

Energy storage materials: the conversion-type for lithium rechargeable batteries

Qingsong Wang, Ben Breitung

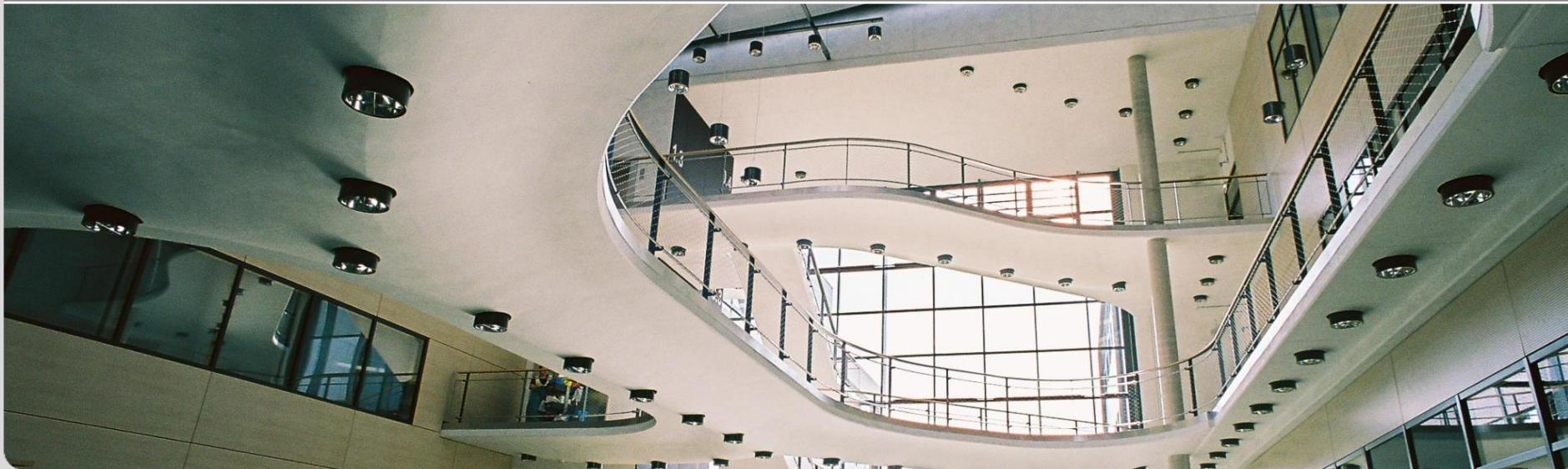
qingsong.wang@kit.edu

Phone: +49 721-608-28102

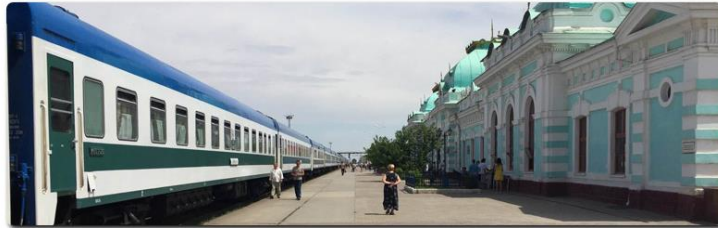
Web-site: <http://www.int.kit.edu/home.php>

July. 2018, NiPS Summer School Perugia , Italy

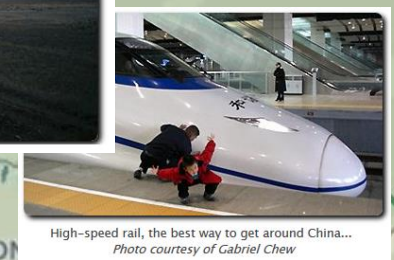
INSTITUTE OF NANOTECHNOLOGY



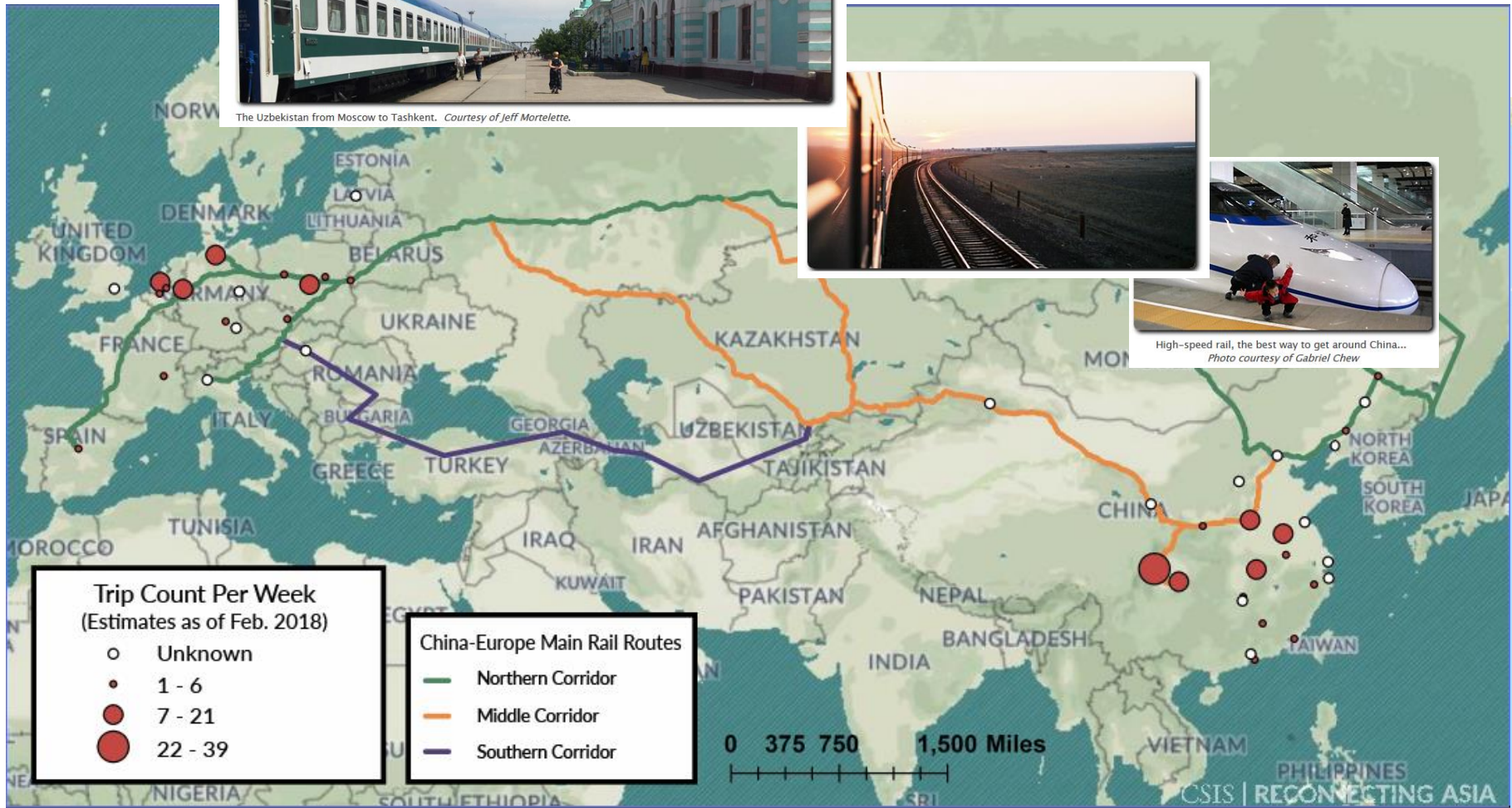




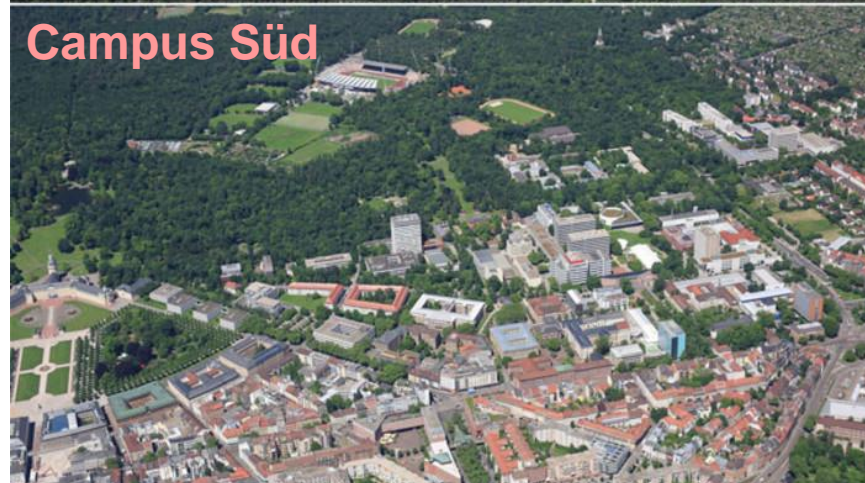
The Uzbekistan from Moscow to Tashkent. Courtesy of Jeff Mortelette.



High-speed rail, the best way to get around China...
Photo courtesy of Gabriel Chew



Germany:
the Länder



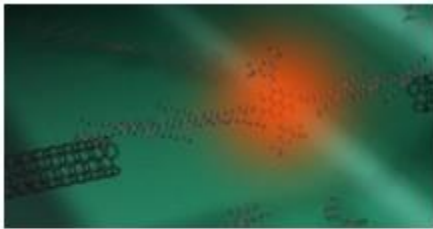
Institute of Nanotechnology

Scientists: ca. 300
Area Labs: **3.596 m²**
Area Offices: **2.600 m²**
Total usable area: **14.158 m²**

Building costs: **23 Mill. €**
Construction time less than 2 years



Research areas



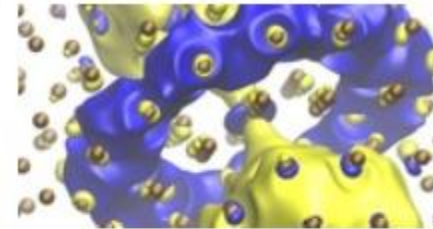
Carbon-based Nanostructures

Nanosystems based on sp^2 -carbon such as fullerenes, carbon nanotubes or graphene are of tremendous scientific and technological interest.



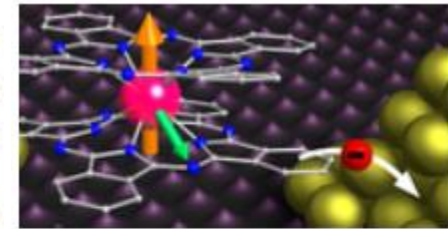
Electrochemical Energy and Hydrogen Storage

Renewable energies such as wind and solar power are in need of efficient energy storage systems.



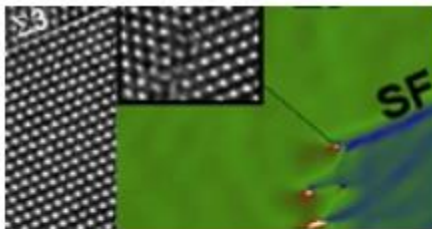
Functional Molecules

Because chemistry allows the synthesis of atomically precise copies of a given molecule, it is the ultimate method of "bottom-up" nanofabrication.



Molecular Electronics

Our work with magnetic molecules showcases the ability to manipulate quantum degrees of freedom in a transport experiment.



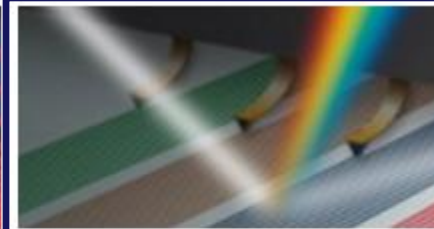
Nanomaterials and Nanocatalysis

Nanomaterials, comprised primarily of surfaces and interfaces, display surprising properties that we can influence through controllable stimuli.



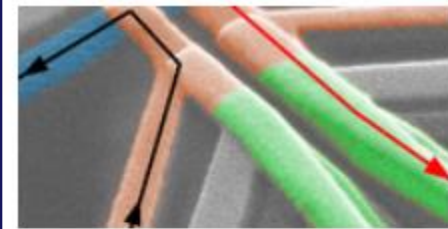
Photonic Nanostructures

By combining STED ideas with direct laser writing (DLW), we are able to produce photonic crystals with band gaps at visible frequencies.



Printable Systems: Materials and Methods

Our research is focused on printing electronic devices based on inorganic nanomaterials and the development of novel printing technologies.

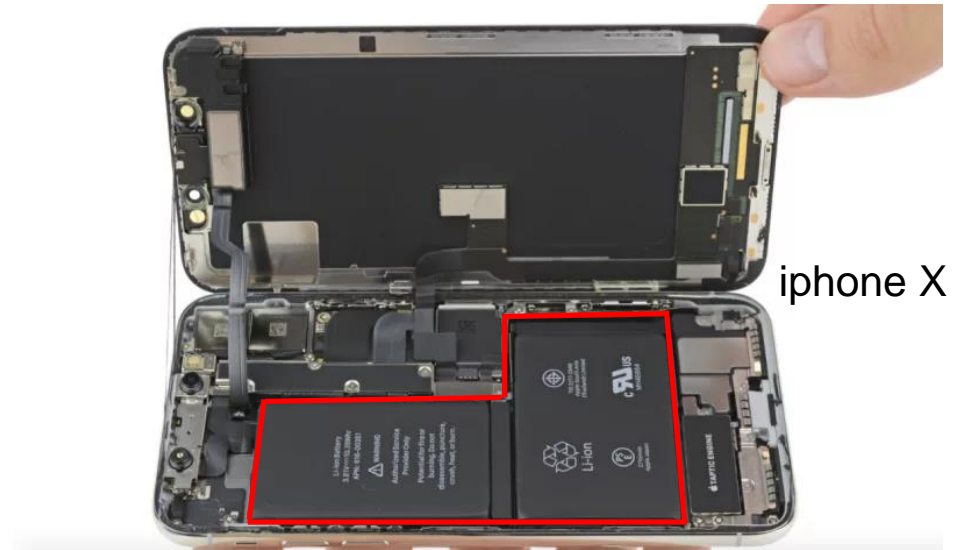


Quantum Transport and Correlations

Advances in nanostructuring allow the fabrication of ever smaller and increasingly complex devices which display spectacular quantum effects in transport.

- Introduction of lithium rechargeable batteries
- Reaction mechanisms of the electrode materials
 - Intercalation/Insertion
 - Alloying
 - Conversion
- Lithium/Sulfur batteries (Ph.D work)
- High Entropy Oxide materials (highlight)

The evolution of the mobile phone



iphone X

iPhone 2007

iPhone 3G 2008

iPhone 3GS 2009

iPhone 4 2010

iPhone 4S 2011

iPhone 5 2012

iPhone 5S 2013

iPhone 6 2014

iPhone 6S 2015

iPhone 7 2016

iPhone X 2017

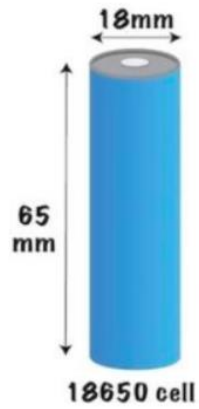


1420 mAh



2716 mAh

Electric cars



Cylinder shape cell: 18650, 21700

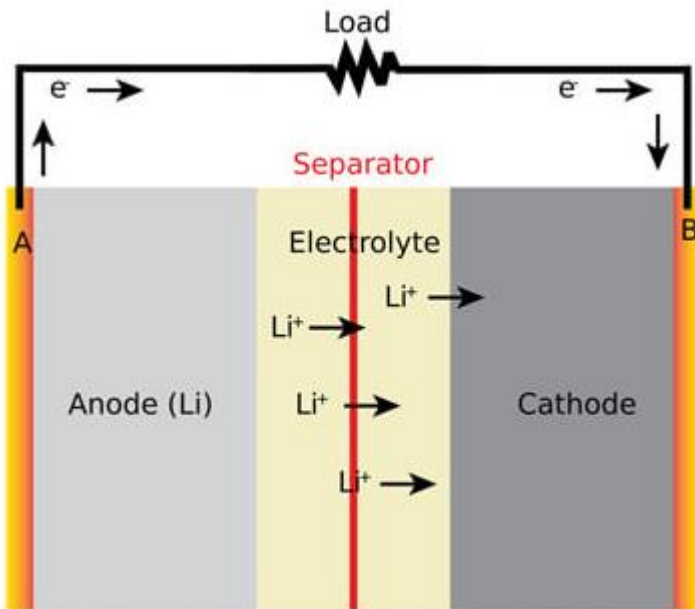
Electrochemical energy storage is an indispensable technology in our daily life!

- Portable devices
- Electric vehicles
- Stationary devices

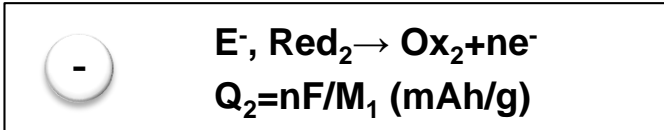
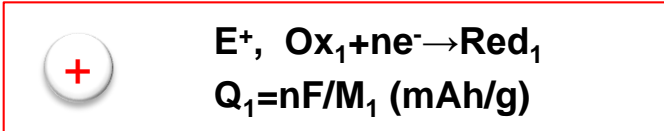


<https://chagedevs.com/newswire/nissan-gm-and-toyota-repurpose-used-ev-batteries-for-stationary-storage/>

Lithium Rechargeable Batteries

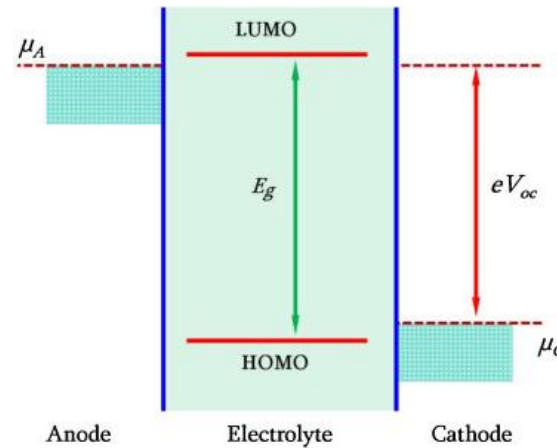


A/B: Current collectors; negative (A), positive (B)

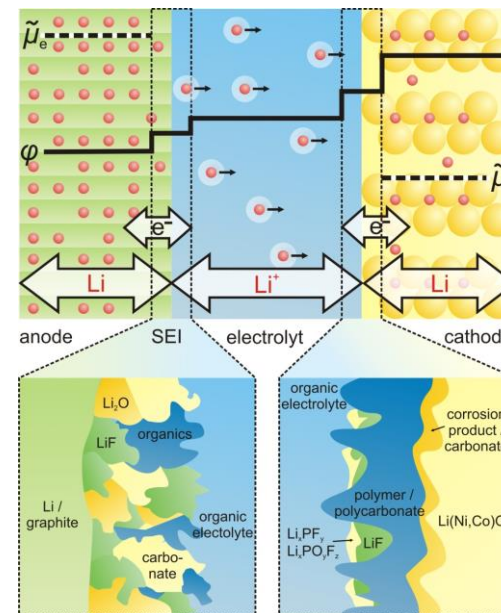


Energy = $\Delta E * Q$ (wh)

<https://doi.org/10.1016/j.mattod.2015.10.009>



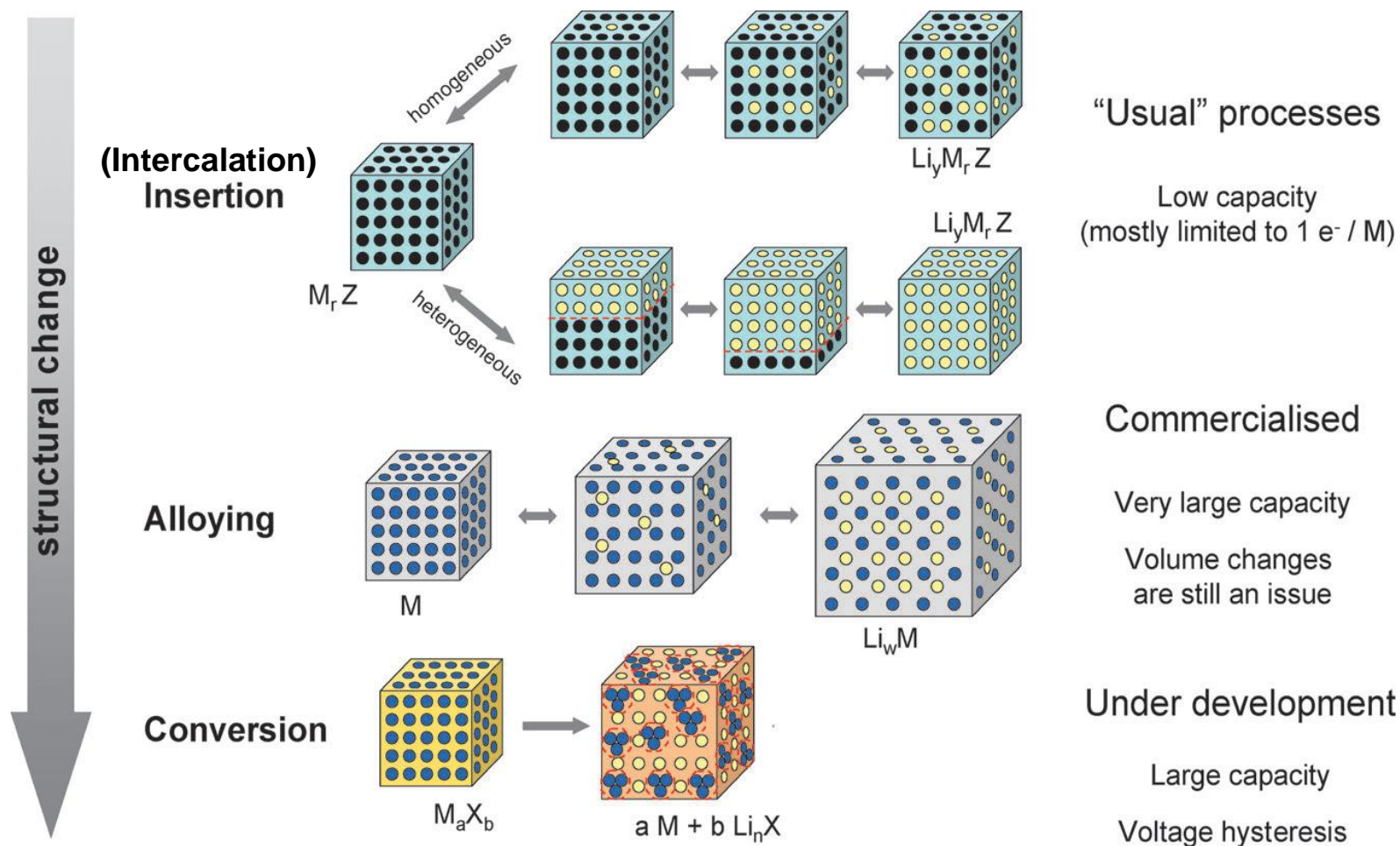
$V_{oc} = (\mu_A - \mu_C) / e$



„SEI“

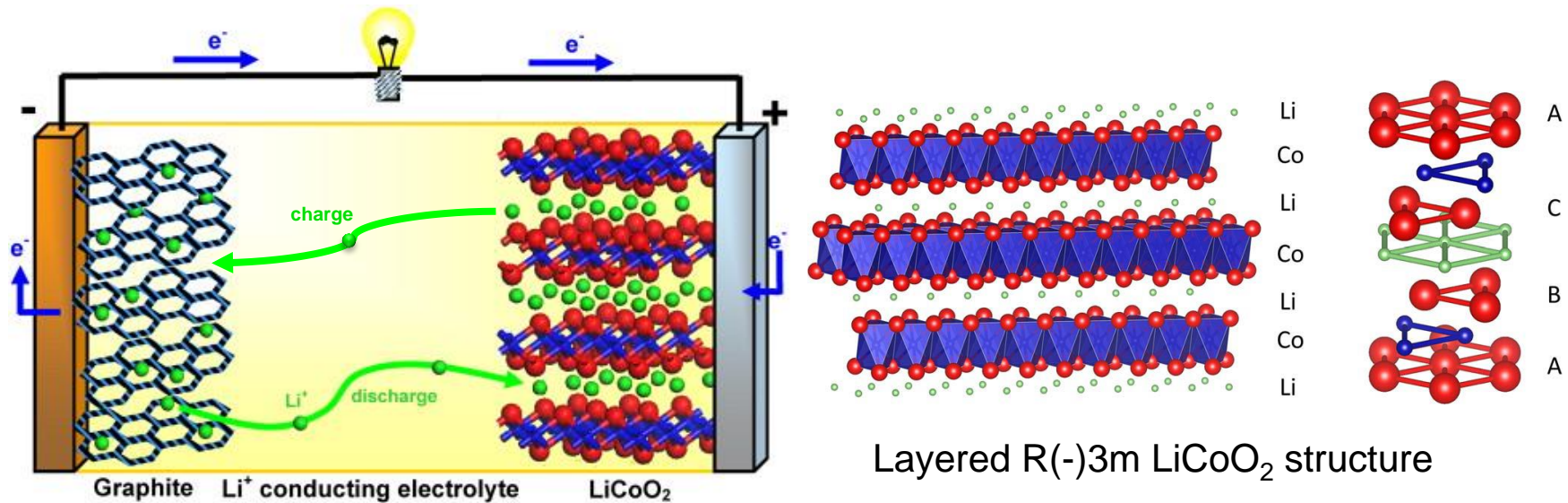
Solid Electrolyte Interphase

Original author: Jürgen Janek

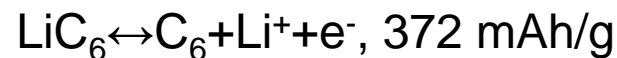


Chem. Soc. Rev., 2009, 38, 2565–2575

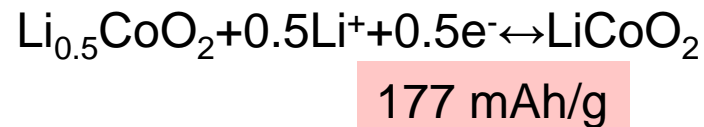
Starting Point: Sony, LiCoO₂, 1991



(-) **Anode: C graphite**



(+) **Cathode: LiCoO₂**

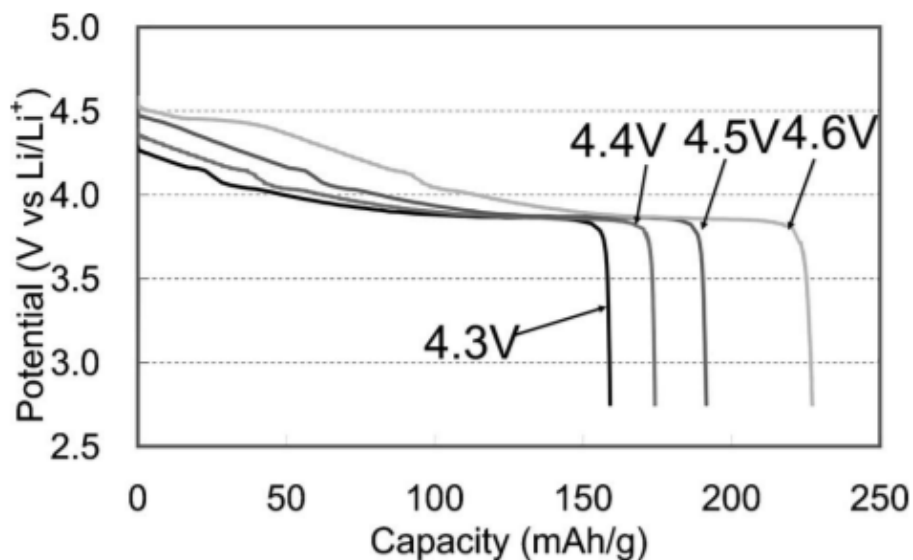


Characteristics:

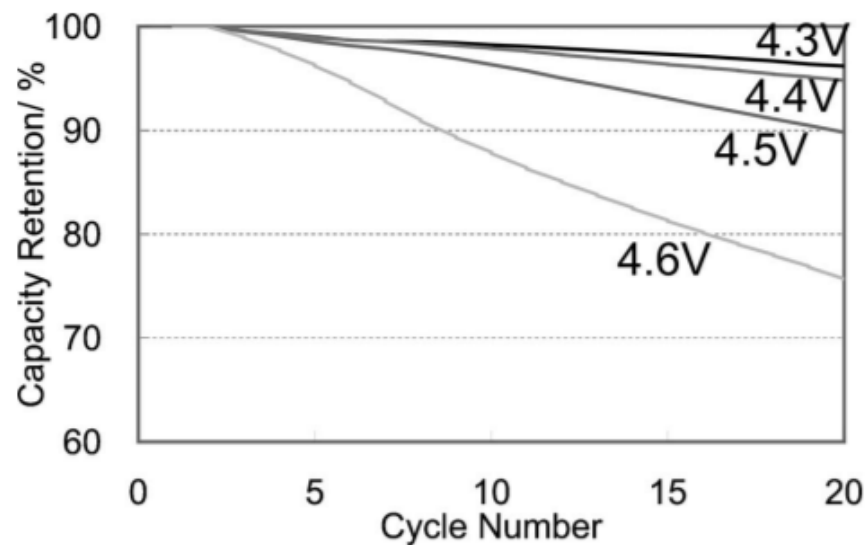
- Li^+ intercalation
- No Li metal
- Non aqueous Electrolyte

Li-ion intercalation at both electrodes

Journal of The Electrochemical Society, **164** (1) A6220-A6228 (2017)



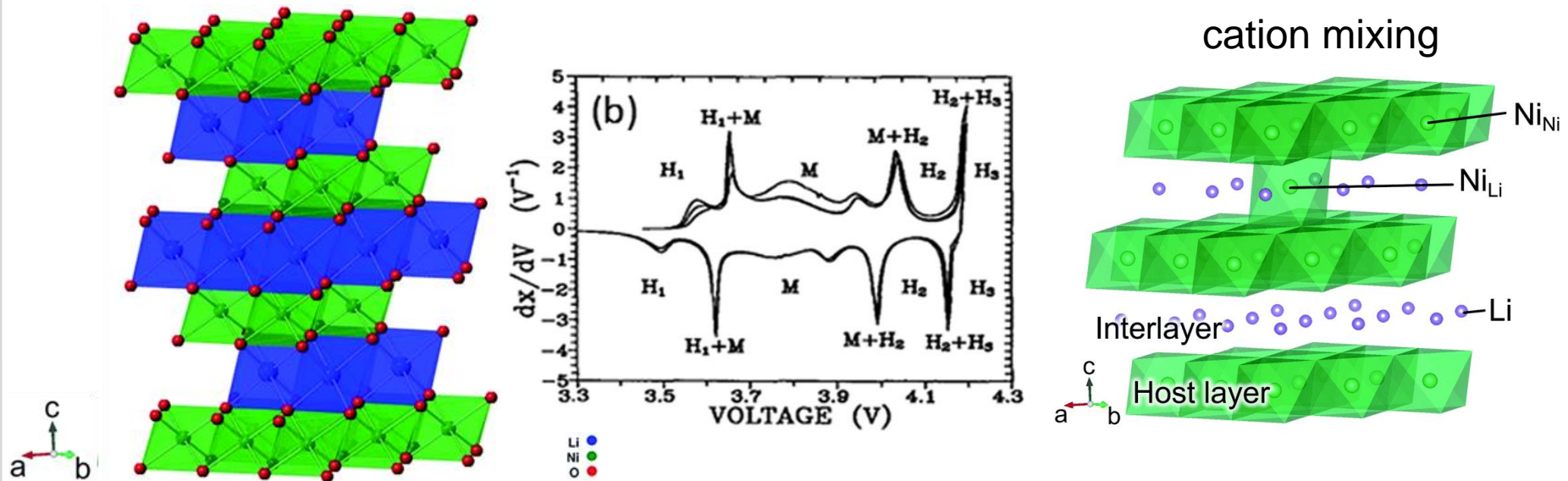
Initial discharge characteristics of LiCoO₂ between the charge cut-off potential of 4.3, 4.4, 4.5, 4.6 V vs Li/Li⁺ and the discharge cut-off potential of 2.75 V vs Li/Li⁺.



Cycle characteristics of LiCoO₂ between the charge cut-off potential of 4.3, 4.4, 4.5, 4.6 V vs Li/Li⁺ and the discharge cut-off potential of 2.75 V vs Li/Li⁺.

Higher cut-off voltage, higher capacity, but faster capacity decaying

Advantages: isostructural, Ni abundant, cheaper alternative

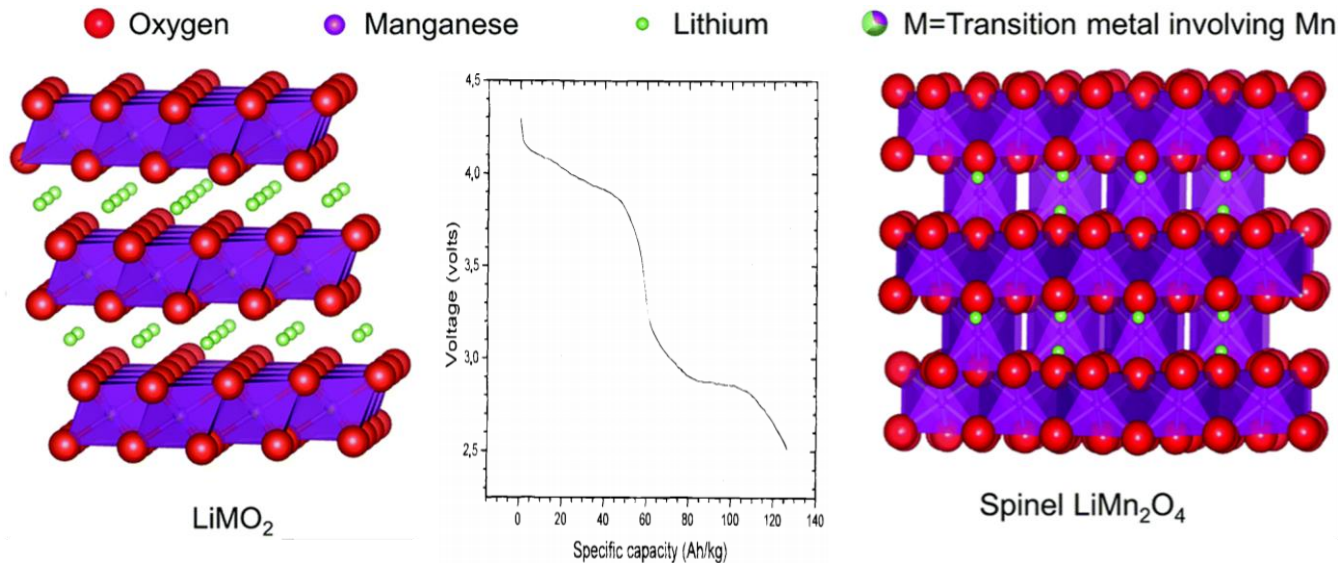


Disadvantages:

critical synthesis condition, Ni³⁺ reduction to Ni²⁺
 cation mixing, phase transformation, capacity fading
 thermally unstable, sensitive to moisture

Phys. Chem. Chem. Phys., 2015, 17, 14064-14070
J. Mater. Chem. A, 2017, 5, 874-901

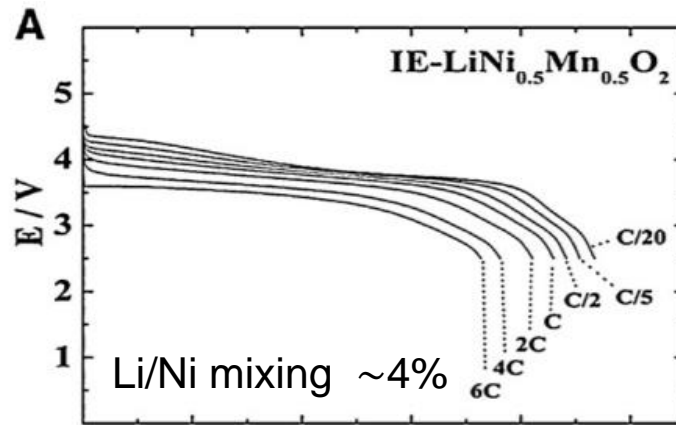
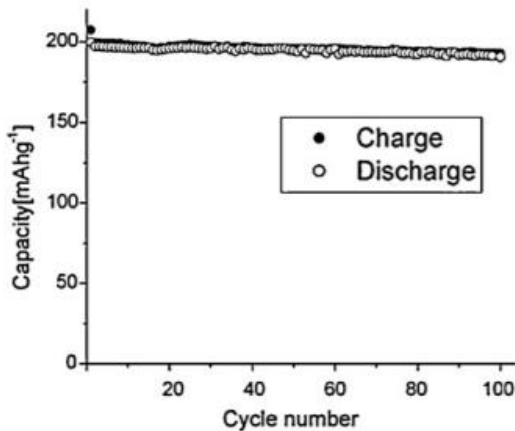
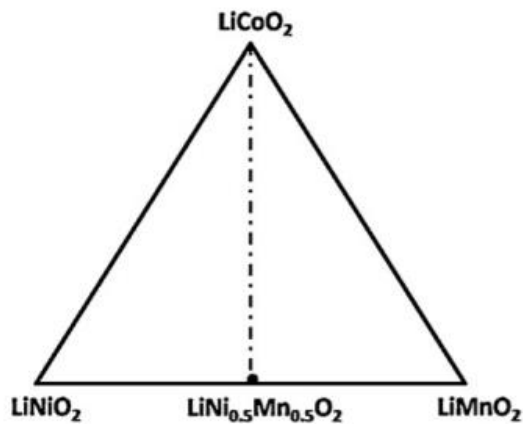
Advantages: cheaper alternative, environmental benign



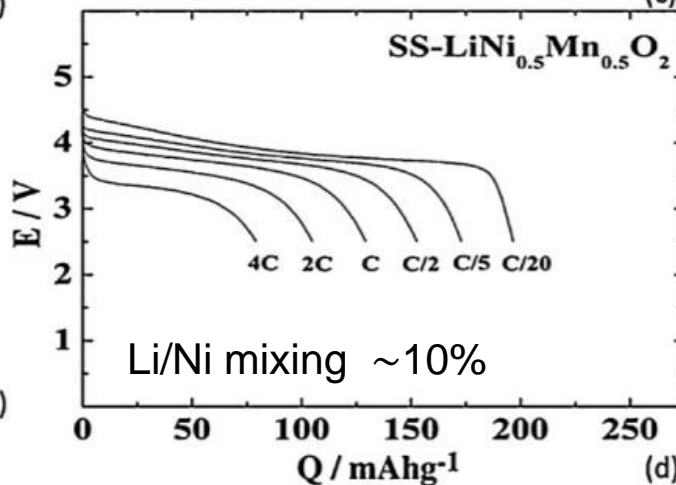
➔ Mn dissolution
HF formation

Disadvantages:
difficult synthesis (undesired orthorhombic)
structural rearrangement, fast capacity fading

J. Electrochem. Soc. 1997,144 (10), 3323, 3330



(a)



(b)

- Ni²⁺ Mn⁴⁺
- Oxidation: Ni²⁺ → Ni⁴⁺
- Higher capacity compared to M³⁺ → M⁴⁺

Li-Ni cation mixing, low Li diffusion coefficient

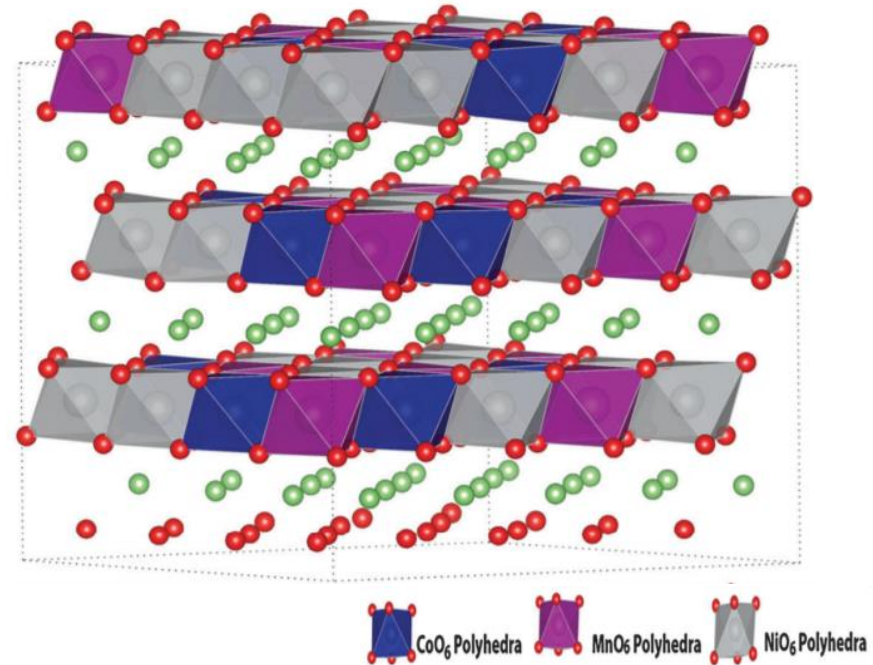
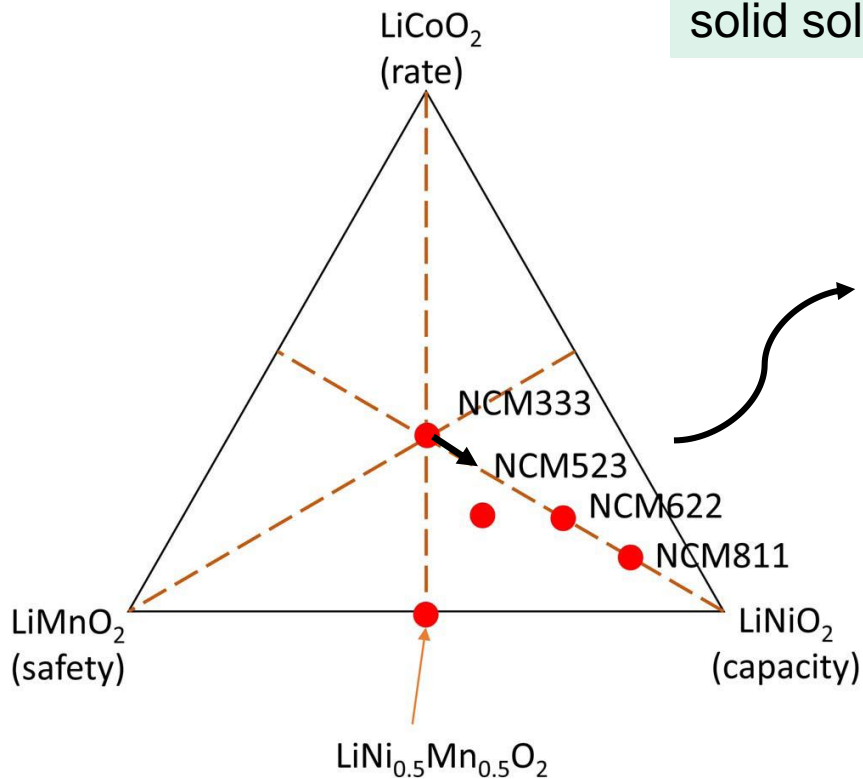
Science 311 (2006) 977–980

Chemistry of Materials 15 (2003) 3161–3169

Journal of Power Sources 184 (2008) 489–493

Li[Ni_{1-x-y}Co_xMn_y]O₂ –Layered NCM

solid solution of LiCoO₂, LiNiO₂ and LiMnO₂



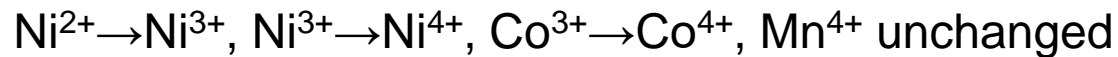
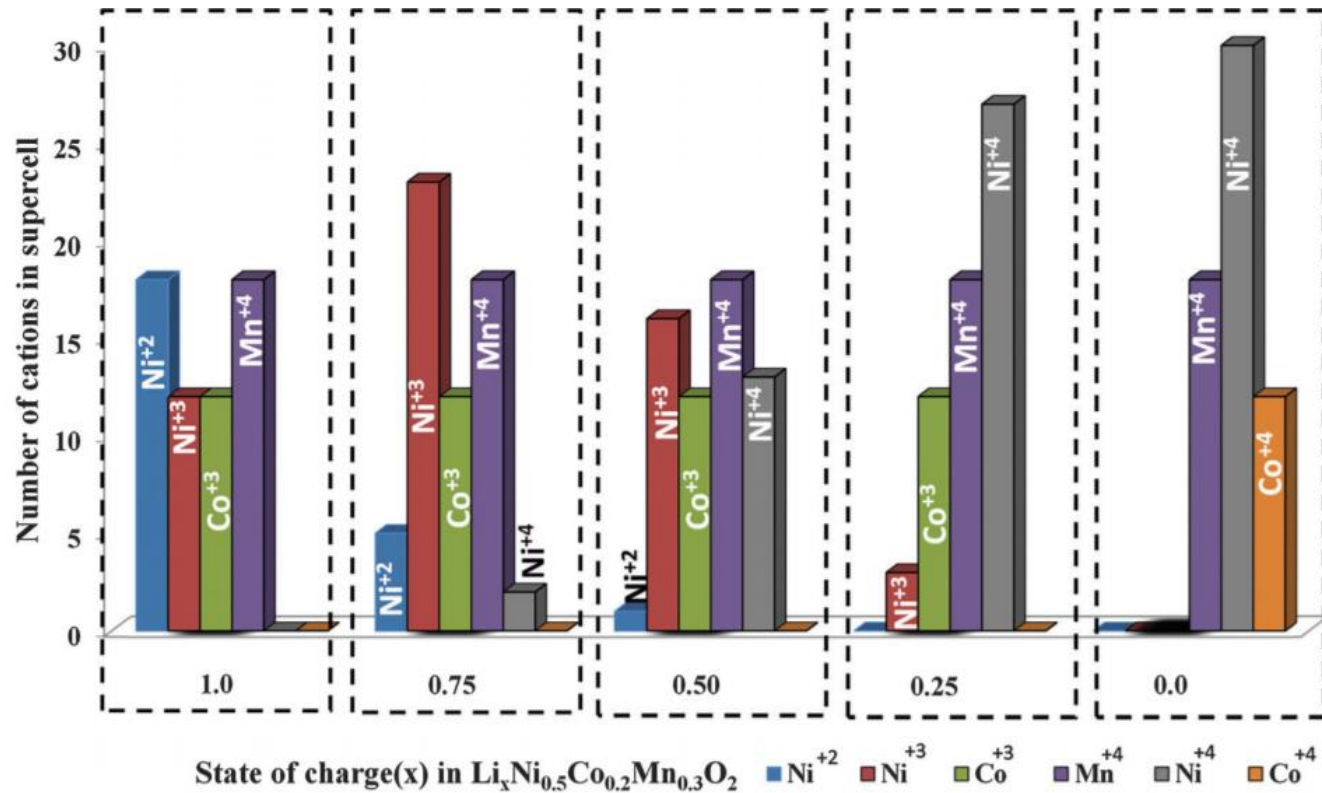
Phase diagram of the ternary system

- Ni²⁺/Ni³⁺/Ni⁴⁺
- high performances, lower cost, and higher safety

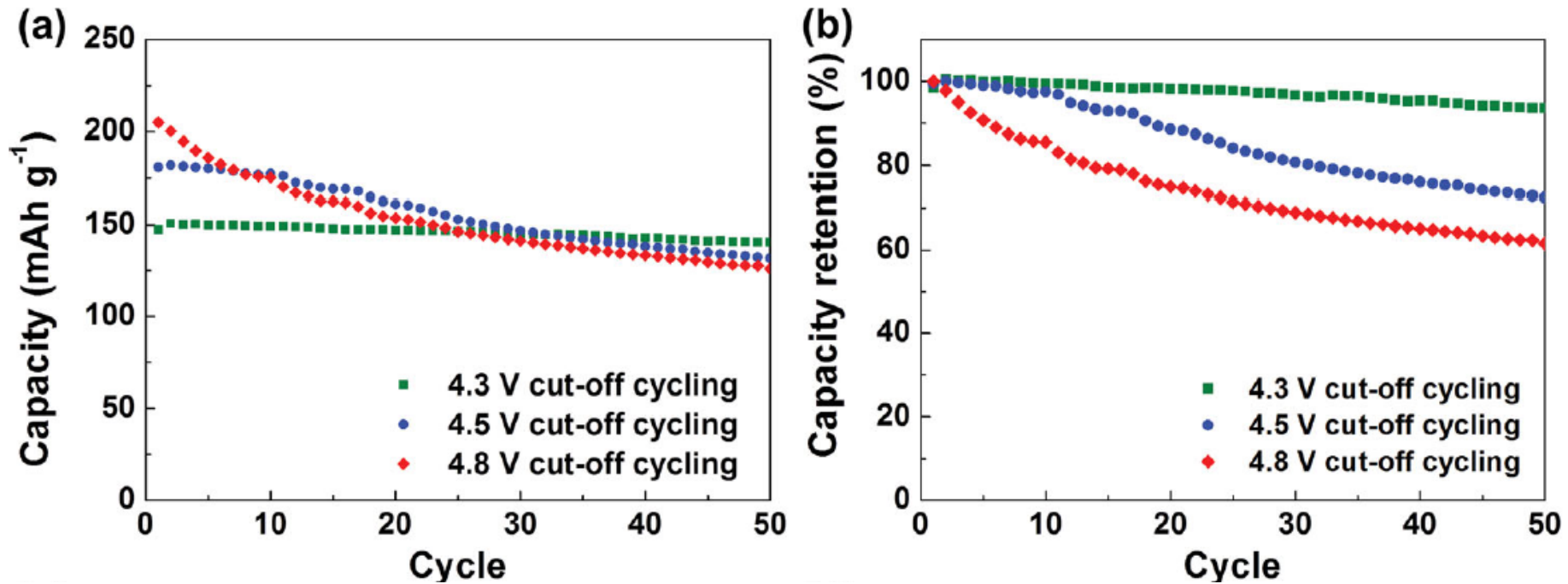
J. Mater. Chem. A, 2016, 4, 16073

Journal of The Electrochemical Society, **164** (1) A6220-A6228 (2017)

Intercalation example : $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523)

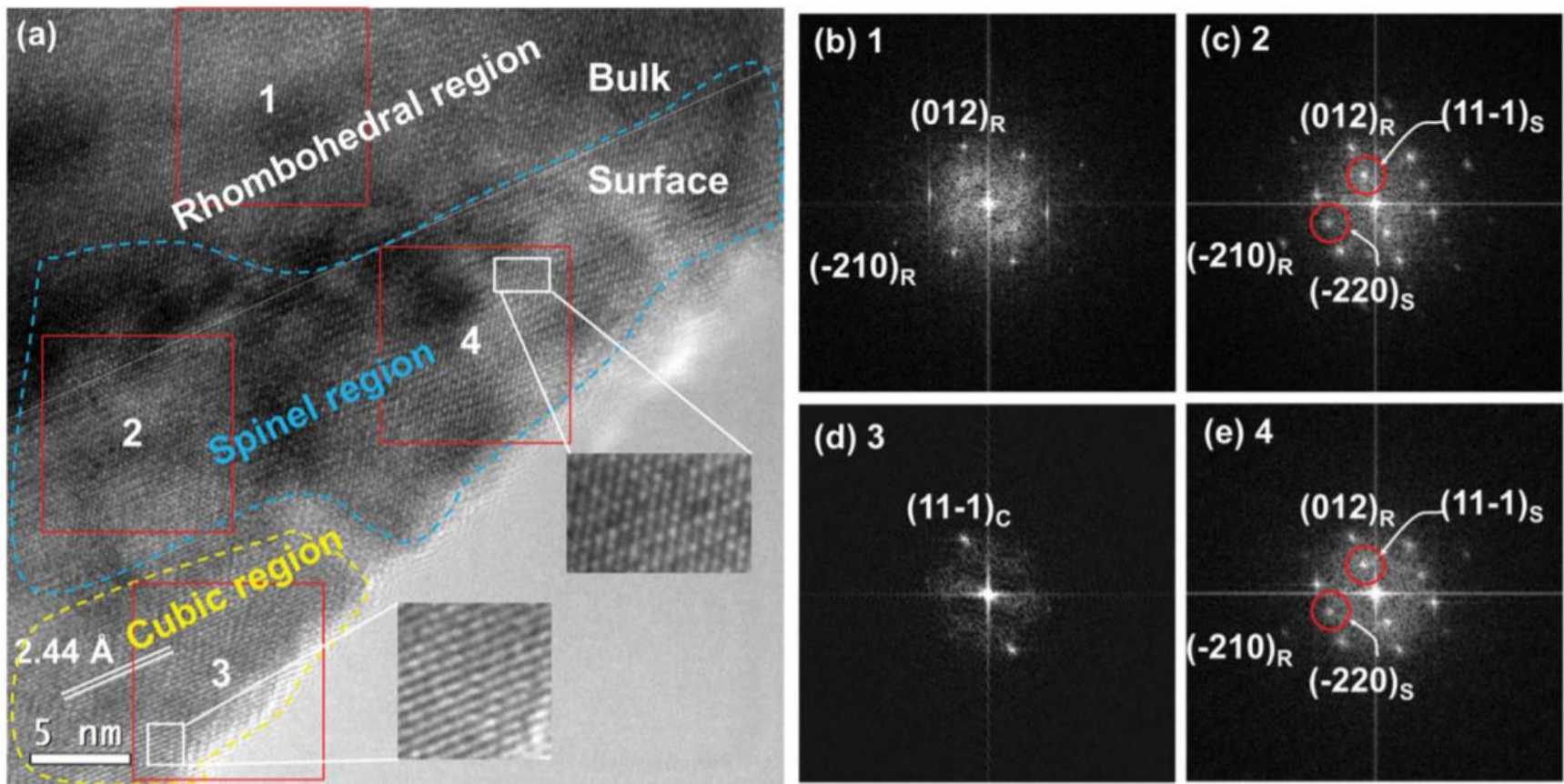


Capacity retention with cutoff voltages (NCM523)

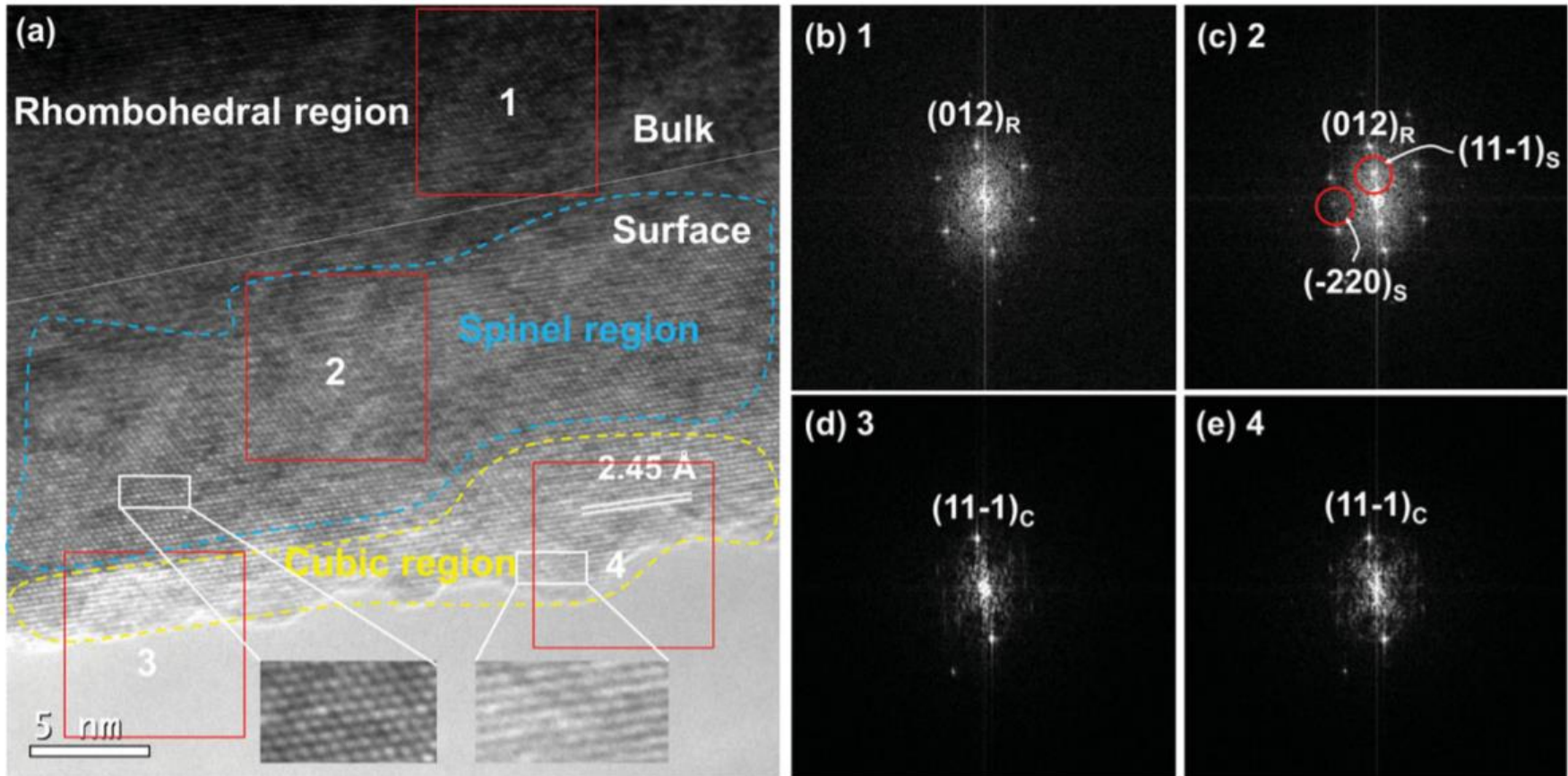


Cycle performance and discharge capacity retention at various cutoff voltages

Adv. Energy Mater. 2014, 4, 1300787



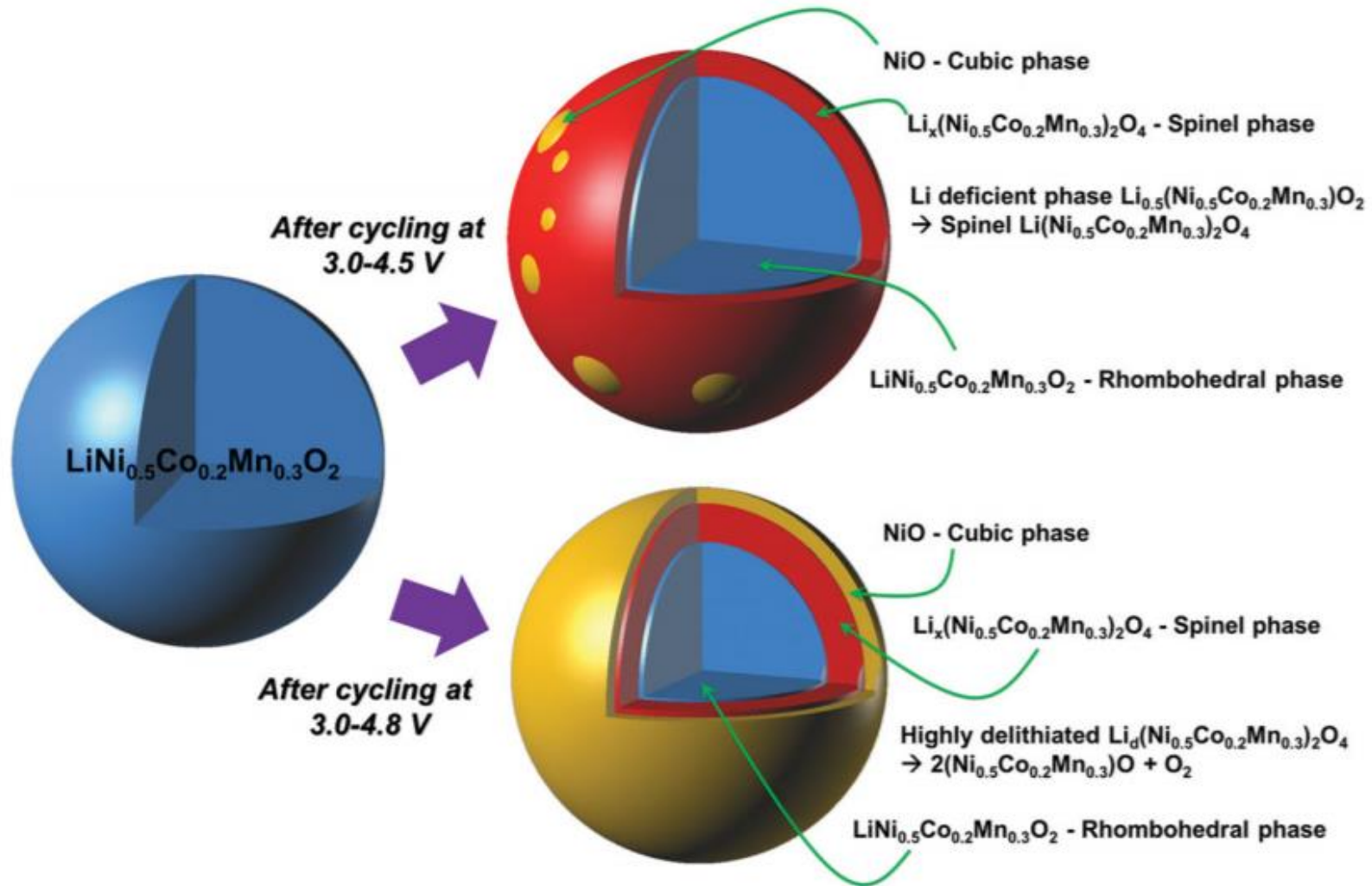
HR-TEM images and FFTs after 50 cycles under 3.0-4.5 V conditions



HR-TEM images and FFTs after 50 cycles under 3.0-4.8 V conditions

Rock-salt: NiO (2.42 Å), CoO (2.46 Å), ionically insulator

Degradation mechanisms

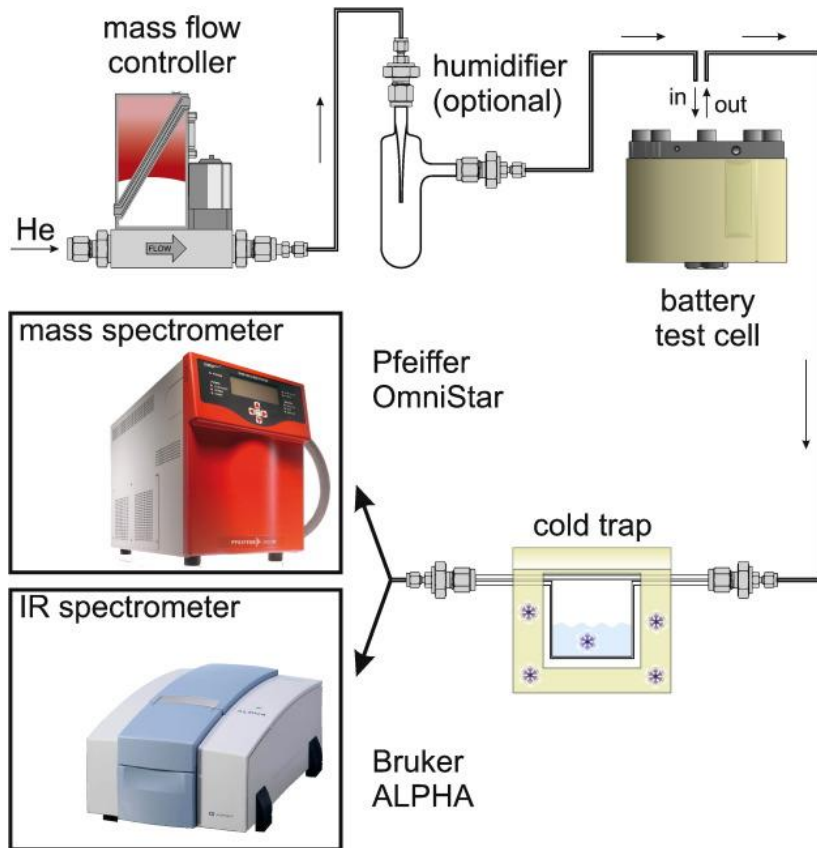


Samsung Galaxy Note 7

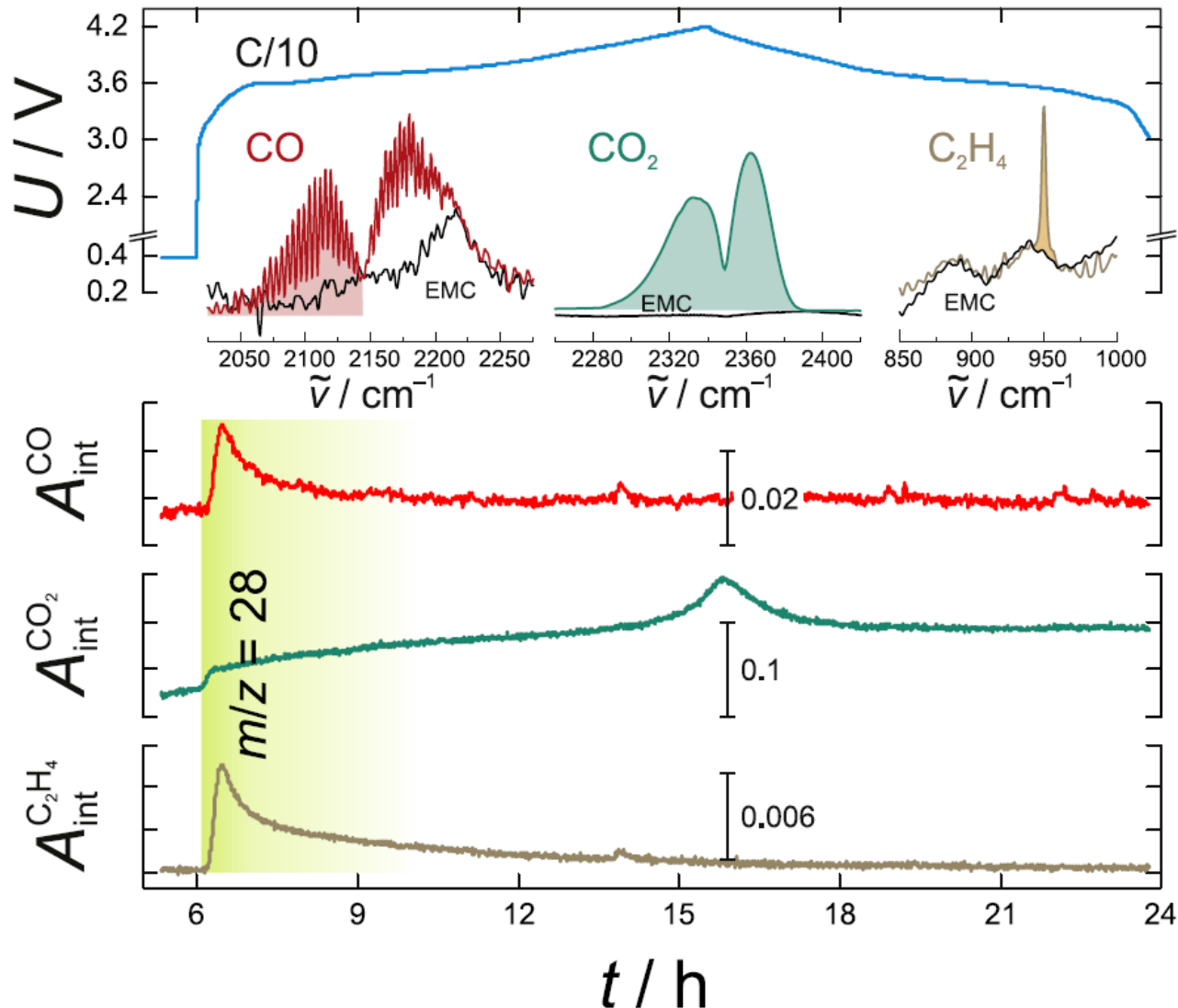


In situ characterization of gas evolution

DEMS-DEIRS: differential electrochemical mass spectrometry- differential electrochemical infrared spectroscopy

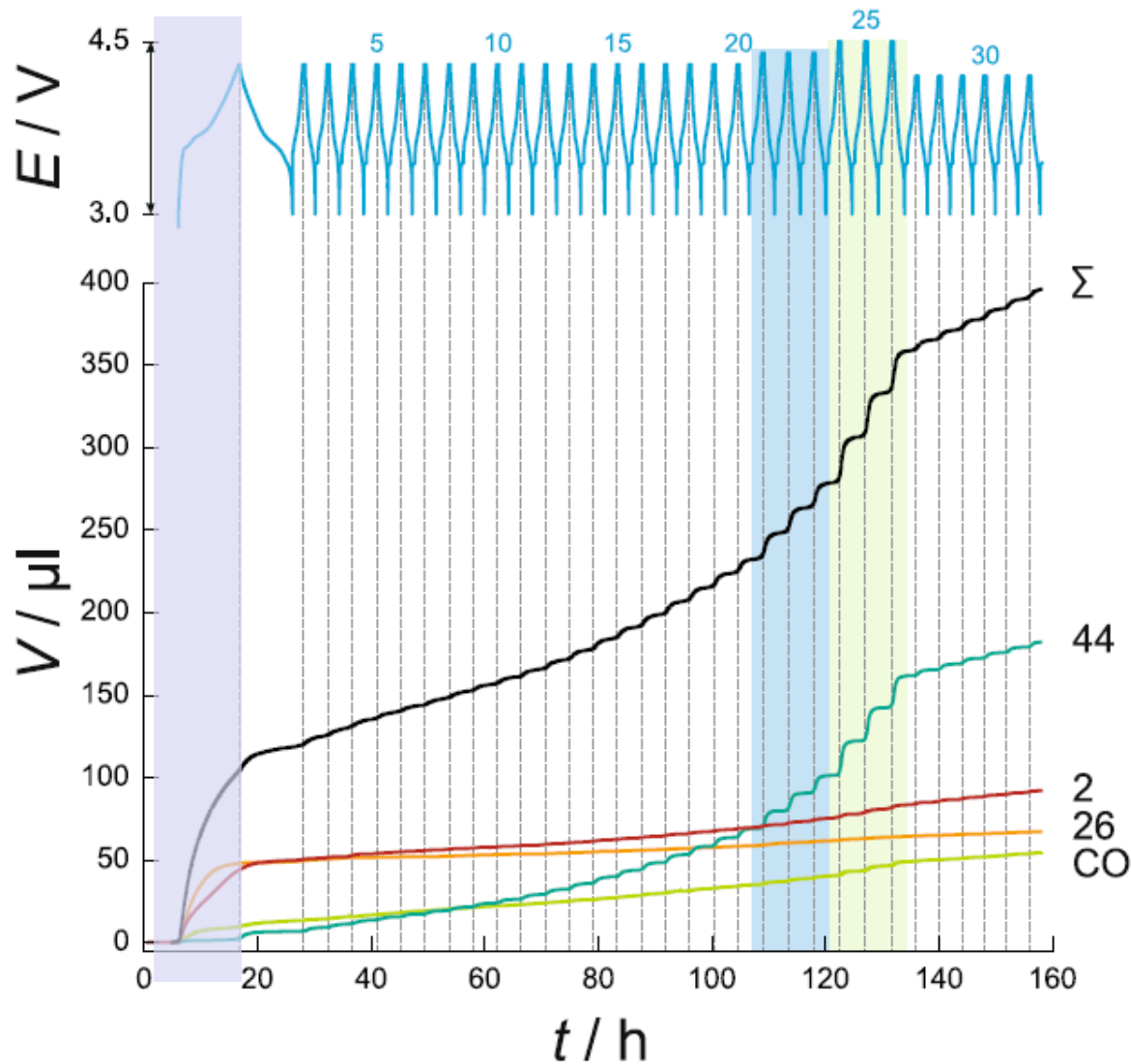


- Mass Flow Control: 2.5 cm³/min
- Temperature controlled
battery cell: 25 °C
- Cold trap -30 °C
- Cathode: LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (2 mAh/cm², 40 mm)
- Anode: Gr (0.6 mm thick, 40 mm)
- Electrolyte : LP57
- Separator: GF/D 42 mm



First charge/discharge cycle of the NCM 523/graphite cell using LP57 and corresponding DEIRS signals

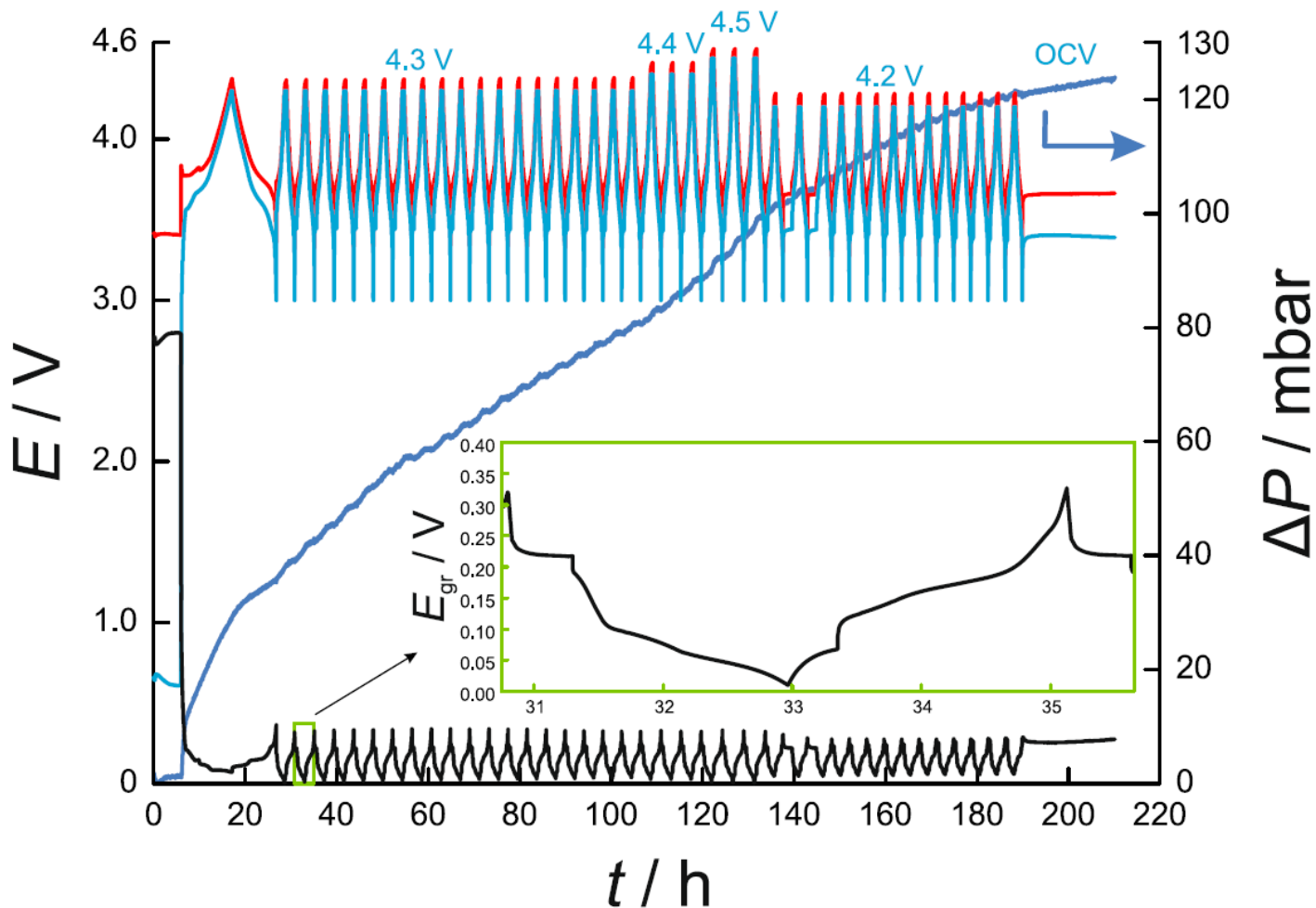
Balázs B. Berkes et.al. *Electrochemistry Communications* 60 (2015) 64–69



- Initial charging process, fast gassing evolution → SEI
- High cut-off voltage

Amount of individual gases (here C_2H_4 , H_2 , CO , and CO_2) along with their sum

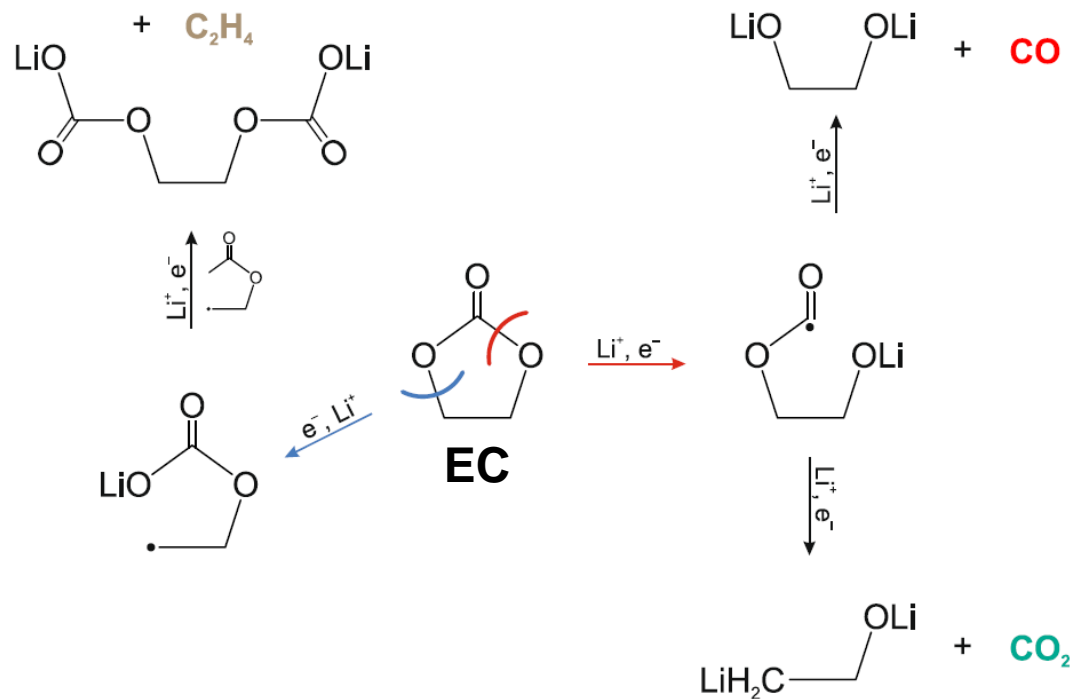
Balázs B. Berkes *et.al.* J. Solid State Electrochem (2016) 20: 2961-2967



Pressure measurement. The test cell contained a Li reference electrode. The potentials of cathode (*red line*) and anode (*black line*) are shown versus Li along with the terminal voltage of the battery (*blue line*).

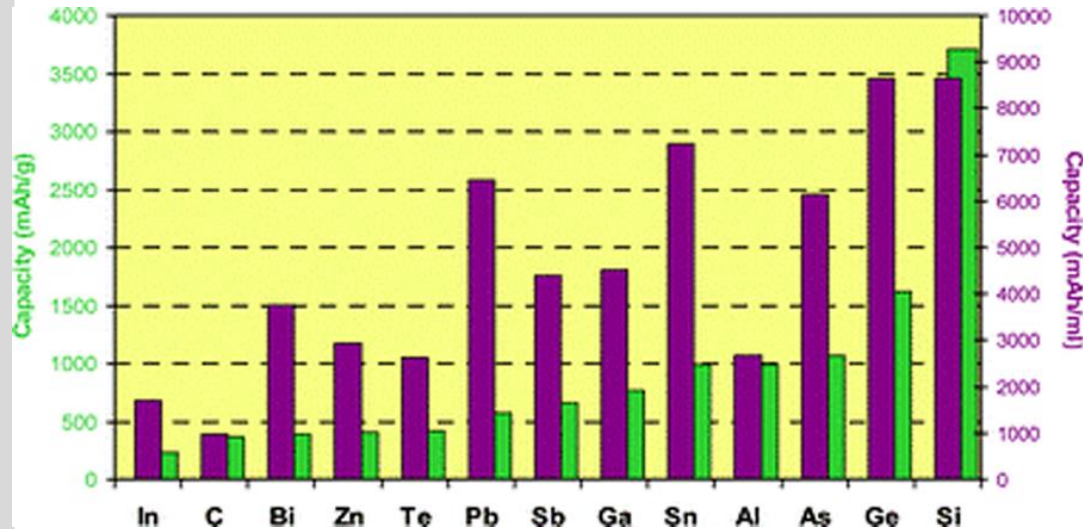
Balázs B. Berkes *et.al.* J. Solid State Electrochem (2016) 20: 2961-2967

Possible reaction routes

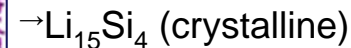
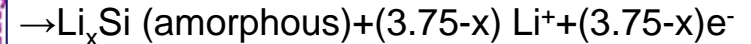


Possible reaction routes in the reduction of Ethylene Carbonate

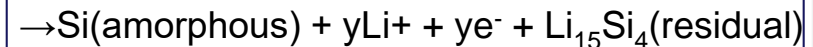
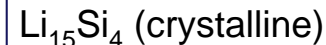
Alloying: Si anode



During discharge:



During charge:

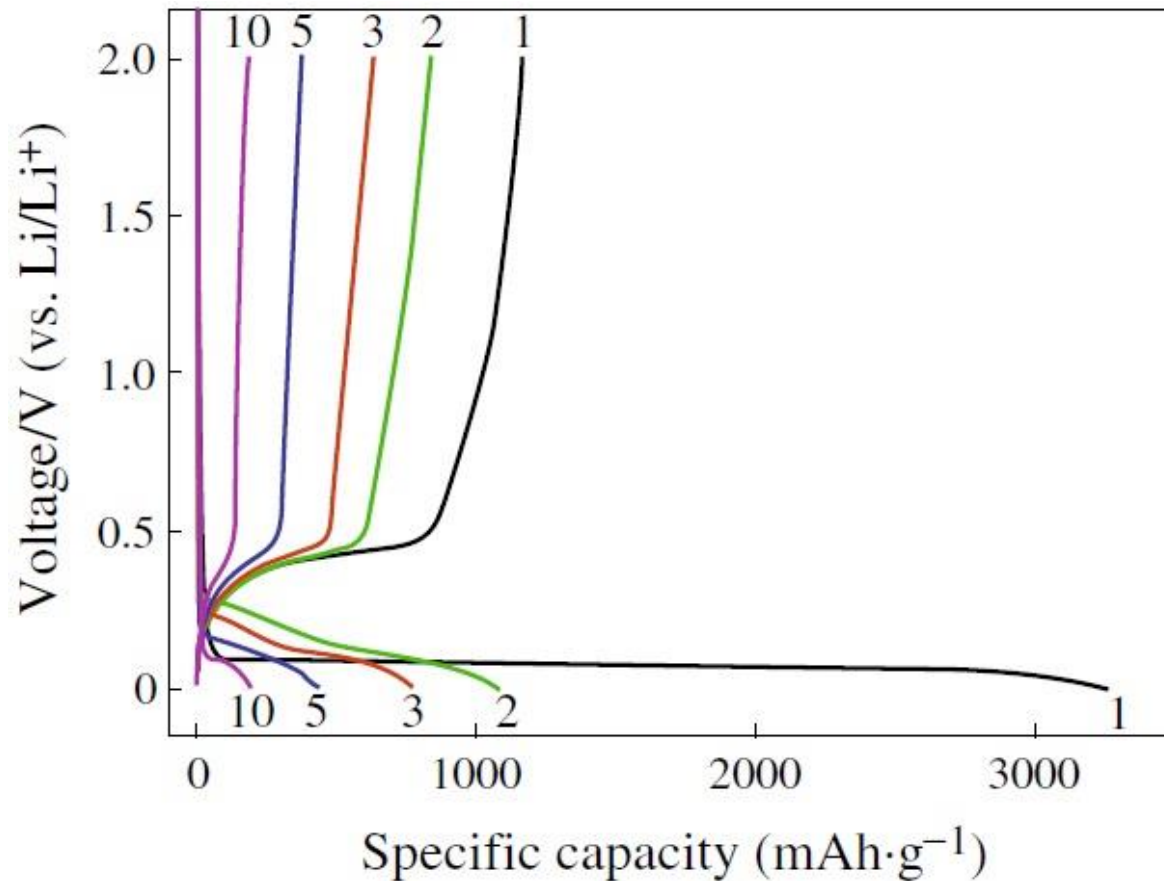


- **Gravimetric capacity**
(4200 mAh g⁻¹, Li₂₂Si₅)
- **Volumetric capacity**
(9786 mAh cm⁻³)

- **The second most abundant element**
- **Cost effective**
- **Environmentally benign**
- **A low electrochemical potential (0.37-0.45 V vs. Li/Li⁺)**

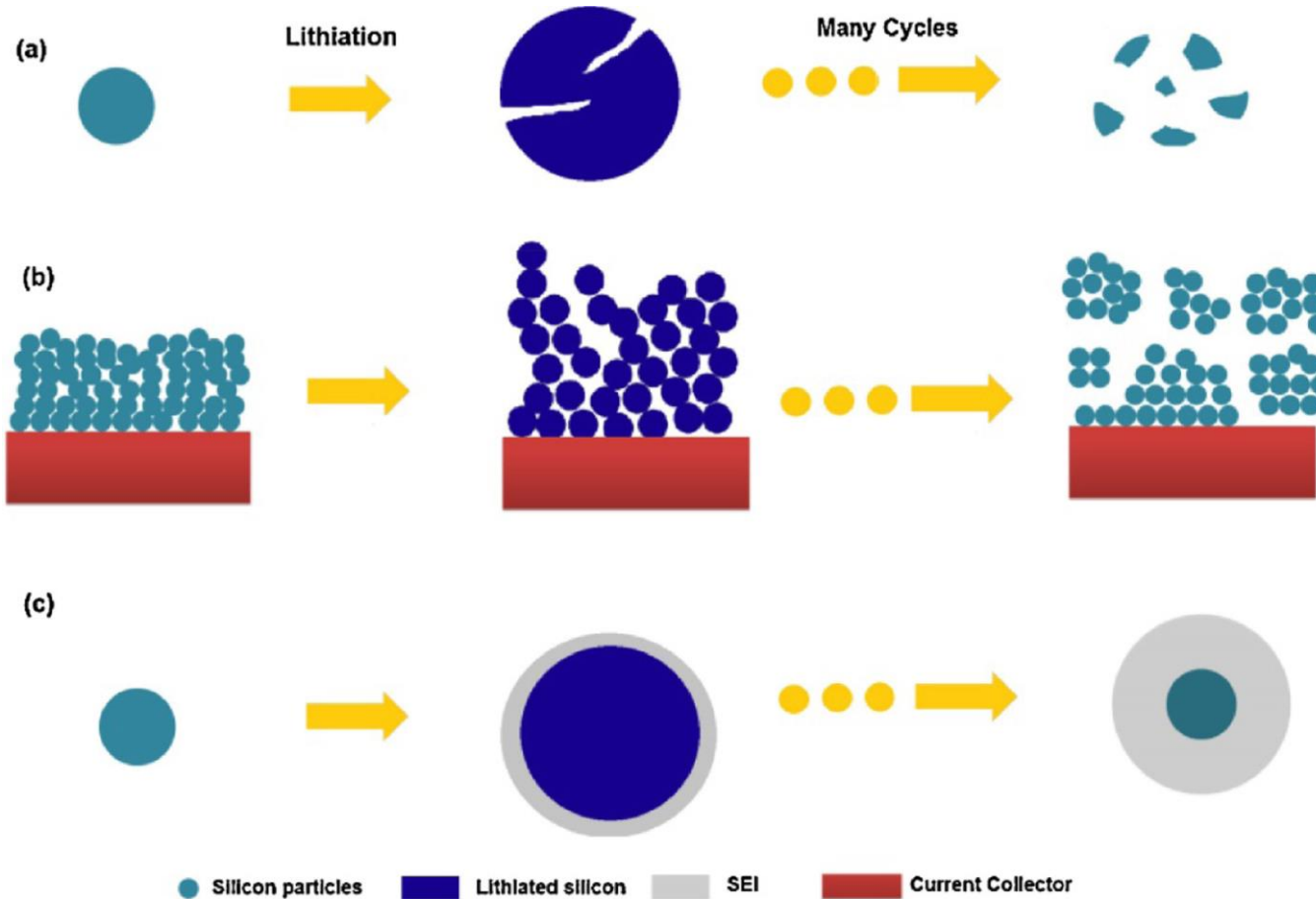
J. Mater. Chem., 2007, 17, 3759-3772
 Nano-Micro Lett. (2014) 6(4):347–358

Si anode: fast capacity decay



Charge-discharge voltage profiles of Si powder anode

Electrochemical and Solid-State Letters, 7 (10) A306-A309 (2004)

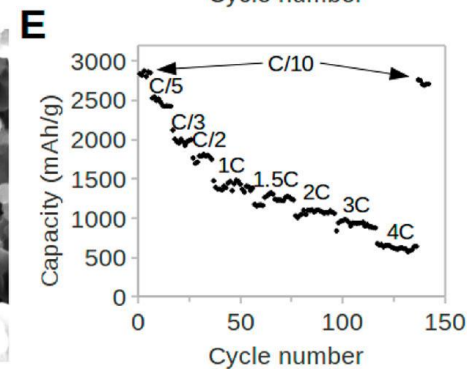
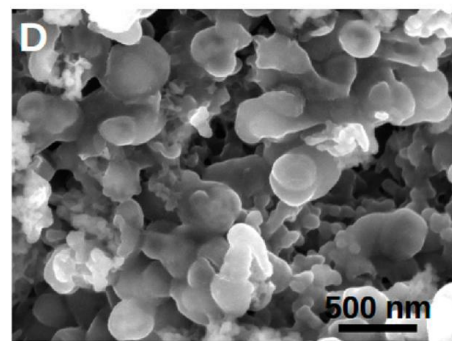
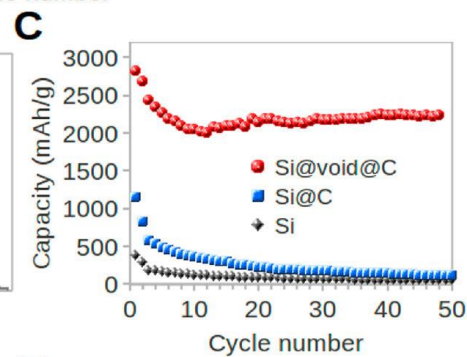
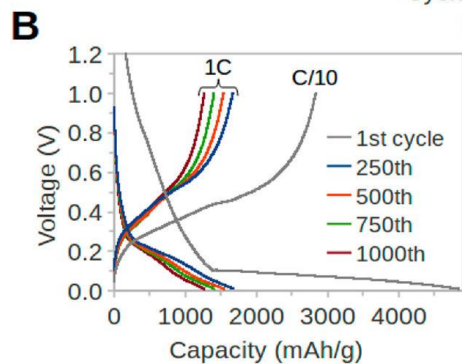
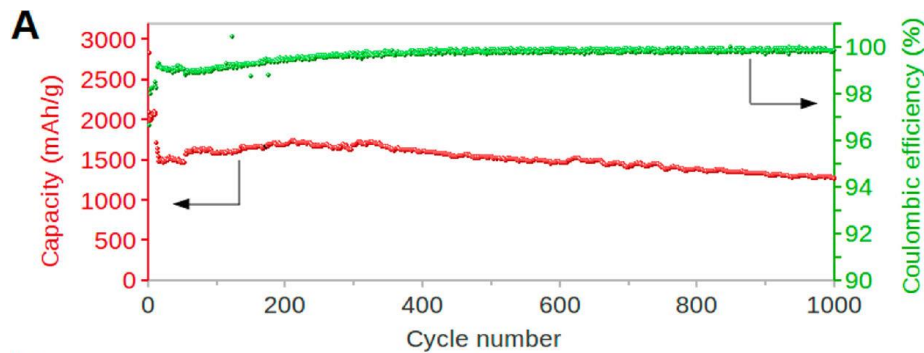
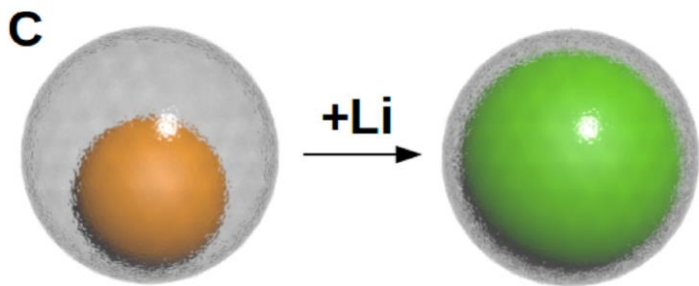
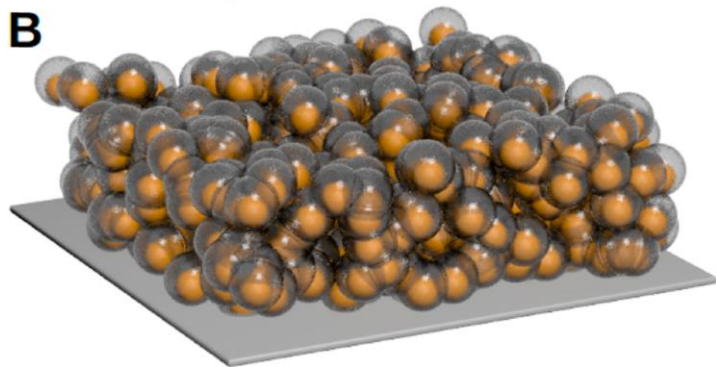
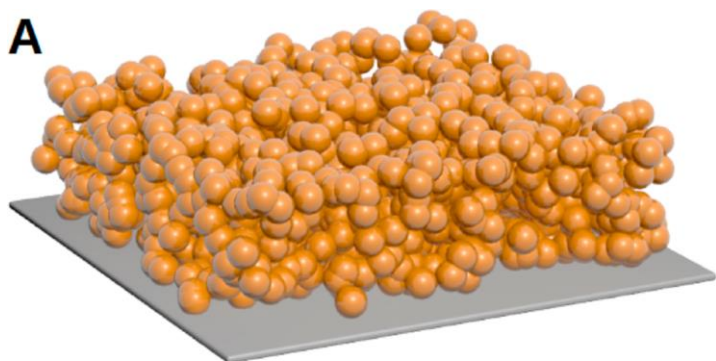


Failure mechanism of Si electrode

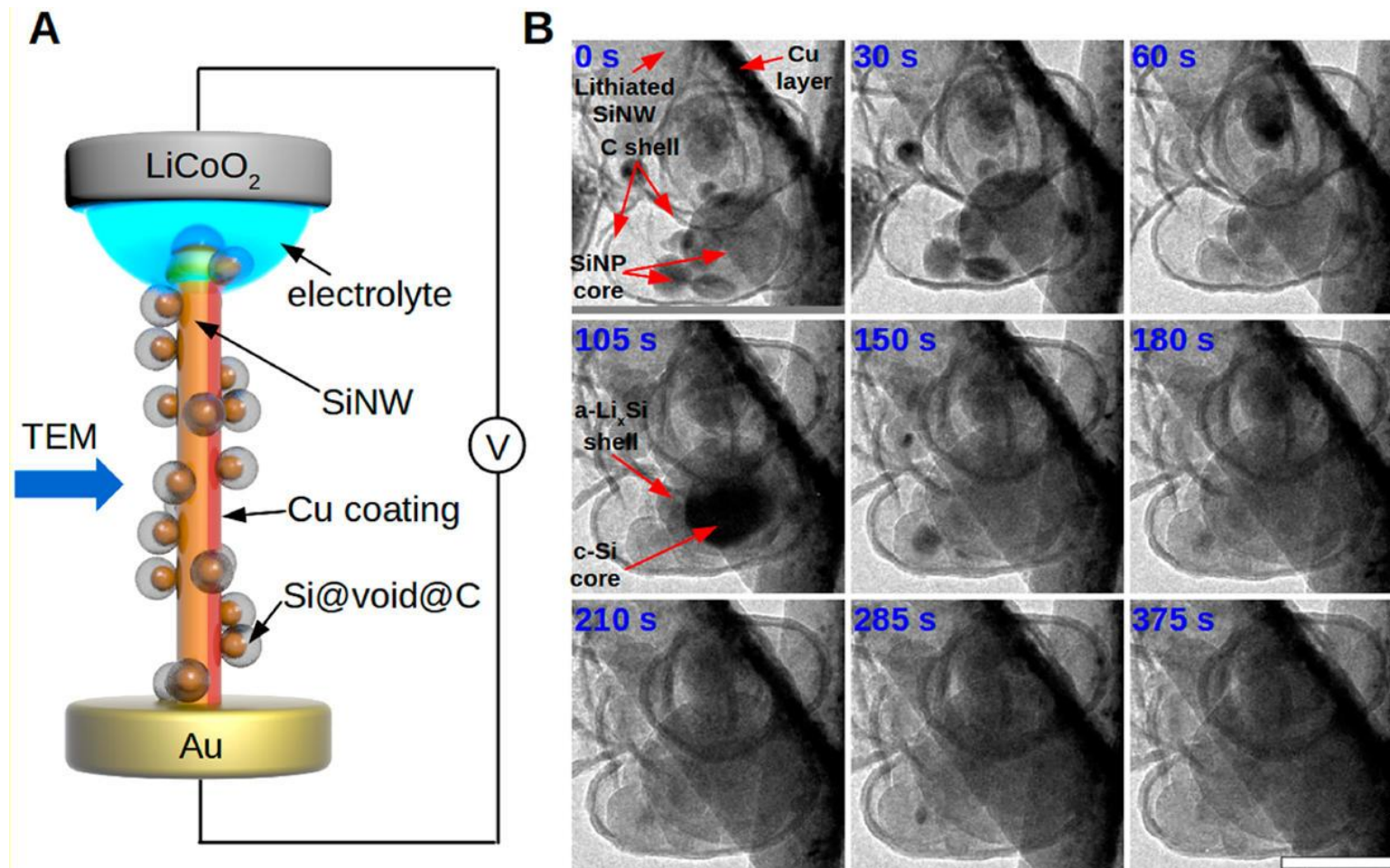


- Nanostructures
- porous structures
- unusual design
- Composites
- SEI formation
- binders

Yolk-Shell Design

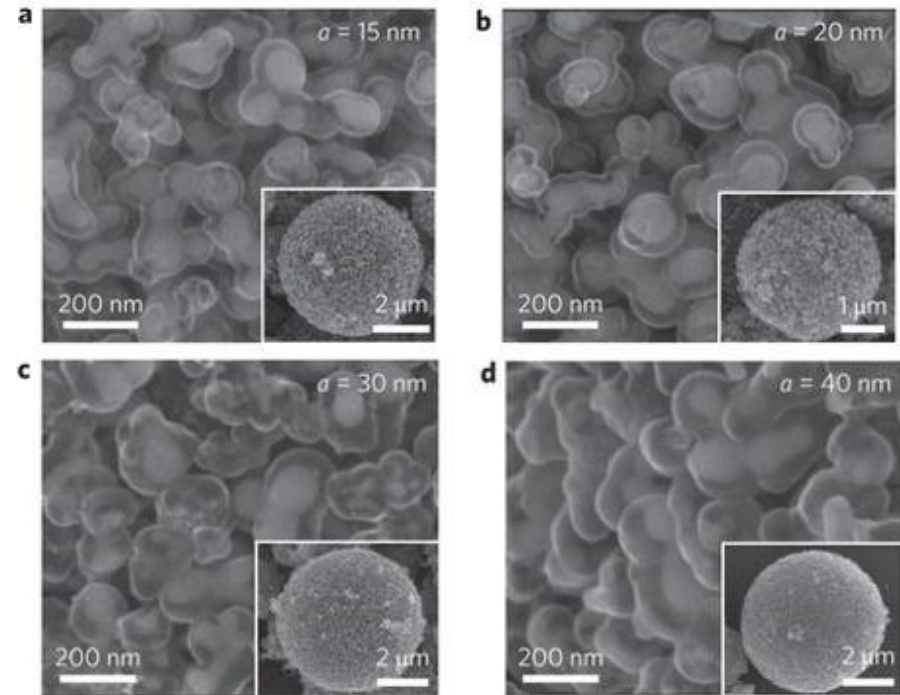
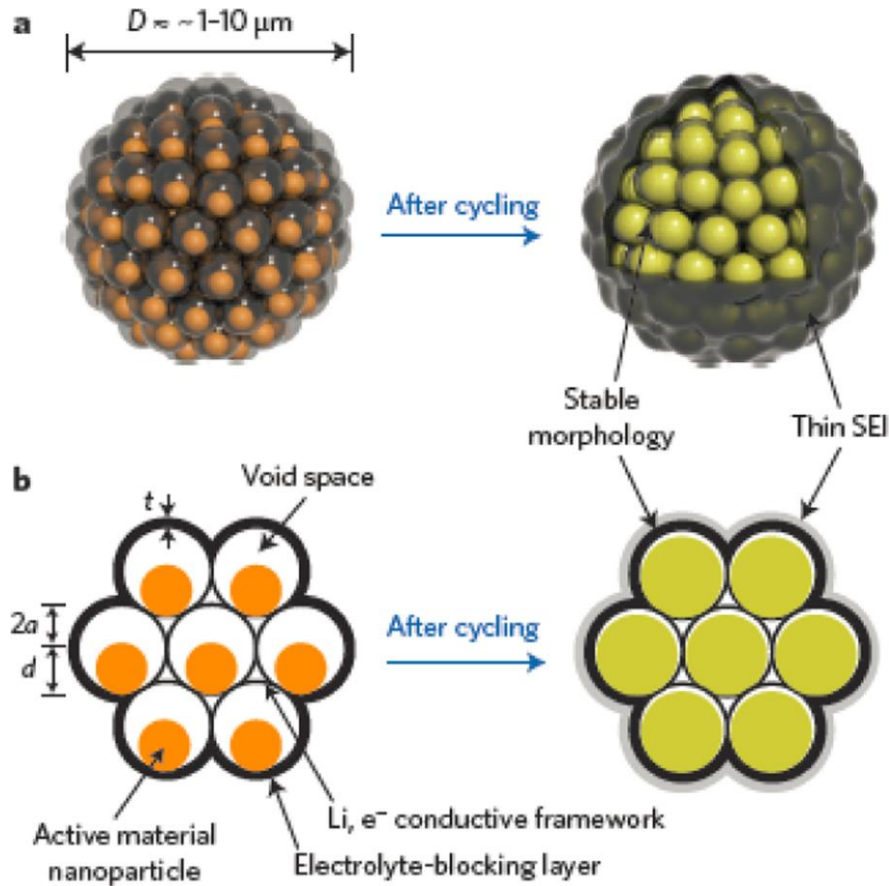


Nano Lett. 2012, 12, 3315–3321



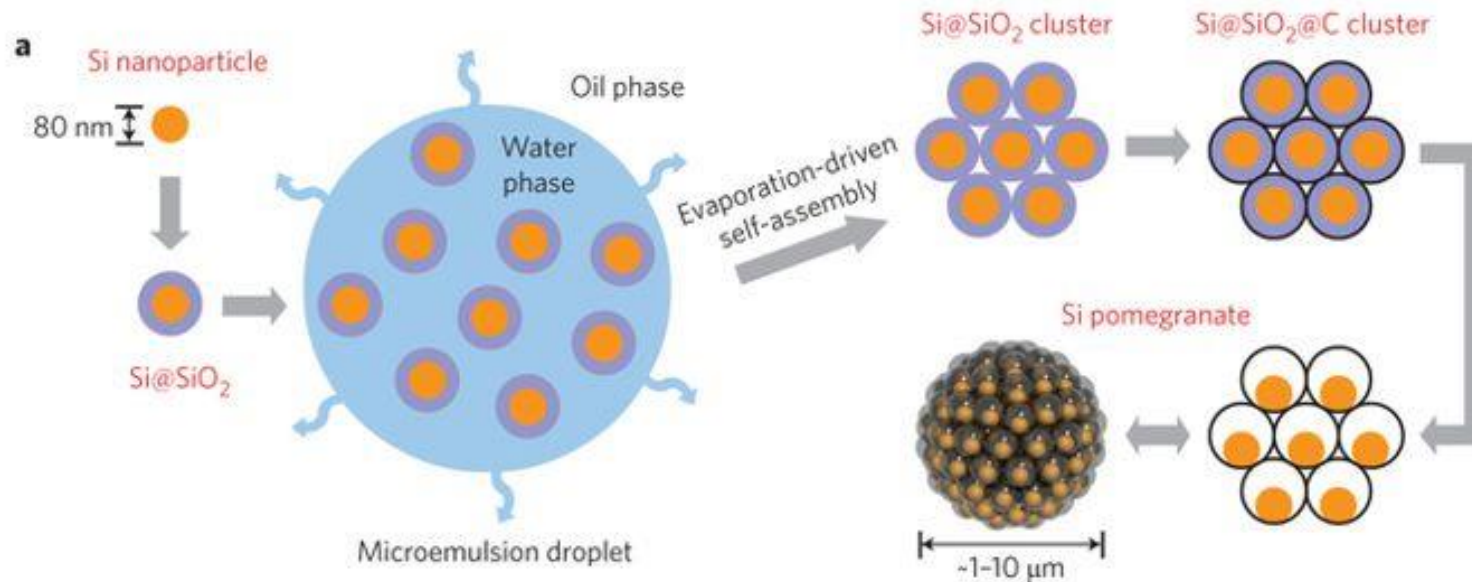
✓ no fracture ✓ Close contact Si core/C shell ✓ enough void space to accommodate expansion

Pomegranate Design



Nature Nanotechnology vol 9, p187–192 (2014)

□ bottom-up microemulsion

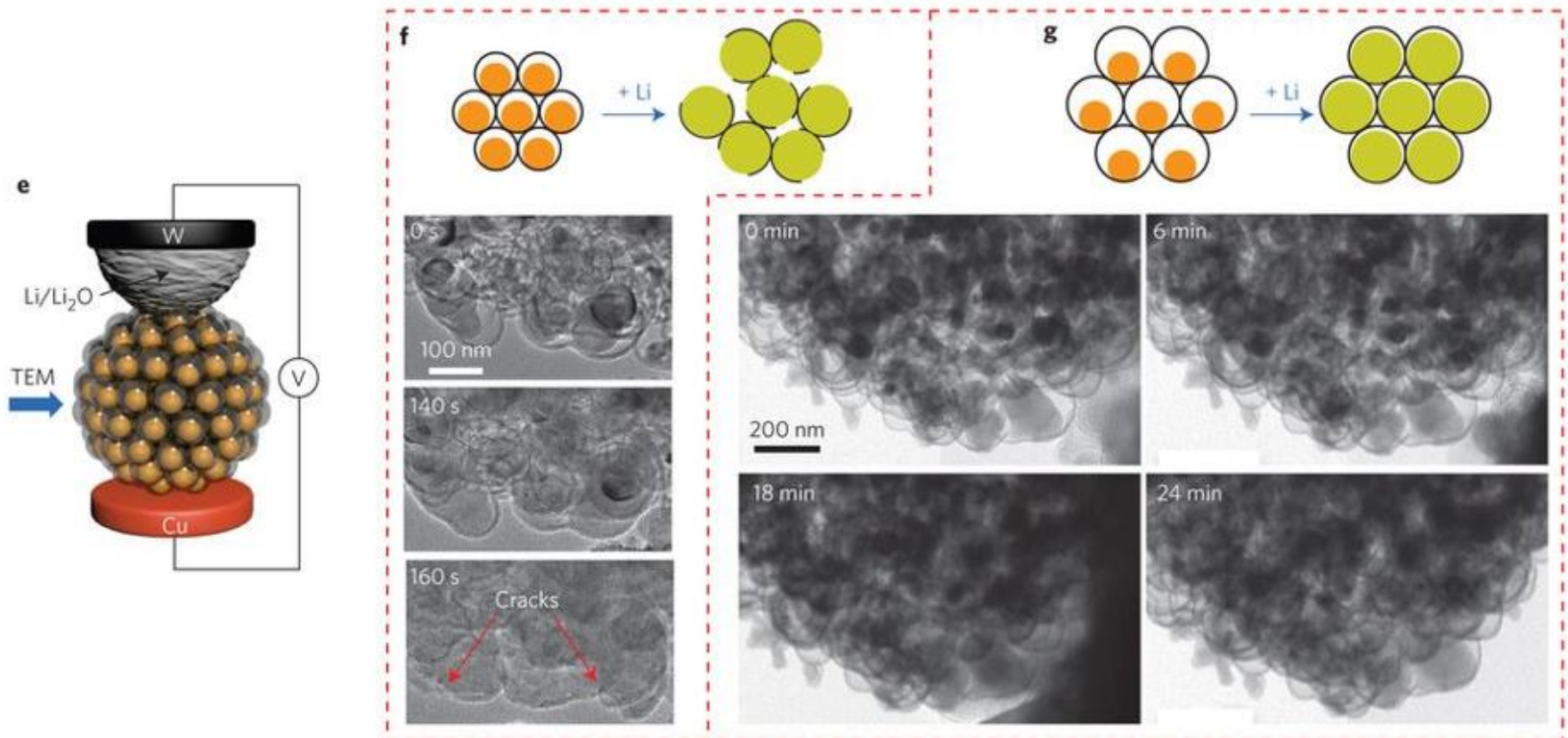


1. Synthesis of Si@SiO₂ nanoparticles
2. Microemulsion-based assembly of Si@SiO₂ nanoparticles into clusters
3. Carbon coating on Clusters
4. Silica layer etching

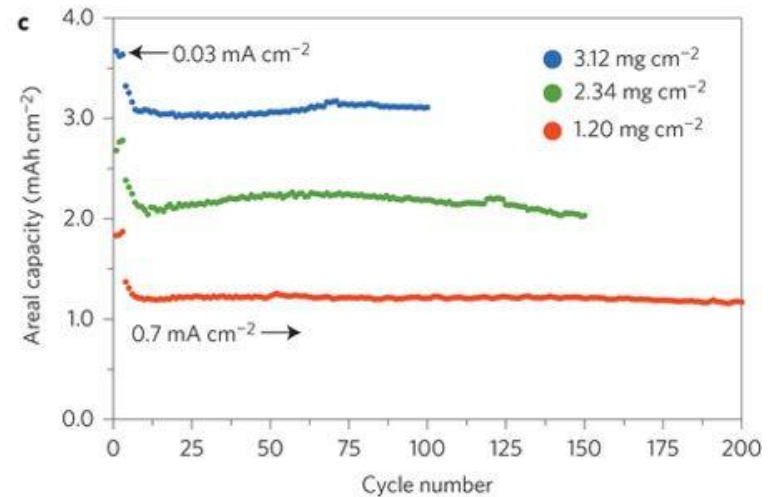
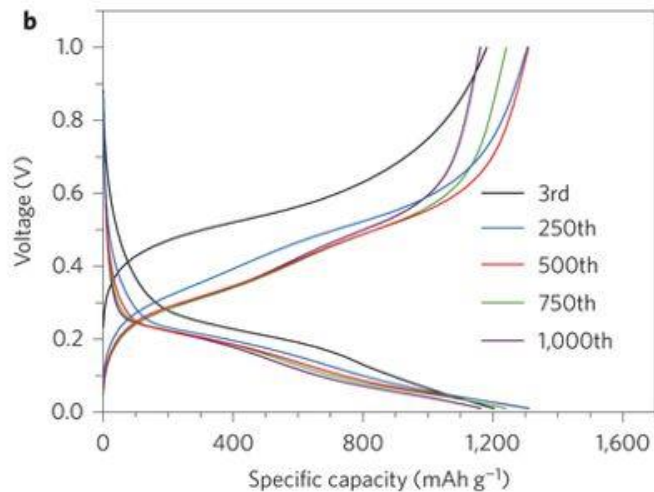
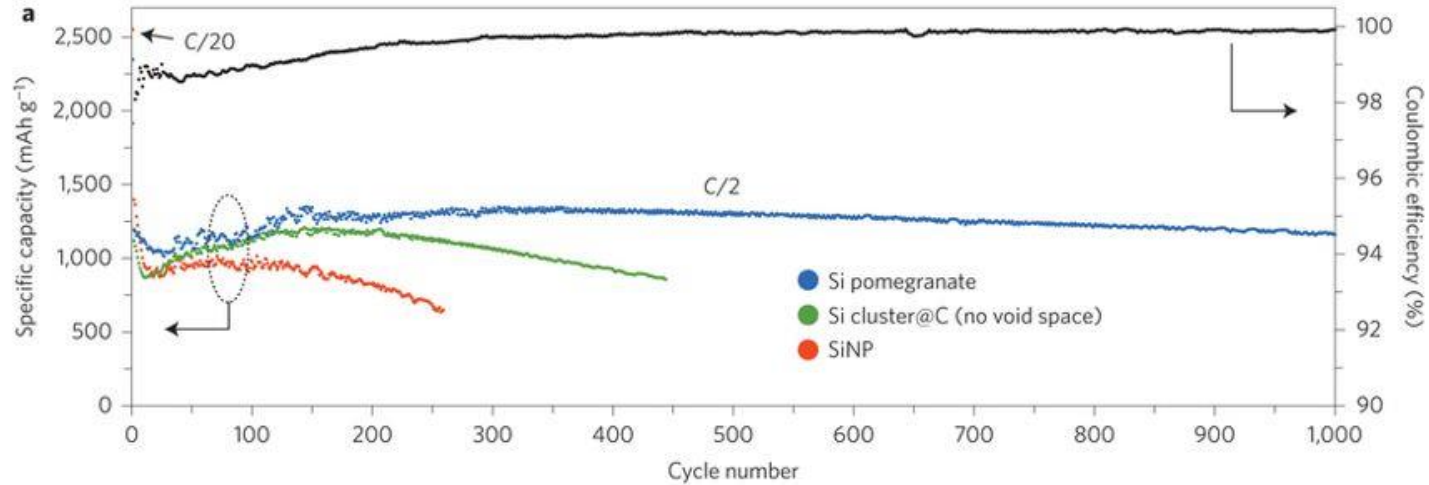
In situ TEM study

- enough void space is required to accommodate the volume expansion

Insufficient void (~15 nm) Sufficient void (~40 nm)



Ultra-stable electrochemical performance



conversion reaction



M = transition metal

X = anion

n = formal oxidation state of X

	X = O		X = S		X = N		X = P		X = F	
	Phase	E_{conv} [V] [a]	Phase	E_{conv} [V]	Phase	E_{conv} [V]	Phase	E_{conv} [V]	Phase	E_{conv} [V]
M = Ti									TiF ₃	0.95 [258]
M = V									VF ₃	0.4 [258]
M = Cr	Cr ₂ O ₃	0.2 [33]	CrS	0.85 [192]	CrN	0.2 [225]			CrF ₃	1.8[c] [259]
M = Mn	MnO ₂	0.4 [38]	MnS	0.7 [165]			MnP ₄	0.2[d] [231]		
	Mn ₂ O ₃	0.3 [42]								
	MnO	0.2 [46]								
M = Fe	Fe ₂ O ₃	0.8 [304]	FeS ₂	1.5 [173]			FeP ₂	0.3 [241]	FeF ₃	2.0 [c] [260]
	Fe ₃ O ₄	0.8 [67]	FeS	1.3 [178]	Fe ₃ N	0.7 [224]	FeP	0.1 [241]		
	FeO	0.75 [13]								
M = Co	Co ₃ O ₄	1.1 [87]	CoS ₂	1.65–1.3 [b] [187]	CoN	0.8 [221]	CoP ₃	0.3 [244]	CoF ₂	2.2 [c] [261]
	CoO	0.8 [87]	Co _{0.92} S	1.4 [192]	Co ₃ N	1.0 [224]				
			Co ₉ S ₈	1.1 [189]						
M = Ni	NiO	0.6 [13]	NiS ₂	1.6 [194]	Ni ₃ N	0.6 [223]	NiP ₃	0.7 [250]	NiF ₂	1.9 [c] [261]
			NiS	1.5 [196]			NiP ₂	0.5-0.3 [b] [233]		
			Ni ₃ S ₂	1.4 [199]			Ni ₃ P	Slope [249]		
M = Cu	CuO	1.4 [125]	CuS	2.0-1.7 [b] [209]	Cu ₃ N	[229]	CuP ₂	0.7 [251]	CuF ₂	3.0 [c] [270]
	Cu ₂ O	1.4 [129]	Cu ₂ S	1.7 [208]			Cu ₃ P	0.8 [252]		
M = Mo	MoO ₃	0.45 [148]	MoS ₂	0.6 [214]						
	MoO ₂	Slope [151]								
M = W			WS ₂	0.8–0.6 [b] [218]						
M = Ru	RuO ₂	0.9 [155]								

Challenges

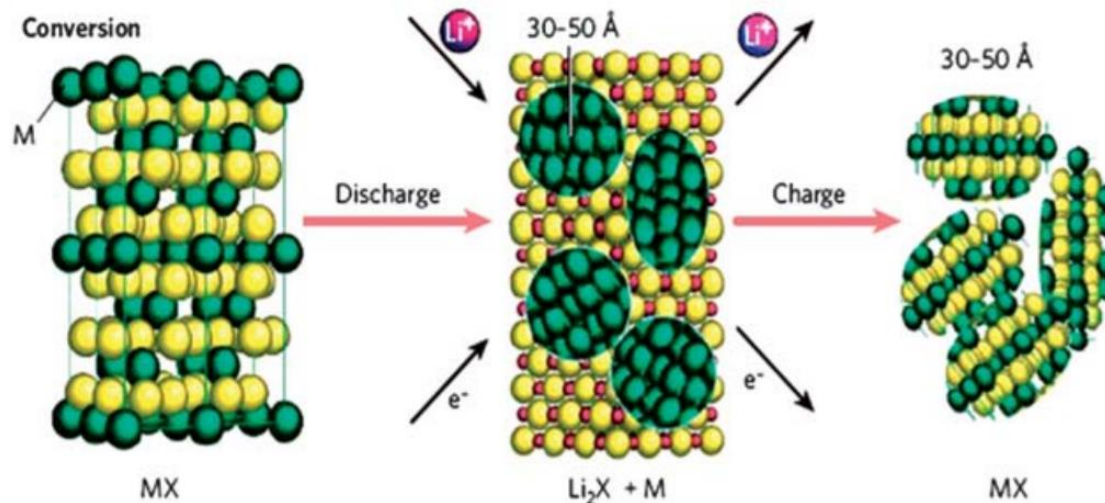
conversion reaction



M = transition metal

X = anion

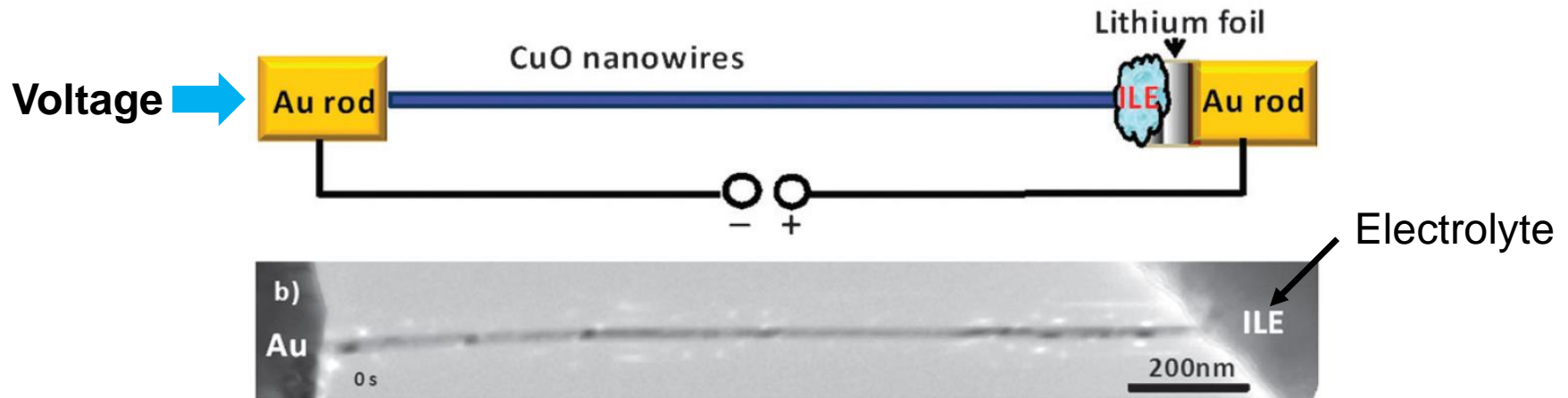
n = formal oxidation state of X



- Completely change
- Volume change
- Large initial irreversible capacity loss

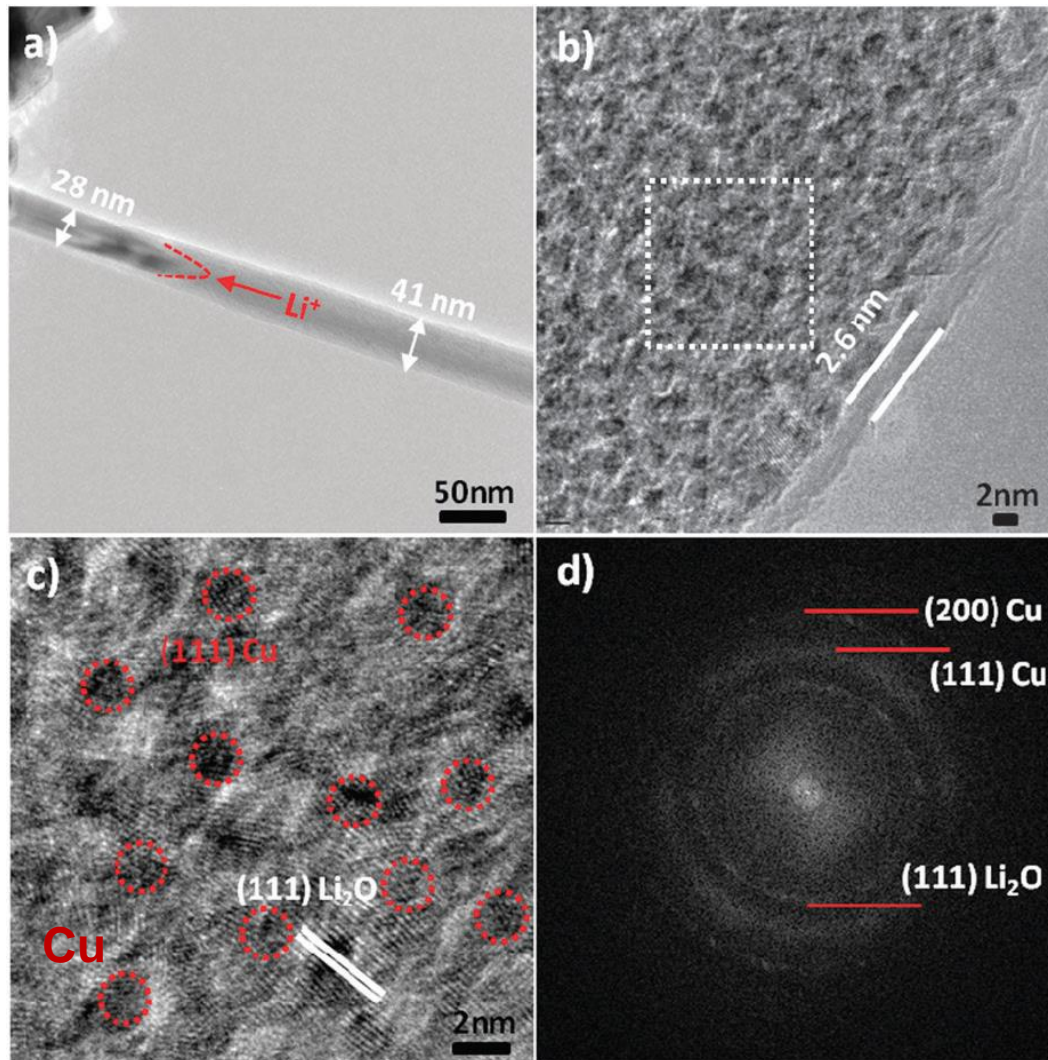
CuO as an example

Conversion mechanism of CuO nanowires during lithiation–delithiation by *in situ* transmission electron microscopy

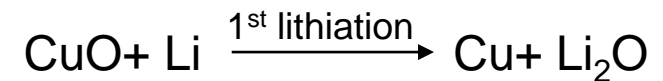


Schematic illustration and corresponding TEM image of a nano-LIB device constructed inside TEM

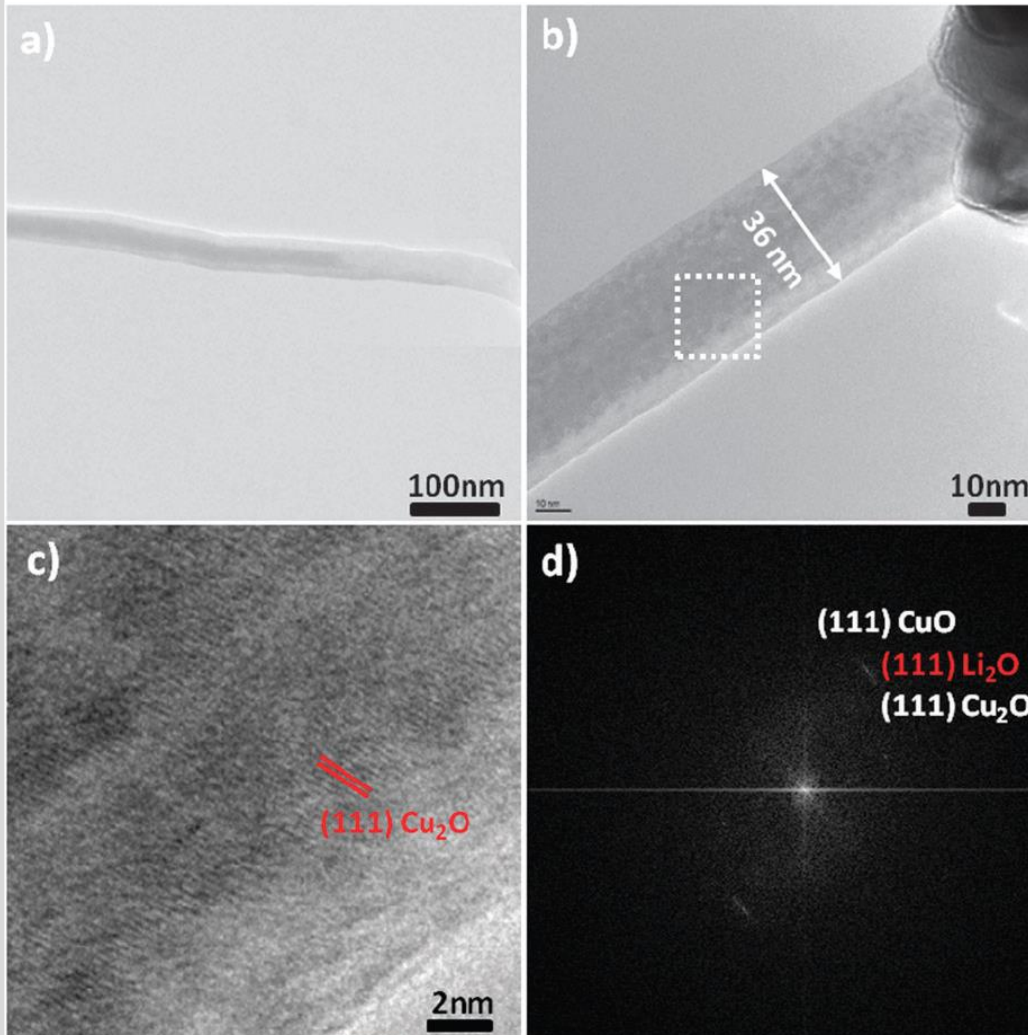
1st lithiation process



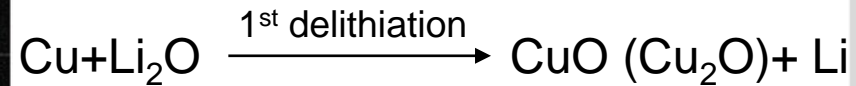
- Expanded, longitudinal and radial
- Volume expansion, 256%
- Lithiation, surface towards center
- SEI
- Li_2O matrix, Cu nanocrystals

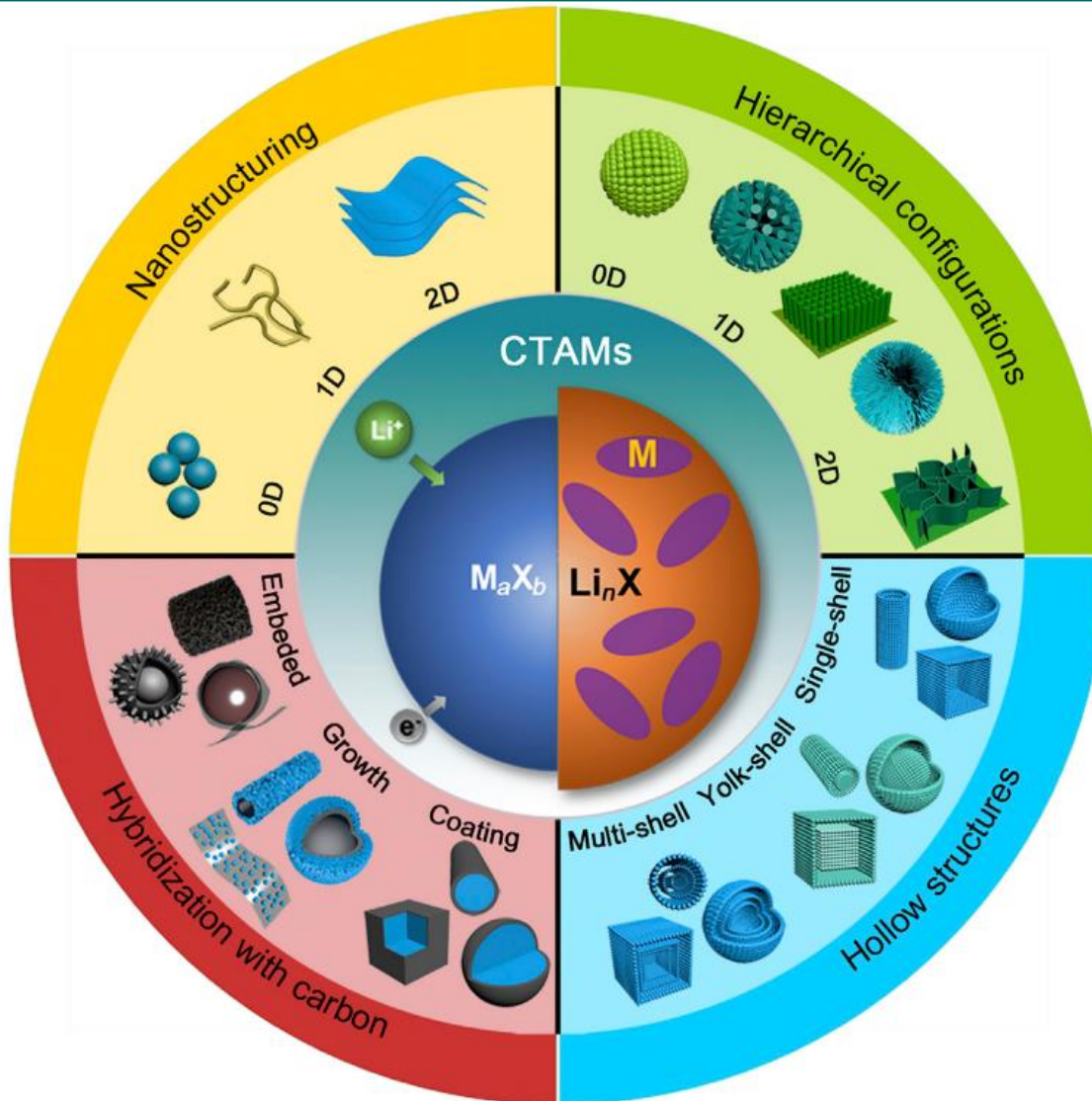


1st delithiation process



- ❑ Shrank, longitudinal and radial
- ❑ Volume expansion, 165%
- ❑ Irreversible volume changes
- ❑ Cu_2O , incomplete oxidation
- ❑ Li_2O , irreversible capacity loss

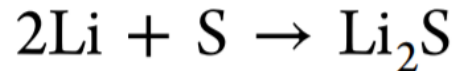
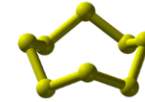




- Nanostructuring
- Hybridization with carbon
- Hollow structures
- Hierarchical configurations

Chem 4, 972–996, May 10, 2018

Conceptually conversion: The Li-S Battery



Theoretical capacity: 1675 mA h/g @ 2V

ARTICLES

PUBLISHED ONLINE: 17 MAY 2009 | DOI: 10.1038/NMAT2460

nature
materials

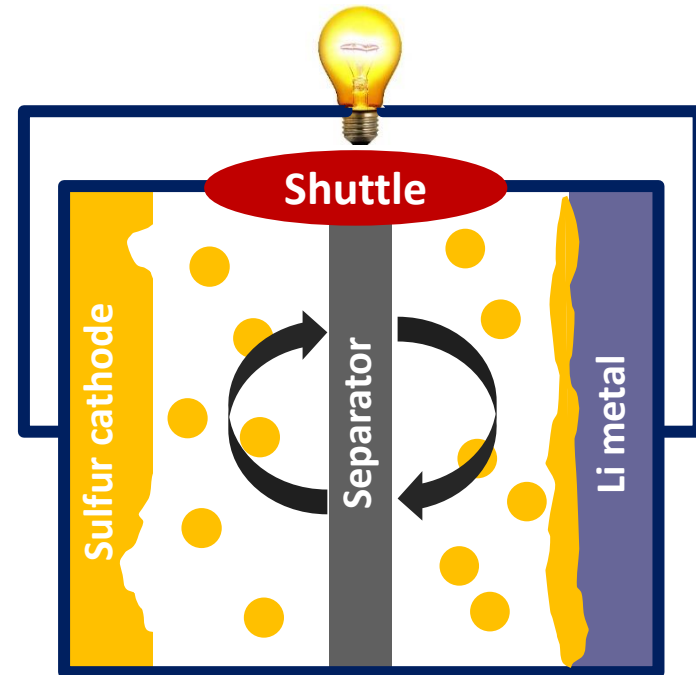
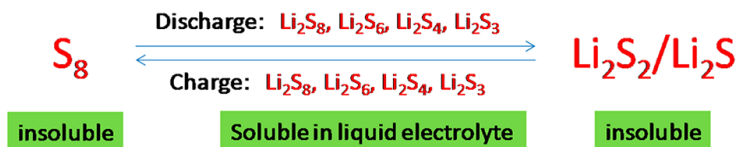
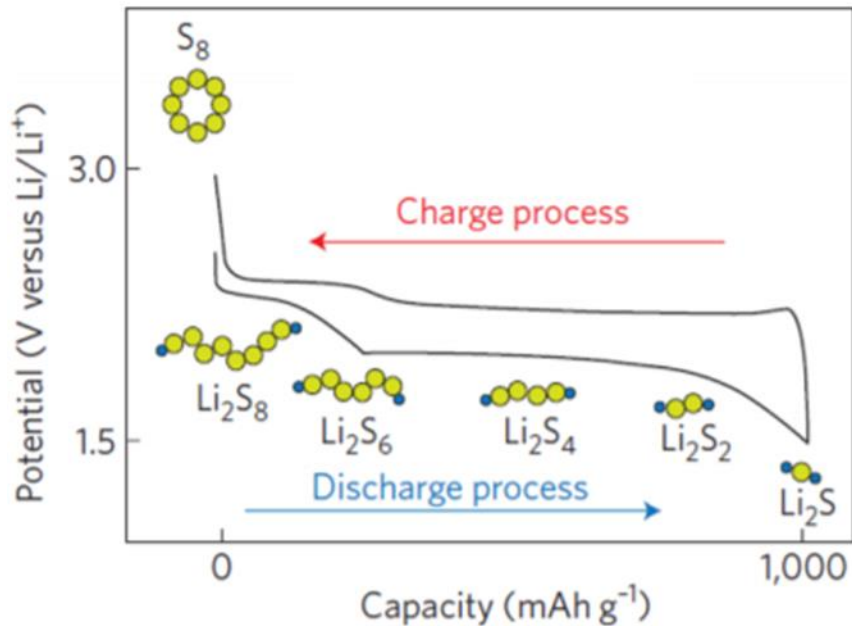
Properties for different cathode materials for Li-ion and Li-S batteries.

Cathode material	Theoretical gravimetric capacity (mAh/g)	Experimental capacity (mAh/g)	Theoretical volumetric capacity (mAh/cm ³)	Average voltage (V)	Level of development
LiCoO ₂	274	130–150	1363	3.8	Commercialized
LiNi _{0.33} Co _{0.33} Mn _{0.33} O ₂	280	150–170	1333	3.7	Commercialized
LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	279	180–200	1284	3.7	Commercialized
LiMn ₂ O ₄	148	100–120	596	4.1	Commercialized
Li ₂ MnO ₃	458	180–190	1708	3.8	Research
LiFePO ₄	170	160–165	589	3.4	Commercialized
LiCoPO ₄	167	110–130	510	3.24	Research
Sulfur	1675	200–1400	2567	2.1	Research

Li-S Batteries: The Challenges, Chemistry, Materials, And Future Perspectives
A Manthiram, Y Fu, SH Chung, C Zu, YS Su Chem. Rev., 2014, 114 (23), 11751
X Ji, KT Lee, LF Nazar *Nature materials*, 2009, 8 (6), 500

The Li-S Battery and the Redox Shuttle

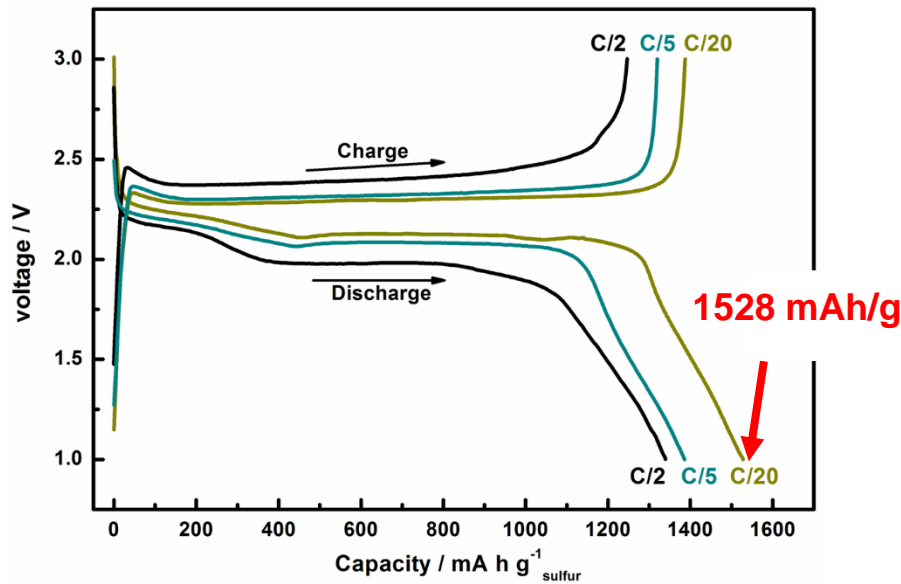
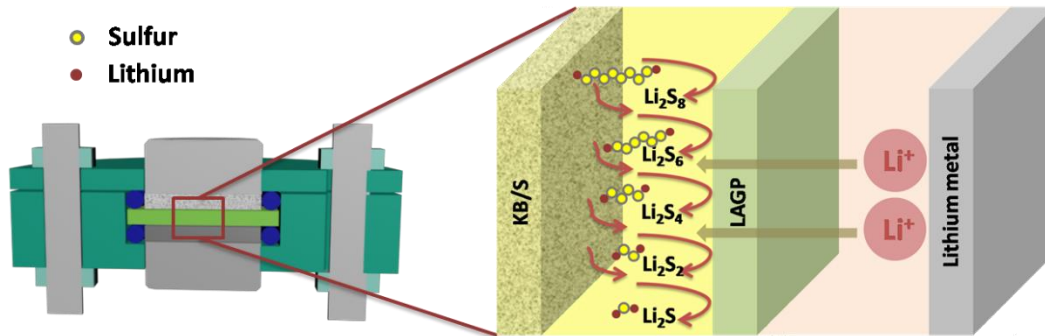
Polysulfides dissolution



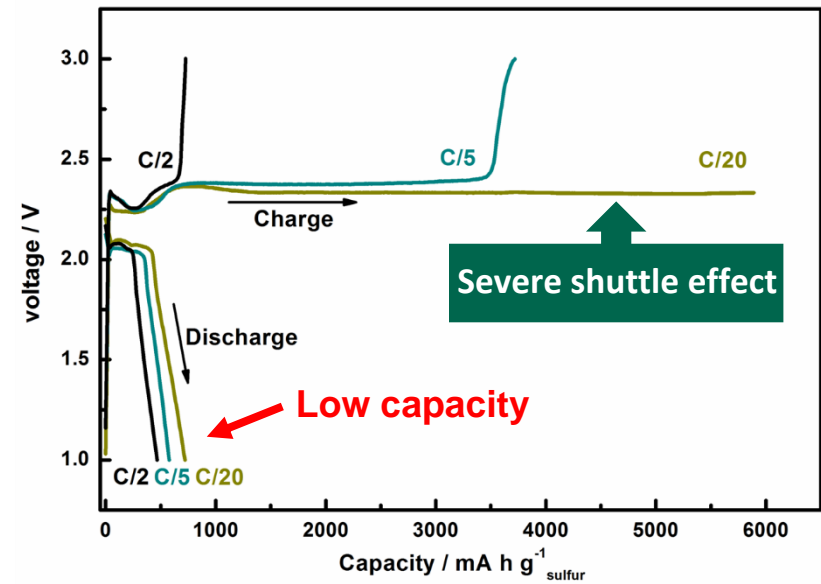
- Inner short circuit
- Cathode active material loss
- Metal anode passivation

Nat. Mater. 2012, 11, 19.

Shuttle Free Li-S battery



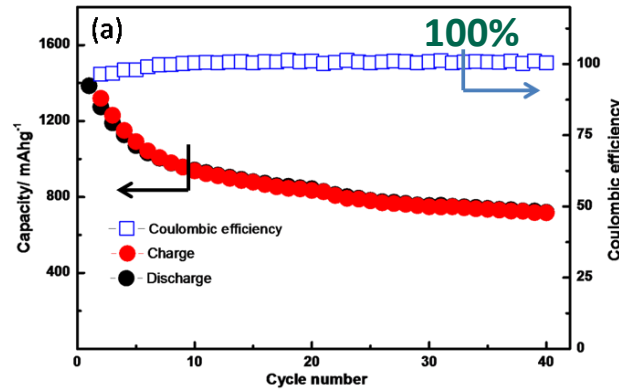
Hybrid electrolyte Li-S cells



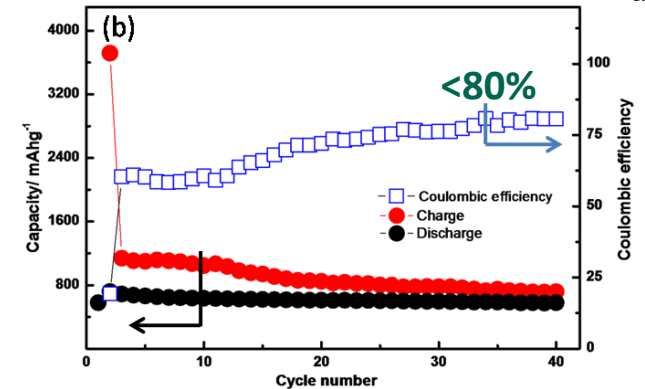
Liquid electrolyte Li-S cells

Q. Wang, J. Jin, X. Wu, G. M. J. Yang, Z. Wen *Phys. Chem. Chem. Phys.*, 2014, 16, 21225-21229

Coulombic efficiency of 100% is achieved



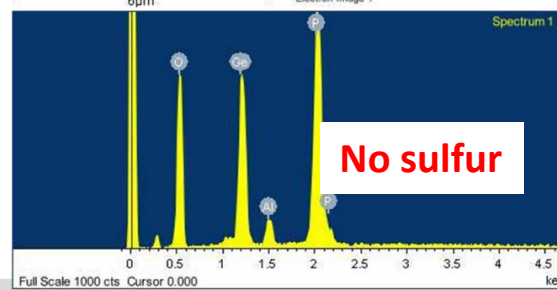
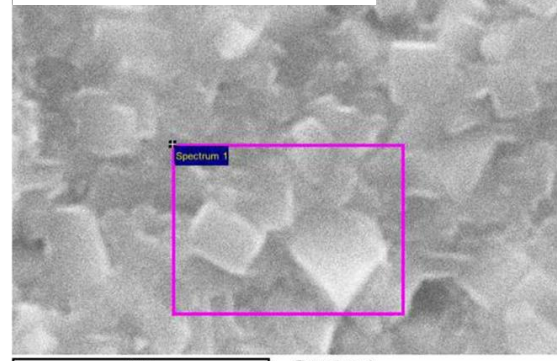
Hybrid electrolyte Li-S cells



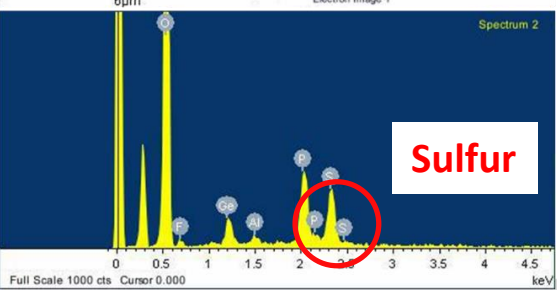
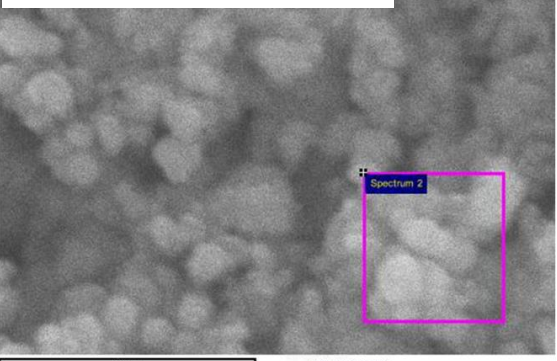
Liquid electrolyte Li-S cells

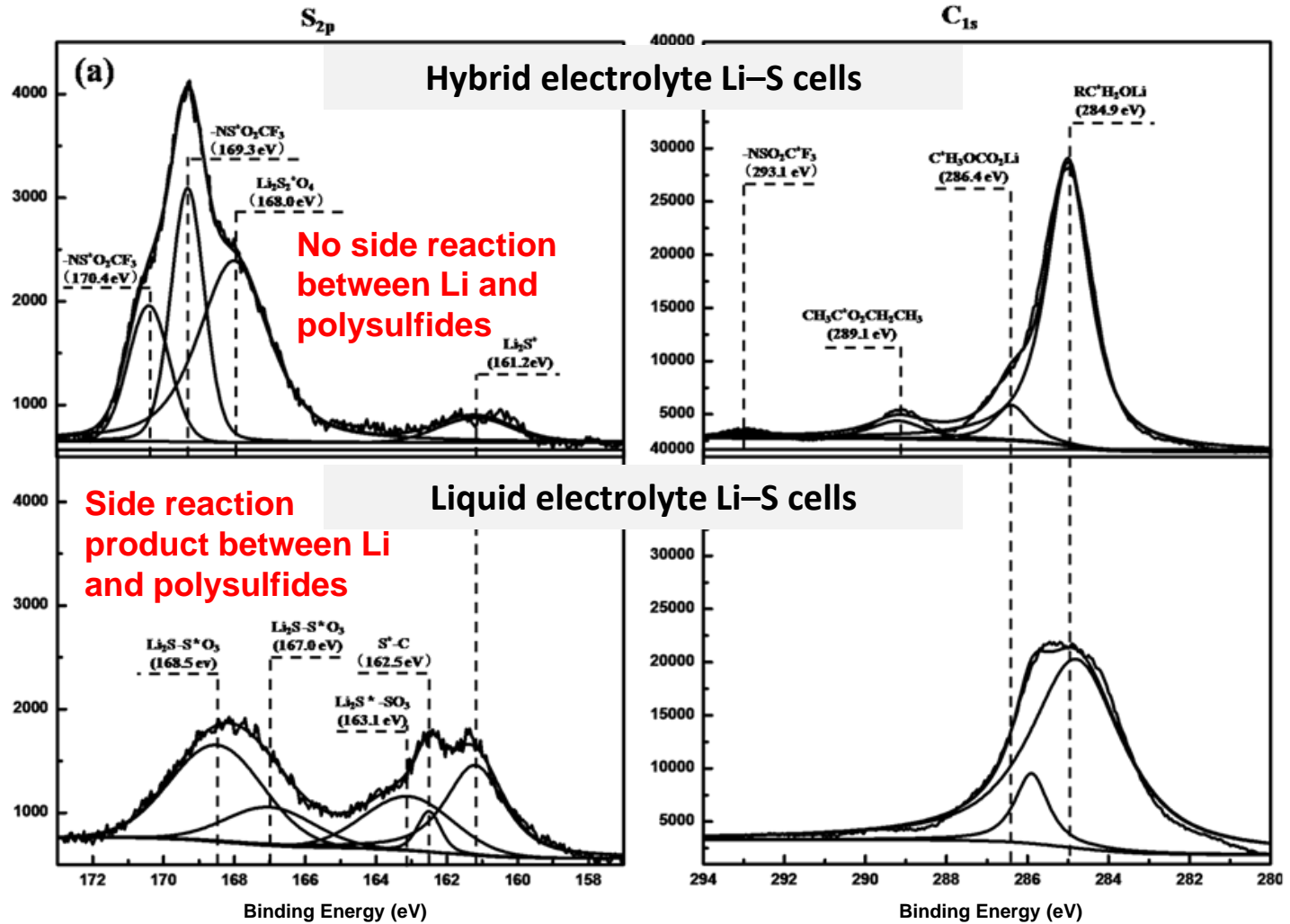
No sulfur is observed on the surface of cycled LAGP

Closed to anode side

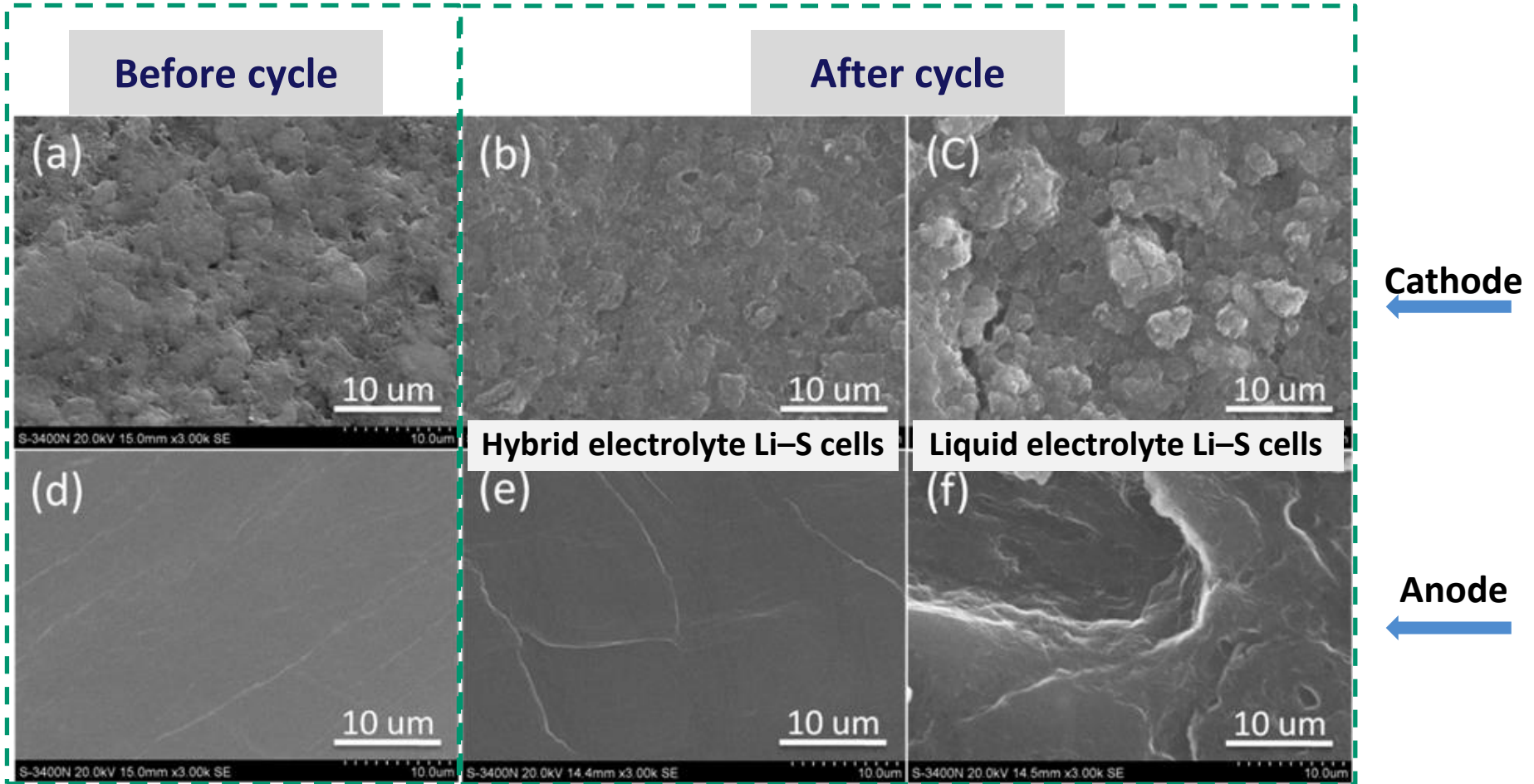


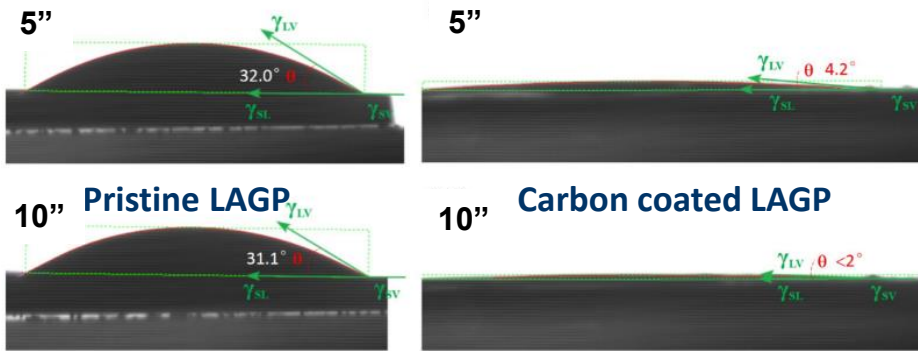
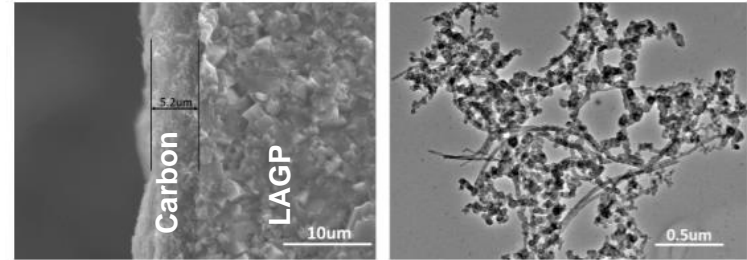
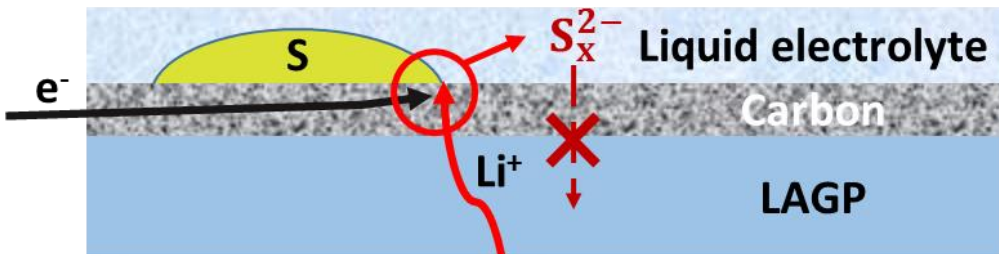
Closed to cathode side



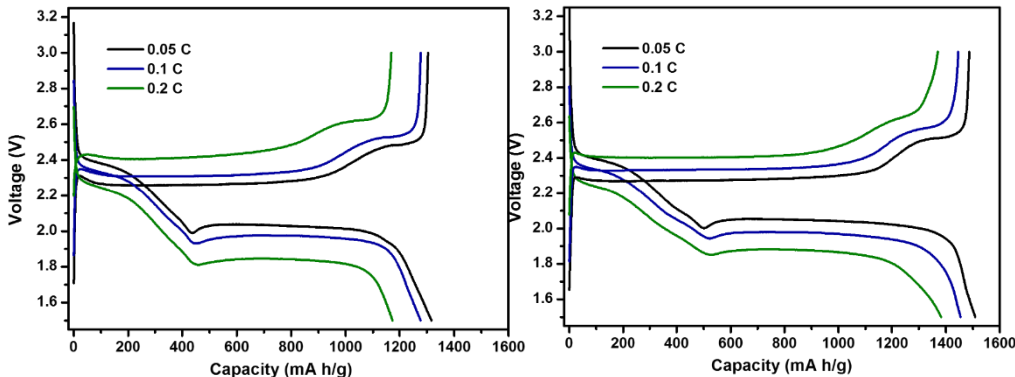


XPS spectra from the lithium anode





Wettability toward electrolytes

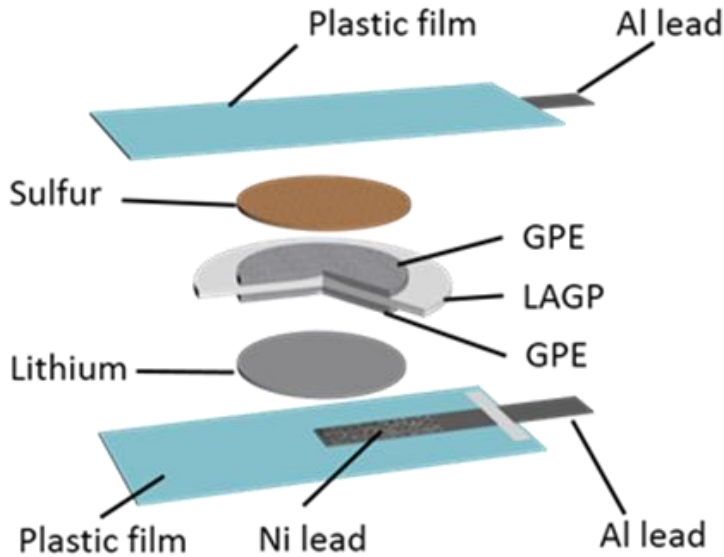


Pristine LAGP

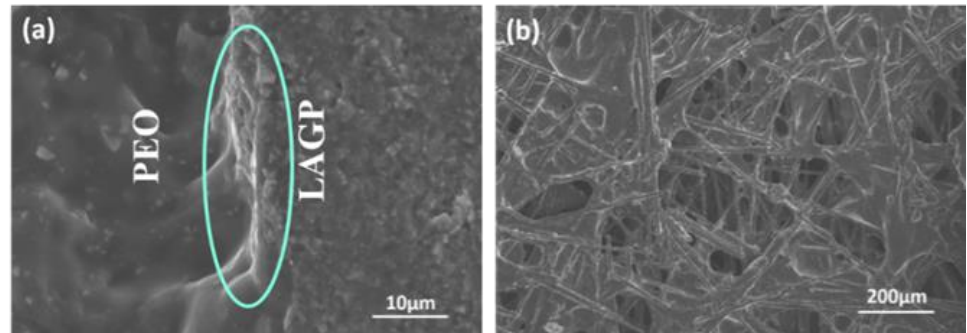
Carbon coated LAGP

- ✓ The carbon-coating serves as an upper current collector to facilitate electron transport for high active-material utilization.
- ✓ The carbon coating layer on the LAGP ceramic helps to enhance the wettability toward electrolytes.
- ✓ Enhanced electrochemical performance is demonstrated

Q. Wang *et al.* *Solid State Ionics* 300 (2017) 67–72

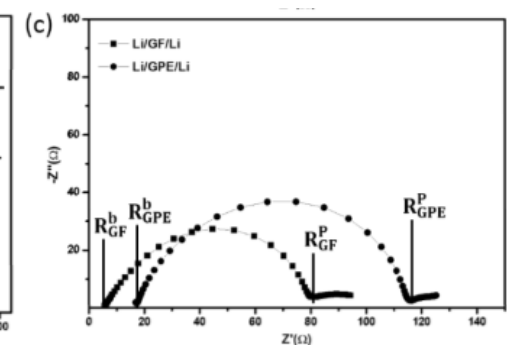
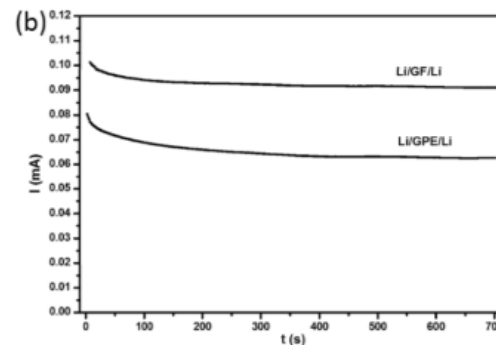


Gel Polymer Electrolyte (GPE)-PEO based



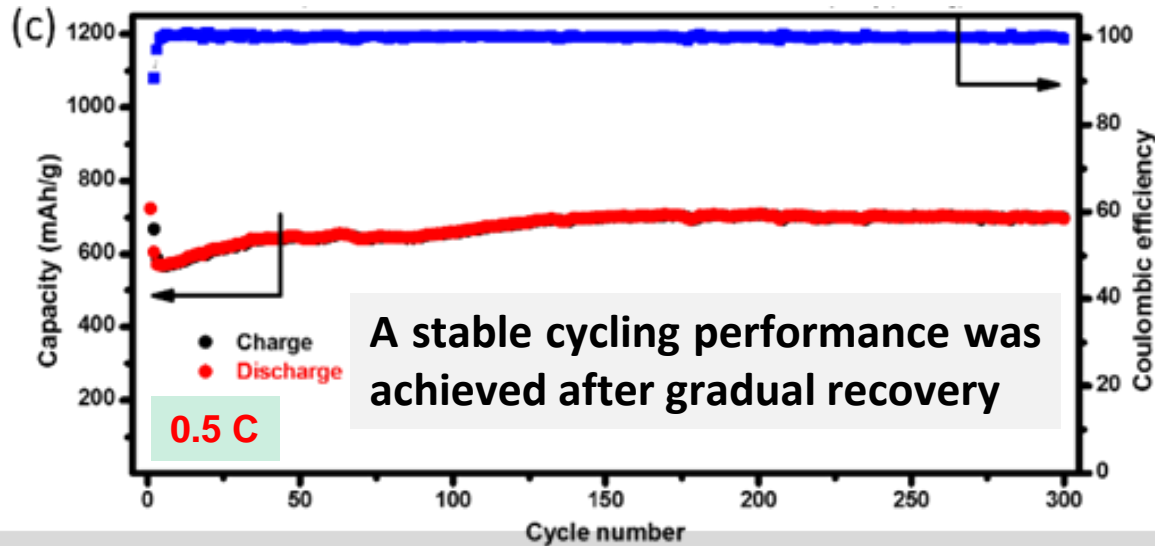
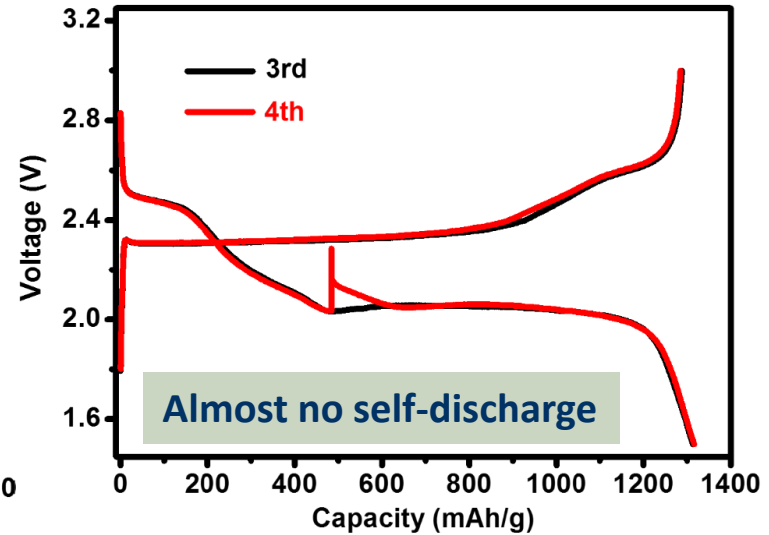
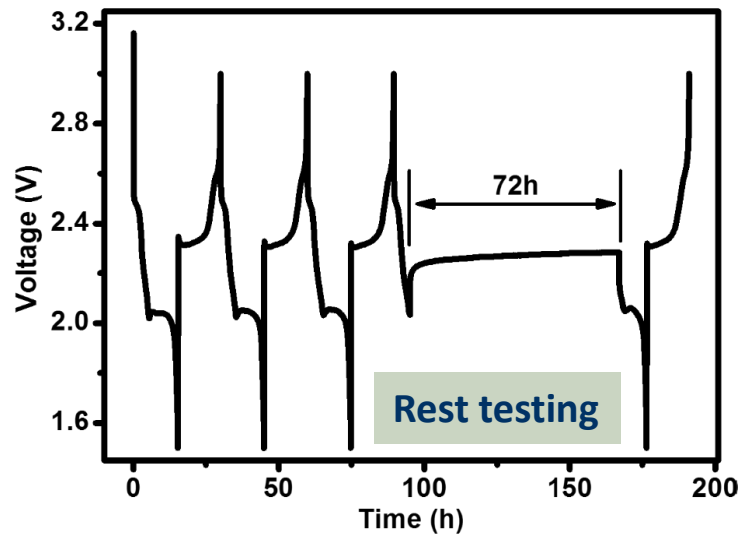
Advantages of GPE

- ✓ Has acceptably high room-temperature conductivity and reasonable mechanical flexibility
- ✓ Helps to decrease the contact resistance of the interface



σ : $11.5 \times 10^{-4} \text{ S cm}^{-1}$, t_{Li^+} : 0.28

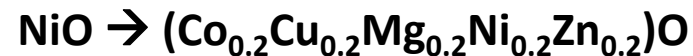
Q. Wang *et al.* *Chem. Commun.*, 2016, 52, 1637-1640



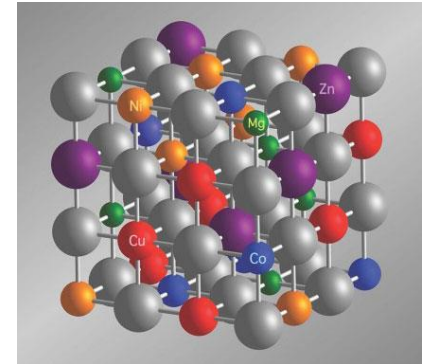
— 300 cycles
 700 mA h/g

What are high entropy oxides (HEOs)?

- Adding multiple cations (≥ 5) on a particular Wyckoff site:
- Achieve a single phase



Rocksalt



$Fm\bar{3}m$

- Why are these called high entropy oxides?

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta S = \Delta S_T + \Delta S_{config}$$

$$\Delta S_{config} = -R \sum_{i=1}^n x_i \ln x_i$$

Maximum; all elements in equiatomic amounts
R: ideal gas constant

- In high entropy materials (high entropy alloys, etc.)

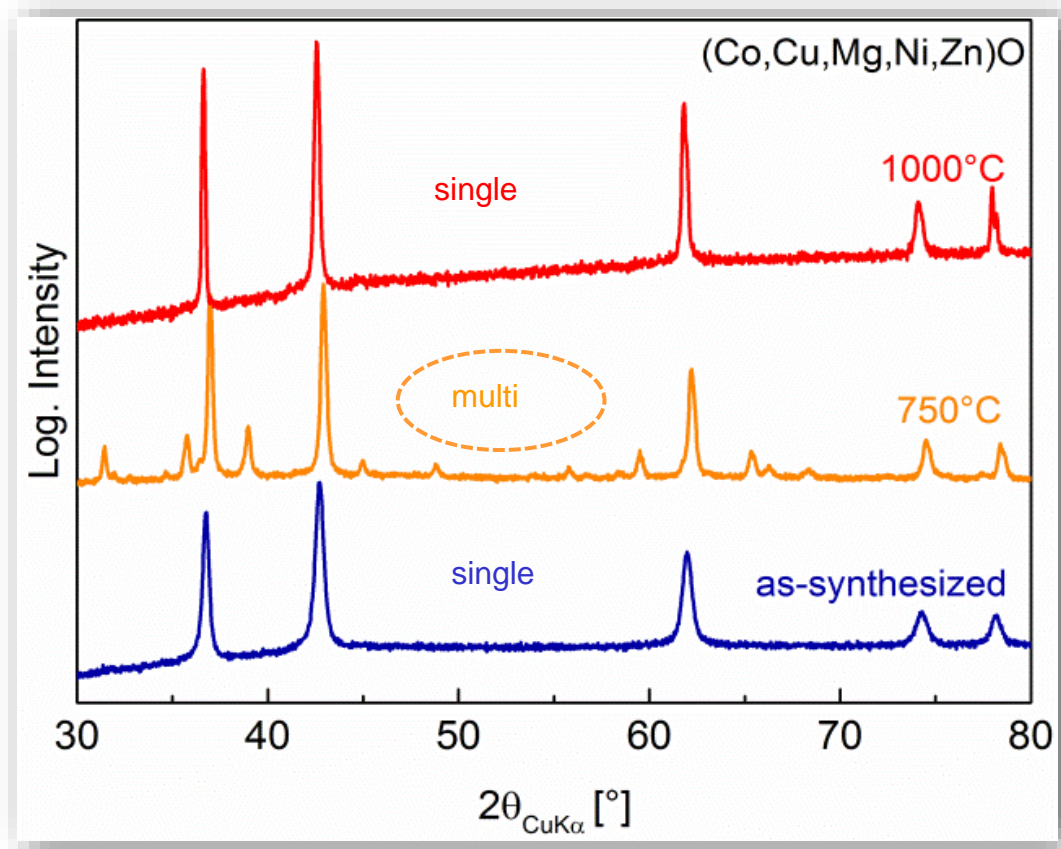
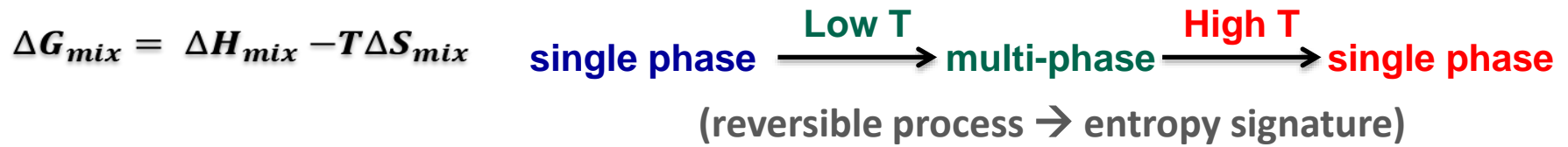
$$\Delta S_{config} > 1.5R$$

$$T\Delta S_{mix} > \Delta H_{mix}$$

Rost C. M. *et al.*, *Nat. Commun.* **6**, 8485 (2015)

Murty B. S. *et al.*, *High Entropy Alloys* (2014)

Structure and role of entropy

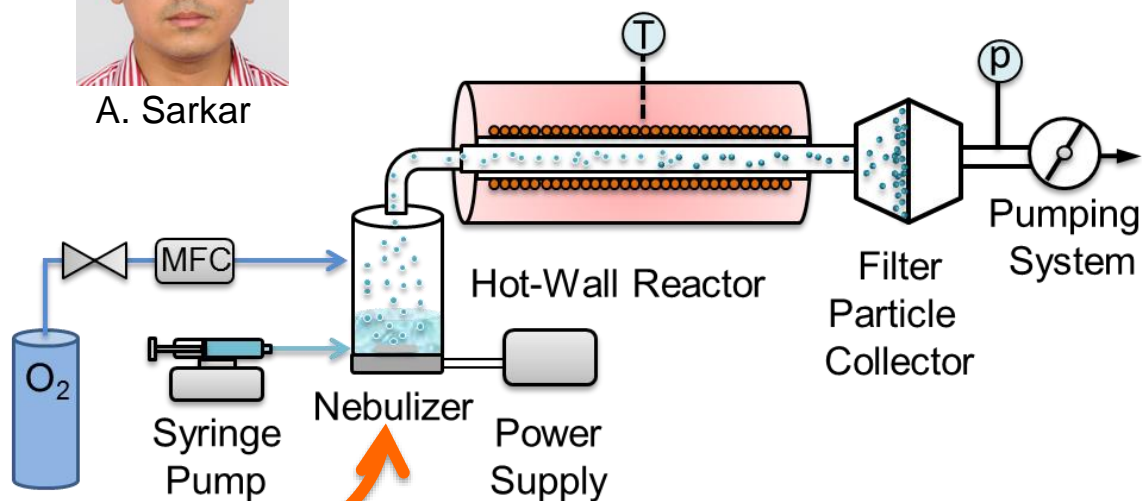


Rost C. M. *et al.*, *Nat. Commun.* (2015)

A. Sarkar, *et al.*, *J. Eur. Cer. Soc.* (2017)



A. Sarkar



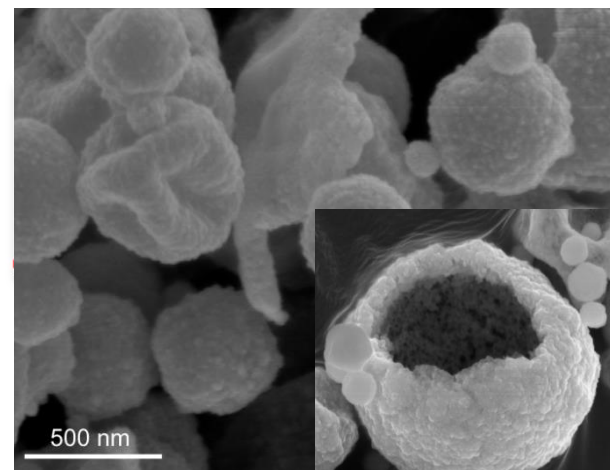
Precursors

Solution of nitrate salts of all elements

Experimental conditions

$T = 1000 - 1200 \text{ } ^\circ\text{C}$
 $p = 900 \text{ mbar}$

Nebulized Spray Pyrolysis



Powder morphology

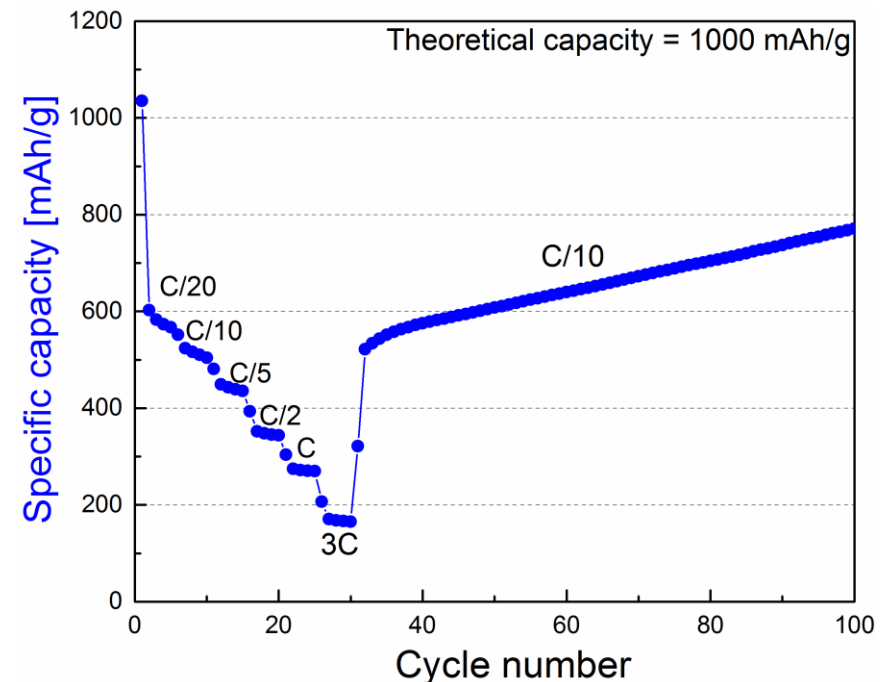
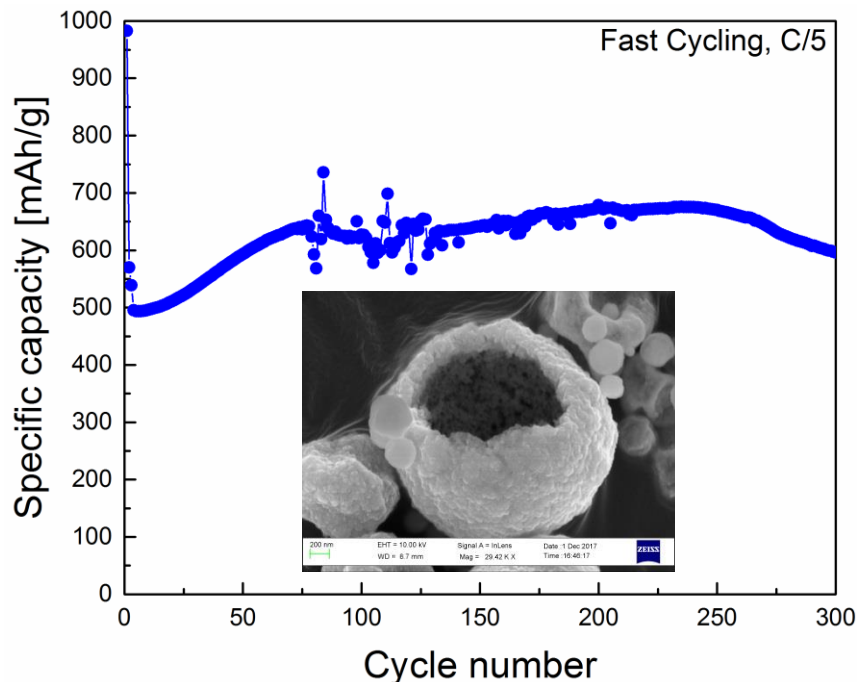
Hollow spherical
Broad particle size distribution

A. Sarkar, *et al.*, J. Eur. Cer. Soc. (2017)

High Entropy Oxides for Reversible Energy Storage

Half cell- charged against Li (as counter electrode)

- Specific capacity > 600 mAh/g (in spite of the big particles)
- High reversibility
- Rate capability



A. Sarkar, *et al.*, Nat. Comm. accepted.

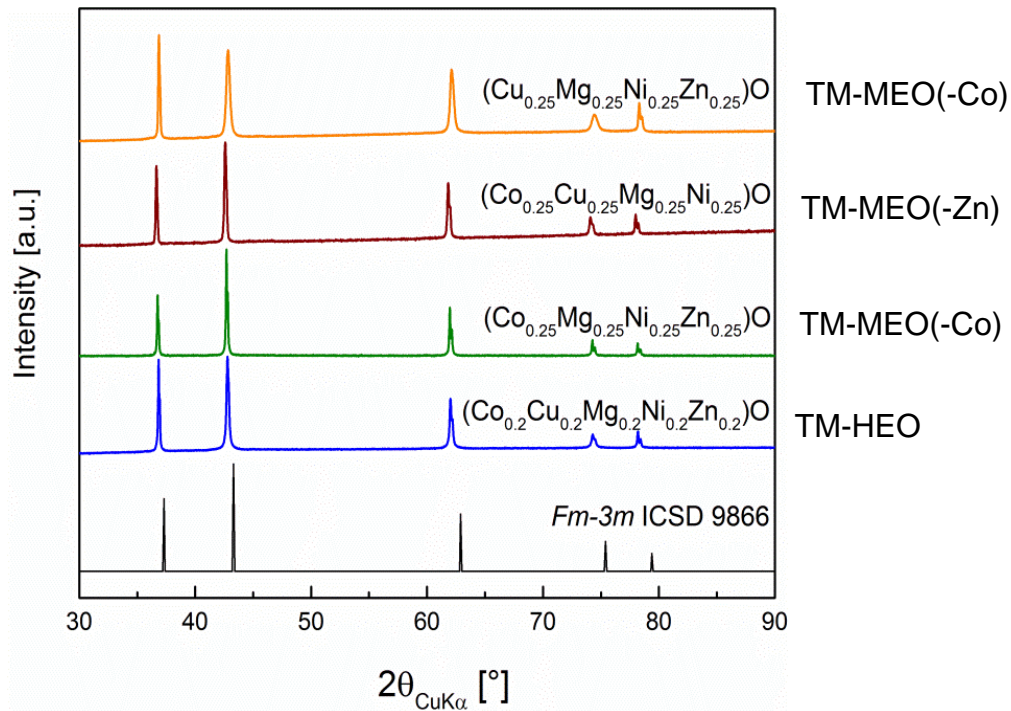
Medium entropy oxides (MEO)

$$\Delta S_{config} = -R \sum_{i=1}^n x_i \ln x_i$$

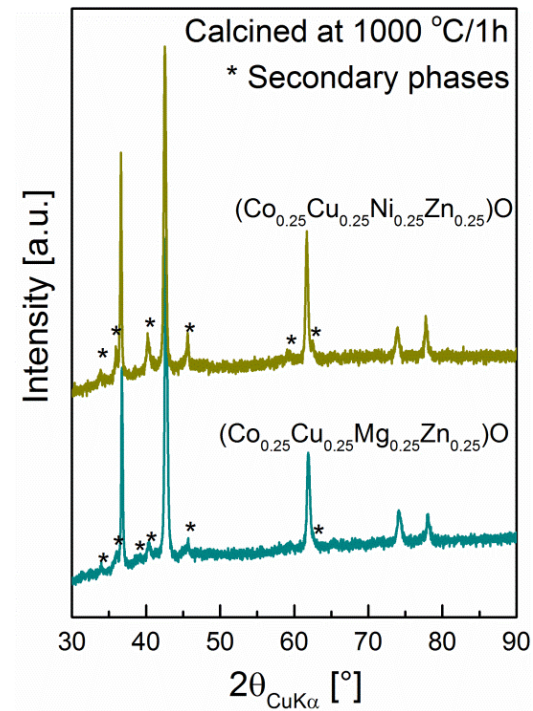
$$\Delta S_{config} > 1.5 R \text{ (HEO)}$$

$$1.5 R > \Delta S_{config} > 1.0 R \text{ (MEO)}$$

$$4\text{-cationic system, } \Delta S_{config} = 1.39 R$$



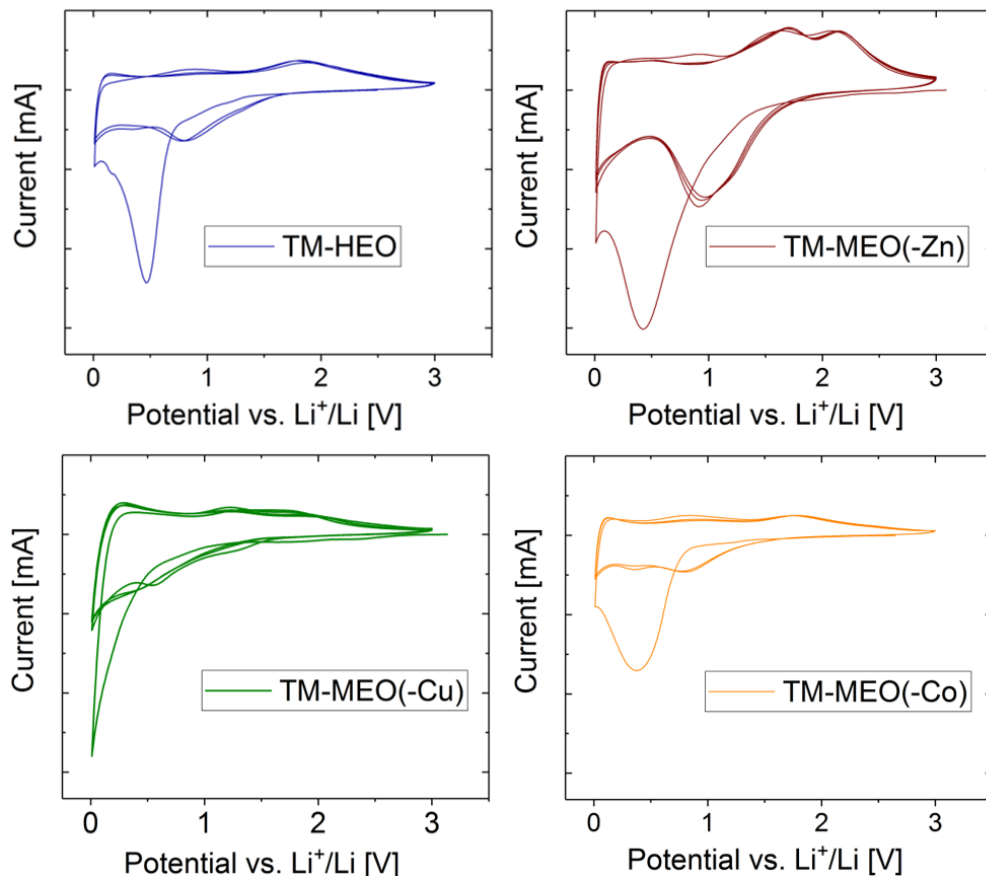
- MEOs needed additional calcination step
- All systems calcined at 1000 °C for comparison



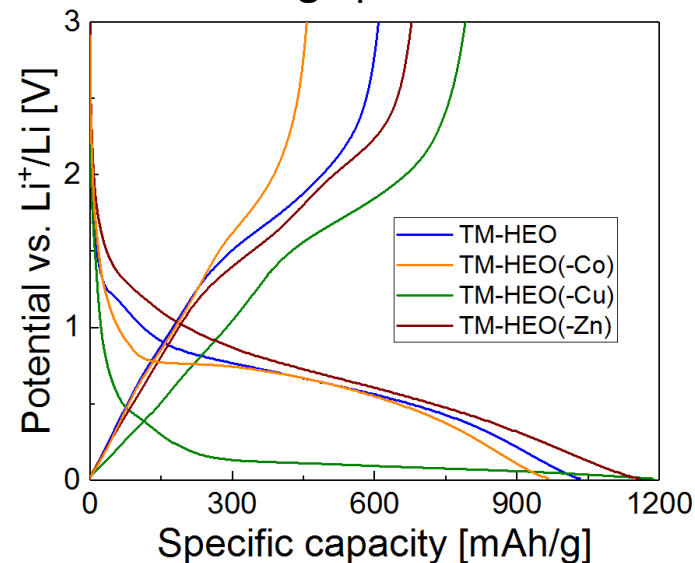
Murty B. S. *et al.*, High Entropy Alloys (2014)

HEO Vs MEO (as electrode)

Cyclic voltammetry (CVs)



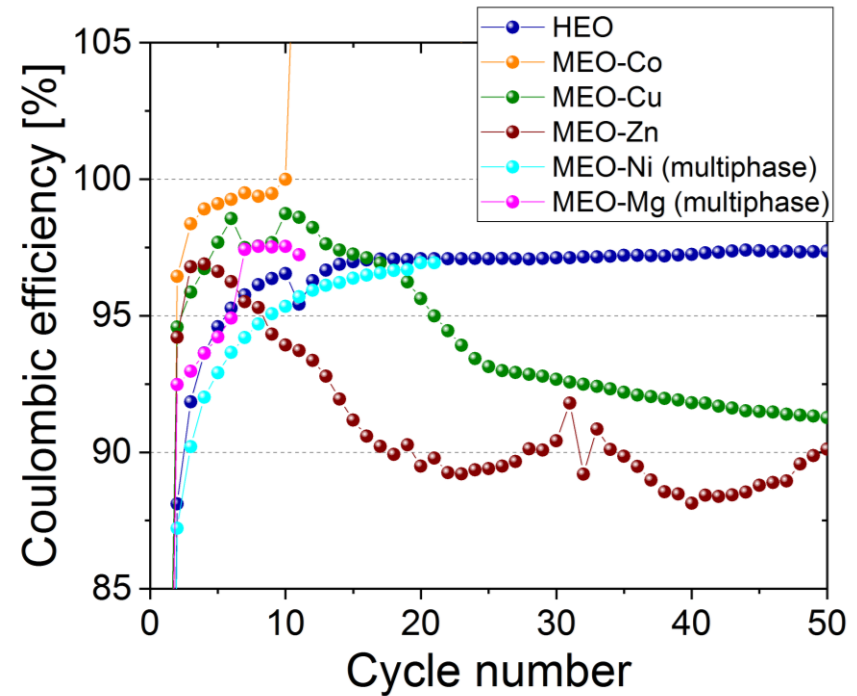
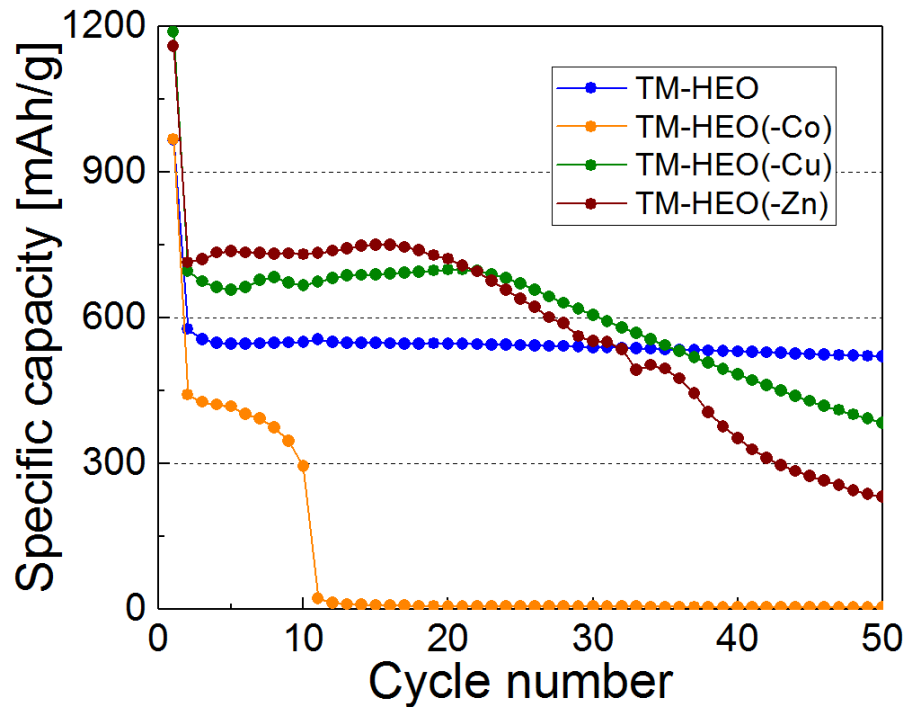
Discharge potentials



- Reaction mechanism completely for different compositions

- Tuning of electrochemical properties by composition

HEO Vs MEO (as electrode)

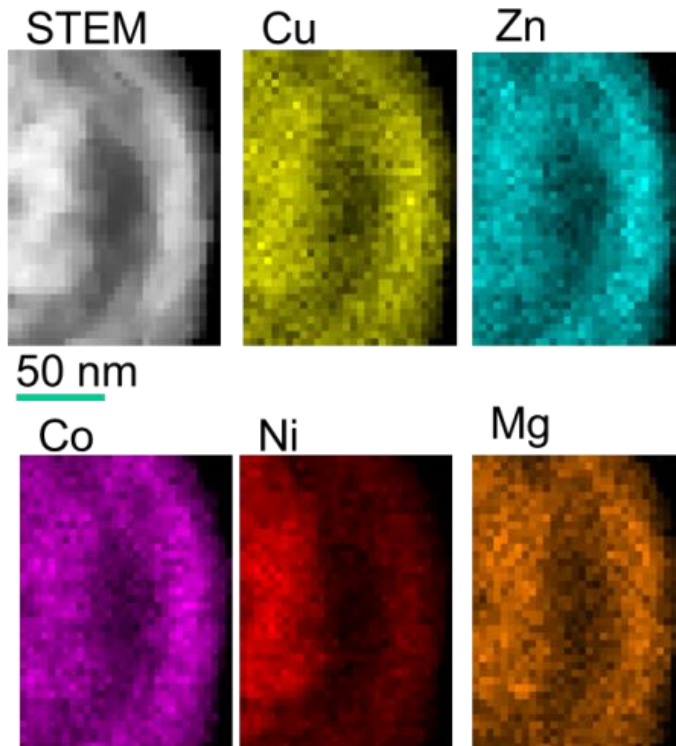


- HEO – better stability
- HEO – better Coulombic efficiency

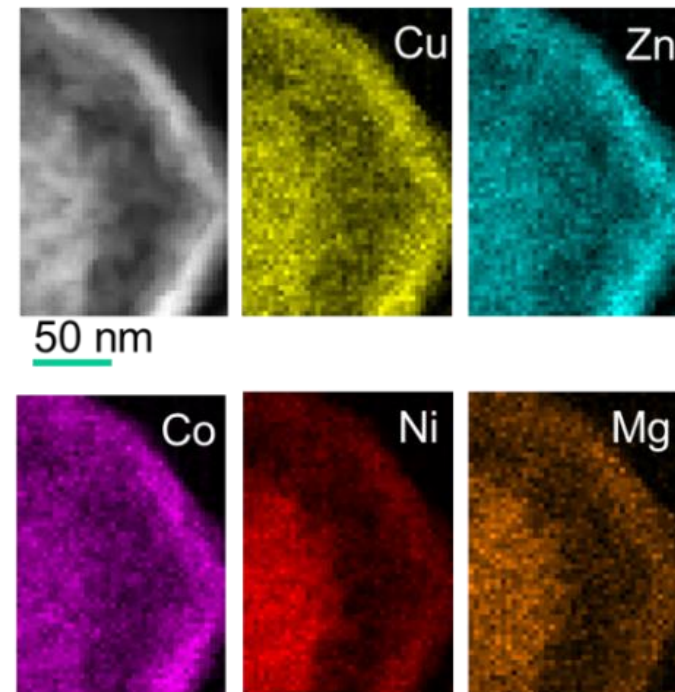
Possible effect of entropy on the electrochemical behaviour

Elemental distribution before and after cycling

Before cycling



After cycling

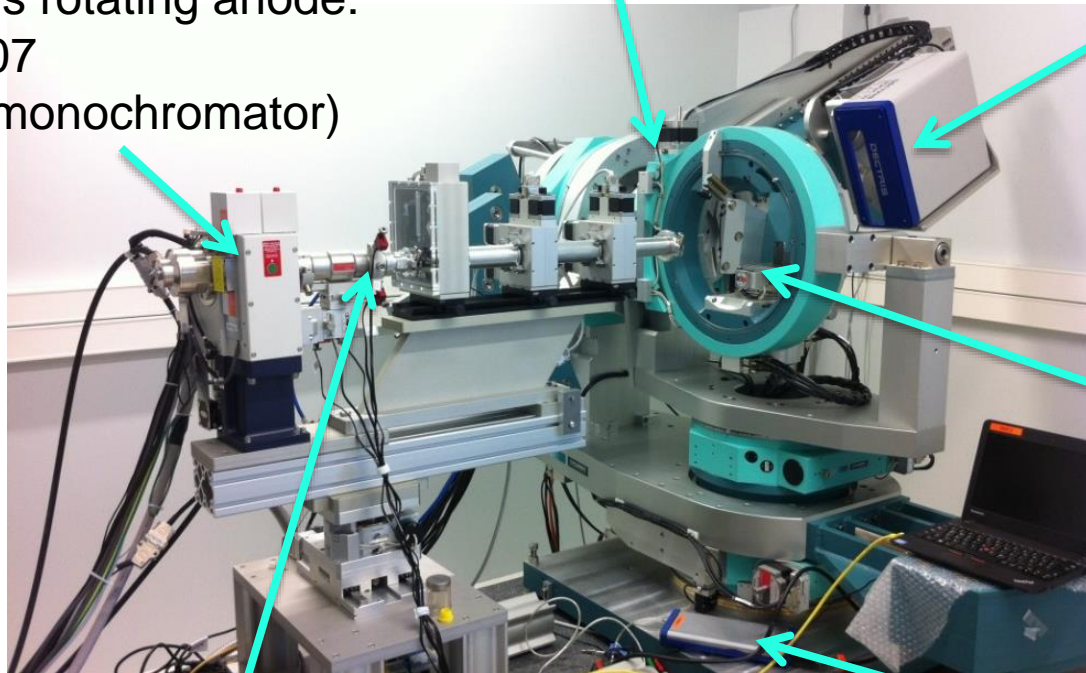


Operando XRD

Mo microfocus rotating anode:
Rigaku MM007
(optional Ge monochromator)

Huber 6-circle goniometer

2-dimensional detector:
Pilatus Dectris 300K-W



Electrochemical
in situ cell

0.6*1.7mm

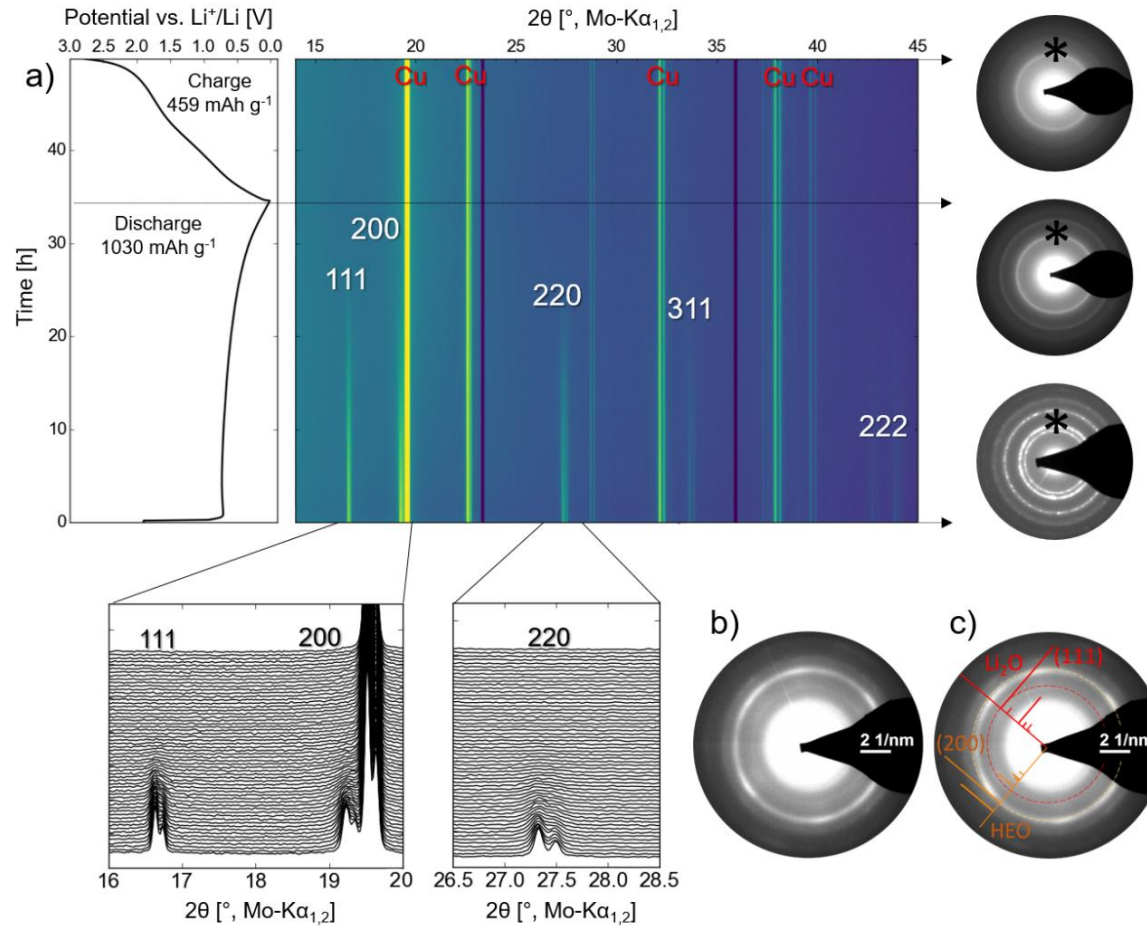
Potentiostat

2D collimating multilayer optic

→ Parallel beam, divergence < 0.3 mrad, $\sim 10^8$ Ph/s

Debye-Scherrer transmission geometry

Operando XRD and *ex situ* TEM studies



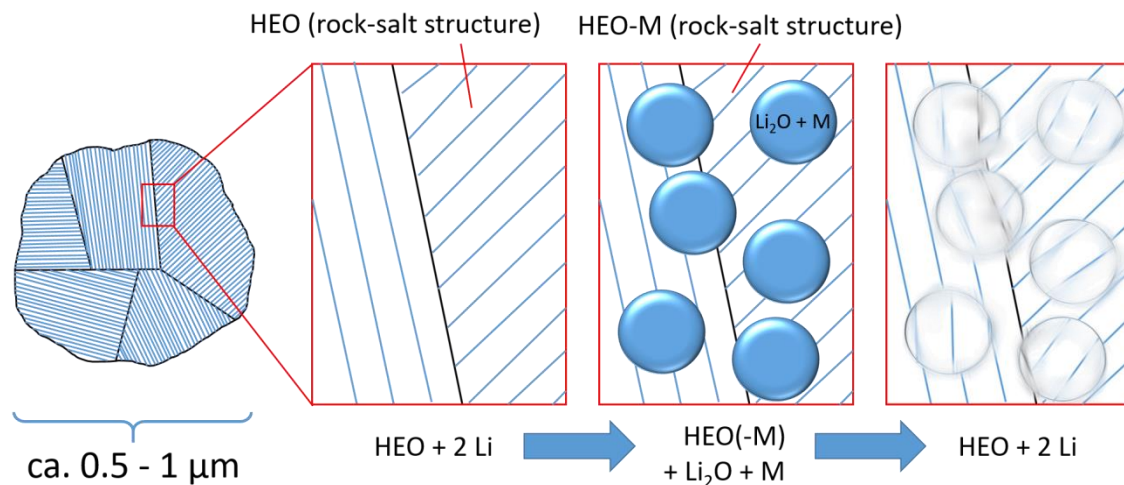
- The HEO structure is maintained even while during discharge
- No segregation of elements during cycling
- Signature of Li_2O after first discharge

Proposed mechanism

Typical Conversion??



- Can't explain the rocksalt phase during discharge
- Possibly some elements keep the HEO structure intact during discharging
- Rest are participating in lithiation and delithiation the process



- ✓ Reaction mechanisms of the electrode materials
 - Intercalation/Insertion ($\text{Li}[\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y]\text{O}_2$)
 - Alloying (Si, volume change, yolk-shell)
 - Conversion (CuO, reaction mechanism)
- ✓ Lithium/Sulfur batteries (shuttle effect)
- ✓ High Entropy Oxide materials (entropy matters)



Thanks very much for your attention!

