



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, $\text{N}\equiv\text{C}-(\text{CH}_2)_n-\text{C}\equiv\text{N}$ 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^+ , $> 120^\circ\text{C}$). 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 fluoroethylene carbonate allowing the realization of Graphite/NMC Li-ion battery. The battery of specific capacity of $135 \text{ mAh}\cdot\text{g}^{-1}$ 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.

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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 $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC: 4.45 V) and $\text{LiNi}_x\text{Mn}_y\text{O}_2$ (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 ethylmethylsulfone 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 ($\text{NC}-(\text{CH}_2)_n-\text{CN}$) 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 LD_{50} 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 (LiPF_6) is too low for battery applications [11], lithium bis(trimethylsulfonyl)imide (LiTFSI), lithium bis(oxalato)borate (LiBOB) and lithium tetrafluoroborate (LiBF_4) are readily

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Table 1
Thermal, physical properties and median lethal dose LD₅₀ of selected dinitriles N≡C-(CH₂)_n-C≡N (n = 2 to 5) [26].

n	name	Vapor pressure/Pa	M _p /°C	B _p /°C	F _p /°C	LD ₅₀ /mg/kg ⁻¹
2	Succinonitrile (SN)	1.04 (25 °C)	53	265	113	129
3	Glutaronitrile (GLN)	<100 (25 °C)	-29	287	>110	266
4	Adiponitrile (ADN)	0.09 (20 °C)	2.3	305	163	155
4	2-Methyl-glutaronitrile (MGLN)	1.9 (20 °C)	-45	213	132	
5	Pimelonitrile (PMN)	2.0 @ 25 °C	-31	175	112	126

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 ($\epsilon_r > 30$) for salt dissociation. The specific gravity is slightly under 1 g cm³ 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/LiMn_{1.5}Ni_{0.5}O₄ 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 sensible 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 PVdF5130 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 $\phi = 1.6 \mu\text{m}$) 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 ultrapure 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.

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