

Better battery electrolytes by optimizing ion transport

Paul Heitjans

Leibniz University Hannover, Hannover, Germany
heitjans@pci.uni-hannover.de

(Received: 2023/08/07, Published online: 2023/08/07)

The scope of *Diffusion Fundamentals (DF)*, both as open-access journal and conference series, has greatly broadened over the past two decades. In fact, most invited lectures of the present 10th jubilee conference deal with spreading phenomena in social sciences and humanities. But even before 2005, the year of the 1st conference when Jörg Kärger and I launched *diffusion-fundamentals.org*, we organized several summer schools [1-3], where we suggested topics for presentations which were clearly beyond our own research areas as both physicists with affinity to chemistry, and, e.g., in [3], I ventured to give a plenary evening talk entitled ‘The phenomenon of diffusion – universal and transdisciplinary’.

In the present contribution, however, I shall rather go back to the roots of diffusion of *particles in matter*. A characteristic cartoon of the energy landscape of a solid material with atomic ions (“migrants”) is shown in Fig. 1.

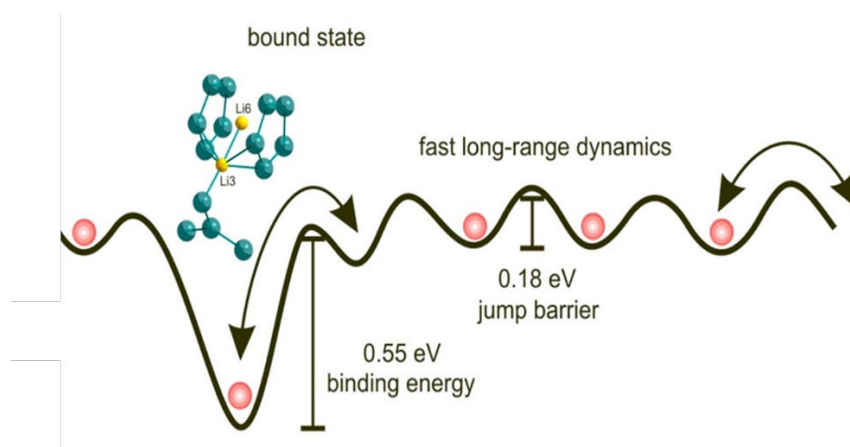


Fig. 1. Sketch of the energy surface of Li (red) in the lithium silicide $\text{Li}_{12}\text{Si}_7$. Long-range diffusion is characterized by a hopping barrier of 0.18 eV. Additionally, there are bound states—sites on which Li is bound more tightly. The long-range process is not interrupted by the bound states (here, it only appears so owing to the 1D projection). Adapted from [4] with permission.

Diffusion and transport of Li ions, in particular, has gained enormous interest in the last decades due their use in rechargeable batteries, which are nowadays ubiquitous. Other light ions such as Na^+ and, e.g., F^- are receiving increased attention for their potential application in batteries, as well.

Details of the Li^+ jumps, e.g., jump rates, activation energies, jump mechanisms and their dimensionality, can be studied by various experimental methods. Among these, the bunch of nuclear magnetic resonance (NMR) techniques (see [5] for an early account in *DF*) is the most versatile one. Besides the elucidation of ion dynamics and transport on large time and space scales, it also allows studies of the local structure (see, e.g., [6] for reviews). A thorough understanding of those fundamentals is key to the improvement of ion transport and, eventually, for better ion batteries with increased energy density, cyclability, safety, etc.

Whereas maximization of the ion conductivity of the electrolyte – preferably in the solid state for safety reasons – together with the search for an optimum electrode pair has been a continuous endeavor since the introduction of the Li ion battery in the 1990s, in recent years, the improvement of the electrolyte/electrode interfaces has received increased attention as being decisive for the optimization of battery performance.

This is indicated in Fig. 2, which shows a scheme of a Li-ion battery where interface engineering has been done by, e.g., a lithium niobate insertion layer.

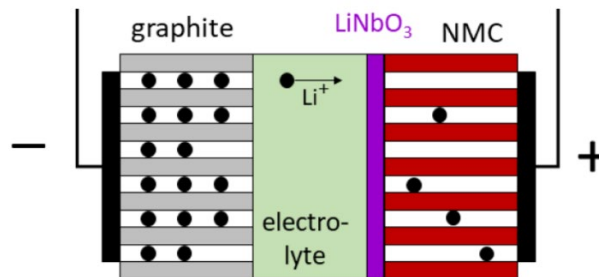


Fig. 2. Schematized commercial Li-ion battery with graphite as negative electrode (anode) and the layer structured oxide NMC ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$) as positive electrode (cathode). During discharge (represented here), the Li ions are de-intercalated from the anode, pass the electrolyte and are inserted into the cathode. The flow of Li ions is compensated by electrons in the external circuit (not shown), driving portable electronics or electric cars. Ideally, the electrolyte is a fast-Li-ion conducting compound (all-solid-state battery). Between electrolyte and electrode an insertion layer (marked in violet) of lithium niobate is indicated. Adapted from [7] with permission.

Insertion layers based on Li-Nb-O (thickness typically 10 nm) are a good example known to protect the electrodes and electrolytes from unwanted reactions and to enhance Li transport across interfaces.

In conclusion, diffusion of the most elementary entities in the materials world not only bears insight into the fascinating fundamentals of particle migration but is also at the heart of applications profoundly accompanying our everyday life.

References

- [1] J. Kärger, P. Heitjans, R. Haberland, WE-Heraeus-Ferienkurs für Physik, *Diffusion in Condensed Matter*, Leipzig 2.–13. 9. 1996, Phys. Bl. 52(5) (1996) 472.
- [2] P. Heitjans, J. Kärger, Sommeruniversität der Studienstiftung des deutschen Volkes, Akademie VI, *Diffusion*, Molveno 27. 8.–9. 9. 2000, Jahresbericht 2000, p. 102, Studienstiftung des deutschen Volkes (Ed.).
- [3] J. Kärger, P. Heitjans, Sommeruniversität der Studienstiftung des deutschen Volkes, Akademie VI, *Diffusion - ein Zufallsprozess mit bemerkenswerten Gesetzmäßigkeiten*, Alpbach 31. 8.–13. 9. 2003, Jahresbericht 2003, p. 120, Studienstiftung des deutschen Volkes (Ed.).
- [4] A. Kuhn, S. Dupke, M. Kunze, S. Puravankara, T. Langer, R. Pöttgen, M. Winter, H.-D. Wiemhöfer, H. Eckert, P. Heitjans, Insight into the Li Ion Dynamics in $\text{Li}_{12}\text{Si}_7$: Combining Field Gradient NMR, 1D/2D MAS NMR, and NMR Relaxometry, *J. Phys. Chem. C* 118 (2014) 28350–28360.
- [5] P. Heitjans, S. Indris, M. Wilkening, Solid-State Diffusion and NMR, *Diffusion Fundamentals* 2 (2005) 45.1–45.20.
- [6] C. V. Chandran, P. Heitjans, Solid-State NMR Studies of Lithium Ion Dynamics Across Materials Classes, *Ann. Rep. NMR Spectrosc.* 89 (2016) 1–102; *Ibid.*: Review Update, 106 (2022) 1–51.
- [7] E. Hüger, L. Riedel, J. Zhu, J. Stahn, P. Heitjans, H. Schmidt, Lithium Niobate for Fast Cycling in Li-Ion Batteries: Review and New Experimental Results, *Batteries* 9 (2023) 244.1–244.36.