The (in-)stability of highly concentrated LiTFSI - acetonitrile electrolytes

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Highly concentrated electrolytes have been launched as promising candidates for a new generation of Li-ion batteries, based on that an increased salt concentration leads to an extended electrochemical stability window of the electrolyte, allowing the use of solvents that otherwise would be unstable. [1] This is foremost due to a change in the local ion-solvent coordination within the electrolyte – in both bulk and interfaces/interphases – with very few "free" solvent molecules available. This lowers the volatility of the electrolyte, increasing battery safety, and also increases the stability vs. various electrode materials and inhibits Al corrosion. [2] Highly concentrated LiTFSI - acetonitrile electrolytes, approx. 4 M, have been shown to stabilize Al current collectors, graphite electrodes in Li-ion batteries, and lithium metal – all in stark contrast to the behaviour of the corresponding 1 M electrolyte. [3]

We here revisit the LiTFSI - acetonitrile system, initially aiming at optimizing the salt concentration. However, cycling our supposedly stable graphite|Li cell surprisingly reveal instability vs. lithium metal at modest currents also for the highly concentrated electrolytes – clear also from inspection of the separators after cell disassembly (Fig. 1). Using graphite|$LiFePO_4$ cells we observe a clear improvement as a function of salt concentration, but the performance is still unsatisfactory – likely caused by insufficient stability of the solid electrolyte interphase (SEI) at the graphite electrode. By paused galvanostatic cycling we show SEI dissolution to occur and the largely irreversible self-discharge to be connected to the SEI reformation. In all, the (in-)stability of this electrolyte system points to less relevance for application in Li-ion cells.

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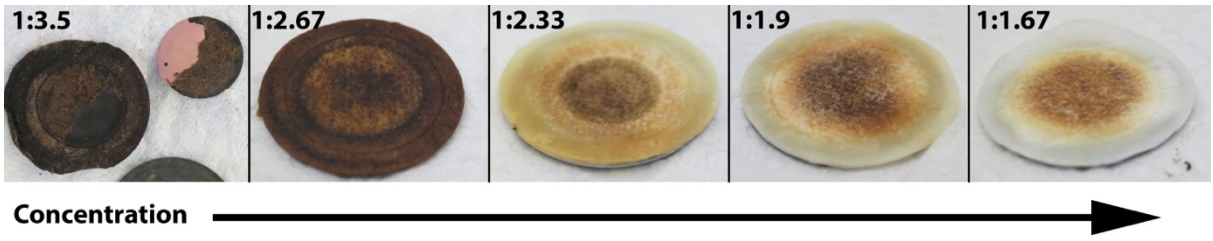

Figure 1: Separators after 50 cycles in graphite|$LiFePO_4$ cells with the concentration provided as the LiTFSI:acetonitrile molar ratios (1:1.67 ≈ 4.5 M).

References:

[1] Y. Yamada, K. Usui, C. H. Chiang, K. Kikuchi, K. Furukawa, A. Yamada, ACS Appl. Mater. Interfaces. 6 (2014) 10892–10899.
[2] D. W. McOwen, D. M. Seo, O. Borodin, J. Vatamanu, P. D. Boyle, W. A. Henderson, Energy Environ. Sci. 7 (2013) 416–426.
[3] Y. Yamada, K. Furukawa, K Sodeyama, K. Kikuchi, M. Yaegashi, Y. Tateyama, A. Yamada, JACS. 136 (2014) 5039–5046.