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Critical evaluation of the stability of highly concentrated LiTFSI - Acetonitrile electrolytes *vs.* graphite, lithium metal and $LiFePO_4$ electrodes

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HIGHLIGHTS

- Electrolytes are tested in full cells with relevant graphite mass loading.
- The stability of Li metal is very sensitive to the current density.
- The SEI stability is investigated using paused galvanostatic cycling.
- Aluminium current collector exhibits irreversible oxidation activated over time.

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ABSTRACT

Highly concentrated LiTFSI - acetonitrile electrolytes have recently been shown to stabilize graphite electrodes in lithium-ion batteries (LIBs) much better than comparable more dilute systems. Here we revisit this system in order to optimise the salt concentration *vs.* both graphite and lithium metal electrodes with respect to electrochemical stability. However, we observe an instability regardless of concentration, making lithium metal unsuitable as a counter electrode, and this also affects evaluation of *e.g.* graphite electrodes. While the highly concentrated electrolytes have much improved electrochemical stabilities, their reductive decomposition below *ca.* 1.2 V *vs.* Li^+/Li° still makes them less practical *vs.* graphite electrodes, and the oxidative reaction with Al at *ca.* 4.1 V *vs.* Li^+/Li° makes them problematic for high voltage LIB cells. The former originates in an insufficiently stable solid electrolyte interphase (SEI) dissolving and continuously reforming – causing self-discharge, as observed by paused galvanostatic cycling, while the latter is likely caused by aluminium current collector corrosion. Yet, we show that medium voltage $LiFePO_4$ positive electrodes can successfully be used as counter and reference electrodes.

1. Introduction

The ongoing electrification of vehicles for road transport puts increasing demands on the capacity, safety and lifetime of the electrochemical energy storage systems. The commonly used lithium-ion batteries (LIBs) basically all contain an electrolyte based on 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) or diethyl carbonate (DEC), a graphite-based negative electrode, and a positive electrode based on a complex oxide [1]. The poor thermal and electrochemical stabilities of both salt and solvents of the electrolyte, however, lead to LIB safety issues and capacity degradation, resulting in a reduced lifespan [2,3] as well as a need for expensive mitigating additives [4,5]. In addition, if lithium metal rather than graphite based negative electrodes, and high voltage positive electrodes could be used, the energy density at the cell level could increase by more than 30% for a state of the art NMC cell (based on data by Hagen et al. [6]). For the lithium metal electrodes, dendrite formation upon cycling, amplified by the electrochemical instability of the electrolyte, is the main limiting factor [7]. For application of high voltage electrodes, the oxidative decomposition of the electrolyte is problematic. Hence there is an urge for novel LIB electrolyte materials and/or concepts.

One starting point could be to replace the electrolyte salt; both $Li[N(SO_2CF_3)_2]$ (LiTFSI) and $Li[N(SO_2F)_2]$ (LiFSI) have shown to be thermally more stable than $LiPF_6$ [8]. They also avoid the problem of HF formation, leading to cell degradation [3]. However, both these salts cause aluminium current collector corrosion when used with high voltage electrodes [9–12]. The Al corrosion for cells using LiFSI-based electrolytes has been attributed to Cl^- impurities and the conductivity

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of these are higher than for LiTFSI-based electrolytes [8], but there are still reasons to rather consider the latter. The decomposition temperature and oxidation potential are both higher; *ca.* 200 °C for LiFSI [13] *vs.* > 330 °C for LiTFSI [14] and *ca.* 4 V *vs.* Li^+/Li° for LiFSI *vs.* > 5 V *vs.* Li^+/Li° for LiTFSI [14]. The aluminium corrosion generally associated with LiTFSI can be circumvented by using a minor amount of $LiPF_6$ as an electrolyte additive [15].

Rather recently, highly concentrated electrolytes [16] based on these salts have been shown to supress the aluminium corrosion [11,17,18]. Furthermore, increasing the concentration of the electrolyte reduces the vapour pressure [19], significantly lowering the solvent volatility at elevated temperatures [18], and can widen the electrochemical stability window by more than 1 V [20,21]. All of this is often claimed to originate in an altered solvation structure of the electrolyte, with no “free” solvent molecules present [22,23], and most ions participating in contact ion pairs or larger aggregates [24], forming network-like structures. This ion-dense structure can cause shifts of the electronic energy levels of both anion and solvent on the order of 1 eV, leading to *e.g.* an increased reduction potential promoting a better passivation [25] or to an increased oxidation potential of the solvent [20]. However, even if special conditions apply to highly concentrated electrolytes [26], the bulk electrolyte structure is not necessarily maintained close to the electrode surface where the concentration varies within the diffusion layer [27]. The concentration is expected to be lower at the negative electrode during LIB charging [28], which may cause solvent reduction if the electrode surface is not properly passivated.

In general, the passivating layer or the “solid electrolyte interphase” (SEI) [29] on the LIB negative electrode is formed by adsorbed products from electrolyte reduction. These form a dense film preventing further electrolyte reduction, while allowing Li^+ transport and preventing solvent co-intercalation [5,30]. In a charged cell, this electrolyte reduction can happen spontaneously by oxidizing (de-intercalating) the lithium and is observed as self-discharge of the cell and growth of the SEI. By introducing a pause in the cell cycling scheme, the SEI growth and dissolution in the electrolyte can be probed [31–33]. Most often a stable SEI on graphite is created by inclusion of EC in the electrolyte, due to its low reduction stability and good film-forming ability [5,30], but with drawbacks of decreased performance below −20 °C [34] and low compatibility with high voltage electrodes [35]. Alternative chemistries for stable SEI creation make use of homologues without the C=O group, but remains to be proven for full LIB cell cycling [36,37]. Thus, electrolytes that allow graphite-based cells to cycle without any EC in the electrolyte are urged for from both a performance and battery life point of view.

One way forward is through highly concentrated electrolytes, which have allowed cycling of graphite electrodes in binary electrolytes such as $Li[N(SO_2C_2F_5)_2]$ - propylene carbonate [22], LiTFSI - dimethyl sulfoxide [23], LiTFSI - tetrahydrofuran [38] and LiFSI - 1,2-dimethoxyethane [39]. Acetonitrile (ACN) has been used as a single solvent in highly concentrated electrolytes in particular with LiTFSI as the salt [24,25,40–44]. ACN has a low cost, a low viscosity, and a high dielectric constant, and is furthermore also one of the most commonly used solvents in supercapacitors [45,46]. The physical properties of the LiTFSI - ACN system have been thoroughly investigated; *e.g.* the viscosity of 1:3 LiTFSI:ACN is *ca.* 10–100 times higher than for a 1 M electrolyte [24,41,42], the conductivity at 4.2 M is ca. 1 mS cm^{-1} [41,42], the anodic stability of 1 M electrolyte *vs.* Al is *ca.* 4.15 V *vs.* Li^+/Li° [44]. Concentrations of 1:1.23 LiTFSI:ACN and higher are not liquid at room temperature due to the occurrence of a crystalline phase, 1:1, with a melting point of 37 °C [40,43] A drawback of ACN is its toxicity and the possibly toxic and corrosive degradation products that may form in a case of insufficient passivation [47].

In 2014 Yamada et al. [41] reported reversible intercalation of lithium ions into graphite using a LiTFSI - ACN electrolyte with a concentration of 4.2 M in a Li|graphite cell. Partial reversibility of Li deposition/dissolution on Ni was observed for the 4.2 M electrolyte whereas it was irreversible in the 3 M electrolyte. The oxidation stability *vs.* Pt was determined to *ca.* 5 V *vs.* Li^+/Li°. They also demonstrated that Li metal immersed in the 4.2 M electrolyte is stable, while it is oxidized by ACN in the 1 M electrolyte, and showed the SEI on the graphite electrode to consist of decomposed TFSI rather than of decomposed solvent, explained by a shift in the TFSI lowest occupied molecular orbital (LUMO) to potentials lower than the ACN LUMO and by a solvation structure with less free solvent [41].

Here we re-visit the highly concentrated LiTFSI - ACN electrolyte in order to: i) optimize the salt concentration for stable practical cell performance, ii) elucidate the underlying mechanisms for (poor) cycle-life, and iii) re-assess the oxidative stability of the electrolyte. We focus on electrolytes ranging from 1:16 to 1:1.67 LiTFSI:ACN in composition (*ca.* 1–4.4 M) *vs.* lithium metal and graphite. $LiFePO_4$ (LFP) positive electrodes are evaluated and used as counter electrode (C.E.) and reference electrode (R.E.) because of their high stability and flat, but modest, potential plateau of 3.43 V *vs.* Li^+/Li° [48].

2. Experimental

2.1. Electrolytes

The LiTFSI salts (Solvionic, 99.9% and Ferro) were both dried for > 24 h at 120 °C under dynamic vacuum and subsequently mixed with ACN (Sigma-Aldrich, 99.8%, used as received), to obtain seven different electrolytes with the molar ratios LiTFSI:ACN (x_{LiTFSI}): 1:16 (0.059, ≈1 M), 1:9 (0.1), 1:3.5 (0.222), 1:2.67 (0.27), 1:2.33 (0.3), 1:1.9 (0.345, ≈4.2 M) and 1:1.67 (0.375). All electrolytes except 1:16 and 1:9 were heated to 50 °C to assist the salt dissolution. All handling of the salts and solvents was made in an Ar-filled glovebox (H_2O < 1 ppm, O_2 < 1 ppm). For conductivities of the electrolytes, see supplementary information Fig. S1. The water content of the electrolytes was by Karl-Fischer titration determined to 100–200 ppm. Due to this rather high water content, an additional 1:1.9 electrolyte was made for comparison, starting from an extra dry salt (Solvionic, 99.9%, < 20 ppm H_2O, used as received), and ACN dried over 3 Å molecular sieves, resulting in < 10 ppm water content. Additionally, for comparisons and as reference systems, the standard LP40 electrolyte, i.e. 1 M $LiPF_6$ in EC:DEC 1:1 wt (Merck, < 20 ppm H_2O, < 50 ppm HF, used as received), as well as 0.5 M $LiPF_6$ (Aldrich, 99.99%) in ACN and 1 M LiTFSI (Solvionic, 99.9%) in DMC (Sigma-Aldrich, 99%) electrolytes were used.

2.2. Electrodes

The graphite negative electrodes were manufactured to a composition of 88% graphite (85% Hitachi SMG, 3% Timrex KS6), 2% carbon black (Timcal C65) and 10% polyvinylidene fluoride (PVdF, Arkema Kynar Flex 2801). A slurry was prepared using 2.16:1 N-Methyl-2-pyrrolidone (NMP, VWR) to dry mass. First, the PVdF was dissolved, then the remaining ingredients were added, and subsequently mixed in a planetary ball mill for 1 h at 600 rpm. The LFP positive electrodes were made using 75% LFP (Phostech P2), 10% carbon black (Erachem Super P) and 15% PVdF. A slurry was then prepared with 2.32:1 NMP to dry mass by ball milling for 2 h at 600 rpm.

The slurries were spread on metal foils acting as current collectors, Cu (Goodfellow, 20 μm, > 99.9%) for the negative and Al (KORFF, 20 μm, Alloy 1200, > 99%) for the positive, using a roll-to-roll coater with a 120 °C drying stage. The thicknesses of the electrodes were in general chosen as to give excess positive electrode capacity, resulting in active material mass loadings of *ca.* 1.9 mg cm^{-2} for graphite and 7.6 mg cm^{-2} for LFP. Thinner graphite electrodes with lower mass loadings, *ca.* 0.3 mg cm^{-2}, were made by diluting the slurry with additional NMP until a thin enough layer was achieved.

Lithium (Cyprus Foote Mineral, 125 μm), stainless steel (Empiro AB,