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# Improving sulfolane-based electrolyte for high voltage Li-ion cells with electrolyte additives



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## HIGHLIGHTS

- Sulfolane:ethylmethyl carbonate-based electrolytes with additives are studied.
- The additive combination of vinylene carbonate and tri-allyl phosphate is best.
- Li(Ni<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>)O<sub>2</sub>/graphite cells with such electrolytes operate well to 4.5 V.

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## ABSTRACT

An electrolyte mixture containing 1 M LiPF<sub>6</sub> in sulfolane:ethylmethyl carbonate 3:7 with vinylene carbonate and other electrolyte additives exhibited promising cycling and storage performance in high voltage Li(Ni<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>)O<sub>2</sub>/graphite pouch type Li-ion cells tested to 4.5 V. Voltage drop during storage, coulombic efficiency, charge endpoint capacity slippage during ultra high precision cycling, charge-transfer resistance after storage or cycling, gas evolution during storage and cycling as well as capacity retention during long-term cycling were examined. The results for cells with sulfolane-based electrolytes were compared with those for cells with ethylene carbonate-based electrolytes containing state-of-the-art electrolyte additives. This survey showed that the combination of vinylene carbonate and triallyl phosphate as electrolyte additives in sulfolane:ethylmethyl carbonate electrolyte yielded cells capable of better performance during tests to 4.5 V than cells with ethylene carbonate-based electrolytes. These results suggest that sulfolane-based electrolytes may be promising for high voltage Li-ion cells.

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## 1. Introduction

Li-ion batteries have been extensively used as power sources in applications such as mobile devices, electric vehicles (EVs), hybrid EVs (HEVs) and grid energy storage. Improvements in energy density as well as cycle or calendar lifetime are desired for these applications [1]. While the lifetime of all Li-ion cells can be improved by using suitable electrolyte additives, the energy density depends on the choice of electrode materials [2,3]. Efforts to increase energy density have led to the development of positive and negative electrode materials with higher specific capacities as well as the positive electrode materials with a higher average potential vs Li/Li<sup>+</sup>. Some high potential positive electrode materials have been developed such as LiCoPO<sub>4</sub> [4,5], Li<sub>2</sub>CoPO<sub>4</sub>F [6], Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> [7], LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> [8], and Li[Ni<sub>x</sub>Mn<sub>x</sub>Co<sub>1-2x</sub>]O<sub>2</sub> [9]. Long-term

performance of Li-ion cells operating to potentials above 4.4 V has been poor due to increased electrolyte oxidation at the surface of positive electrode as the potential increases [10–12]. These issues with Li-ion cells, even incorporating state of the art electrolytes, begin to appear at 4.3 V [13] and become very problematic at or above 4.5 V during cell operation [14,15].

One solution to the electrolyte oxidation problem is to find new alternative electrolyte formulations with high anodic stability. Sulfone-based electrolytes have been developed since they have high dielectric constant and high electrochemical oxidation potential compared with carbonate-based electrolytes [16–20]. However, sulfone-based electrolytes also suffer from their high melting point, high viscosity and most importantly inability to passivate the graphite electrode well. Therefore, a secondary solvent that can decrease viscosity and proper electrolyte additives that can passivate the graphite electrode are needed. Recently, Xia et al. [21] demonstrated an electrolyte system composed of sulfolane (SL), ethylmethyl carbonate (EMC) and vinylene carbonate

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(VC) which showed good cycling and storage performance in NMC442/graphite Li-ion pouch cells. Problems with SL:EMC:VC electrolyte are gas evolution during cycling and storage at high temperatures. Therefore, it is quite crucial and interesting to find electrolyte additives which could function as a gas reducer in SL:EMC electrolytes and, when used together with VC, are competitive or better than state-of-the-art EC-based electrolytes containing electrolyte additives.

Some sulfur containing additives such as prop-1-ene-1,3-sultone (PES) [22,23], methylene methanedisulfonate (MMDS) [24] and trimethylene sulfate (TMS) [25] have been shown to be good gas reducers in NMC111/graphite Li-ion pouch cells. The beneficial effect of these additives is enhanced when combined with a third electrolyte additive, namely, tris(trimethylsilyl) phosphite (TTSPi). Several combinations have shown good storage and cycling performance as well as improved safety features in both NMC111/graphite and NMC442/graphite Li-ion pouch cells [26–28]. Beside these sulfur-containing additives, triallyl phosphate (TAP) was also studied as a good gas reducer at high temperatures in NMC442/graphite pouch cells [29]. When TAP was used together with PES, gas evolution was further decreased while the cycling and storage performance were improved [30].

In this paper, the SL:EMC:VC solvent mixtures with various different electrolyte additives were studied in NMC442/graphite Li-ion pouch cells. Experiments were made using Ultra High Precision Coulometry (UHPC) [31], a precision storage system [32], an *ex-situ* gas evolution apparatus [33] as well as electrochemical impedance spectroscopy (EIS) [34]. Long-term cycling results were also conducted to compare the SL:EMC:VC electrolyte system with EC-based electrolyte systems containing some promising additive blends.

## 2. Experimental

1 M LiPF<sub>6</sub> EC/EMC (3:7 wt% ratio, BASF, 99.99%) was used as the control electrolyte. 1 M LiPF<sub>6</sub> Sulfolane/EMC (3:7 wt% ratio) was used as the studied electrolyte. The sulfolane was obtained from Novolyte Technologies, now BASF (99.99% pure with 9.2 ppm water). The additives were added at 1–8 wt% to the studied electrolyte. These additives included vinylene carbonate (VC), prop-1-ene-1,3-sultone (PES), methylene methanedisulfonate (MMDS), ethylene sulfite (ES), Propanediol cyclic sulfate (trimethylene sulfate - TMS), 1,3,2-dioxathiolan-2,2-oxide (ethylene sulfate - DTD), tris(trimethylsilyl) phosphite (TTSPi) as well as triallyl phosphate (TAP). Fig. S1a (supporting information) shows the chemical structure of additives that were studied in this paper. The reasons for choosing these additives are explained in Refs. [26] and [29]. The purities and the suppliers of the additives used are listed in Table 1 (supporting information). Some promising electrolyte additive combinations in 1 M LiPF<sub>6</sub> EC:EMC (3:7 by wt.) electrolyte include 2% PES + 1% MMDS (or DTD) + 1% TTSPi (PES211) and 2% PES + 2%TAP were also used for comparison in some of the experiments. The details of the PES211 electrolyte have been reported in Ref. [14].

The 402035-size pouch cells employed in this study were all Li [Ni<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>]O<sub>2</sub> (NMC442)/graphite cells with a capacity of 245 mAh balanced for 4.7 V operation. Fig. S2 shows SEM images of the top surfaces of the NMC442 and graphite electrodes so that readers can appreciate the morphology of the particles that make up the electrodes. The cells were produced by Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). The pouch cells were vacuum sealed without electrolyte in China and then shipped to our laboratory in Canada. Details about the electrode loadings, thicknesses, compressed electrode density, separator, etc., can be found in Ref. [35].

Before filling with electrolyte, the cells were cut just below the heat seal and dried at 80 °C under vacuum for 14 h to attempt to remove residual water. Then the cells were transferred immediately to an argon-filled glove box for filling and vacuum sealing. The NMC442/graphite pouch cells were filled with 0.75 mL of electrolyte (0.90 g for EC:EMC 3:7 electrolyte and 0.86 g for SL:EMC 3:7 electrolyte). After filling, cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.). First, cells were placed in a temperature box at 40 °C where they were held at 1.5 V for 24 h, to allow for the completion of wetting. Then, cells were charged at 12 mA (C/20) to 3.5 V. This step is called formation step 1. After formation step 1, cells were transferred into the glove box, cut open to release any gas generated and vacuum sealed again. These cells were then charged again from 3.5 V at 12 mA (C/20) to 4.5 V. This step is called formation step 2. After formation step 2, the cells were transferred into the glove box, cut open to release gas generated and then vacuum sealed again. These degassing voltages were selected based on the in-situ gas evolution experiments that show most of the gas evolves in the formation step at voltages below 3.5 V and above 4.3 V [36]. After the two degassing processes, cells were then discharged to 3.8 V where impedance spectra were measured.

The cycling/storage procedure was carried out using the Ultra High Precision Charger (UHPC) at Dalhousie University [31]. Testing was between 2.8 and 4.4 V at 40 ± 0.1 °C. Cells were first charged to 4.400 V using currents corresponding to C/10, stored open circuit at 4.400 V for 20.00 h and then discharged to 2.800 V using currents corresponding to C/10. This process was repeated on the UHPC for 15 cycles where comparisons were made. The cycling/storage procedure was designed so that the cells were exposed to higher potentials for significant fractions of their testing time [37]. For storage experiments, cells were first discharged to 2.8 V and charged to 4.5 V two times. Then the cells were held at 4.5 V until the measured current decreased to 0.0025 C. A Maccor series 4000 cyler was used for the preparation of the cells prior to storage. After the pre-cycling process, cells were carefully moved to the storage system which monitored their open circuit voltage every 6 h during a total storage time of 500 h. Storage experiments were made at both 40 and 60 °C.

*Ex-situ* (static) gas measurements were used to measure gas evolution during formation and during cycling [33]. The measurements were made using Archimedes' principle with cells suspended from a balance while submerged in liquid. The changes in the weight of the cell suspended in fluid, before and after testing are directly related to the volume changes through the change in the buoyant force. The change in mass of a cell,  $\Delta m$ , suspended in a fluid of density,  $\rho$ , is related to the change in cell volume,  $\Delta v$ , by

$$\Delta v = -\Delta m/\rho \quad (1)$$

*Ex-situ* measurements were made by suspending pouch cells from a fine wire "hook" attached under a Shimadzu balance (AUW200D). The pouch cells were immersed in a beaker of de-ionized "nanopure" water (18.2 M $\Omega$ ) that was at 20. ± 1 °C for measurement.

Electrochemical impedance spectroscopy (EIS) measurements were conducted on NMC111/graphite pouch cells after formation and also after cycling on the UHPC [34]. Cells were charged or discharged to 3.80 V before they were moved to a 10 ± 0.1 °C temperature box. Alternating current (AC) impedance spectra were collected with ten points per decade from 100 kHz to 10 mHz with a signal amplitude of 10 mV at 10 ± 0.1 °C. A Biologic VMP-3 was used to collect these data.

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