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NANO-STRUCTURED BINARY INTERMETALLICS AS NEGATIVE ELECTRODE FOR LITHIUM ION BATTERIES

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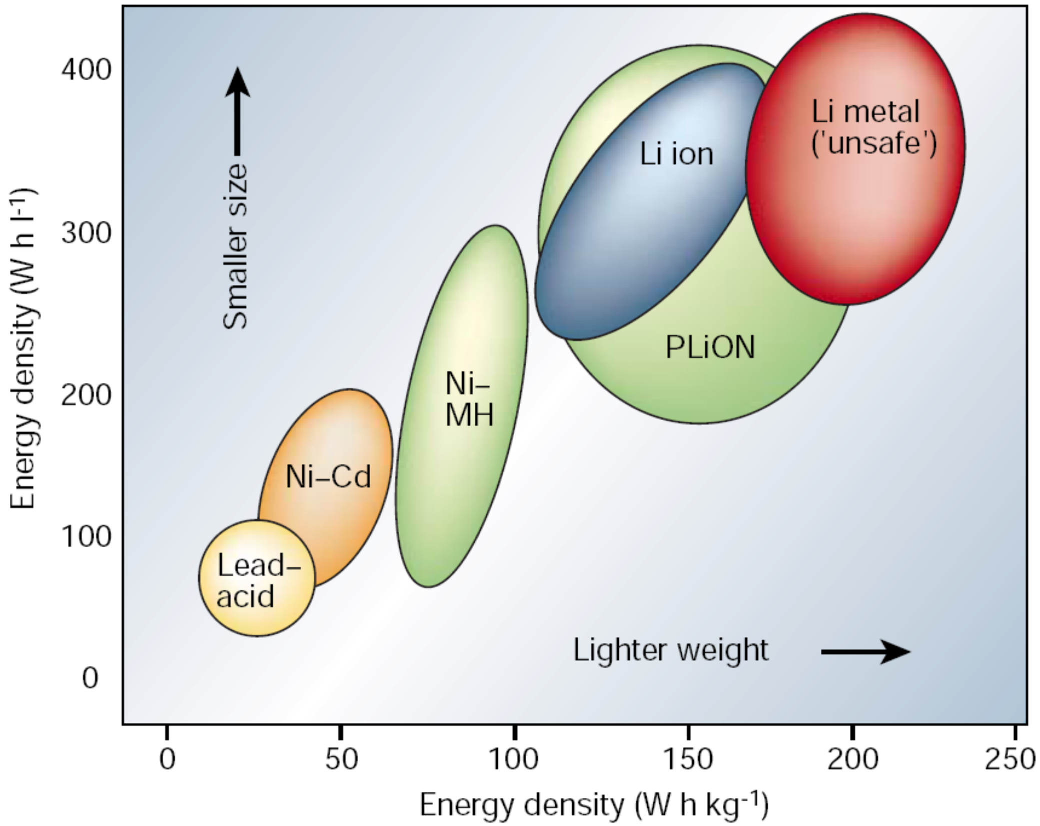
Lithium Ion Battery (LIB)



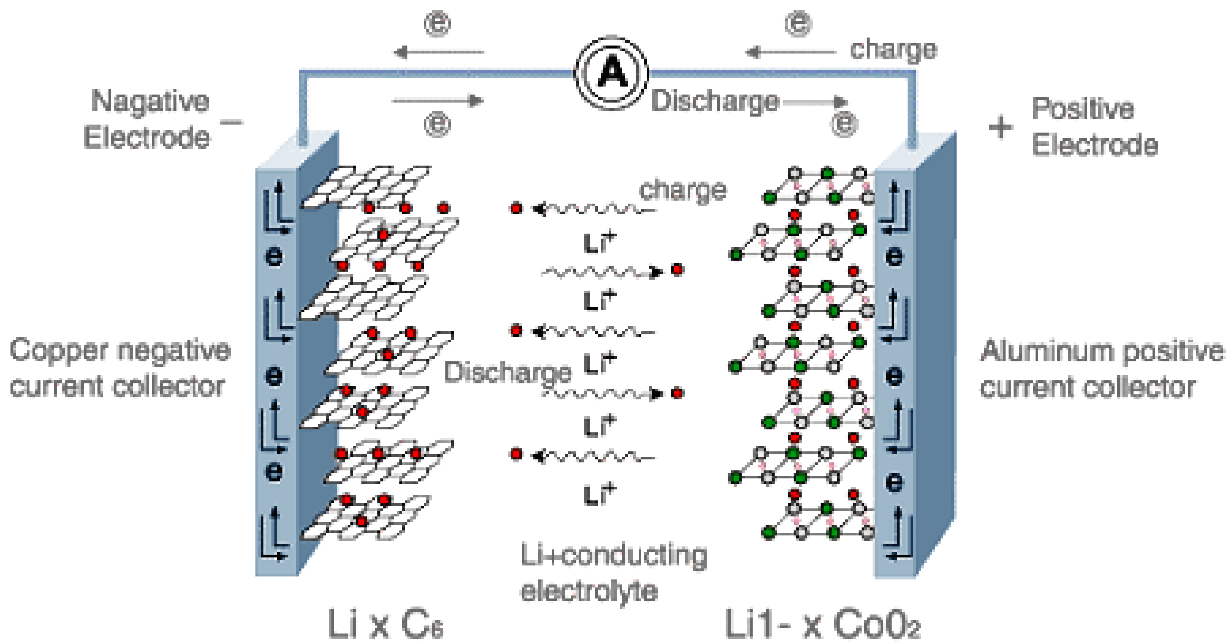
J. M. Tarascon et al., *Nature* **414**, 359 (2001).

- High energy density
- High voltage
- High rate discharge/Fast charge
- No memory effect
- Long cycle life
- High storage characteristics
- Minimal self-discharge
- Reliability

At present: Mobile phones, Note book PCs, Power tools

Future: HEV, Robotics, Electricity Storage

Charge/Discharge Mechanism of LIB



Graphite powder (MCMB) 10-20 μm

O (Oxygen)
Co (Cobalt)
C (Carbon)
Li+ (Li-ion)

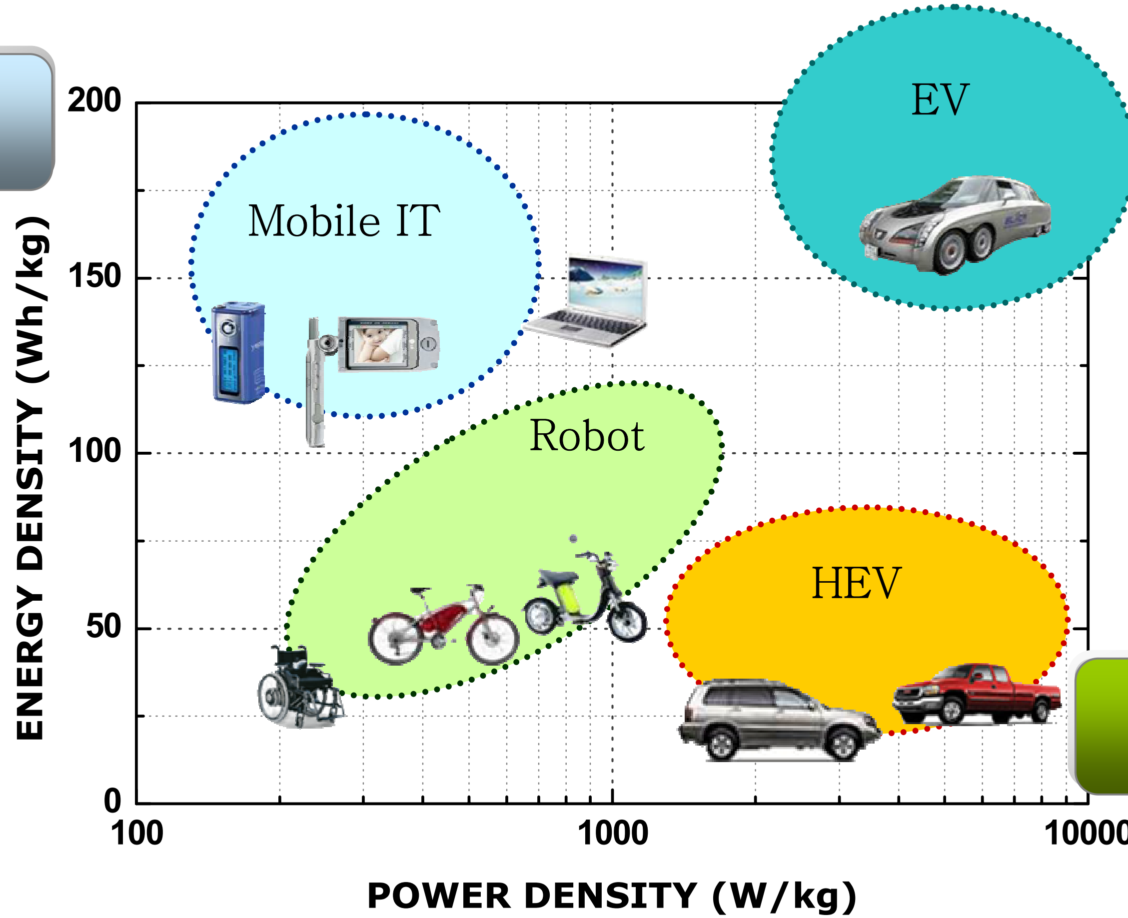
$LiCoO_2$ powder 10-20 μm

$$LiCo0_2 + C_6 \underset{\text{Discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li1\text{-}xCo0_2 + LixC_6$$

http://www.samsungsdi.com/

Electrode materials for each application

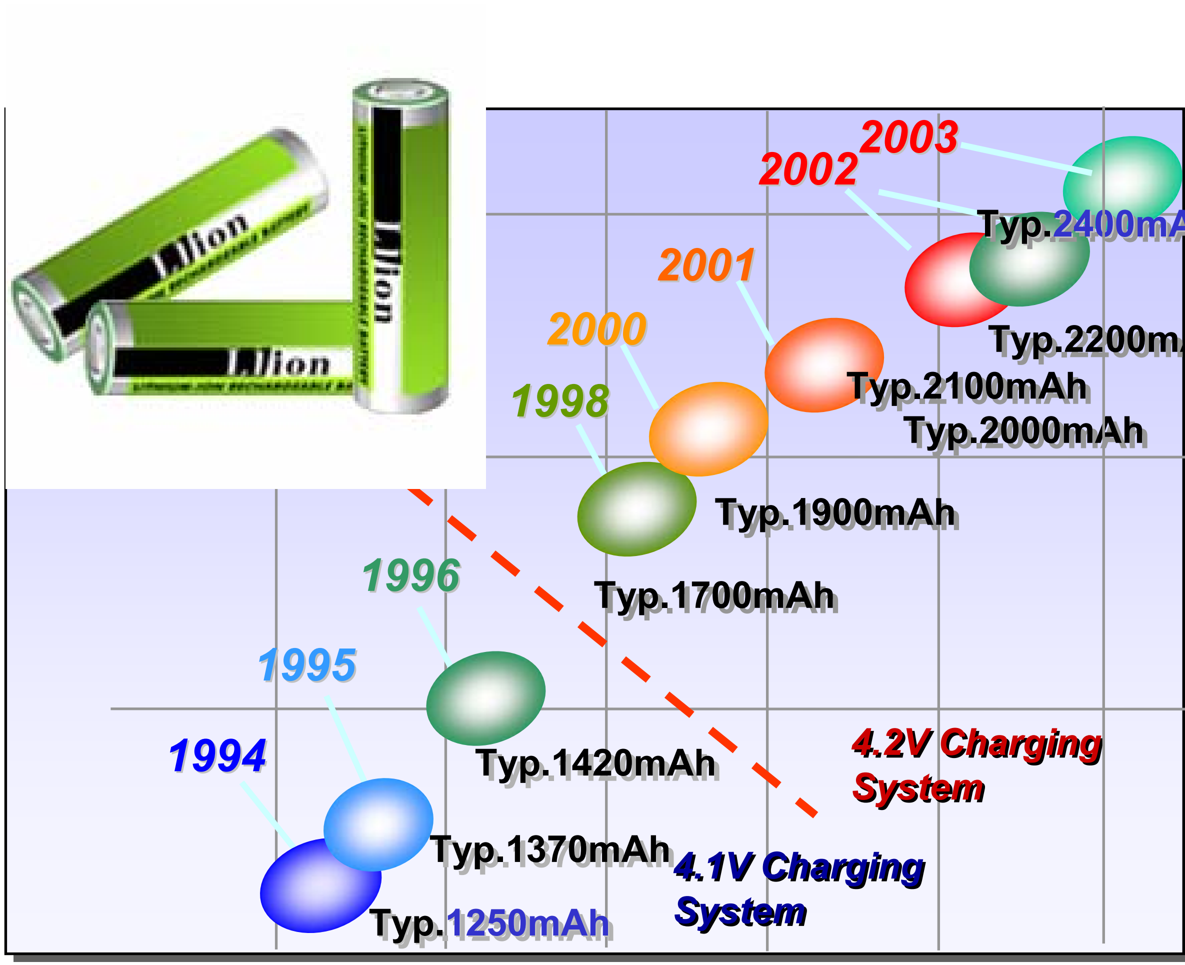
High loading, thicker plate



Large area, thinner plate

Electrode materials, design: specified for each application

LIB for Note Book PC



Cylindrical 18650 LIB:
Capacity doubles
for 10 years
(Improvement in design)

To have 3000 mAh cells:
New electrode materials

Nanotechnology for Advanced Electrode Materials ?

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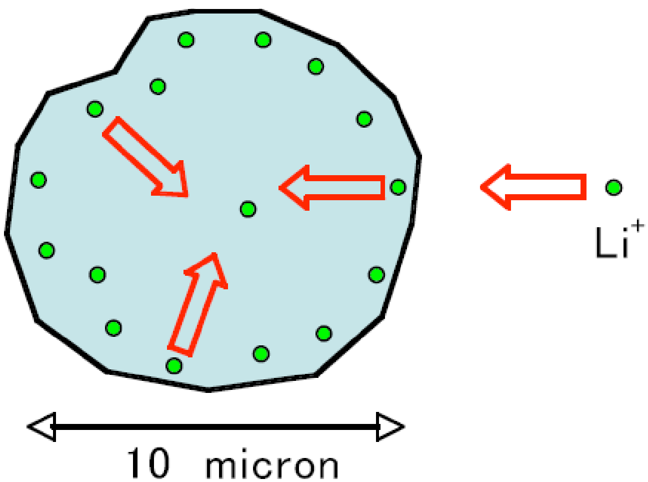
- **Nano-sized electrode materials (vs. nano-structured materials)**
  - Advantage
    - Larger electrode/electrolyte contact area ; **higher charge/discharge rates**
    - **Short path length** for Li^+ transport; **higher charge/discharge rates**
    - **Better accommodation of strain** induced by lithium insertion/removal, improving cycle life
  - Disadvantage
    - **Undesirable electrode/electrolyte reactions** due to higher surface area, leading to self-discharge, poor cycling and calendar life
    - Hard to handle **unstable ultra-fine** powders; in mixing and slurry making processes
    - Potentially more **complex synthesis**
    - **Environmental, health and safety issues**

Nano-sized Electrode Materials ($LiFePO_4$)

- High power cell using nano phosphate (A 123Systems)
  - $LiFePO_4$: poor electronic/ionic conductor

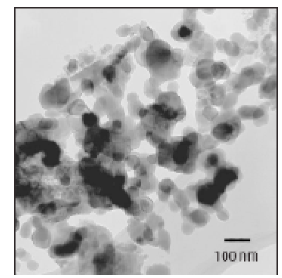
Oxides based Li Ion (conventional technology)

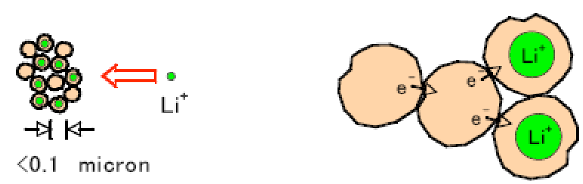


Conventional Li Ion diffusion: particle size needs to be large in order to prevent side-reactions and for safety reasons, as a result conventional Li Ion has poor rate capability

A123 doped nanophosphate

Better battery enabled by new nano-materials





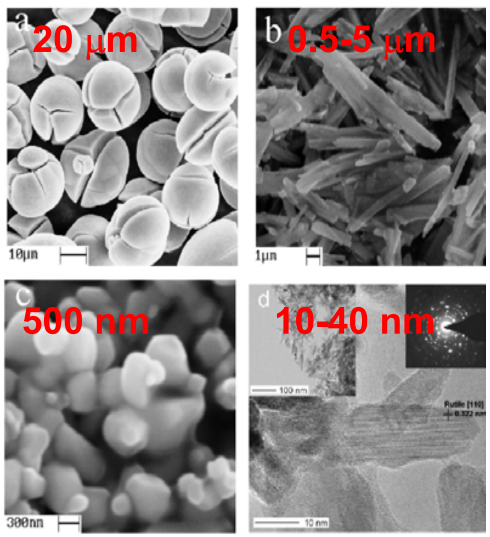
100 times smaller than conventional oxides.

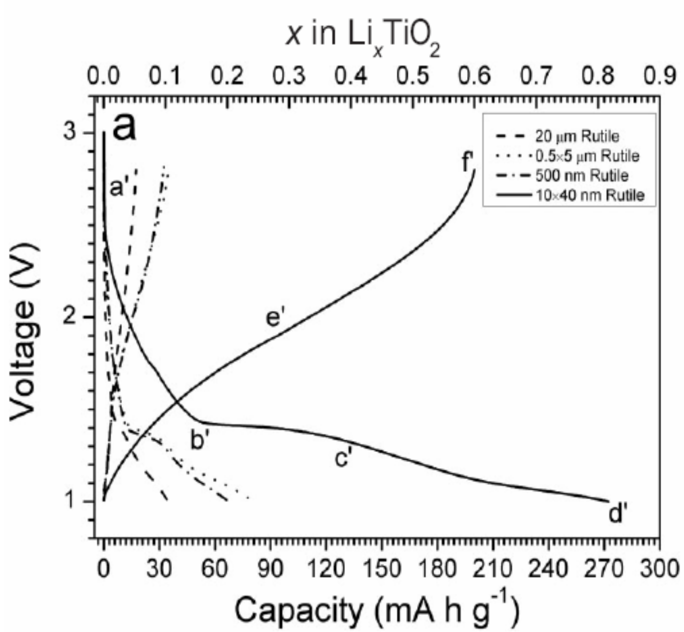
Orders of magnitude more conductive than conventional phosphates

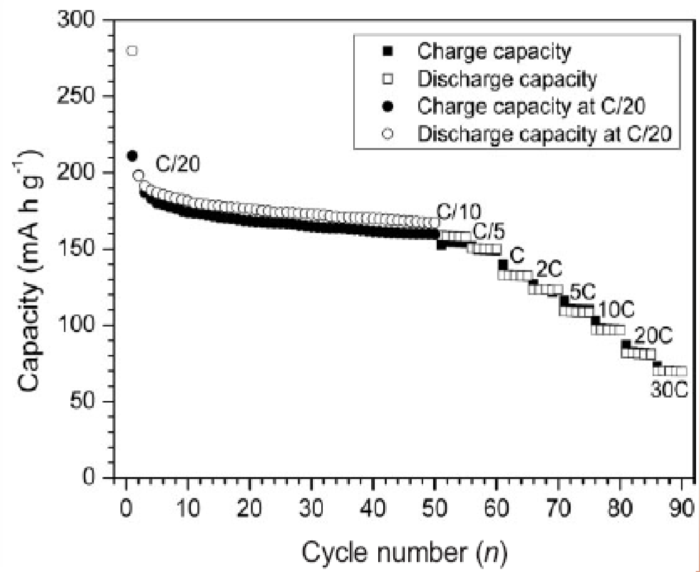
A123Systems active materials are so intrinsically stable that particle size can be reduced to nano-scales for drastically increased power without safety or life degradation

Nano-sized rutile TiO_2

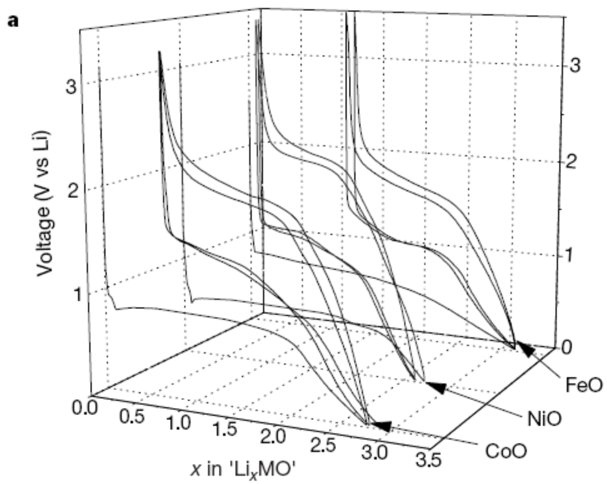
- High lithium electroactivity of nano-sized rutile TiO_2 (Y. Hu et al., *Adv. Mater.* **18**, 1421 (2006))
  - Rutile TiO_2 (known to be inactive) becomes active by using **nano-sized** particles!
  - Nano-sized rutile TiO_2 exhibits excellent rate performance.

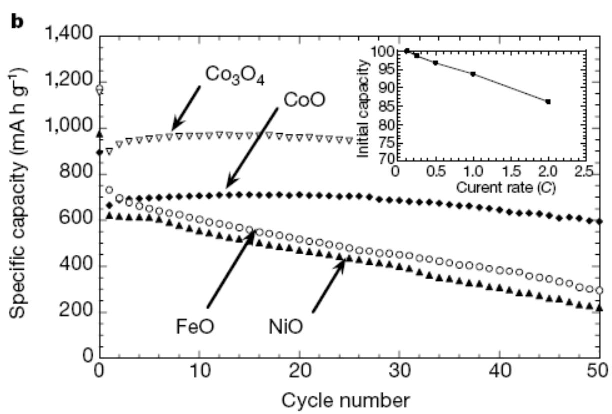


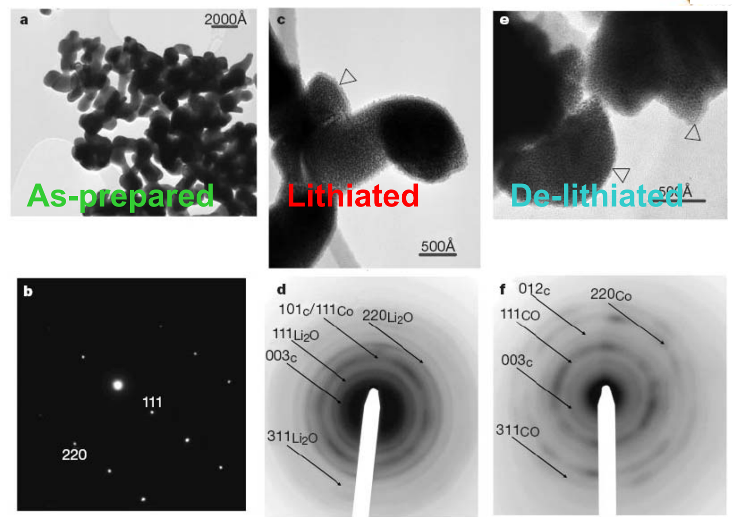




Nano-structured Materials (Unexpected Reaction)







nano-sized

- Unexpected reaction: Reverse reaction
  - Nano-sized Co ; enhances the electrochemical activity towards the decomposition of Li_2O.

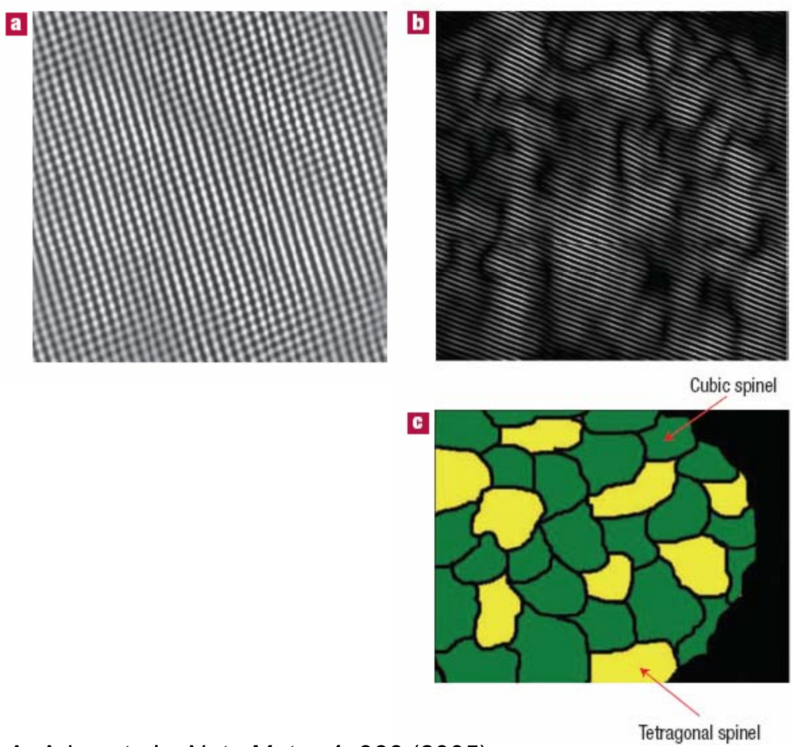
◆(P. Poizot et al., *Nature* **407**, 496 (2000))

Nano-structured Materials

- Nano-domain structure of $Li_xMn_{2-y}O_4$ derived from layered $Li_xMn_{1-y}O_2$

Regular $Li_xMn_{2-y}O_4$ spinel

$Li_xMn_{2-y}O_4$ spinel obtained on cycling layered $Li_xMn_{1-y}O_2$



A. Arico et al., *Nat.. Mater.* 4, 366 (2005).

– Spinel $LiMn_2O_4$

Cubic to tetragonal phase transition leads to capacity fading

– Layered $LiMnO_2$

  – **Nanodomain structure** formed during the layered-to-spinel transformation enables the system to **accommodate the strain induced by cubic to tetragonal transition**

Introduction: Binary Intermetallics

- **Intermetallic compounds; Active/inactive A-B type**
  - One approach to enhance the poor cyclability of alloying anode materials (Sn, Si, Ga)
  - Inactive B; buffering role against volume change of active A.

- **Reaction mechanism of binary intermetallics**
  - $Li + A_yB \leftrightarrow LiA_yB$: Addition reaction
    - Cu_6Sn_5, Cu_2Sb, etc
  - $Li + A_yB \leftrightarrow LiA_y + B$: Conversion reaction
    - SnSb, CoSb, InSb, Sn_2Fe, Mg_2Si, etc
    - Bond cleavage between A-B
    - Inactive B is extracted and active A is lithiated

Outline

- Thin film $CuGa_2$ electrode; active/inactive AB-type intermetallics
- Li^+ uptake mechanism
- Favorable roles of nano-domain structure

$$CuGa_2 + 4Li^+ + 4e \leftrightarrow 2Li_2Ga + Cu$$

Experimental

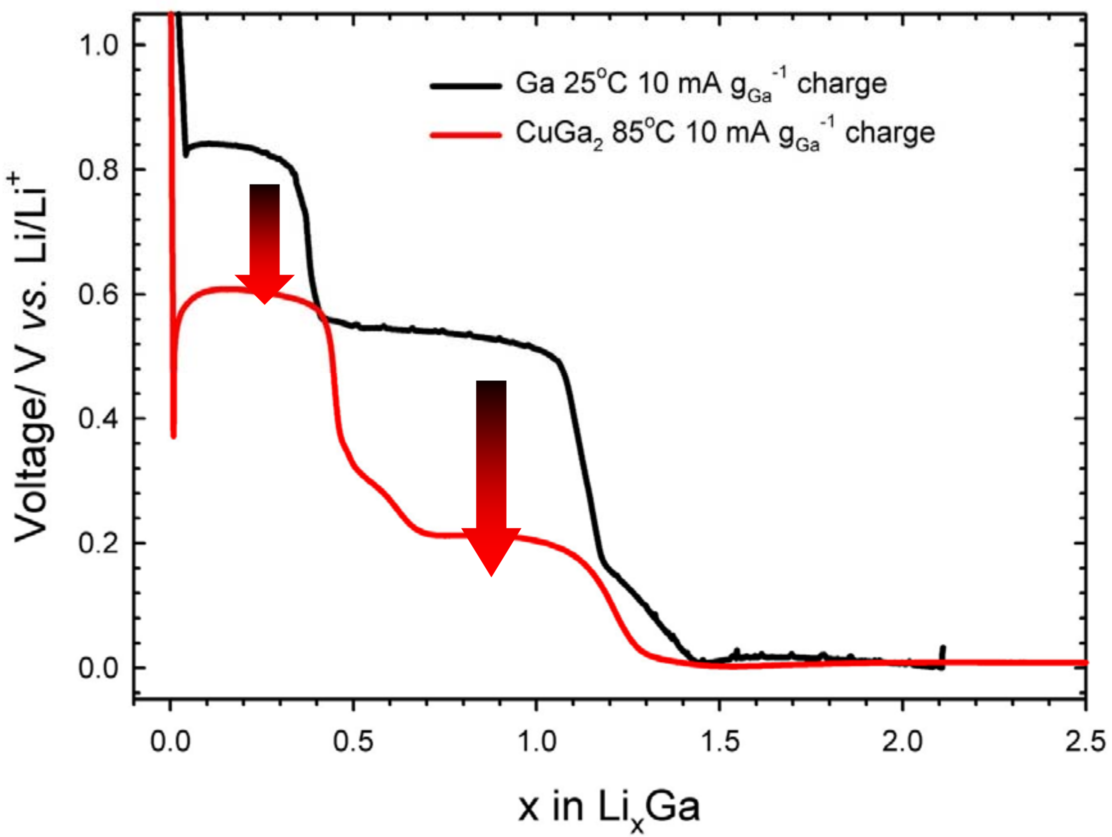
- Electrode preparation
  - **Ga** electrode
    - Spreading liquid Ga on Cu foil
  - **$CuGa_2$** electrode
    - Spreading liquid Ga on Cu foil and annealing at 120°C for 1 day
  - Thin film electrodes (> a few micron thick).

- Cell tests at 25, 120°C
  - Electrolyte: LiBOB/EC+DEC or LiBeti/PC

- In-situ XRD at 120°C

Li-uptake Mechanism; $CuGa_2$

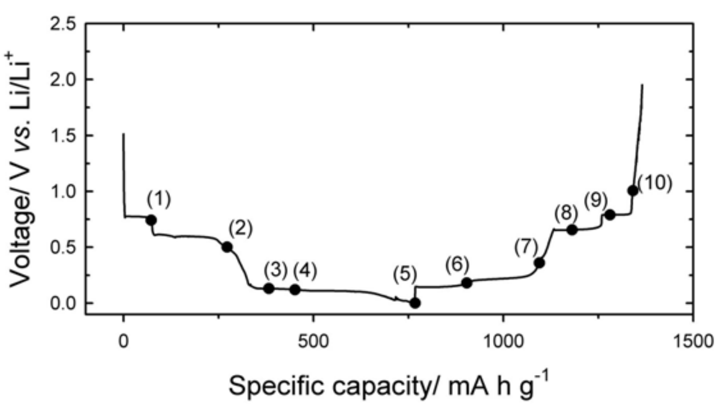
- Similar lithiation profile but larger polarization for $CuGa_2$ electrode

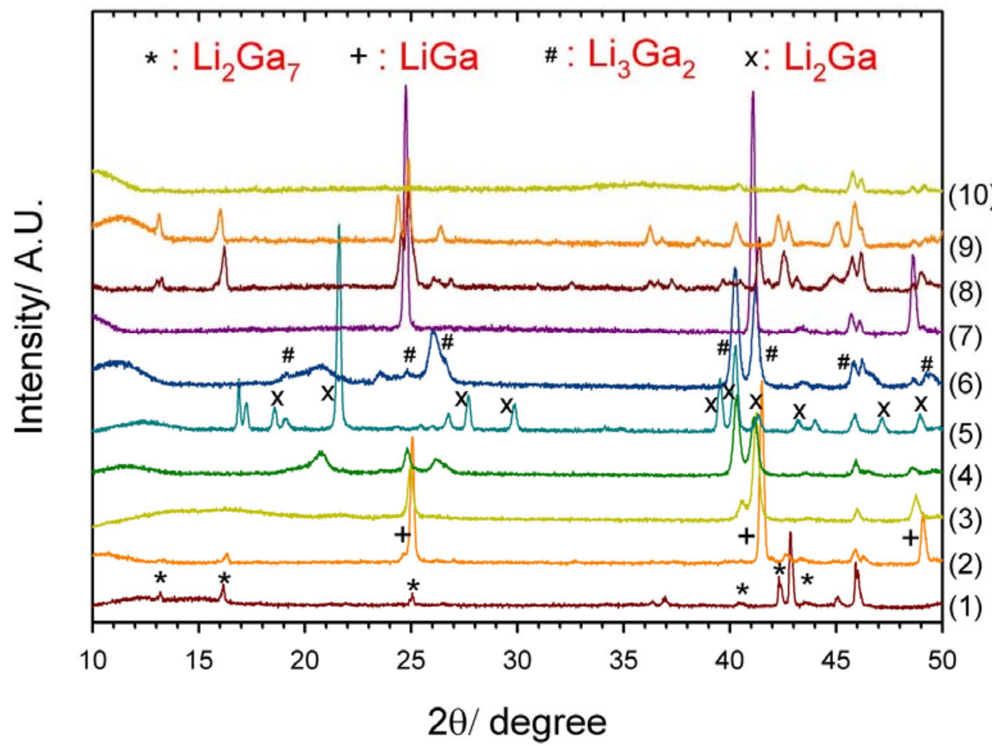


– $CuGa_2 + 4Li^+ + 4e \leftrightarrow 2Li_2Ga + Cu$: Conversion reaction (Cu extraction)

– Larger polarization for bond cleavage; Cu-Ga

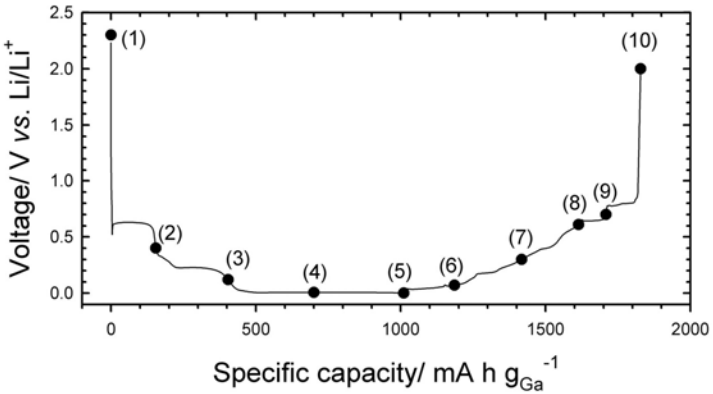
In-situ XRD on Ga electrode at 120°C

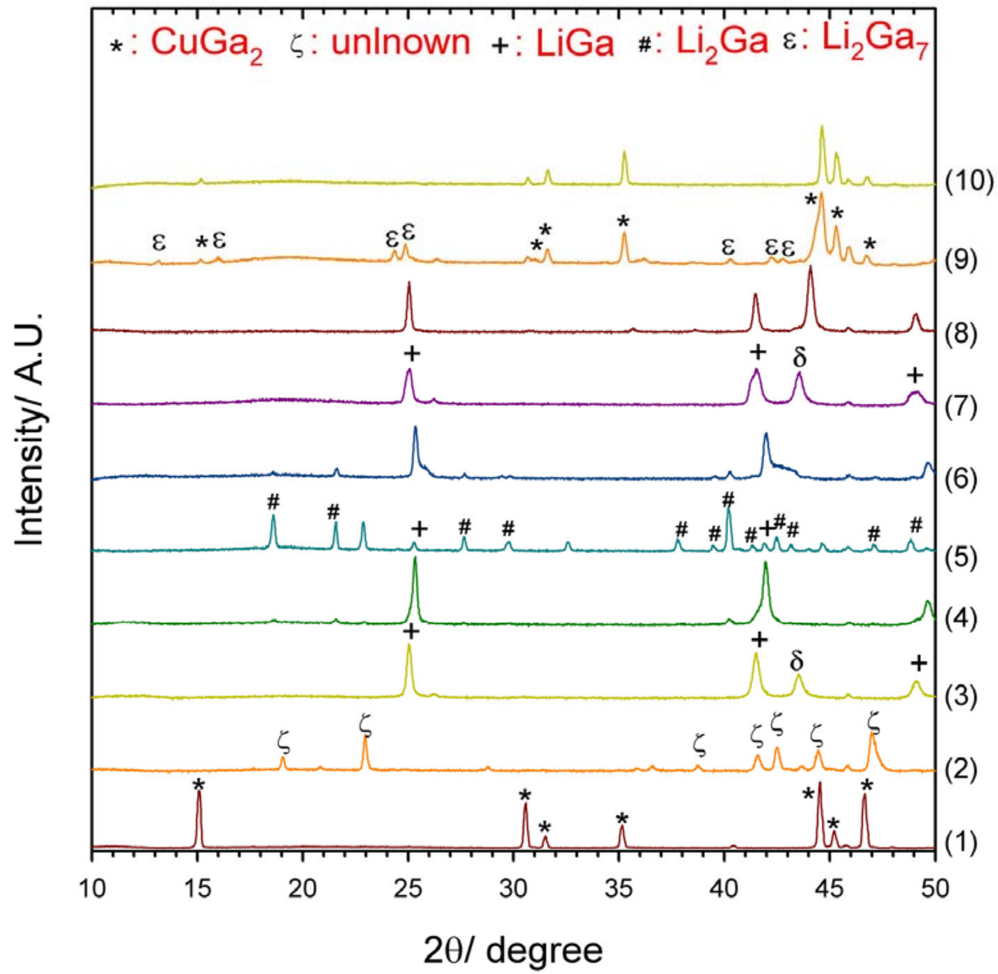




$$Ga + 2Li^+ + 2e \leftrightarrow Li_2Ga$$

In-situ XRD on $CuGa_2$ electrode at 120ºC

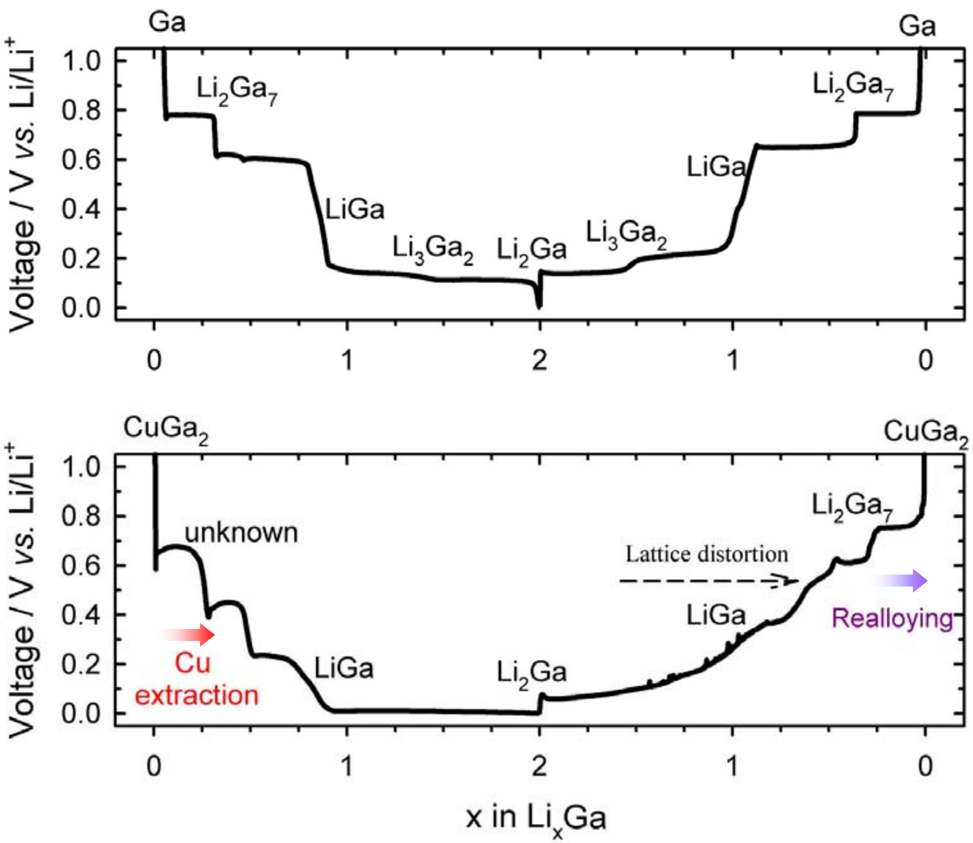




$$CuGa_2 + 4Li^+ + 4e \leftrightarrow 2Li_2Ga + Cu$$

Reaction Mechanism in Ga and $CuGa_2$ at 120ºC

$$Ga + 2Li^+ + 2e \leftrightarrow Li_2Ga$$

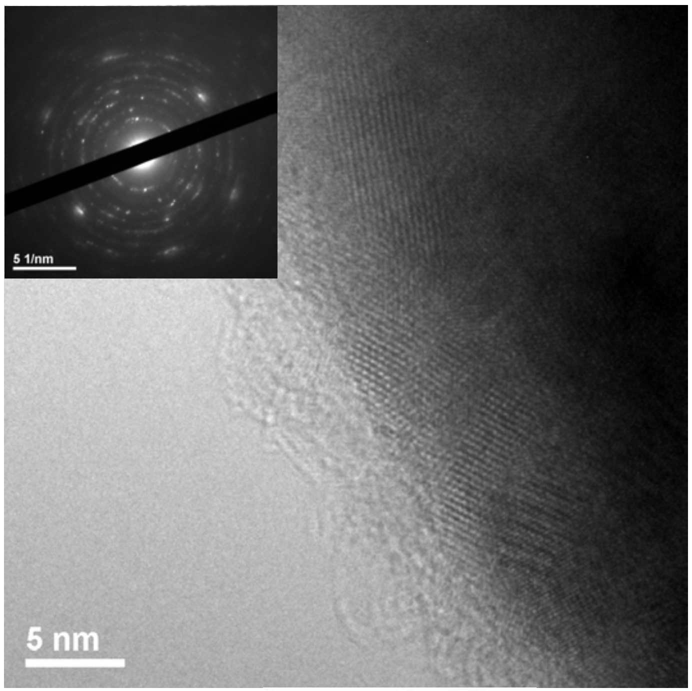


- Similar lithiation mechanism
- Noticeable difference in de-lithiation mechanism
- Any interaction between Li_2Ga and metallic Cu ?

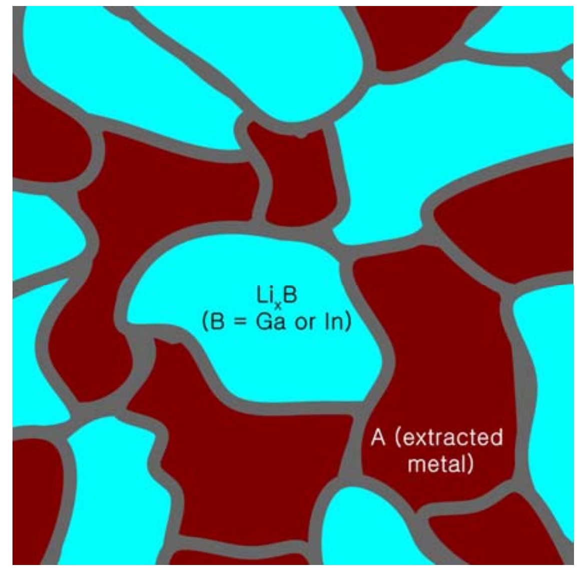
$$CuGa_2 + 4Li^+ + 4e \leftrightarrow 2Li_2Ga + Cu$$

HR-TEM Image; Nano-domain of Li_xGa and Cu

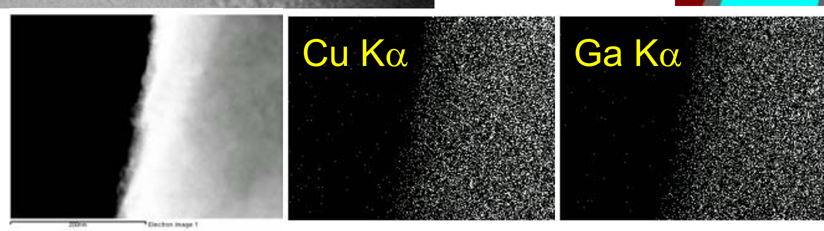
Lithiated to LiGa with 100 mA g_{Ga}^{-1} at 55°C



Schematic diagram representing the nano-structured domain

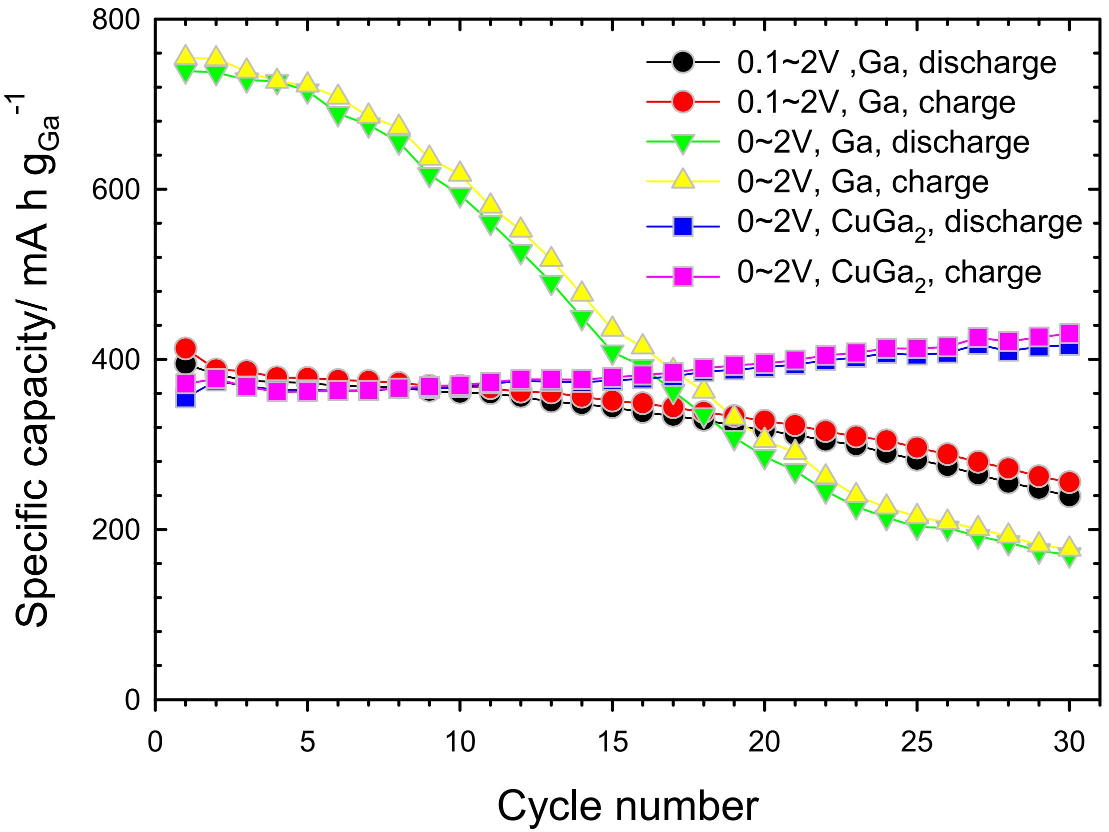


EDS Results



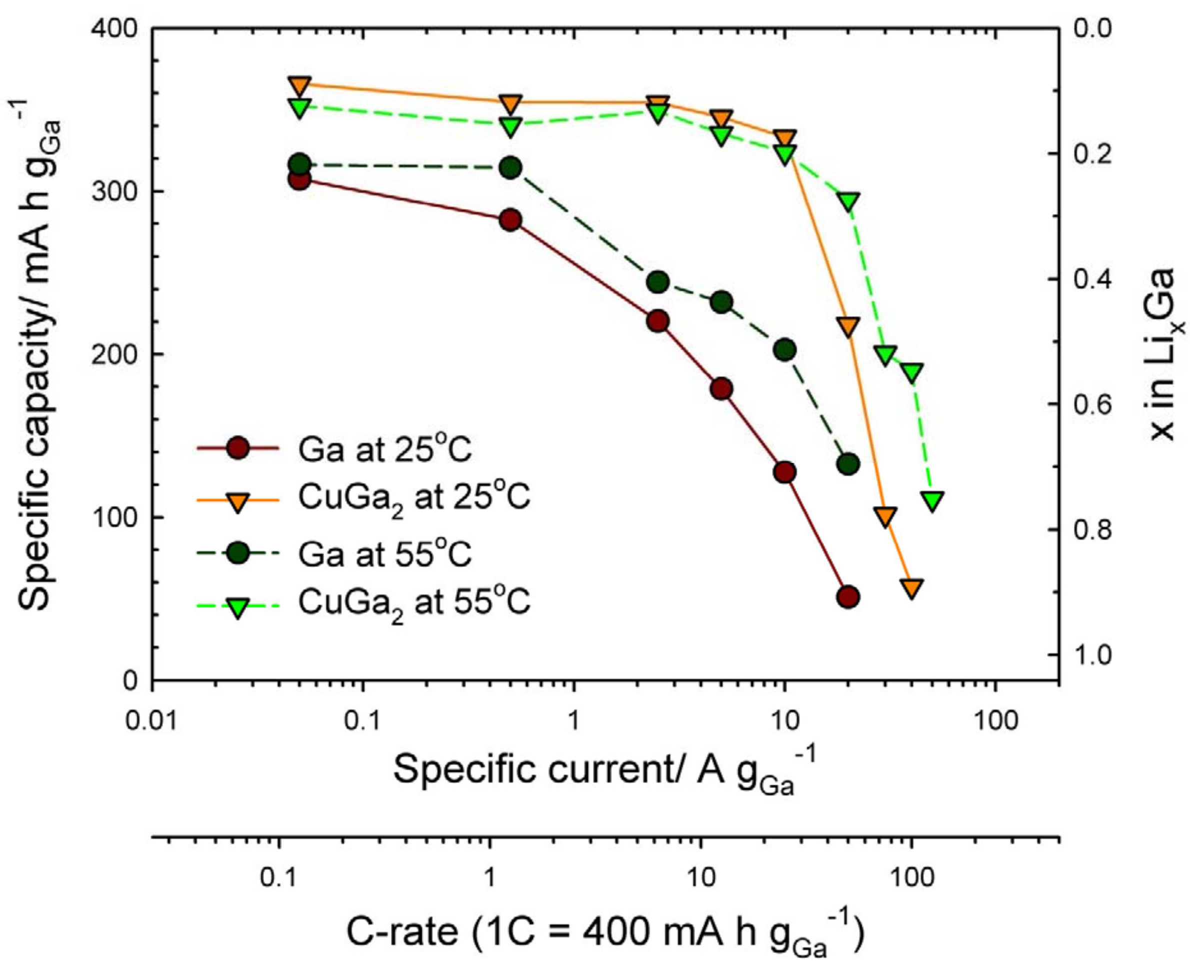
- Nano-domains of Li_xGa and extracted Cu are formed after Li uptake
- Large contact area between two domains; any favorable behaviors ?

Cycle Performance of Ga and $CuGa_2$ electrode



- $CuGa_2$ electrode:
  - Negligible 1st irreversible capacity !
  - Excellent cyclablity !

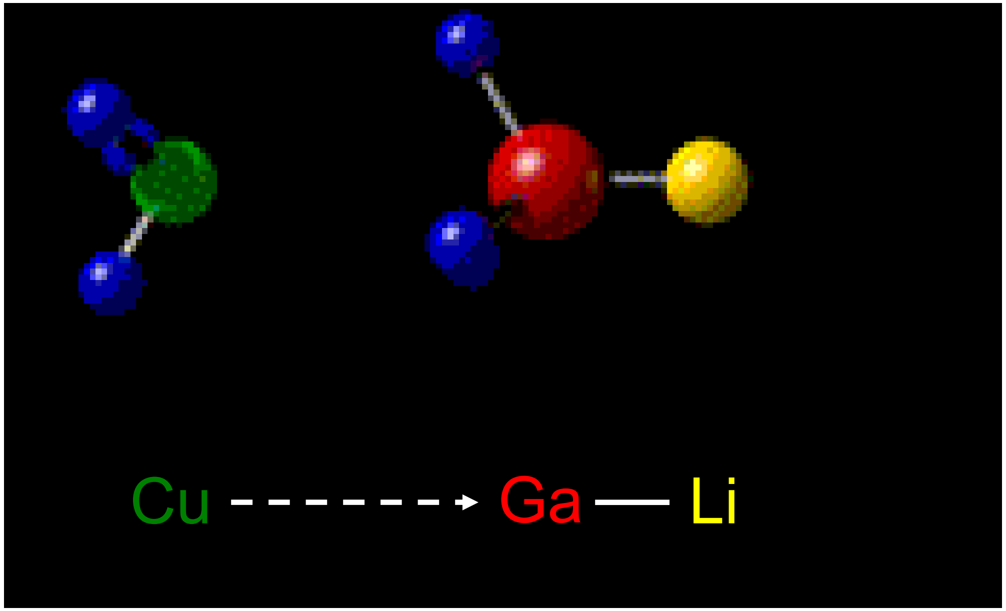
High Discharge (De-lithiation) Rate; $CuGa_2$



- *A very high discharge rate !*
- *A good candidate as the negative electrode for high-power LIB*

High De-lithiation Rate: partial bonding

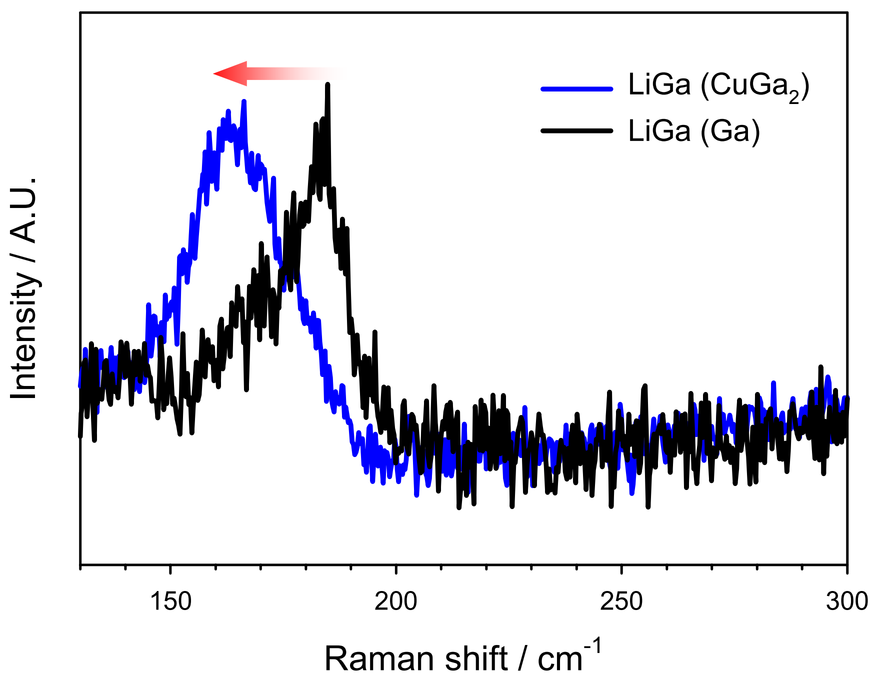
- Analogous to **SN2 reaction** in organic chemistry
  - Partial bond between Ga in Li_xGa and extracted Cu weakens Li-Ga bond. Thereby, delithiation rate is dramatically increased.



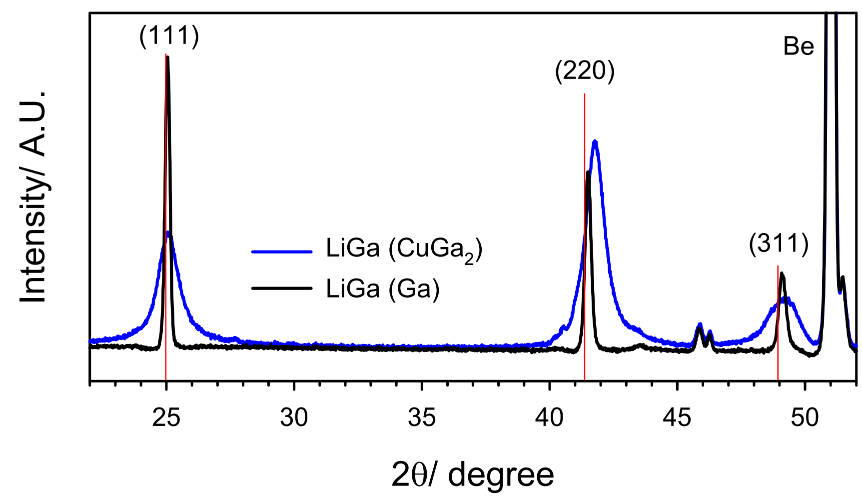
$$Cu + 2Li_2Ga \leftrightarrow CuGa_2 + 4Li^+ + 4e$$

Evidences for Partial Bonding

Raman spectra



XRD patterns



- **Raman shift to lower frequency; stretching of Li-Ga bond**

Cu-Ga-Li

Weaker Li-Ga bond strength due to partial bonding between Cu-Ga.

(220) peak shift in XRD pattern; Distortion of LiGa structure; may be induced by the partial bonding.

Conclusion

1) $CuGa_2$ electrode; lithiated by conversion reaction

: Nano-structured Li_xGa and Cu domains are formed

: Slower lithiation than pure Ga electrode

2) Large contact area between two domains;

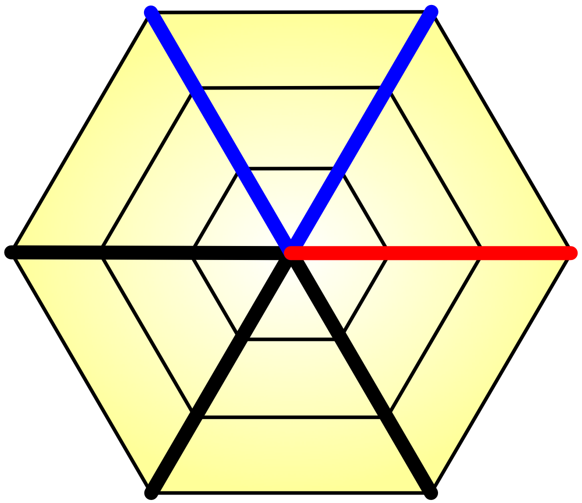
Partial bonding between Cu-Ga → weakens the Li-Ga bond

→ enhances the de-lithiation rate

Similar results with Cu_3Si, Cu_3Sn

Electrochemically driven nano-structured materials: interesting for fundamental research and practical application

Performance requirements for applications



Capacity

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