



Improving the long-term cycling performance of lithium-ion batteries at elevated temperature with electrolyte additives



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HIGHLIGHTS

- NMC111/graphite cells with PES-based electrolytes show excellent high temperature lifetime.
- Short term coulombic efficiency measurements and initial gas production predict long term lifetime.
- Over 1000 cycles with less than 20% capacity loss at C/2.5 was obtained for the best cells at 55 °C.

ARTICLE INFO

Article history:

Received 20 January 2015

Received in revised form

2 April 2015

Accepted 13 April 2015

Available online

Keywords:

Electrolyte additives

Li-ion batteries

Propene sultone

Vinylene carbonate

Cycle life

ABSTRACT

The effects of vinylene carbonate-based and prop-1-ene-1,3-sultone-based electrolyte additives on the cycling behavior of Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O₂/graphite pouch type cells at elevated temperature have been systematically studied. Capacity fade during cycling, charge-transfer resistance before and after cycling as well as gas evolution during formation and also during cycling were examined and compared. For vinylene carbonate-based additive blends, only 3% vinylene carbonate, 2% vinylene carbonate + 1% 1,3,2-dioxathiolane-2,2-dioxide + 1% tris(trimethylsilyl) phosphite or 2% vinylene carbonate + 1% methylene methyl disulfonate + 1% tris(trimethylsilyl) phosphite showed less capacity fade than 2% vinylene carbonate alone. Cells with all of these vinylene carbonate-based electrolyte additive blends lost more than 20% of their initial capacity after ~1000 cycles at 55 °C and all the vinylene carbonate-based cells swelled more than 10% of their initial volume during this test. Cells containing all prop-1-ene-1,3-sultone-based additive blends generally produced much less gas than the vinylene carbonate-based blends. Many cells containing prop-1-ene-1,3-sultone-based additive blends lost less than 20% of their initial capacity after 1000 cycles. Moreover, the impedance of these prop-1-ene-1,3-sultone-based electrolytes decreased after long-term cycling. These results suggest that prop-1-ene-1,3-sultone-based electrolytes are more useful than vinylene carbonate-based electrolytes at high temperatures in Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O₂/graphite cells.

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1. Introduction

During cycling and storage of a Li-ion cell, the degradation of electrolyte solvents and/or lithium salts can occur and lead to the formation or growth of solid electrolyte interphases (SEI) on both electrodes [1]. When lithium-ion cells are subjected prolonged charge–discharge cycling, elevated operating temperature or elevated operating voltage, the formed SEI layers either grow in

thickness or become compromised, leading to a decrease in lifetime and to cell failures [2–4]. The use of electrolyte additives has been shown to be one of the most effective ways to improve cycle life, calendar life and safety of Li-ion batteries [5].

Electrolyte additives such as vinylene carbonate (VC) [6], fluoroethylene carbonate (FEC) [7] and vinyl ethylene carbonate (VEC) [8] are commonly used SEI forming additives. These additives can be reduced on the graphite surface before solvents, such as ethylene carbonate (EC), during the formation cycles and participate in the SEI forming process to form a more protective SEI film. Besides these cyclic carbonate additives, organic sulfur containing additives such as ethylene sulfite (ES) [9,10], 1,4-butane sultone (BS) [11], 1,3-propane sultone (PS) [12], prop-1-ene-1,3-sultone (PES)

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[13] and 3-fluoro-1,3-propane sultone (FPS) [14], 1,3-dioxathiolane-2,2-dioxide (DTD) [15] and trimethylene sulfate (TMS) [15] have also proposed as SEI forming additives. These sulfur-containing additives are generally soluble and have higher reduction potential (vs. Li/Li^+) than that of EC and thus can participate in the SEI forming process at the negative electrode. Cell containing these sulfur-containing additives reported in the above literature generally delivered better charge–discharge cycling performance than control cells without additives.

Recently, our group has begun studying cyclic sulfur-containing additives and their combinations with VC [15–19]. The results of these experiments showed that the combinations of VC with DTD, TMS or methylene methane disulfonate (MMDS) as additives can give better performance than VC alone in NMC(111)/graphite cells balanced for operation to 4.2 V [15,16]. The results also confirmed that ES acts as an impedance reducer [17] while PES acts as a gas reducer [18]. Among these additives, only PES imparts similar effects to Li-ion cells as VC when used as a single additive in terms of coulombic efficiency and electrolyte oxidation improvements [18,19]. Very recently, Wang et al. [20] studied more than 110 electrolyte additive sets and proposed a “Figure of Merit” approach, based on high precision coulometry, to rank the additive blends from “best to worst”. They found that electrolytes containing combinations of additives with a base additive of either VC or PES, a sulfur containing additive such as MMDS, ES or DTD and tris(trimethylsilyl) phosphate (TTSP) and/or tris(trimethylsilyl) phosphite (TTSPi) generally led to NMC111/graphite cells with excellent performance. Although these additive combinations illustrated superior performance during a few charge–discharge cycles in experiments using the Ultra High Precision Charger (UHPC) at Dalhousie University, long term cycle life of Li-ion cells using these additive blends has not yet been systematically explored.

In this paper, the long-term cycling properties of 12 electrolyte additive blends that focus on VC as their primary component and 11 electrolyte additive blends that focus on PES as their primary component are reported. The reasons for choosing these additives are explained in Ref. [19]. Fig. 1 shows the structures of these selected electrolyte additives. Long-term cycling stability at 55 °C, impedance before and after cycling as well as cell swelling before and after long-term cycling were measured and compared. These results should be of interest to battery manufacturers and

researchers who want to develop Li-ion batteries with longer cycle life and less gas evolution (or swelling) at elevated temperatures.

2. Experimental

1 M LiPF_6 ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 wt.% ratio, BASF) was used as the control electrolyte in the studies reported here. To this electrolyte, the additives vinylene carbonate (VC, BASF, 99.97%) or prop-1-ene-1,3-sultone (PES, Lianchuang Medicinal Chemistry Co., Ltd., China, 98.20%) were added either singly or in combination with other additives. Additive components were added at 1, 2 or 3% by weight in the electrolyte. The other additives, their purities and their suppliers are listed in Table 1.

$\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]\text{O}_2$ (NMC111)/graphite pouch cells without electrolyte (220 mAh) were obtained from Whenergy (Shandong, China) (Whenergy has been renamed as LiFun Technology and has moved to Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000, China). The pouch cells were vacuum sealed without electrolyte in China and then shipped to our laboratory in Canada. Before filling with electrolyte, the cells were cut just below the heat seal and dried at 80 °C under vacuum for 12 h to remove any residual water. Then the cells were transferred immediately to an argon-filled glove box for filling and vacuum sealing. The NMC111/graphite pouch cells were filled with 0.9 g of electrolyte. After filling, cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.). The formation process is described as follows. First, cells were placed in a temperature box at 40.0 °C where they were held at 1.5 V for 24 h, to allow for the completion of wetting. Then, cells were charged at 11 mA (C/20) to 3.8 V. After the first charge to 3.8 V, cells were transferred and moved into the glove box, cut open to release gas generated and then vacuum sealed again. This process is known as degassing. After the degassing step, the formation process was complete. Also after degassing, impedance spectra of the cells were measured at 3.8 V as described later below.

For long-term cycling, the cells were charged and discharged at 80 mA (C/2.5) between 2.8 and 4.2 V at 55.0 ± 0.5 °C using a Neware (Shenzhen, China) charger system. All cells were cycled unclamped, that is the pouch was entirely free.

Coulombic efficiency (CE) measurements were made using the Ultra High Precision Charger (UHPC) at Dalhousie University [21].

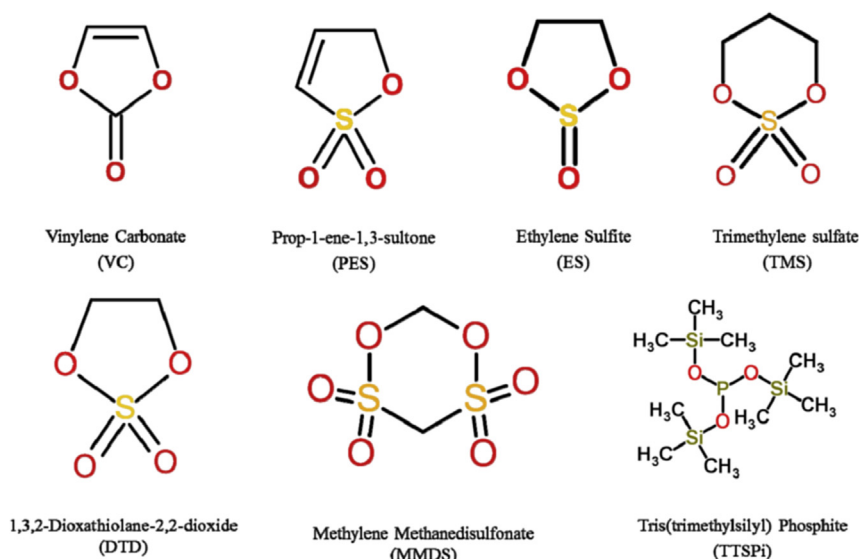


Fig. 1. Molecular formula and structural information of additives studied in this paper.

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