

Lithium Batteries, Past, Present and Future

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SMART MOBILITY SUMMIT 2019

Issues

- **Past:** Lithium metal batteries
- **Present:** Lithium ion batteries with graphite anode protected by a Solid Electrolyte Interphase (SEI) **are the Power Source of Electric Mobility**
- **Future:** Advanced lithium batteries with better anode, cathode and SEI



Calculated Mass of Batteries Electric Vehicles*

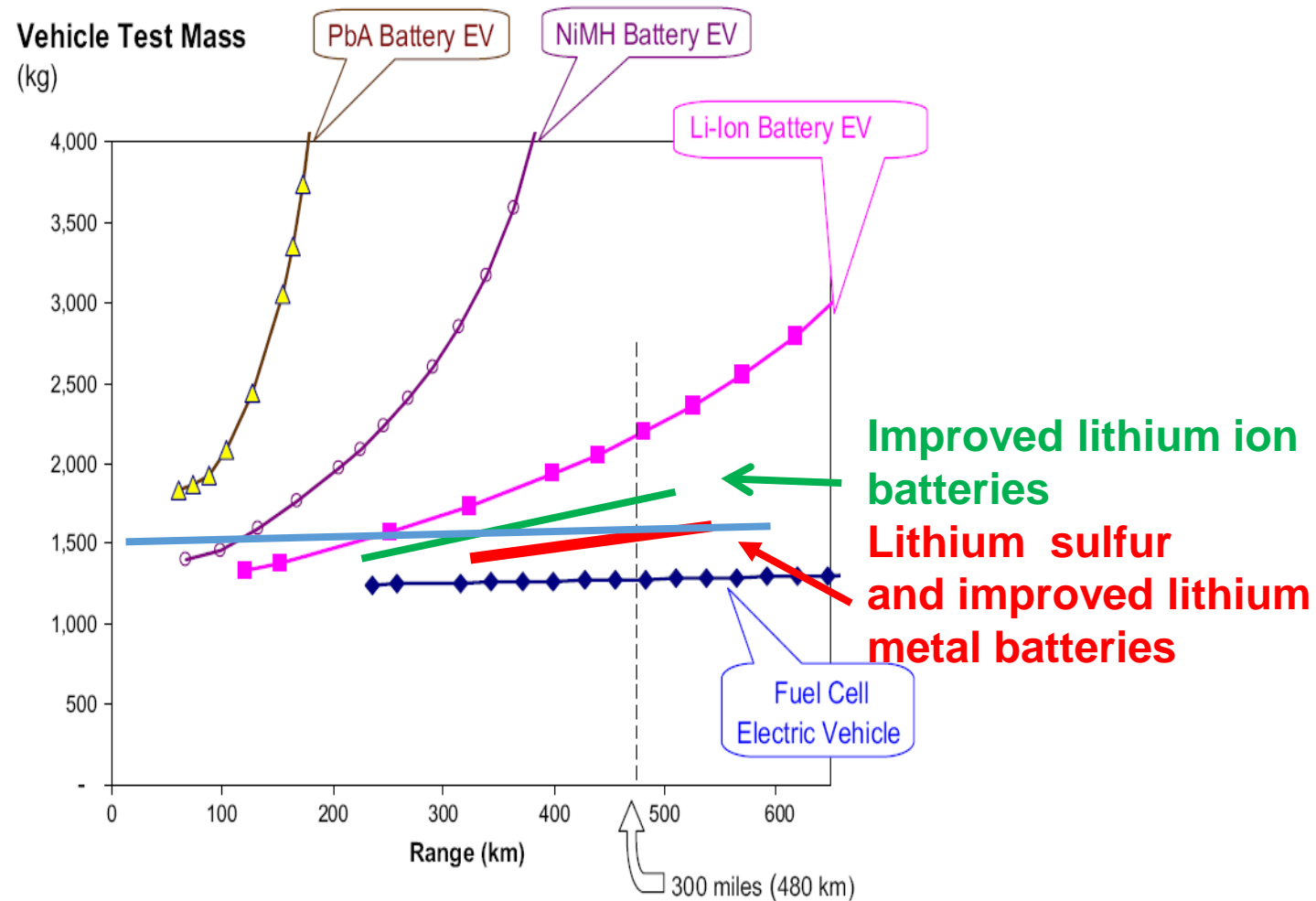


Fig. 6 – Calculated mass of fuel cell electric vehicles and battery electric vehicles as a function of the vehicle range; the power trains of all vehicles are adjusted to provide a zero to 97 km/hr (60 mph) acceleration time of 10 s.

* *Fuel Cell and Battery Electric Vehicles Compared*, C. E. Thomas 2009

Introduction:

- Batteries consist of anode (negative) cathode (positive) and electrolyte (solution containing ions)
- Lithium is a very active and high capacity metal

Past, in the seventies:

Several researchers developed batteries with **lithium metal anode***

Several prototypes were manufactured, but safety issues and inadequate cycle durability lead to the termination of their production

From the 2019 Nobel committee report

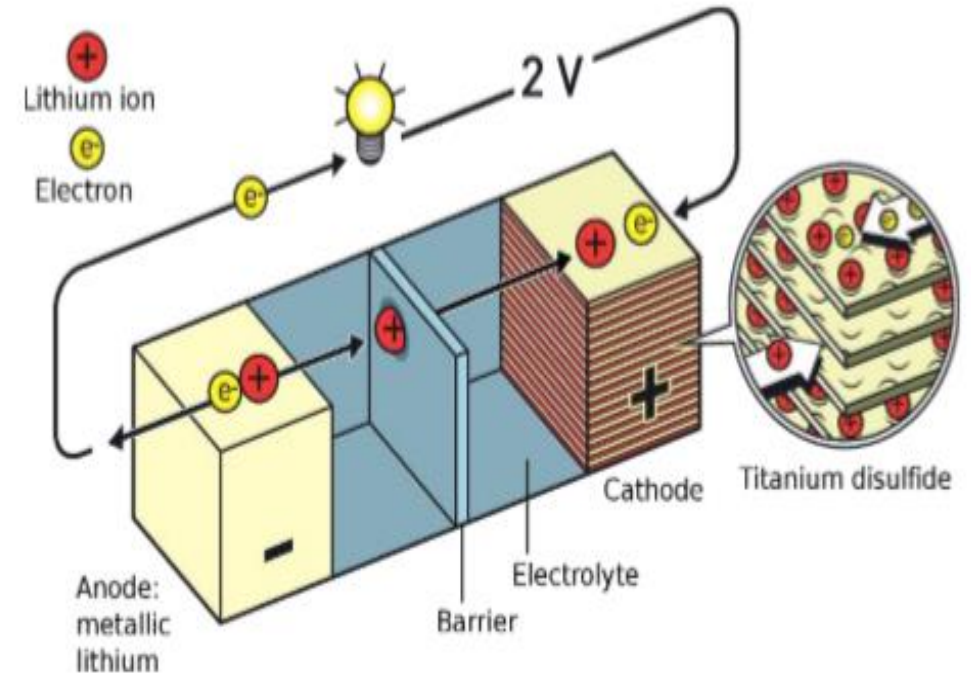


Figure 4. Lithium-based battery using Li_xTiS_2 as the cathode.

* *M.S. Whittingham (2019 Nobel Prize laureate);*

Electrointercalation in Transition-Metal Disulphides. J. Chem. Soc., Chem. Commun. 1974, 328–329

The wrong working assumption of batteries experts, prior to 1980, was that **on charge of lithium batteries** there is a **direct transfer** of electrons from the lithium anode to lithium ions in the solution

lithium ion in the solution + electron (coming from the electrode) gives lithium metal deposited on the electrode

Researcher's major task was to purify the electrolyte as much as they can in order to avoid lithium anode passivation

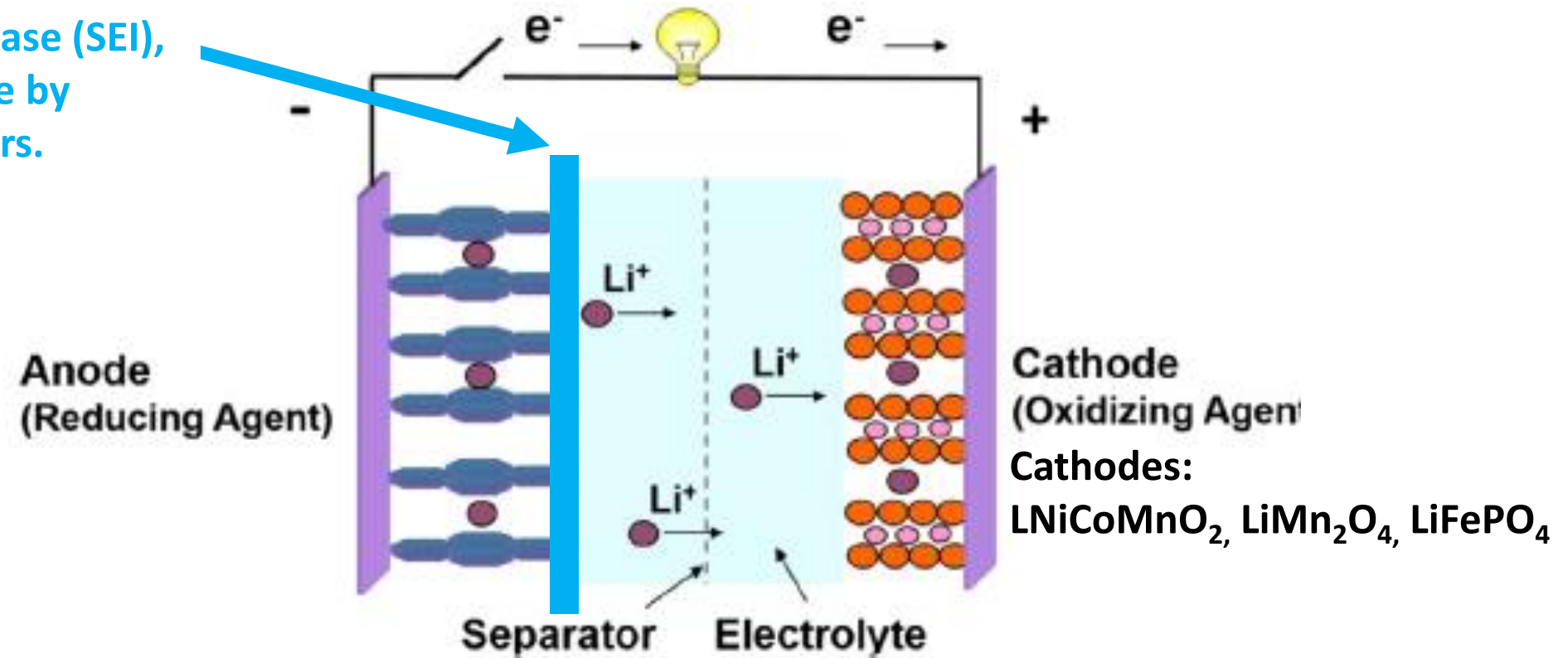
This research direction delays the development of lithium batteries

The solid electrolyte interphase (SEI) model, to be presented, proved that this is a wrong path

Present: Lithium Ion Batteries are the Power Source of Electric Mobility

Schematic view of a Li-ion battery during discharge.

A few nano-meter thick
Solid Electrolyte Interphase (SEI),
formed at the first charge by
reactions of SEI precursors.



Non aqueous organic electrolyte

Present anode:
Graphite, **370 mAh/gc**
(in all commercial cells)

Future anode:
Silicon, **4000mAh/gSi**
Nano particles or Nano wires,
(in a development stage)

Cathodes:
 LiNiCoMnO_2 , LiMn_2O_4 , LiFePO_4

The Necessity of Forming an Anode SEI

Two reactions occur in parallel in **SEI-free lithium batteries**:

1. Dissolution of the lithium metal to give lithium ions in the solution
2. Electrons are going out of the lithium metal into the solution to form “**solvated electrons**”

This reaction was revealed, for the first time, by Peled in the SEI paper

Prior to 1980 the battery experts were unaware of this reaction

Solvated electrons attack the cathode leading to a fast battery self discharge.

In addition, solvated electrons **attack the electrolyte** leading to its decomposition

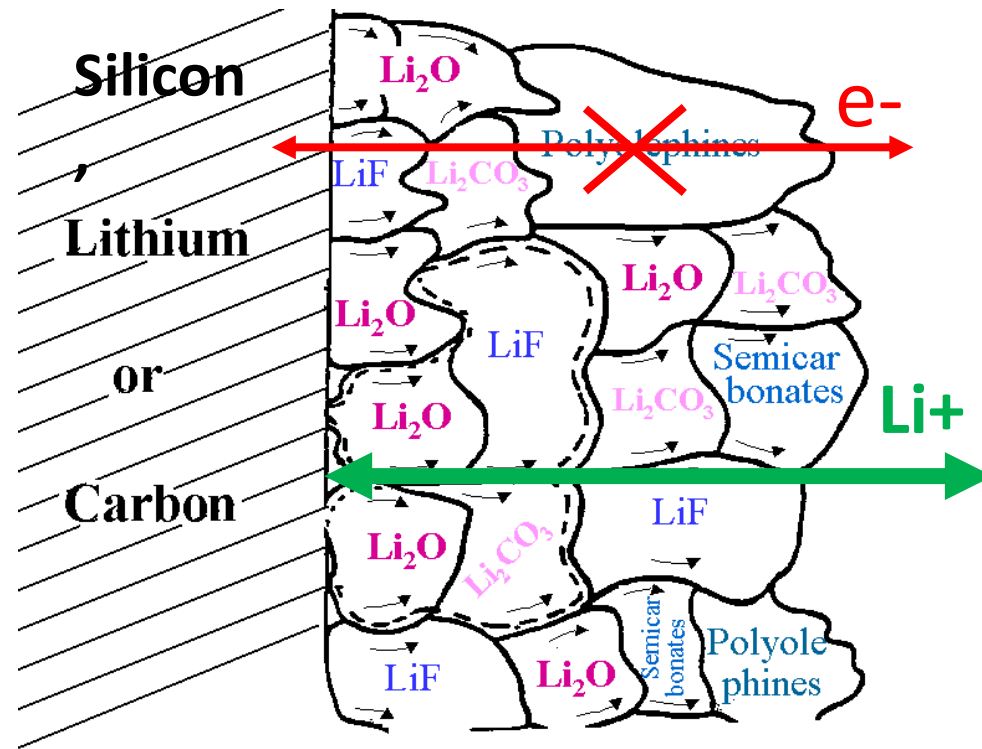
On charge instead of electroplating of **lithium metal we get dissolution of solvated electrons**

Conclusions:

1. In SEI free systems the battery can't be charged and will undergo a fast self discharge, or **a SEI free battery can't exist.**
1. SEI is required to **stop the electrons transfer from the lithium anode to the electrolyte, forming solvated electrons.**

SEI model - In all Lithium batteries the anode is completely covered by a few nm thick, electronically insulating SEI (Peled 1979*)

We need to add to the electrolyte **SEI precursor molecules** that react with the lithium anode to form the SEI (many patents – **secret** of the battery manufacturers).



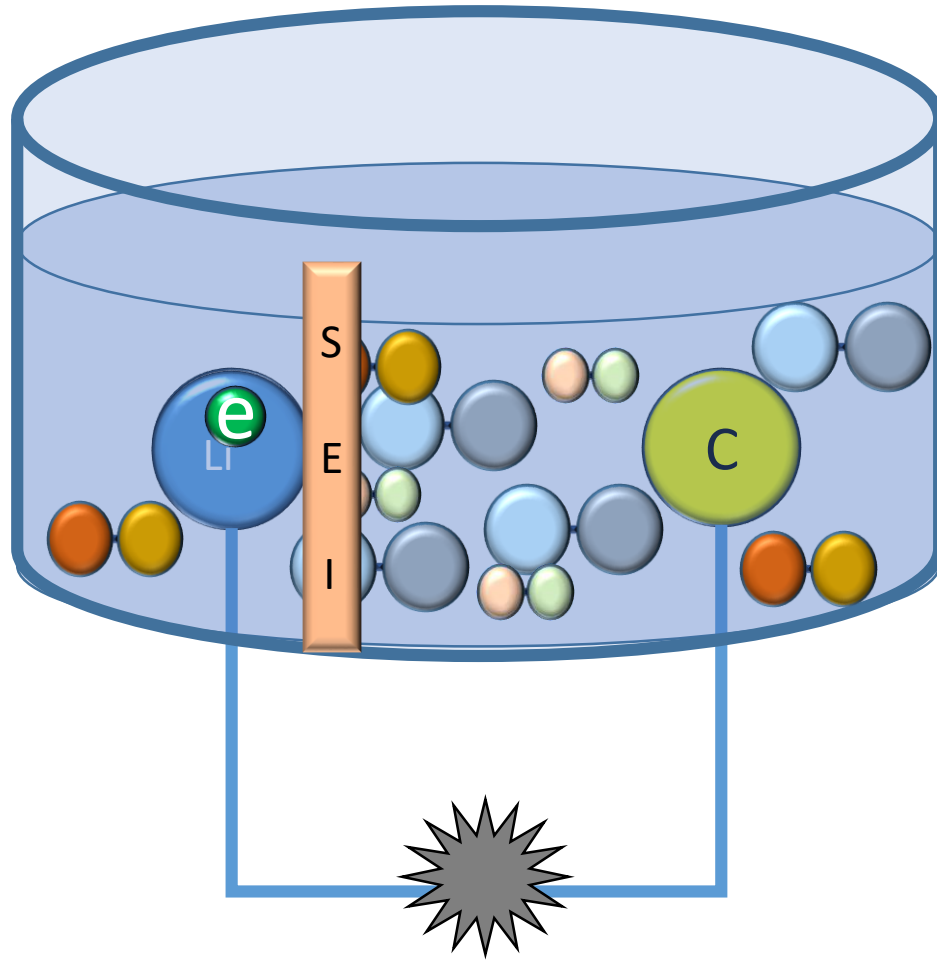
SOLID ELECTROLYTE INTERPHASE

The SEI Affects:

1. Safety of the battery
2. Self discharge rate
3. Cycle life
4. Maximum operating Temp
5. Power

* E. Peled, "The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Nonaqueous Battery Systems -The Solid Electrolyte Interphase (SEI) Model"; J. Electrochem. Soc. 126, 2047-2051 (1979).

Molecular Animation for SEI Formation and Role (A.P.)



Present: The SEI model is the **foundation stone** of the lithium battery electrochemistry

- It explains how lithium batteries work, provides equations for the kinetics of lithium reactions, lithium-anode corrosion, the resistivity of the SEI, the growth rate of the SEI, the capacity loss at the first charge and more.
- It enables the development of safer, higher energy and long duration lithium ion batteries
- The Royal Swedish Academy of Science's cites three JES articles **critical** to the development of the Lithium-ion batteries, **one of them is Peled's 1979 SEI Model paper**
- Our 2017 SEI paper received, in two years, over **20,000 downloads (700-800 per month)**
- It was marked by the Web of Science as a **"Hot Paper" and highly cited paper**

Review-SEI: Past, Present and Future

By: **Peled, E.**; Menkin, S.

JOURNAL OF THE ELECTROCHEMICAL SOCIETY Volume: 164
Issue: 7 Pages: A1703-A1719 Published: 2017

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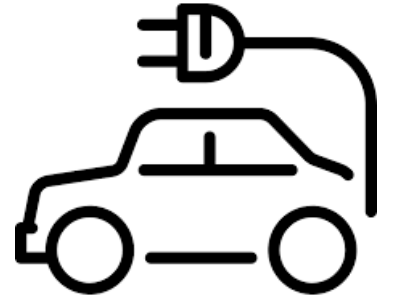
Times Cited: 107
(from Web of Science Core Collection)

 **Hot Paper**
 **Highly Cited Paper**

Future lithium battery candidates:

1. **Lithium ion** battery with a silicon anode, better cathodes (higher voltage, greater capacity) and a better SEI.
2. **Lithium metal** sulfur battery with a better SEI (long term).
3. **Lithium metal** batteries with better cathodes and better SEI (long term)

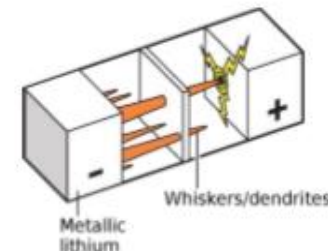
In order to increase the market share and the **driving range of electric vehicles (EVs) from 300 to 500km** we need to develop lighter, lower-cost and durable batteries



From the 2019 Nobel committee report

The following SEI properties must be improved:

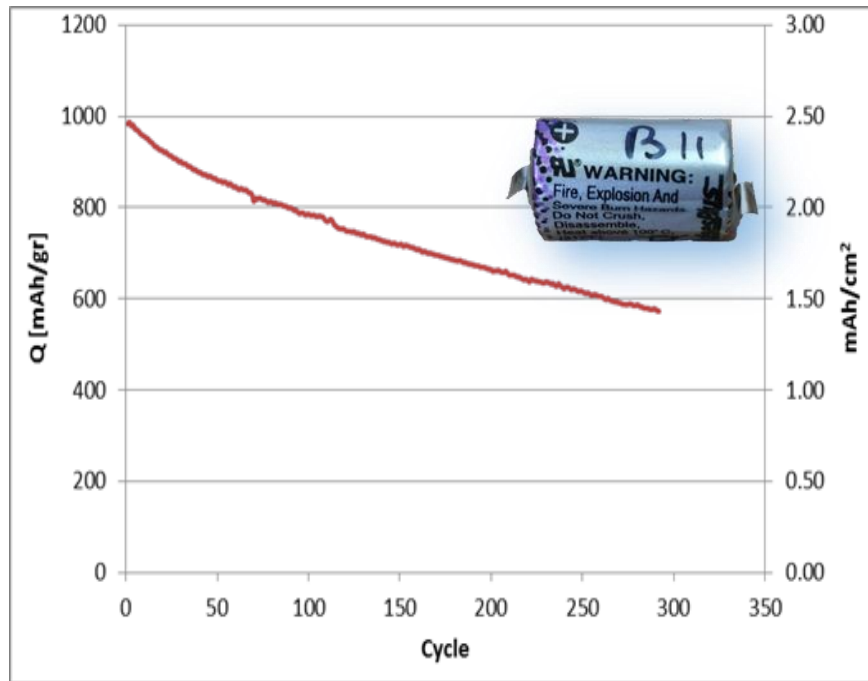
- Thermal stability (**to avoid thermal runaway situation**)
- Flexibility (especially in the case of silicon anode).
- Amorphous structure (to minimize dendrite growth and **to avoid dangerous short circuit**)



Lithium dendrite growth leads to internal short circuits

Future - Lithium battery with **silicon anode** is expected to increase the driving range of **EVs by more than 40%**

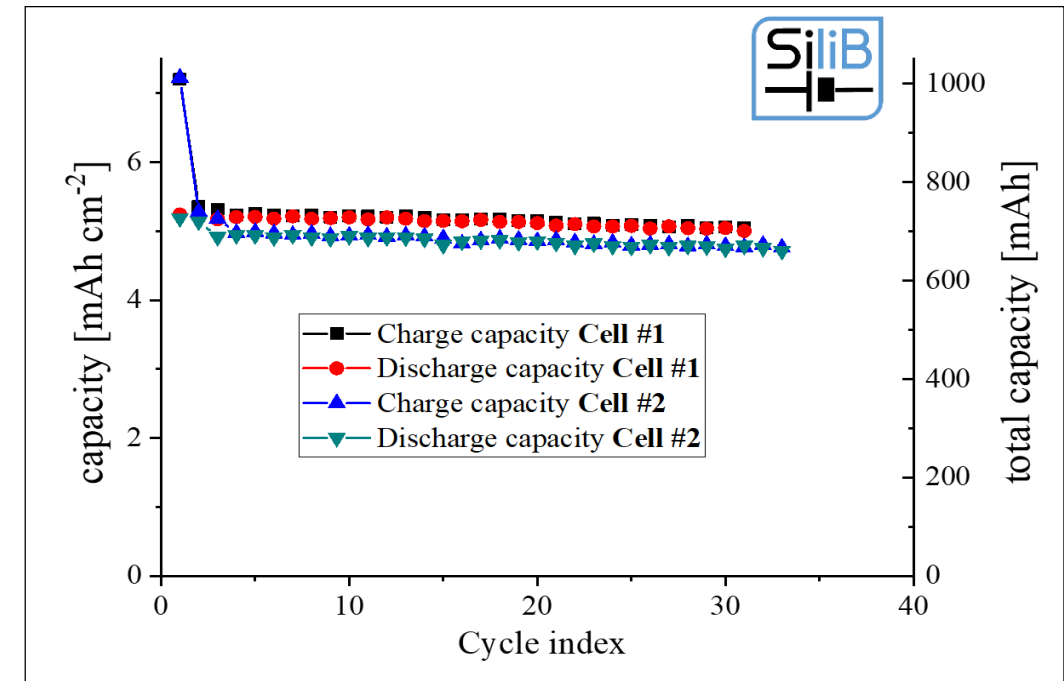
A cell with **TAU Silicon-nickel nano particles** anode was made and tested by Tadiran



TAU
demonstrated
three times
the capacity of
the common
graphite
anode!

Cell assembled with NCA cathodes by Tadiran

Scaling up to a 0.7Ah pouch cell with **TAU Silicon-Nano-Wires** anodes (Momentum funds)



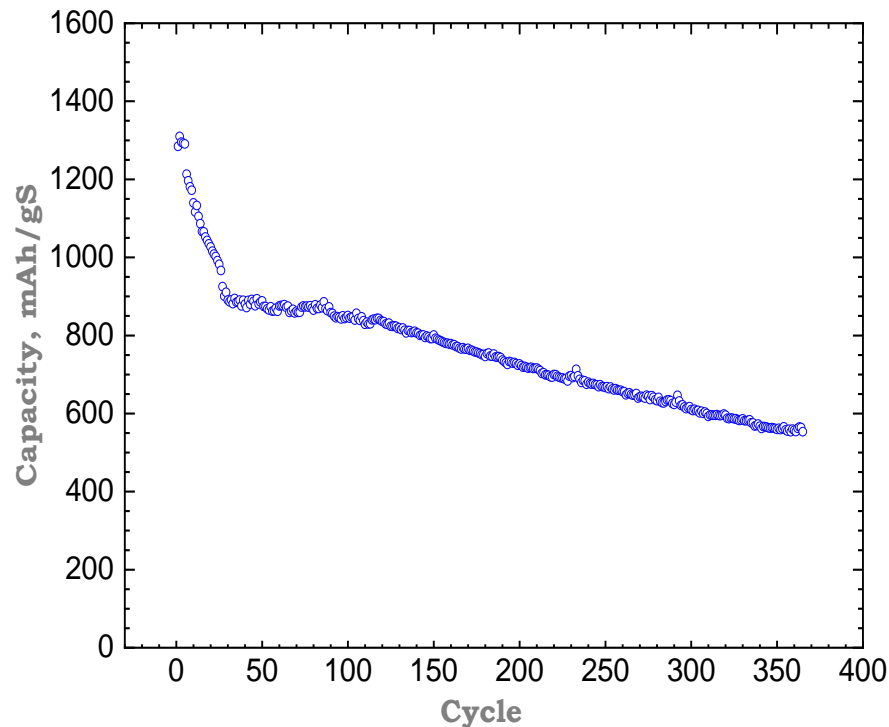
Cell assembled with NMC cathodes by ETV energy

Future – Lithium Sulfur Battery.

Expected to increase the EVs driving range by **more than 50%**

The Lithium Sulfur couple has **high theoretical specific energy** (2567 Wh.kg^{-1}), **five times higher** than that of common lithium ion batteries.

Cycle life of **TAU 2019 Lithium – Sulfur** Batteries. They demonstrated up to **four times** the capacity of common lithium ion battery cathode and **350 cycles**.



The first Lithium Sulfur battery composed of porous carbon loaded sulfur, **was developed** by Peled in 1989. It demonstrated **only 50 cycles**.

Thank you for your attention

I wish to thank Prof. Diana Golodnitsky for many years of fruitful cooperation
and all my collaborators, graduate and post-graduate students