

Challenges and opportunities of dual-graphite cells based on ionic liquid electrolytes

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In recent publications, electrochemical energy storage systems using graphites as positive electrode material have been proposed as so-called dual-ion cells [1-3].

In this type of electrochemical cell, the lithium ions from the electrolyte are inserted/deposited into/on the negative electrode (e. g. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /metallic lithium) and the corresponding electrolyte anions are intercalated into the positive graphite electrode during charge. During discharge, both anions and lithium ions are released back into the electrolyte. Hence, the electrolyte in this system does not only act as charge carrier, but also as active material [1-3].

For the special case that graphite/carbon is applied as negative electrode material, this system is named dual-graphite or dual-carbon cell. The concept of this type of cell was first introduced by McCullough et al. and Carlin et al. [4, 5] and further studied by Seel and Dahn [6]. Regarding the work of Seel and Dahn, their system was focused on PF_6^- anion intercalation from organic solvent-based electrolytes. However, such electrolytes suffer from oxidative decomposition and thus result in insufficient coulombic efficiencies, due to the high cathode working potentials which exceed 5 V vs. Li/Li^+ [6].

The dual-ion system described above makes use of an ionic liquid-based electrolyte, namely a mixture of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in N-butyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl) imide ($\text{Pyr}_{14}\text{TFSI}$) [1-3]. This type of ionic liquid exhibits several beneficial properties compared to the state-of-the-art organic solvent based electrolytes, such as a broad electrochemical stability window with a high stability vs. oxidation and low safety hazards (a very low volatility at ambient pressure and nonflammability) [7, 8]. Overall, the dual-ion system displays a highly reversible anion uptake and release, an excellent cycling stability and coulombic efficiencies exceeding 99% [2].

The focus of this work is on the study of a dual-graphite cell using graphite as both anode and cathode material and the $\text{LiTFSI-Pyr}_{14}\text{TFSI}$ ionic liquid as electrolyte, whereas the TFSI anions are intercalated into the positive electrode during charge. Since the compatibility of this ionic liquid with graphite anodes is relatively poor [9], the influence of SEI-forming electrolyte additives, such as ethylene sulfite (ES), is studied.

The overall cell performance was studied in terms of upper charging end voltage, cycling stability, rate performance and self-discharge. Depending on the upper charging end voltage and specific current, coulombic efficiencies of more than 99% and discharge capacities exceeding 120 mAh g^{-1} (based on graphite cathode weight) can be achieved (see Figure 1). Furthermore, this system provides an excellent cycling stability with a capacity retention of more than 95% after 500 charge/discharge cycles.

One main advantage of this dual-graphite system is the fact that it makes use of inexpensive electrode materials (graphite/carbon) which in addition can be manufactured to composite electrodes by an aqueous processing route using the environmentally friendly binder sodium carboxymethyl cellulose (Na-CMC).

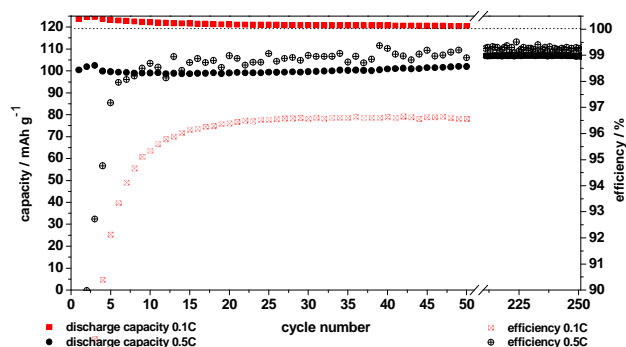


Figure 1. Charge/discharge cycling of a dual-graphite cell; measurement was performed in a three-electrode setup with metallic lithium as reference electrode; electrolyte: $\text{Pyr}_{14}\text{TFSI}$ 1M LiTFSI + additive. Cell voltage range 3.0 V – 5.2 V. Specific currents: 10 mA g^{-1} (= 0.1 C) and 50 mA g^{-1} (= 0.5 C).

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