TI *Live!* BATTERY MANAGEMENT SYSTEMS SEMINAR

TI POWER

YEVGEN BARSUKOV

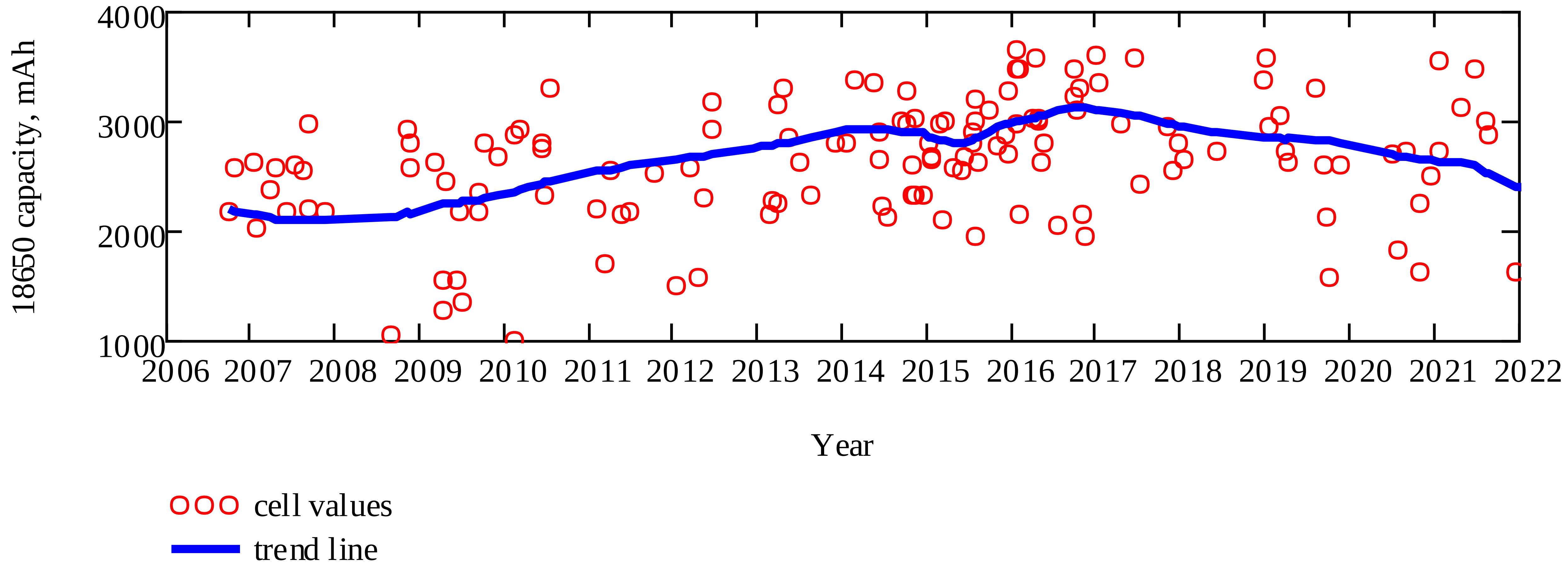
BATTERY TECHNOLOGY UPDATE

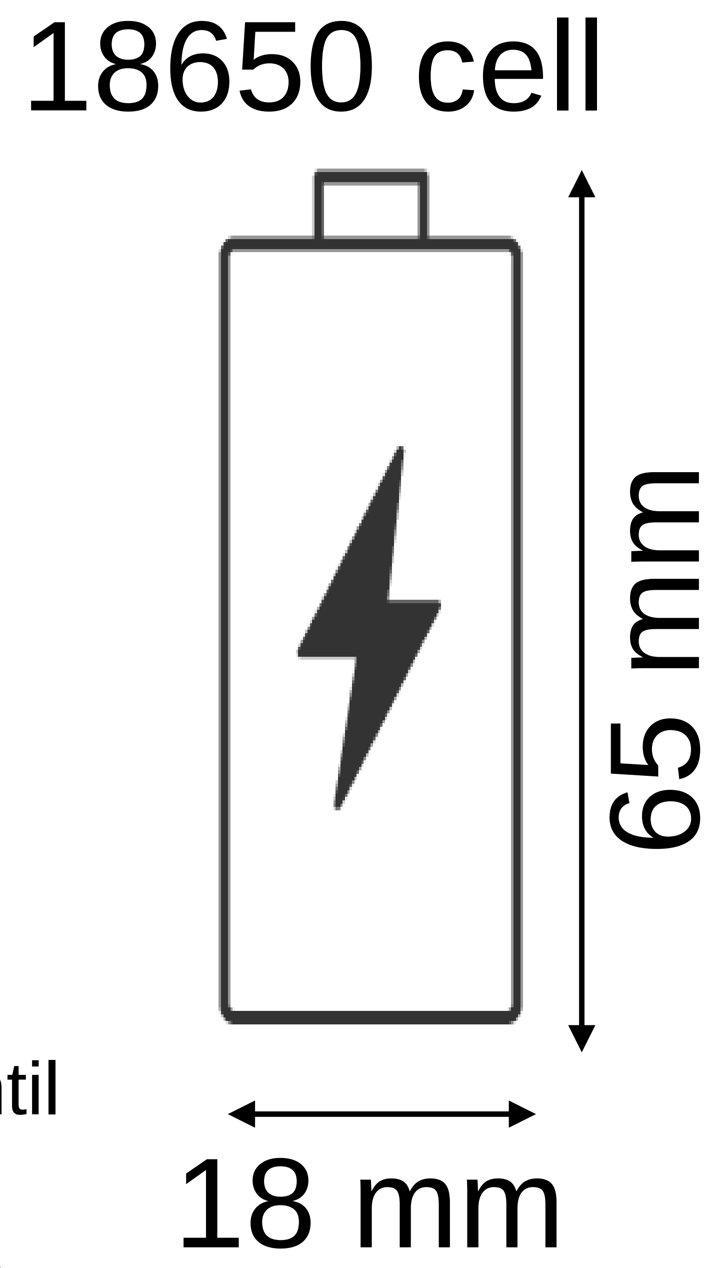
Agenda

New battery technology development

- Capacity and impedance trends.
- What is available now:
  - Highest energy: phones, tablets.
  - Cost reduction: less Co, Ni.
  - Higher charge/discharge rates.
  - High longevity: backup, grid management, automotive.
- Next 5 years.
- Futuristic technologies.

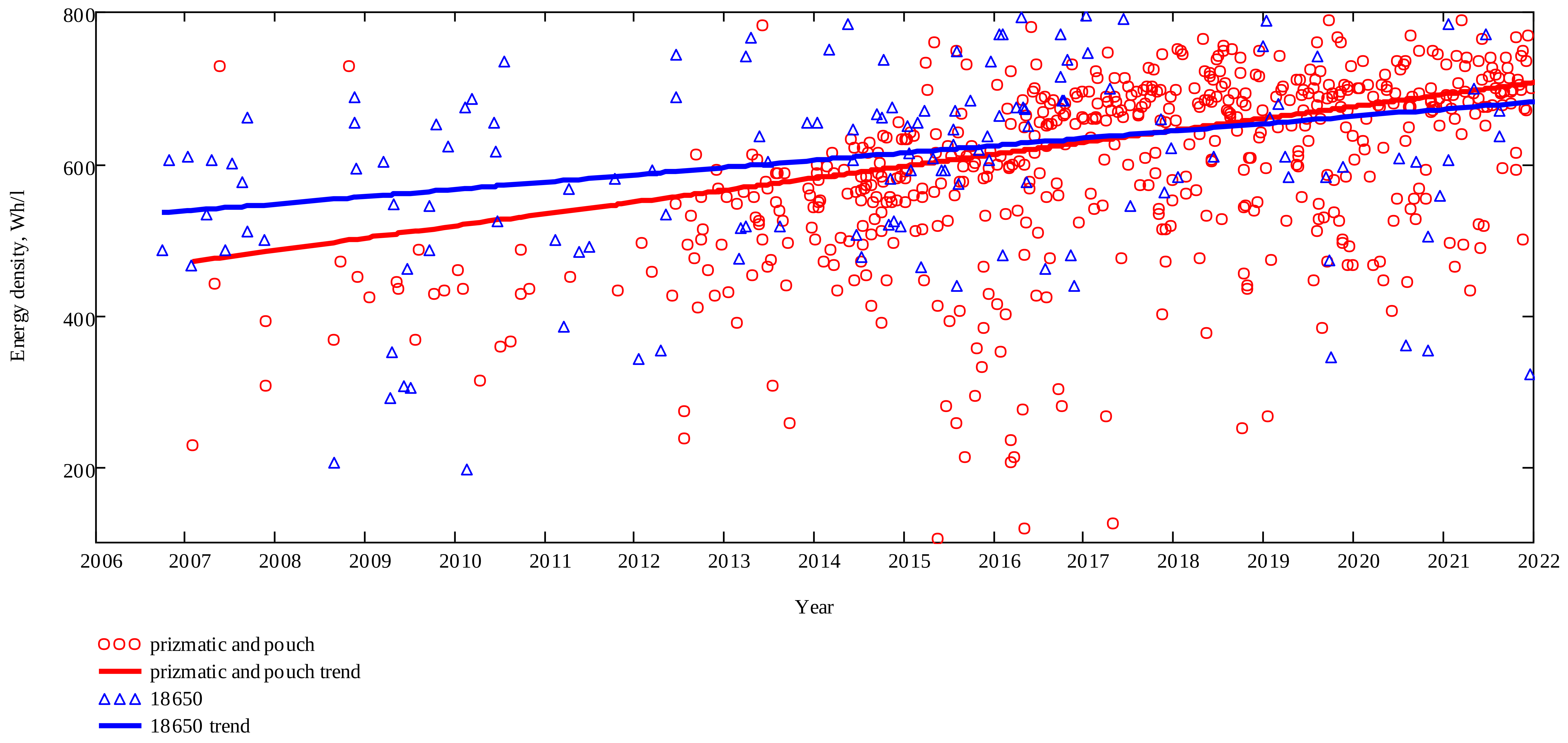
18650 Li-ion cell capacity development trend





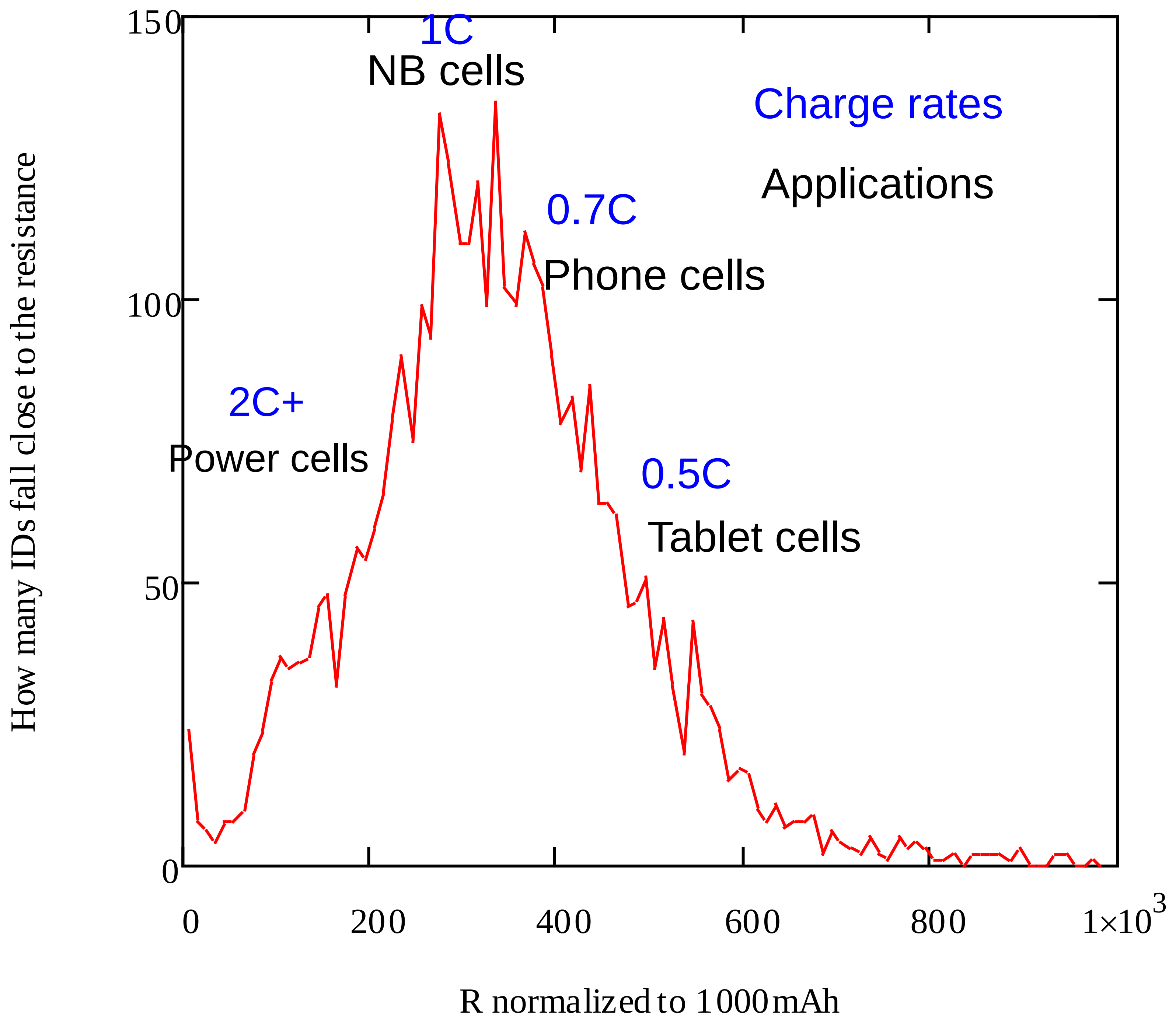
- 18650: Cylindrical, 65-mm length, 18-mm diameter.
- 120 mAh/year average increase rate until 2007, slowed down to 75 mAh/year until 2015 and slightly decreasing since then.
- Most new developments are focusing on pouch cells except in automotive space. Tesla is in mass production with 2170 cell, in future moving to tabless 4680.

Average pouch cells energy density overtook 18650 cells



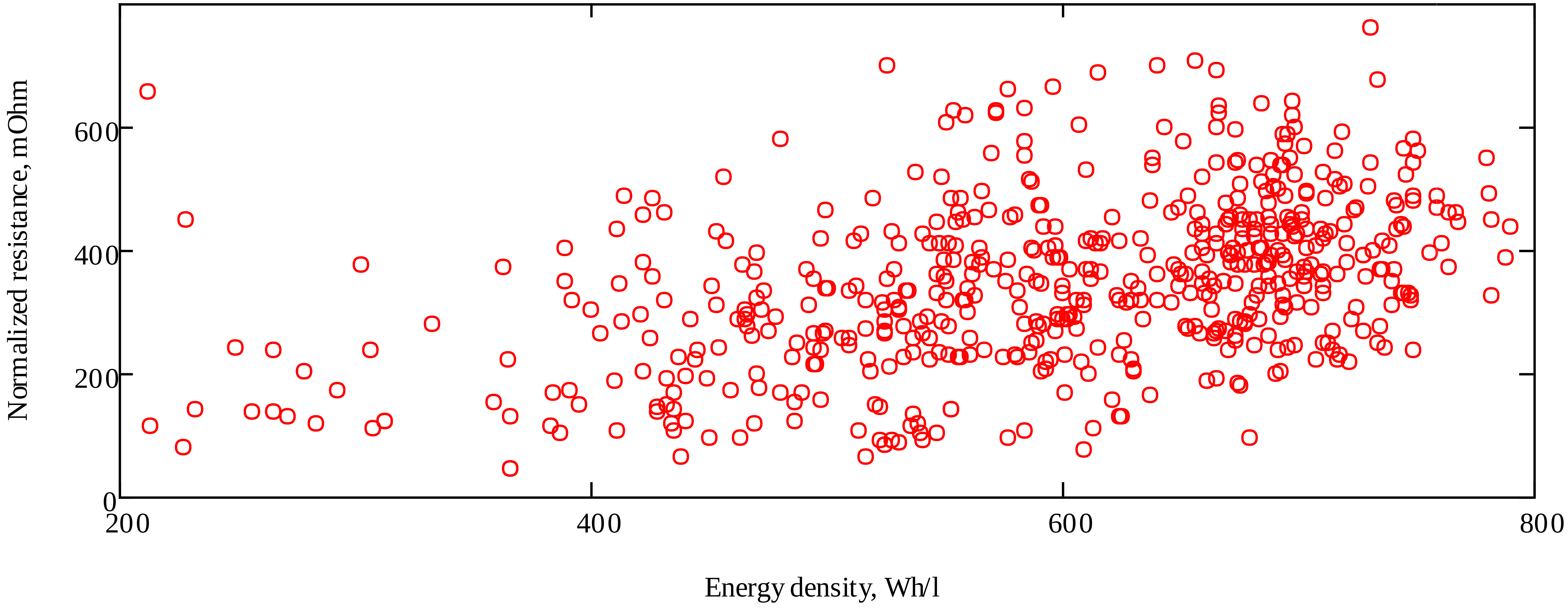
*Data summarized from TI chemical ID database

Normalized impedance distribution



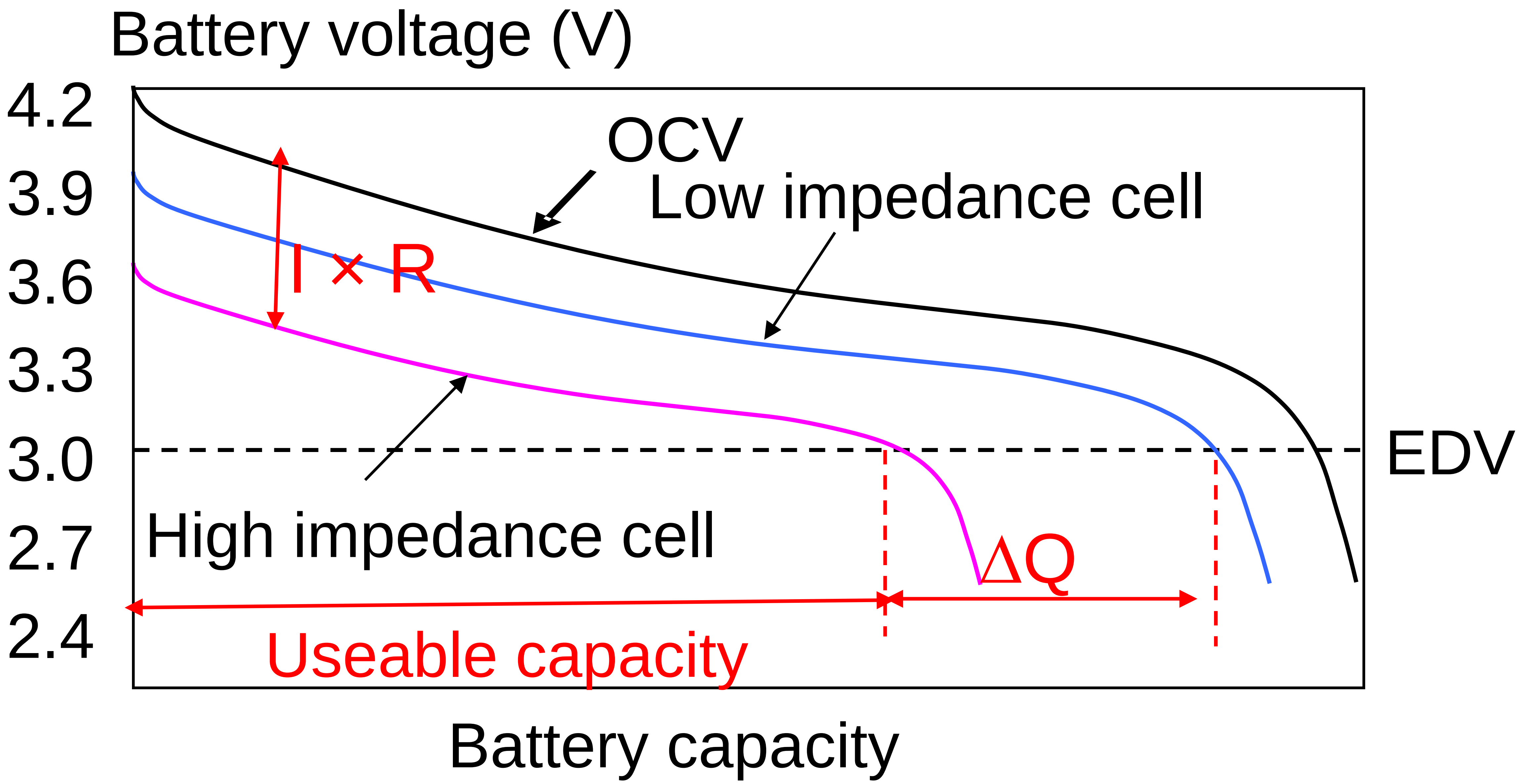
- Impedance for same cell type is inversely proportional to capacity.
- To compare different capacity cells, impedance data for all existing chem IDs is normalized to 1000 mAh.
- Impedance values correspond to low frequency (1 mHz) and depth of discharge (DOD) of 70%.

Normalized resistance increase with energy density – high rate vs. high energy compromise



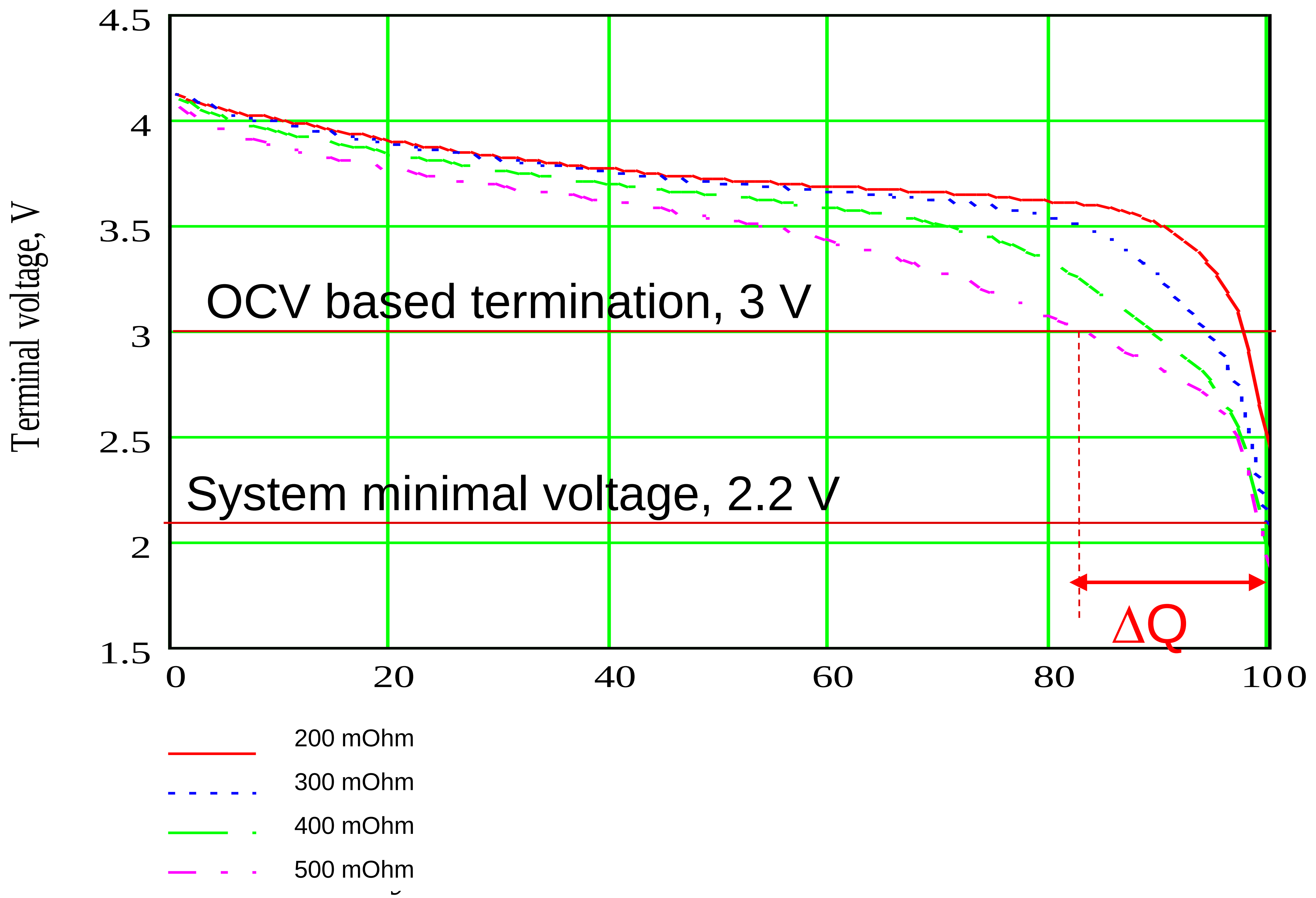
*Resistance is normalized by scaling it to 1000-mAh cell size. Pouch cells data are used for comparable design.

Effect of battery impedance on run-time



- High internal resistance causes large I × R drop.
- End of discharge voltage (EDV) is reached too early, reducing useable capacity.

Useable capacity increase using Impedance Track™ gauge with rate compensation

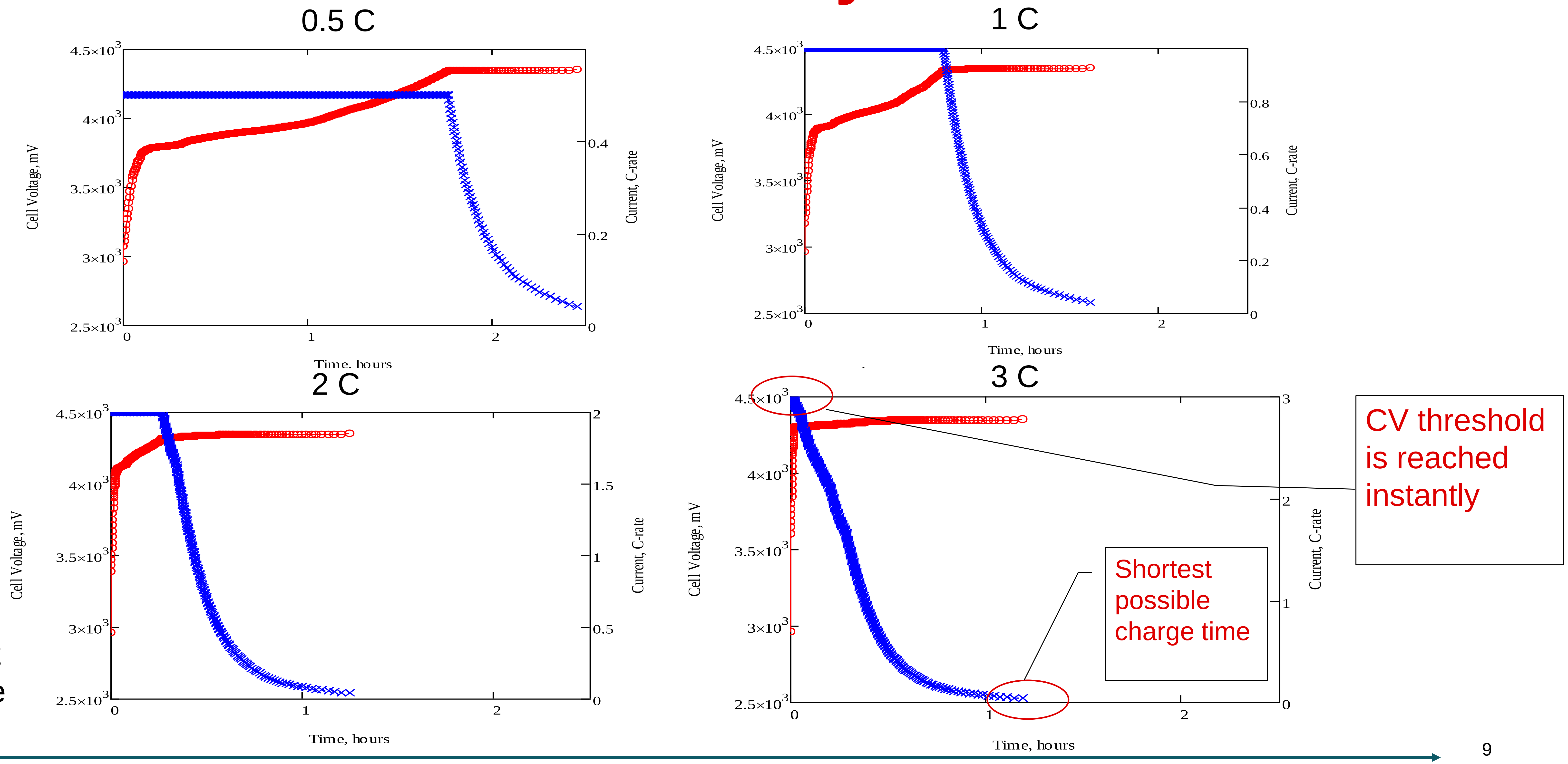


*1 C constant power discharge rate

- Typical fixed termination voltage: 3 V
  - Use of this termination voltage results in run-time loss that increases with impedance of battery
- Commonly used in notebooks – power supplies have minimal operation voltage 2.2 V/cell for 3 s pack
- Early termination is done not because of system needs but because of wrong estimation of true state of charge based on voltage
- Use of true capacity estimation would increase useable capacity from 200-mOhm to 500-mOhm battery by: 2%, 6%, 11%, 17%
- This effect is increased with battery age and at higher discharge rates
- Set in data flash terminate voltage = minimal system voltage to take full advantage of Impedance Track run time increase

Each battery has a “critical” charging C-rate where CV threshold is reached instantly

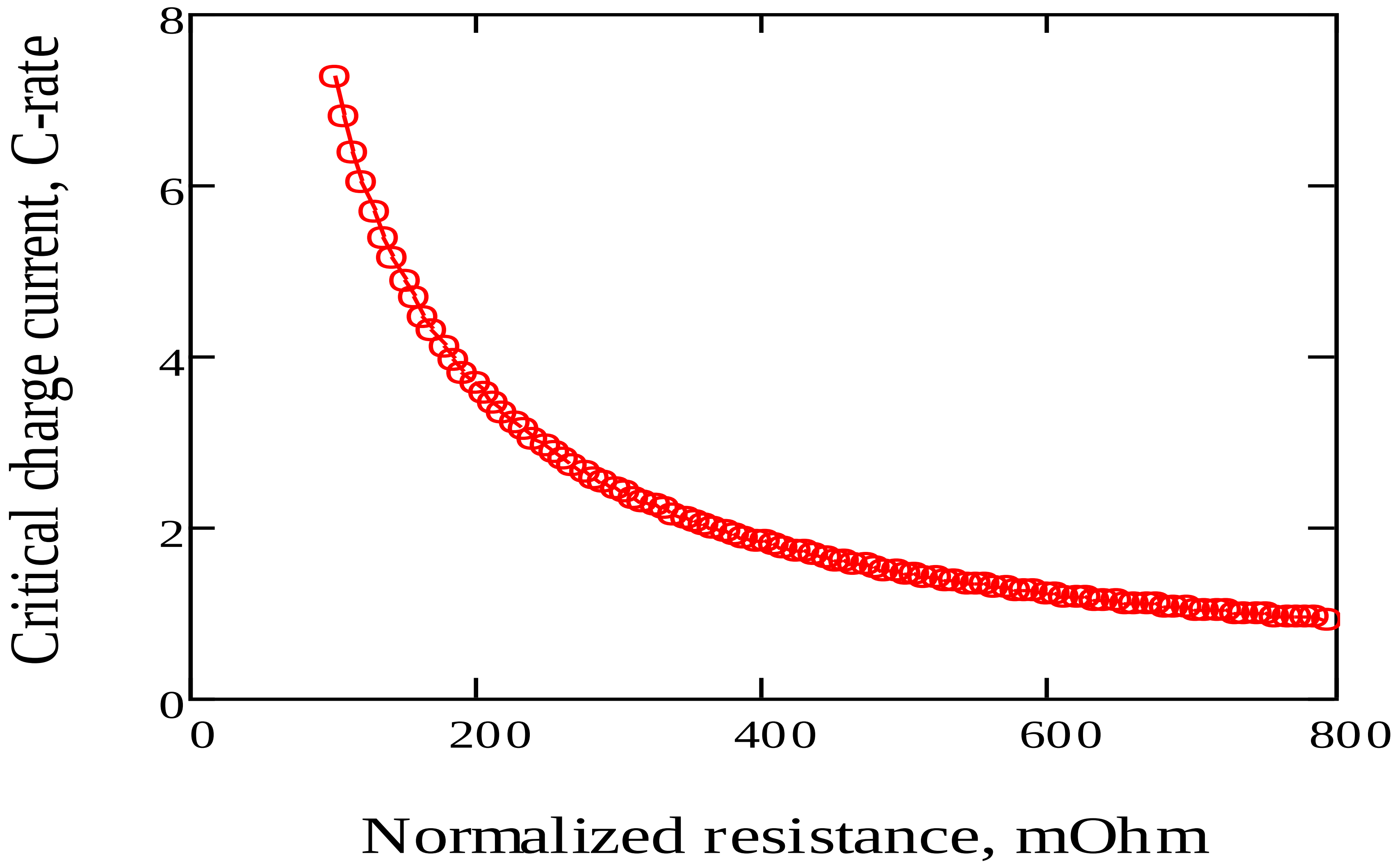
Legend:
- Voltage
- Current

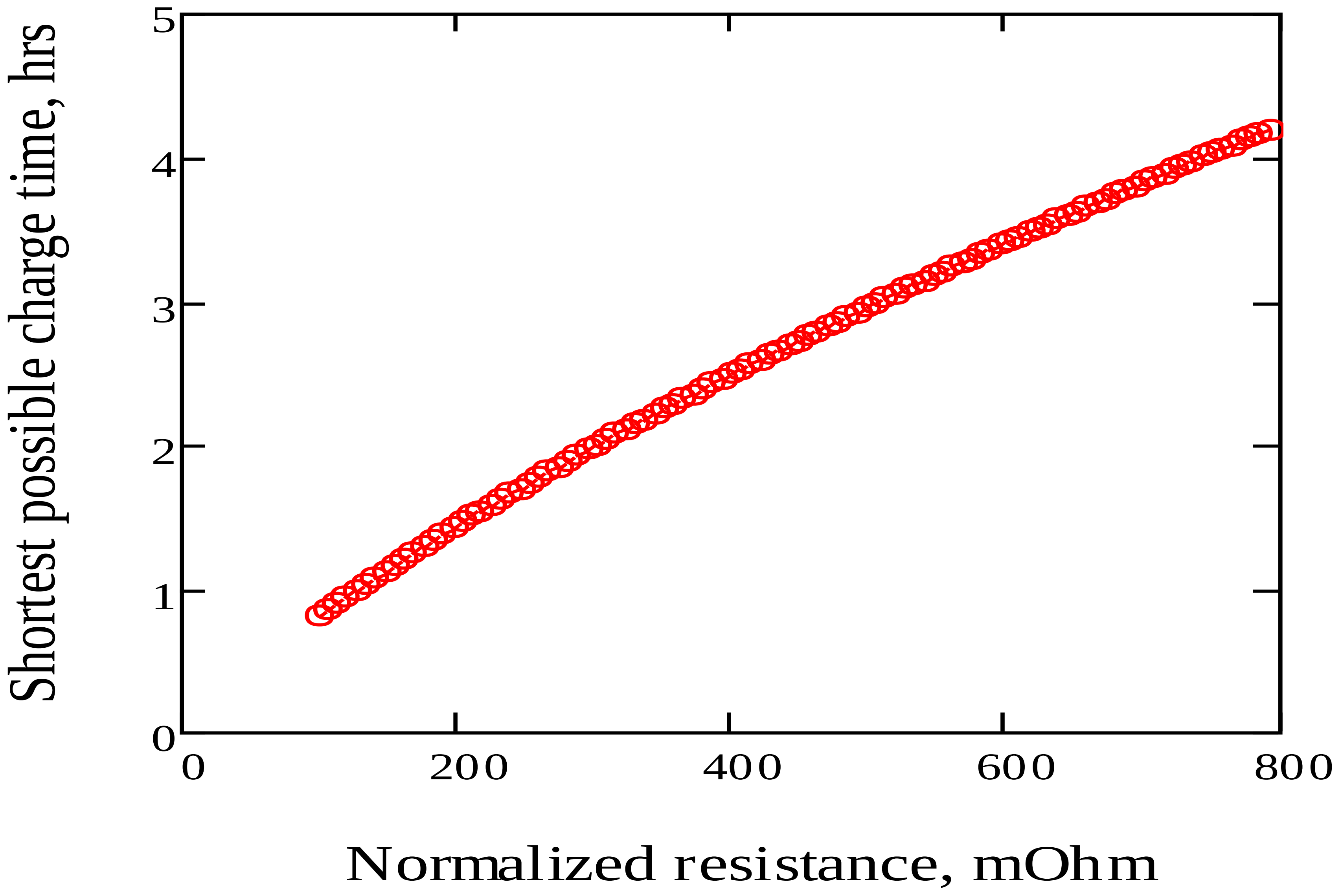


Increasing constant current (CC) charge rate

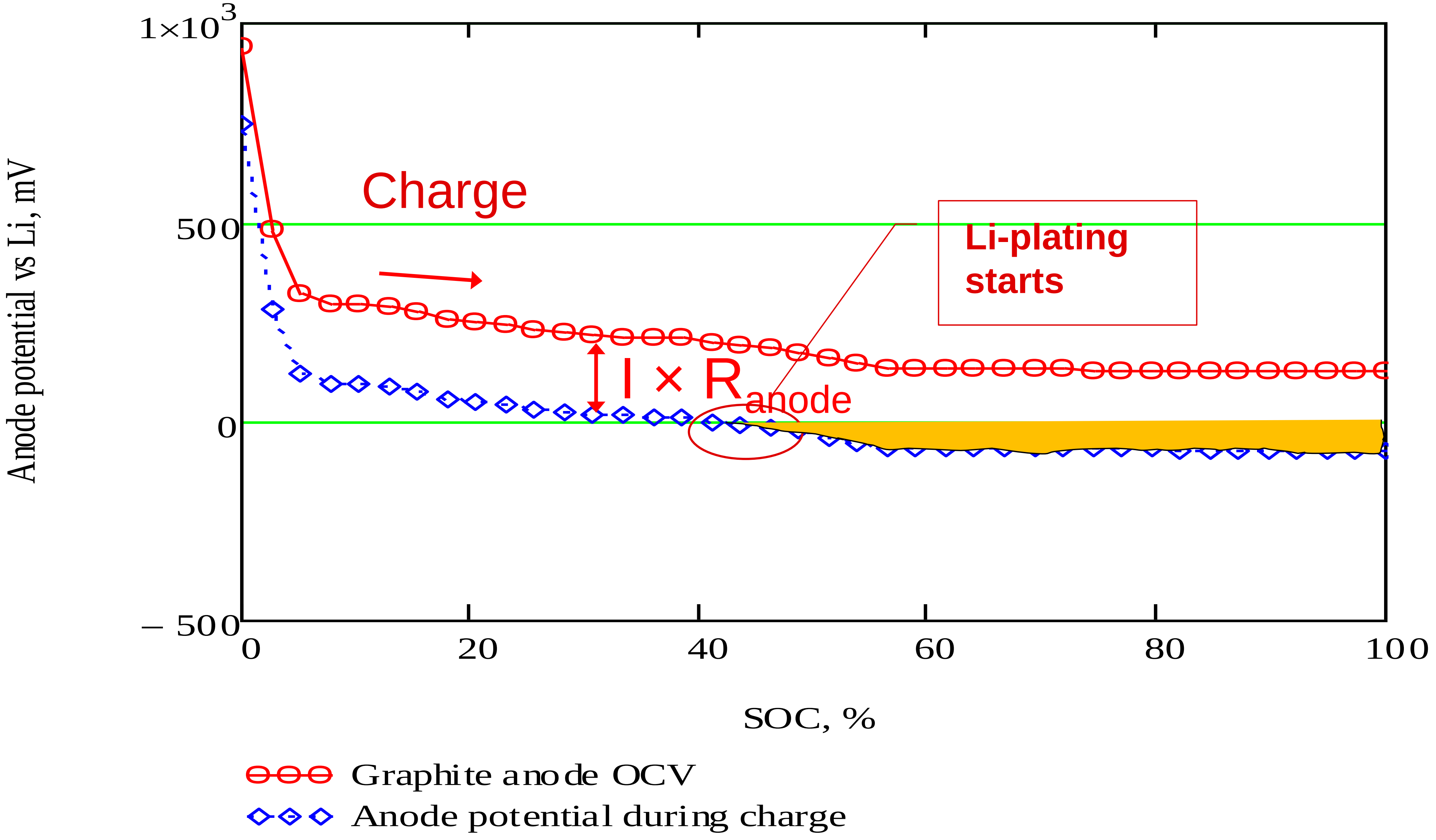
TEXAS INSTRUMENTS

Normalized resistance effect on shortest possible charge time for CC/CV charge



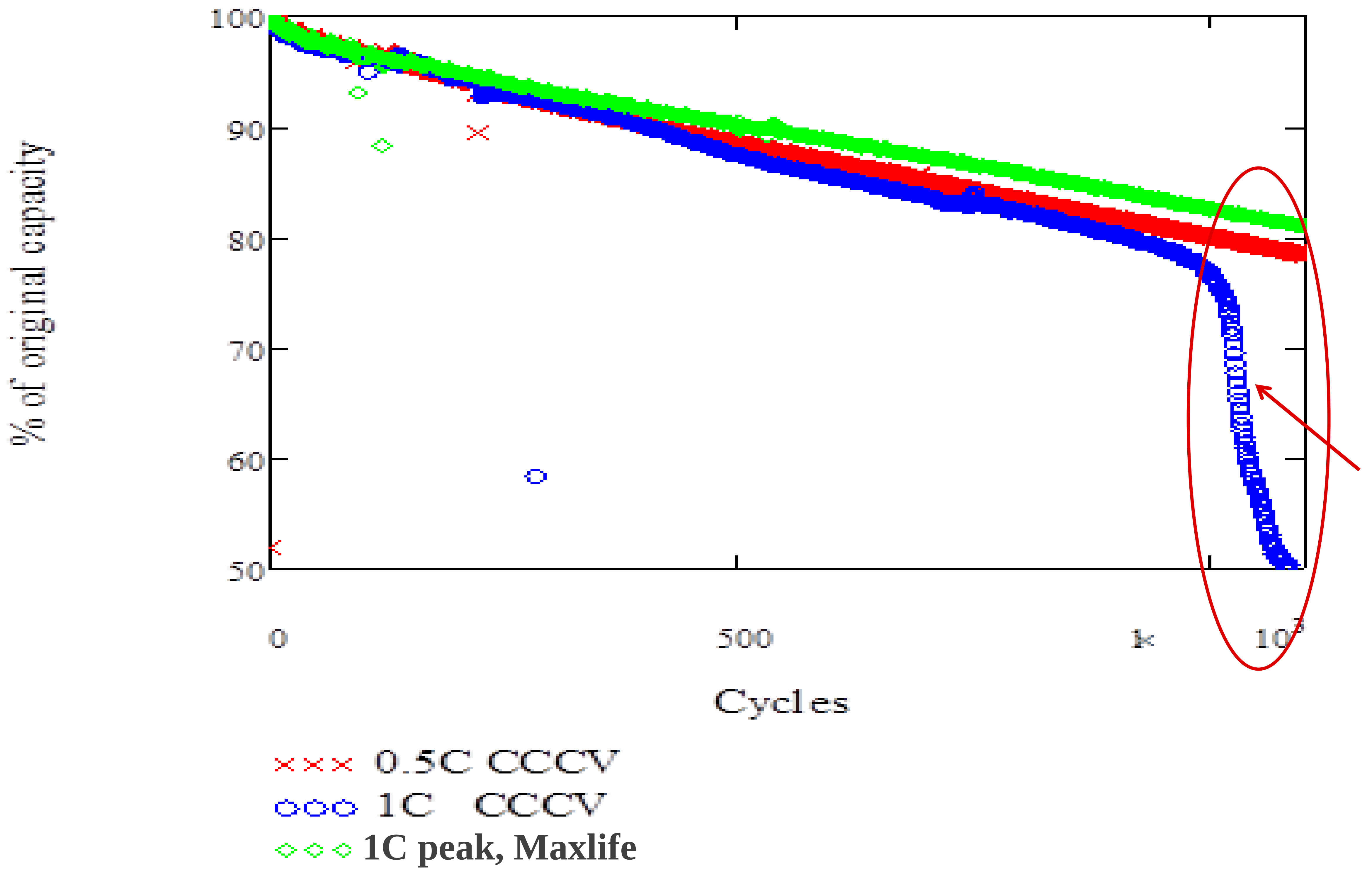


Charge rate limitation due to Li-plating



- Graphite open circuit potential is above Li potential during entire charge period
- However, at **high charge rates, low temperatures** or for **aged cells,** I x R drop across anode can cause anode potential to go below zero potential, causing Li-plating

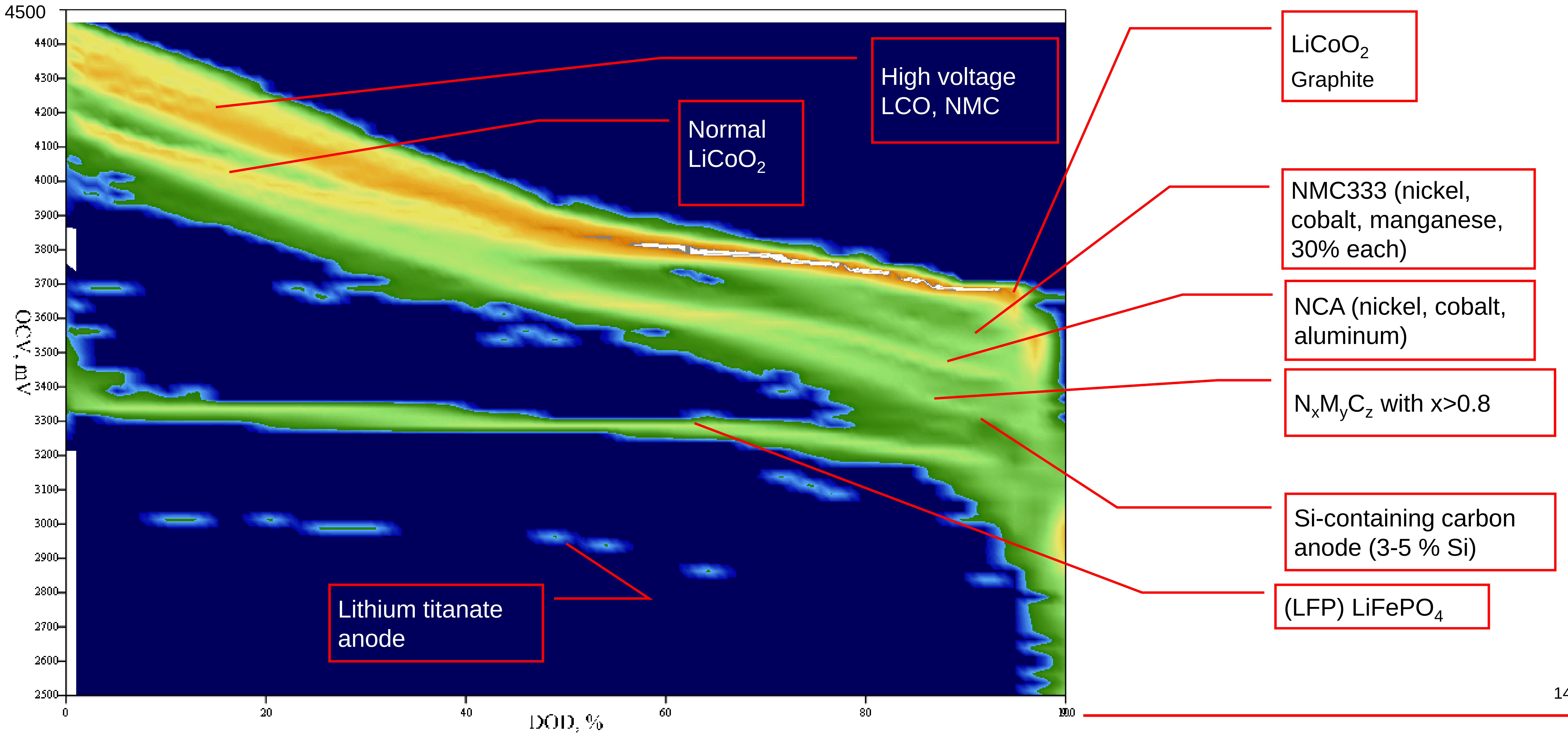
Li-plating caused by resistance increase of an aged cell



- Exponential capacity drop due to Li-plating
- Possible Li-dendrite formation, safety issues
- With the same 1 C peak current, Maxlife™ prevents capacity drop

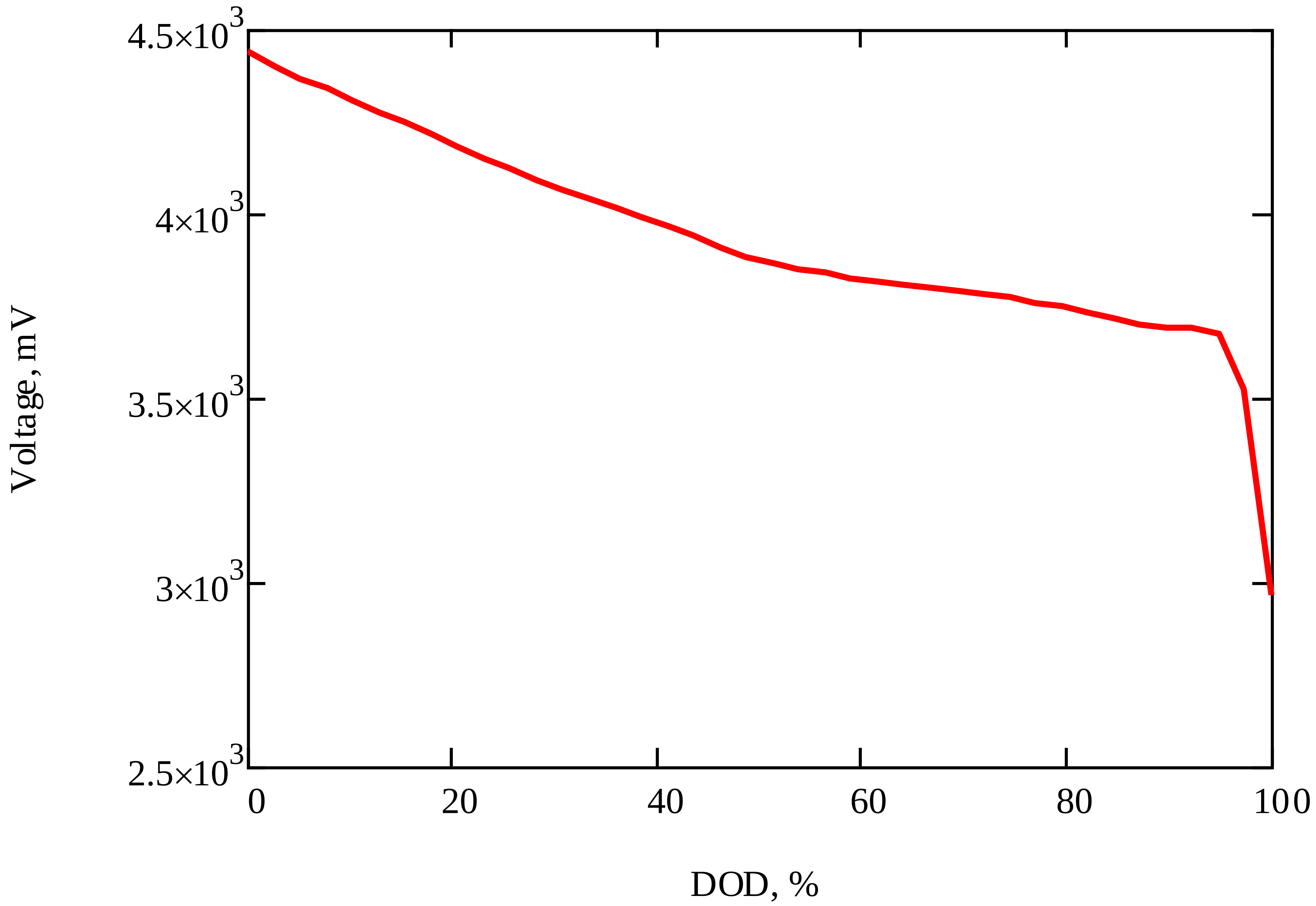
State of the art

Present market snapshot: Probability of open circuit voltage (OCV) based on chemistry occurrence in the market



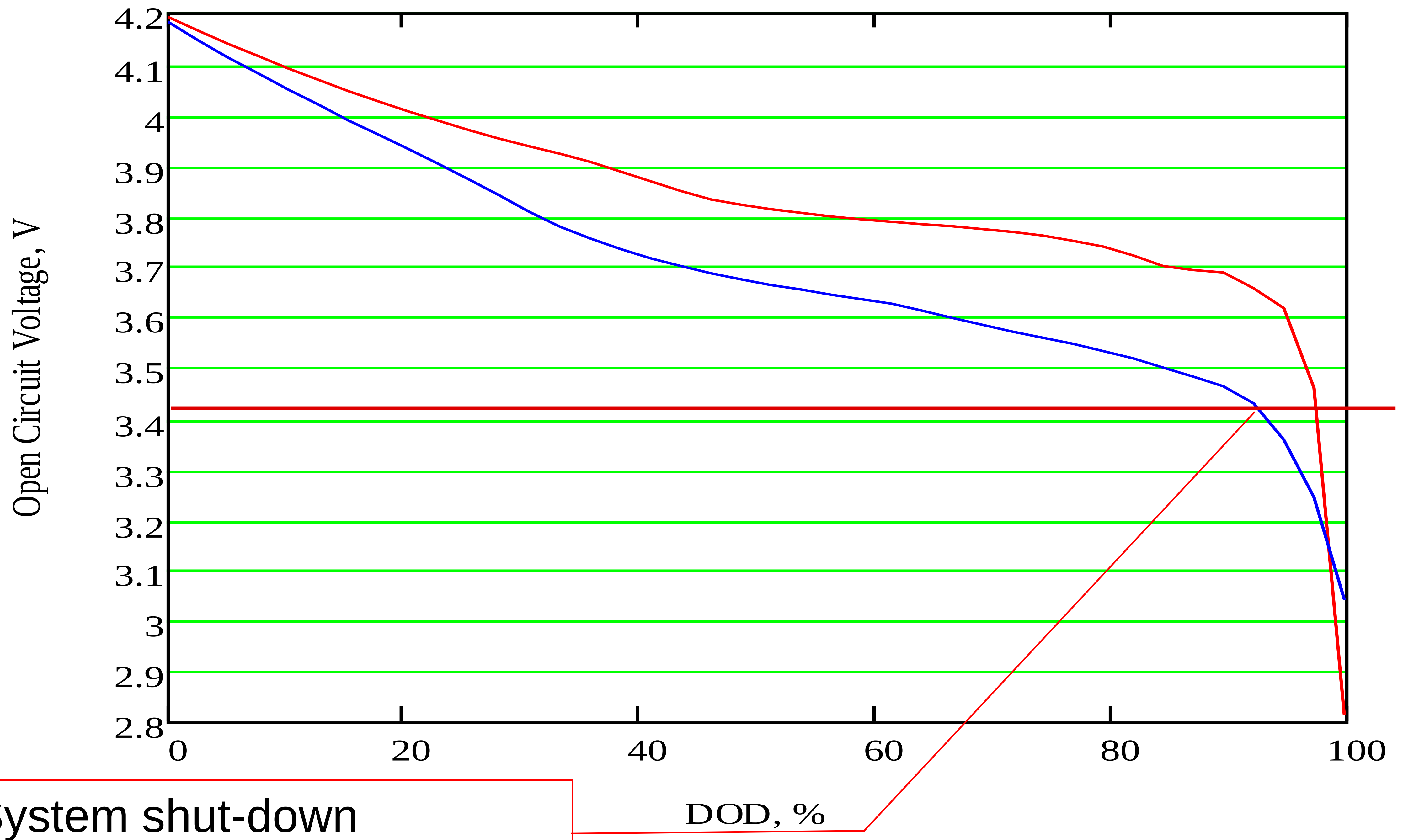
* Hotter color means more common

Highest energy choice now – $LiCoO_2$ charged to 4.45 V



- Improved electrolytes and ceramic coating on separator enabled higher voltages
- Highest energy is provided due to high voltage and increased capacity due to higher cathode utilization
- Instability of $LiCoO_2$ at higher voltages will likely prevent further increases

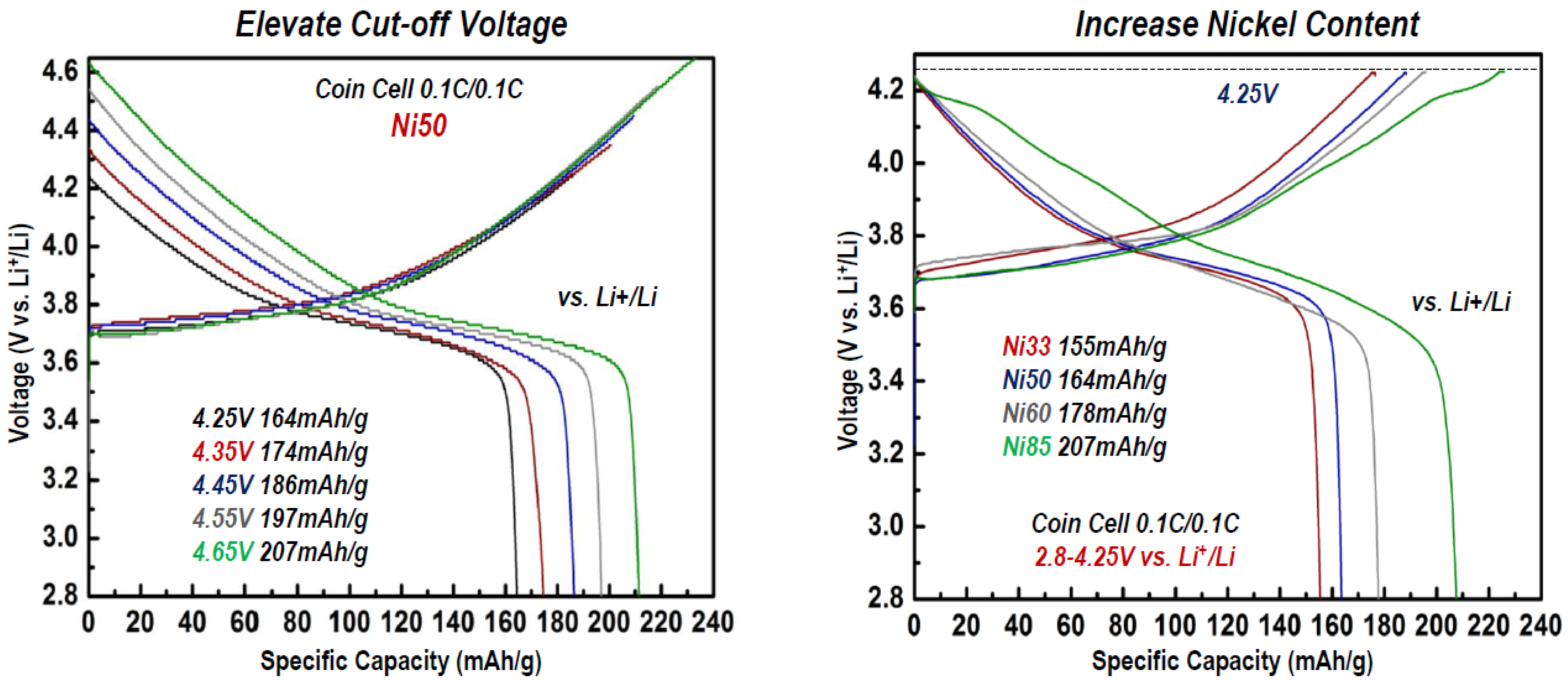
Cost reduction: Replace more Co – NCA, NMC, enable with lower termination voltages



System shut-down

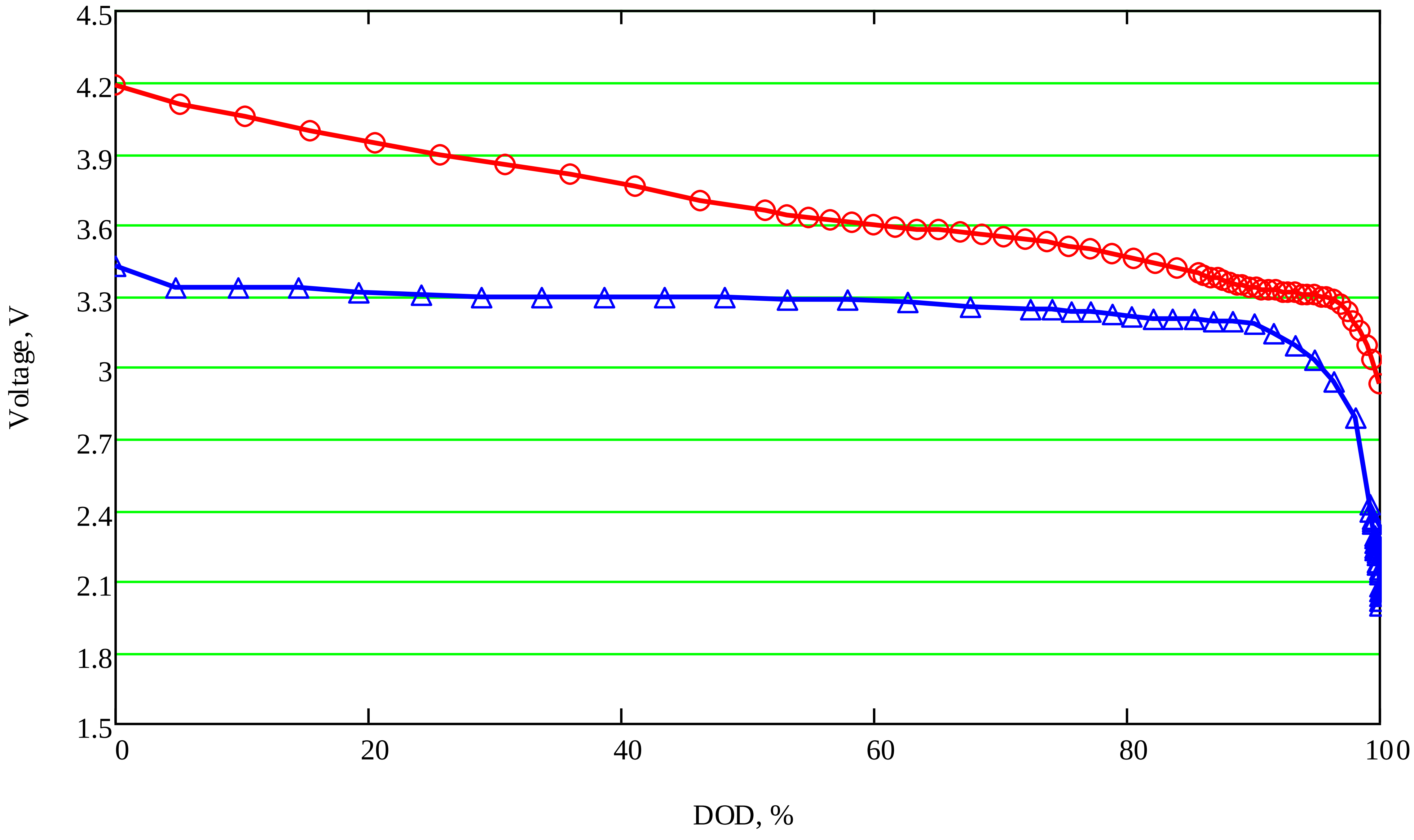
- Replacing some Co with Ni and Mn reduces cost, for example in NMC 532: $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$
- High system shut down voltages in the range of 3.2-3.4 V are favoring $LiCoO_2$ vs Ni-based chemistry
- This is one reason why Ni-containing chemistries (NCA, NMC) have little penetration in single-cell smart phone or tablet systems, but lots of use in 2-4 cell laptops and automotive
- Future improvements in power management such as use of step-up regulators can open opportunities for lower voltage cells

Higher nickel content and higher voltage – future energy increases in NMC (333→ 811)

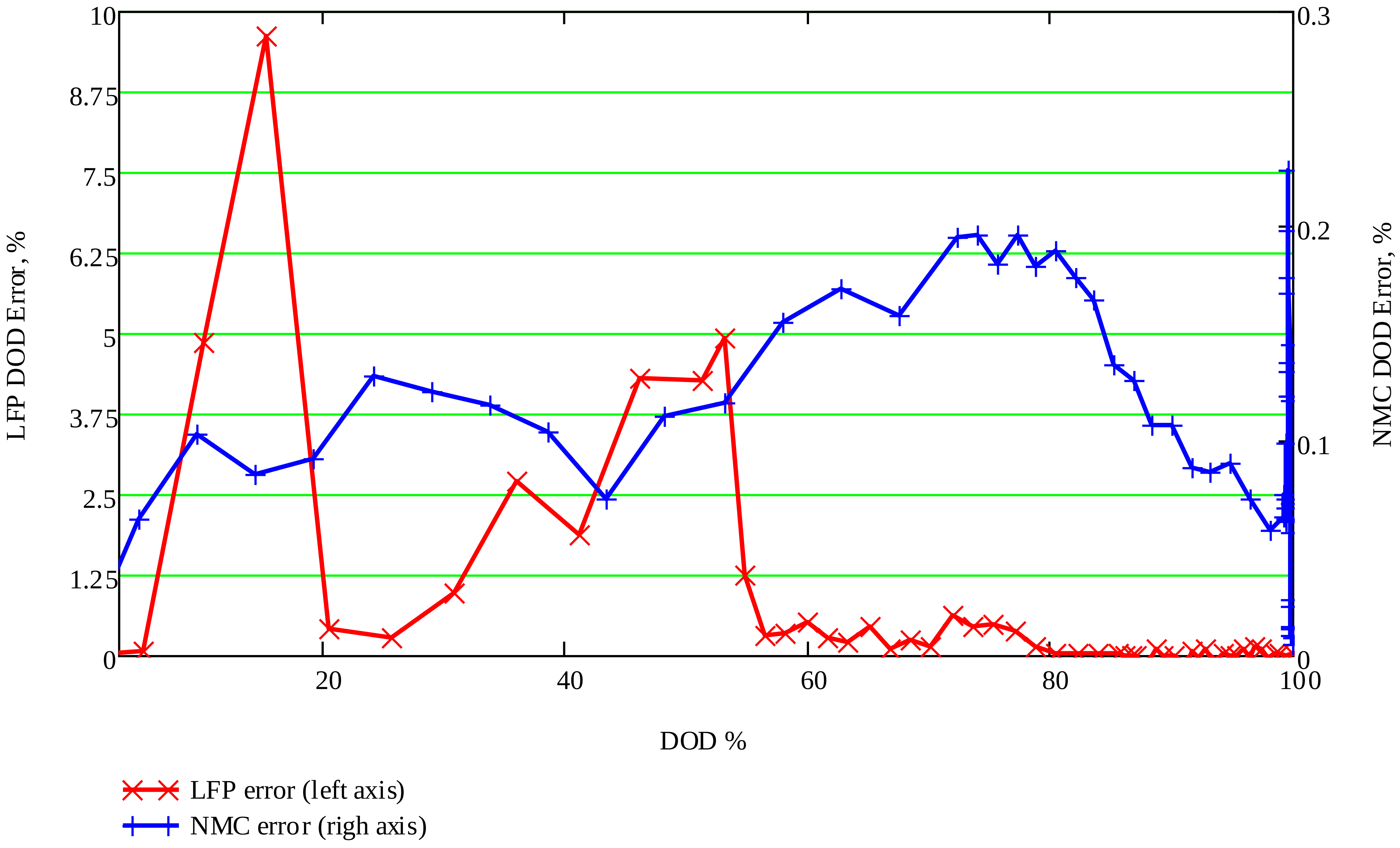


*CATL presentation in Advanced Automotive Battery Conference Europe, Liang Tao, Mainz, Feb. 2nd 2017

$LiFePO_4$ – Ni not needed!
Very flat OCV profile, Here NMC vs $LiFePO_4$



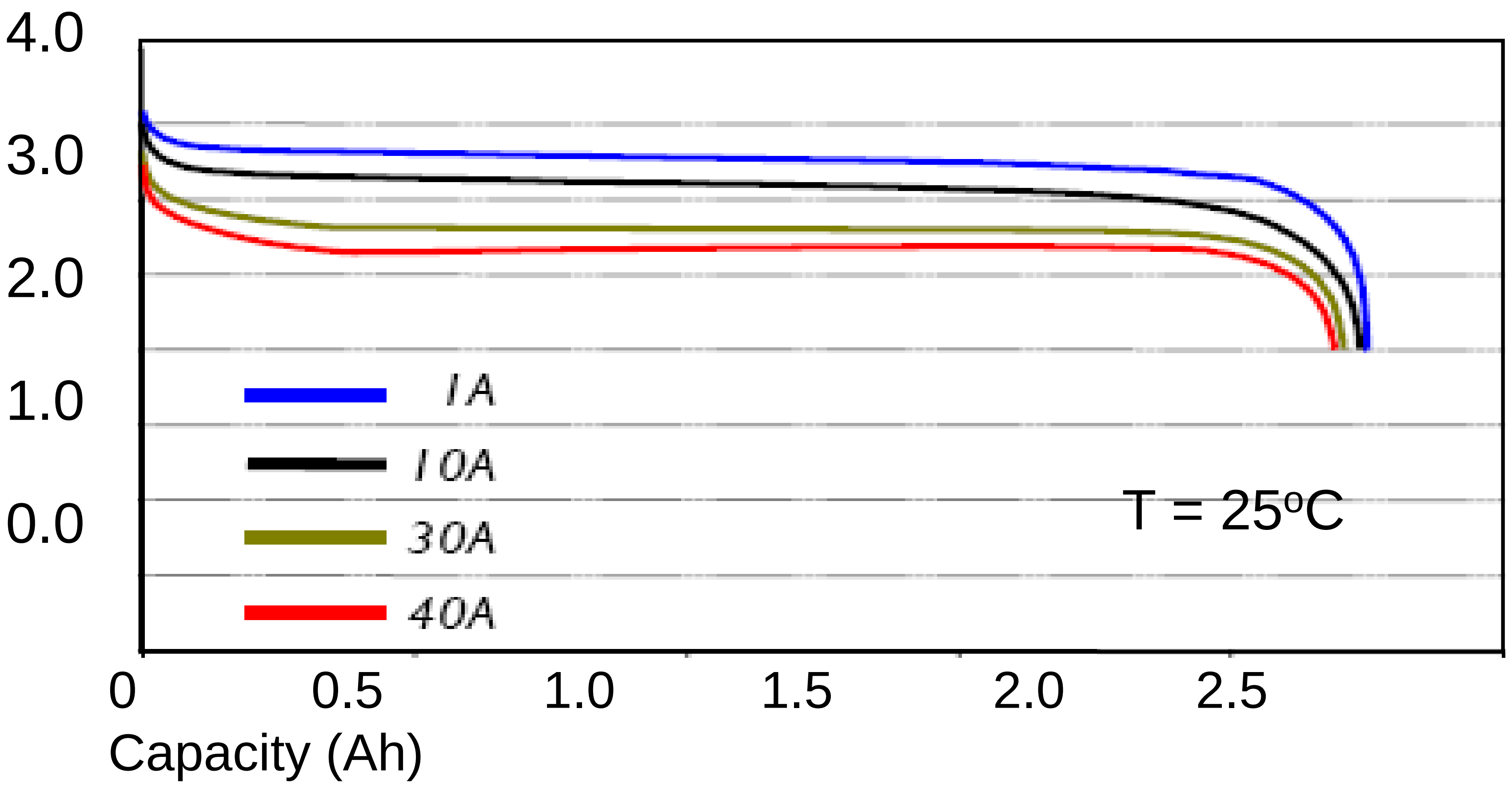
Correlation error in DOD, % for NMC vs LiFePO4, given 1mV measurement error – 20 times higher!

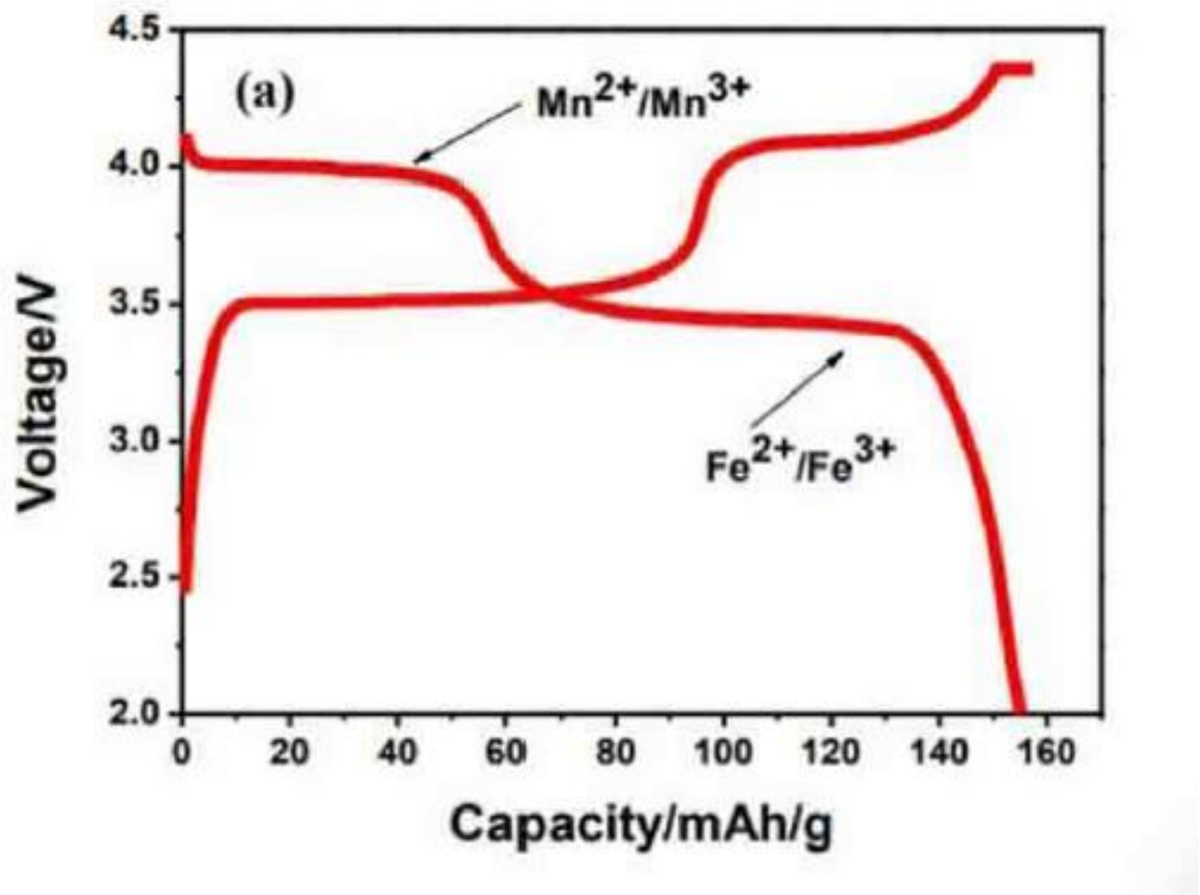


LFP Summary

- Pros:
  - Higher Safety: 350 °C thermal runaway;
  - Low Cost
  - No supply contains, as no Ni or Co needed
- Cons:
  - Lower volumetric energy density by 30%
  - Flat voltage profile requires higher voltage measurement accuracy

- Improvements: LMFP development by CATL, $LiFe_xMn_{1-x}PO4$, energy density improves by 25%.

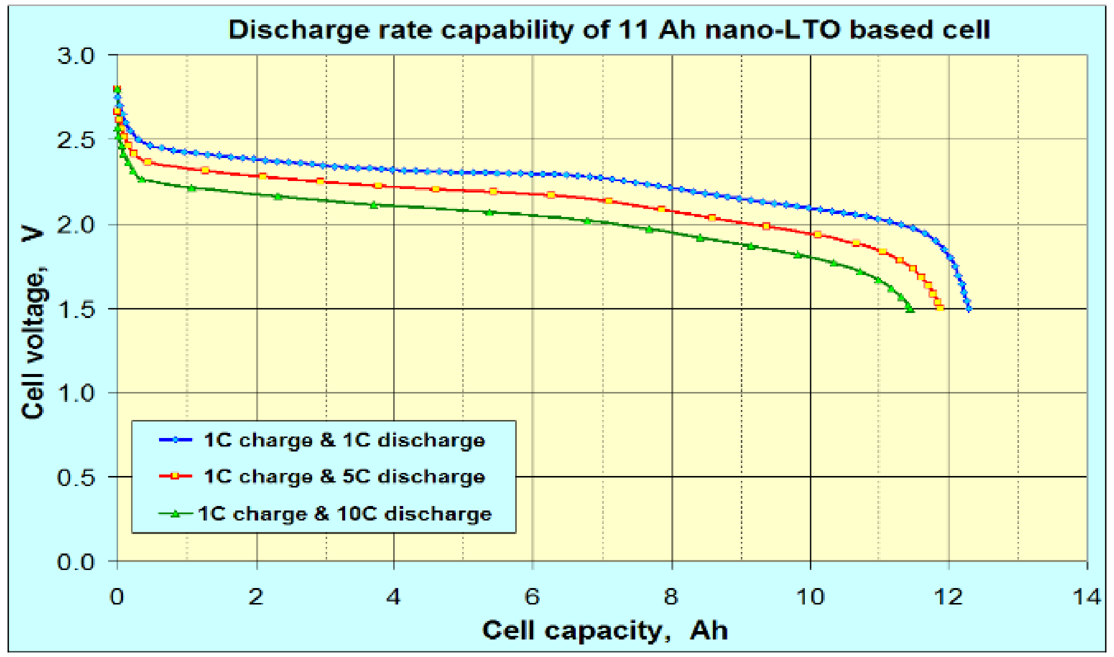


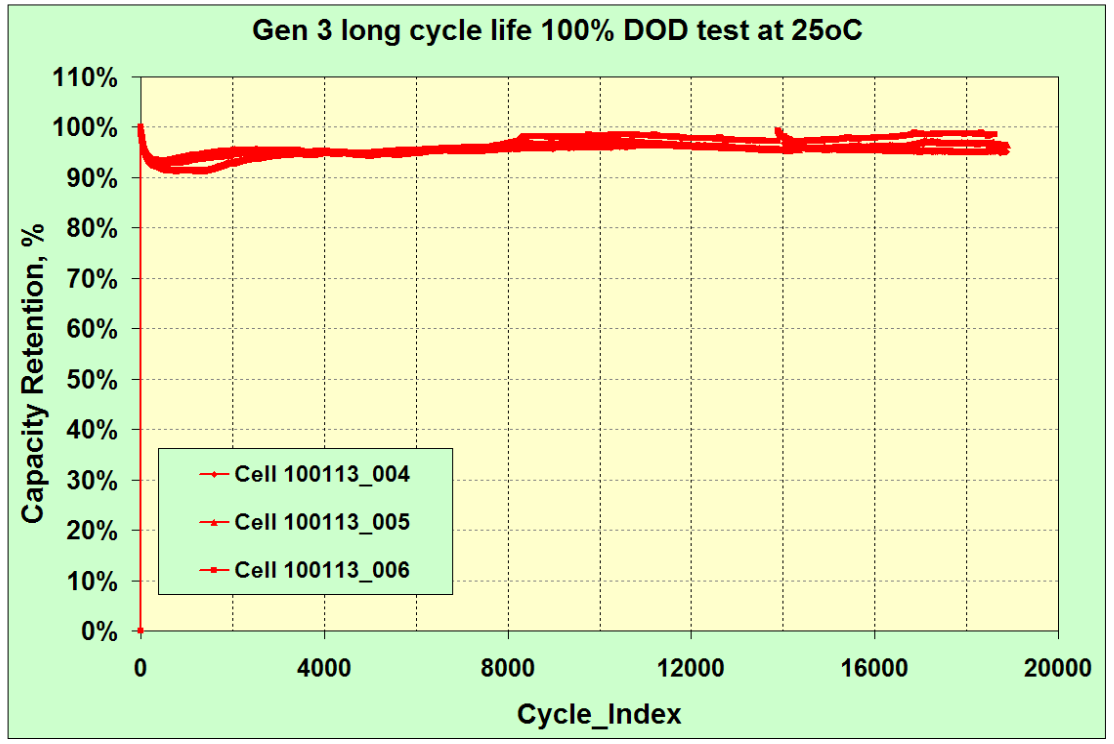


*http://www.a123systems.com

**Tycorun Energy, LMFP industry special report 2022

Power backup applications – longevity, high rate capability is needed





Li-titanate anode, $Li_4Ti_5O_{12}$

Pros:

- Cycle life over 20000 cycles
- Lowest impedance
- Best low temperature performance

Cons:

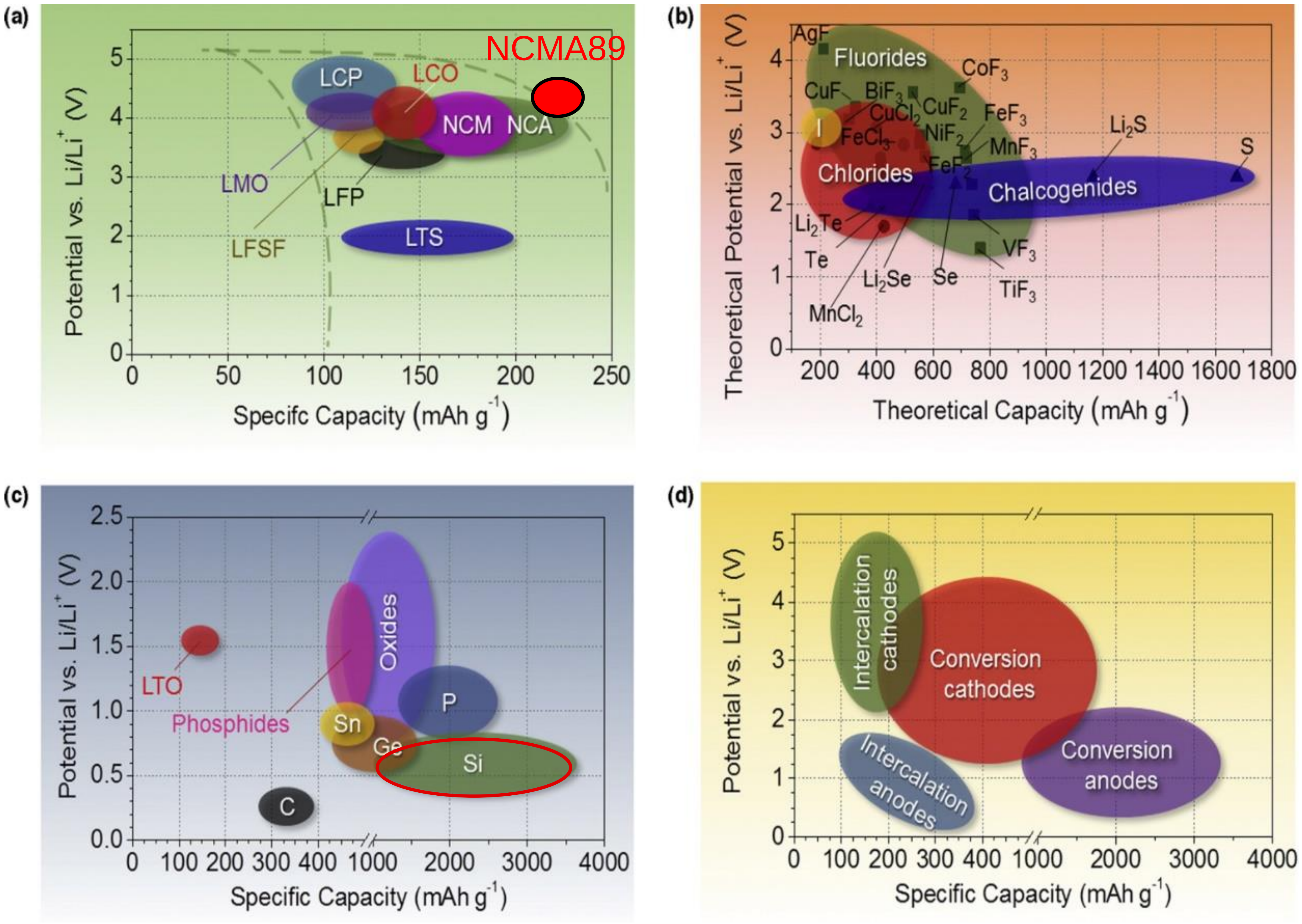
- High price of titanate
- Low energy density due to voltage range from 2.6 V to 1.5 V
- NMC is a cheaper alternative, with less cycle life. Used solar backup batteries and in server backup applications. Usually charged to 4.1 V or less for better calendar life.

*Altairnano, Batteries 2012, October 24th-26th 2012, Nice, France

Where do we go from here in the near term (<5 years)?

Choices in materials to increase capacity

Intercalation | Conversion

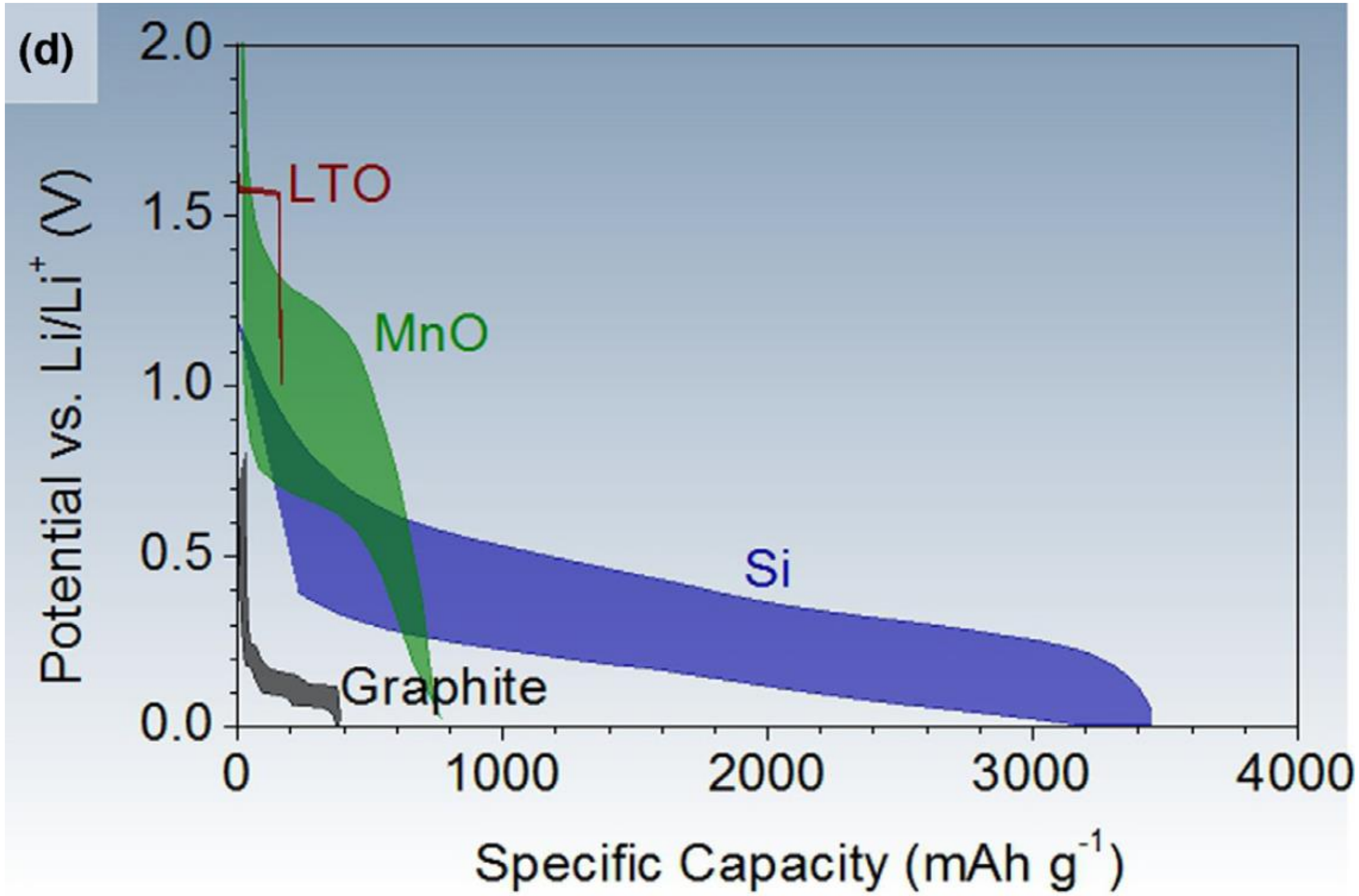


Cathode materials

Anode materials

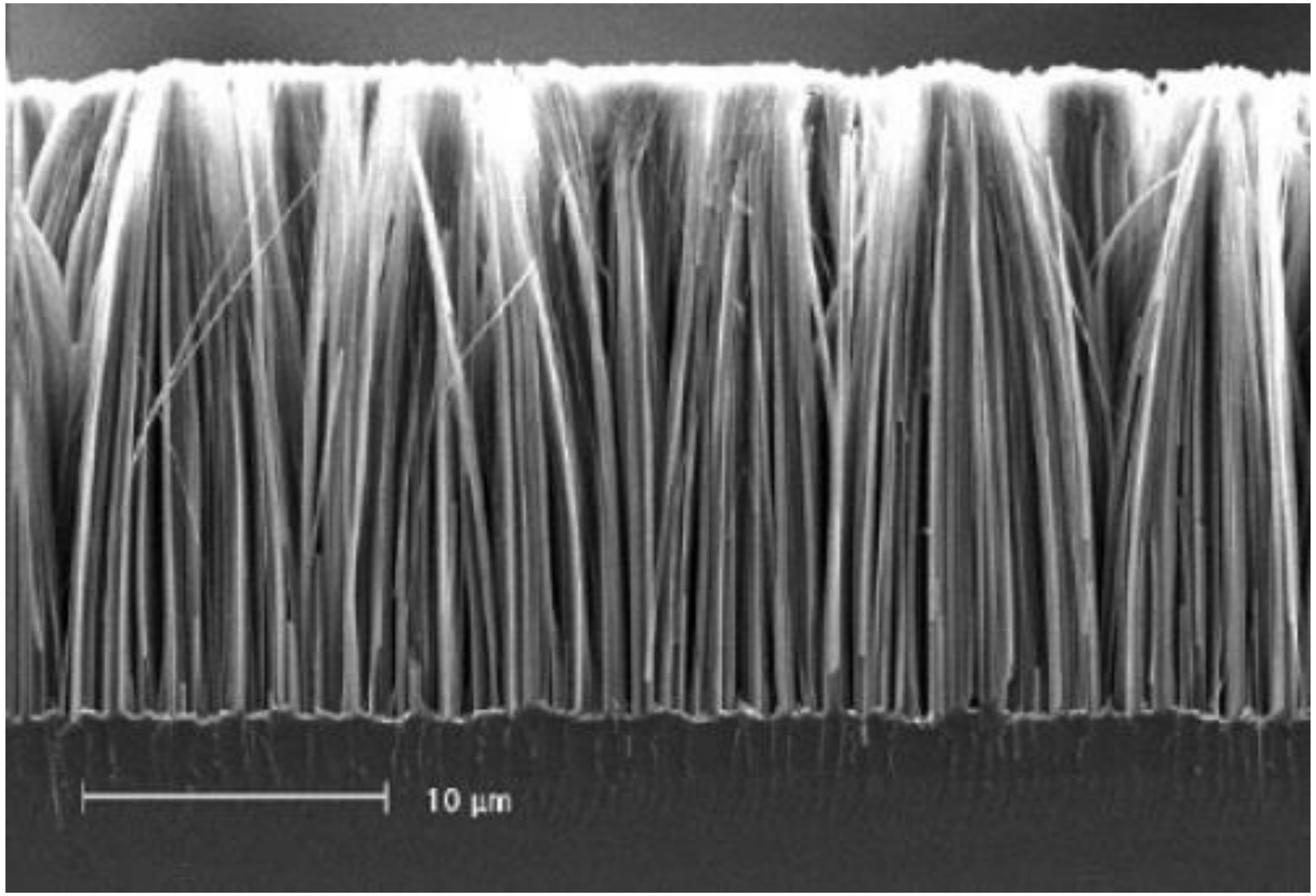
*Li-ion battery materials: present and future Naoki Nitta et al. Materials Today, 18/5, 2015

Higher capacity by improving anode material: Si is on its way



*Li-ion battery materials: present and future Naoki Nitta et al. Materials Today, 18/5, 2015

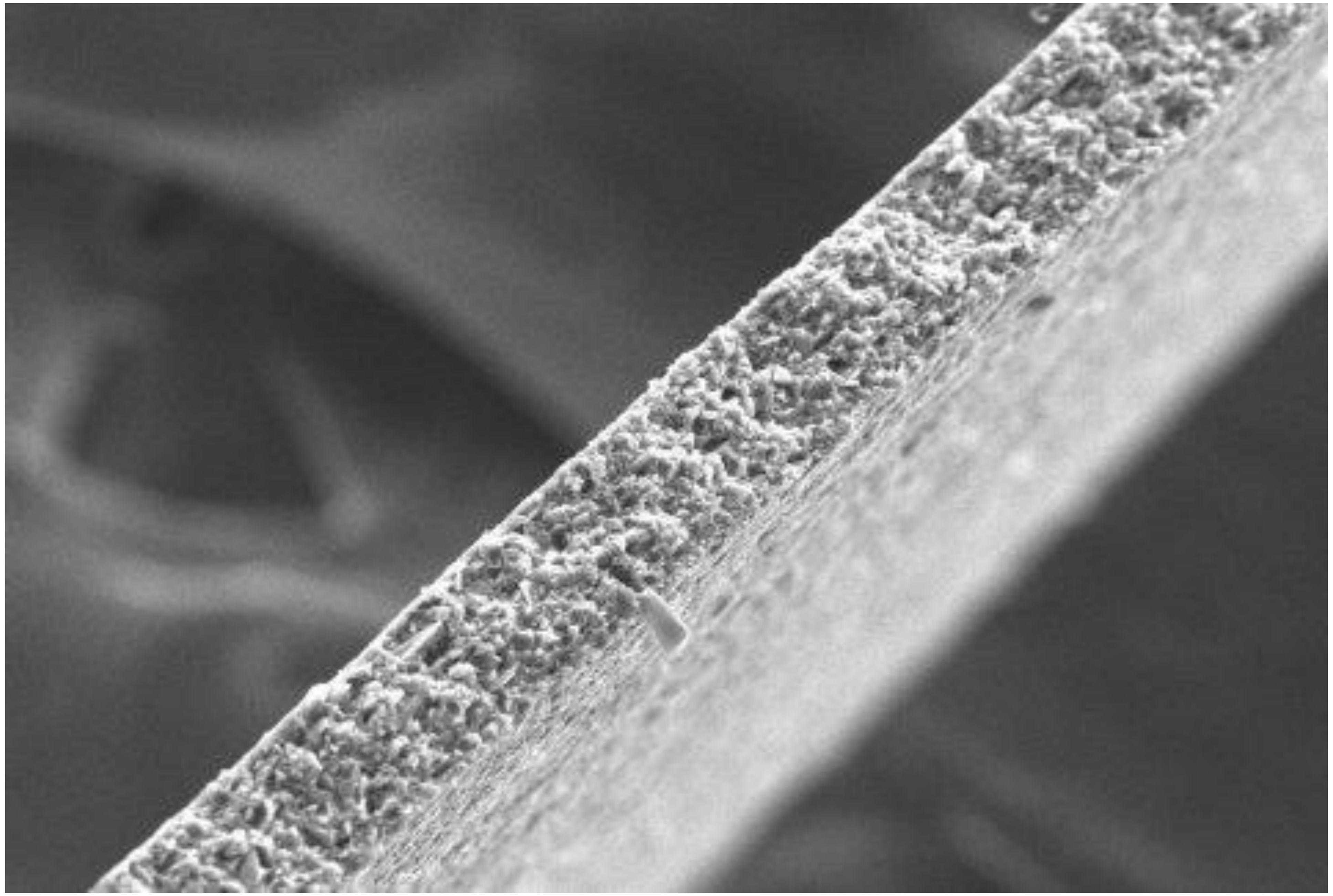
Latest news on Si: Nanowires and nanoparticles



Cross section of Si-nanowires electrode
(Photo: Global Silicon Nanowires Market 2018)

- Si-nanowires achieve good cycle ability and Si-utilization.
- Several startup companies are working on reducing cost of Si-nanowires synthesis.
- Mass production using carbon-coated Si particles material started – cell is used in a fitness tracker.

Latest news on Si: Micromatrix method



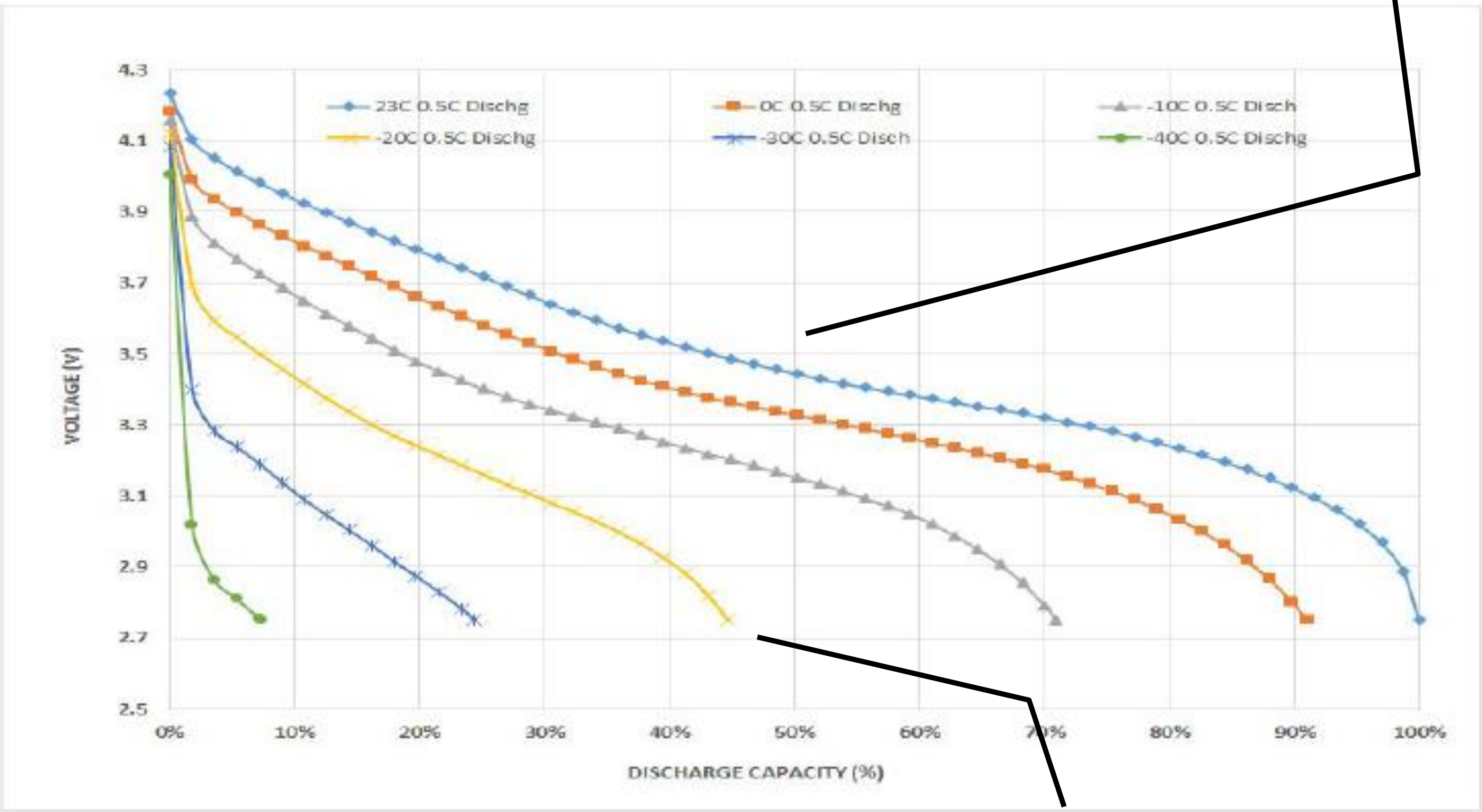
Cross section of Enevate's HD-Energy Anode utilizing a silicon-dominant micromatrix (Photo: Business Wire)

- Micromatrix with high Si-content has emerged as a cost-effective method to achieve good cycle life.
- High Si cells have advantage of fast charging due to Li-alloying reaction, high surface area and potential that is far from Li level.
- A startup company is partnering with automotive cell makers with a high silicon cell: 750 Wh/L, 5 min charge to 75%.
- Another startup is utilizing nano-scale metalloids (Sn, Si, others) to achieve 10 C rate, 5 min. charge.

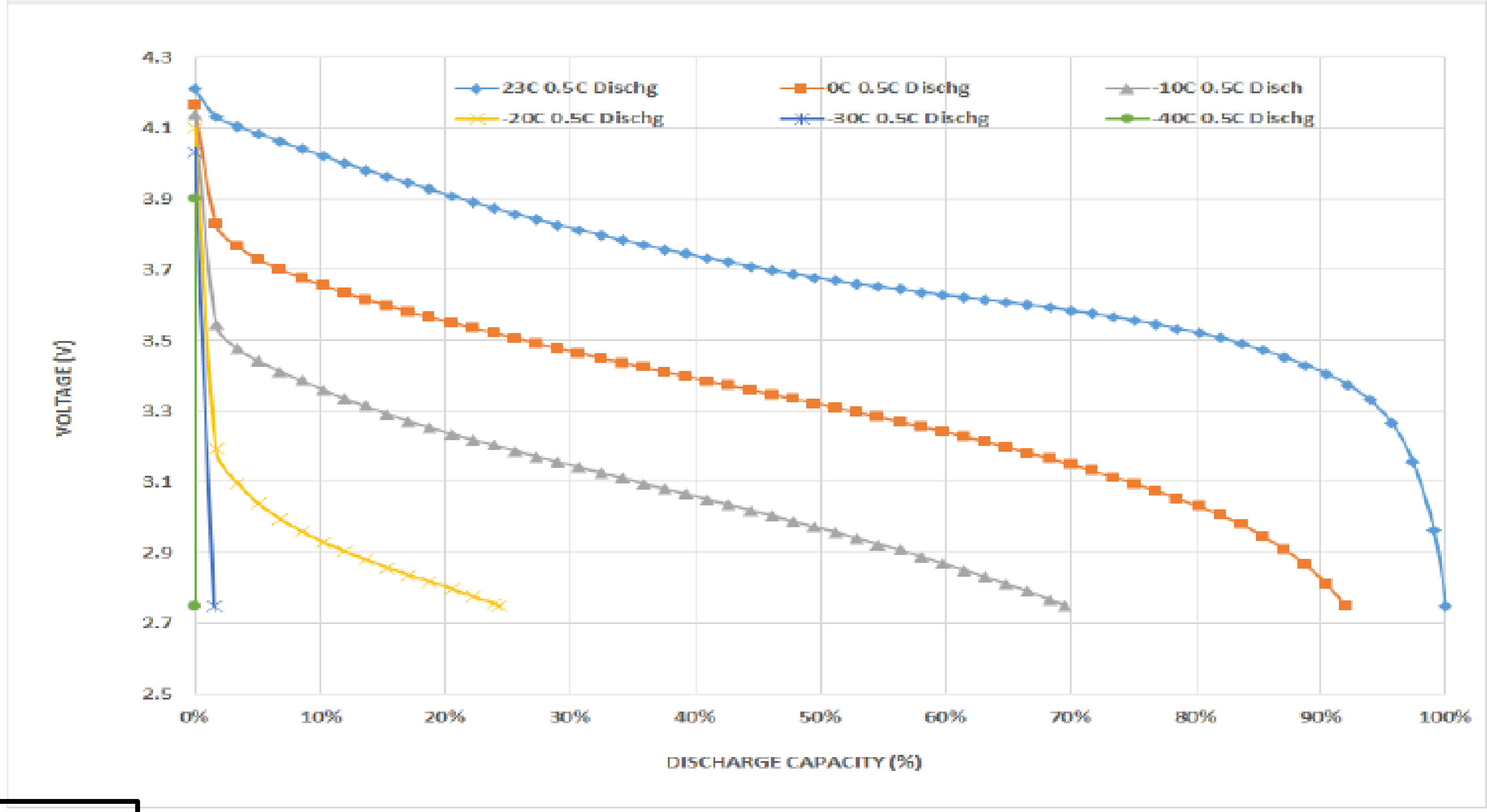
Rate and temperature performance of Si-cells

Not for single-cell devices: most capacity is below 3.5 V

Micro-matrix design Si cell



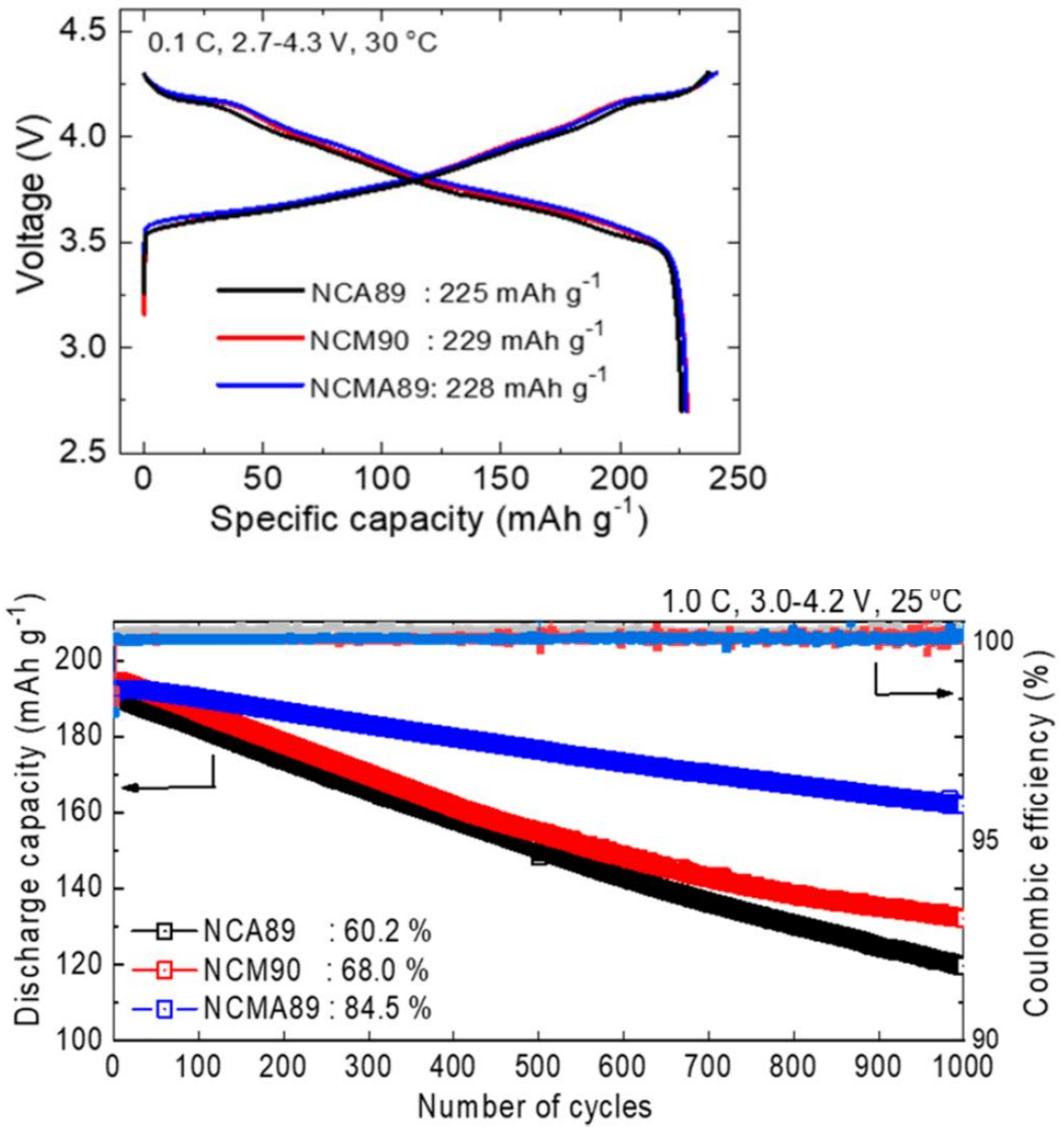
Conventional graphite anode cell



Great at low temperature: Close to 50% capacity still available at -20 °C

*Enevate, "Ultrafast Charging Silicon-Dominant Anode and Li-ion Cell Technology for EV Applications", International Battery Seminar and Exhibit, Florida 2017

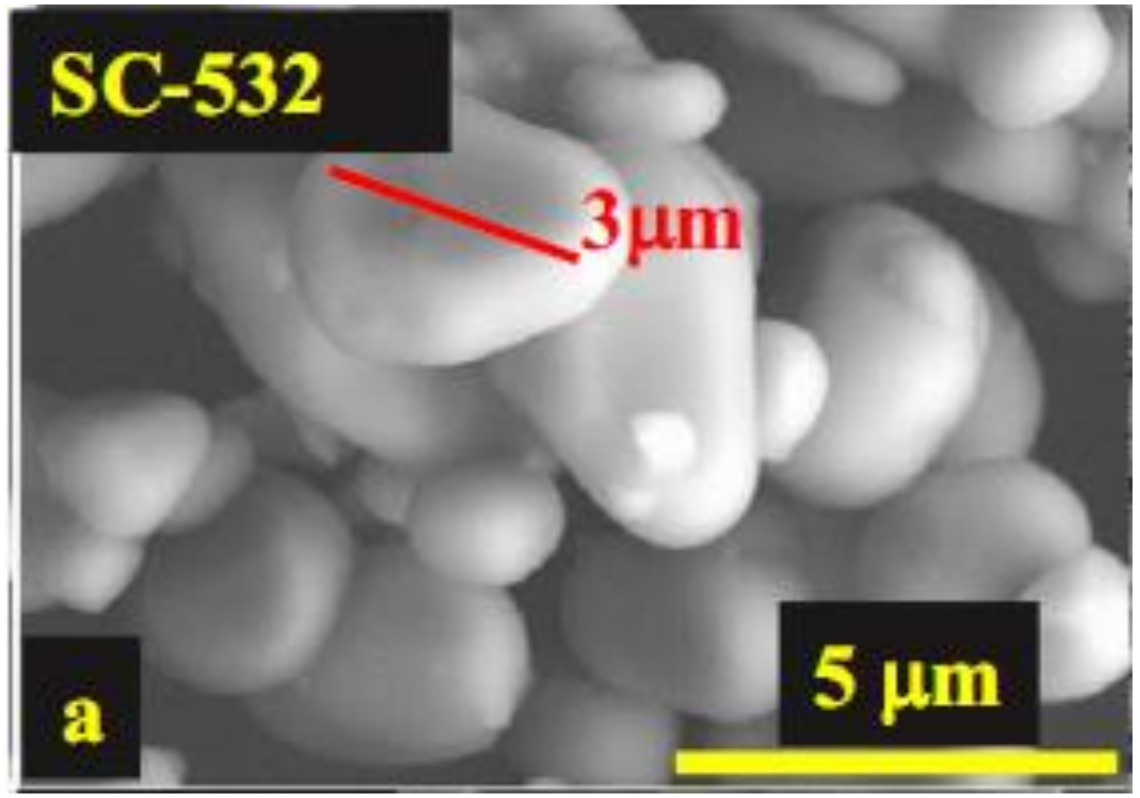
Pushing nickel content in NCMx to the limit: NCMA89



- More Ni is cheaper and more available.
- Can we go beyond 80% Ni?
- NCA89 and NCM90 are unstable, but if you layer them together – excellent cycle life.
- NCMA with 89% Ni will by used by two large EV automakers in 2022.

**Un-Hyuck Kim,Liang-Yin Kuo,Payam Kaghazchi,Chong S. Yoon, and Yang-Kook Sun,*
ACS Energy Lett. 2019, 4, 576−582

Longer cycle life without sacrificing energy: single crystal NMC532 ($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$)



SEM image of single crystal NMC532 powder (SC-532)

5000 full cycles with only 10% capacity loss

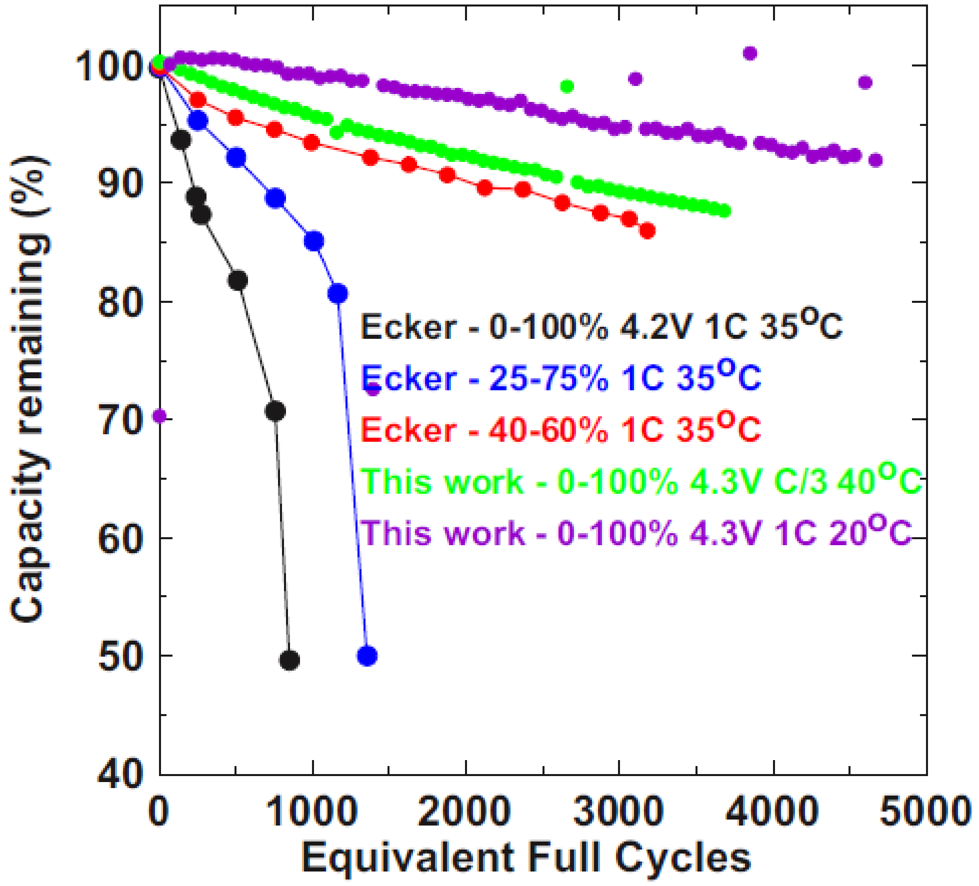


Figure 1. Long-term cycling data plotted as percent initial capacity versus equivalent full cycles for NMC/graphite cells as described in the legend. The

Million mile capable automotive battery enabled

Needed for high cycling with V2G!

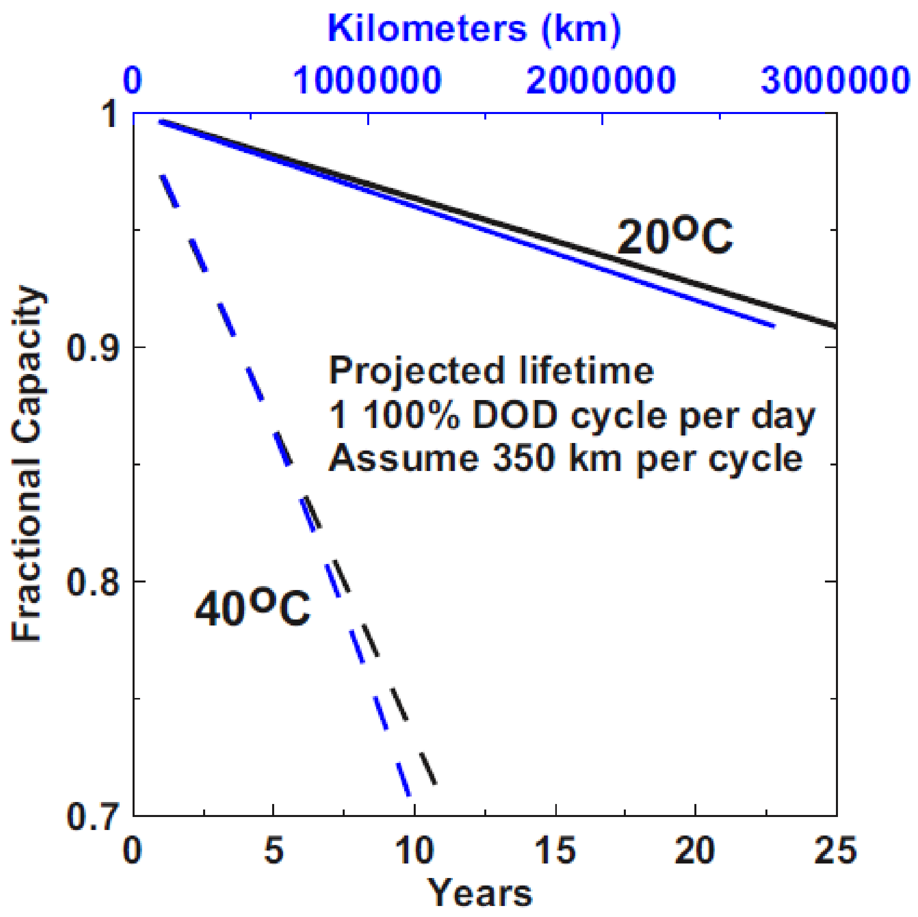
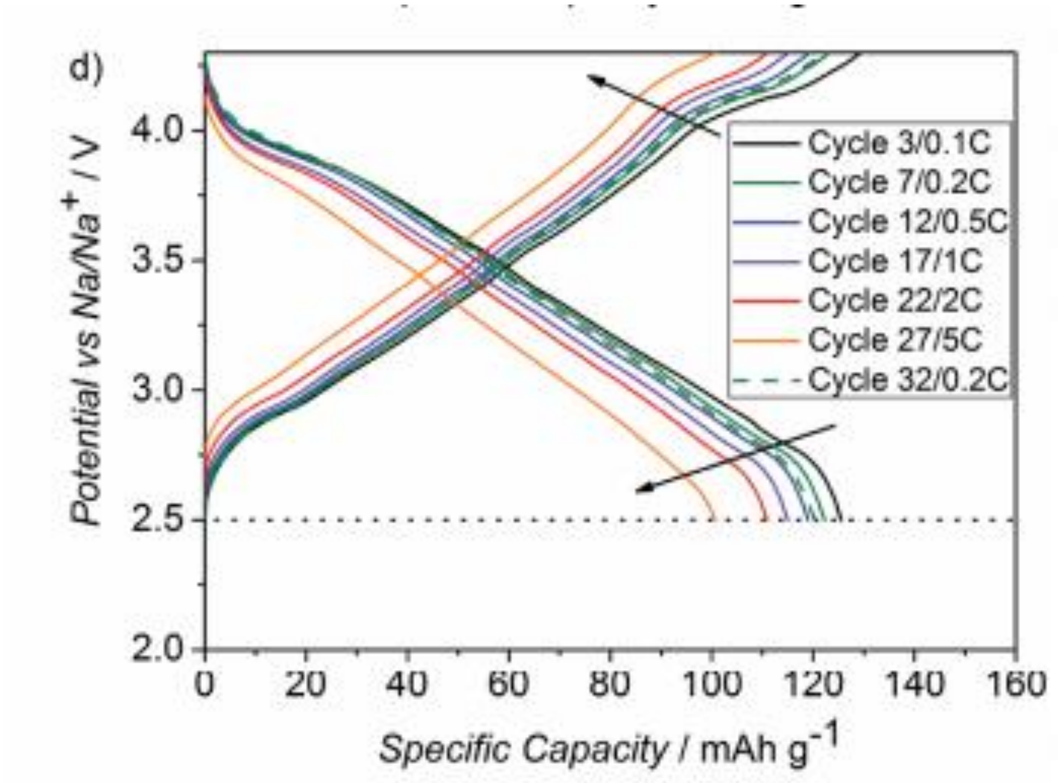


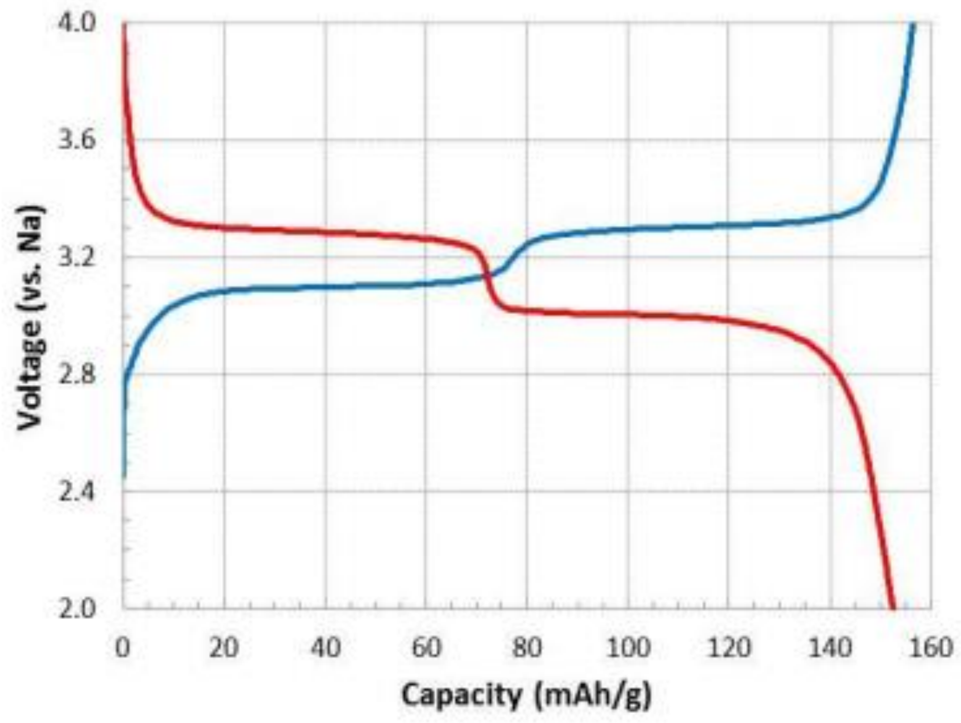
Figure 23. Worst-case scenario lifetime and total driving range projections for the NMC532/graphite cells with 2% VC + 1% DTD at 20 and 40°C.

Journal of The Electrochemical Society*, **166 (13) A3031-A3044 (2019), Jessie E. Harlow, Xiaowei Ma, Jing Li, Eric Logan, Yulong Liu,1,2 Ning Zhang, Lin Ma, Stephen L. Glazier, Marc M. E. Cormier, Matthew Genovese, Samuel Buteau, Andrew Cameron, Jamie E. Stark,and J. R. Dahn

Low cost for storage: Sodium-ion battery



Layered oxide cathode based sodium battery[1]



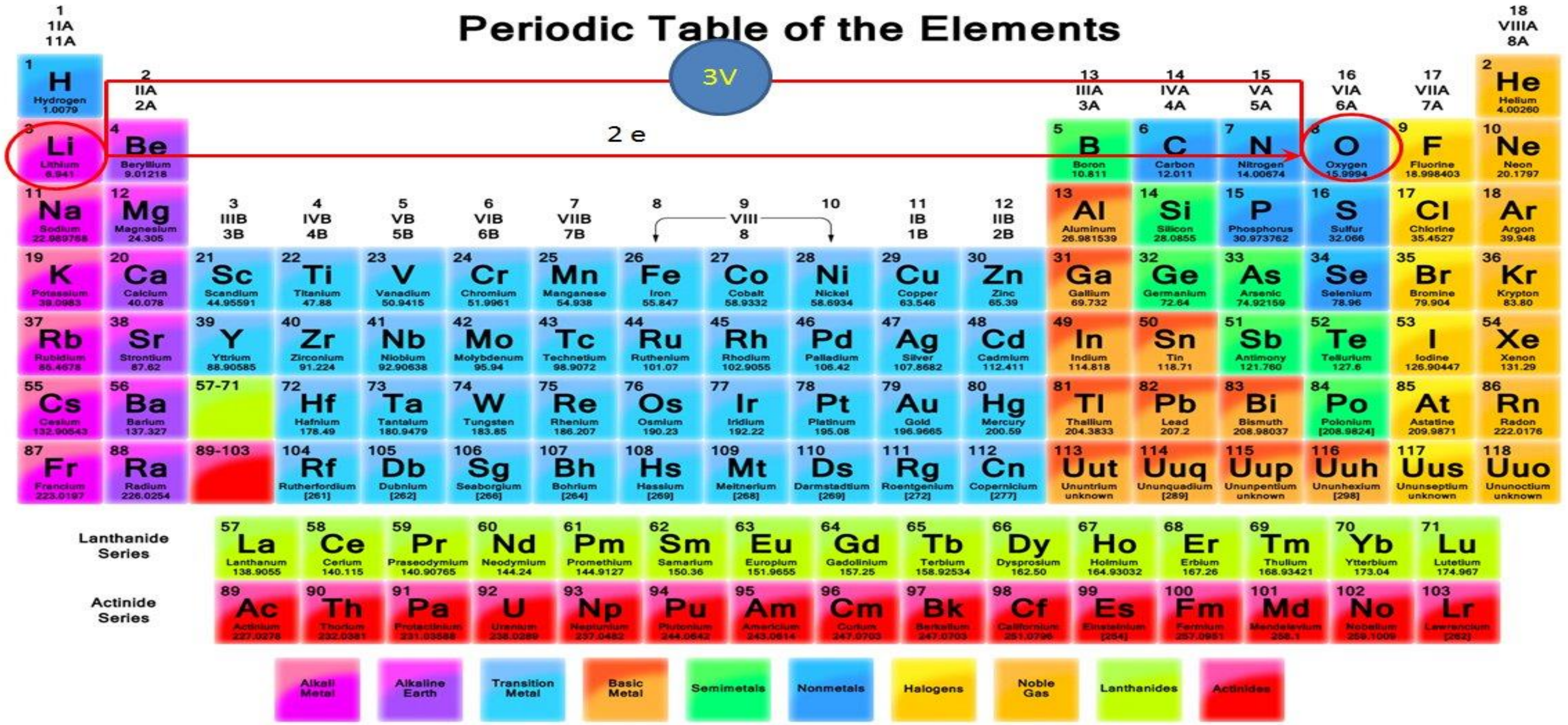
Prussian blue based sodium battery[2]

- Sodium is much cheaper and more available than Li.
- Will always have lower energy density (larger weight), but could be good for solar/wind storage.
- Different cathodes are being considered, including layered mixed oxides and Prussian blue, $Na_2MnFe(CN)_6$ (particularly CATL).
- Can achieve 190 Wh/l and 145 Ah/Kg.

1: *Adv. Energy Mater*. **2016**, *6*, 1501555, *Marlou Keller , Daniel Buchholz ,* and Stefano Passerini*
2: Sharp Labs of America, Dr. JJ Lee, DOE symposium 2015

Looking to the future

Periodic table cathode and anode selection



- Pick anode from top (lightest) left (strongest electron donor).
- Pick cathode from top (lightest) right (strongest electron acceptor).

Highest theoretical energy densities

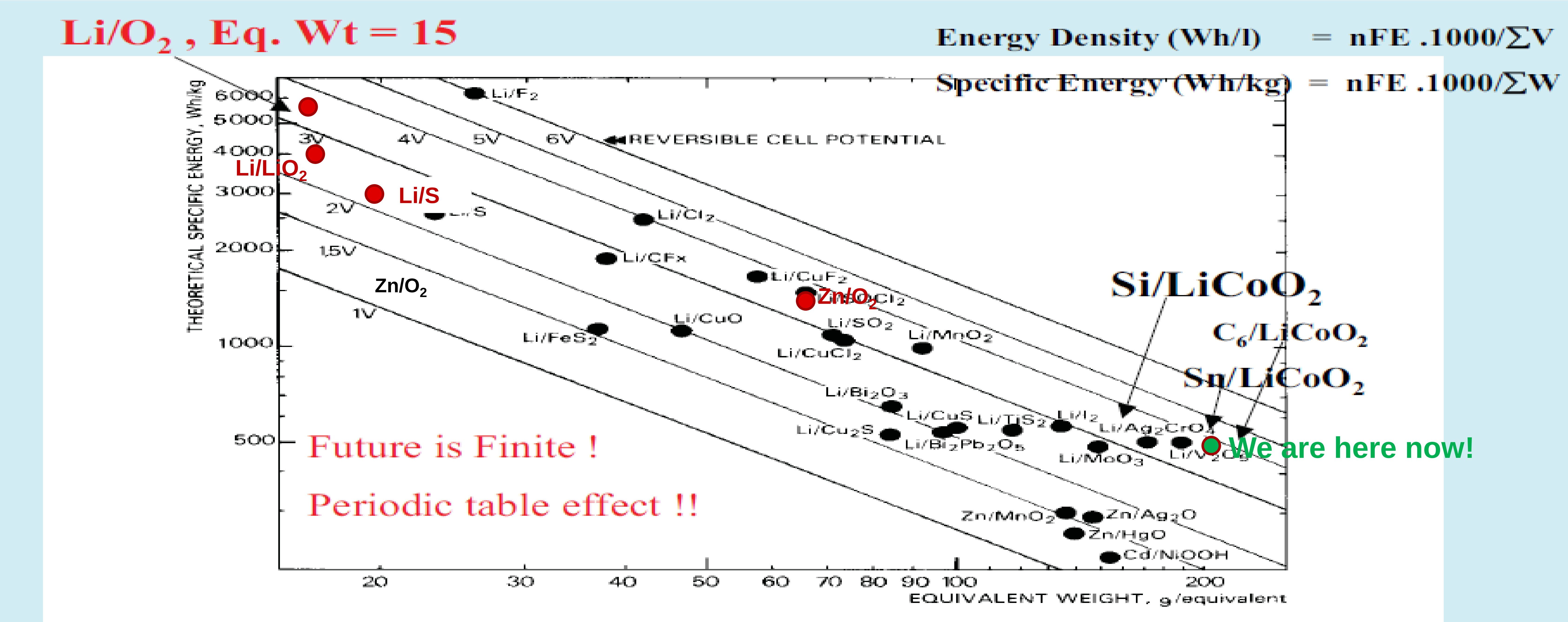
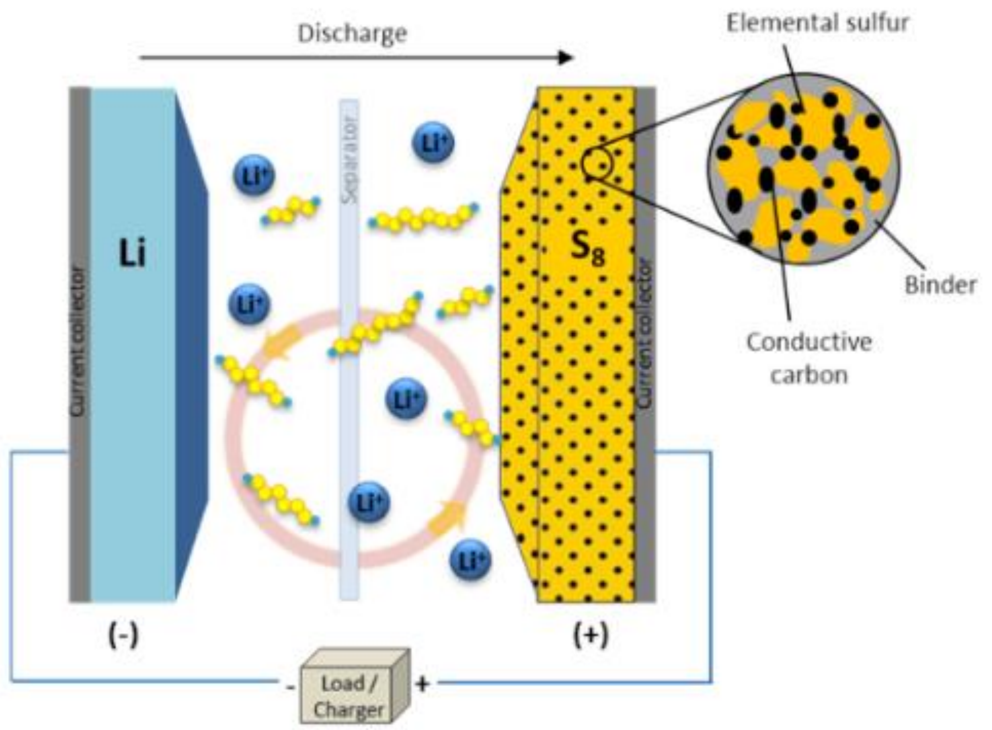


Fig. 1. Effect of the difference of electronegativity between anode and cathode (as reflected by the cell reversible voltage) and of the equivalent weight (of anode plus cathode materials) on the theoretical specific energy on weight basis of various electrochemical systems

*K.M. Abraham, Twenty Seventh International Battery Seminar, Fort Lauderdale, FL, 2010

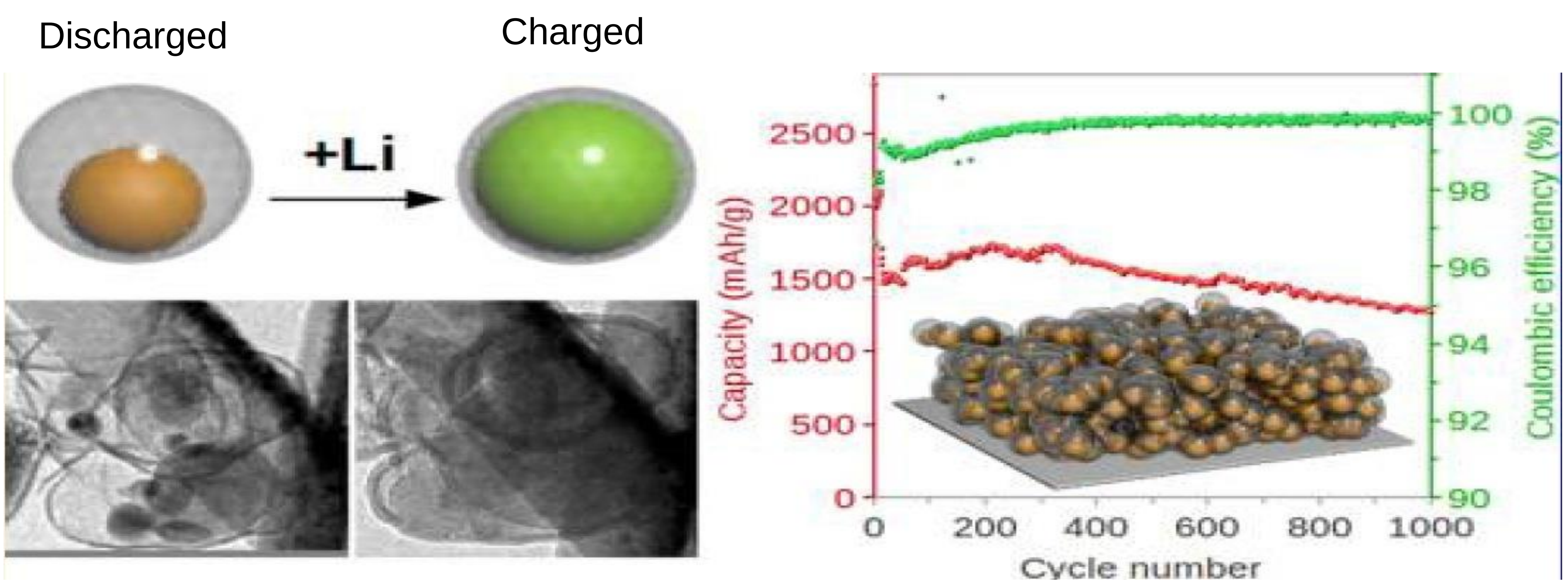
Futuristic chemistries: Li-sulfur

- Theoretical energy density 2550 Wh/kg and 2862 Wh/l.
- Practical cells are still at 325 Wh/kg and 320 Wh/l because of low conductivity of sulfur.
- Low cycle ability and issues with reaching capacity targets.
- Safety concerns about using metallic lithium.
- High self discharge.
- Safety is problematic due to toxic SO_2 production when burning – OK for remote storage batteries.
- Recent improvements to cycle life due to suppression of self-discharge with lithium nitrate, self-healing by saturated LiS_x solution and by using yolk-shell or other nano-encapsulation.
- One startup company has pilot production, improved electrolytes and protective layers.



*From Oxis web-site

Yolk-shell encapsulation



- Yolk-shell encapsulation can be used for both cathode (shown for sulfur) and anode (like Si, Sn), already used by Sila nanotechnologies.
- Eliminates main degradation mechanism due to cracking of passivating layer from expansion/contraction, since outer shell stays constant.

*A Yolk-Shell Design for Stabilized and Scalable Li-Ion Battery Alloy Anodes, Nian Liu, Hui Wu,⊥
Matthew T. McDowell, Yan Yao, Chongmin Wang, and Yi Cui

Futuristic chemistries: Li-air

Table I. Characteristics of some metal/oxygen battery couples.

Metal/O_2 Couple	Idealized cell reaction[a]	Calculated open-circuit voltage (V)	Theoretical specific energy[b] (Wh/kg) Including O_2	Theoretical specific energy[b] (Wh/kg) Excluding O_2
Li/O_2	$4Li + O_2 \rightarrow 2Li_2O$	2.91	5,200	11,140
Al/O_2	$4Al + 3\,O_2 \rightarrow 2Al_2O_3$	2.73	4,300	8,130
Ca/O_2	$2Ca + O_2 \rightarrow 2CaO$	3.12	2,990	4,180
Zn/O_2	$2Zn + O_2 \rightarrow 2ZnO$	1.65	1,090	1,350

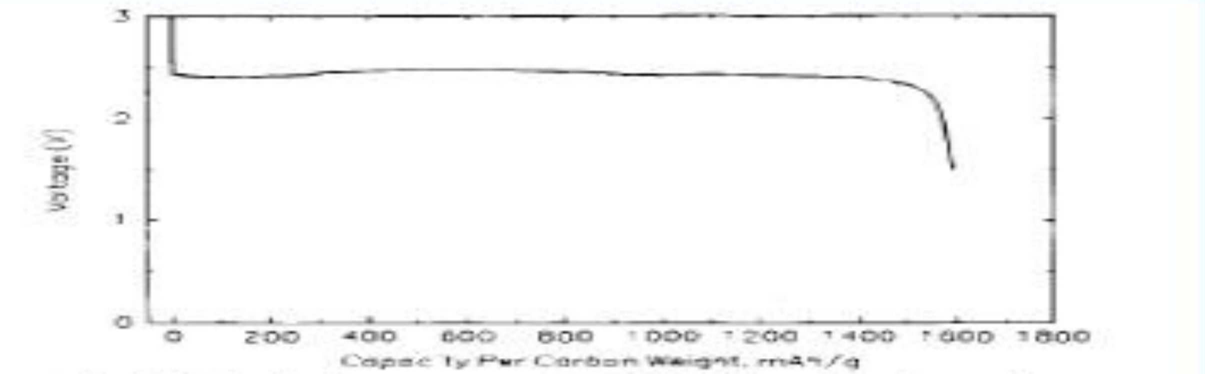
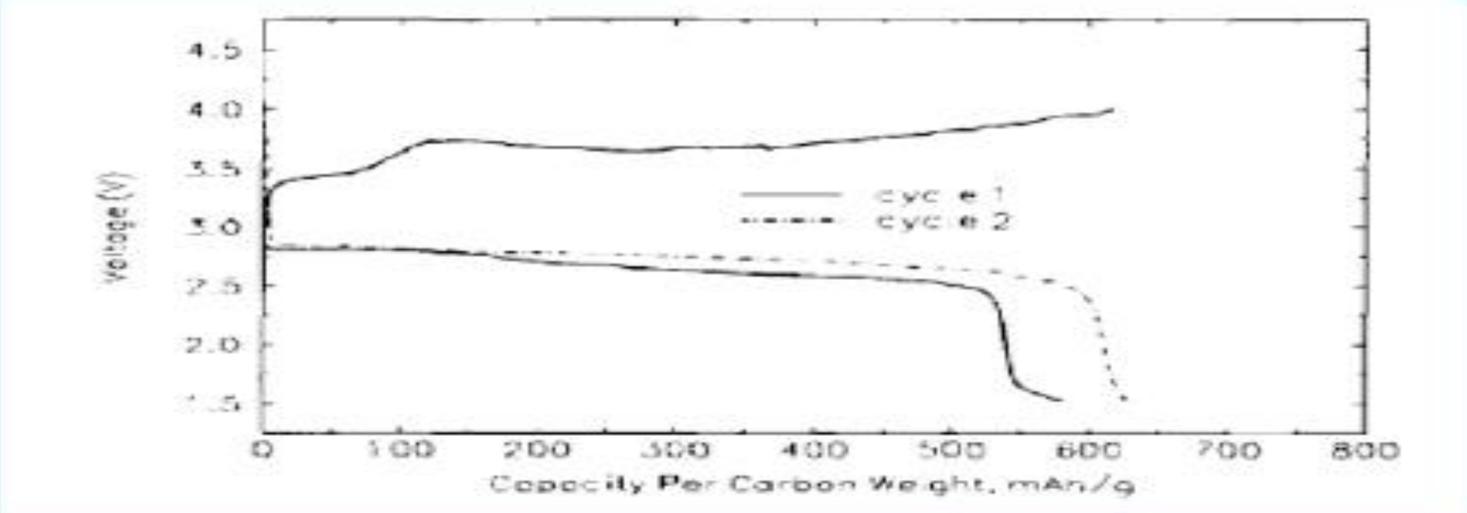
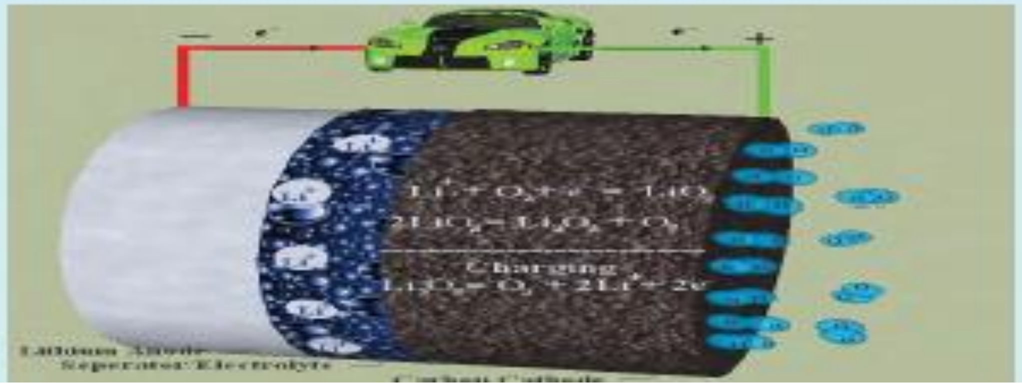


Fig. 2. The discharge curve of a Li/PAN-based polymer electrolyte/oxygen cell at a current density of 0.1 mA/cm² at room temperature. The cathode contained Chevron acetylene black carbon. The cell was packaged in metallized plastic envelope and discharged by exposing the carbon electrode to laboratory air.

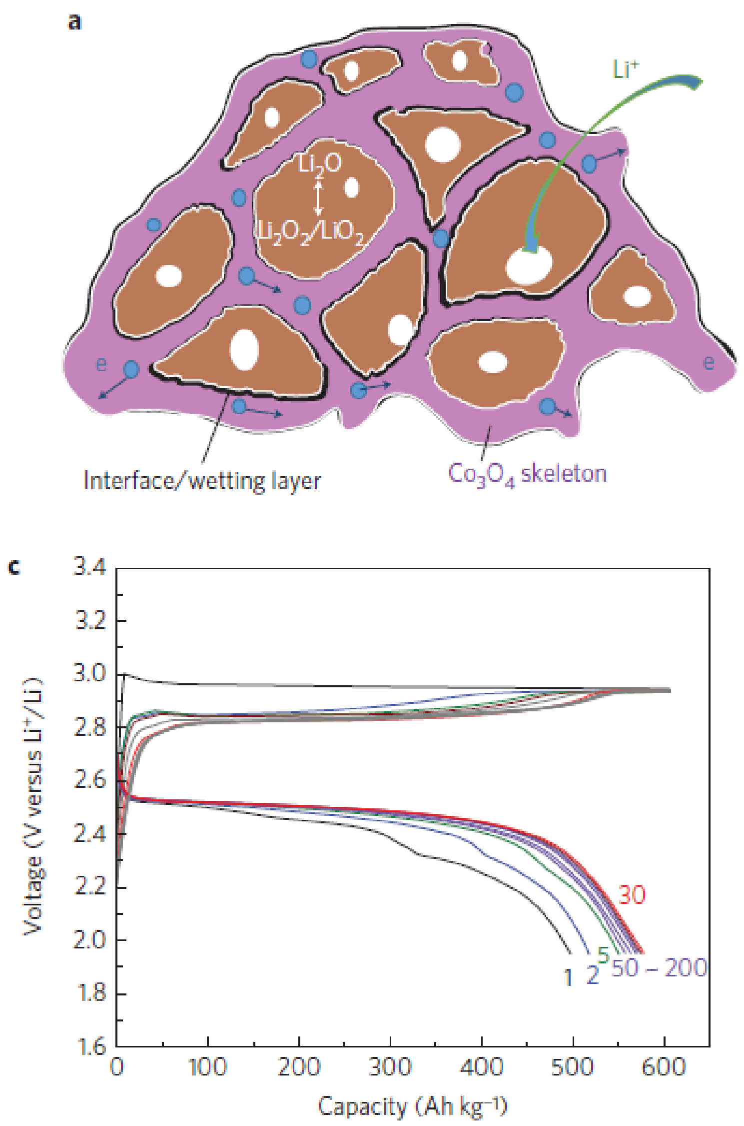


K.M.Abraham and Z. Jiang ; J. Elctrochem. Soc., 143, 1 (1996)
US Patent 5,510,209 (1996)
J. Phys. Chem. C 2009, *113*, 20127–20134



*K.M. Abraham, Twenty Seventh International Battery Seminar, Fort Lauderdale, FL, 2010

Futuristic chemistries: Li-air and Li-Li peroxide



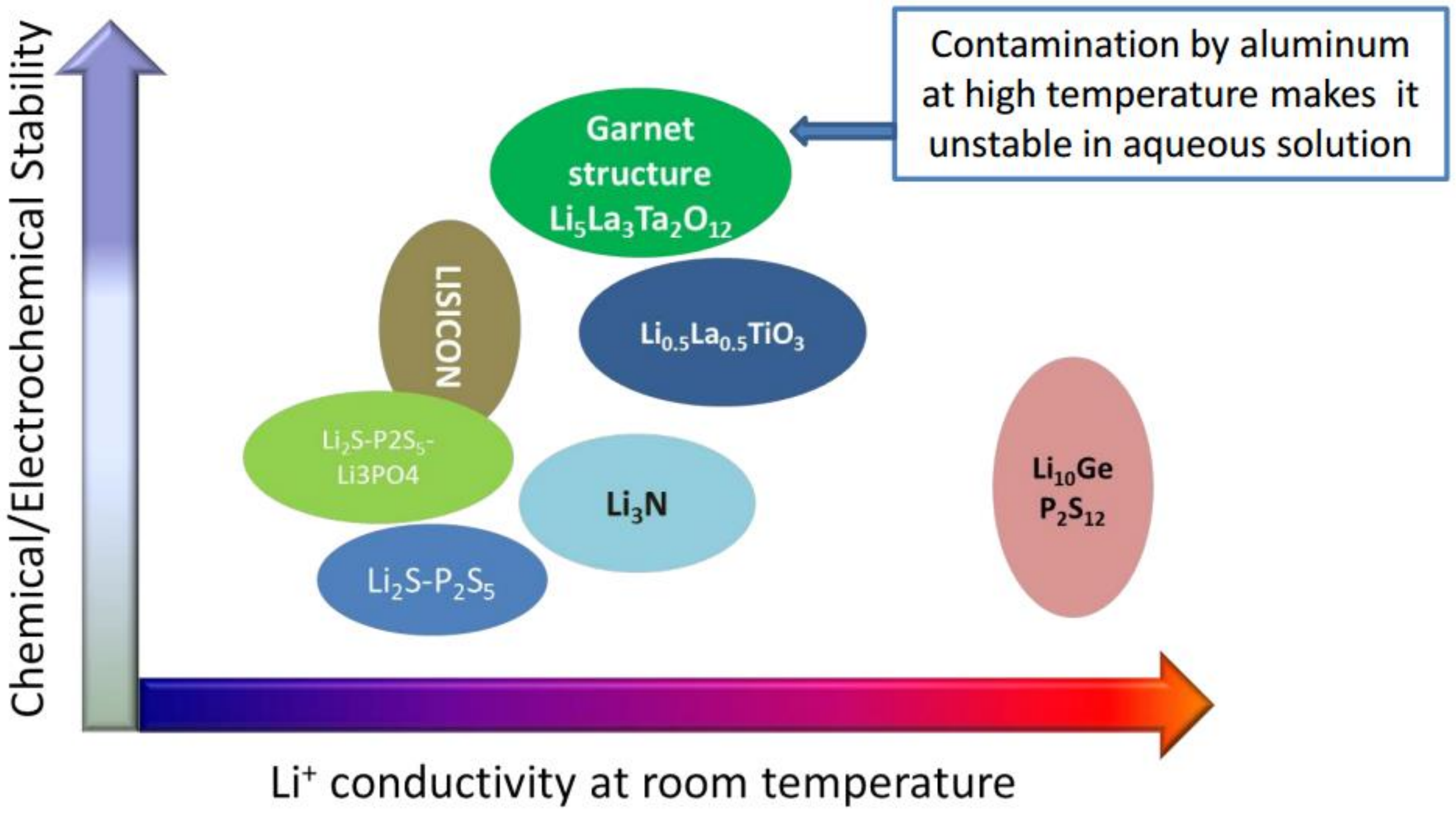
$$Li_2O_2 + 2Li^+ + 2e^- = 2Li_2O \quad U_1^0 = 2.86\,V \qquad (1)$$

$$LiO_2 + 3Li^+ + 3e^- = 2Li_2O \quad U_2^0 = 2.88\,V \qquad (2)$$

- Li / air rechargeable battery is being actively developed. Since Li is the lightest high-energy metal, this battery has the highest theoretically possible energy density for any battery.
- Low discharge rate due to air cathode intrinsic low rate capability.
- Cycle ability issues due to exposure of aggressive materials to air.
- Li-safety: progress with solid electrolyte with conductivity similar to liquid by Goodenough group and other researchers.
- First likely as a low-rate primary battery to displace Zn/Air used in hearing aid applications.
- Li Peroxide / Li – can be assembled in passive state as neutral Li_2O / Cu current collector and than charged to peroxide LiO_2 / Lithium. Theoretical capacity 1341 Ah/kg, e.g. at 2.5 V average voltage 3352 Wh/kg – higher than Li / S.

**Nature Energy, 2016,* Ju Li, Zhi Zhu at MIT

Ceramic solid electrolytes – solid state battery



*John B. Goodenough, Long Wang, DOE Vehicle Technologies Annual Merit Review Meeting

**M. H. Braga,N. S. Grundish,A. J. Murchisona and J. B. Goodenough , Energy Environ. Sci., 2017,10, 331-33

- Main safety hazard comes from organic electrolyte (burning 10 times more energy when compared to electric energy).
- Solid electrolyte can not burn, but power capability is reduced because of low conductivity compared to liquid.
- Allows to use metallic Li, which has higher energy density than graphite.
- One startup company demonstrated 20 layered cell using sulfur-based solid electrolytes
- Another startup has demonstrated 20 min. charge rate and good cycle life over 500 cycles probably using $Li_7La_3Zr_2O_{12}$ (LLZO)
- **Cost and manufacturability** remain main problems that make the mass production of such large size brittle ceramic films with perfect quality to assure protection from Li-dendrites highly questionable

Battery trends summary

- 18650 Li-ion cell reached 3516 mAh, growth **stopped in year 2015.** Popular in automotive: 2170 cell in future moving to tabless 4680.
- New developments are focused on **pouch cells**, targeting cell phones, tablets, ultrabooks. **Energy density of pouch cell exceeded 18650**!
- Normalized cell **impedance peak is increasing** from 200 to 400 mOhm due to high energy cells. Needs for impedance aware power management!
- **Now:**
  - Mixed cathodes with high Ni and Mn content are mainstream in multi-cell designs as low-cost option (**NCA, NMC**)
  - **Lower voltages** (down to **2.5 V**) need to be supported to take advantage of NMC and NCA Ni-rich cathodes, Si-anode and LFP
  - Further increase of Ni-content in **NMC (333 -→532→ 811**) and increase of charging voltage will keep energy density increasing and cost decreasing. Safety has to be addressed!
  - **LFP** becomes a cost effective choice to address **supply shortage of Ni** – but lower energy density. LMFP helps with energy. High V-accuracy needed for both due to extreme flatness.
  - **Si and SiO** anode now 3-5% addition to carbon. Several Startups show good cycle life and charge rate results with **high Si-content** cells. Large EV maker committed to high-Si for next gen anodes.
  - High charge rate capability: **3C** Manganese spinel (low cost), NMC, Li-titanate of LiFePO4, **10C**: high Si and nano-metal containing cells
  - Power backup and Grid energy management (high longevity, low cost): Li-FePO4 and Li-titanate, sodium-ion
- **Near term** (up to 5 years from now):
  - Low utilization **Li / sulfur** (10% of theoretical): One startup is in pilot production now
  - **High Si-content** cells using nano-technology or particles in matrix
  - Higher Ni cathodes (**NCMA89**) higher voltage Ni-cathodes made stable using particle nano-structure engineering
  - **single crystal NMC532** gives long life high energy option! Million mile car battery possible and needed for V2G high cycling!
- **Long term**: Li / sulfur, Li / air, Li / peroxide, solid electrolytes