

Anion intercalation into graphite from organic solvent based electrolytes with high oxidative stability

O. Fromm*, P. Meister, S. Rothermel, J. Huesker,
H.-W. Meyer, T. Placke, M. Winter

University of Münster, Institute of Physical Chemistry,
MEET Battery Research Center,
Corrensstraße 46, 48149 Münster, Germany

*olga.fromm@uni-muenster.de

Graphite is a redox-amphoteric intercalation host and can be intercalated by cations or anions yielding to so-called donor-type or acceptor-type graphite intercalation compounds (GICs) [1, 2]. Examples for anionic species that are capable to form acceptor-type GICs are hexa- or tetrafluoride guests, such as PF_6^- , AsF_6^- or BF_4^- [3], and even large carbon-based anions, like tris(trifluoromethanesulfonyl) methide ($(\text{CF}_3\text{SO}_2)_3\text{C}^-$), bis-(perfluoroethanesulfonyl)imide ($(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^- = \text{BETI}^-$) [4] and also bis(trifluoromethanesulfonyl) imide ($(\text{CF}_3\text{SO}_2)_2\text{N}^- = \text{TFSI}^-$) [5, 6].

Graphite as the positive electrode in electrochemical energy storage systems has been first introduced by the patents of McCullough and the publications of Carlin [7] et al. in the 1990s. In their work, they build a so-called “dual-carbon cell” using graphite as both the negative and positive electrode. This system found further examination in the work of Seel and Dahn, where the anion intercalation process of PF_6^- from organic solvents, e. g. sulfones, was the subject of the study [8]. Recently, different types of anion intercalation based energy storage systems are in the focus of research. In the work of Placke et al. [9, 10] some promising results for anion intercalation into graphite from ionic liquid based electrolytes (ILs) were presented. The examined electrochemical system, named “dual-ion cell” is based on the intercalation of the TFSI^- anion into the graphite cathode and the lithium ion insertion into LTO or lithium deposition on metallic lithium as anode. Both ions derive from an electrolyte containing LiTFSI in the ionic liquid *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ($\text{Pyr}_{14}\text{TFSI}$).

Ionic liquids, such as $\text{Pyr}_{14}\text{TFSI}$, have an alignment of favorable properties, since: they are non-flammable, non-volatile and in addition display a high anodic stability [11]. Nevertheless, ILs have some major drawbacks, including high molecular masses, which decreases the specific energy of the cell or the high costs compared to the state-of-the-art organic solvent-based electrolytes. Therefore, the examination of the compatibility of organic solvent-based electrolytes that exhibit a high stability vs. oxidative decomposition, e. g. sulfones like ethyl methyl sulfone (EMS), is required to reduce the costs of the electrolyte system and increase the specific energy of the dual-ion system. However, not only the electrolyte solvent needs to exhibit a high anodic stability, in particular the intercalated anions require a sufficient stability. Examples are fluorinated anions such as TFSI^- or BETI^- (Figure 1).

A further issue that has to be considered in this case is the electrochemical stability of the aluminum current collector and thus the issue of anodic dissolution. To suppress the anodic dissolution, electrolyte additives that support the stability of the current collector have been

investigated.

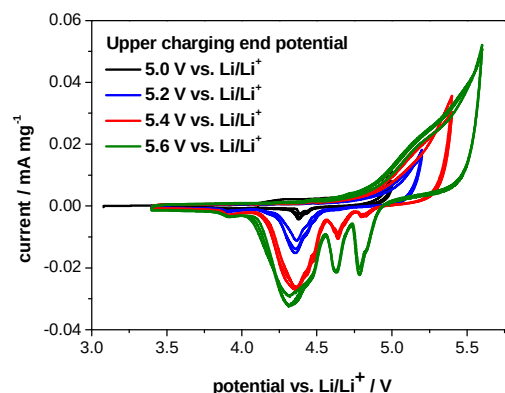


Figure 1. CV plots of 1M LiBETI in EMS electrolyte at different cut-off potentials vs. Li/Li^+ . Counter and reference electrode: lithium metal.

References

- [1] J.O. Besenhard, H.P. Fritz, *Angewandte Chemie-International Edition in English*, 22 (1983) 950-975.
- [2] R. Santhanam, M. Noel, *Journal of Power Sources*, 76 (1998) 147-152.
- [3] D. Billaud, A. Pron, F. Lincoln Vogel, *Synthetic Metals*, 2 (1980) 177-184.
- [4] Y. Ein-Eli, *Lithium Batteries*, in, 1999, pp. 416-422.
- [5] X. Zhang, N. Sukpirom, M.M. Lerner, *Materials Research Bulletin*, 34 (1999) 363-372.
- [6] M. Winter, Doctoral Thesis, Westfälische Wilhelms-Universität Münster, (April 1995).
- [7] R.T. Carlin, H.C. Delong, J. Fuller, P.C. Trulove, *Journal of the Electrochemical Society*, 141 (1994) L73-L76.
- [8] J.A. Seel, J.R. Dahn, *Journal of the Electrochemical Society*, 147 (2000) 892-898.
- [9] T. Placke, P. Bieker, S.F. Lux, O. Fromm, H.W. Meyer, S. Passerini, M. Winter, *Z. Phys. Chem.*, 226 (2012) 391-407.
- [10] T. Placke, O. Fromm, S.F. Lux, P. Bieker, S. Rothermel, H.W. Meyer, S. Passerini, M. Winter, *Journal of the Electrochemical Society*, 159 (2012) A1755-A1765.
- [11] G.T. Kim, G.B. Appetecchi, M. Montanino, F. Alessandrini, S. Passerini, *Ecs Transactions*, 25 (2010) 127-138.