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Solid Electrolyte Based on Succinonitrile and LiBOB

Interface Stability and Application in Lithium Batteries

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This paper reports physical and electrochemical properties of a solid electrolyte for lithium batteries formed by doping a plastic crystal solvent, succinonitrile, with lithium bioxalato borate (LiBOB). Thermal properties, solubility limits, conductivity, compatibility with lithium, and range of electrochemical stability have been studied. Succinonitrile doped with 4 mol % LiBOB is a solid at room temperature and melts near 50°C. Electrochemical cells employing either $LiFePO_4$ or $Li_{1.2}Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$ as the active cathode material and lithium metal as the anode were evaluated. This solid electrolyte showed excellent performance when combined with a $LiFePO_4$ cathode, delivering a reversible discharge capacity of ~142 mAh g^{-1} with very good capacity retention. However, with the $Li_{1.2}Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$ cathode, the cell's capacity retention was not as good exhibiting a discharge capacity that decreased from 194 mAh g^{-1} in the first cycle to 149 mAh g^{-1} at 20th cycle.
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Lithium-ion batteries have been widely used as power sources for modern portable electronic devices, such as laptop computers, cellular phones, and video cameras. However, these batteries use liquid electrolytes with organic solvents, which are flammable and easy to ignite on exposure to high temperatures. To solve this safety problem, there is a strong desire to switch to non- or less-flammable electrolytes. Crystal plastic solid electrolytes have been emerging as a suitable class of materials that can substitute for polymer and liquid electrolytes in lithium-based rechargeable batteries.[1-3] The ionic transport characteristic of crystal plastic electrolytes is of critical importance to the optimization of theses electrolytes for applications in batteries and fuel cells. Using solid electrolytes, instead of conventional liquid electrolytes in electrochemical systems, improves the safety through reduction of vapor pressure and elimination of electrolyte leakage. In comparison to the polymer electrolytes, crystal plastic electrolytes have been shown to have higher ionic conductivites[3,4] and can provide good room-temperature performance.[5,6] The lithium-ion transference number, the electrochemical window, the crystal plastic temperature range, and the stability vs lithium determine the utility of these materials as electrolytes for lithium batteries.

A few prior studies have been reported on lithium batteries using crystal plastic electrolytes.[3,5-8] The electrolytes used were a mixture of a plastic crystal solvent from the pyrazolium imide family or succinonitrile (SCN) with lithium bis-trifluoromethanesulfonyl imide $[Li(CF_3SO_2)_2N]$ (LiTFSI) salt. In these previous investigations, it was observed that 5 mol % LiTFSI in succinonitrile was sufficient to reach a useful ionic conductivity for room-temperature application, whereas for other plastic crystal electrolytes, such as 5-methyl-5,6,7,8-tetrahydropyrazolo[1,2-a]pyridazin-4-ium trifluoromethanesulfonimide, *N*,*N*′-pentamethylene pyrazolium bis(trifluoromethanesulfonyl)imide, or *N*,*N*′-diethy1-3-methylpyrazolium bis(trifluoromethanesulfonyl)imide a composition higher than 10 mol % LiTFSI was necessary.[6-8]

In this paper, we present an investigation of the thermal behavior and conductivity of a plastic crystal electrolyte formed by doping succinonitrile with 4 mol % lithium bioxalato borate $[Li(C_2O_4)_2B]$ (LiBOB), and a study of the formation and stability of the lithium-electrolyte interface. We also report on the results of electrochemical studies of this solid electrolyte in lithium metal batteries with $LiFePO_4$ or $Li_{1.2}Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$ cathodes.

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Experimental

The preparation of a crystal plastic electrolyte as freestanding thin film is not practical due to the moisture sensitivity of the lithium salt component in ambient air. Consequently, all preparation and handling of these batteries was performed inside an Ar-filled glove box. The lithium salt-doped succinonitrile was heated until melting and then spread as a viscous liquid onto the cathode and the porous separator. For the preparation of cathode disks, a slurry was formed by mixing the active material (84 wt %) with Super S carbon black (4 wt %), graphite (4 wt %), and binder (8 wt %) from a solution of polyvinylidene fluoride (Kynarflex 2800) dissolved in *N*-methyl-2-pyrrolidone. The slurry was coated onto an aluminum current collector. The cathodes were dried under vacuum at 110°C overnight and then disks of 14.2 mm diam were punched and weighed. The electrodes were pressed under 0.3 MPa for 1 min, and the weight of active material in the electrode sheet was ~5 mg cm^{-2}. Electrochemical performances of these solid electrolytes were investigated in coin cells (size 2325), using internal spring and spacer. Batteries were assembled in an argon-filled glove box with lithium foil as the anode and either $LiFePO_4$ or $Li_{1.2}Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$ for the cathode. Cell tests were conducted at 40°C by galvanostatic cycling on an Arbin battery cycler. Cyclic voltammetry was performed in the voltage range of −0.5 to 5 V at a scan rate of 10 mV s^{-1} on a Princeton Applied Research potentiostat/galvanostat (Parstat 2263) with the electrolyte sandwiched between lithium and stainless steel (SS) electrodes. The electrochemical impedance measurements were carried out by applying 2 MHz to 0.01 Hz frequency ranges with oscillation amplitude of 10 mV using a Princeton Applied Research potentiostat/galvanostat (Parstat 2263). The thermal data were obtained with a differential scanning calorimeter module (TA Instruments 2920) at a heating rate of 10°C/min in nitrogen atmosphere.

Results

Succinonitrile exists in the plastic crystal phase between −44°C and 55°C[9,10] and exhibits a body-centered crystal structure. In this phase, the molecules exist in two isometric conformations: a gauche and a transisomer.[10]

Lithium bioxalato borate (LiBOB) is a lithium battery electrolyte salt[11] characterized by its higher thermal stability and ability to form a good solid electrolyte interface (SEI) with lithium. However, the disadvantage of the LiBOB is its lower solubility in organic solvents. The same behavior is observed with succinonitrile, in which the limit of solubility is only 4 mol %.

For the differential scanning calorimetry (DSC) studies, a hermetically sealed pan was slowly cooled to −100°C and then heated to 150°C at a scan rate of 10°C/min. Figure 1 shows the DSC profile for succinonitrile doped with 4% LiBOB. The first endother-

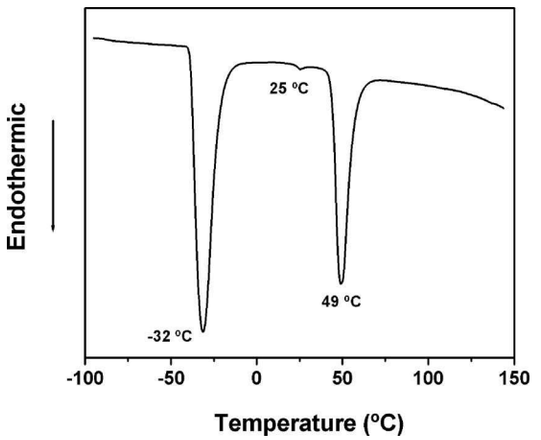

Figure 1. DSC scan of 4% LiBOB doped succinonitrile at a heating rate of 10°C/min.

mic peak at −32°C shows the transformation from the rigid solid state to a plastic crystalline state. The second strong endothermic peak at 49°C is indicating the melting point. The weak endothermic peak at 25°C is probably due to the presence of a eutectic as is observed for the $LiBF_4$–SCN and LiTFSI–SCN systems.[12]

The temperature dependency of the conductivity of succinonitrile doped with 4% LiBOB is shown in Fig. 2. Room-temperature conductivity is $>10^{-4}$ S/cm, and at 40°C, the conductivity reaches a level high enough for practical use in lithium cells, 1.4×10^{-3} S/cm. Although a dependence of ionic conductivity on defect volume was observed for *N*-methyl *N*-ethyl pyrrolidinium TFSI,[13] this model cannot necessarily be applied to salt-doped succinonitrile. The conductivity depends on the nature of salt (anion and cation) and can be influenced by the presence of a eutectic or the formation of adducts.[3,14] For example, the presence of the crystalline adduct $LiPF_6(SCN)_2$ in the XRD data of 4% $LiPF_6$-doped succinonitrile explains its poor conductivity.[12] The formation of a crystalline adduct at low salt concentration was not observed for succinonitrile doped with $LiBF_4$ or LiTFSI; however, these salts form a eutectic with succinonitrile.[13]

Electrochemistry impedance spectroscopy (EIS) analysis can be used to investigate the interfacial reactions between a solid electrolyte and lithium metal.[15] The electrochemical impedance spectroscopy measurements are typically represented as a Nyquist plot. The time evolution of the impedance response was monitored for a Li/4% LiBOB-SCN/Li cell at open circuit potential for 72 h. The low-frequency semicircle in the EIS spectra of Li/4% LiBOB-SCN/Li is attributed to the bulk resistance of the electrolyte. The response plotted in Fig. 3 shows that after 24 h a small expansion occurs in the first semicircle and the formation of a second semicircle is observed. The small expansion of the first semicircle is most probably due to a corrosion reaction between the lithium metal and the electrolyte and is minimized by the formation of a passivation film (second semicircle). In measurements taken after 48 h and 72 h, the impedance responses are very similar to the response after 24 h. This indicates that a passivation film is formed within 24 h and quite stable thereafter.

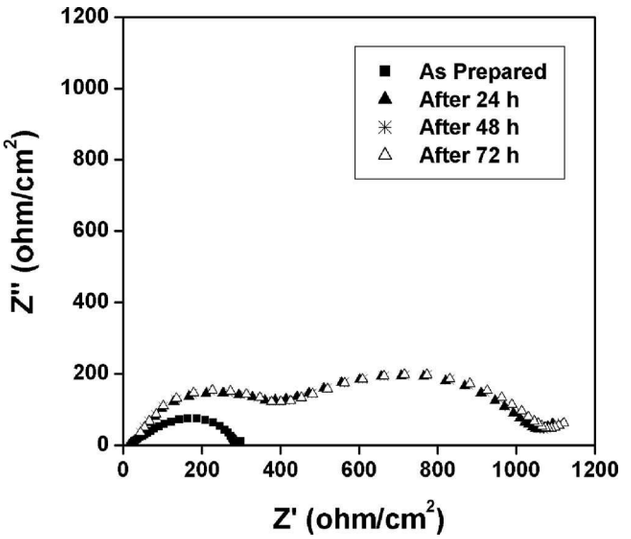

Figure 3. Time evolution of the impedance response of a Li/SCN–4% LiBOB/Li cell at 40°C.

The electrochemical stability window of the 4% LiBOB–SCN electrolyte was measured by cyclic voltammetry at 40 and 50°C in an electrochemical cell at a scan rate of 10 mV/s (Fig. 4). A stainless working electrode was separated from a lithium metal disk,

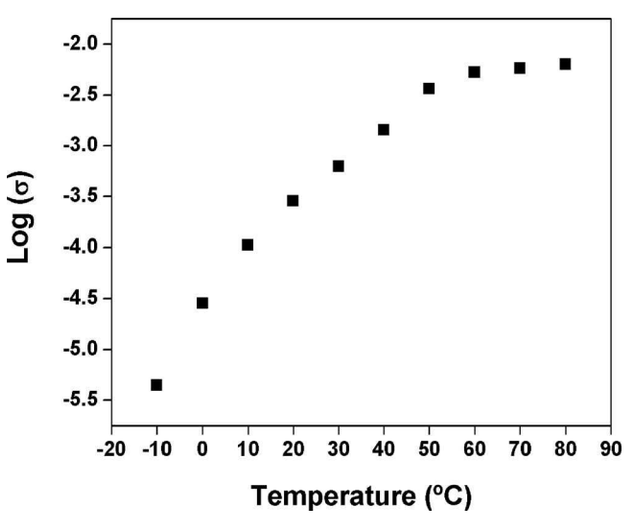

Figure 2. Conductivity of 4% LiBOB doped succinonitrile.

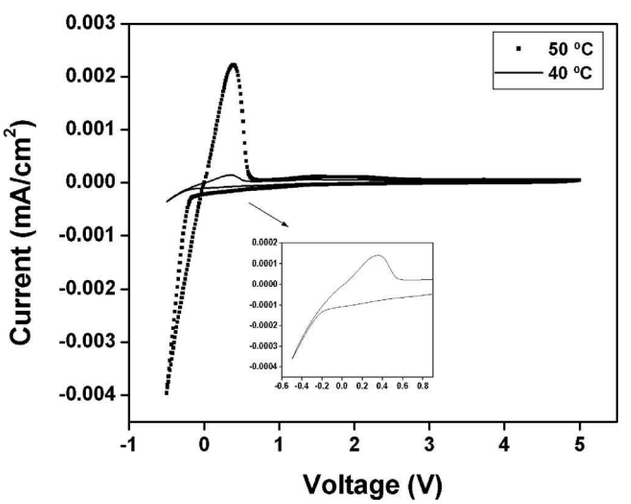

Figure 4. Cyclic voltammograms of SCN–4% LiBOB using lithium as blocking electrode and stainless steel as working electrode at a scan rate of 10 mV s^{-1}. Inset shows detail of 40°C data at low voltage.

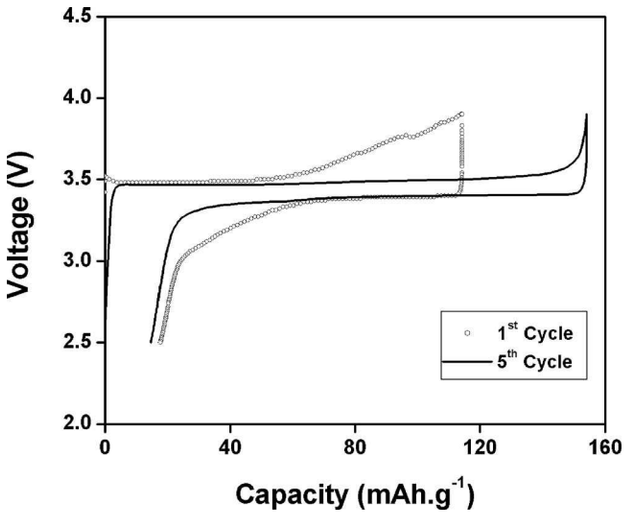

Figure 5. First and fifth galvanostatic (*C*/12) charge-discharge cycles taken at 40°C of a Li/SCN–4% LiBOB/$LiFePO_4$ cell.

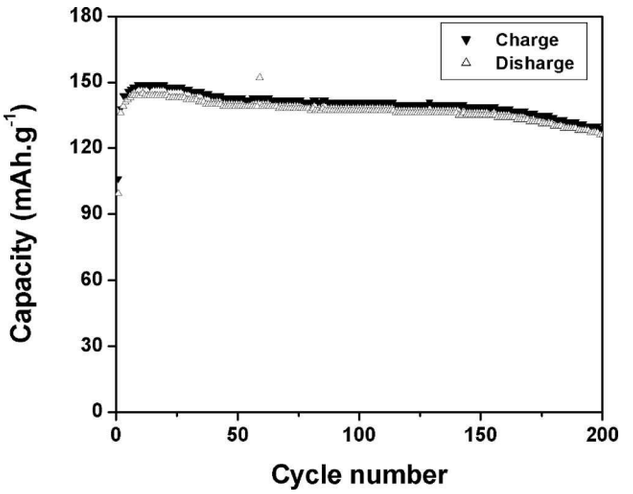

Figure 6. Specific charge-discharge capacity vs cycle number for a Li/SCN–4% LiBOB/$LiFePO_4$ cells cycled at 40°C.

which served as both the reference and counter electrodes by a sheet of microporous separator Celgard 3501 impregnated with the electrolyte. At 40°C, after the lithium stripping at 0.36 V and the lithium deposition at −0.48 V, no onset voltage is observed for either anodic and cathodic currents even at 5 V vs Li/Li+. This indicates that this electrolyte has exceptional electrochemical stability and should be suitable for use in lithium secondary cells with high-voltage cathodes, such as the layered $Li_{1+x}Mn_{0.4}Ni_{0.4-y}Co_yO_2$ oxides. The same behavior is observed at 50°C, except that the current densities for the deposition and the stripping of lithium are increased by 2.7 orders of magnitude due to melting of the plastic crystal electrolyte (shown at 49°C by DSC).

In order to evaluate the electrochemical performance of this plastic crystal electrolyte, test cells were constructed using the 4% LiBOB–succinonitrile electrolyte, a lithium metal anode, and a $LiFePO_4$ cathode. These cells were then cycled at 40°C. Figure 5 presents the variations of voltage vs charge/discharge capacity at the first, and fifth cycles for the Li/4% LiBOB/$LiFePO_4$ cell. For these tests, the voltage range was 2.5–3.9 V vs Li/Li^+, and the current density was *C*/12 (14.2 mA g^{-1}). A voltage plateau near 3.5 V was observed. The initial cycle showed a large ohmic resistance and low capacity, but on cycling, the ohmic resistance between the anode and the cathode decreased (Fig. 5). The total discharge capacity increased from only 97 mAh g^{-1} at the first cycle to 141 mAh g^{-1} by the fifth cycle. The evolution of capacity during cycling in the potential range of 2.5–3.9 V at *C*/12 rate is presented in Fig. 6. The cycle performance was excellent, even after 200 cycles the discharge capacity was still 124 mAh g^{-1}.

The rate performance of Li/SCN–4% LiBOB/$LiFePO_4$ cells were measured at various current densities and are given in Table I. The same current densities were used for both the charge and the discharge. The discharge capacity decreased by only 10% on increasing the rate from *C*/24 to *C*/12, with a discharge capacity of 157 mAh g^{-1} at *C*/24 and 142 mAh g^{-1} at *C*/12. However for higher rates, *C*/8 and *C*/6, the discharge capacities delivered decreased to 93 mAh g^{-1} and 91 mAh g^{-1}, respectively.

The electrochemical performance of lithium metal cells containing 4% LiBOB–SCN electrolyte and $Li_{1.2}Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$ cathodes were also investigated. Figure 7 compares the initial and the fifth cycle charge-discharge capacities for a Li/SCN–4% LiBOB/$Li_{1.2}$ $Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$ cell cycled between 2.5 V and 4.6 V at *C*/24 rate (with $C = 240$ mAh g^{-1}). The cell has a higher charge capacity (~240 mAh g^{-1}) and also a higher discharge capacity (193 mAh g^{-1}) than the previous cell with a $LiFePO_4$ cathode. A low coulombic efficiency in the first few cycles is characteristic of the $Li_{1.2}Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$ system and is believed to be due to an irreversible process that involves removal of lithium and oxygen from the material.[16] However, as shown in Fig. 8, the coulombic efficiency improves after a few cycles to near 99%. But as can also be seen in Fig. 8, the capacity decreased gradually on cycling to be only 149 mAh g^{-1} by the 20th cycle.

Conclusion

We have reported electrochemical studies of lithium bioxalato borate (LiBOB) doped succinonitrile electrolyte. This solid electrolyte shows good thermal stability, high ionic conductivity, a wide electrochemical stability window, and good compatibility with

Table I. Li/SCN–4% LiBOB/$LiFePO_4$ cell discharge capacities at different discharge rate.

Current	*C*/24	*C*/12	*C*/8	*C*/6
Discharge capacity (mAh g^{-1})	157	142	93	91

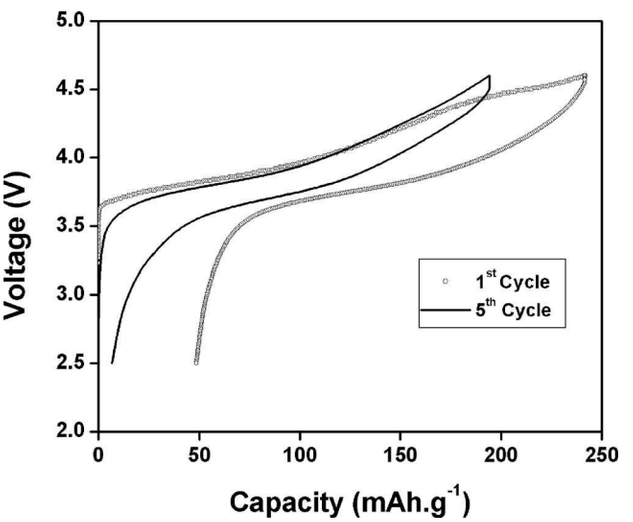

Figure 7. First and fifth galvanostatic (*C*/12) charge-discharge cycles taken at 40°C for a Li/SCN–4% LiBOB/$Li_{1.2}Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$ cell.

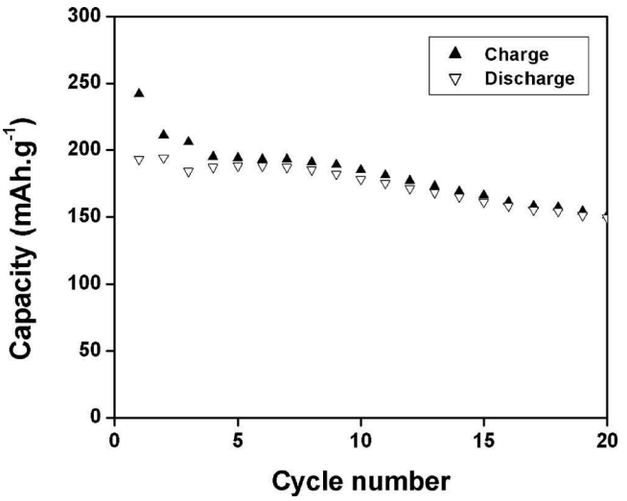

Figure 8. Specific charge-discharge capacity vs cycle number for a Li/SCN–4% LiBOB/$Li_{1.2}Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$ cell cycled galvanostatically between 2.5 V and 4.6 V at *C*/12 rate.

lithium metal. Electrochemical evaluations in lithium batteries have demonstrated that 4% LiBOB-doped succinonitrile is a good solid electrolyte for use with lower voltage cathodes, such as $LiFePO_4$, but further optimization is needed for use with higher voltage cathodes, such as $Li_{1.2}Mn_{0.4}Ni_{0.3}Co_{0.1}O_2$.

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