Towards high-voltage Li-ion batteries: Reversible cycling of graphite anodes and Li-ion batteries in adiponitrile-based electrolytes

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Abstract

Due to their low vapor pressure and their promising electrochemical and thermal stability, N=C-(CH2)n-C≡N dinitriles are proposed as an electrolyte solvent for Li-ion batteries. Adiponitrile (ADN) has substantial advantages, especially for applications requiring high potential cathodes, because it has high electrochemical/thermal stability (up to 6 V vs. Li/Li+) [120°C]. However, to obtain very high voltage batteries, ADN electrolytes must also passivate the anode of the battery. In this work, reversible cycling of graphite in adiponitrile was successfully achieved by adding a few percent of fluorethylene carbonate allowing the realization of Graphite/NMC Li-ion battery. The battery of specific capacity of 135 mAh g⁻¹ showed a cycling stability for more than 40 cycles. The composition of the solid electrolyte interphase (SEI) was determined as a function of the FEC concentration as well as the state of charge of the graphite anode using hard X-ray photoelectron spectroscopy (HAXPES) and XPS. With FEC, the SEI layer is thinner and depends on the SOC of the anode, but does not depend on the FEC concentration. SEM characterizations clearly showed that the surface of the anode is completely covered by the SEI layer, regardless of the concentration of FEC. Indeed, 2% of FEC is sufficient to suppress the reduction of adiponitrile which is explained by a specific adsorption of FEC on the graphite anode.

1. Introduction

Lithium-ion batteries (LiB) have now become the most popular type of rechargeable batteries for portable electronics [1,2] and larger scale applications such as electric vehicles [3–6]. As the demand for stored energy is increasing, it is critical to increase the specific energy of this kind of batteries. For that, there are two ways, which can be combined: (1) is to increase the cell voltage and (2) is to increase the specific capacity of the active materials both at the cathodic and anodic sides. New materials such as Ni-rich LiNi,MnₓCo₁₋ₓO₂ (NMC: 4.45 V) and LiNi,MnₓO₂ (LMNO: 4.9 V) [7] are able to reach, at least partially, this goal. Nevertheless, the question of the electrolyte stability at high voltages remains open. The main difficulty is to find an electrolyte formulation which will be compatible with a low voltage anode such as graphite and a 4.5–5 V class cathode. For this purpose, fluorinated alkyl carbonates [8] and solvents highly resistant to oxidation like dinitriles (DN) [9–11] or sulfones [12,13] have been proposed. As a matter of fact, dinitriles like glutaronitrile or adiponitrile (ADN) or sulfones like ethylmethysulfone or tetramethylsulfone [9,10,14,15] are exceptionally stable at high potentials and until at least 5.5 V [16]. As displayed in Table 1, DN (NC-(CH2)n-CN) exhibit interesting properties such as high boiling points (over 250°C), low vapor pressures at ambient temperature, flash points are over 100°C [17] and self-ignition temperatures over 450°C [15]. Hence, they can be considered as hardly flammable solvents. As the LD₅₀ is relatively low, which is the amount of a toxic agent that is sufficient to kill 50% of a population of animals usually within a certain time, DN are considered toxic by ingestion or inhalation but without the potential for bioaccumulation [18]. Based on available data and according to EU regulation (EC) 1272/2008, ADN is not classified as dangerous for the environment. DN are able to solubilize many compounds (ionic or not) and even though the solubility of lithium hexafluorophosphate [LiPF₆] is too low for battery applications [11], lithium bis[(trimethylsilyl)imide] (LiTFSI), lithium bis(oxalato)borate (LiBOB) and lithium tetrafluoroborate (LiBF₄) are readily...
soluble [17]. Hence, DN are very good candidates as solvents for battery electrolyte as they exhibit a high dipole moment for solvating Li⁺ ions and high dielectric constant (ε₉ > 30) for salt dissociation. The specific gravity is slightly under 1 g cm⁻³ at room temperature which is advantageous in term of weight but their high viscosity could be considered as a major drawback as it will strongly affect the ion mobilities. ADN has been chosen as solvent as it presents one of the best compromises among available DN (n = 2 to 5) in terms physical properties and safety. When using a graphite anode, the quality of the solid electrolyte interphase (SEI) layer is critical to achieve high cycle life and high rate performances of Li-ion batteries. However, SEI layers formed on graphite anodes when using pure DN solvents are not stable and cycling can only be achieved by adding a co-solvent to the electrolyte like EC or DMC [19]. Another solution to this problem can be the use of SEI-forming additives such as FEC. These are expected to build a uniform deposit on the electrode surface and to form a mechanically and chemically stable coating. Successful SEI-forming candidates are already known like vinylene carbonate (VC) [20,21] or fluoroethylene carbonate (FEC) [22], and their ability to form stable films on graphite [23–25] has been proved.

In earlier works, Abu-Lebdeh and co-workers have investigated mixtures of dinitriles and cyclic alkyl carbonate as a possible safe and stable electrolyte for Li-ion batteries. Based on their work, good performance could be obtained using a mixture containing 50:50 (v:v) % of dinitriles: ethylene carbonate. Furthermore, Duncan et al. have investigated a series of binary and ternary solvent mixtures containing aliphatic dinitriles with alkylcarbonates. However, these authors highlight that good electrochemical performance in a Li/LiMn₁.₅Ni₀.₅O₄ Li-ion half-cell could be only achieved using high alkylcarbonate concentrations, e.g. higher than 50% by volume.

In this work, we report on the impact of adding FEC to adiponitrile-LiTFSI electrolyte on the cyclability of graphite anode in lithium-ion batteries. The effect of FEC was investigated as a function of its concentration in electrolytes using SEM observations, electrochemical cycling and impedance spectroscopy. The surface chemistry of the graphite anode was studied using different FEC contents and state of charge of the electrode. Moreover, the performance of graphite/NMC full lithium-ion batteries is reported.

The ADN based electrolyte used in this study contains lithium bis-(trifluoromethane sulfonyl) imide (LiTFSI) as lithium salt instead of the more popular LiPF₆. The advantages of using LiTFSI is its solubility in ADN and its chemical and thermal stability. Moreover, it is not sensitive to traces of water and hence does not decompose to HF, POF₃, and other harmful compounds.

### 2. Experimental

#### 2.1. Electrolyte, solvent mixture and cell preparation

Adiponitrile (ADN) (99%) and Fluoroethylene carbonate (FEC) were commercially available from Aldrich, metallic lithium from Alfa Aesar. Lithium bis-(trifluoromethane sulfonyl) imide (LiTFSI) was purchased from Solvionic and used as received. FEC is used as received without any further purification. However, ADN was used after distillation under partial vacuum in our laboratory.

Electrolyte preparations and cell assembly were carried out under a dry argon atmosphere in a glove box (MBraun) (<1 ppm of O₂ and H₂O). The electrolyte used was 1 M LiTFSI in Adiponitrile (ADN) (reference electrolyte). FEC was added with an amount of 2 and 10% by mass to the respective electrolyte formulations.

Half-cells and full-cells were fabricated with two-electrode Teflon Swagelok or coin-cell systems with metallic lithium foil as the counter electrode. Graphite/Li half-cells were tested using graphite Timcal SLP 30 coated on a copper disk current collector (1 cm diameter, average loading: 5.1 mg cm⁻²) as working electrode and metallic lithium as counter electrode. LiNi1/3Mn1/3Co1/3O2 (NMC)/Graphite full cells were also performed. The NMC cathodes consisted of 90 wt% active mass (Umicore MX6 for NMC), 5 wt% Super P carbon and 5 wt% of PVDVF5130 in an organic medium coated on an aluminum disk current collector (1 cm diameter, average loading ~14.1 mg cm⁻²). A microporous glass-fiber paper (WHATMAN, pore diameter Φ = 16 μm) filled with the electrolyte solution was used as a separator. Graphite and NMC electrodes and separators were dried at 80 °C under vacuum for 24 h under vacuum. They were then transferred and stored in a glove box (MBRAUN UniLab) with water contents and O₂ < 10 ppm.

#### 2.2. Experimental methods

Density and viscosity measurements were carried out from 10 °C to 80 °C using an Anton Parr digital vibrating tube densitometer (model 60/602, Anton Parr, France) and an Anton Parr rolling-ball viscometer (Lovis 2000 M/ME, Anton Parr, France), respectively. In both cases, the cell temperature was regulated within ±0.02 °C. Dynamic viscosity values reported in this paper were calculated by taking into account the effect of the sample density and the buoyancy of the ball in each sample as a function of temperature. The densitometer was firstly calibrated at all temperatures with degassed water and dehumidified air at atmospheric pressure as recommended by the manufacturer while ultra-pure water was used to calibrate the viscometer. The uncertainty of the density and viscosity measurements were better than 5 × 10⁻⁵ g cm⁻³ and 1%, respectively.

#### 2.3. Electrochemical methods

Electrochemical measurements were recorded on a multi-channel potentiostatic—galvanostatic VMP system (Biologic) for galvanostatic charge-discharge and electrochemical impedance spectroscopy. Two batteries were cycled for each test to check the reproducibility of the measurements. Galvanostatic charge-discharge tests were carried out under C/20 rate using cutoff potentials of 0.02 V vs. Li/Li⁺ for discharge and 2 V vs. Li/Li⁺ for a charge. The electrochemical impedance spectroscopy (EIS) measurements were performed at the open circuit voltage, with frequency of 1 MHz—10 MHz, and signal amplitude of 50 mV.
2.4. Surface characterization

The morphologies of the electrodes after cycling were investigated by scanning electron microscopy using Zeiss ULTRA Plus Field Emission Microscope. The organic components of the SEI layers were characterized by Fourier Transform Infrared (FT-IR) Spectroscopy.

For the photoelectron spectroscopy (PES) analysis of the SEI formation, the graphite electrodes were cycled in Gr/Li half-cells using coin cells to the specified voltages (OCV, 0.9 V after expected FEC decomposition, 0.02 V fully lithiated, 1.5 V delithiated). In total, three different electrolyte compositions were studied: i) ADN-LiTFSI (1 M) (no additive), ii) ADN-LiTFSI (1 M) +2 wt% FEC, iii) ADN-LiTFSI (1 M) +10 wt% FEC. After the electrochemical cycling, the electrodes were retrieved from the batteries, washed twice in DMC solvent and then dried under vacuum to remove residual electrolyte solvent and lithium salts. Samples were shipped to Uppsala for the PES measurements. The samples were characterized by Fourier Transform Infrared (FT-IR) Spectroscopy.

Spectroscopy.

Additionally, hard x-ray photoelectron spectroscopy was performed using a PHI 5500 spectrometer with monochromatized Al Kα radiation (1486.6 eV). The spectra were recorded at 23.5 eV pass energy and 0.1 eV step size. Additionally, hard x-ray photoelectron spectroscopy was performed at 2005 eV and 6015 eV excitation energies to probe deeper into or even through the SEI layers to the bulk active material. These hard x-ray photoelectron spectroscopy (HAXPES) measurements were carried out at the HIKE instrument (KMC-1 beamline) at the synchrotron facility BESSY II at Helmholtz-Zentrum Berlin. All obtained spectra are referenced in binding energy with respect to the surface hydrocarbon at 285 eV and represented normalized to the total peak area to allow changes in relative intensities. Data evaluation was performed using Multipak V6.1A and Igor Pro 6.34A software packages as well as tabulated atomic sensitivity factors.

Contact angle measurements were performed using Krüss DSA 10 optical instrument (version 1.90.014) using the “sessile drop fitting” method in a chamber at a temperature of 25 °C. The measurements were made by depositing three or four drops of the electrolyte in several places on graphite surface, to check the reproducibility of the measurements. The contact angle, on the right and left, is then measured by digitizing the image displayed on the screen of the computer that controls the device. The average of the two measurements of the contact angle is calculated.

The surface tension (γSL), contact angles (θ) and solid-liquid interfacial energy (γSL) has been determined for a graphite electrode immersed in ADN-LiTFSI electrolyte solutions containing FEC. The dispersive (γLd) and polar (γLp) components of the surface tension of the electrolyte and the free interface energy between the solid and the liquid (γSL) were then calculated using the Young models [27] (Equation (1)) and Owens-Wendt [28] (Equation (2)):

\[
\cos \theta = \frac{\gamma_S - \gamma_L}{\gamma_L}
\]

And:

\[
\gamma_L = \gamma_{Ld} + \gamma_{Lp}
\]

\[
\gamma_{SL}(1 + \cos \theta) = 2\sqrt{(\gamma_{Ld} + \gamma_{Lp}) + 2\sqrt{(\gamma_{Ld}p + \gamma_{Lp})}}
\]

The surface energy (γS) of the graphite electrode is deduced from the contact angle data of two reference solvents, for which γLd and γLp are known, using the Owens and Wendt approach previously described [29].

3. Results and discussion

3.1. Electrochemistry

The passivation layer formation during cycling using dinitrile electrolyte solvents is studied on graphite negative electrodes. For this purpose, ADN has been used as electrolyte solvents and LiTFSI as a lithium salt. In order to compare the impact of the SEI-forming additives on the graphite anode, an amount of 2 wt% and 10 wt% in FEC will be added to the electrolyte formulation. Galvanostatic cycling results obtained in lithium half-cell and the two first cycles are reported in Fig. 1 at a charge/discharge rate of C/20 from 2 to 2.4.

Fig. 1. Galvanostatic cycling of a graphite sample in ADN based electrolytes with LiTFSI 1 M with or without FEC.
20 mV vs. Li/Li$^+$ for the three electrolyte formulations (no additive, 2 wt% FEC, and 10 wt% FEC).

In the case of LiTFSI-ADN without additive, the irreversible capacity (120 mAh.g$^{-1}$) at the first cycle (Fig. 1a) is very high and the reversible capacity is 199 mAh.g$^{-1}$. In the second cycle (Fig. 1b), the reversible capacity drops significantly to only 29 mAh.g$^{-1}$.

The shape of the delithiation curve for the electrolyte without additives shows that there is an important ohmic drop probably related to a very resistive interface and low permeability to lithium ions. The profile of the charge/discharge curves with FEC (2 and 10 wt %) shows a significant improvement in the reversibility of the graphite electrode.

On the galvanostatic charge-discharge curves we can clearly distinguish the action of the additives which drastically reduce the irreversible charge between 1 and 0.25 V during the first cycle, then, a typical behavior of a lithium ion insertion into the graphite electrode can be observed as seen by the insertion plateaus between 0.25 and 0.02 V vs Li/Li$^+$. The delithiation capacities obtained at the first cycle is 338 and 350 mAh.g$^{-1}$ in the presence of 2% and 5% FEC respectively. This capacity increases of about 10 mAh.g$^{-1}$ during the second cycle. In order to evaluate the efficiency of this passivation layer, the irreversible capacity and the reversible capacities at the first and the 5th cycles have been determined and the results are reported in Table 2.

In order to study the passivation layer in detail, dQ/dV curves at the first cycle are reported in Fig. 2. In the case of ADN without additives, almost no de-intercalation peaks of Li$^+$ between 0 and 0.3 V are observed. The zoom (1) in the potential range between 0.2 and 1.4 V vs. Li/Li$^+$ shows a peak at 0.4 V in ADN-LiTFSI (1 M) without FEC, which can be attributed to the ADN reduction and corresponds to the potential plateau observed in Fig. 1 lower voltages than alkyl carbonates (0.8V-0.6 V) [30]. The absence of lithium de-intercalation peak means that the surface of the graphite electrode is totally blocked by the ADN decomposition products. When FEC is used in the electrolyte, on zoom (1) it can be noted that the peak at 0.4 V (of ADN reduction) is no longer visible, whereas new peaks appear at potentials below 1.4 V vs. Li/Li$^+$. These peaks correspond to FEC reduction on graphite: 1.1 V and 1.2 V for 2 and 10% FEC, respectively, which is comparable to literature [24]. These reduction potentials are situated above that of ADN. Therefore, FEC forms an SEI earlier than ADN and prevents or at least significantly minimizes reductive ADN decomposition on the graphite surface. The graphs show that the reduction potential is shifted to higher values as the additive quantity increases.

Furthermore, FEC is previously adsorbed on the electrode surface before being reduced due to the symmetrical shape of the peak. This reduction peaks, although the adsorbed amount remains constant since the electrical charge due to FEC reduction remains almost the same independent of the initial FEC concentration in the electrolyte. This could indicate that surface saturation by FEC is reached as early as 2%. This may explain why the SEI formed by FEC always exhibits similar electrochemical properties even by varying the

Table 2
Cycling results for Gr/Li half cells using ADN-LiTFSI (1 M) with or without FEC.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>1st cycle</th>
<th>5th cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_lithiation (mAh$^{-1}$)</td>
<td>C_delithiation (mAh$^{-1}$)</td>
</tr>
<tr>
<td>ADN</td>
<td>318.2</td>
<td>199.5</td>
</tr>
<tr>
<td>ADN +2%FEC</td>
<td>406.1</td>
<td>338.7</td>
</tr>
<tr>
<td>ADN +10%FEC</td>
<td>397.6</td>
<td>348.05</td>
</tr>
</tbody>
</table>

Fig. 2. Differential dQ/dV curves vs. Li/Li$^+$ for Gr/Li half cells in ADN-LiTFSI (1 M) with or without FEC.
amount of FEC in the electrolyte. These results show that 2% by weight of FEC is sufficient to obtain a reversible behavior of the graphite electrode in ADN based electrolyte.

Table 3 shows that the addition of FEC additive induces a decrease of the contact angle as well as that of the free interfacial energy. This implies that the additive increases the wettability of the electrode material. $\gamma_{SL}$ values decrease in presence of FEC, this means also that the additive is the is preferentially adsorbed at the S/L interface [29]. The fact that the $\gamma_{SL}$ do not vary significantly with the additive concentration (from 5 to 10%) means that the surface is almost saturated even at low contents (5%). Hence selective adsorption occurs which could explain why similar quantity of charge is obtained for FEC reduction regardless the concentration (Fig. 2).

The evolution of the delithiation capacity of Gr/Li half cells with FEC-containing electrolyte is shown in Fig. 3a. Cells were cycled for 5 cycles at C/20 (in order to stabilize the SEI and the electrolyte/FEC-containing electrolyte is shown in Fig. 3a. Cells were cycled for 350 mAh/g. The delithiation capacity is stable and the values are about 14.5 mAh/g at C/20 and 33 mAh/g at C/10 with significant capacity retention for at least 35 charge/discharge cycles.

The evolution of coulombic efficiencies upon cycling is shown in Fig. 3b. The 1st cycle, the efficiency is about 84% in presence of 2% FEC and 87% in presence of 10% FEC. However, it increases to reach values higher than 96% from the 2nd cycle and close to 100% from the 5th cycle for both electrolytes.

3.2. EIS measurements

Electrochemical impedance spectroscopy analysis was used in order to study the interfacial reactions between the electrolyte and the lithium metal. Fig. 4 shows the impedance changes for a symmetrical Li/Li cells in ADN without and with 10% FEC, measured at different storage times. The impedance spectra present two semi-circles: the first one in the high frequencies domain corresponds to the SEI layer formed on the Li electrodes, and the second one at low frequencies corresponds to the charge transfer resistance at the Li/SEI interfaces [31,32]. The impedance spectra are fitted using an equivalent circuit which comprises two $R/Q$ branches in series ($R_1+ R_2/Q_2 + R_3/Q_3$) where $R_1$ represents the resistance due to the electrolyte/separator, $R_2$ the SEI layer resistance, and $R_3$ the charge transfer resistance. $Q$ is a constant phase element representing a no ideal capacitance ($Q_2$ is for the SEI layer capacitance and $Q_3$ is for the double layer capacitance).

The role of the additive is clearly observed in the changing shape of the spectra, and it affects both semi-circles. The additive lowers the charge transfer resistance and more importantly, it stabilizes its value since no increase of the diameter of the low frequencies semi-circle was observed over time. $R_{SEI}$ is higher in the presence of FEC, however, the charge transfer resistance is much lower than that obtained without additive. It can be seen that the SEI evolves over time, which is probably due to its destruction/reconstitution during the dissolution/deposition of lithium during the application of amplitude (50 mV). However, we can note that the charge transfer resistance remains almost constant in the presence of FEC.

Impedance measurements of Gr/Li half cells in ADN-based electrolytes were performed in presence of FEC. Results obtained at the end of the 1st the 2nd lithiation (at 20 mV vs. Li/Li') are displayed in Fig. 5 (a and b) for two FEC concentrations. The spectra consist of two flat capacitive semi-circles, typical of an intercalation anode material at the end of its lithiation followed by a sloping line at lower frequencies. Generally, the high-frequency semi-circle is assigned to the SEI/graphite interface ($R_{SEI}$) and the lower-frequency semi-circle is assigned to the charge transfer resistance ($R_{ct}$) [33,34]. It is worth noting that the impedance spectra recorded for the Gr/Li half-cell show some similarity with the spectra already shown for Li/Li cell. However, the characteristic frequencies of the semi-circles are different. Moreover, the presence of the sloping line at very low frequencies is characteristic of an insertion anode material. At low frequency, the evolution of the spectra is attributed to diffusion into the electrode material (Warburg) and the interception with the abscissa axis at the high frequencies region represents the resistance of the electrolyte $R_s$. Since these spectra have

![Fig. 3](image-url)
been recorded using a half-cell containing a polarized reference to lithium, it is not possible to exclude a contribution of the lithium electrode to the total cell impedance. It is thus difficult to interpret accurately the evolution of the electrolyte/graphite interface independently of that of the lithium electrode. These EIS spectra are therefore discussed qualitatively in terms of the evolution of the contributions on the two interfaces of the cell (graphite and lithium).

In order to determine the $R_{\text{SEI}}$, the impedance spectra are fitted using a simplified Randles circuit (inserted in Fig. 5a) with: $R/C$ reflects the electrode/electrolyte interfaces (SEI on the two electrodes) in series with $R/C$ which translates the charge transfer to the electrodes (mainly on the graphite due to the very high reversibility of metallic lithium). The values of $R_s$ and $R_{\text{SEI}}$ at the end of the 1st and 2nd lithiation are given in Table 4. The evolution of $R_s$ between the first and the second cycle is larger for ADN without FEC (33–306 Ω) than for electrolyte with FEC (15.9–13.5 for 2% FEC and 43 to 51 for 10% FEC). This could be attributed to the irreversible consumption of the electrolyte during the electrode passivation during the first cycles, which has been already reported in the literature [35,36]. However, the $R_s$ value is stable with 2% FEC and increases slightly with 10% FEC, but remains much lower compared to the value obtained without additive. The $R_s$ values show the impact of FEC, which limits the irreversible consumption

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**Fig. 4.** Impedance spectra of Li/Li cells in ADN-LiTFSI with and without FEC. The impedance spectra are recorded at T = 2 h after assembling the cell (a) and at T = 10 h (b). Measurements were conducted at 25 °C. In insert of figure a, the electrical equivalent circuit obtained by fitting impedance data.

**Fig. 5.** Impedance spectra after 1st (a) and 2nd (b) lithiation for Gr/Li half-cells cycled in ADN with 2 wt% and 10 wt% FEC, respectively. In insert of figure a, the electrical equivalent circuit obtained by fitting impedance data.
of electrolyte and the consequent drop in conductivity due to the irreversible reduction of the electrolyte. The results show that the resistances to the interfaces (RSEI) are lower in the presence of additives. RSEI values obtained with 2 and 10% FEC are similar, in good agreement with the obtained irreversible capacities already shown in Table 2.

After the 2nd lithiation, a strong increase of the impedance (RSEI) is observed in ADN without additives, thus confirming the blocking character of the SEI in this case. When FEC is used in the electrolyte, RSEI is stable between 1st and 2nd lithiation and an increase of only of 15 Ω for 2% FEC and 2 Ω for 10% FEC, respectively, is observed. The results obtained by the EIS measurements are thus in good agreement with our previous observations on the impact of the additives on the formation of a less resistive, more stable interface.

### 3.3. SEM observation

The morphology of the graphite electrodes before and after cycling in ADN based electrolytes was visualized by scanning electron microscopy and the images are displayed in Fig. 6. The comparison of SEM images of uncycled graphite electrode and electrodes cycled in ADN shows clearly the formation of a surface film in all cases but its morphology and nature differ depending on the electrolyte composition. For the samples cycled in ADN without FEC (Fig. 6b), the graphite electrode is coated with a porous, filamentous and inhomogeneous layer. Overall, this layer also seems to be thicker. As we can see, the addition of the additive clearly modifies the morphology and the electrode surfaces are completely covered with a compact surface layer which appears to be quite homogeneous.

The figure shows that the SEI layer formed in the presence of 2 and 10% FEC has a similar morphology with a granular shape. Generally, a porous structure is related to a gas evolution during the SEI formation reaction. The presence of a thick layer without FEC may explain the poor cyclability as the electrode seems blocked. Thus, the SEM observations appear to be in agreement with the previously discussed electrochemical results. This means that the SEI layer is ineffective and that it is not surprising that no cycling can be achieved.

### 3.4. XPS analysis

The SEI formation on graphite in ADN based electrolytes is studied using XPS in order to investigate the composition of this layer and the influence of the FEC additive. The surface analysis was carried out as a function of i) the potential of the graphite (OCV (not cycled), 0.9 V, 0.35 V, 0.02 V and discharged at 1.5 V) and ii) the electrolyte composition (no additive, 2% FEC, 10% FEC). The spectra for carbon, fluorine and nitrogen are shown in Fig. 7. Furthermore, oxygen, sulfur and lithium spectra were recorded and are shown for completeness in the supplementary information.

The C1s spectra of the graphite electrodes cycled to various states of lithiation for the three different electrolyte compositions are shown in Fig. 7a. For the non-cycled electrodes (i.e. OCV), the C1s spectra dominated by the graphite peak (CC) at 284.2 eV and a hydrocarbon peak

### Table 4

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>1st lithiation</th>
<th>2nd lithiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs (Ω)</td>
<td>Rs (Ω)</td>
<td>RSEI (Ω)</td>
</tr>
<tr>
<td>ADN</td>
<td>33</td>
<td>229</td>
</tr>
<tr>
<td>ADN + 2% FEC</td>
<td>15.9</td>
<td>146</td>
</tr>
<tr>
<td>ADN + 10% FEC</td>
<td>43</td>
<td>150.9</td>
</tr>
</tbody>
</table>

Fig. 6. SEM images of graphite electrodes before and after cycling in the three different electrolyte formulations.
Fig. 7. C1s, F1s, and N1s, spectra of graphite electrodes in 1 M LiTFSI in ADN electrolyte without additive (left), with 2% FEC (middle) and with 10% FEC (right).
(CH) at 285 eV independent of the electrolyte composition. Furthermore, carbon-oxygen groups (at 286.8 eV and 288.6 eV) can be observed which most likely stem from the CMC binder. Additionally, a low intensity CF$_3$ peak from LiTFSI salt residues can be observed at 293 eV. Upon cycling, for all electrolyte formulations, the graphite peak intensity decreases and the hydrocarbon intensity increases. Despite the different electrolyte formulations, the C1s spectra are similar in structure. Therefore, it is reasonable to believe that the newly evolving peaks stem from the common electrolyte components such as the salt. In the early cycling stages, this is further supported by the presence of LiF in the F1s spectra (Fig. 7b) and new Sulfur species in the S2p spectra (see SI Fig. S1). According to Shterenberg [37], the salt TFSI anion can decompose at potentials < 1 V vs Li$^+$/Li to compounds including C$_6$F$_3$Li and C$_3$F$_5$SO$_2$Li. The C$_2$Fx fragment gives rise to a peak at about 290 eV [37], shaded in red in Fig. 7a. In the case of the FEC containing electrolytes, this signal overlaps with the carbonate peak from the FEC reduction. In the case of 2 and 10% FEC, further carbonate-additive characteristic SEI components such as ethers (286.5 eV), carboxylates (288.8 eV), and esters (288 eV) are observed.

The two sets of samples cycled in FEC-containing electrolytes show very similar C 1s spectra during cycling. However, at potentials of 0.35 V and 0.02 V vs Li$^+$/Li, the carbonate and potentially CHF$_2$OCO$_2$ type compounds at 291 eV binding energy are more pronounced in case of 10% FEC possibly related to the higher lithium concentration in the electrolyte.

At 0.02 V vs Li$^+$/Li (fully lithiated), no graphite peak can be observed anymore independent of the electrolyte formulation indicating an SEI thickness larger than the XPS probing depth of approximately 10 nm. At 1.5 V (delithiation), for the FEC containing electrolytes, the graphite peak can be observed again indicating reduced SEI thickness. This is not the case when no additive is present, thus the SEI remains fairly thick in this range, in agreement to the SEM-observations.

The effect of the FEC additive can be further seen in the F1s spectra (Fig. 7b).

In the F1s spectra for all electrodes and electrolyte compositions, a LiTFSI salt peak can be observed at 689 eV. In the OCV state, all samples, in addition, show LiF contribution at 685 eV binding energy. This indicates salt instability even at open circuit potential and is in agreement to recent observations of chemical decomposition in the Mg$_2$TFSI-DME system [38].

After cycling the electrodes to 0.9 V, the relative LiF intensity increases for the electrolytes containing FEC which is a further indication for the desired FEC decomposition at this cycling stage. Interestingly, in case of no additives, the LiF component almost disappears at the lithiated state (0.02 V). This coincides with an additional peak observed in the N1s spectra (Fig. 7c) of this electrode at approx. 399 eV binding energy. Due to the absence of clear LiF signal for the 0.02 V sample without additive as well as no indication of pronounced salt decomposition in the S2p spectra for this voltage (see Fig. S1 in supporting information), this additional N1s contribution could indicate ADN solvent decomposition at low potentials vs Li$^+$/Li. This decomposition of ADN leads most likely to a R–N=N–R' and polymeric compounds such as poly (ethylenimine) [39], giving rise to the intensity increase around 398–399 eV binding energy. As this is not observed for the samples cycled in electrolytes containing FEC, the additive seems to form an SEI that can prevent solvent decomposition at low potentials. This can potentially explain why cycling graphite in di-nitrite electrolytes without carbonate-based electrolytes does not work with high reversibility.

### 3.5. Evaluation of the surface composition

Using the integrated areas of the elemental peaks as well as tabulated, instrument specific atomic sensitivity factors [40], the surface composition of each sample was calculated. The results are given in Table 5. The sodium contribution stems from the Na-cellulose salt used as a binder.

Generally, the carbon content decreases during cycling for all electrolyte compositions. This is most likely due to the coverage of the graphite surface by surface layer components. Interestingly, the fluorine content is in the range of 3–9% for all samples (except in case of 2% FEC cycled to 0.02 V). This reflects that the main F contribution stems from the SEI-incorporated salt or salt residues on the surface and is therefore not dependent on the FEC concentration in the electrolyte.

The reduced salt contributions in case of 0.02 V in the 2% FEC electrolyte could be due to local inhomogeneity as well as a more efficient washing for this specific sample. The very low salt contributions can also be observed in the core level spectra in the very high noise level for the F1s, N1s, and S2p emissions for that specific sample.

Independent of the electrolyte formulation, the Lithium content increases from below 10% for the OCV and 0.9 V samples to around 15% (and even higher for the 10% FEC electrolyte) when the samples were cycled to 0.35 V and lower. This can indicate increased SEI formation incorporating lithium species (such as LiF, Li$_2$O, Li$_2$CO$_3$) in ROLi) but also the beginning of lithium insertion to graphite, which usually starts around 0.4 V vs Li$^+$/Li. Only in the case where 10% FEC were used in the electrolyte, a decrease in lithium concentration can be observed after the batteries underwent a delithiation step up to 1.5 V.

| Table 5 | Element composition of the graphite surface film for samples cycled in ADN electrolyte without additive, with 2% and 10% FEC. |
|---|---|---|---|---|---|---|---|---|
| No additives | OCV | 69% | 15% | 7.7% | 1.4% | 2.1% | 3.8% | 0.2% |
| | 0.9 V | 61% | 23% | 4.1% | 1.7% | 1.0% | 9.0% | 0.1% |
| | 0.35 V | 50% | 30% | 2.7% | 1.7% | 0.7% | 15% | 0.3% |
| | 0.02 V | 58% | 24% | 3.9% | 2.0% | 1.1% | 12% | 0.0% |
| | 1.5 V | 42% | 33% | 4.9% | 2.0% | 1.4% | 17% | 0.1% |
| 2% FEC | OCV | 76% | 11% | 5.7% | 0.9% | 1.4% | 4.0% | 0.5% |
| | 0.9 V | 59% | 22% | 7.6% | 1.1% | 1.0% | 8.8% | 0.4% |
| | 0.35 V | 60% | 24% | 3.7% | 0.8% | 0.6% | 11% | 0.2% |
| | 0.02 V | 65% | 21% | 0.9% | 0.2% | 0.3% | 12% | 0.0% |
| | 1.5 V | 51% | 27% | 5.8% | 1.1% | 1.2% | 13% | 0.5% |
| 10% FEC | OCV | 66% | 17% | 8.6% | 1.0% | 2.1% | 4.8% | 0.3% |
| | 0.9 V | 73% | 17% | 4.3% | 0.7% | 0.8% | 3.9% | 0.4% |
| | 0.35 V | 45% | 31% | 6.2% | 1.0% | 0.5% | 16% | 0.6% |
| | 0.02 V | 35% | 36% | 3.8% | 0.6% | 0.6% | 23% | 0.1% |
| | 1.5 V | 45% | 30% | 6.2% | 1.1% | 0.9% | 16% | 0.5% |
3.6. HAXPES analysis

To gain further understanding on how the SEI on graphite is built up in case of ADN-FEC based electrolytes, cycled graphite electrodes were also characterized using hard x-ray photoelectron spectroscopy (HAXPES). This analysis was performed on graphite electrodes cycled vs. Li metal as counter electrode using 1 M LiTFSI in ADN electrolyte including 10% FEC. The same cut-off-potentials as in section 2.4 were chosen (i.e. OCV, 0.9 V, 0.35 V, 0.02 V, and 1.5 V). In addition, graphite electrodes after 10 (7 for in-house) complete cycles of lithiation and delithiation were characterized. In Fig. 8, the C 1s and O 1s spectra recorded at 2005 eV and 6015 eV.
excitation energy are shown in comparison to the in-house XPS data (see also Fig. 7 a, SI) to visualize the depth evolution.

Generally, the spectra obtained using synchrotron radiation show the same features for carbon and oxygen as observed in-house. One important difference to highlight is however that the detection of the bulk graphite peak (CC) even for the fully lithiated sample (see Fig. 8a) is possible using these higher excitation energies. Thus, one can estimate, that the SEI thickness in case of the electrolyte containing 10% FEC is above 10 nm (probing depth for in-house) but below 20 nm which corresponds to the approximate information depth for 2005 eV excitation energy.

Additionally, clear relative binding energy shifts between surface hydrocarbon (CH) and bulk graphite (CC) depending on the degree of lithiation can be observed. This is in line with our recent publication [41] on interpreting HAXPES results from battery electrodes and is attributed to an electric potential gradient at the interface between SEI and bulk electrode material. Interestingly, the relative binding energy shift between the CC and the CH peak in case of the electrode cycled 10 times and left in delithiated state is closer to the shift for the fully lithiated electrode after than to that after 1 cycle in delithiated state. The magnitude of the relative binding energy shift between surface and bulk seems to correlate to the presence of Li2O (see Fig. 8b). A pronounced Li2O signal could only be detected for the samples that showed a very pronounced relative peak shift between CH and CC, i.e. for the sample after the first complete lithiation and after 10 cycles. Furthermore, Li2O becomes more visible using higher excitation energies and therefore seems to accumulate in the deeper layers SEI or at the buried interface.

### 3.7. Proof of concept: high voltage graphite NMC full cells using ADN-based electrolyte

After studying ADN based electrolytes in the Gr/Li, Gr/NMC full cells were assembled in order to examine the compatibility and the electrochemical performance using this electrolyte. On the other hand, we have already reported in our previous results [42], that there is no corrosion of aluminum current collectors, used for the positive electrode, which may occurs in ADN-LiTFSI based electrolyte. ADN-LiTFSI (1 mol L−1) with 10% FEC was used as electrolyte, based on the results obtained in half-cells. Fig. 9 shows first and second galvanostatic charge/discharge curves of Gr/NMC cells at C/20 in potential window of 3−4.2 V. The first cycle shows good cycling of Gr/NMC batteries with a discharge capacity of 135 mAh.g−1 and irreversible capacity of 24 mAh.g−1 (Table 6). At the 5th cycle, the discharge capacity decreases to 124 mAh.g−1 which means a loss of 10 mAh.g−1 after 5 cycles.

The irreversible capacity loss is almost ten times lower in the 5th cycle than in the 1st, i.e. 2.6 mAh.g−1 with 10% FEC. Assuming that most capacity losses are due to interfaces stabilization and SEI formation, this could indicate that such phenomena only take place during the few first cycles.

Fig. 10 shows the variation of discharge capacity at different scan rates from C/20 to C/5 for Gr/NMC cells in ADN+10%FEC. As we can show, discharge capacities decrease from 120 mAh.g−1 at C/20 to 115 mAh.g−1 at C/15, and to 105 mAh.g−1 when C/5 rate is applied. Moreover, a long cycling at C/10 rate was performed and shows a 10% decrease of the capacity after 45 cycles compared to the initial value (Fig. 10b). This result is somewhat interesting since similar performances have been already shown using alkyl carbonate based electrolyte [43,44]. The capacity fading has been described by other groups as cathode active materials losses and dissolution. Several strategies have been used to improve NMC cathode cyclability [45–48]. However, such issues are out of the scope of the present study.

### 4. Conclusion

In this paper, we evaluated the effect of SEI-forming additives in ADN-LiTFSI based electrolyte. Dinitriles hold the promise of realizing high voltage batteries due to their improved stability against oxidative decomposition as compared to the traditionally used carbonate solvents. However, nitriles are known for their inherent inability to form stable SEI on graphite. Our study shows that they can, however, be used if additives, favoring the formation of a stable and conductive SEI layer, are added. In a first step, an in-depth Gr/Li half-cell study was carried out in ADN without additive. The results confirmed that this electrolyte is not compatible with graphite anodes. This is related to the decomposition of the electrolyte solvent which leads to a blocking surface layer which seems to be impermeable for Li ions. However, in presence of FEC, an additive known for its ability to efficiently passivate the graphite anode, a marked improvement in reversible capacity is observed and values close to the theoretical values for graphite at the first charge/discharge are obtained (330−350 mAh.g−1) stable for more than 35 cycles. The results show that a small percentage of additive (2%) may be sufficient to improve the behavior of the graphite anode in ADN. SEM images confirm the presence of a homogeneous and covering SEI on the surface of the electrodes. Surface analysis by XPS and HAXPES shows that the composition of the surface layers is rather similar for ADN-based electrolytes in the early stages of the

### Table 6

Charge, discharge and irreversible capacities at 1st and 5th cycles for Gr/NMC full cells cycled in ADN-LiTFSI with 10% FEC.

<table>
<thead>
<tr>
<th>ADN-LiTFSI + 10%FEC</th>
<th>1st cycle</th>
<th>5th cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{charge}}$ (mAhg$^{-1}$)</td>
<td>$C_{\text{discharge}}$ (mAhg$^{-1}$)</td>
<td>$C_{\text{irrev}}$ (mAhg$^{-1}$)</td>
</tr>
<tr>
<td>159</td>
<td>135</td>
<td>24</td>
</tr>
<tr>
<td>126.9</td>
<td>124.3</td>
<td>2.6</td>
</tr>
</tbody>
</table>
References


[21] L. El Ouattari, R. Dedryvere, C. Siret, P. Biensan, S. Reynaud, P. Iratxabal, D. Gonbeau, The effect of vinylene carbonate additive on surface film electrochemical cycling, which seems mostly due to chemical instability of the LiTFSI salt. At lower potentials, the composition differs and in case of no additive and ADN solvent decomposition could not be prevented. Combined with the electrochemical results, it seems that these solvent decomposition products that lead to a Li-ion blocking surface film on graphite. With the additive FEC, solvent decomposition seems minimal at low potentials and the final SEI composition is comparable to other carbonate-based SEI layers. Moreover, electrochemical impedance measurements and XPS analyzes indicate that in the presence of the additives the formed SEI is thinner, more stable and therefore more permeable for Li ions and favorable to the charge/discharge processes. Furthermore, promising electrochemical performances and cyclability have been proven using adiponitrile-based electrolyte in graphite/NMC full cells. Indeed, the battery exhibited a specific capacity of 135 mAh g⁻¹ and only 10% capacity fading during cycling which is comparable to batteries using alkyl carbonate based electrolyte. These promising results obtained using Li-ion full cell battery open new perspectives in developing safer and more stable electrolytes for high voltage Li-ion batteries.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2018.05.133.

Fig. 10. Evolution of discharge capacity as a function of the scan rate (a) and cycle number at C/10 (b) of the Gr/NMC cells cycled in ADN-LITFSI with 10% FEC.


[34] X. Li, J. Liu, M.N. Banis, A. Lushington, R. Li, M. Cai, X. Sun, Atomic layer deposition of solid-state electrolyte coated cathode materials with superior high-voltage cycling behavior for lithium ion battery application, Environ. Sci. (2017) 7, 768, https://doi.org/10.1039/C6EE42704A.


