Ethylene Carbonate-Free, Adiponitrile-Based Electrolytes Compatible with Graphite Anodes

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Adiponitrile-based, ethylene carbonate-free electrolytes were investigated for a use in room temperature, 4.5V Li-ion batteries including graphite electrodes. The use of DMC as co-solvent in a 1/1, (wt/wt) ratio and the incorporation of lithium bis(fluorosulfonyl)imide (LiFSI) and lithium difluorooxalatoborate (LiDFOB) anions allows reaching conductivities of 5.8 mS cm⁻¹ and 3.4 mS cm⁻¹ at 20°C, respectively. Electrochemical stability windows of more than 5.0V were obtained with both salts. The cycling of graphite electrodes of *c.a.* 7.5 mg cm⁻² is demonstrated with LiDFOB, even without the use of SEI additives, given the SEI-forming properties of the salt. The addition of fluoroethylene carbonate allows improving further the electrolyte performance to 99.9% efficiency. As for cathode operation, cycling of 15 mg cm⁻² LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ was achieved in the 3V - 4.5V potential range (Vs Li⁺/Li) with only a 0.2% capacity decay per cycle.

Introduction

Increasing the energy density of Li-ion batteries to push further their application for powering electric vehicle implies, at the material level, increasing either the electrodes capacity or the battery (i.e. cathode) operating voltage. However, the limiting factor for operating cathodes at high voltage, be them NMC above 4.3[1], or LiMn_{1.5}Ni_{0.5}O₄ up to 4.8V - 5.0V, is the limited anodic stability of state-of-the-art alkyl carbonates-based electrolytes. Thus, the use of alternative solvents such as alkyl-sulfone, ionic liquids, fluorinated alkylcarbonates has been proposed[2].

Among them, aliphatic alkyl dinitrile (CN(CH₂)_nCN, n = 3-8), and adiponitrile (ADN, n = 4) in particular, offer high anodic stabilities[3,4]. However, the preparation of high-energy Li-ion cells requires, in most cases, the use of graphite-based anodes. Thus, solutions have to be found for the operation of graphite electrodes, given their insufficient cathodic stability and poor ability to form solid electrolyte interphase (SEI) [5,6] at the surface of graphite, which is a prerequisite for it suse a Li-ion anode..

In fact, using EC as co-solvent in ADN-based electrolytes allowed the cycling of either full graphite/LiCoO₂ cells or graphite half-cells with either LiTFSI [3] or LiBF₄[7]. However, EC is considered responsible for both the poor low temperature performance of the electrolytes[8] and their failure at high voltage[1] and efforts have thus been directed toward EC-free electrolytes as well. Gmitter *et al.*[8], in particular, demonstrated successful cycling of MCMB/LiCoO₂ cells, by

using VC or FEC as additives and LiBF_4 as a co-salt for a LiTFSI/ADN-based electrolyte. However, as MCMB are known for allowing the use of PC-based electrolytes, which are usually incompatible with graphite[9], the possibility of operating graphite anodes with adiponitrile, EC-free electrolytes have not been demonstrated up to now.

In fact, the low solubility of typical inorganic salts such as LiPF_6 and LiBF_4 in pure alkyl dinitriles initially led toward the use of LiTFSI[3], a salt with high thermal and electrochemical stability and low lattice energy. However, this salt does not possess intrinsic SEI forming ability (when used as single salt in the electrolyte) and it induces Al current collector corrosion. However, other salts, such as lithium difluorooxalatoborate (LiDFOB) and lithium bis(fluorosulfonyl)imide (LiFSI) are good candidates for substituting LiPF_6 as they provide enhanced SEI forming ability in various type of electrolytes. In addition, they are usually more soluble in organic solvents, including those with lower dissociating properties than typical EC mixtures. Thus, we report here on the electrochemical characterizations of EC-free electrolytes based on ADN:DMC mixtures with LiDFOB or LiFSI , for a use in 4.5V, graphite-based, Li-ion batteries at room temperature.

2. Experimental part

Electrolyte preparation: ADN (Aldrich, 99%) was distilled under vacuum and dried on molecular sieve at room temperature until the water content dropped below 20 ppm as determined by coulometric Karl-Fischer titration (KF 851 Titrand, Mettler Toledo). Dimethyl carbonate (DMC) (BASF, Selectilyte™) and fluoroethylene carbonate (FEC) (BASF, Selectilyte™) were used as received. The lithium salts were either used as received (LiPF_6 (BASF, Selectilyte™, 99.99%)) or dried under vacuum for 48h at 80°C for LiDFOB (Aldrich), and 90°C for LiFSI (PROVISO CZ). Electrolyte solutions were prepared and stored in a Mbraun glove box filled with argon (< 1 ppm H_2O & O_2).

Electrode preparation: Graphite electrode of 96 wt% active mass loading and 7.5 mg cm^{-2} were provided by CEA-LITEN (France). $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ electrodes of 86 wt% active mass loading and 15 mg cm^{-2} were purchased from Custom Cells (Germany) and used as received

Electrochemical testing: All electrochemical testing was done in 3 electrode Swagelok™ cells assembled in a glove box (MBraun) with O_2 and H_2O level below 1 ppm with Li counter and reference electrodes (99.99%, Rockwood lithium) using a stack of 6 layers of Freudenberg FS2026 non-woven polypropylene separator drenched with 200 μl of electrolyte. Voltamperometries were performed on a VMP3 (Bio-logic) potentiostat-galvanostat and cycling was done on a Maccor 4300 with cells placed in a temperature controlled chamber (KB400, Binder GmbH) at 20°C. Conductivities were measured using a, impedance-based conductimeter (MCS10, Bio-Logic) between -60°C and 25°C using a steps of 5°C with 20 minutes ramps in between each steps 5°C per step going from high to low temperature. The electrodes were charged using a constant current step at C/10 for the first two cycles and C/2 for the following cycles, followed by a constant voltage step using a C/50 current limit. A Full-cell was assembled using the same electrodes and cycled in two electrode configuration with similar cycling protocol, excepted for the constant voltage step at the cut-off voltage during charge.

3. Results and discussion

3.1. Conductivity of the electrolytes

The conductivity curves of the 1M ADN/DMC (1/1, wt/wt) electrolytes are shown in Figure 1. It is worth mentioning that the 1M LiPF₆ electrolyte was not liquid at room temperature, but had the appearance of a gel-like paste, probably due to insufficient solubility of LiPF₆ or to the formation of solid LiPF₆/solvent complexes. Accordingly, the conductivity curve has an irregular shape with several transitions. The conductivities stays well below those of the two other salts tested with only c.a. 1 mS cm⁻¹ at 20°C. For LiFSI, a conductivity of 5.8 mS cm⁻¹ is reached at 20°C while that of LiDFOB is lower at 3.3 mS cm⁻¹. For comparison, the conductivity of the 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) + 0.1M lithium bis(oxalate) borate (LiBOB) and 1M LiBF₄ + 0.1M LiBOB in EC:ADN (1/1, v/v) are 3.6 mS cm⁻¹ [10] and 2.1 mS cm⁻¹ [4] respectively. The LiFSI electrolyte stayed liquid until -20°C before crystallizing, which is on the curve as a strong conductivity drop. The LiDFOB electrolyte start partially crystallizing between -5°C and -10°C, which translates to a deviation to the Vogel-Tammann-Fulcher (VTF) behavior below this point with a further crystallization occurring below -20°C which induces a stronger conductivity drop.

Figure 1: Conductivity plot of the 1m ADN/DMC (1/1, wt/wt) electrolytes

3.2. Electrochemical stability windows

Figure 2 shows the voltamperograms of the 1M electrolytes electrochemical stability window for the 1M ADN/DMC electrolytes. In reduction, only low background currents between 7 and 11 $\mu\text{A cm}^{-2}$ are observed before Li metal plating occurs, probably due to electrode passivation. On the anodic scan, the two electrolytes containing FEC exhibit similar decomposition potential at *c.a.* 5.5V. The LiFSI, FEC-containing electrolyte exhibits the strongest background oxidation current, which, however, does not raise above 5 $\mu\text{A cm}^{-2}$ even in this case. The LiDFOB electrolyte without additive decomposes at lower potential, at *c.a.* 5.2V.

Figure 2: Voltamperogram of 1M ADN/DMC (1/1, wt/wt) electrolytes at 0.1 mV s^{-1} . WE: Pt (anodic scan) and Ni (cathodic scan), RE & CE: Li

3.3. Graphite electrode cycling

Figure 3a. shows the cycling performance of standard high mass loading graphite electrodes in 1M LiDFOB ADN/DMC electrolytes with and without the addition of 2 wt% FEC as SEI forming additive. The efficiencies in the first cycles are rather high in both cases, with respectively 90.4% and 92.2%. It is remarkable, considering the absence of EC as solid electrolyte (SEI) forming co-solvent. The efficiencies then raise above 99.9% for the FEC containing electrolyte, whereas those of the additive-free electrolyte stays lower and only reach 99.7%. It is possible that, in half cells, especially with high mass loading electrodes, the Li metal electrode influences the efficiency results, as FEC might as well favor quick SEI formation/reformation at the counter

electrode as well and limit shuttling of electrolyte reduction products to the cathode. The capacity retention is rather high in both cases with, however, an advantage for the FEC containing electrolyte.

Figure 3: Graphite electrodes 7.5 mg cm⁻² cycled in 3 electrode cells in 1M LiDFOB, ADN/DMC (1/1, wt/wt) with or without FEC (a) Comparison of cycling stability and efficiency (b) Comparison of voltage profiles for selected cycles (1C = 372 mA g⁻¹)

As can be seen on the potential profiles, shown in figure 3b, the lithium insertion and de-insertion plateaus are well defined at C/10 for both electrolytes, but at C/2, only c.a. 175 mAh g⁻¹ are inserted during the constant current step in the 3rd cycle. Because of the higher ohmic drop, only the two first insertion plateau are then seen upon lithium insertion. In addition, over cycling, the voltage

profiles evolves with more marked ohmic drops. While in the case of the electrolyte without FEC, the slope during de-insertion becomes more marked, due to Li^+ transport limitation by diffusion, in the case of the FEC-containing electrolyte, mainly a ohmic drop effect is seen and the curves remain relatively parallel to each other's upon cycling. It probably results from a better SEI formation on the surface of graphite in the FEC-containing electrolyte (*i.e.* a more protective and thinner SEI in which limited diffusion occurs and which does not lead to as much accumulation of degradation products on its outer layer upon cycling). In the case of the FEC-free electrolyte, although a SEI forms and allows graphite operation, it is probably less protecting and grows over time, which could explain the increase Li^+ transport limitations over cycling (electrode clogging) and would be consistent with the lower efficiencies observed. On the other hand, increased ohmic drop could simply be a result of electrolyte consumption at the Li counter electrode (even in 3 electrode cell configuration, as the reference electrode is placed in between the graphite electrode and the counter electrode, half of the ohmic drop linked to the electrolyte resistance is still seen on the potential profiles).

3.4. Cycling of $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ up to 4.5V

Figure 4a. shows the cycling stability of a commercial 7.5 mg cm^{-2} standard NMC electrode in 1M LiDFOB ADN/DMC + 2 wt% FEC. As can be seen, the capacity retention at C/2 is rather good with only a 0.2% decay per cycle at C/2, although the capacity cycled at C/2 is somewhat low, as compared to what can be reached in conventionnal 1M LiPF_6 EC/DMC electrolyte. The corresponding voltage profiles are shown on figure 4.b and show that the ohmic drop at the beginning of the charge decreases between the first and second cycle, but then increases. As this corresponds to Li plating step, it is likely that

Figure 4: NMC electrodes cycled in half-cell in 1M LiDFOB with 2w% FEC, ADN/DMC (1/1, wt/wt), cycling stability and efficiency

3.5. Graphite/NMC full cell

To confirm the role of Li metal counter electrode, a full cell was assembled, using the same electrodes (i.e. not balanced for full cell at 4.5V) and the voltage profiles at C/10 and C/2 are shown in figure 5. As can be seen, the charged at C/2 is, in this case much closer to that at C/10, with only

limited increase of ohmic drop at the beginning of the first charge at C/2 and similar charged capacities as at C/10, which shows that the lithium metal electrode does affect the ohmic drop significantly. Unfortunately, at C/2, Li plating occurs upon charge, as seen upon discharge by the location of the first graphite plateau, which is detrimental for cycling stability and result into a lowering of overvoltage during the first charge at C/2.

Figure 5: Voltage profile of a Graphite/NMC full cell at C/10 (2nd cycle) and C/2 (3rd cycle). Specific capacity refers to the cathode.

Conclusion

The conductivities and electrochemical stability window of AND/DMC electrolyte containing 1 M LiFSI and or LiDFOB have been measured to be in the range of commercial li-ion electrolytes for LiFSI and slightly lower for LiDFOB. The LiDFOB electrolyte as been shown to allow graghte cycling with and without the addition of FEC as SEI forming additive and cycling efficiencies above 99.9% have been achieved with the use of FEC as well as stable capacities, using a constant voltage step. However, in half-cells, lithium insertion is slow and only a fraction of the full graphite capacity can be reached at C/2 during lithium insertion. Cycling of NMC cathode was also possible with a 0.2% capacity decay per cycle. A full-cell was assembled to asses the influence of the Li metal electrode in half cells and it was found that, although the cathide is oveerdimensionned, the ohmic drop at the beginning of charge is reduced in this case, although lithium platig occurs before the end of the charge and result in short cycle life in the following cycles. While this result are preliminary, the composition of the SEI formed on graphite in the absence of EC deserves further investigations.

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