

# Computational study of Li segregation and diffusion at grain boundaries in Cu: implications for Li-ion current collectors

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Adoption of Li-ion batteries for stationary energy storage requires to prolong their operational lifetimes to several decades calling to inhibit all degradation mechanisms. It is widely accepted that copper current collector used on the anode side of a commercial Li-ion battery is stable in contact with metallic lithium or LiC<sub>6</sub>. However, looking at Li-Cu phase diagram one can discover that up to 18-23 at. % of Li dissolves in copper at room T [1]. The thermodynamically favourable formation of Cu-Li alloy upon electrochemical cycling of a Li-ion battery should be accompanied by gradual loss of lithium, increase of the current collector electrical resistivity, and potential decohesion of anode material due to the volumetric expansion of a current collector. Even though such processes are slow, they can limit the lifetime of Li-ion batteries intended to operate during 10-20 years, such as used in electric cars and grid storage.

Indeed, Li penetration into copper foil of a cycled cell was detected by Nagpure et al. using neutron profiling in depth (NPD) method [2]. The penetration depth exceeded 0.8  $\mu\text{m}$  constituting a non-negligible part (~8 %) of a typical current collector foil. The irreversible Li uptake shows that Li is indeed dissolved in copper, while the speed of this process is governed by Li diffusion. The lithium depth profiles by time-of-flight secondary-ion mass spectrometry study shows that Li diffusivity in a single crystal Cu at room T is  $1.3 \times 10^{-20} \text{ cm}^2/\text{s}$ , while in a polycrystalline Cu it is increased by three orders up to  $1.4 \times 10^{-17} \text{ cm}^2/\text{s}$  due to the enhanced grain boundary diffusion [3].

Interestingly, the nature of Li diffusion in Cu remains poorly understood even in the case of a single crystal. The origin of much faster Li diffusion at Cu grain boundaries (GB) also remains obscure. No information is available about Li segregation at GBs and its impact on vacancy formation and migration energies.

In this study we address the phenomena of Li grain boundary segregation and diffusion in copper by performing density functional theory calculations and explain the origin of favourable Li segregation and decrease of migration barriers using electronic structure analysis. We consider the thoroughly

studied  $\Sigma 5(310)[001]$  symmetric tilt GB (Figure 1) and two experimentally observed twin boundaries:  $\Sigma 3(112)[110]$  and  $\Sigma 9(221)[110]$  tilt grain boundaries and generalize results to a wide range of special grain boundaries.

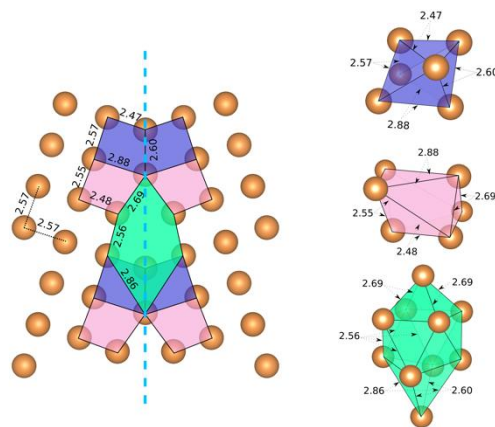


Figure 1. The structure of  $\Sigma 5(310)[001]$  grain boundary and considered substitutional and interstitial positions for Li segregation and migration.

Overall, we show that grain boundaries promote Li penetration inside the copper thin films due to Li segregation and accelerated GB diffusion which can be a reason for slow Cu electrodes degradation in Li-ion batteries.

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## References

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