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Study of triallyl phosphate as an electrolyte additive for high voltage lithium-ion cells

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HIGHLIGHTS

- Cells with TAP show excellent charge discharge capacity retention at high V.
- Coulombic efficiency measurements and gas production predict long term lifetime.
- TAP polymerizes at the surface of each electrode creating thick stable SEI films.
- The only problem with TAP is impedance increase associated with too much TAP.

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ABSTRACT

The role of triallyl phosphate as an electrolyte additive in Li($Ni_{0.42}Mn_{0.42}Co_{0.16}$)$O_2$/graphite pouch cells was studied using *ex-situ* gas measurements, ultra high precision coulometry, automated storage experiments, electrochemical impedance spectroscopy, long-term cycling and X-ray photoelectron spectroscopy. Cells containing triallyl phosphate produced less gas during formation, cycling and storage than control cells. The use of triallyl phosphate led to higher coulombic efficiency and smaller charge endpoint capacity slippage during ultra high precision charger testing. Cells containing triallyl phosphate showed smaller potential drop during 500 h storage at 40 °C and 60 °C and the voltage drop decreased as the triallyl phosphate content in the electrolyte increased. However, large amounts of triallyl phosphate (>3% by weight in the electrolyte) led to large impedance after cycling and storage. Symmetric cell studies showed large amounts of triallyl phosphate (5% or more) led to significant impedance increase at both negative and positive electrodes. X-ray photoelectron spectroscopy studies suggested that the high impedance came from the polymerization of triallyl phosphate molecules which formed thick solid electrolyte interphase films at the surfaces of both negative and positive electrodes. An optimal amount of 2%–3% triallyl phosphate led to better capacity retention during long term cycling.

1. Introduction

High potential lithium-ion cells are of interest for battery manufacturers and electric vehicle makers. However, cycling cells to high potential normally results in relatively low coulombic efficiency (CE) and poor lifetime [1–3]. The poor cycling stability is mainly caused by the oxidation of the electrolyte at the surface of positive material as the potential increases [4]. The use of electrolyte additives can improve the properties of the solid electrolyte interface (SEI) on the surfaces of both positive and negative electrodes and thus can improve both cycle and calendar life as well as cycling performance of Li-ion cells [5–7].

Some electrolyte additives such as succinic anhydride [8], lithium bis(oxalato) borate (LiBOB) [9,10], lithium difluoro(oxalato) borate (LiDFOB) [11], 1,3-propane sultone [12] and methylene methanedisulfonate [13] have shown beneficial effects on high potential positive electrode materials. Tarnopolskiy et al. [8] investigated a series of 40 different electrolyte additives and found that only succinic anhydride improved the self-discharge of $LiNi_{0.5}Mn_{1.5}O_4$/Li half cells while also showing an enhanced coulombic efficiency and a decreased capacity loss per cycle. Aravindan et al. [14] found that adding LiBOB (>0.1 wt. %) to 1 M $LiPF_6$

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EC:DEC 1:1 wt. % electrolyte can greatly improve the cycling performance of Li/$LiCoPO_4$ half-cells between 3.5 and 5.2 V. However, these works mainly referred to coin cell studies where the electrolyte and active Li are in excess. Also, electrolyte oxidation at high potential almost always generates gaseous products that are not detected in coin-type cells.

The effect of both electrolyte additives and solvents in Li$[Ni_{0.42}Mn_{0.42}Co_{0.16}]O_2$ (NMC442)/graphite pouch type cells balanced for 4.7 V has been studied. These highly repeatable machine-made pouch cells allow comparison of small differences in CE, charge endpoint capacity slippage as well as gas evolution and impedance growth caused by the addition of various additives to the electrolyte. Ma et al. [15,16] and Downie et al. [17] confirmed the beneficial impact of 2% prop-1-ene-1,3-sultone (PES) + 1% methylene methanedisulfonate (MMDS) + 1% tris(trimethylsilyl) phosphite (TTSPi) ("PES-211") in suppressing impedance growth, reducing the parasitic heat flow and extending cycle life in NMC442/graphite pouch cells operating up to or above 4.4 V. Nie et al. [18] showed that adding pyridine-boron trifluoride (PBF) as an electrolyte additive brings special advantages for high energy density NMC442/graphite cells. Petibon et al. [19] and Xia et al. [20] showed that the ethyl acetate- and sulfolane-based electrolytes provide an interesting alternative to EC-based electrolytes for NMC442/graphite cells. Electrolyte additives as well as atypical solvents can therefore play a huge part in the successful implementation of high potential Li-ion cells.

In this paper, the effects of triallyl phosphate (TAP) in $LaPO_4$-coated NMC442/graphite pouch cells were studied using *ex-situ* gas measurements, ultra high precision coulometry (UHPC) [21], automated precision storage experiments [22], electrochemical impedance spectroscopy (EIS) [23] as well as long-term cycling. X-ray photoelectron spectroscopy (XPS) was also used to analyze the SEI films formed at the surface of both graphite and NMC442 electrodes and correlate chemical differences to the electrochemical differences observed between electrolytes. These results should be of interest to those developing high potential Li-ion batteries with longer lifetime.

2. Experimental

1 M $LiPF_6$ ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 wt. % ratio, BASF, 99.99%) was used as control electrolyte. To this electrolyte, triallyl phosphate (TAP, TCL, >94.0%) was added as an additive at 1, 2, 3, 5 or 8% by weight. Prop-1-ene-1,3-sultone (PES, Lianchuang Medicinal Chemistry Co., Ltd., China, 98.20%), was also chosen as an electrolyte additive for comparison in some of the experiments.

The pouch cells employed in this study were $LaPO_4$-coated Li$[Ni_{0.42}Mn_{0.42}Co_{0.16}]O_2$ (NMC442)/graphite cells with a capacity of 180 mAh balanced for 4.7 V operation. The positive NMC442 active material was coated with 3 wt. % of $LaPO_4$, which appears as nanoparticles on the NMC442 particle surfaces. The NMC442 was prepared by Umicore Co. and the $LaPO_4$ coating was applied by 3 M Co. Fig. S1 shows SEM images and EDS spectra of the top surfaces of the coated NMC442 and graphite electrodes so that readers can appreciate the morphology and components of the particles that make up the electrodes. The pouch cells were manufactured by Li-Fun Technology (Zhuzhou, China), sealed without electrolyte in China 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 14 h to remove any residual water. The cells were then transferred immediately to an argon-filled glove box for filling and vacuum sealing. The NMC442/graphite pouch cells were filled with 0.75 mL (0.90 g) of electrolyte. After filling, cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.). The cells were then weighed while submerged under water. Next, the 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. Cells were then charged at 12 mA (C/20) to 3.5 V. This step is called "formation step 1". The cells were weighed while submerged under water again, to determine the cell volume change by Archimedes principle [25]. 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 to 4.5 V at 12 mA (C/20). This step is called "formation step 2". Archimedes volume measurements were taken a third time. 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 potentials were selected based on the *in-situ* gas evolution experiments, described below, that shows that most of the gas evolves in the formation step at potentials below 3.5 V and above 4.3 V. After the two degassing steps, cells were discharged to 3.8 V, at which point impedance spectra were measured. The potential of 3.8 V was chosen for the EIS and ex-situ gas measurements because at this voltage both graphite and NMC electrodes are at about 50% state of charge. This is important because both the degassing procedure and EIS measurements take some time and the cells are stable at 3.8 V.

The cycling/storage procedure was carried out using the ultra high precision charger (UHPC) at Dalhousie University [21]. Testing was performed between 2.800 and 4.400 V at 40 ± 0.1 °C. Cells were first charged to 4.400 V using currents corresponding to C/10, stored open circuit beginning 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 for 15 cycles. The cycling/storage procedure was designed so that the cells were exposed to higher potentials for significant fractions of their testing time. All pouch cells were cycled without clamps.

For the dQ/dV *vs.* V analysis, the graphite potential was estimated as follows. High-precision reference potential-specific capacity data for Li/graphite and Li/NMC442 cells as well as the full NMC442/graphite pouch cell potential-capacity behavior were first measured. Then, from these data, the dV/dQ *vs.* Q behavior of a NMC442/graphite pouch cell was calculated and compared to the experimental curve using a differential potential analysis software previously developed at Dalhousie University [24] which alleviates the need of a 3rd electrode to obtain the anode potential. This was done so that features in dQ/dV vs V during formation of the two-electrode pouch cells could be placed relative to the potential of Li/Li^+.

For 500 h storage experiments, cells were first discharged to 2.8 V and charged to 4.5 V two times at 40 ± 0.1 °C. Then the cells were held at 4.5 V until the measured current decreased to 0.0025C. A Maccor series 4000 cycler 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 potential, recording the potential every 6 h over 500 h of storage [22]. Storage experiments were made at 40 ± 0.1 °C and 60 ± 0.1 °C.

Ex-situ (static) gas measurements were used to measure gas evolution during formation and during cycling [25]. 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 by the change in the buoyant force. The change in mass of a cell, Δm, suspended in a fluid of density, ρ, is related to the change in cell volume, Δv, by

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