Short communication

# Investigation of Li salt doped succinonitrile as potential solid electrolytes for lithium batteries

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## Abstract

Solid ionic conductors with good conductivity at room temperature and mechanical flexibility are very attractive candidates for application as electrolytes for secondary lithium batteries. Plastic crystal electrolytes formed by doping succinonitrile with lithium salts can potentially meet these requirements. In this study, succinonitrile doped with various lithium salts were characterized by differential scanning calorimetry, powder X-ray diffraction, conductivity measurements and in electrochemical studies. The much better conductivities and electrochemical performance of certain lithium salts in comparison to the others studied has been found to be correlated to their propensity to form crystalline adducts with succinonitrile at low molar concentrations. Of the lithium salts studied, only two which did not form crystalline adducts at low concentrations: lithium bis-trifluoromethanesulphonylimide ($Li[CF_3SO_2]_2N$) and lithium tetrafluorborate ($LiBF_4$) had high enough conductivities at ambient temperature for evaluation in lithium cells. Contrary to prior predictions, both showed reasonable capacities, high coulombic efficiencies, and good capacity retention even with metallic lithium as the anode.

*Keywords:* Lithium ion battery; Electrolyte; Succinonitrile

## 1. Introduction

Lithium ion batteries have rapidly come to dominate the market for power sources for portable electronic devices. The characteristics of combining high energy density with excellent charge retention have led to this success. As good as the currently available lithium ion batteries are; there is still much scope for further improvements. While the focus to date has largely been on lithium ion batteries that use liquid electrolytes, this technology's basic design creates problems in terms of packaging format, size, and cost. Recently, questions about the safety of commonly used liquid electrolytes have also been raised [1]. The gelled polymer, lithium ion battery, in which the electrolyte solution is immobilized as a plasticizer in a polymer matrix, alleviates some of these issues to some extent but not completely. Ultimately better safety and flexibility in format could be achieved by using ionically conductive polymers as the electrolyte in lithium ion cells. Polymer electrolytes have also been proposed for usage with metallic lithium anodes [2]. Since anodes of lithium metal have the highest theoretical specific capac-

ity, they offer the potential for smaller, lighter cells with much greater specific energy. The mechanical properties of polymer electrolytes decrease the severity of problems that might arise from the formation of dendrites which can occur when using lithium metal anodes. However, the polymer electrolytes that have shown the most promise for use in lithium batteries have quite low conductivity at room temperature [3] and consequently lithium polymer batteries are typically operated at about 80 °C.

More recently, a new class of solid electrolytes has been developed in which lithium salts are doped into matrices of plastic crystal phases to yield pliable materials with quite good ionic conductivities. Plastic crystals are mesophases formed mainly by quasi-spherical or disk-like molecules exhibiting rotational and/or orientational disorder while retaining the long-range translational order [4]. A result of this type of "disorder" is the high diffusivity and plasticity that enables plastic crystals to compete with other materials with similar mechanical properties such as polymer electrolytes. However, in comparison to polymer electrolytes, the preparation of a plastic crystal electrolyte is very easy, does not require much addition of lithium salt, and does not need any solvent or radiation cross-linking.

MacFarlane et al. [5] reported conductivities as high as $2 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ at 60 °C in lithium doped plastic crystal ionic

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compounds comprised of alkylmethylpyrrolidinium cations and bis(trifluoromethanesulphonyl)imide anions. The fast ion mobility was attributed to the rotational disorder and the existence of vacancies in the plastic crystal lattice. One concern in systems where the host matrix is ionic itself is that the ionic conductivity can result from more that one carrier and the effective transport number of the ion of interest, lithium, may be less than 1.

Non-ionic, molecular plastic crystal phases with good solvent properties can also be used to form solid electrolytes. In this case the molecular plastic crystal must be polar enough to dissolve the ionic salt. The plastic crystal phase of succinonitrile has been recognized as an excellent matrix for the formation of many solid-state ionic conductors [6,7]. In particular, room temperature ionic conductivities as high as $3.4 \times 10^{-4}\,S\,cm^{-1}$ [6] and $1.47 \times 10^{-3}\,S\,cm^{-1}$ [7] were found at 2 and 5 mol% doping, respectively, of lithium bis-trifluoromethanesulfonylimide ($Li[CF_3SO_2]_2N$) into the plastic crystal form of succinonitrile. With conductivities at room temperature comparable to conventional liquid electrolytes for secondary lithium batteries ($10^{-3}\,S\,cm^{-1}$) and good mechanical properties, crystal plastic electrolytes are one of the most promising alternatives to liquid or gelled electrolytes.

Succinonitrile (abbreviated in some of the figures as SCN) exhibits plastic crystal phase formation at temperatures between $-40$ and $58\,°C$ [8]. In the liquid and plastic crystal forms, succinonitrile exists in rotational isomers: gauche and trans. However, at temperatures below $-44\,°C$ only the gauche form exists [9]. When doped with 5 mol% of $Li[CF_3SO_2]_2N$ the plastic crystal range is reduced to $-40$ to $44\,°C$, and with 5 mol% of $LiBF_4$ the plastic crystal phase is found between $-30$ and $41\,°C$ [7]. The conductivities of succinonitrile–lithium salts have already been discussed in prior publications [6,7]. Amongst the lithium salts evaluated, $Li[CF_3SO_2]_2N$ and $LiBF_4$ show the highest conductivities at $1.47 \times 10^{-3}\,S\,cm^{-1}$ for 5 mol% $Li[CF_3SO_2]_2N$–succinonitrile and more than $10^{-4}\,S\,cm^{-1}$ for 5 mol% $LiBF_4$–succinonitrile at room temperature [7]. These conductivities are good enough to use these electrolytes in lithium batteries at room temperature. Lithium ion cells using $Li[CF_3SO_2]_2N$–succinonitrile electrolytes have already been demonstrated and quite good electrochemical performances have been obtained using 5 mol% $Li[CF_3SO_2]_2N$–succinonitrile with a $Li_4Ti_5O_{12}$ anode and either $LiFePO_4$ or $LiCoO_2$ as the cathode material [7,10]. However, the voltage outputs of these cells are only 1.9 V for $LiFePO_4$ and 2.3 V for $LiCoO_2$, and consequently, theses cells cannot deliver high energy densities.

Although prior studies reported that a broad range of lithium salts could be dissolved into succinonitrile, it was found that only a few lithium salts: $Li[CF_3SO_2]_2N$, $LiBF_4$ and LiSCN showed useful conductivities at temperatures below melting [7]. Given that in all cases, ionic salts were being dissolved in a reasonably polar solvent, succinonitrile, these differences in conductivity were not easily understood. In an effort to better understand the cause of the dependence of the conductivities on the nature of the salt, we have conducted powder X-ray diffraction, conductivity and electrochemical characterizations of numerous lithium salt–succinonitrile solutions.

Additionally, for succinonitrile electrolytes, it was believed that metallic lithium anodes could not be used due to the expectation of $Li^0$ catalyzing the polymerization of the succinonitrile [7]. In this paper we report on the first rechargeable lithium metal batteries using succinonitrile–lithium salts electrolytes. Two lithium salts were used: $Li[CF_3SO_2]_2N$ (which is abbreviated as LiTFSI in some of the figures) and $LiBF_4$.

## 2. Experimental

The lithium salts: $LiBF_4$ (Aesar), $Li[CF_3SO_2]_2N$ (Aldrich), $LiClO_4$ (Alfa Products), $LiPF_6$ (Aldrich), and $LiAsF_6$ (USS Agri-chemical) were used as received as was the succinonitrile (Aldrich).

### 2.1. X-ray diffraction

For the X-ray diffraction studies, samples were prepared in two ways. In the first method, samples of lithium salts at 4 mol% concentration were prepared by melting the succinonitrile and then dissolving the required amount of lithium salt in the molten succinonitrile. These molten solutions were injected into 1 mm capillaries in an Argon-filled glove box and then sealed with wax. In the second method, ethanolic solutions of Li salts and succinonitrile were mixed in a 1:2 molar ratio, and then the ethanol was slowly removed under vacuum in a glove-box antichamber. White powders formed readily for $LiAsF_6$, $LiPF_6$ and $LiClO_4$, while a colourless and flakey, 'plastic'-like material slowly formed for $Li(CF_3SO_2)_2N$. The crystals formed for the $LiBF_4$ were some where in between in texture and were cream coloured. None of these 1:2 molar compounds had ever been investigated or even reported previously. These samples were then loaded into 1 mm capillaries in an Argon-filled glove box and heat-sealed.

The X-ray diffraction data were obtained in transmission mode on a Bruker D8 with primary Goebel mirror and a Våntec PSD detector with radial Soller slits. The crystal structures of the adducts of succinonitrile with certain of these lithium salts were indexed, solved and refined from the powder diffraction data with Topas 3. Indexing was done using the singular value decomposition technique and the structure solution using simulated annealing.

### 2.2. DSC and conductivity measurements

Differential scanning calorimetric analysis was performed using a TA Instruments 2920. All the samples were sealed in aluminum DSC pans in an Argon-filled glove box and then scanned from $-100$ to $150\,°C$ at $10\,°C\,min^{-1}$.

Conductivity measurements were performed by the impedance spectroscopy technique between 0.1 Hz and 5 MHz using a Solatron SI 1260 and a platinum conductivity cell ($K = 1\,S\,cm^{-1}$). Samples were heated until melting and then cooled slowly to $-15\,°C$. Conductivity measurements were taken as the temperature was increased from $-15$ to $80\,°C$, allowing 30 min for thermal equilibration at each temperature. The resistance of the sample was taken as the value at which

the low-frequency end of the semi-circle crosses the x-axis of the complex impedance plot.

## 2.3. Electrochemical characterization

Only the two salts that were found to have high conductivities at ambient temperatures, $Li[CF_3SO_2]_2N$ and $LiBF_4$, were evaluated in electrochemical cells. Electrolytes were prepared by dissolving the pre-weighted amounts of either $Li[CF_3SO_2]_2N$ or $LiBF_4$ into molten (70 °C) succinonitrile in an Argon-filled glove box. A concentration of 4 mol% salt to succinonitrile was used for both salts. Electrochemical evaluations were carried out in coin cells (size 2325) using lithium metal discs (Foote Mineral) as anodes. Composite cathodes containing 84:8:8 (w/w) ratios of $LiFePO_4$ (Phostech), Super S carbon black and polyvinylidene fluoride (Kynarflex 2800) binder, respectively, were prepared as slurries in N-methyl pyrrolidinone (Aldrich). The resulting paste was applied to an aluminum film current-collector by the doctor-blade method. The electrode casts were dried in a convection oven at 80 °C prior to use. The active material loading was about 4.5 mg cm$^{-2}$ and the geometric surface area of the cathode was always 1.5 cm$^2$. A separator (Celgard 3501) was imbibed with a melt of the $Li[CF_3SO_2]_2N$- or $LiBF_4$-doped succinonitrile at 70 °C and then positioned on top of the cathode. The lithium metal anodes were positioned on top of the electrolyte film once it had cooled slightly. The cells were assembled in an Argon-filled glove box. Cell tests were conducted at room temperature by galvanostatic cycling at C/24 rate on an Arbin battery cycler. Cyclic voltammograms were obtained at 1 mV s$^{-1}$ scan rate on a Princeton Applied Research potentiostat/galvanostat (model 273A) with the electrolyte sandwiched between lithium and stainless steel (SS) electrodes.

## 3. Results

Although conductivity and DSC studies on the plastic crystal phases of succinonitrile doped with a variety of lithium salts has been reported previously [6,7], no investigations of the crystal structures or phase diagrams were reported. In the paper from Armand's group, three lithium solutes in particular showed high conductivities ($10^{-4}$ to $10^{-3}$ S cm$^{-1}$) at temperatures near ambient: LiSCN, $Li(CF_3SO_2)_2N$, and $LiBF_4$. While others such as $LiPF_6$, $LiCF_3SO_3$ and $LiCF_3CO_2$ had quite low conductivities ($<10^{-5}$ S cm$^{-1}$ at ambient temperature). The DSC data did not suggest any clear differences between the two groups of salts. All showed a rigid to plastic crystal phase transition at −35 °C and melting points lower than neat succinonitrile. To investigate the cause of the differences in the behaviours of the various lithium salt dopants, a study by X-ray powder diffraction patterns was undertaken.

## 3.1. X-ray diffraction characterization

The X-ray diffraction patterns of plastic crystal phases of succinonitrile doped with 4 mol% of various lithium salts, taken in sealed capillaries and at room temperature, are shown in Fig. 1. The pattern of neat succinonitrile is provided for comparison.
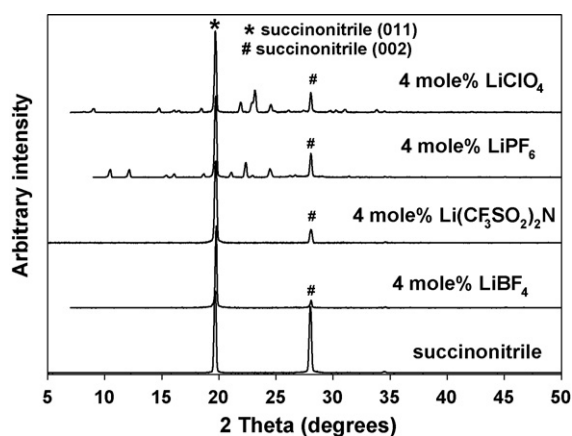


Fig. 1. Room temperature diffraction patterns of 4 mol% LiX in succinonitrile.

Of the salts studied, only two, $Li(CF_3SO_2)_2N$ and $LiBF_4$, had simple diffraction patterns consistent with having only a crystal plastic phase closely related to that of neat succinonitrile. The diffraction patterns of succinonitrile doped with 4 mol% of $LiClO_4$ or $LiPF_6$ both show the presence of a crystalline material with a high degree of ordering in addition to the peaks for a plastic crystal phase related to that of succinonitrile.

Since it was known that 1:2 mixtures of AgX salts and succinonitrile produce crystalline self-assembling network coordination compounds [11], it was postulated that the crystalline material present in the $LiPF_6$ and $LiClO_4$ samples were analogues of known structures with Ag salts. Consequently, a similar synthesis route, of precipitation from an ethanolic solution, was attempted for Li salts of interest: $Li(CF_3SO_2)_2N$, $LiBF_4$, $LiClO_4$, $LiPF_6$, and $LiAsF_6$ (as a possible heavy atom analogue of $LiPF_6$).

The diffraction patterns for 1:2 compositions of lithium salts in succinonitrile are shown in Fig. 2. A comparison to the patterns in Fig. 1 readily shows that the additional crystalline phases in the 4 mol% compositions of $LiClO_4$, and $LiPF_6$ do indeed match that observed from the crystallization of 1:2 molar mixtures of lithium salt and succinonitrile. Although crystalline phases are also formed for $LiBF_4$ and $Li(CF_3SO_2)_2N$, their absence in the diffraction patterns at 4 mol% composi-
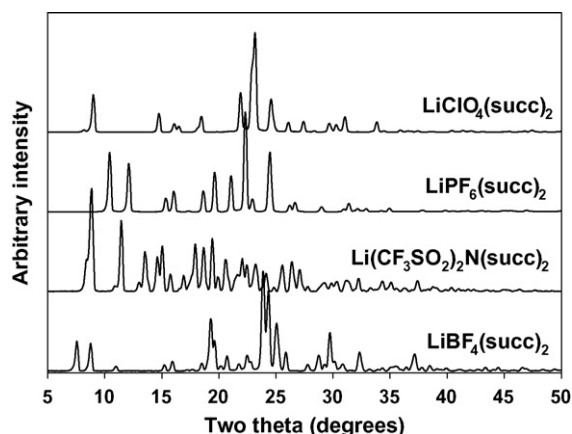


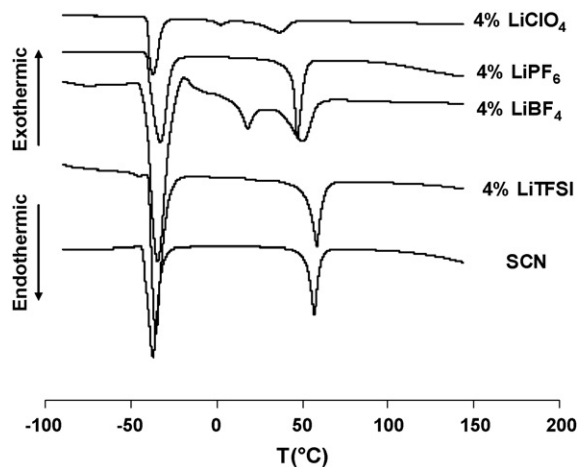Fig. 2. Room temperature diffraction patterns of 1:2 molar ratios of LiX:succinonitrile.

Fig. 3. DSC measurements of 4 mol% solutions of various lithium salts in succinonitrile.

tion correlates with high conductivities being observed at room temperature.

From a comparison to the structures reported previously of the analogous silver salt adducts [11], it was readily determined that the Li salts do not produce direct structural analogues and may have more complex structural changes between anions than those reported for the Ag salts. However, the diffraction patterns for LiPF$_6$, LiClO$_4$ and LiAsF$_6$ could be indexed to single crystallographic unit cells. Details of the crystal structures of the lithium salt adducts will be reported in a separate paper [12].

### 3.2. DSC and conductivity measurements

The DSC measurements for 4 mol% compositions of lithium salts in succinonitrile, shown in Fig. 3, are virtually identical to those reported earlier for 5 mol% solutions [7], with the exception that LiClO$_4$ had not been investigated previously.

The choice of salt has only a small affect on the temperature of the transition from normal solid to plastic crystal phase at temperatures near −35 °C but in all cases, except for Li[CF$_3$SO$_2$]$_2$N, lowering of the temperature of melting of the plastic crystal phase can be observed. Two salts, LiBF$_4$ and LiClO$_4$ have additional endothermic peaks at 18 and 2 °C, respectively. For LiBF$_4$,
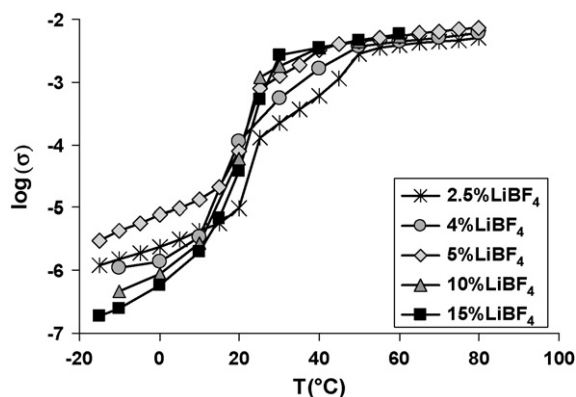


Fig. 4. Conductivity measurement of LiBF$_4$ in succinonitrile at molar concentrations of 2.5–15%.
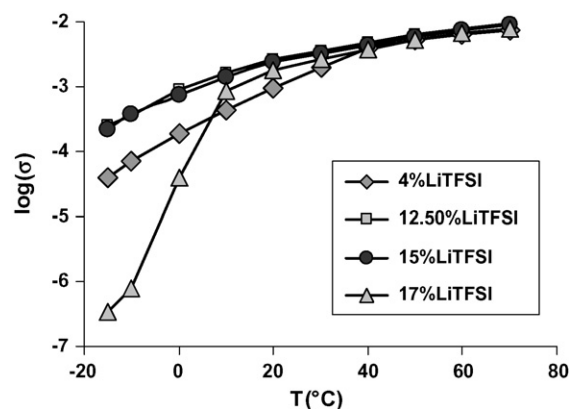


Fig. 5. Conductivity measurement of LiBF$_4$ in succinonitrile at molar concentrations of 2.5–15%.

this additional peak was suggested to be due to a transition from one plastic crystal phase to another [7].

Conductivity measurements for LiBF$_4$ at concentrations from 2.5 to 18 mol% are shown in Fig. 4. It is of interest to note that the conductivity does not increase substantially until temperatures above 18 °C, a temperature that correlates with the additional endothermic event in the DSC scan.

The conductivities of compositions of Li[CF$_3$SO$_2$]$_2$N in succinonitrile from 4 to 17 mol% are shown in Fig. 5. For Li[CF$_3$SO$_2$]$_2$N the conductivities remain high to temperatures well below ambient for compositions up to 15 mol%.

### 3.3. Electrochemical characterization

The electrochemical stability of succinonitrile–4 mol% Li[CF$_3$SO$_2$]$_2$N (abbreviated as LiTFSI in figures) and succinonitrile–4 mol% LiBF$_4$ was investigated by cyclic voltammetry. Fig. 6 shows the cyclic voltammograms, taken at room temperature, of those electrolytes sandwiched between a stain-
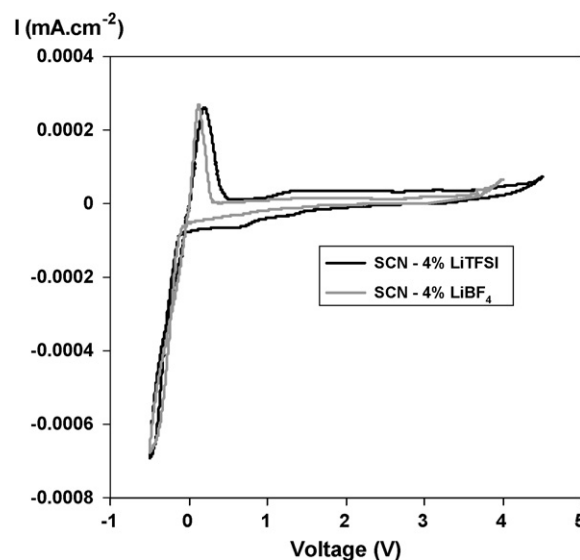


Fig. 6. Cyclic voltammograms of succinonitrile–4% Li[CF$_3$SO$_2$]$_2$N and succinonitrile–4% LiBF$_4$ using lithium as the blocking electrode and stainless steel as the working electrode at a scan rate of 1 mV s$^{-1}$.

less steel electrode and a lithium metal electrode at a scan rate of $1 \, mV \, s^{-1}$. For succinonitrile–4 mol% $Li[CF_3SO_2]_2N$, the voltammogram clearly shows the deposition of metallic lithium at the cathodic limit and stripping of lithium in the returning anodic scan. In the anodic scan, irreversible oxidation started at 4.5 V versus $Li/Li^+$. Consequently, the composite succinonitrile–4 mol% $Li[CF_3SO_2]_2N$ was stable up to 4.5 V. This is a lesser stability than the result that was obtained previously using a silver electrode [7] which found a good stability up to 5.5 V at a scan rate of $20 \, mV \, s^{-1}$. For succinonitrile–4 mol% $LiBF_4$, a cyclic voltammogram again shows the deposition and the stripping of lithium onto the stainless steel electrode. The current responses were negligible below 3.9 V versus $Li/Li^+$. This implies that there is no decomposition of any components in this potential region and that succinonitrile–4% $LiBF_4$ has a suitable electrochemical stability for 3.4 V cathode materials like $LiFePO_4$.

Lithium batteries using either succinonitrile–4% $Li[CF_3SO_2]_2N$ or succinonitrile–4% $LiBF_4$ as the electrolyte were tested at a constant current corresponding to $C/24$ rate. The voltage limits were adjusted to be well within the electrolyte's stability range. For succinonitrile–4% $Li[CF_3SO_2]_2N$ limits of 2.0 and 3.9 V were used, and for succinonitrile–4% $LiBF_4$ the limits were set to 2.0 and 3.7 V. The voltage profiles of those batteries are plotted in Fig. 7. For the cell with succinonitrile–$Li[CF_3SO_2]_2N$ electrolyte, the $Fe^{3+}/Fe^{2+}$ couple is observed at 3.49 V on oxidation and at 3.39 V on reduction. The oxidation and reduction peaks shift only slightly with succinonitrile–$LiBF_4$ electrolyte to 3.50 V on oxidation and 3.38 V on reduction. Such separations between the oxidation and reduction peaks indicate moderate polarization and a reasonable reversibility in the electrochemical process.

The Li/succinonitrile–4% $Li[CF_3SO_2]_2N$/$LiFePO_4$ cell delivered 109 mAh g$^{-1}$ of $LiFePO_4$ in the first cycle and the capacity increased slowly over the first few cycles to stabilize at about 115 mAh g$^{-1}$ (Fig. 8). This capacity is not untypical of $LiFePO_4$ cathodes. Charge/discharge efficiencies of >98% were observed from the second cycle and efficiencies near 100% were found from the sixth cycle onwards.
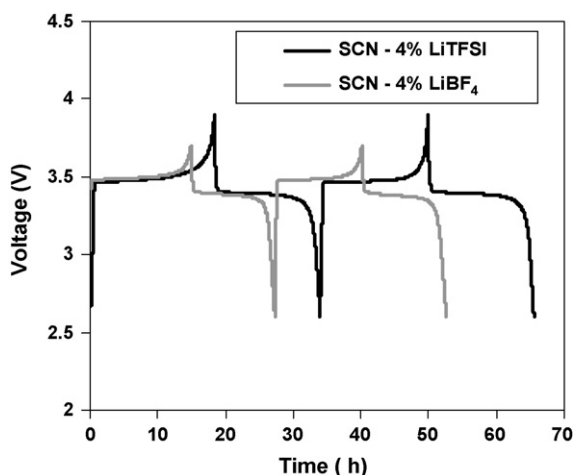


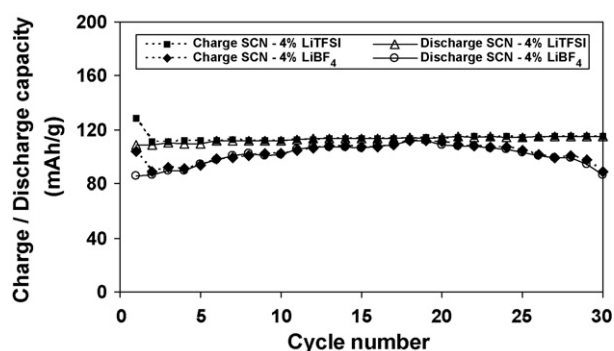Fig. 7. First and second galvanostatic charge–discharge cycles of Li/succinonitrile–4% lithium salt/$LiFePO_4$ cells at $C/24$ rate.



Fig. 8. Specific charge–discharge capacities vs. cycle number for Li/succinonitrile–4% lithium salt/$LiFePO_4$ cells.

The results obtained with succinonitrile–4% $LiBF_4$ electrolyte were not quite as good, with a discharge capacity of only 86 mAh g$^{-1}$ of $LiFePO_4$ and a charge/discharge efficiency of only 83% on the first cycle. The capacities improved somewhat after a few cycles and then decreased again. Given the marked dependence of the conductivity on temperature at temperatures near 20 °C (Fig. 4), the variability in the capacities is most likely due to small changes in the ambient temperature. The capacities being lower than for $Li[CF_3SO_2]_2N$ is due to the lower voltage limit on charging and the higher polarization. However, after the initial cycles, the charge/discharge efficiencies were near 100%.

These results are the first demonstration that contrary to prior predictions succinonitrile-based electrolytes can be successfully used with metallic lithium anodes.

## 4. Conclusions

From X-ray diffraction studies it has been determined that the solubility for certain lithium salts in succinonitrile is much lower than previously thought and that solid crystalline adducts with succinonitrile are formed even at quite low salt concentrations. Consequently, these compositions show no significant conductivity before melting to form ionic solutions. These adducts of succinonitrile with lithium salts had not been reported previously. The two lithium salts studied, $LiBF_4$ and $Li[CF_3SO_2]_2N$, that did not show evidence of adduct formation by X-ray diffraction on room temperature samples at 4 mol% composition were further characterized by DSC, conductivity and electrochemical studies. More detailed studies on the phase diagrams of both $LiBF_4$ and $Li[CF_3SO_2]_2N$ in succinonitrile by variable temperature X-ray diffraction studies have revealed that these systems are actually quite complex [12].

For $LiBF_4$ there is a strong correspondence of the conductivity to the additional endothermic event at 18 °C. This results in strong temperature dependence in electrochemical performance. Additionally, the electrochemical stability is somewhat less than that reported previously [7] and is poorer than for $Li[CF_3SO_2]_2N$. However, it is still adequate for use with lower voltage cathodes such as $LiFePO_4$.

$Li[CF_3SO_2]_2N$, in comparison, shows good conductivity in succinonitrile over a broad range of compositions and temperatures. Furthermore, the electrochemical stability of

Li[CF$_3$SO$_2$]$_2$N–succinonitrile makes it feasible to consider for use with higher voltage cathodes such as Li[Mn, Ni, Co]O$_2$.

The feasibility of using plastic crystal electrolytes for secondary lithium cells has been demonstrated for the first time. Plastic crystal electrolytes formed by doping succinonitrile with either Li[CF$_3$SO$_2$]$_2$N or LiBF$_4$ at low enough concentrations to remain in a plastic crystal form have been shown to have quite reasonable stability in contact with metallic lithium anodes. A lithium secondary cell built with LiFePO$_4$ cathodes and succinonitrile–Li[CF$_3$SO$_2$]$_2$N electrolyte was shown to cycle with high coulombic efficiency and good capacity retention.

Plastic crystal electrolytes, in general, and particularly those formed from succinonitrile and lithium salts can be viewed as a serious alternative to polymer electrolytes for lithium batteries. Very little research on crystal plastic electrolytes has been reported to date, and this has mostly been from two groups: MacFarlane's group at Monash University and Armand's group at the University of Montreal. Their work has opened the way for further research in plastic crystal-salt systems (i.e. to synthesize a crystal plastic with an extended crystal plasticity temperature domain), and for research on electrode–crystal plastic electrolyte interfaces.

## Acknowledgement

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