

How do the graphite characteristics influence the anion intercalation into a graphite-based cathode in dual-ion cells?

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

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

*tobiasplacke@uni-muenster.de

Graphite as positive electrode in electrochemical energy storage systems has been first introduced by patents of McCullough and the publications of Carlin et al. in the 1990s [1, 2]. In their work, they build a so-called “dual-carbon cell” using graphite as both the negative and positive electrode. This concept was further examined in the works of Seel and Dahn, where they investigated the intercalation of PF_6^- anions into graphite from organic solvent based electrolytes such as sulfones [3]. There are different types of anion intercalation-based energy storage systems, which are in the focus of research. Examples include the so-called hybrid supercapacitors [4], or systems that are based on a graphite cathode and a metal oxide anode, such as TiO_2 or MoO_3 , working at potentials above 1 V vs. Li/Li^+ [5, 6]. These systems are therefore proposed as safe energy storage systems as there is no possibility of oxygen generation at the cathode and no risk of lithium plating or dendrite formation at the anode.

However, one major drawback of these systems is the limited oxidative electrolyte stability at the high working potentials of the graphite positive electrode. As the cathode potential during anion intercalation approaches 5 V vs. Li/Li^+ or even beyond, the organic solvent-based electrolytes suffer from the highly oxidizing conditions and subsequently electrolyte oxidation takes place, resulting in insufficient discharge/charge efficiencies and continuous electrolyte degradation.

Recently, we reported about so-called “dual-ion cells”, which are based on the anion intercalation into a graphite-based cathode from ionic liquid-based electrolytes [7, 8]. Here, the study’s main focus is on the intercalation of bis(trifluoromethanesulfonyl) imide anions (TFSI) into a graphite cathode from N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ($\text{Pyr}_{14}\text{TFSI}$) [7, 8]. Overall, these systems exhibit an excellent cycling stability and a capacity retention of more than 99% after 500 charge/discharge cycles, outperforming reported organic solvent-based dual-graphite/dual-ion cells. Furthermore, it was pointed out that depending on the upper charging end potential (see Figure 1) and cycling temperature, coulombic efficiencies of more than 99% and specific discharge capacities exceeding 100 mAh g^{-1} (based on the graphite cathode weight) can be obtained [7, 8]. In addition, the intercalant guest gallery height and thus the maximum stoichiometry of the TFSI-intercalated graphite could be calculated by use of *in-situ* XRD measurements [9]. Here, a gallery height of ca. 8 \AA could be determined, which is associated with a volume increase of up to about 140% for the TFSI anion uptake.

The focus of this investigation is on the influence of the graphite properties, such as the particle size distribution and surface characteristics, i. e. the specific surface area, in particular the ratio of the basal plane to

the “non-basal plane” surface area (which accumulates the prismatic and “defect” surface area), the surface morphology or the surface functional groups, on the overall electrochemical performance of TFSI anion intercalation. In addition, the rate performance at $20 \text{ }^\circ\text{C}$ and $60 \text{ }^\circ\text{C}$ as well as the long-term cycling behavior of TFSI anion intercalation-based dual-ion cells will be discussed.

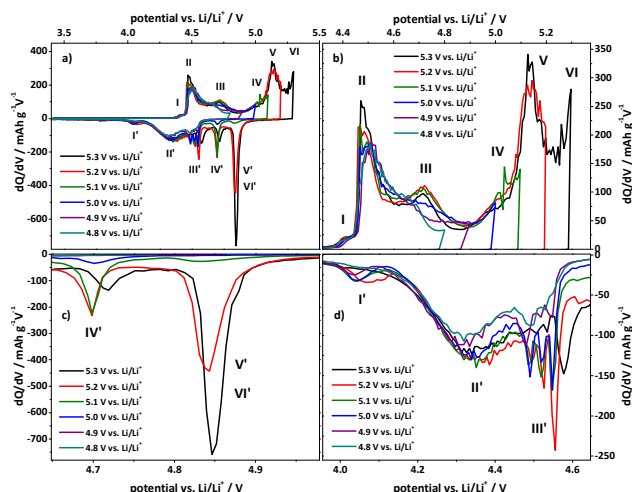


Figure 1. Differential capacity profiles of the metallic lithium (anode)-graphite (cathode) dual-ion cell during constant current charge/discharge cycling with a specific current of 50 mA g^{-1} at different upper charging end potentials (4.80 V to 5.30 V vs. Li/Li^+). (b), (c) and (d) are magnified sections of the total profiles (a). In each case, the 50th charge/discharge cycle is displayed.

References

- McCullough, F. P., *U.S. Pat.*, 5,518,836 **1996**.
- Carlin, R. T.; Delong, H. C.; Fuller, J.; Trulove, P. C., *Journal of the Electrochemical Society* **1994**, 141, (7), L73-L76.
- Seel, J. A.; Dahn, J. R., *Journal of the Electrochemical Society* **2000**, 147, (3), 892-898.
- Ishihara, T.; Yokoyama, Y.; Kozono, F.; Hayashi, H., *Journal of Power Sources* **2011**, 196, (16), 6956-6959.
- Thapa, A. K.; Park, G.; Nakamura, H.; Ishihara, T.; Moriyama, N.; Kawamura, T.; Wang, H. Y.; Yoshio, M., *Electrochimica Acta* **2010**, 55, (24), 7305-7309.
- Gunawardhana, N.; Park, G.-J.; Dimov, N.; Thapa, A. K.; Nakamura, H.; Wang, H.; Ishihara, T.; Yoshio, M., *Journal of Power Sources* **2011**, 196, (18), 7886-7890.
- Placke, T.; Bieker, P.; Lux, S. F.; Fromm, O.; Meyer, H. W.; Passerini, S.; Winter, M., *Zeitschrift für Physikalische Chemie* **2012**, 226, 391-407.
- Placke, T.; Fromm, O.; Lux, S. F.; Bieker, P.; Rothermel, S.; Meyer, H. W.; Passerini, S.; Winter, M., *Journal of the Electrochemical Society* **2012**, 159, (11), A1755-A1765.
- Schmuelling, G.; Placke, T.; Kloepsch, R.; Fromm, O.; Meyer, H. W.; Passerini, S.; Winter, M., *Journal of Power Sources* **2013**, DOI: 10.1016/j.jpowsour.2013.03.064.