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Concentrated Electrolytes for Enhanced Stability of Al-Alloy Negative Electrodes in Li-Ion Batteries

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Reprint graphite with alloying Al negative electrodes would allow for the development of high energy density Li-ion batteries. However, large volume changes associated with the alloying/dealloying process often result in pulverization of the electrode and rapid capacity fade during cycling due to the continuous formation of solid electrolyte interphase (SEI) layers and loss of electronic contact. In this study, we report that increasing salt concentration in the electrolyte to > 5 mol dm$^{-3}$ led to enhanced capacity retention during cycling of Li-Al half-cells, which was accompanied by nearly constant impedance for the Al electrode in lithium bis(fluorosulfonyl)imide (LiFSI)/dimethyl carbonate (DMC) 1:1 (mol/mol) superconcentrated electrolyte. X-ray photoelectron spectroscopy (XPS) revealed that a potential hold in the superconcentrated electrolyte formed an SEI layer with a greater LiF content than in standard 1 mol dm$^{-3}$ solution. This was supported by Raman spectroscopy of LiFSI solutions in DMC, supplemented with density functional theory calculations, which showed an increased driving force for the reduction of FSI$^{-}$ anions to form LiF from Li$^{+}$-coordinated DMC complexes with increasing salt concentration. Therefore, the enhanced capacity retention and stability can be attributed to the stability of LiF-rich SEI layers which limit carbonate reduction and charge transfer impedance growth.

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Current Li-ion battery technology relies on the use of graphite in the negative electrode, which has low average potentials (~0.1 V vs. Li/Li$^+$) and little irreversible capacity as well as high rate capability, cycle life and electronic conductivity. It is well known that a solid electrolyte interphase (SEI) forms on the graphite edge plane in ethylene carbonate (EC)-based electrolytes, which allows lithium ions to reversibly intercalate into the graphitic carbon structure. This behavior has been attributed to the reductive decomposition of EC to form an electronically insulating yet ionically conductive SEI layer on the graphite surface, preventing further decomposition of the electrolyte and co-intercalation of solvent into the graphite. Alloying negative electrode materials, such as Al, Si$^{10}$ and Sn$^{12,13}$ exhibit much higher theoretical capacities due to the formation of Li-rich Li-M binaries, making them attractive for implementation in advanced high-energy Li-ion batteries. However, the large volume changes required to accommodate the alloying process$^{14,15}$ have been linked to pulverization of the electrodes, resulting in a loss of electronic contact and destabilization of the SEI. With these materials, the poor robustness of the SEI repeatedly exposes pristine active material, leading to the continuous formation of electrolyte degradation layers. Consequently, significant capacity fade has been observed during cycling which has so far hindered the application of alloying negative electrode materials in practical Li-ion batteries.$^{7,8,16}$ The electrochemical properties of several candidate negative electrode materials are compared to those of graphite in Table S1. Notably, Si negative electrodes have a very high specific capacity (3579 mAh g$^{-1}$ for Li$_{14}$Si$_4$) but undergo the most extreme volume change during lithiation (280%) out of the candidate materials; as such, a large number of battery researchers have focused on addressing this problem.$^{11,15}$ Despite a lower specific capacity than Si (993 mAh g$^{-1}$ for LiAl), the density of Al lends itself to a relatively high volumetric capacity and therefore a high estimated energy increase in a full-cell. Al electrodes also undergo a much smaller volume change than Si of 97% upon lithiation. However, the use of Al electrodes presents its own host of challenges, such as the issue of cost, safety and the significant component of resistive Al$_2$O$_3$ passivation layers in electrodes made using active material nanoparticles, which is a common solution to alleviate fracture in Si electrodes.$^9$ Therefore, studying how Al-alloy negative electrodes can be stabilized, particularly through understanding of the SEI layer which forms on the negative electrode, may assist in the design and development of high energy density Li-ion batteries with long cycle lives.

A potential solution to stabilize the SEI for Al electrodes is the use of concentrated electrolytes, which have attracted recent attention due to the tunability of physicochemical and electrochemical properties simply by increasing the salt concentration. Electrolyte solutions with these high salt concentrations (≥ 3 mol dm$^{-3}$) have recently been termed “solvent-in-salt” and/or “superconcentrated” electrolytes.$^{20}$ Generally, Li$^+$ ions are coordinated by solvent molecules in the solution to form a [Li(solvent)$_3$]$^+$ structure, where the solvation number $n$ is most often reported to be around four.$^{21-23}$ Typical electrolyte concentrations used for Li-ion batteries are around 1 mol dm$^{-3}$ (solute/Li$^+$ ratio ~ 10) and therefore ~ 60% of solvent molecules are “free” from Li$^+$. As the salt concentration is increased, the activity of free solvent molecules which do not interact with Li$^+$ cations decreases.$^{24}$ As a result of this low free solvent activity, interesting phenomena have been widely reported such as high thermal stability, low volatility,$^{25,26}$ suppression of transition metal/reaction intermediate/collector dissolution,$^{26-31}$ expansion of the electrochemical window$^{25,33,34}$ and the formation of compact and stable SEI layers for Si and Li metal negative electrodes. These phenomena are especially prevalent when the solvent/Li$^+$ ratio is less than the common solvation number of four (corresponding to a Li salt concentration greater than ~ 3 mol dm$^{-3}$)$^{11,29}$ Although SEI layer formation in superconcentrated solutions is not well understood, their stability has been explained by the reduction of salt anions to form a protective LiF film which prevents further electrolyte reductive decom-
position and/or Li dendrite formation. In particular, concentrated electrolytes with lithium bis(fluorosulfonyl)imide (LiFSI) salt have exhibited fast charge transfer and the formation of a protective SEI layer on Si and Li metal due to low Lewis basicity, small anion size and a relatively weak S-F bond in the molecular structure. The stability of SEI layers formed from LiFSI salt solutions can be attributed to LiF formation through co-adsorption of dissociated Li⁺ and FSI⁻ and breaking of the S-F bond to leave F⁻(SO²)₂⁻N and LiF. 

In this study, galvanostatic cycling and electrochemical impedance spectroscopy (EIS) measurements showed that Li-Al half-cells cycled in LiFSI/DMC 1:1.1 (mol/mol) electrolytes exhibited greater capacity retention than those cycled in more dilute solutions as well as nearly constant charge transfer impedance. Through a combination of Raman spectroscopy and density functional theory (DFT) calculations, the solvation structures in superconcentrated and standard electrolytes were used to rationalize the observed electrochemical stability by showing that the driving force for the reduction of FSI⁻ anions to form LiF is higher in the superconcentrated electrolyte. Supported by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) analysis, these results suggested that the superconcentrated electrolyte promoted FSI⁻ reduction and therefore the formation of a passivating LiF-rich SEI layer to prevent continuous electrolyte degradation and SEI growth on the negative electrode.

**Methods**

**Experimental methods.**—Lithium bis(fluorosulfonyl)imide (LiFSI, >99%) salt purchased from Oakwood Chemical was used as received. Electrolytes were prepared by mixing LiFSI with dimethyl carbonate (DMC, battery-grade BASF). The residual water contents in the electrolytes were measured by Karl Fischer titration and were below 100 ppm. Viscosities and densities of the electrolytes were measured using a Stabinger viscometer (SVM3001, Anton Paar). Ionic conductivity was determined using a Traceable 23226-505 conductivity meter.

Composite Al electrodes were prepared by mixing 80 wt% Alumnum powder (Alfa Aesar, 7–15 μm or US Research Nanomaterials Inc., 100 nm), 10 wt% polyvinylidene fluoride (Kynar) and 10 wt% acetylene black (Chevron) in N-methyl-2-pyrrolidone (Sigma Aldrich). The slurry was then spread onto copper foil (25 μm thickness) using a gap bar coater and dried at 80°C. Electrodes (1/2 in. diameter, 1.27 cm² area) were punched and dried overnight under dynamic vacuum (120°C). Active material mass loading of the composite was 1.5 mg cm⁻² and 0.4 mg cm⁻² for composite Al nanoparticle electrodes. Aluminum foil electrodes were punched out of aluminum foil (1/2 in. diameter, 16 mm thickness) and dried overnight under dynamic vacuum (120°C).

Raman spectra of the electrolytes were measured using a microscope Raman spectrometer system (LabRAM HR, Horiba) with 532 nm laser excitations calibrated with a Si standard. Electrolytes were sealed in a capillary tube and held at 25°C during measurement (T95 system controller, Linkam Scientific). After baseline correction of the spectral range, the integrated intensity of the DMC band (890–990 cm⁻¹) was normalized by fixing the C1s photoemission peak of adventitious carbon (285 eV) to the same value. Energy dispersive X-ray (EDX) analysis was performed using a monochromatized Al Kα source and a charge neutralizer. The Al working electrode was then charged to an end-of-charge potential of 0.1 V Li, held at 0.1C (99.3 mA g⁻¹) and then discharged at 0.01 V Li for a given number of cycles at a 0.1 C rate (¬0.1 mA cm⁻² gov., 99.3 mA g⁻¹), calculated from the theoretical specific capacity of LiAl (993 mAh g⁻¹). In this paper, the Li⁺ alyloying process into the Al electrode (Li⁺ + Al + e⁻ → LiAl) is defined as “charging”. Cells were then de-crimped in the glove box and rinsed with 200 μL of DMC for further characterization. Aluminum foil electrodes were held at a potential of 0.01 V Li in Tomcell type TJ-AC cells with a cutoff charge of 1 mAh/cm² before being opened in the glove box and rinsed with 200 μL of DMC for XPS analysis.

Scanning electron microscopy (SEM) samples were rinsed in an aluminum laminate package with a heat sealer inside the glove box for transport, before being opened and quickly placed into the SEM chamber to minimize air exposure. SEM images of the electrode surface were taken using a JEOL JSM-5910 scanning electron microscope at a 3 kV operating voltage. Energy dispersive X-ray (EDX) analysis was conducted at a 20 kV operating voltage.

Charged aluminum foil electrodes were transferred from the glove box to the chamber of the X-ray photoelectron spectroscopy (XPS) spectrometer using a sample transfer vessel (ULVAC-PHI, INC.). XPS spectra were collected using a PHI 5000 VersaProbe II (ULVAC-PHI, INC.) with a monochromatized Al Kα source and a charge neutralizer. Spectra were recorded with a pass energy of 23.5 eV and calibrated with the Cls photoemission peak of adventitious carbon at 285 eV. After subtraction of a Shirley-type background, photoemission lines were fitted using combined Gaussian-Lorentzian functions. All spectra were normalized by fixing the Cls photoemission peak of adventitious carbon (285 eV) to the same value.

For electrochemical impedance spectroscopy (EIS), three-electrode cells were assembled in the glove box with Li metal foil (15 mm diameter), a Whatman GF/A separator (19 mm diameter), a Li₄Ti₅O₁₂ mesh reference electrode (18 mm diameter), and Al electrode (1/2 in. diameter) from bottom to top, where a mesh Li₄Ti₅O₁₂ reference electrode was placed between positive and negative electrode with two separators and 200 μL of electrolyte. A detailed cell configuration can be found in previous work. A mesh reference electrode was used to avoid an inhomogeneous electric field during EIS measurement, which is known to cause an artefactual EIS response (ex. “spiral” behavior on Nyquist plots with a Li rod reference electrode). Galvanostatic and potentiostatic charge and EIS tests were performed using a VMP3 (potentiostat with a frequency response analyser, Biologic) with cells thermally equilibrated by a thermostat chamber (SU-241, Espec) at 25°C. After cell assembly, the Li₄Ti₅O₁₂ mesh reference electrode was electrochemically lithiated (negatively polarized at a constant current of 500 μA against the Li metal counter electrode with a cutoff voltage of 1.3 V Li) to a stable reference electrode potential of 1.56 V Li. The Al working electrode was then charged to an end-of-charge potential of 0.1 V Li at 0.1C (99.3 mA g⁻¹) and held at that potential. EIS measurements were carried out at the holding potential (0.1 V Li) every hour with a 10 mV amplitude and a frequency range from ~10⁻¹ to 10⁻⁶ Hz.

**Computational methods.**—All calculations were performed using the Gaussian 09 computational package. Geometries were optimized at the B3LYP/6-31G(d,p) level of theory; ground states were verified by the absence of any imaginary frequency. The conductor-like polarizable continuum model (CPCM) and was employed to capture the solvation effects. To mimic the solvation environment in DMC solvent, methyl propanoate was selected as the implicit solvent with the dielectric constant set to 3.1. Single point energy calculations were performed at the B3LYP/6-311++G(d,p) level of theory for vertical reduction energies, where geometry optimization was not allowed for the charged state.

$$G_{\text{Red}} = G(M^+) - G(M)$$

**Results and Discussion**

The concentration-dependent viscosities and ionic conductivities of LiFSI/DMC solutions at 25°C are shown in Figure 1a. Concentrations, ionic conductivities and viscosities can be found in Table S2.
The viscosity of solution increases rapidly at concentrations greater than 4 mol dm\(^{-3}\) due to an increasing number of solvated cations with a larger hydrodynamic radius than free solvent molecules in the solution. This effect is combined with the enhanced Coulombic interaction between solvated Li\(^+\) cations and FSI\(^-\) anions with decreasing distance.\(^{24,34-37}\) The ionic conductivity first increases with increasing LiFSI concentration up to \(\sim\) 1.5 mol dm\(^{-3}\), which can be attributed to increased mobile Li\(^+\) concentration as supported by previous reports with dimethyl sulfoxide (DMSO),\(^{24}\) sulfolane,\(^{58}\) carbonates\(^{29}\) and ethers.\(^{59}\) Beyond 1.5 mol dm\(^{-3}\), the conductivity decreases with increasing Li salt concentration as a result of the decreased mobility of ionic species\(^{30,34}\) associated with increased viscosity.\(^{24,34}\) The decrease in conductivity may also be due to reduced salt dissociation\(^{58,59}\) as a result of direct anion coordination to Li\(^+\) at high salt concentrations when there are insufficient solvent molecules to fully stabilize the cation. These two factors typically yield a maximum ionic conductivity at concentrations of \(\sim\) 1 mol dm\(^{-3}\), as observed extensively for ether- and carbonate-based electrolytes.\(^{21,24,54,55}\)

Concentration-dependent solution Raman spectra were measured in order to investigate the Li\(^+\) solvation structures in LiFSI/DMC solutions. The spectrum shown in Figure 1c shows that pure DMC exhibits a band centered at \(\sim 915\) cm\(^{-1}\) corresponding to the O-CH\(_2\) stretching mode of the DMC solvent.\(^{29,62}\) Dissolving LiFSI into DMC shifts this band to 930 – 935 cm\(^{-1}\), with a clear isosbestic point at \(\sim 923\) cm\(^{-1}\), and introduces a band centered at \(\sim 730\) cm\(^{-1}\) corresponding to the FSI\(^-\) S-N symmetric stretching mode, shown in Figure 1b.\(^{29,63}\) The Raman spectrum of the superconcentrated LiFSI/DMC 1:1.1 solution did not pass through the isosbestic point, which suggests that the coordinated DMC band shifted further to a higher frequency and that the strength of the Li\(^+\)-DMC interaction increased due to a lack of free solvent to stabilize the Li\(^+\) cation (a strong Lewis acid). The presence of distinct solvation structures in superconcentrated and standard solutions agrees with results reported for concentrated solutions of lithium bis(trifluoromethanesulfonyl)amide (Li[TfSA])/N,N-dimethylformamide\(^{56}\) and Li[TfSA]/DMSO.\(^{24}\)

As shown in Figure 1b, there is an increase in Raman shift from \(\sim 728\) cm\(^{-1}\) to 753 cm\(^{-1}\) as the concentration is increased, which is often observed in concentrated amide-based solutions.\(^{29,60,64,65}\) Previous work has shown that a Raman shift of \(\sim 725\) cm\(^{-1}\) can be assigned to aggregate clusters (FSI\(^-\) coordinated to \(\geq 2\) Li\(^+\)) in concentrated LiFSI solutions.\(^{29,61}\) In addition, it has been shown that anion bidentate coordination (two sulfonyl oxygens in FSI\(^-\) interacting with Li\(^+\)) is more favorable in concentrated solutions\(^{29,54,56}\) due to the stability of the bidentate structure in the absence of solvent contributions.\(^{56}\) It was reported that standard concentrations of Li[TfSA]/DMSO solutions had high concentrations of free FSA\(^-\) anions due to the solvent’s high donor number and the dissociative nature of Li[TfSA] salt.\(^{24}\) As LiFSI is also highly dissociative,\(^{29}\) LiFSI/DMSO 1:1.1 (mol/mol) solution can be used as a reference for the Raman shift for free FSI\(^-\). The Raman shift for even the most dilute LiFSI/DMC 1:24 solution still does not reach the value corresponding to free FSI\(^-\). S-N stretching (\(\sim 722\) cm\(^{-1}\)) found by deconvoluting the Raman spectra for LiFSI/DMSO 1:1.0 (mol/mol) solution shown in Figure S1. Therefore, it can be inferred that FSI\(^-\) is still coordinated to Li\(^+\) in the solvation structure in standard LiFSI/DMSO solutions.

DFT-predicted Raman shifts of bidentate (923 cm\(^{-1}\), two ester oxygens in the carbonate molecule interact with Li\(^+\), schematic shown in Figure 1c), monodentate (959 cm\(^{-1}\), carbonyl oxygen in the carbonate molecule interacts with Li\(^+\), schematic shown in Figure 1c) and free DMC (933 cm\(^{-1}\)) were compared to the normalized DMC band in Figure 1c by scaling the DFT-predicted Raman shift for free DMC to 915.3 cm\(^{-1}\). The value determined experimentally from pure DMC. The experimental Raman shift corresponding to coordinated DMC suggests that predominantly monodentate DMC is found in the solvation structures in both standard and concentrated electrolytes. Considering the molar ratio of LiFSI to DMC, the likely Li\(^+\) solvation structure in superconcentrated LiFSI/DMC 1:1.1 solution would contain one bidentate LiFSI and one monodentate DMC molecule (LiFSI-Bi-DMC-Mo). With this configuration, Li\(^+\) is coordinated by only 3 oxygens (one oxygen from monodentate DMC and 2 oxygens from bidentate FSI\(^-\)), which is lower than the common Li\(^+\) solvation number of four.\(^{24}\) Thus, in LiFSI/DMC 1:1.1 solution, Li\(^+\) is energetically frustrated and DMC interacts more strongly with Li\(^+\) than with concentrations \(c_{\text{DMC}}/c_{\text{Li}} \geq 4\), where Li\(^+\) is always coordinated by at
least 4 oxygens. As a result, a high frequency shift of the coordinated DMC band is observed, as discussed above.

The fractional integrated intensity contributions of the free (\sim 915.3 \text{ cm}^{-1}) and coordinated DMC (\sim 935 \text{ cm}^{-1}) were used to determine the Li+ solvation number, \(n\), where the solvation complex was given by [Li(DMC)]\(_n\). Detailed deconvolution spectra are shown in Figure S2. The fractional integrated intensities of Li\(_2\)-coordinated DMC increase linearly while those of free DMC decrease with increasing molar ratio of LiFSI/DMC for \(c_{\text{LiFSI}} / c_{\text{DMC}} \leq 0.25\) (LiFSI/DMC 1:4 or more dilute), as shown in Figure 1d. In less concentrated electrolytes such as LiFSI/DMC 1:10.8 and 1:24, the fraction of free DMC is much greater than the typical solvation number of Li\(^+\) in aprotic solvents (4–5), in agreement with previous work.\(^{29}\) On the other hand, the molar ratio of LiFSI/DMC 1:1.1 in the superconcentrated electrolyte is much greater than the typical solvation number of Li\(^+\). Assuming that the Raman scattering coefficients for free and coordinated DMC are identical, one can relate the fractional integrated intensity to \(n\), where \(I_f\) is the integrated intensity of the coordinated DMC peak, \(I_c\) is the integrated intensity of the free DMC peak and \(c_i\) is the molar concentration of species \(i\):\(^{24}\)

\[
\frac{I_c}{I_f + I_c} = \frac{c_{\text{DMC}(i)}}{c_{\text{DMC}}} = \frac{n_{\text{LiFSI}}}{c_{\text{DMC}}} - \frac{n_{\text{LiFSI}}}{c_{\text{DMC}}}
\]

The solvation number \(n\) was found by fitting the points where \(c_{\text{LiFSI}} / c_{\text{DMC}} \leq 0.25\) in Figure 1d, yielding the dotted line shown with a slope of 2.4 for \(n\). However, DFT calculations have shown that the scattering coefficients are not identical for free and coordinated vibrational modes in DMC; more accurate predictions should divide these solvation numbers by 0.93–0.95.\(^{28,29}\) Thus, we applied this correction to obtain a solvation number \(n\) of 2.5–2.6 (the number of solvent molecules coordinating with Li\(^+\)), indicating the predominant formation of [Li(DMC)]\(_n\) complexes. Therefore, the likely Li\(^+\) solvation structure in standard solution is one monodentate LiFSI and three monodentate DMC molecules (LiFSI-Mo-3DMC-Mo).

The stability of composite Al electrodes was investigated as a function of concentration via half-cell galvanostatic measurements. The charge/discharge curves with LiFSI/DMC 1:1.1 and 1:10.8 electrolytes in Figure 2a and Figure 2b exhibit the features that are to be expected with Li-Al half-cells, but also show enhanced capacity retention during cycling in the superconcentrated electrolyte. A clear plateau at 0.28 V\(_{Li}\) corresponds to the Li allaying reaction (Li\(_2\) + Al + e\(^-\) \rightarrow LiAl) and a plateau at 0.42 V\(_{Li}\) corresponds to the de-allaying reaction (LiAl \rightarrow Li\(^+\) + Al + e\(^-\)).\(^{7,6,9–71}\) The initial charging before reaching the lithiation plateau at 0.28 V\(_{Li}\) is due to reduction of the oxidized surface film,\(^8\) while the overpotential observed for the lithiation reaction can be associated with the nucleation of LiAl phase and the work required to deform the surrounding active material.\(^{72}\) The charge/discharge curves also show that there is no significant polarization resistance growth associated with SEI formation in both cases. The difference between the capacities reached with these practical cells (\sim 500 mAh g\(^-1\)) and the theoretical capacity of 993 mAh g\(^-1\) is due to a combination of the cutoff voltage, inhomogeneous reaction of the active material\(^{72,73}\) and the finite charging rate.\(^{74}\) Charge/discharge curves using LiFSI/DMC 1:4 and 1:24 (mol/mol) are shown in Figure S3. The charge/discharge curves for composite Al nanoparticle electrodes in both LiFSI/DMC 1:1.1 and 1:10.8 (mol/mol) electrolytes are shown in Figure S4, which exhibited capacities < 70 mAh g\(^-1\) and no clear lithiation plateau. Similar pseudocapacitive behavior has been reported in previous work with Al nanoparticle electrodes\(^{65,75}\) and has been linked to an increase in surface area for Al\(_2\)O\(_3\) formation and ability to accommodate mechanical stress during lithiation. As a result, there is a greater cumulative thickness and minimal cracking of Al\(_2\)O\(_3\) surface films such that Li\(^+\) is unable to penetrate through to the active material.\(^9\) Active material nanoparticles are therefore not a viable solution, in this case, to stabilize the electrode material and prevent fracture.

The enhanced capacity in superconcentrated LiFSI/DMC 1:1.1 compared to standard electrolyte concentrations is clear when the specific discharge capacity of the Li-Al half-cells is plotted against cycle number, as shown in Figure 2c. Notably in the case of the superconcentrated electrolyte, there is an initial dip in capacity reaching a minimum at approximately 5 cycles; however, there is an increase in capacity after approximately 15 cycles. Although the ionic conductivities of the standard LiFSI/DMC 1:10.8 and intermediate LiFSI/DMC 1:4 solutions are higher than the superconcentrated solution (Figure 1a), severe capacity fade was observed due to greater free carbonate activity and insufficient reduction of FSI\(^-\) in the electrolyte, leading to the formation of an ineffective SEI which cannot suppress continuous electrolyte decomposition. Unfortunately, Al electrodes cycled in the superconcentrated electrolyte dropped to a low capacity of \leq 100 mAh g\(^-1\) after 30 cycles, suggesting that the electrolyte is unable to stabilize the electrolyte-Al interface over extensive cycling (Figure 2c).

SEM images were used to discern the state of the electrode after cycling and confirmed that cycled Al electrodes were not stable over extensive cycling in both LiFSI/DMC 1:1.1 and 1:10.8 solutions. The SEM images in Figure 3 show that after 5 cycles, the Al particles in both superconcentrated and standard electrolytes fractured to a size of \sim 10 \mu m from an initial size of \sim 50 \mu m after the first cycle. EDX

Figure 2. Galvanostatic charge/discharge curves for Li-Al half-cells using (a) LiFSI/DMC 1:1.1 and (b) LiFSI/DMC 1:10.8 (mol/mol) solutions as the electrolyte with the 1\(^{st}\), 15\(^{th}\) and 30\(^{th}\) cycles shown. Galvanostatic cycling was conducted at 25°C and a rate of 0.1C based on the theoretical capacity of 993 mAh g\(^-1\) in a cutoff voltage range of 0.01 V to 2 V. (c) Specific discharge (de-lithiation) capacity of Li-Al half-cells vs. cycle number in LiFSI/DMC electrolytes. Molar ratios of LiFSI to DMC are shown. Galvanostatic cycling was conducted at 25°C and a rate of 0.1C based on the theoretical capacity of 993 mAh g\(^-1\) in a cutoff voltage range of 0.01 V to 2 V. For molar ratios of 1:1.1 and 1:10.8, the data shown is an average of three tests with error bars representing the standard deviation.
maps in Figure S5 confirm that the grains in question are indeed Al active material. The first dip in the discharge capacity seen in Figure 2c therefore corresponds to the fracture of the Al particles in the composite electrode. The capacity fade during cycling has been related to the depth of lithiation during charge, with cracking and delamination occurring during the volume contraction associated with delithiation.\textsuperscript{72,75} The lithiated LiAl phase has a brittle Zintl phase structure which if over-lithiated, will experience high stresses making it susceptible to fracture.\textsuperscript{72} SEM images taken after 15 cycles show that particle sizes are still \( \sim 10 \, \mu m \) and that fracture has occurred in both electrolytes, despite the large discrepancy in discharge capacity. SEM images of the electrode after 5 and 15 cycles in LiFSI/DMC 1:10.8 solution have much less particle definition than the corresponding samples in the superconcentrated electrolyte, which indicates thicker SEI buildup in the standard electrolyte. SEM images of pristine electrodes and after 30 cycles are shown in Figure S6.

EIS measurements were conducted with a three-electrode configuration to investigate impedance growth related to SEI formation as a function of electrolyte concentration. Two semicircles are typically observed in the Nyquist plot for a Li intercalation or alloying reaction into a composite electrode.\textsuperscript{9,44} It has been proposed that the higher frequency semicircle (left) corresponds to impedance at the electrified interface where Li\textsuperscript{+} migration and adsorption/desorption occurs in the pore structure, coupled with electron migration at the grain boundaries of the composite electrode. The low frequency semicircle (right) has been assigned to the charge transfer resistance through the electrolyte-electrolyte interface.\textsuperscript{44} Earlier studies have shown that the low frequency resistance grows with increasing SEI thickness, which is indicative of an increasing energy barrier for charge transfer through the SEI layer.\textsuperscript{5,44} The Nyquist plot in Figure 4a shows that the electrode held at 0.1 V\textsubscript{Li} in the superconcentrated electrolyte exhibited a very stable electrified interface impedance and charge transfer/SEI impedance with negligible increase after 10 hours. In contrast, the Nyquist plot for the electrode held in the standard electrolyte in Figure 4b shows that there was a continuous increase in charge transfer resistance linked to continuous growth of the SEI layer. On the other hand, the high frequency component did not increase over time in the standard electrolyte, which is consistent with its assignment to the electrified interface impedance (predominantly associated with Li\textsuperscript{+} migration in the pore structure) and should remain constant during a potential hold. Therefore, it can be inferred that the SEI formed in the superconcentrated electrolyte acted as a passivating layer which suppressed further electrolyte decomposition, whereas there was continuous SEI growth in the standard electrolyte.

XPS analysis on aluminum foil electrodes held at 0.01 V\textsubscript{Li} in LiAl half-cells revealed that a potential hold in the superconcentrated electrolyte formed an SEI layer with a greater LiF component than in the standard electrolyte. An aluminum foil electrode was used instead of a composite electrode to avoid any misinterpretation from the presence of conductive carbon and/or PVDF binder.\textsuperscript{91} The F1s photoemission lines in Figure 5 show that LiF and LiF\textsubscript{2} from the degradation of LiFSI, were found in the SEI from both standard and superconcentrated electrolytes. It is clear that after charging in the superconcentrated electrolyte, there was a greater contribution of LiF in the SEI than in the standard electrolyte, indicating that more FSI\textsuperscript{-} anion reduction had occurred. There is also an increase in the LiF contribution compared to the standard solution, which is simply due to the higher salt concentration in the LiFSI/DMC 1:1.1 solution.

In the Li1s spectra for the superconcentrated electrolyte, a greater LiF contribution is also observed along with reduced Al2p signals associated with aluminum oxides and aluminum metal. The reduced yet still detectable Al2p signals in the superconcentrated electrolyte indicate that the SEI layer was thicker than in the standard electrolyte after the first charge but remained thinner than the sampling depth of \( \sim 10 \, \text{nm} \) for XPS.\textsuperscript{98} The thick initial SEI layer formed in the concentrated electrolyte is likely to remain stable with further cycles, whereas the SEI layer in the standard electrolyte will grow thicker over time due to continuous electrolyte degradation.\textsuperscript{91} This conclusion is supported by the continuous growth of the low frequency charge transfer resistance in standard electrolyte concentrations, in contrast with the effectively constant resistance in superconcentrated solution, as previously shown in Figure 4. The contributions of C-O (\( E_{\text{b}} \sim 286.3 \, \text{eV} \))\textsuperscript{86} and CO\textsubscript{2} (\( E_{\text{b}} \sim 290.3 \, \text{eV} \))\textsuperscript{41} in the C1s spectra can be attributed to deposition of carbonaceous species associated with carbonate reduction and SEI formation in carbonate-based electrolytes.\textsuperscript{77,92} The greater intensity of these contributions in
the standard electrolyte suggests that more carbonate reduction had occurred in the first charge, which is consistent with the higher contributions from ROLi (E_b ∼ 531 eV) and surface O/CO/CO_3/CO (E_b ∼ 532 eV) in the O1s spectra.

To connect solvation structure with electrochemical stability, the lowest unoccupied molecular orbitals (LUMOs) of several coordination complexes were calculated. The LUMO can be used to describe the ability to receive electrons and the susceptibility toward reduction complexes were calculated. The LUMO can be used to describe the lowest unoccupied molecular orbitals (LUMOs) of several coordination complexes.

Conclusions

Raman spectroscopy was used to investigate the solvation structure of LiFSI in DMC. In standard concentrations, Li^+ forms solvates [Li(DMC)]_n FSI while [Li(DMC)]_n FSI is formed in superconcentrated solution. A combination of galvanostatic cycling tests and EIS measurements showed that Li-Al half-cells cycled in the superconcentrated electrolyte exhibited higher capacity and capacity retention than more dilute concentrations while maintaining an essentially constant charge transfer impedance. In contrast, the charge transfer impedance increased with time in the standard electrolyte. SEM images showed that the superconcentrated electrolyte was able to prevent buildup of resistive and non-passivating carbonate SEI but was unable to prevent fracture of active material particles. XPS analysis was used to detect a greater LiF concentration and a lower concentration of carbonate degradation products in the SEI layer after a potential hold in concentrated electrolytes.
Figure 6. Computed reduction energies and maps of the lowest unoccupied molecular orbitals (LUMOs) for Li+ solvation structures in LiFSI/DMC solutions: (a) bidentate LiFSI and monodentate DMC (b) monodentate LiFSI and three monodentate DMC. Reduction energies were calculated using B3LYP/6-31+ +G(d,p)/B3LYP/6-31G(d,p) in implicit methyl propanoate with the dielectric constant set to 3.1. Reduction energies for configurations (a) and (b) are shown in (c). The LUMO maps (isovalue = 0.02) were generated using the optimized geometries obtained at B3LYP/6-31G(d,p). Atom color code: gray – carbon, white – hydrogen, red – oxygen, purple – lithium, yellow – sulfur, blue – nitrogen, cyan – fluorine. The red and green regions represent the positive and negative parts of the orbital wave functions, respectively. Solvation structure (a) is likely in superconcentrated solution, while solvation structure (b) is likely in standard concentrations.

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