



Sulfone-carbonate ternary electrolyte with further increased capacity retention and burn resistance for high voltage lithium ion batteries



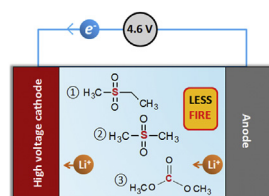
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HIGHLIGHTS

- Much improved sulfone-carbonate high voltage electrolyte, by small sulfone inclusion.
- Striking threefold decrease in capacity fade, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode over 300 cycles.
- Electrolyte conductivity increased by factor of 2, to approach all-carbonate value.
- Low fire risk property further enhanced by elimination of another $-\text{CH}_3$ group.
- Finally, DSC studies show improved low temperature stability by eutectic effect.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 April 2015

Received in revised form

17 June 2015

Accepted 24 June 2015

Available online 11 July 2015

Keywords:

Lithium ion battery

Electrolytes

Low flammability

High voltage

Sulfone eutectic

ABSTRACT

Safety and high energy density are the two focus issues for current lithium ion batteries. For safety, it has been demonstrated that sulfone electrolytes are much less flammable than the prevailing all-carbonate type, and they are also promising for high voltage batteries due to the high oxidation resistance. However, the high melting points and viscosities greatly restricted their application. Based on our previous work on use of fluidity-enhancing cosolvents to make binary sulfone-carbonate electrolytes, we report here a three-component system that is more conductive and should be even less flammable while additionally having better low temperature stability. The conductivity–viscosity relations have been determined for this electrolyte and are comparable to those of the “standard” carbonate electrolyte. The additional component also produces much improved capacity retention for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode. As with carbonate electrolytes, increase of temperature to 55 °C leads to rapid capacity decrease during cycling, but the capacity loss is due to the salt, not the solvent. The high discharge capacity observed at 25 °C when LiBF_4 replaces LiPF_6 , is fully retained at 55 °C.

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1. Introduction

Rare but fiery accidents with all-electric vehicles serve as a reminder that electrochemical technology has not yet provided us

with fully safe emission-free automobile power trains. Risk lies mainly in the electrolytes, highly flammable acyclic carbonate being the leading risk solvent in current batteries. We have recently shown that electrolytes with high sulfone content can provide excellent electrochemical performance with high voltage cathodes [1], while Amine and others [2–4] have shown that such electrolytes are much less flammable than the standard (carbonate) electrolytes.

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The oxidation resistance of acyclic sulfones has actually been recognized for some time [5,6]. What has been more recently discovered is that sulfones can be combined with less oxidation resistant but fluidity-enhancing cosolvents without losing their oxidation resistance [1,6]. This has been shown, by simulation studies [7], to be due to a preferential (and protective) ordering of sulfone molecules near the electron-rich highly positive-charged surface of the cathode. With the emergence of 5 V class spinel $[\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4]$ (LNMO, 4.6 V) [8] or cobalt phosphate (LiCoPO_4 , 4.8 V) [9] cathodes, whose operating potentials lie beyond the expected stability limits of the carbonate-based electrolytes (4.5 V) [10], this sulfone-carbonate electrolyte synergism would seem to be an important development. While there is some concomitant decrease in safety from the carbonate co-solvent addition, the sulfone-carbonate binary electrolyte is still far safer than the commercialized all-carbonate electrolytes.

In recent papers [1,11] we explored the ionicities, and half cell performances, of 1M LiPF_6 solutions in a variety of binary solvents that contain one or other sulfone as the polar (ion solvating) component together with a low dielectric constant but high fluidity acyclic carbonate, as the co-solvent. We showed that the combination ethylmethylsulfone (EMS) + dimethyl carbonate (DMC) provides very favorable electrochemistry at both the high voltage LNMO cathode and the lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) anode.

In the present extension of our studies, we have incorporated the smaller, more highly polar, but higher melting dimethyl sulfone (DMS) in proportions to minimize the binary sulfone liquidus temperature [12,13]. The eutectic temperature of the simple binary system lies at 23 °C, far below the melting point of DMS (110 °C) and also EMS (36.5 °C). The addition of electrolyte salt and the low-melting DMC of course lead to a substantial further stabilization of the liquid, which we document herein. The design consideration of this ternary electrolyte can be outlined as in Fig. 1.

While stabilizing the electrolyte for lower temperature application is important, our initial interest was in finding whether the conductivity and ionicity could be incrementally increased by incorporation of the smaller, highly polar sulfone DMS. While this improvement has indeed been realized, a more important and unexpected improvement has been found. This is that, in half-cell testing with the high voltage LNMO cathode, we find we have obtained a much smaller rate of capacity loss than the already small value for the two component solvent case reported previously [1]. Moreover, with only two CH_3 groups per molecular DMS (see Fig. 1)

compared with the four in sulfolane [2], the burn resistance should also be enhanced.

Not surprisingly, the excellent performance found with the ternary solvent electrolyte is not maintained at 55 °C, but this is not a solvent problem. It is due to intrinsic PF_6^- thermal instability, which we establish by replacing the PF_6^- anion with the more thermally stable BF_4^- anion and showing we can obtain a temperature independent cycling performance. We report these substantial improvements in sulfone electrolyte technology below.

2. Experimental

EMS (>98.0%) and DMC (>98.0%) were purchased from TCI company, and all other chemicals used were bought from Sigma-Aldrich, all used without further purification. A known mass of EMS was first heated at 50 °C to obtain the liquid state, and the mass of DMS needed for the desired sulfone composition then dissolved. The EMS 85mol%-DMS 15mol% mixture stays liquid at room temperature due to proximity to the eutectic composition. DMC was then added to obtain (EMS85-DMS15)-DMC ternary solvent, which is reported in weight % DMC, or weight ratio DMC. Finally LiPF_6 was added to the solvent to obtain an electrolyte with a concentration of 1 mol L^{-1} .

For the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode, preformed sheets were provided by Hydroquebec Co. under arrangement with the DOE LBL-BATT research program. They comprised LNMO 89%, carbon black 3%, vapor grown carbon fiber (VGCF) 3% and polyvinyl difluoride (PVDF) 5% in mass.

Viscosity measurements were performed using a Cannon-Manning viscometer, which was calibrated by the manufacturer. The temperature was controlled to ± 0.1 °C by means of a water circulating bath (LC20, Lauda).

Solution densities were measured with accuracy sufficient for obtaining equivalent conductivities for our Walden plots (~1%), simply by measuring the weight of the sample filling a 1 mL volumetric flask at different temperatures. Before each measurement, the flask was maintained in an aluminum block at the desired temperature for 0.5 h to obtain a uniform temperature.

Ionic conductivities were measured by the standard complex impedance method, using a PARSTAT2273 apparatus (Princeton Applied Research) with a frequency range of 10 Hz to 1 MHz. The electrolytes were contained in a dip-type cell with twin platinum electrodes. The cell constant of 17.07 cm^{-1} was determined using

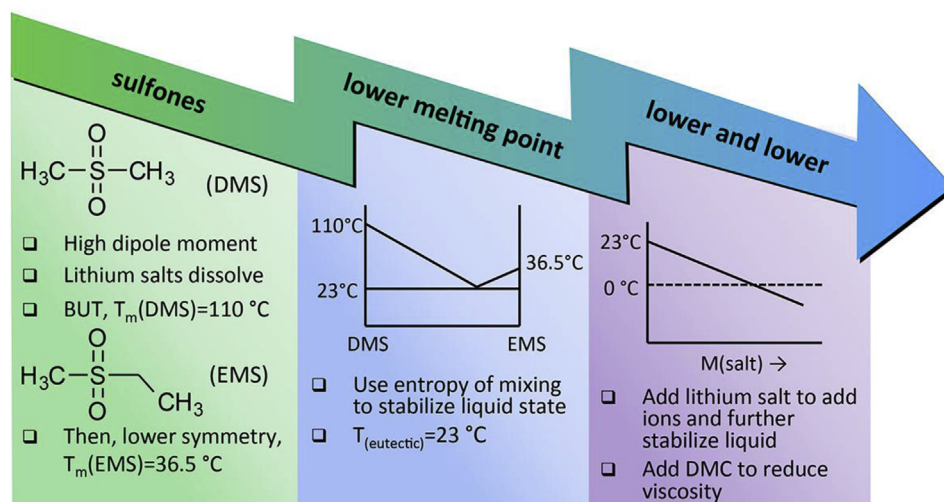


Fig. 1. Schematic presentation of the design of sulfone-carbonate ternary electrolyte.

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