Short communication

New electrolytes based on glutaronitrile for high energy/power Li-ion batteries

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A B S T R A C T

Glutaronitrile, $CN[CH_2]_3CN$, is evaluated as a co-solvent in thermally and (anodically) electrochemically stable electrolyte mixtures suitable for high energy/power Li-ion batteries. Linear sweep voltammetry scans indicate an electrochemical anodic stability of more than 6 V versus Li^+/Li for the 1 M LiTFSI electrolytes. Glutaronitrile and its ethylene carbonate electrolyte solutions show high ionic conductivities and low viscosities reaching $5\,mS\,cm^{-1}$ and 7 cP, respectively, at 20 °C. Aluminum corrosion tests of the solutions showed an improved protective resistance up to 4.4 V. Lithium ion batteries incorporating graphite as an anode and $LiCoO_2$ as the cathode material were assembled using a glutaronitrile electrolyte mixture, whose stability on graphite was greatly enhanced by the use of ethylene carbonate as a co-solvent and Li (bioxalatoborate) (LiBOB) as a co-salt, and these cells showed moderately good discharge capacities with low capacity fade up to the 100th cycle.

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1. Introduction

The use of Li-ion batteries in portable consumer electronics has proven to be so highly successful that there is a great deal of interest not only in enhancing their performance for consumer electronics but also in extending their use to other applications [1,2]. One application that is under intensive research and development is electrical storage systems for electric vehicles in their different forms as pure (EV), hybrid (HEV), and plug-in hybrid (PHEV) [3]. This application is more demanding on the battery and requires an enhancement of its specifications particularly, increasing the power and energy densities and cycle life, and most importantly, rendering them safer and lowering their cost [4]. One way to increase the energy density of the battery and possibly its capacity is to use new cathode materials operating at high voltages, that unfortunately current electrolytes based on organic carbonates cannot typically sustain [5,6]. Another disadvantage of the carbonate mixture electrolytes are their volatile, flammable and the highly corrosive salt typically used in these electrolytes (namely $LiPF_6$). These issues could be overcome by using more thermally stable solvents and a less reactive salt.

From the work of Makoto Ue et al. on double layer capacitors it was demonstrated that aliphatic dinitrile solvents like gluotaronitrile (GLN) ($n = 3$) and adiponitrile (ADN) ($n = 4$) exhibit exceptional

resistance to electrochemical oxidation to voltages reaching as high as ∼5 V versus SCE (∼8.3 versus Li^+/Li) [7,8]. This extra stability is much higher than that of most aprotic solvents used in Li-ion batteries including those from carbonate family and even the more-stable sulfone family [9,10]. Despite the high stability and excellent physical and thermal properties of some mono- and di-nitriles, their use in rechargeable Lithium batteries has been long perceived as infeasible due to the ease of reduction of nitriles by common anode materials such as lithium metal or graphite, which does not result in the compact, ionically conducting SEI, necessary for the functioning of the battery. We recently revisited the subject and demonstrated that this incompatibility can be overcome in the case of the graphite anode by the addition of known SEI forming solvents like ethylene carbonate (EC) or salts like LiBOB. In our previous work, we reported on aliphatic dinitrile solvents, $CN[CH_2]_nCN$ with various alkane chain lengths ($n = 3$–8) and showed that their 1 M LiTFSI electrolyte solutions exhibit a 6 V electrochemical window, measured using a platinum microelectrode [11,12]. The two solvents with the shortest alkane chain in the study, GLN ($n = 3$) and ADN ($n = 4$) show the best thermal (high boiling point, flash point) and physical (high dielectric constant, low viscosity) properties of all the dinitrile solvents, with GLN being slightly superior due to the shorter alkane chain. GLN has been briefly mentioned in a few patents as a possible solvent electrolyte [13], or an electrolyte additive [14] for capacitors or batteries and it has also been used in $\bar{I}/\bar{I}_3$ redox electrolytes for dye sensitized solar cells [15]. As far as we are aware, there is no detailed study on the physical and electrochemical properties of lithium electrolytes based on GLN and herein we report on the

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results of that investigation, and for the first time the Li-ion battery performance using graphite as anode.

2. Experimental

The electrolytes were prepared by dissolving the appropriate amount of the lithium bis-(trifluoromethanesulfonly)imide salt, LiTFSI, (3 M), and in some cases, lithium bioxalato borate, LiBOB (chemmetal) into the solvent (glutaronitrile, Fluka) or solvent mixtures (ethylene carbonate, Aldrich) at the appropriate ratios. The electrolyte solutions were mixed properly and if necessary heated until complete dissolution. Conductivity measurements were performed using the AC impedance spectroscopy technique where the electrolyte solutions were poured into a two-platinum-electrode conductivity cell with a cell constant of 0.96. The frequency was swept between 1 kHz and 1 Hz using a Solartron Frequency Analyzer. The temperature was varied between −20 and 80 °C allowing 20 min^{-1} for thermal equilibration. Cyclic and linear sweep voltammograms were realized with a platinum microelectrode (Ø 25 μm) for the electrochemical window measurements or with aluminum wire (Ø 0.58 mm) for corrosion studies, and using in both cases a silver wire as a counter and pseudo reference electrode. The true potential was established with butyl-ferrocene (Aldrich) and was found to be around 3.2 V versus Li$^+$/Li. The scan rate was 10 mV s^{-1} and all measurements were conducted at ambient temperature.

Battery investigations were carried out with coin-type cells. Cathode and anode materials were prepared by mixing 85:5:5:5 (w/w) ratios of active material, carbon black, super S and poly(vinylidene difluoride) binder dissolved in *N*-methyl pyrrolidinone, respectively. The resulting pastes were applied to an aluminum or copper foil current collector and then were dried, first at room temperature and then at 150 °C under vacuum for 2 days. A Celgard® separator (30 μm thickness) was put between the electrodes and soaked with electrolyte. The cells were assembled in an Ar-filled dry box at room temperature. Cell performance was evaluated by galvanostatic experiments carried out on a multichannel Arbin battery cycler. The cells were first charged and then discharged at constant current density (*C*/12) between two 2.5 and 4.1 V at 20 °C. Differential scanning calorimetric analysis was performed using a TA Instruments 2920. All the samples were sealed in aluminum pans inside an Argon-filled glove box and then scanned from −100 to 150 °C at 10 °C min^{-1} rate. Viscosity measurements were conducted using a CANNON® viscometer (E455, 100). All experiments and handling of chemicals were performed in an Ar-filled glove box.

3. Results and discussion

3.1. Electrochemical stability

Glutaronitrile is a liquid with a melting point of −29 °C, a boiling point of 287 °C and a flash point of 110 °C. It shows a viscosity of 5.3 cP and has a high dielectric constant of 37. This makes it the aliphatic dinitrile solvent with the best thermal and physical properties. Electrolytes of GLN and the lithium salt LiTFSI were prepared and the salt dissolved readily over all concentrations. The 1 M electrolyte solution was used to record an anodic voltammetry scan on a Pt microelectrode (25 μm) and is shown in Fig. 1. The scan was first recorded using the as-received GLN solvent, which has a light brown color, and showed an irreversible oxidation plateau that starts at 4 V versus Li$^+$/Li before the oxidation of the electrolyte at 6.3 V, that is mainly due to imide anion oxidation, which is known to be less stable compared to other delocalized anions such as PF6$^-$ [16]. The plateau is mainly due to the presence of impurities rather
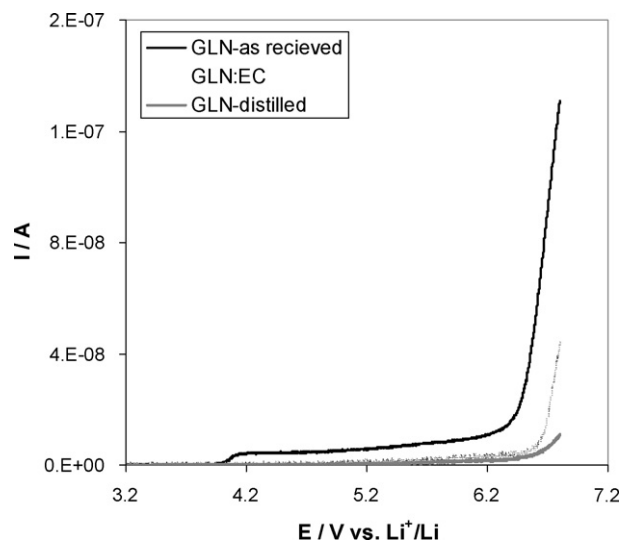

Fig. 1. Linear sweep voltammetry scans of a 1 M LiTFSI electrolyte solutions in GLN before and after purification and in a GLN:EC solvent mixture (1:1 by volume) recorded on a Pt electrode (25 μm) at a scan rate of 10 mV s^{-1}.

than what was suggested by Angell et al. as a slow oxidation of dinitriles [9]. This is supported by the CV scans of the rest of the liquid dinitriles, not shown here, [14] and our earlier work on the plastic crystal dinitrile, succinonitrile (*n* = 2) [17] that showed no apparent oxidation peaks before that of the TFSI$^-$ anion. After purifying GLN by double distillation the solvent became colorless and when its anodic scan was recorded, the oxidation plateau near 4 V disappeared. However, a gradual increase in the current was observed at around 5 versus Li$^+$/Li, and ongoing more positive in the voltage it increased significantly until eventually showed decomposition at 6.5 V versus Li$^+$/Li. Fig. 1 also shows the anodic scan of the GLN:EC (1:1 by volume) electrolyte, that exhibit a similar behavior to the distilled GLN with a slightly higher oxidation currents. We have previously discussed the electrochemical stability of aliphatic dinitriles with an alkane chain length between 3 and 8 and showed that they all exhibit remarkable anodic stability that is higher than what is reported for carbonate and sulphone-based electrolytes, and even ionic liquid electrolytes [14]. As shown here and elsewhere in the text, GLN is an exception and its abnormality is brought about by the presence of impurities and we believe that a more sophisticated and efficient purification method should improve its anodic stability.

3.2. Conductivity and viscosity measurements

The room temperature conductivity of LiTFSI electrolyte solutions in GLN and GLN:EC (1:1 by volume) were measured as a function of concentration using an AC impedance spectroscopy technique and the results are is shown in Fig. 2. The conductivity of the two systems follows a typical behavior by increasing gradually at low concentrations and going through a maximum, in this case, around the 1 M concentration. Then the conductivity decreased at higher concentrations possibly due to ion pairing or to a viscosity increase. The maximum conductivities observed were 3.8 mS cm^{-1} in the case of the GLN and 4.9 mS cm^{-1} for the GLN:EC electrolyte solution. EC shows a significant increase in the conductivity of the electrolyte solutions throughout the concentration range. The conductivity of the 1 M electrolyte solutions were also measured as a function of temperature in the range between −20 and 80 °C as shown in, Fig. 3. The conductivity increased from 0.4 mS cm^{-1} at −20 °C to 1.7 mS cm^{-1} at 20 °C and reaching 8.0 mS cm^{-1} at 80 °C.
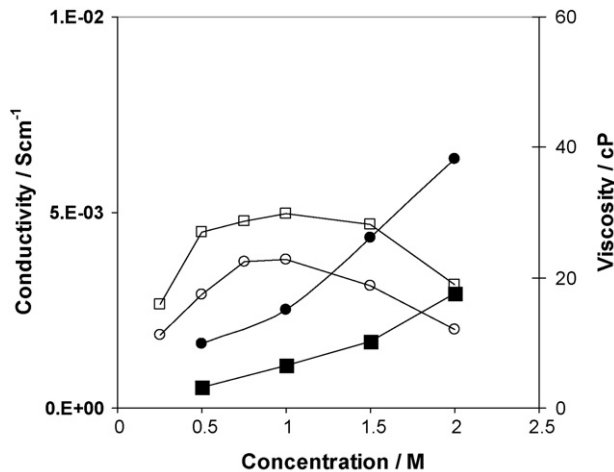
Fig. 2. Conductivity (open) and viscosity (filled) as a function of concentration of LiTFSI in GLN (circles) and its EC electrolyte solutions (squares).

The EC showed a significant increase in the conductivity which was more profound at low temperatures. It increased from $0.6\,mS\,cm^{-1}$ at $-20\,°C$ to $3.6\,mS\,cm^{-1}$ at $20\,°C$ and reaching $12.3\,mS\,cm^{-1}$ at $80\,°C$.

The viscosity of the GLN solvent was measured at room temperature and found to be 5.8 cP, a value that increased to 15.8 cP by the addition of LiTFSI (1 M) and even higher to 27.2 cP for the 1.5 M solution explaining the decrease in the high-concentration-end of the concentration-conductivity figure. We also separately investigated the effect of EC on the viscosity of GLN and found that it decreased from 5.8 to 2.8 cP, upon the addition of EC in 1:1 by volume, which in turn increased to 7.5 cP when LiTFSI (1 M) was added. A slightly higher viscosity 8.2 cP was obtained for the higher concentration solution of LiTFSI (1.5 M). We can see that EC has a positive effect in off-setting the viscosity increase due to the addition of LiTFSI bringing it to a level similar in value to that of neat GLN.

3.3. DSC scans

Fig. 4 shows the DSC scans of the 1 M LITFSI GLN and GLN:EC electrolytes. It can be observed that the GLN electrolyte showed
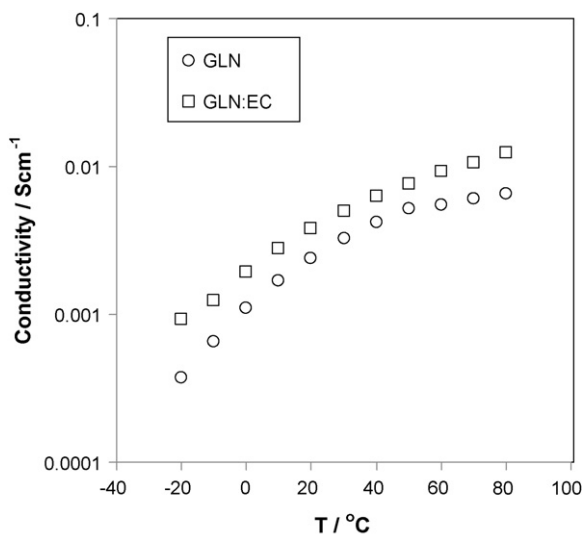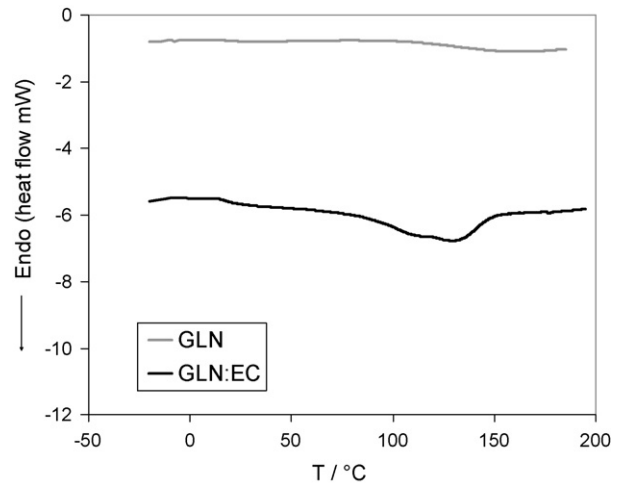

Fig. 4. DSC scans of 1 M LiTFSI electrolyte solutions of GLN and of GLN:EC (1:1 by volume).

good thermal stability at low temperatures but undergoes a slow evaporation process at $110\,°C$ and that peaks at $165\,°C$ in the tested temperature range between -20 and $180\,°C$. This could be attributed to the presence of impurities that are still present after purification by double distillation as evidenced also by the voltammetric scans. One possible impurity is 1,3-dibromopropane the precursor that is used to synthesize GLN by reacting it with KCN, that has a boiling point of $165\,°C$, the same evaporation temperature observed in the scan [18]. The GLN:EC electrolyte mixture on the other hand showed similar stability but in this case a broad but small peak appear in the scan and is centered at around $130\,°C$.

3.4. Battery performance

We have previously reported on the use of dinitriles, specifically ADN with an alkane chain length of 4, in Li-ion batteries utilizing an incompatible graphite anode, and showed that the use of a co-solvent, ethylene carbonate, and a co-salt, LiBOB, in the electrolyte mixture stabilizes the graphite/dinitrile interface, and that the battery shows good cyclability [15]. This behavior was also corroborated by in situ IR measurements of the interface
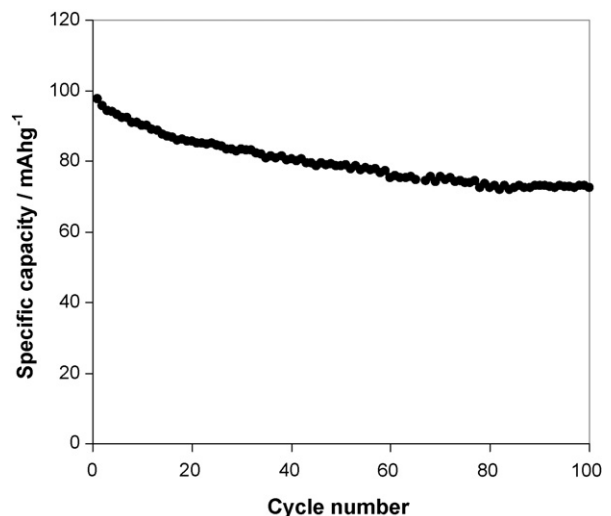

Fig. 3. Conductivity as a function of temperature of the 1 M LiTFSI in GLN and in GLN:EC (1:1 by volume) electrolyte solutions.

Fig. 5. Cycling performance of a MCMB/LiCoO₂ battery at C/12 rate incorporating the 1 M LiTFSI, 0.1 M LiBOB in GLN:EC (1:1 by volume) electrolyte.
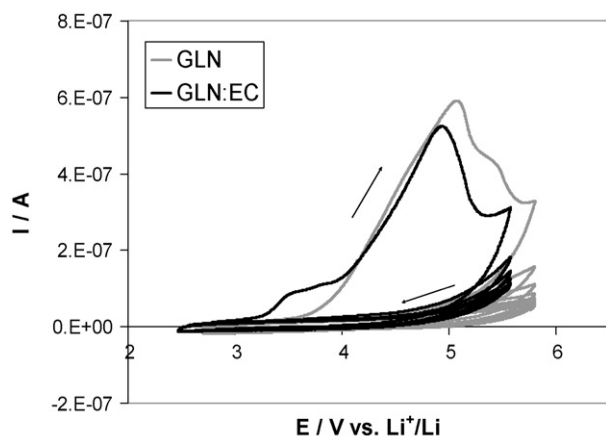
Fig. 6. Cyclic voltammetry of an Al wire in 1 M LiTFSI electrolyte solutions of GLN and of GLN:EC (1:1 by volume).

which we found to be formed by the reduction products of EC and LiBOB, with no contribution from ADN [13]. In this work we have tested MCMB/LiCoO$_2$ batteries with 1 M LiTFSI electrolytes containing GLN, EC and LiBOB in different ratios and observed the same behavior as in the ADN system.

Fig. 5 shows the cycling performance of a Li-ion battery employing conventional electrodes, MCMB/LiCoO$_2$, and an electrolyte composed of GLN:EC in a 1:1 ratio by volume containing 1 M LiTFSI and 0.1 M LiBOB. The battery showed an initial discharge capacity of 98 mAh g^{-1} that decreased gradually on cycling reaching a steady value corresponding to 74% of initial capacity at the 80th cycle and beyond to the 100th cycle. These values are lower than what we previously found for the ADN system with the similar electrolyte composition, despite the higher conductivity and lower viscosity of the GLN system, a behavior that can only be attributed to the presence of impurities that might interfere with the SEI as also evidenced by the LSV and DSC scans.

3.5. Stability against aluminum corrosion

Aluminum corrosion was evaluated in the GLN and GLN:EC electrolytes because of the fact that the LiTFSI salt, a good lithium salt alternative to LiPF$_6$, causes severe corrosion to the Al current collector commonly used in lithium ion batteries at potentials higher than 3.7 V versus Li$^+$/Li [19]. An electrochemical cell was assembled using an Al wire as a working electrode and an Ag wire as reference and counter electrodes. The cell showed an open circuit potential of 2.2 V and 2.3 V versus Li$^+$/Li for GLN and GLN:EC, respectively. These values became more positive with time, increasing slowly to reach 2.8 V versus Li$^+$/Li for GLN and 2.5 V versus Li$^+$/Li for GLN:EC over a period of 3 h, indicating a slow passivating behavior. However, these new values are still much more positive than what was reported for LiTFSI electrolyte solutions in EC:DMC (1.63 V versus Li$^+$/Li) or an ionic liquid (2.05 V versus Li$^+$/Li) [20] indicating a better ability of GLN to passivate the Al surface.

Fig. 6 shows the cyclic voltammetry scans recorded for GLN and GLN:EC electrolytes during 10 cycles. It can be seen that during the first cycle the two electrolytes showed a similar passivating behavior that is different from the typical hysteresis loop char-

acteristic of a pitting corrosion usually observed in the carbonate system. Instead, the electrolytes showed a gradual increase in the current in the forward scan, starting at a more positive value for the GLN electrolyte, that decreased in the reverse scan to lower values indicative of the formation of a protective layer that might have formed from any combination of Al^{+3} and TFSI$^-$ ions depositing on the surface [20] or its passivation by the nitrile groups through the lone pair electrons on the nitrogen atom, similar to what is observed in other LiTFSI/nitrile electrolytes [21]. Moreover, by the third cycle the two electrolytes showed an excellent passivating behavior with currents dropping to very insignificant values above 4.5 V versus Li$^+$/Li.

4. Conclusion

Lithium electrolytes based on glutaronitrile were prepared and tested in Li-ion batteries. Glutaronitrile was chosen for this study due to its high anodic and thermal stability as well as due to it having the best physical properties in the aliphatic dinitrile family of solvents. Its application in batteries using graphite as an anode was made possible by the addition of EC as a co-solvent (GLN:EC 1:1 by volume) and a co-salt (0.1 M LiBOB). The cathodic stabilization effects of both EC and LiBOB were found to be imperative to obtaining good battery performance in graphite/LiCoO$_2$ cells. This we believe is a step in the right direction towards assembling safer, higher energy/power batteries with cathodes having higher potentials and/or capacities.

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