

## Dual graphite cells utilizing anodes with pre-formed SEI

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Graphite as a redox-amphoteric intercalation host can be intercalated by cations or anions yielding to so-called donor-type or acceptor-type graphite intercalation compounds [1, 2]. Examples for anions capable to form acceptor-type GICs are hexa- or tetrafluoride guest species such as  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$  or  $\text{BF}_4^-$  [3] and even large carbon-based anions such as tris(trifluoromethanesulfonyl) methide ( $(\text{CF}_3\text{SO}_2)_3\text{C}^-$ ) or bis(trifluoromethanesulfonyl) imide ( $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ) [4, 5]. Donor type GICs are formed by cations, for example lithium.

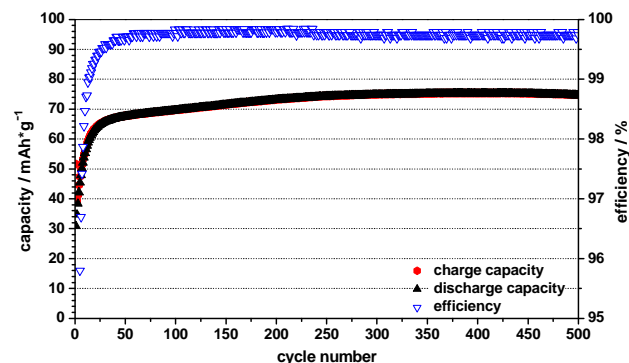
Graphite as the positive electrode in electrochemical energy storage systems has been first introduced by patents of McCullough and the publications of Carlin et al. in the 1990s [6]. In their work, they built a “dual-carbon cell” using graphite as both the negative and positive electrode. This concept was further examined in the work of Seel and Dahn, who investigated the intercalation of  $\text{PF}_6^-$  anions into graphite from organic solvent based electrolytes such as sulfones [7]. Recently, different types of anion intercalation based energy storage systems are in the focus of research. Examples are the dual-ion cells using graphite as cathode and for example metallic lithium as anode [8], which is therefore proposed as an alternative energy storage system with conventional transition metal oxide based cathodes replaced by graphite.

Nevertheless, 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.  $\text{Li}/\text{Li}^+$  or even beyond, organic solvent based electrolytes suffer from these highly oxidizing conditions and electrolyte oxidation takes place, resulting in insufficient discharge/charge efficiencies and continuous electrolyte degradation subsequently followed by early termination of the cell operation. A further issue concerning the organic solvent based electrolytes is the fact that solvent co-intercalation between the graphite interlayer gaps can occur which therefore eventually lead to graphite exfoliation reactions.

In this contribution, we present promising results for dual graphite cells using ionic liquid based electrolytes (ILs), namely *N*-Butyl-*N*-Methylpyrrolidinium bis(trifluoromethanesulfonyl) imide. As the compatibility of ILs with graphite negative electrodes is poor [9], we investigated graphite anodes with pre-formed SEI. The preforming of the SEI was achieved in a half cell using a graphite anode and an organic electrolyte cycled versus metallic lithium at a low rate for three cycles. The dual-graphite cell was subsequently assembled using the pre-formed anode, the ionic liquid *N*-Butyl-*N*-Methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ( $\text{Pyr}_{14}\text{TFSI}$ ) with 1M lithium bis(tri-

fluoromethanesulfonyl) imide ( $\text{LiTFSI}$ ) as electrolyte and a graphite as cathode.

The electrochemical system is based on intercalation of the TFSI anion into the graphite cathode and the lithium cation intercalation into the graphitic anode. The performance of these dual graphite cells has been studied in terms of cell cut-off voltage, rate and electrolyte composition which is used to form the SEI.



**Figure 1.** Charge/discharge cycling performance for a dual-graphite cell at a cut-off voltage of 5 V.

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