

Review of symmetry and structure relationships of the stage-I graphite intercalation compounds (GICs) structure family

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Graphite and materials made of graphite have historically been of huge technological importance due to their manifold interesting properties. Many of the properties arise due to graphite being an anisotropic material with a layered structure, featuring very strong covalent bonds within the single layers of graphene, while the interlayers connect only through very weak van-der-Waals forces. Due to that, graphite materials undergo intercalation reactions and form graphite intercalation compounds (GICs). In

these GICs, metallic ions intercalate between separated layers of graphene, showing interesting properties [1]. For example, graphite itself is very conductive in the graphene layer, but conductivity perpendicular to these layers is many orders of magnitude lower. Another important feature is that the intercalation to GICs is highly reversible, which is utilized in high performance lithium-ion batteries (LIBs), where graphite-based anode materials are most commonly used. Through the intercalation of graphite with Li-ions up to the so-called stage-1 compound with maximum lithium content LiC_6 , energy is chemically stored in the structure and released upon the reversible reaction in a LIB when paired with an appropriate cathode material, which in turn must be capable to take up the released Li ions from the LiC_6 -GIC. The transformation to LiC_6 however is complex and between the two terminal points, graphite and LiC_6 , many intermediate stages exist [2]. However, our understanding of the phase transition mechanism and reaction pathway, especially in the Li-graphite system, remains incomplete, due to the profound complexity and peculiarities of this “staging” reaction. Although a full understanding is imperative in order to control aging and cell performance characteristics of lithium ion batteries. We review published binary stage-1 GIC structures from the ICSD-database, fundamental structural aspects like bonding distances and packing arrangements and explore their symmetry relationships applying group-subgroup considerations. Our findings will improve the understanding of the intermediate stages occurring during the electrochemical intercalation of lithium ions in LIBs and enhance the analysis of measured diffraction data.

- [1] Dresselhaus M. S., Dresselhaus G. "Intercalation compounds of graphite." *Adv. Phys.* 51(1), 1-186 (2002)
[2] Didier C., Pang W. K., Guo Z., Schmid S., Peterson V. K. "Phase Evolution and Intermittent Disorder in Electrochemically Lithiated Graphite Determined Using in Operando Neutron Diffraction." *Chem. Mater.* 32(6), 2518-2531 (2020)

The project thanks the BMBF (Federal Ministry of Education and Research, Germany) for funding within grant number 03XP0255.

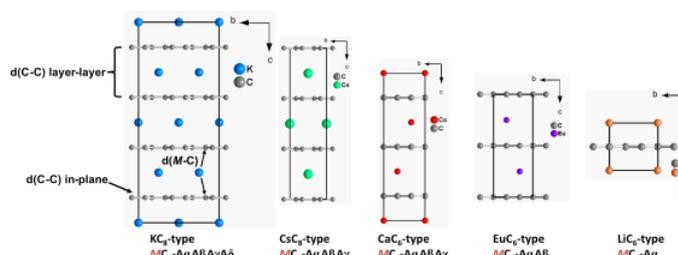


Fig. 1 The five binary M-GIC structure types shown in projection along the a-axis. Different stacking arrangements are visible. However, a full disambiguation of the arrangement requires projections along two perpendicular axes. Shown below are assigned structure type labels. Uppercase Latin letters depict symmetry equivalent carbon layers, lowercase Greek letters show equivalent metal ion layers.