



# Mixtures of Ionic Liquid and Sulfolane as Electrolytes for Li-Ion Batteries



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## ABSTRACT

In this study, novel temperature stable electrolyte mixtures are investigated with respect to their use in Li-ion cells. Sulfolane, 3-methylsulfolane, and the ionic liquid N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl) azanide (DMMA-TFSA) are chosen as main components in the electrolyte mixtures. The electrolytes are studied in cell tests with LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (NMC) as cathode and graphite as anode material. The performance of the cells is tested at room temperature and at elevated temperatures (40 °C) which demonstrates the significant improvement of the cell performance by raising the temperature slightly. Furthermore, the additives vinylene carbonate and hexamethyldisilazane are used to improve the electrolyte properties with respect to cell performance and long term stability.

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## 1. Introduction

Lithium-ion batteries are the most prospective chemical energy storage tools for high power electrical applications like the automotive sector. However, there are still challenges regarding safety (flammability), high voltage, and toxicity issues for Li-ion cells. Therefore, alternative electrolyte mixtures are besides the electrode investigation still one of the main focus areas of the battery researchers.

Up to date, most commercial electrolytes are mixtures based on organic carbonates and LiPF<sub>6</sub>. Namely, dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylmethyl carbonate (EMC) are used extensively in spite of their high flammability. Therefore, the battery has to be prepared with different kinds of safety tools which reduce the risk of fire or explosion, but increase the cost and weight of the cell pack. Thus, electrolyte mixtures should be developed which enable an improvement in the intrinsic cell safety.

One interesting class of electrolyte solvents regarding high voltage applications and high safety are sulfolane derivatives [1–4].

An outstanding electrochemical oxidation stability, a moderate conductivity, an appropriate dipole moment and dielectric constant, a high flash point and boiling point, and the stability of aluminum against dissolution at high potentials are main advantages [5–8] of these class of compounds. As expected, the anion of the lithium salt contributes and affects the electrochemical properties of such sulfolane-conducting salt mixtures significantly [5]. However, the cell performance is considerably reduced compared to carbonate-based mixtures because of the increased viscosity [8]. Furthermore, additives are mentioned to be necessary to obtain an accurate solid electrolyte interface (SEI) film onto negative graphite electrodes [8,9]. Sedlarikova et al. demonstrated the principal use of sulfolane (SL) and mixtures of sulfolane (SL) with carbonates (DMC, propylene carbonate (PC)) and the conducting salt LiClO<sub>4</sub> in Li-ion based cells [6]. However, a fast fading was observed against graphite anodes [6]. Li et al. proved mixtures of SL and sulfites with lithium bis(oxalato) borate (LiBOB) as conducting salt to be an option as electrolyte solvents for Li-ion cells [10], but the addition of these compounds reduce the flash points significantly.

Another approach to enhance the safety of the battery cell is the use of ionic liquids (IL) as electrolyte component or additive because of the negligible vapor pressure and high flash points (> 300 °C) [11–13]. It is found that N,N-diethyl-N-methyl-N-(2-

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methoxyethyl) ammonium bis(trifluoromethylsulfonyl) azanide (DMMA-TFSA) effectively hampers the aluminum dissolution at high voltages against Li/Li<sup>+</sup> [14] and provides an acceptable ionic conductivity [15,16] which makes it very attractive as electrolyte component. In addition, the replacement of the conducting salt LiPF<sub>6</sub> with more temperature stable salts like LiBOB or lithium bis(trifluoromethanesulfonyl) azanide (LiTFSA) increases the safety properties, too [17,18]. However, there are still challenges based on the long term stability of such electrolyte mixtures because of aluminum dissolution at high cell voltages, solid electrolyte interface (SEI) stability and capacity fading [19].

Very recently, Xiang et al. published the usability of mixtures of sulfolane and ionic liquid (piperidinium based IL) as electrolytes for Li-ion half cells (Li/LiFePO<sub>4</sub> and Li/Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub>) for up to 50 cycles [20]. However, lithium cannot be used in commercial cells because of the growth of Li dendrites onto the surface of Li. Furthermore, a quasi-infinite reservoir of Li impedes the analysis of the cell regarding lithium fading, solid electrolyte interface (SEI) stability, long-time stability, and continuous consumption of Li for the SEI layer.

The aim of this study is to evaluate the feasibility of novel sulfolane (SL) and DMMA-TFSA mixtures including the sulfolane derivative 3-methylsulfolane (M-SL) as electrolyte component in Li-ion based batteries against graphite. Therefore, the electrolytes are studied in the cell system graphite and LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>. In addition, the effects of selected additives are investigated, namely vinylene carbonate (VC) and hexamethyldisilazane (HMDS which are necessary to obtain a stable SEI layer and preferably reduced traces of water and capacity fading.

## 2. Experimental

N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)azanide (DMMA-TFSA, IoLiTec > 99.8%), lithium bis(trifluoromethylsulfonyl)azanide (LiTFSA, IoLiTec > 99.5%), sulfolane (SL, Sigma-Aldrich, 99%), and 3-methylsulfolane (M-SL, TCI europe, >98%, 725 ppm H<sub>2</sub>O) were dried at 120 °C (Karl-Fischer). Vinylene carbonate (VC, Aldrich, 97%), hexamethyldisilazane (HMDS, Sigma-Aldrich, 99%), lithium foil (Alfa Aesar, 0.75 mm thick), and aluminum foil (Hohsen Corp., Japan, current collector quality) were used as received. The preparation of the electrolytes was performed in an argon-filled glove box (MBraun GmbH) with oxygen and water levels below 0.5 ppm. During the preparation of the electrolyte mixtures it is observed that the glass vial is silanized for very high concentrations (8 m.-%) and that the solubility limit is nearly reached. Calandered electrodes based on graphite and NMC with a content of approximately 90% of active material were provided in cooperation.

For the drying procedure and the verification of the water content, a coulombmetric Karl-Fischer titrator was used. The

titrator consists of a 831 KF Coulometer and a 860 KF Thermoprep oven from Metrohm. The water content of the solvents was less than 10 ppm.

In this study common coin cells (type: CR 2032, Hohsen Corp.) were used with a coin cell crimper from BT Innovations (Canada). The cells were assembled in an argon-filled glove box according to standard procedures. Precisely, a graphite anode (Ø = 15 mm), a NMC cathode (Ø = 15 cm), and a glass fiber separator (Whatman<sup>®</sup>, GF/B and QMA 450; Ø = 16 mm) were used inside a coin type cell with one spring and one stainless steel spacer (electrolyte volume: 140 µl).

The ionic conductivity of the electrolytes was measured by the standard complex impedance method, using a Zahner Zennium IM6 electrochemical workstation in the frequency range from 1 kHz to 1 MHz. A 1.6 ml closed cell (0.85 ml solvent) from RHD instruments is used for the measurements. The temperature dependence (0–80 °C) of the ionic conductivity was recorded by placing the test cells in a temperature and humidity chamber (ThermoTec Espec, SH-261). Before each measurement the cells were thermally equilibrated for at least 30 min. In the phase minimum (~ 0°) the impedance value | → Z<sup>+</sup> | was used for calculating the specific conductivity κ according to κ = C/| → Z<sup>+</sup> | with the cell constant C = 17.0139 cm<sup>-1</sup>. The cell constant was received by measuring a standard solution (1.413 mS cm<sup>-1</sup> at 25 °C, Hanna instruments, HI 70,031). The internal resistance of the cells were measured via complex impedance. The value of the resistance, which is mentioned in the text, was extracted from the Bode-plot in the minimum of the phase (~ 0°).

The cyclovoltammograms were measured at a Zahner XPOT potentiostat (software: PPseries, Potentiostat XPot Zahner elektrik 6.4). The potential range was 2.5 – 6 V vs. Li/Li<sup>+</sup> with platinum as working electrode. The cells were measured in 3-electrode configuration (EE-Cells manufactured by EL-Cell GmbH) with reference and working electrodes composed of lithium. The scan speed applied for all CV tests was 5 mV/s. A potential with significant increase in the current density is used as limit for the oxidative stability.

The battery tests were performed on a lithium cell cycler (LICCY, development of KIT, Institute of Data Processing and Electronics) with a maximum current of 10 mA and a voltage range of 0 – 10 V. The cut-off voltage is given in the text. The potentials reported in this paper are that of the positive electrode with respect to the counter electrode. The charging and discharging cycles were conducted with constant current based on the C-rate of the material used. A detailed description can be found in Ref. [21]. Dynamic viscosity was measured using a Malvern Gemini HR Nano rotational rheometer with 40/1° cone geometry and a gap of 30 µm. These experiments were performed by using a solvent evaporation protecting cover in air. The density of the electrolyte mixtures was obtained by repeated measurement of the mass of

**Table 1**

Composition, viscosity data, conductivity data and oxidative stability of electrolyte mixtures and solvents.

sample	solvents(ratio/wt.-%)	conducting salt (c/molkg <sup>-1</sup> )	additives (c[wt.-%])	E <sub>ox</sub> , Li Pt[V]	viscosity η(25 °C)[mPa s]	conductivity κ(25 °C)[mS cm <sup>-1</sup> ]
SL	SL	–	–	> 5 V <sup>a</sup>	11.4(30 °C)	< 0.004
M-SL	M-SL	–	–	> 5 V <sup>a</sup>	14.5	< 0.004
DMMA	DMMA	–	–	5.6 ± 0.1	82.2	2.11
EM-0	EC/DMC(1:1)	LiPF <sub>6</sub> (0.787)	–	5.6 ± 0.1	4.0	11.68
EM-1	SL	LiTFSA (1)	VC (5), HMDS (1)	5.0 ± 0.1	49.9	2.32
EM-2	M-SL	LiTFSA (1)	VC (5), HMDS (1)	5.0 ± 0.1	57.1	1.64
EM-3	DMMA	LiTFSA (1)	VC (5), HMDS (1)	5.0 ± 0.1	434.2	0.44
EM-4	SL/DMMA(1:1)	LiTFSA (1)	VC (5), HMDS (1)	4.9 ± 0.1	100.0	1.58
EM-5	M-SL/DMMA(1:1)	LiTFSA (1)	VC (5), HMDS (1)	4.9 ± 0.1	122.0	1.24
EM-6	SL/DMMA(2:1)	LiTFSA (1)	VC (5), HMDS (1)	5.1 ± 0.1	67.0	2.08
EM-7	M-SL/DMMA(2:1)	LiTFSA (1)	VC (5), HMDS (1)	5.1 ± 0.1	87.3	1.41

<sup>a</sup> No significant increase of the current density is observed up to 6 V.

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