

# Multistage Lithium Intercalation in Bilayer Graphene

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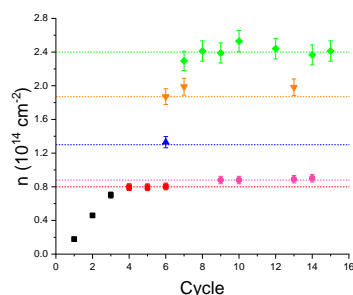
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Intercalation of  $\text{Li}^+$  ions into bulk crystals such as graphite is a key process in the functioning of batteries and energy storage. Bilayer graphene is an ultimate building block for intercalated graphite and is therefore a promising system for investigation of the storage capacity, structural characteristics and dynamics of the intercalation process. We used device-level intercalation of bilayer graphene with  $\text{Li}^+$  ions driven from a solid LiTFSI:PEO electrolyte by an external electric field. Intercalation was monitored by measuring graphene's resistivity and carrier density as entering  $\text{Li}^+$  ions cause electron doping of graphene to maintain charge neutrality. Unlike the previous studies using a similar setup [1], intercalation was monitored over a long time (up to several hours) and 15 intercalation-deintercalation cycles. Surprisingly, we found that the system exhibits five different stages of intercalation seen as well-defined values of the device resistance and carrier density (Fig. 1). The latter remain stable over extended periods of time and are uniform along the  $\sim 20\mu\text{m}$  device. Such multistage intercalation in a bilayer is unexpected and has not been reported previously. Our analysis shows that different stages correspond to metastable configurations of  $\text{Li}^+$  ions in the bilayer, such that an increasing Li density is achieved via discontinuous jumps between  $\text{Li}^+$  positions corresponding to local energy minima [2], Fig. 2. We attribute the existence of multiple quasi-stable  $\text{Li}^+$  configurations to cyclic changes of layer stacking from AB to AA, similar to graphite: While the formation energy for Li intercalation is significantly lower for AA stacking, ion diffusion is limited by energy barriers for  $\text{Li}^+$  jumping between neighbouring carbon rings [2]. In later cycles we observe that some stages are skipped and denser stages are reached in shorter times, in agreement with the expectation that the energy barriers become lower as the interlayer distance increases with intercalation. The maximum Li density achieved in our experiment is  $2.4 \times 10^{14} \text{ cm}^{-2}$ , similar to previous studies. Our findings shed light on the dynamics of the intercalation process and provide an explanation to empirical observations that ion storage capacity and efficiency of intercalation improve over the course of initial cycles.

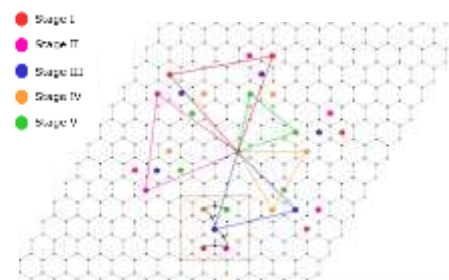
## References

- [1] Kühne, M., Paolucci, F., Popovic, J. *et al. Nature Nanotech* **12**, (2017) 895–900.  
[2] Shirodkar, S. N. & Kaxiras, E. *Phys. Rev. B* **93**, (2016) 1–5.

## Figures



**Figure 1:** Carrier densities of the 15 cycles. Dashed lines correspond Li densities in Fig. 2.



**Figure 2:** Lithium configurations corresponding to measured carrier densities for each stage.