



# Towards more thermally stable Li-ion battery electrolytes with salts and solvents sharing nitrile functionality



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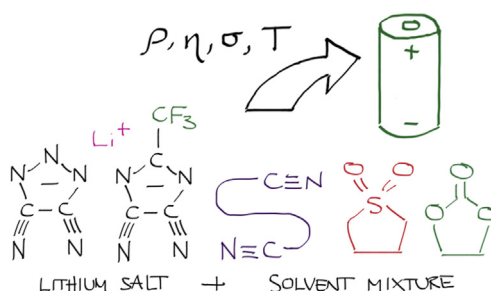
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## HIGHLIGHTS

- Solvents and salts with nitrile groups are combined into novel electrolytes.
- Sulfolane in adiponitrile provides thermally stable, high flashpoint electrolytes.
- LiDCTA and LiTDI electrolytes have high oxidation stability (4.5 V vs Li<sup>+</sup>/Li<sup>0</sup>).
- Ethylene carbonate is decomposed into CO<sub>2</sub> in the presence of lithium salt.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The overall safety of Li-ion batteries is compromised by the state-of-the-art electrolytes; the thermally unstable lithium salt, lithium hexafluorophosphate (LiPF<sub>6</sub>), and flammable carbonate solvent mixtures. The problem is best addressed by new electrolyte compositions with thermally robust salts in low flammability solvents. In this work we introduce electrolytes with either of two lithium nitrile salts, lithium 4,5-dicyano-1,2,3-triazolate (LiDCTA) or lithium 4,5-dicyano-2-trifluoromethylimidazolidine (LiTDI), in solvent mixtures with high flashpoint adiponitrile (ADN), as the main component. With sulfolane (SL) and ethylene carbonate (EC) as co-solvents the liquid temperature range of the electrolytes are extended to lower temperatures without lowering the flashpoint, but at the expense of high viscosities and moderate ionic conductivities. The anodic stabilities of the electrolytes are sufficient for LiFePO<sub>4</sub> cathodes and can be charged/discharged for 20 cycles in Li/LiFePO<sub>4</sub> cells with coulombic efficiencies exceeding 99% at best. The excellent thermal stabilities of the electrolytes with the solvent combination ADN:SL are promising for future electrochemical investigations at elevated temperatures (> 60 °C) to compensate the moderate transport properties and rate capability. The electrolytes with EC as a co-solvent, however, release CO<sub>2</sub> by decomposition of EC in presence of a lithium salt, which potentially makes EC unsuitable for any application targeting higher operating temperatures.

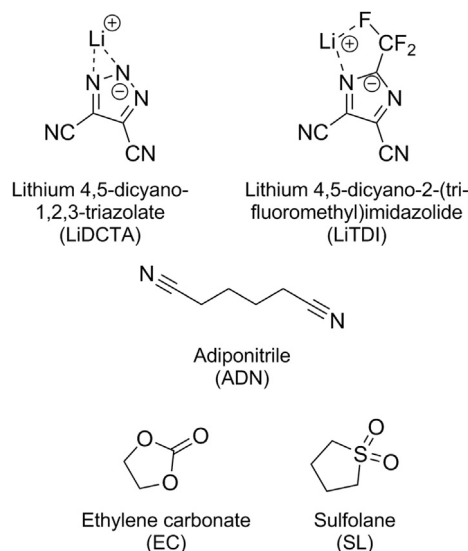
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## 1. Introduction

The Li-ion battery is a successful story that has enabled generations of energy demanding consumer electronics. However, to

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**Fig. 1. Chemical structures** LiDCTA, LiTDI, and the solvents ADN, EC, and SL. The  $\text{Li}^+$  coordination modes of the anions have been proposed and discussed elsewhere [11,16,33].

meet the needs of new applications there is a need to improve Li-ion battery cell performance, operation conditions, safety, and cost beyond current limitations. Safety is of particular concern and intimately connects to properties of the state-of-the-art liquid electrolyte. The typical electrolyte consists of at least three components; a lithium salt dissolved in a binary or ternary solvent mixture, where the solvents offer different, and sometimes synergistic, advantages for salt dissolution, fast ion transport, thermal and electrochemical integrity [1]. The industry standard is *ca* 1 mol  $\text{dm}^{-3}$  lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in a mixture of ethylene carbonate (EC) and one or several linear dialkyl carbonates [2]. Despite many advantages of these electrolytes, there are critical limits to their use; the significant decomposition of  $\text{LiPF}_6$  at  $T \geq 60^\circ\text{C}$  [3,4], the near room-temperature flash points of linear carbonates [5], and the extensive heat generated when both linear and cyclic carbonates are decomposed [2,5].

More thermally stable alternatives to  $\text{LiPF}_6$  have been suggested and reviewed thoroughly elsewhere [6–8]. In this work we focus on two closely related lithium salts including heterocyclic anions with nitrile functionality; lithium 4,5-dicyano-1,2,3-triazolate (LiDCTA)<sup>\*</sup> and lithium 4,5-dicyano-2-trifluoromethylimidazolidine (LiTDI, Fig. 1) [9,10]. LiDCTA is thermally stable to  $300^\circ\text{C}$  and one of few alternatives to  $\text{PF}_6^-$  that is free of both fluoro and oxygen atoms, which brings advantages in terms of low cost synthesis (no fluorine) [9] and potentially weak interactions with  $\text{Li}^+$  (no oxygen) [11]. In solid poly(ethylene oxide) (PEO) electrolytes, LiDCTA has a positive plasticizing effect and offers a high  $\text{Li}^+$  transference number [12]. In a few typical liquid aprotic solvents, and mixtures thereof, it is soluble in molar concentrations [9,12–14], but in others it has poor solubility and a strong tendency to form ionic aggregates [15]. Moderate ion conductivities (at best  $2.7 \text{ mS cm}^{-1}$  in EC:DMC at  $20^\circ\text{C}$  [14]) and a low oxidation stability (*ca* 4 V vs.  $\text{Li}^+/\text{Li}^\circ$  [13]) has made it a less attractive salt compared to LiTDI, but it is still a conceptually interesting fluorine-free salt.

TDI differs from DCTA only by  $-\text{C}-\text{CF}_3$  replacing the central ring nitrogen atom of the latter (Fig. 1). Computational results suggest the fluoromethyl group to weaken the interaction with  $\text{Li}^+$  [16],

which is supported experimentally by an improved miscibility of LiTDI over LiDCTA in some aprotic solvents [15] and a higher electrolyte conductivity ( $6.7 \text{ mS cm}^{-1}$  in EC:DMC at  $20^\circ\text{C}$  [14]). TDI is predicted to have a slightly lower oxidation stability than DCTA [16], but experimentally some LiTDI electrolytes are found to be more stable ( $\leq 4.5 \text{ V}$  vs.  $\text{Li}^+/\text{Li}^\circ$  [14,17]). LiTDI is thermally stable to  $250^\circ\text{C}$  and has been scrutinized against  $\text{LiPF}_6$  in various carbonate solvent mixtures [17–19]. However, it should be recognized that i) these solvents are optimized for use with  $\text{LiPF}_6$  and ii) the low flashpoints and heat evolution of these solvents motivate their replacement as well. Therefore, it is instructive to find more suitable solvent alternatives [20], where ideally positive synergistic effects between solvents and salts can make both LiDCTA and LiTDI interesting solutes in altogether new types of electrolytes for Li-ion batteries.

Aprotic molecular liquids are the most interesting solvents for low cost electrolytes near-term, while in the long-term ionic liquids based on either the DCTA or TDI anions may be another alternative [21,22]. Limiting our scope to the former class of solvents, 1,2-dicyanobutane (adiponitrile, ADN) was chosen as the main component of our electrolytes. ADN and other dinitriles have high oxidation stabilities [23] and nitriles in general can have a positive impact on anion stability, exemplified by the increased aluminium corrosion potential of electrolytes with lithium perfluoroalkylsulfonyl imides [24]. Mixtures of ADN with EC form high flashpoint electrolytes that are compatible with graphite anodes [25,26], although additional solvents or salts seem to be required for compatibility with certain high-voltage cathodes [23]. Tetrahydrothiophene 1,1-dioxide (Sulfolane, SL) has for long been considered as a co-solvent for lithium metal [27–29] and Li-ion cells [30] and is together with related sulfones (and nitriles) a target for high-voltage or oxidation tolerant electrolytes [31]. SL has been shown to significantly decrease the heat generation at Li-ion cell failure when partially replacing EC [2,32], which makes it an interesting co-solvent also from a safety perspective.

In this work we highlight key properties of new electrolyte compositions where salts and solvents share nitrile functionality. The focus of the study is on the physico-chemical properties of these novel electrolytes and the basic electrochemistry of Li-metal/cathode half-cells at room temperature. The choice of co-solvents turns out to be crucial for salt solubility, a wide liquid range, and electrolyte thermal stability; with EC as a co-solvent, carbon dioxide is generated at intermediate temperatures ( $\geq 60^\circ\text{C}$ ), which represents a critical drawback, since increased high temperature tolerance is an important line of electrolyte development. For the here investigated nitrile based electrolytes, the moderate cycle performance and poor rate performance at room temperature suggests that higher temperatures are necessary to yield transport properties and performances that are competitive with the state-of-the-art electrolytes. The ADN:SL electrolytes is of potential interest for use at higher temperatures, but for universality, thermal stability should optimally be combined with good performance also at lower temperatures. For this, further screening of suitable solvent compositions is necessary. Our work supports the previous results that the ionic conductivity of electrolytes with LiTDI is higher compared to LiDCTA [14], but not the stipulated difference in oxidation stability, and both salts remain interesting alternatives to  $\text{LiPF}_6$  in the wait of a solvent breakthrough.

## 2. Experimental

**Electrolyte preparation:** Adiponitrile ( $M = 108.14 \text{ g mol}^{-1}$ , 99%, Sigma-Aldrich) and sulfolane ( $M = 120.17 \text{ g mol}^{-1}$ , 99% Sigma-Aldrich) were dried over molecular sieves (4 Å) and mixed in mole ratios with ethylene carbonate ( $M = 88.06$ , 99%, Sigma-

<sup>\*</sup> Alternatively 1,2,3-triazole-4,5-dicarbonitrile (LiTADC).

Aldrich) to give one ternary (ADN:SL:EC 2:1:1 n:n:n) and two binary (ADN:SL and ADN:EC 2:1 n:n) solvent mixtures with ADN as the main component. For the sake of brevity we from this point refer to the mixtures by using only the first letter of each solvent i.e. “AS” for ADN:SL, “AE” for ADN:EC, and “ASE” for ADN:SL:EC.

LiDCTA and LiTDI were provided by collaborators and their synthesis is described elsewhere [13,34]. Both salts were dried 4 days at 60 °C in a Büchi B-580 vacuum oven, before dissolved in the solvent mixtures, or single solvent ADN, at a concentration of 0.67 m (mol kg<sup>-1</sup> solvent, corresponding molarities are given in Suppl. Table S1). The only exception is LiDCTA at a concentration of 0.5 m in ADN because of limited solubility. All steps were performed in an argon-filled glove box (H<sub>2</sub>O < 1 ppm, O<sub>2</sub> < 1 ppm). The water content of all electrolytes were confirmed to be < 100 ppm by Karl Fischer titration (Metrohm).

**Differential scanning calorimetry (DSC):** Heating traces were recorded with a Q1000 from TA instruments. Samples of 10–20 mg were hermetically sealed in an aluminium crucible, cooled to –150 °C before heated up to 170 °C at a rate of 10 °C/min. The melting point was defined as the minimum of the appropriate endothermic peak.

**Density/Viscosity:** Densities and viscosities were determined with an Anton Paar DMA 4500 M density meter and a Lovis 2000 M rolling-ball viscometer module. The dynamic viscosities were measured with the falling sphere method using a steel ball ( $\varnothing = 1.5$  mm,  $\rho = 7.70$  g cm<sup>-3</sup>) and a capillary ( $\varnothing = 1.59$  mm). Temperatures were measured from 20 to 80 °C in 10 °C steps. The results were confirmed by repeating the measurements going down in temperature.

**Ionic conductivity:** Ionic conductivities were obtained by dielectric spectroscopy measurements in the frequency range 100 MHz – 10 MHz using a Concept 80 broadband dielectric spectrometer from Novocontrol. The dielectric cells were assembled in the glove box and the samples were filled into a Teflon<sup>®</sup> spacer (thickness = 0.25 mm,  $\varnothing_{\text{inner}} = 16$  mm) which was placed between two stainless steel electrodes. Data were collected from –30 to 110 °C in 10 °C steps and the cells thermally equilibrated for 15 min at each temperature before the measurements. The DC conductivity at each temperature was extracted from the frequency plateau in the corresponding frequency region.

**Flashpoint:** Flashpoints were determined with a Grabner Mini-FLASH TOUCH according to the D6450 standard for closed cups. A stainless steel cup with 1 ml of sample was placed in contact with an electric arc and heated from a temperature approximately –18 °C from the anticipated flashpoint. A discharge once per °C by the electric arc results in a pressure increase in the closed cup. The flashpoint is determined as the temperature where the pressure reaches 20 kPa under a given air flow, and a heating rate of 5.5 °C min<sup>-1</sup>.

**Thermal gravimetric analysis (TGA):** A TG 209 F1 Iris from Netzsch was loaded with aluminium pans holding samples of 10–15 mg. The pans were heated from 25 °C to 250 °C at 5 °C min<sup>-1</sup>. Thermal stabilities were determined by setting a 1% mass loss as the decomposition temperature. Additionally, isothermal measurements were performed at 80 °C for 1 h to study “long-term” stabilities. All evolved gases were transferred through a Teflon<sup>®</sup> capillary and gas cell (both at 200 °C) where a Vector 22 Bruker FT-IR continuously recorded FT-IR spectra between 620 and 4400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. To assign a temperature to each FT-IR spectra, it was estimated that it takes 1 min for the transfer of the evolved gases from the TGA chamber to the FT-IR cell.

**Linear sweep voltammetry (LSV):** The anodic stability was determined by linear sweep voltammetry of Li/electrolyte/SS (Stainless-steel) Swagelok<sup>®</sup> cells using a multi-channel

electrochemical analyser (Ivium-n-Stat instrument, Ivium Technologies) at room temperature with a scan rate of 1 mV s<sup>-1</sup> between 2 and 5.5 V vs Li<sup>+</sup>/Li<sup>0</sup>. A microporous electrospun polyacrylonitrile (PAN) membrane, described in more detail elsewhere [13], was soaked with the electrolyte and sandwiched between the electrodes.

**Coin cell assembly and battery testing:** Carbon-coated (5%) lithium iron phosphate (LiFePO<sub>4</sub>) was prepared and used as the active cathode material [35]. A slurry of LiFePO<sub>4</sub>, Super-P conductive carbon and poly(vinylidene fluoride) (PVDF, Sigma-Aldrich) as binder, were mixed in a weight ratio of 80:10:10 in *N*-methyl pyrrolidone (NMP) and casted on an aluminium foil. Two-electrode coin cells were assembled with a lithium metal anode (thickness = 300 µm, from Cyprus Foote Mineral Co.) and the carbon-coated LiFePO<sub>4</sub> electrode as the cathode. Approximately 120–170 µl of electrolyte, depending on separator weight, was penetrated into a PAN or Celgard 2400 separator, which was placed between the electrodes. The galvanostatic charge/discharge tests of the Li/electrolyte/LiFePO<sub>4</sub> cells (2.5–4.4 V, 1 C-rate, 25 °C) were performed with a WBCS3000 battery cyler from WonATech. Co.

**Solubility modeling:** Molecular structures were built in the graphical user interface of TmoleX 4.1 and quantum chemical calculations performed with the TURBOMOLE [36,37] V7.0 program package. Geometries were optimized using the BP86-functional [38,39] and TZVP basis set [40] in gas phase and for the perfect conductor-like screening model (COSMO:  $\epsilon = \infty$ ). Additionally, a single point calculation at BP86/TZVPD/COSMO//BP86/TZVP/COSMO level of theory was performed in order to generate a fine grid cavity surface (FINE) for the molecules, which is saved in a COSMO-file. The COSMO-RS calculations (RS = *Real Solvents*) were performed with the COSMOthermX program [41] and the salt-solubility module using the BP\_TZVPD\_FINE\_C30\_1501 parameterization at a temperature setting of 25 °C (298.15 K). See the [supplementary information](#) for more details.

### 3. Results and discussion

In the following the physical properties of the electrolytes are reported; melting points, densities, viscosities, and ionic conductivities, which determine the low temperature limit and electrolyte transport properties. Based on the results, the most promising electrolytes were tested for their oxidation stabilities and cycled in Li/LiFePO<sub>4</sub> cells. Finally, TGA FT-IR and flashpoint tests were made to assess the thermal stability and flammability of the electrolytes.

#### 3.1. Physical properties

##### 3.1.1. Modeling suggests co-solvents to adiponitrile to increase salt solubility

The molar solubilities of LiTDI and LiDCTA in ADN, SL, AS 2:1, AE 2:1 and ASE 2:1:1 were calculated using COSMO-RS (Suppl. Table S1). Qualitatively, the salt solubility increases in the order ADN < AE  $\approx$  AS < ASE < SL, which indicates that from a solubility perspective SL and/or EC are both appropriate co-solvents to ADN. These results are consistent with our experimental observations. Quantitatively, the calculated molar solubilities for LiTDI underestimate, but are of similar magnitude as the experimental results. The  $\Delta_{\text{fus}}G$  of ca. 6 kcal mol<sup>-1</sup> for LiTDI (based on thermochemical data) is larger than 2.6 kcal mol<sup>-1</sup> for LiDCTA (based on a single solubility reference), but limited data for estimating the latter makes a direct comparison of the salt solubilities difficult. However, the lower  $\Delta_{\text{fus}}G$  and higher decomposition temperature of LiDCTA (ca 320 °C vs. 250 °C) suggest a denser crystal structure, a  $\Delta_{\text{fus}}H$ -driven solubility process, and an overall lower solubility compared to LiTDI. Also, a simple structural argument, comparing

the planar DCTA with the more bulky TDI, with its freely rotating  $\text{CF}_3$ -group, suggests LiTDI to be the easier soluble salt.

### 3.1.2. Co-solvents decrease the melting temperature of adiponitrile

The melting temperature ( $T_m$ ) of ADN ( $2^\circ\text{C}$ ) decreases when SL is added as a co-solvent, but it is little affected by EC (Fig. 2). For the stoichiometric mixtures here, the lowest  $T_m = -20^\circ\text{C}$  is observed for the ternary solution ASE. The  $T_m$  sequence  $\text{ASE} < \text{AS} < \text{AE} \approx \text{ADN}$  remains unaffected by the addition of the lithium salt LiTDI (Fig. 2) or LiDCTA (not shown). Thus, a co-solvent to ADN is essential for sub-zero applications. For comparison, Abu-Lebdeh et al. did not observe any clear melting point for their solvent mixture AE (1:1 v:v  $\approx 1:1.7$  n:n), which suggests that a higher concentration of co-solvent can suppress the melting point further [25].

### 3.1.3. Co-solvents increase the density and viscosity of adiponitrile

The neat solvent ADN has a lower density than the solvent mixtures (Fig. 3a). The densities increase with the addition of LiDCTA and more so with LiTDI. The viscosity of ASE is similar to that of ADN (overlapping curves, Fig. 3b) and smaller than that of AS. The lower viscosity of ASE compared to AS is reasonable, since AE mixtures have lower viscosities in comparison with ADN [25] and, thus, EC counteract the viscosity increase by SL. The viscosities of all solvents increase with the addition of salt, again with a stronger effect by LiTDI. The exception is ASE, for which both salts have a similar effect. Overall, the electrolyte viscosities range from 12 to  $20 \text{ mPa s}^{-1}$  at  $20^\circ\text{C}$  to  $2\text{--}4 \text{ mPa s}^{-1}$  at  $80^\circ\text{C}$ . The lowest electrolyte viscosities here are in the same range as the  $ca\ 15 \text{ mPa s}^{-1}$  reported for LiTFSI ADN and LiTFSI AE (1:1 v:v) electrolytes at comparable concentrations [25].

In general, viscosities are inversely proportional to ionic conductivities and, therefore, offer a rough first indication how the electrolytes may affect the rate performance of Li-ion cells. Considering that commercial electrolytes have much lower viscosities, e.g.  $5.1 \text{ mPa s}^{-1}$  at  $20^\circ\text{C}$  for 1 M LiPF<sub>6</sub> in EC:DEC [42], the here measured electrolytes show comparable viscosities only at  $70\text{--}80^\circ\text{C}$ . Lower room temperature viscosities,  $ca\ 8 \text{ mPa s}^{-1}$ , are possible in ternary electrolytes (ADN:EC:DMC 2:1:1 v:v) by the conventional strategy to include low flashpoint linear carbonates

[23], but operation at elevated temperatures with thermally more stable and less flammable electrolytes may ultimately be a more reasonable approach.

### 3.1.4. Electrolytes have higher ionic conductivities with LiTDI compared to LiDCTA

The ionic conductivities of the LiTDI electrolytes at room temperature and above all meet the often stated requirement of  $1 \text{ mS cm}^{-1}$  for battery electrolytes (Fig. 4a) [43]. The highest conductivities are obtained with ADN as a single solvent, but the co-solvents are needed to lower the melting point and maintain sufficient ionic conductivities at low temperatures.

The LiDCTA electrolytes have lower ionic conductivities than the LiTDI electrolytes and require slightly higher temperatures ( $\geq 40^\circ\text{C}$ ) to exceed  $1 \text{ mS cm}^{-1}$  (Fig. 4b). This is counter-intuitive considering the lower viscosities of the former, but such exceptions exist and are observed also for LiTDI in comparison with LiPF<sub>6</sub> or LiTFSI in EC:DMC electrolytes [19]. Differences in anion shape and ion association (concentration of ion pairs and aggregates) are likely part of the explanation. The conductivities of the ADN-based electrolytes do not come close to those of LiTDI and LiDCTA in carbonate mixtures [14,19], but the absence of low flashpoint solvents may permit higher operating temperatures and improved transport properties to increase the performance.

In summary, the physical properties reveal that AS and ASE based electrolytes offer a wider liquid range as compared to AE or the single solvent ADN electrolytes, which is important at least for avoiding electrolyte crystallization at low temperature conditions. However, for sufficiently low viscosities and high conductivities, elevated temperatures are needed. In the following section we compare the electrochemical properties of the AS and ASE electrolytes.

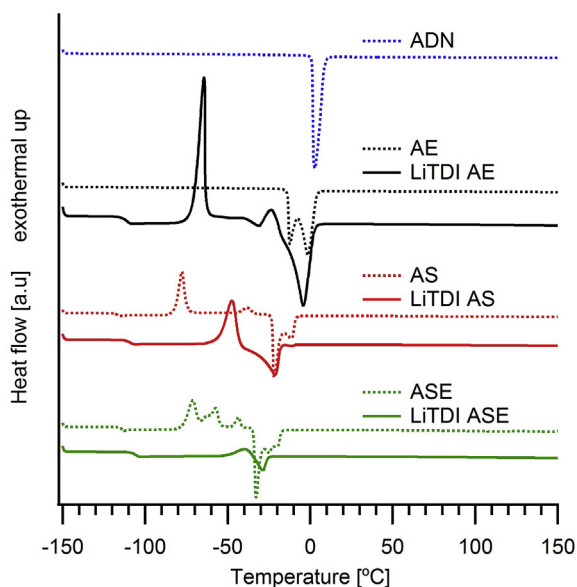
## 3.2. Electrochemical properties

### 3.2.1. High stability solvents improve DCTA oxidation stability

The oxidation potentials of the AS and ASE electrolytes are approximately  $4.5 \text{ V}$  vs  $\text{Li}^+/\text{Li}^\circ$  based on LSV measurements in Li/SS (stainless steel) cells (Fig. 5). The stabilities are comparable to that of LiTDI in carbonate electrolytes [14], but the reported difference between DCTA and TDI [9] is not observed here. These results, together with the  $< 4.0 \text{ V}$  vs.  $\text{Li}^+/\text{Li}^\circ$  oxidation potential of LiDCTA in PC [13], suggest that ADN and SL have a positive effect on the stability of DCTA. The results should, however, be considered guiding, since it is known that the higher surface area and possible catalytic effects of specific electrode particles may dramatically influence the results for a given application [1,44,45]. On a detailed level, there are some very small currents observed in all electrolytes already at  $3.5 \text{ V}$  vs.  $\text{Li}^+/\text{Li}^\circ$ , such small currents are normally neglected when determining the oxidation potential, but may be of importance for the long-term stability [45].

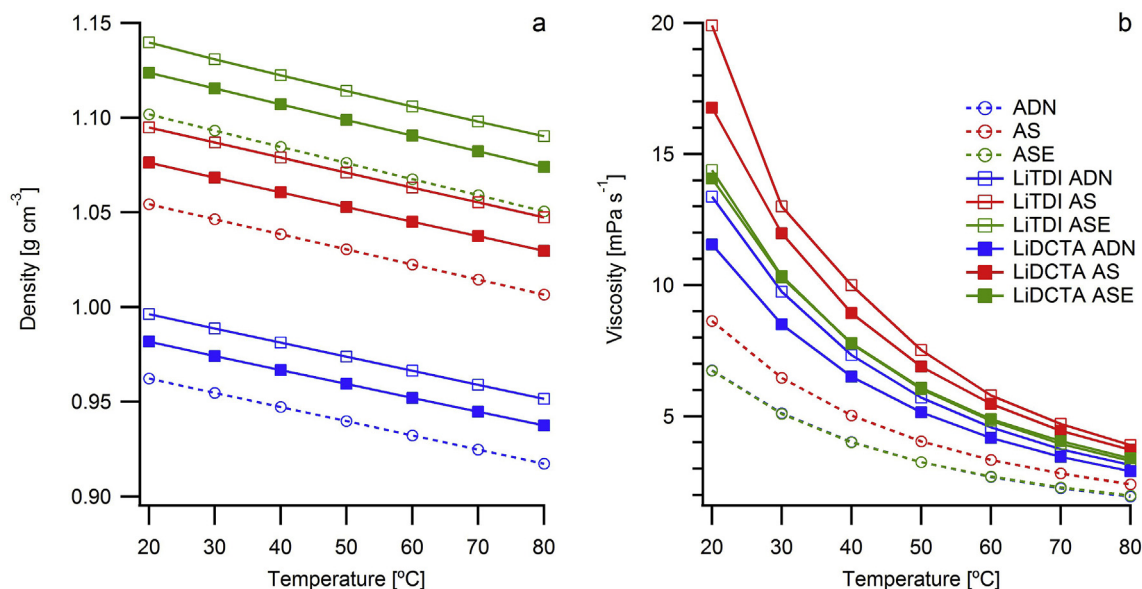
### 3.2.2. Charge/discharge tests show stable cycling but poor rate capability

Charge/discharge tests of Li/LiFePO<sub>4</sub> cells (20 cycles) were carried out between  $2.5$  and  $4.4 \text{ V}$  vs.  $\text{Li}^+/\text{Li}^\circ$  ( $4.5 \text{ V}$  in the case of LiDCTA ASE). The cells with ASE electrolytes delivered the highest average discharge capacities ( $\sim 145 \text{ mAh g}^{-1}$ ). After a few initial cycles with irreversible capacity losses the performance stabilized and average coulombic efficiencies (cycles 5–20) were 97.5 (LiTDI ASE) and 95.8% (LiDCTA ASE) (Fig. 6). These rather low coulombic efficiencies may arise from side-reactions, which are only noticeable in the ternary electrolytes. A big difference in appearance of the 20th compared to the 1st cycle of the LiDCTA ASE electrolyte (Fig. S1), and the lower coulombic efficiency, shows that the extended upper cut-off of  $4.5 \text{ V}$

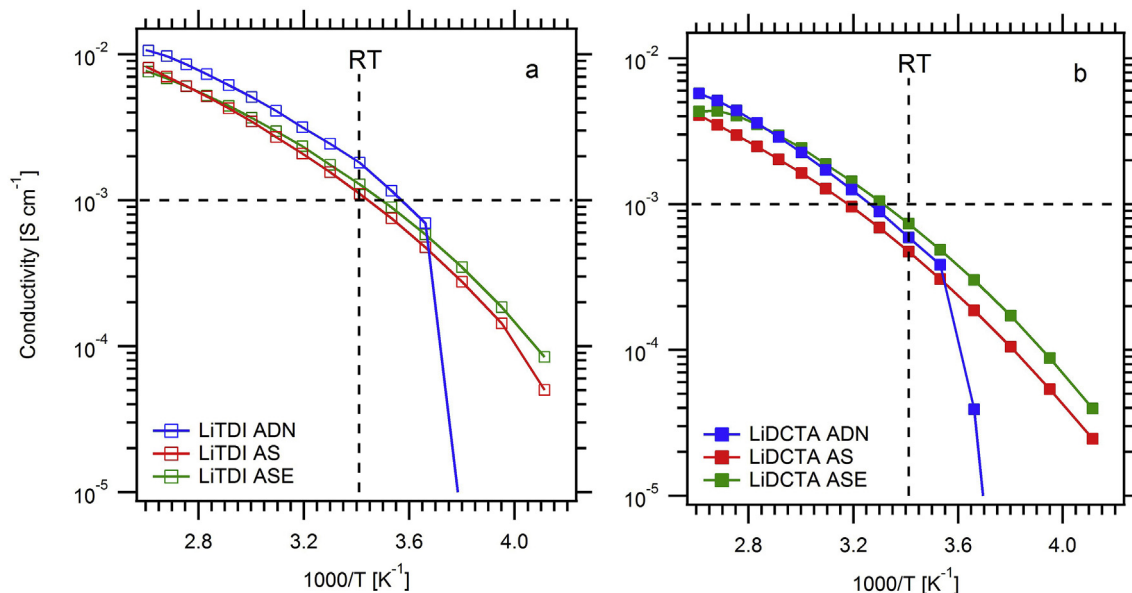


**Fig. 2. Liquid range** The melting temperature  $T_m$  of ADN (A) decreases with EC (E) and/or SL (S) as co-solvents. LiTDI or LiDCTA (not shown) has only a small effect on  $T_m$ .





**Fig. 3.** Densities and viscosities a) Densities and b) viscosities of ADN (A), the solvent mixtures AS and ASE and the corresponding electrolytes. The viscosity curves of ADN and ASE are overlapping.



**Fig. 4.** Ionic conductivities a) of electrolytes with LiTDI or b) LiDCTA in ADN, AS, and ASE. The LiTDI electrolytes reach a conductivity of  $> 1 \text{ mS cm}^{-1}$  at room temperature (RT), the LiDCTA electrolytes at ca  $40^{\circ}\text{C}$ .

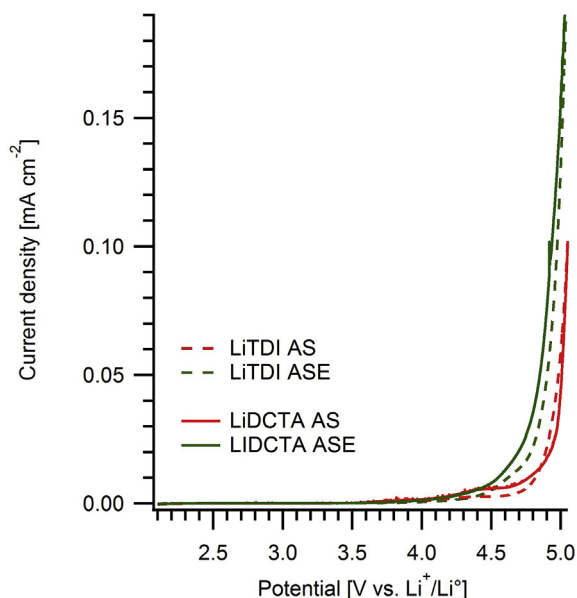
vs.  $\text{Li}^+/\text{Li}^{\circ}$  strongly negatively effects the reversibility of the reaction. The relatively high coulombic efficiencies for the AS electrolytes; 99.6% (LiTDI AS) and 99.8% (LiDCTA AS), based on cycles 5–20, are promising – despite slightly lower discharge capacities than the ASE electrolytes – and offer an overall improvement compared to the cells with 1 M LiDCTA in PEGDME [13].

The conceptually interesting fluorine-free LiDCTA ASE electrolyte was further tested in cells with different separators and C-rates. The cell with a Celgard separator performed very poorly, which we interpret as an insufficient ability of the electrolyte to wet the separator (Fig. S2). This may be a result of the high viscosity of the electrolyte in combination with the small pore size ( $0.04 \mu\text{m}$ ) of the polypropylene based Celgard separator [46]. Similar wetting issues have been reported for other sulfone-based electrolytes [28]. The

rate test was performed with a PAN separator using a more cautious charge/discharge window of 2.5–4.0 V vs.  $\text{Li}^+/\text{Li}^{\circ}$  to focus exclusively on the rate effect. The inability of the cell to cope with a 2C-rate (Fig. 6b) further highlights the problem related to the high viscosity of the electrolyte and stresses that their potential use in practical Li-ion batteries will require higher operating temperature and/or a solvent combination that enables lower viscosity electrolytes. Furthermore, the decreased coulombic efficiency, when returning to 0.1 C-rate, is a possible sign of some irreversible process occurring already below 4.0 V vs.  $\text{Li}^+/\text{Li}^{\circ}$ .

### 3.3. Thermal properties and electrolyte flammability

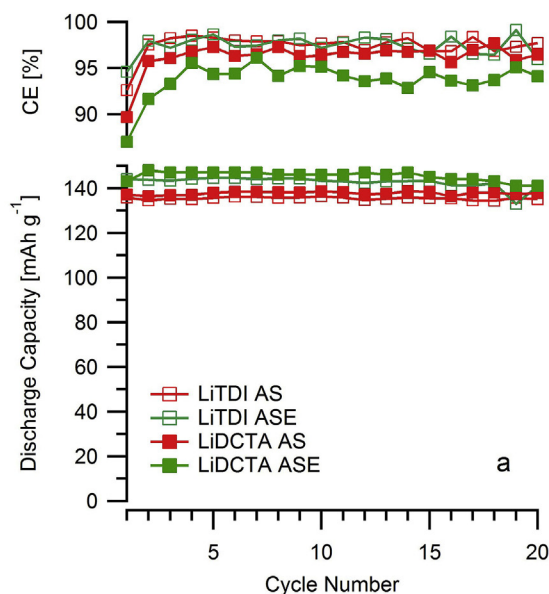
From previous sections it is clear that elevated temperatures



**Fig. 5.** Anodic stabilities of the AS and ASE electrolytes with LiTDI or LiDCTA. All electrolytes are stable up to ca 4.5 V vs.  $\text{Li}^+/\text{Li}^0$  in a Li/SS cell.

would be required to compensate for the higher viscosities, lower conductivities, and overall poorer transport properties of the ADN based electrolytes compared to the state-of-the-art. At the same time, elevated temperatures impose rougher conditions for the materials. In this section a few critical material properties are investigated as a function of temperature to address the applicability of the electrolytes at temperatures ( $> 60^\circ\text{C}$ ) where the state-of-the-art cannot be used.

The first design features for safer electrolytes are the exclusive use of high flashpoint solvents and more thermally stable lithium salts than  $\text{LiPF}_6$ . The flashpoints for all solvent mixtures and electrolytes used here fall in the range of  $150\text{--}160^\circ\text{C}$  (Fig. S3), which is more than  $100^\circ\text{C}$  higher than for a typical organic solvent mixture, such as EC:DEC (3:7 w:w) [26].



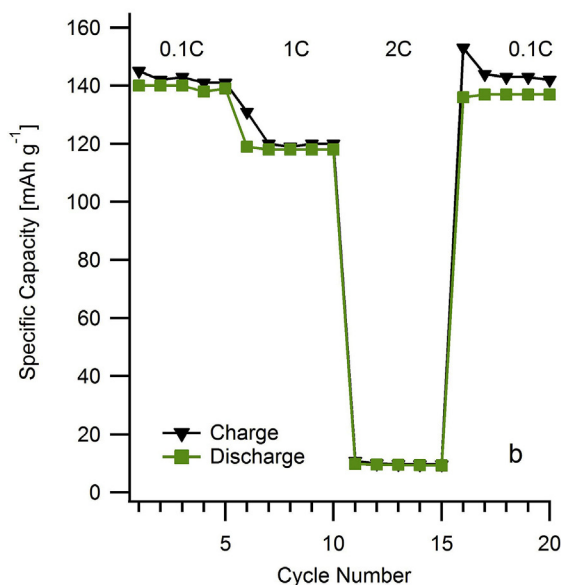
### 3.3.1. Electrolyte mass loss is dictated by the co-solvent

The thermal stabilities derived from dynamic TGA (Fig. 7a) show only minor differences between the electrolytes – they are all stable to at least  $110^\circ\text{C}$  ( $\leq 1\%$  mass loss). Isothermal TGA, however, reveals mass losses already at  $80^\circ\text{C}$ , where the extent of the mass loss depends on the solvent combination; the ASE electrolytes lose 3.5% of the initial mass during an hour at  $80^\circ\text{C}$ , while the AS electrolytes lose 2.1% (Fig. 7b). The mass loss processes are, however, not completed by the end of the measurements. The difference between the ASE and AS electrolytes correlates with the much faster mass loss rate of EC, as is evident from the dynamic TGA results and the analysis of the exhaust gases by FT-IR spectroscopy, to be discussed in more detail next.

### 3.3.2. Ethylene carbonate is decomposed in the presence of lithium salt

The analysis of the exhaust gases by FT-IR spectroscopy suggests that alternative reaction channels govern the decomposition of the different electrolytes. When EC is part of the electrolyte, bands from evaporated EC at approximately  $1100$  and  $1870\text{ cm}^{-1}$  [47] (Fig. 8) are the first to appear (LiTDI ASE at  $78^\circ\text{C}$ ; LiDCTA ASE at  $60^\circ\text{C}$ ). Surprisingly, these are followed shortly by an envelope of bands centered at ca  $2350\text{ cm}^{-1}$  (LiTDI ASE at  $110^\circ\text{C}$ ; LiDCTA ASE at  $70^\circ\text{C}$ ), which we ascribe to  $\text{CO}_2$ . With increasing temperature these features dominate the spectra until, we assume, all EC is consumed. The  $\text{CO}_2$  bands appear neither in the spectra of neat EC nor the ASE solvent mixture (free of salt), which suggests a catalytic effect by the lithium salt.

It is well known that thermal decomposition products of  $\text{PF}_6^-$  in state-of-the-art electrolytes trigger EC decomposition and  $\text{CO}_2$  evolution [4,48], but nothing suggests DCTA and TDI to be unstable at such low temperatures. However, anion-solvent interactions have been suggested to lower the oxidation stability of PC and EC in electrolytes [49,50]. A bit speculative at this stage, strong anion-EC interactions in these electrolytes could be responsible for the low temperature decomposition of EC. Alternatively,  $\text{Li}^+$  is the culprit; in ionic liquids, for example, a lowering of the thermal stability has been observed when introducing a lithium salt – where  $\text{Li}^+$  is the only new species of the ionic liquid electrolyte [42]. A third



**Fig. 6.** Galvanostatic charge/discharge a) Coulombic efficiencies (CE) for Li/LFP cells with AS and ASE electrolytes (2.5–4.4 V vs.  $\text{Li}^+/\text{Li}^0$ ) and b) specific capacity as a function of different discharge rates for Li/LFP cells with LiDCTA ASE electrolytes (2.5–4.0 V vs.  $\text{Li}^+/\text{Li}^0$ ).

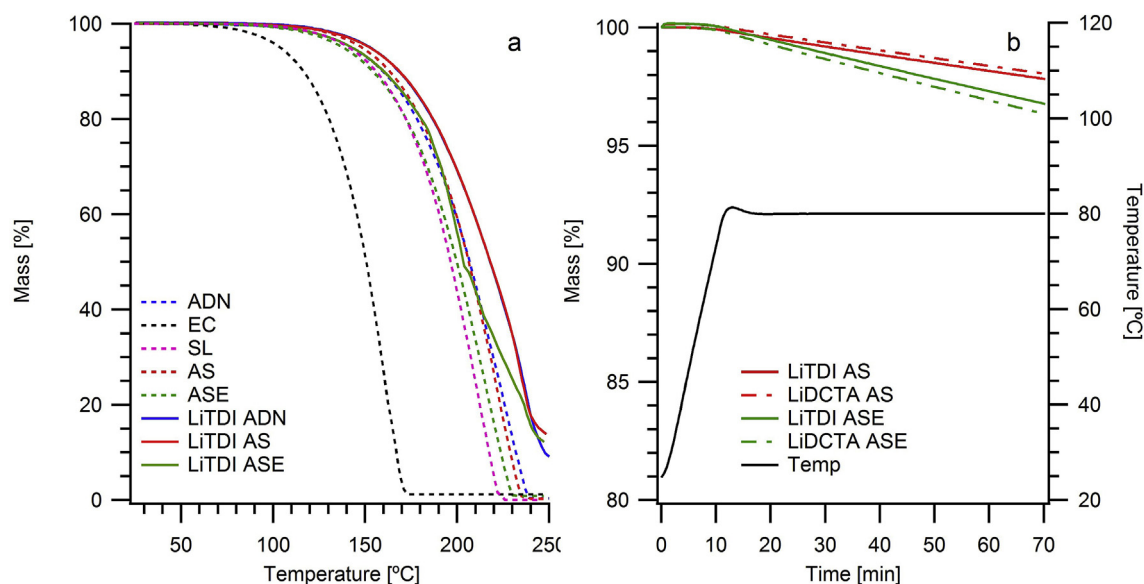


Fig. 7. Thermal stabilities a) Dynamic thermal stabilities of the solvents and the LiTDI electrolytes and b) isothermal (80 °C) electrolyte stabilities.

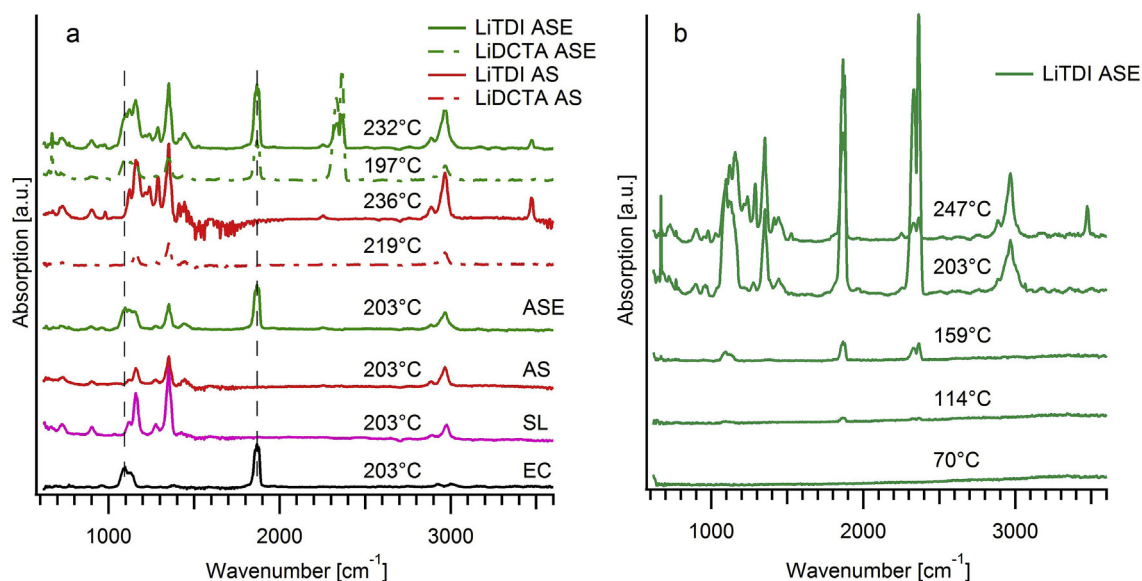


Fig. 8. Gas phase FT-IR spectra a) of the different electrolytes at maximum absorption and solvents at 203 °C and b) time evolution of the spectra for LiTDI ASE. Dashed lines indicate evaporated EC.

possibility is that the electrolytes, when loaded into the TGA instrument and briefly contacted with the atmosphere, absorb some moisture that drives hydrolysis of EC [51]. In strong contrast to the ASE electrolytes, the first features of the AS and ADN electrolytes appear at approximately 150 °C, and do not, as expected from the absence of carbonates, show any signatures of CO<sub>2</sub>.

The evaporation and decomposition of EC at relatively low temperatures is an important result, since EC is a standard component for the protective solid electrolyte interphase (SEI) on the anode [52,53], and therefore a constituent of many electrolytes. The decomposition of EC is not only detrimental to the cell operation, but a safety hazard, since evolution of CO<sub>2</sub> builds up pressure inside the cell. Taking into account the role of EC for rapid heat evolution [32], EC does not seem to be a suitable component, at co-solvent concentrations, for electrolytes targeting applications at elevated temperatures.

### 3.3.3. The anion influences the decomposition products at high temperatures

At high temperatures (> 200 °C) additional spectral features start to appear that are related to the choice of lithium salt. For all the LiTDI electrolytes there is a band at ca 3500 cm<sup>-1</sup> (LiTDI:ADN not shown), which is most likely due to TDI decomposition, since the band is not observed in any of the corresponding LiDCTA electrolytes (Fig. 8). No additional features from the decomposition of LiDCTA were observed, which is in agreement with the higher decomposition temperature of LiDCTA [9]. Decomposition products with small IR cross-sections or hidden by the absorption bands of the solvents can, however, not be ruled out. Finally, the possible release of toxic hydrogen cyanide (HCN) is a general concern for nitrile containing compounds [25]. We do not find any bands of HCN in the FT-IR spectra for any of the electrolytes below 250 °C. This does not exclude the formation of HCN under all

circumstances, but supports the argument that other nitrile containing reaction products are more likely to form [25].

#### 4. Conclusions

We have investigated combinations of lithium salts and solvents with nitrile functionality with the hope of forming thermally more stable, high-performing electrolytes for Li-ion battery application. The physical properties of the electrolytes were characterized over a wide temperature range and show an extended liquid range for the mixed solvent electrolytes compared to single solvent electrolytes. The electrochemical cycling performances were moderate, possibly due to high electrolyte viscosities and slow mass transport, which leaves room for further improved nitrile based solvent mixtures. The electrolytes show some advantages over conventional electrolytes in terms of thermal stability, where the ADN and AS electrolytes show high flashpoints, slow solvent evaporation, and no CO<sub>2</sub> release. The ASE electrolytes, however, evaporate EC at relatively low temperatures (from approximately 70 °C) and release CO<sub>2</sub> shortly thereafter, which makes them a safety risk and unsuitable for application in Li-ion batteries. Furthermore, the absence of CO<sub>2</sub> evolution from the neat ASE mixture (no salt) suggests a direct or indirect catalytic effect by Li<sup>+</sup> and/or the anion. The results may be of relevance for related electrolytes with EC intended for use at elevated temperatures. We conclude that the electrolytes with the AS solvent combination are the most suitable electrolytes overall, with high flashpoints and thermal stabilities, and good electrochemical performance, but their electrochemical performance at elevated temperatures remains to be investigated. In general, further optimization of the transport properties of nitrile based electrolytes should be possible by a more careful screening of solvent compositions and identification of additional, suitable, co-solvents without compromising the thermal integrity.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2016.09.101>.

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