Metal Anode



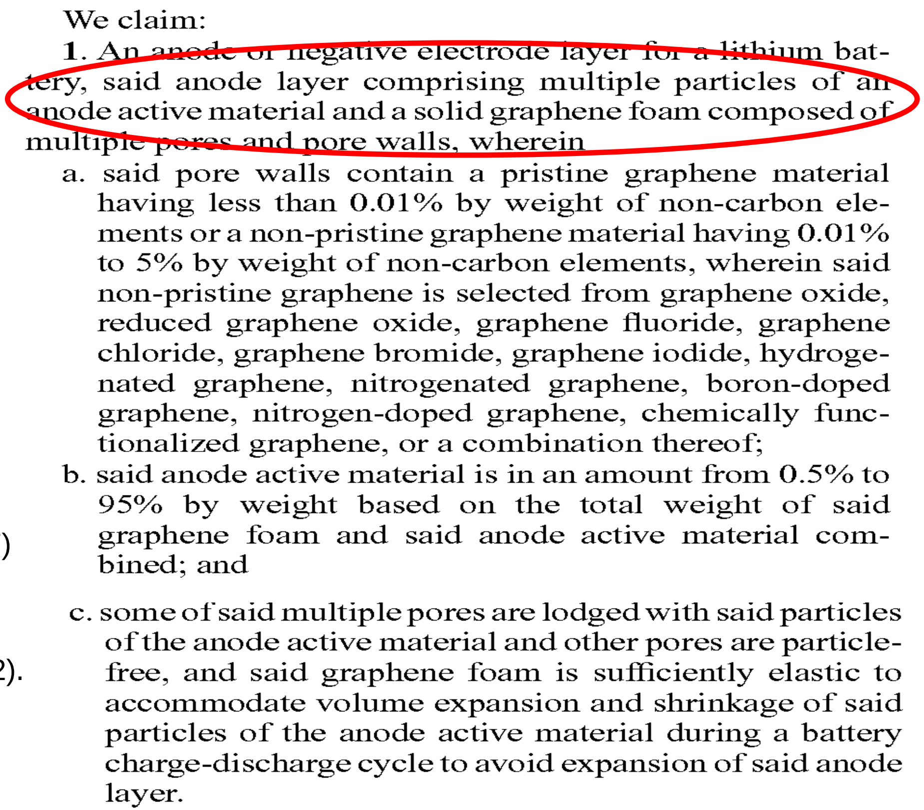
4. The anode layer of claim **1**, wherein said anode active material contains a prelithiated Si, prelithiated Ge, prelithiated Sn, prelithiated SnO_x, prelithiated SiO_x, prelithiated iron oxide, prelithiated VO_2, prelithiated Co_3O_4, prelithiated Ni_3O_4, or a combination thereof, wherein x=1 to 2.



Jie Zhao, et al.

Aruna Zhamu and Bor Z. Jang, "Graphene Foam-Protected Anode Active Materials for Lithium Batteries," US Patent Application No. 14/121,151 (08/07/2014); now US Patent No. 9,742,001 (08/22/2017)

Aruna Zhamu and Bor Z. Jang, "Method of Producing A Prelithiated Anode for Secondary Lithium Ion Battery," US Pat. Appl. No. 12/291,689 (11/13/2008); Now US Patent No. 8,158,282 (04/17/2012).
Aruna Zhamu and Bor Z. Jang, "Secondary Lithium Ion Battery Containing A Prelithiated Anode," US Pat. Appl. No. 12/319,114 (01/02/2009); now US Patent No. 8,241,793 (08/14/2012).



We claim:

1. An anode or negative electrode layer for a lithium battery, said anode layer comprising multiple particles of an anode active material and a solid graphene foam composed of multiple pores and pore walls, wherein

a. said pore walls contain a pristine graphene material having less than 0.01% by weight of non-carbon elements or a non-pristine graphene material having 0.01% to 5% by weight of non-carbon elements, wherein said non-pristine graphene is selected from graphene oxide, reduced graphene oxide, graphene fluoride, graphene chloride, graphene bromide, graphene iodide, hydrogenated graphene, nitrogenated graphene, boron-doped graphene, nitrogen-doped graphene, chemically functionalized graphene, or a combination thereof;

b. said anode active material is in an amount from 0.5% to 95% by weight based on the total weight of said graphene foam and said anode active material combined; and

c. some of said multiple pores are lodged with said particles of the anode active material and other pores are particle-free, and said graphene foam is sufficiently elastic to accommodate volume expansion and shrinkage of said particles of the anode active material during a battery charge-discharge cycle to avoid expansion of said anode layer.

Major Types of Rechargeable Lithium Metal Batteries

Type	Anode current collector	Anode active material	Electrolyte	Cathode active material	Cathode current collector
Conventional Li metal cell	Cu foil	Li metal foil or powder	Liquid or polymer gel	Non-lithiated metal oxides (V_2O_5), sulfides (MoS_2, $TiSe_2$), etc.	Al foil
Solid-state Li metal cell	Cu foil	Li metal foil or powder	Solid electrolyte (organic, inorganic, or composite)	NCA, NCM, etc.	Al foil
Lithium-sulfur cells (Li-S)	Cu foil	Li metal foil or powder	Liquid (solid possible)	S or Li polysulfides + carbon (high %)	Al foil
HBC's Li-S cells	Graphene-protected Cu foil	Li metal or pre-lithiated Si	Quasi-solid or liquid	Graphene-protected S (as a product of HBC)	Graphene-coated Al foil
Anode-less Li metal cells	Cu foil	Initially Li metal- free	Solid-state electrolyte	NCA, NCM, etc.	Al foil
HBC's anode-less Li metal cells	Protected Cu foil	Initially Li metal-free	Quasi-solid or solid-state electrolyte	NCA, NCM, etc.	Graphene-coated Al foil

(Other types, such as Li-air and Li-Se, not discussed here)

Summary

- G^3 has all the required technologies to overcome the technical barriers that have thus far impeded the emergence of next-generation lithium metal batteries:
  - Liquid electrolyte-lithium metal reactions
  - Lithium dendrite-induced internal shorting and formation of inactive lithium particles
  - Large solid electrolyte-electrode gap and high interfacial impedance
- G^3's protected lithium metal technology will make all types of lithium metal secondary batteries technically feasible and economically viable.
- In combination with G^3's non-flammable electrolytes, the protected anode technologies will help reduce or eliminate fire/explosion hazards from EV batteries.

Thank you!

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