



The use of ethyl acetate and methyl propanoate in combination with vinylene carbonate as ethylene carbonate-free solvent blends for electrolytes in Li-ion batteries



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ABSTRACT

Li[Ni_{0.33}Mn_{0.33}Co_{0.33}]O₂/graphite and LiCoO₂/graphite pouch cells filled with a combination of ethyl acetate (EA) and vinylene carbonate (VC), or methyl propanoate (MP) and VC with 1 M LiPF₆ function very well, even though these cells contain no ethylene carbonate, thought to be essential for the negative electrode solid electrolyte interphase (SEI). Cells filled with 1 M LiPF₆ in MP:VC (95:5 w:w) showed similar capacity retention and impedance after 1700 h of cycling at 40 °C as cells filled with 1 M LiPF₆ in EC:ethyl methyl carbonate (EMC) + 2% VC. Cells filled with these ester containing electrolytes also showed better rate performance when cycled at -14 °C, delivering 40% of the discharge energy at a current equivalent to 4C, while cells filled with EC:EMC + 2% VC failed to deliver any capacity at a current of 3C. High precision coulometry measurements also showed that cells filled with 1 M LiPF₆ in MP:VC (95:5 w:w) had similar coulombic efficiency and charge endpoint capacity slippage as cells filled with 1 M LiPF₆ EC:EMC + 2% VC which indicates ester based electrolytes can have long lifetime.

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1. Introduction

Li-ion batteries are used in consumer electronics and electrified vehicles (EV). EV applications require the batteries to function well at both low temperature (below 0 °C) and relatively high temperature (40 °C and above). Low temperature operation is problematic due to reduced electrolyte conductivity and high temperature operation requires electrolytes yielding low parasitic currents due to electrolyte/electrode reactions [1–3].

Most electrolytes for Li-ion cells use a mixture of ethylene carbonate and other linear organic carbonates such as diethyl carbonate (DEC), ethyl methyl carbonate (EMC), or dimethyl carbonate (DMC) with LiPF₆ as the conductive salt. In these carbonate-based electrolytes, the presence of EC is normally necessary if a graphite electrode is used [4]. The use of such electrolytes, in combination with small weight percentages of electrolyte additives have been shown to yield quite long lived cells [1] with low parasitic currents when cycled up to 4.2 V [5,6]. However, the presence of EC increases the viscosity of the

electrolyte (see Table 1 for the viscosities of some pure solvents) which lowers its conductivity compared to EC-free electrolytes, especially at low temperatures. The electrolyte conductivity can still be tuned to some extent by using higher weight fractions of low viscosity linear carbonate based co-solvents as demonstrated by Smart et al. [7].

In order to further lower the viscosity of EC-based electrolytes, co-solvents having even lower viscosity than linear carbonates have been used. For instance, Smart et al. [8,9] demonstrated that the use of low molecular weight organic esters in EC:DMC:DEC: ester quaternary solvent blends improved the electrolyte conductivity (especially at low temperature) compared to ternary EC:DMC:DEC blends. They also showed that the resistivity and the stability of the solid electrolyte interphase (SEI) film created by the addition of esters greatly depended on the ester introduced. Sazhi et al. also developed electrolytes containing ternary solvent blends with EC:EMC:ethyl propanoate (EP) and EC:DEC:EP [10]. Even though the electrolyte conductivity was greatly enhanced, these electrolyte blends still contained 20–30% of EC.

The inability of most solvents to form a protective layer at the surface of graphite requires the use of additives if no EC is added. Several researchers, for example, used additives that are known to form surface films at the lithiated graphite surface to design new

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solvents blends. Ein-Eli et al. showed that the addition of SO₂ allows the use of different single solvents such as methyl formate, propylene carbonate, DMC and DEC with graphite, without the use of EC [11]. The use of SO₂ is impractical in pouch type Li-ion cells which are vacuum sealed. The vacuum sealing step would remove most of the SO₂ from the electrolyte. In another instance, Zhang et al. showed that the use of 5% VC in PC allows the graphite to be cycled without any EC [12]. Many other examples have been presented in detail in other references [13–20].

Based on the previous studies mentioned above, low molecular weight esters such as ethyl acetate and methyl propanoate are good solvent candidates from an electrolyte conductivity standpoint. The use of known film forming additives in combination with these esters should make such blends suitable for their use in Li-ion cells with a lithiated graphite anode. Table 1 lists some physical characteristics of common cyclic and linear organic carbonates and two organic esters (ethyl acetate and methyl propanoate, also called methyl propionate). Table 1 shows that the two esters have lower viscosity and lower melting point than any of the linear carbonates. This makes them suitable for low temperature applications. The additive VC is a very well-known and extensively studied additive [2,12,13,21–33]. It has been shown to form an SEI film at the lithiated graphite surface which enables the use of PC-based electrolytes without any EC. It then stands to reason that electrolytes consisting of a blend of an ester with VC should be kinetically stable against lithiated graphite and should show good rate performance at low temperature.

2. Experimental

Dry wound 220 mAh Li[Ni_{0.33}Mn_{0.33}Co_{0.33}]O₂/graphite (NMC (111)/graphite) pouch cells from Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000) and 320 mAh LiCoO₂/graphite (LCO/graphite) pouch cells from BAK Co. (Shenzhen, China) were used in this study. The negative electrode of both the NMC and LCO pouch cells were made out of 15–30 μm and 10–25 μm artificial graphite, respectively. The negative to positive active mass ratio of the NMC(111)/graphite and LCO/graphite pouch cells were adjusted so the cells could be cycled to 4.2 V without lithium plating. The pouch cells were vacuum sealed in China without electrolyte and then shipped to Canada. In Canada, the pouch bag of the pouch cells was cut open and the cells were first vacuum dried at 80 °C for 10 to 14 h to remove any residual water. The NMC (111)/graphite and LCO/graphite pouch cells were then filled with 0.75 mL and 1.0 mL of formulated electrolytes, respectively. The cells were then sealed under vacuum at a gauge pressure of -85 kPa (relative to atmospheric pressure). After filling, the pouch cells were connected to a Maccor 4000 series charger and held at 1.5 V for 24 h in a 40 °C box to promote wetting. The cells were then charged to either 3.5 V or 3.8 V at a current density corresponding

to C/20. In order to remove the gas formed early on during the formation charge [34] the pouch cells were then moved to an argon-filled glove-box to be opened and re-sealed under vacuum.

All chemicals used in the electrolytes were obtained from BASF (LiPF₆, purity 99.94%, water content 14 ppm, EC:EMC, 3:7 by weight, water content < 20 ppm, VC, purity > 99.8%, water content < 100 ppm, EA, purity 99.99%, water content < 20 ppm, MP, purity 99.99%, water content < 20 ppm, fluoroethylene carbonate (FEC), purity 99.94%, water content < 20 ppm). All base electrolyte formulations used in this study contained a concentration of LiPF₆ of 1 M.

Electrochemical impedance spectra were measured using a BioLogic VMP3 equipped with 2 EIS boards. In order to automate the process somewhat, the output of one VMP3 EIS board was connected to a Keithley 705 scanner and the output of the other to a Keithley 706 scanner. Each scanner housed two Keithley 7053 10-channel high current scanner cards. In-house software was designed and written so that each scanner could connect up to 16 cells sequentially to have their EIS spectra measured automatically overnight. All impedance spectra were collected at a cell potential of 3.80 V and constant temperature by housing the cells in temperature-controlled boxes at 10 °C (+/-0.1 °C). All impedance measurements were made using a 10 mV input signal from 100 kHz to 100 mHz.

The volume of gas produced during the formation cycle and after cycling was measured ex-situ using Archimedes' principle. Cells were weighed while submerged in deionized water (18 MΩ·cm) before and after the experiment. The difference in weight, Δw, of the pouch cell while submerged in water is then directly proportional to the volume of gas produced, Δv, following Eq. (1):

$$\Delta v = \Delta w / \rho, \quad (1)$$

where ρ is the density of water.

Long term cycling was performed using a Neware (Shenzhen, China) battery testing system at 40.0 ± 0.1 °C.

The analysis of the solvent composition of the electrolyte after cycling was done using the GC-MS procedure described by Petibon et al. in an earlier publication [35]. This procedure allows for potentially damaging salts such as LiPF₆ to be removed in a simple fashion. Prior to GC-MS analysis, cells were first discharged to an open circuit voltage near 0.0 V to render them safe for opening. Then the cells were opened rapidly outside the glove box. The jelly roll was then immediately put in a perfluoroalkoxy polymer (PFA) vial containing 10 mL of dichloromethane. The vial was then shaken automatically for 15–20 min to extract the electrolyte from the jelly roll. The supernatant was then filtered using a syringe filter with a PTFE membrane and 0.2–0.45 μm pores. A few drops of the filtrate were then added to a vial containing 5.0 mL of dichloromethane and 0.25 mL of distilled water, shaken for 5–10 min and centrifuged at 300 g-force for 10–15 min to eliminate any potential emulsion. The

Table 1
Physical characteristics of selected organic carbonates and esters

Chemical name	Abbreviation	Viscosity at 25 °C/cP	Melting point/°C	Boiling point/°C
Ethylene carbonate	EC	1.86 (40 °C) ^a	39 ^a	248 ^a
Propylene carbonate	PC	2.5 ^a	-48 ^a	242 ^a
Diethyl carbonate	DEC	0.75 ^a	-43 ^a	126 ^a
Ethyl methyl carbonate	EMC	0.65 ^a	-55 ^a	109 ^a
Dimethyl Carbonate	DMC	0.59 ^a	4 ^a	90 ^a
Ethyl acetate	EA	0.441 (25 °C) ^b	-84 ^b	77 ^b
Methyl propanoate	MP	0.43 (25 °C) ^c	-87 ^b	80 ^b
Or Methyl propionate				

^a reference [46],

^b reference [47],

^c reference [48].

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