Ultrafast diffusion and superdense ordering of Lithium in a single van der Waals gap

Jurgen H. Smet
M. Kühne, S. Fecher, F. Paolucci, J. Popovic, P.M. Ostrovsky, D. Samuelis, J. Maier

Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

F. Börrnert, J. Biskupek, U. Kaiser

Materialwissenschaftliche Elektronenmikroskopie, Universität Ulm, D-89081 Ulm, Germany

M. Ghorbani-Asl, A.V. Krasheninnikov

Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden Rossendorf, D-01328 Dresden, Germany

j.smet@fkf.mpg.de

Solids that simultaneously conduct electrons and ions are key elements for the mass transfer and storage required in battery electrodes. Single-phase materials with a high electronic and high ionic conductivity at room temperature are hard to come by, and therefore multiphase systems with separate ion and electron channels have been put forward instead. Here we report on bilayer graphene as a single-phase mixed conductor and demonstrate the diffusion of lithium faster than in graphite and even surpassing the diffusion of sodium chloride in liquid water [1]. To measure diffusion of lithium we have developed an on-chip electrochemical cell architecture in which the redox reaction, that forces lithium intercalation, is localized at a protrusion of the device only. This geometry has the advantage of allowing for a well-defined one dimensional diffusion front so the 2D material can be operated as a true single-phase mixed conductor and also leaving the graphene bilayer unperturbed from the electrolyte during operation. Time-dependent Hall measurements across spatially displaced Hall probes enable to monitor the in-plane diffusion kinetics within the single van der Waals gap of the bilayer. The intercalation is reversible. The device concept with a peremetrial galvanic cell is transferrable to other 2D materials and thin films and the immediate accessibility of the mixed conductor surface also offers the possibility of deploying local probe and surface analysis techniques to study the local kinetics and ordering of an intercalate otherwise hidden underneath the electrolyte. Here, we have chosen to perform transmission electron microscopy even though probing light elements such as lithium ions and carbon atoms is severely hampered by their low scattering cross section for impinging electrons and their susceptibility to knock-on damage. Working at low acceleration voltage becomes crucial, but demands the use of spherical and chromatic aberration correctors to maintain true atomic resolution. We achieve true atomic resolution and contrary to expectation, we observe the formation of a high density, multi-layered crystalline phase of lithium in between the graphene sheets. The associated storage capacity exceeds by far the densest configuration realized in bulk graphitic carbon under similar conditions.

References

[1] M. Kühne, F. Paolucci, J. Popovic, P.M. Ostrovsky, J. Maier, J.H. Smet, Nature Nanotechnology **12** (2017) 895.
[2] M. Kühne, F. Börrnert, S. Fecher, M. Ghorbani-Asl, J. Biskupek, D. Samuelis, A. Krasheninnikov, U. Kaiser, J.H. Smet, Reversible superdense ordering of lithium between two graphene sheets, submitted.