



## Towards high-performance dual-graphite batteries using highly concentrated organic electrolytes

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### ABSTRACT

Dual-ion batteries (DIBs) and dual-graphite batteries (DGBs) attract increasing attention as an alternative approach for stationary energy storage due to their environmental, cost and safety benefits over other state-of-the-art battery technologies. In order to realize an extraordinary cell performance of DGBs, it is of particular importance to stabilize the interphases between electrolyte and electrode, for both the negative and positive electrodes. In this work, we present the implementation of highly concentrated electrolytes (HCEs) in DIBs and DGBs, *i.e.* electrolyte formulations based on either LiPF<sub>6</sub> or LiTFSI in dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethyl methyl carbonate (EMC). A reversible cycling stability of the graphitic negative electrode is proven as well as the stability of the HCEs against oxidative decomposition at the positive electrode at a cathode potential of 5V vs. Li/Li<sup>+</sup>. Additionally, we demonstrate that the anodic dissolution of the aluminum (Al) current collector is successfully suppressed by using LiTFSI-based HCEs, which show a comparable resistivity against Al dissolution as LiPF<sub>6</sub>-based electrolytes. Furthermore, a strong dependence of concentration and onset potential of anion intercalation is observed and comprehensively discussed with respect to the thermodynamic environment of the electrolyte. Overall, the use of HCEs enables a highly reversible cycling stability, providing extraordinary high specific discharge capacities of 80–100 mAh g<sup>-1</sup> for lithium metal-based DIBs and DGBs. The evaluation of voltage efficiency (VE) and energy efficiency (EE) reveals the highest values for the EMC/LiPF<sub>6</sub>-based electrolyte, *i.e.* 96% (VE) and 95% (EE). In summary, the use of HCEs is a promising strategy to further optimize the electrochemical performance of DIBs and DGBs in terms of high reversible capacity and cycling stability and decreased parasitic side reactions.

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## 1. Introduction

The development of secondary battery technologies is of particular importance for the implementation of renewable energy sources and for the broad market acceptance of electro-mobility. As rapid feeding of renewable energies into the available power networks may result in temporary grid fluctuations, stationary battery storage systems gained significant interest to counterbalance or even avoid such peak loads. In this case, not necessarily high

specific energy or energy density of the battery but rather affordable cost structures, long-term stability and operational safety are relevant. Besides state-of-the-art lithium ion batteries (LIBs), other rechargeable battery technologies get in the focus of interest as potential candidates for stationary energy storage [1–3].

Battery systems based on the dual-ion intercalation mechanism are promising candidates that currently gain increasing interest for such applications. Among them, the most prominent representatives include dual-ion (DIB), dual-carbon (DCB) or dual-graphite batteries (DGB). The battery concepts are distinguished based on the active material at both the negative (anode) and positive electrode (cathode). The term dual-ion batteries serves as “umbrella term” for all systems and chemistries in which both the electrolyte cations as well as anions participate in the electrochemical energy storage mechanism [4–6]. DCBs and DGBs can be considered as special cases where both the anode and cathode active materials

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consist of carbonaceous or graphitic materials, respectively [7–16]. Besides graphite-based cathode materials, also different anion-hosting cathodes have been reported recently including metal organic frameworks [17], hydrocarbons [18] or thianthrene, poly(vinylthiazine) or coronene-based organic cathodes [18–21].

Furthermore, dual-ion chemistries based on other cations than  $\text{Li}^+$ , including  $\text{Na}^+$  [22–26] and  $\text{K}^+$  [11,12,14] have been reported, recently. The DCB and DGB systems enable the replacement of rather expensive transition metal-based cathode materials typically used in LIBs [27] by non-toxic affordable graphites and carbons, thereby providing benefits in recycling and overall cell costs [6,8,10,13]. Notably, the actual cell safety can be further enhanced utilizing hardly flammable electrolytes such as ionic liquids [4] or highly concentrated electrolytes (HCEs) [16,28].

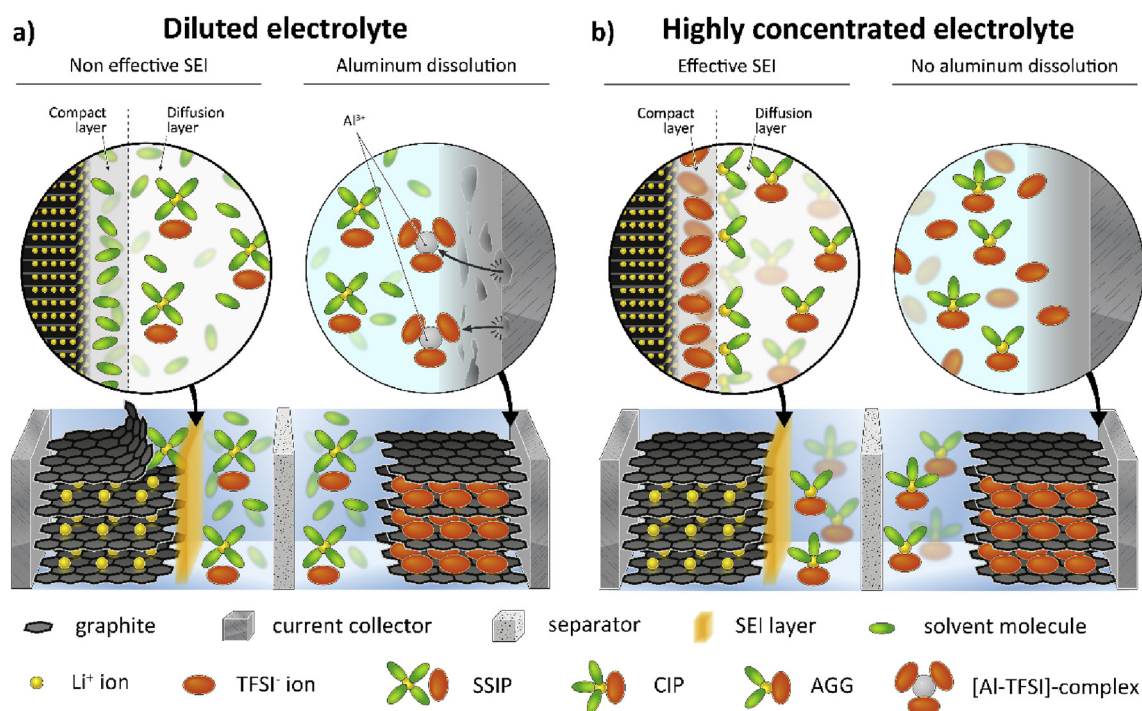
Moreover, excellent electrochemical performance and high reversibility of the anion intercalation/de-intercalation into graphitic carbons have been reported [4,5,29]. Up to now, a variety of different electrolyte formulations and particularly different anions has been investigated for application in dual-ion systems [30–34], however, some compositions suffer from significant electrolyte decomposition and anodic dissolution [56] of the aluminum (Al) current collector resulting in poor Coulombic efficiency during cell operation. In particular, diluted or low concentrated electrolytes (<2 M salt content in solution) [34,35] and few imide-based ionic liquids [36,37] demonstrated a rather poor cell performance at cathode working potentials of >5 V vs.  $\text{Li}/\text{Li}^+$ . In order to prevent or reduce Al dissolution, several feasible strategies including utilization of  $\text{Pyr}_{14}\text{TFSI}$  and  $\text{LiTFSI}$  ionic liquid based mixtures [38], highly concentrated electrolytes (HCEs) [39], ceramic coatings on the Al current collector [40,41] or the addition of electrolyte salts as additives that result in passivation layers on Al surfaces (e.g.  $\text{LiPF}_6$ ) have been evaluated [42,43].

Indeed, HCEs appear quite attractive and suitable for application in DGBs, as such electrolytes provide remarkably increased reductive stabilities as well as highly reversible  $\text{Li}^+$  uptake or release at

graphite negative electrodes due to synergistic effects of salt and solvent molecules forming an effective solid electrolyte interphase (SEI) [44] without EC as electrolyte component [28,45]. Furthermore, an increased stability against oxidative electrolyte decomposition at the corresponding positive electrode [46,47], accompanied by a suppressed Al dissolution for salt-solvent combinations, which do not form a protecting fluoride layer at the Al-surface in diluted solutions, such as imide-based salt electrolyte formulations [39,41,48,49], could be identified. Notably, an application of HCEs better the achievable cell safety by reducing the solvent vapor pressure and enhancing the thermal stability [28,39]. Nevertheless, the substantially higher demand of electroactive salts introduces higher electrolyte costs and often reduced ionic conductivities, but the available benefits in terms of electrochemical performance may outweigh these drawbacks (Fig. 1). In case of diluted electrolytes, inappropriate compositions can lead to graphite exfoliation and/or massive Al dissolution, hence rapid cell failure, which clearly can be mitigated by HCEs.

So far, only a few reports describe the use of HCEs for DGBs. Miyoshi et al. studied a Li-DGB with different amounts of  $\text{LiPF}_6$  in dimethyl carbonate (DMC) [16], demonstrating a reversible (de-) intercalation into the graphite lattice without exfoliation and remarkably increased cell capacities. Nevertheless,  $\text{LiPF}_6$  is not an attractive choice in view of health and environmental concerns due to its tendency to decompose in the presence of trace amounts of  $\text{H}_2\text{O}$ , releasing HF and other toxic reaction products [50,51]. Therefore, efforts should be devoted to replace  $\text{LiPF}_6$  with more (electro-) chemically stable electrolyte salts such as  $\text{LiTFSI}$ , to increase cell safety.

In this work, we study  $\text{LiTFSI}$ -based and  $\text{LiPF}_6$ -based HCEs for application in DGBs and lithium metal-based DIBs. In particular, we focus on the charge/discharge characteristics of both diluted and highly concentrated electrolytes to explain the possible effects of increased cell performance, i.e. reversible capacity, Coulombic efficiency, voltage efficiency and energy efficiency. We also unravel



**Fig. 1.** Working principles and (dis-)advantages of the dual-graphite battery using a) diluted and b) highly concentrated electrolytes. The abbreviation SSIP denotes a solvent-separated ion pair, CIP designates contact ion pair and AGG corresponds to aggregated ions.

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