



A study of highly conductive ester co-solvents in Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O₂/Graphite pouch cells

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ABSTRACT

The effect of low viscosity esters on rate capability and lifetime of Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O₂/graphite pouch cells was studied using a variety of methods including ultra high precision coulometry, isothermal calorimetry and long term cycle testing. Methyl acetate (MA) and methyl propionate (MP) were selected as the ester co-solvents in ethylene carbonate (EC): ethyl methyl carbonate (EMC): dimethyl carbonate (DMC) (25:5:70 vol%) blended solvent along with 2% vinylene carbonate (VC) or 2% fluoroethylene carbonate (FEC) additives. Cells containing electrolytes with 20% or 40% MA or MP could support higher charging rates without unwanted lithium plating than those without esters. All electrolytes with 2% FEC could support higher charging rates without unwanted lithium plating compared to corresponding electrolytes with 2% VC. However, UHPC and microcalorimetry measurements indicate that both the use of esters and the use of FEC over VC lead to lifetime penalties which were confirmed by long term cycling tests. Useful electrolytes, detailed in this report, that yield a good compromise between high charging rates and long lifetime are those that contain 20% MA by weight.

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1. Introduction

Rapid charging capability is desirable for electric vehicles equipped with Li-ion batteries (LIBs). Unfortunately, fast charging or low temperature charging can cause unwanted lithium plating on the graphite negative electrode of Li-ion cells, which can drastically reduce the capacity and cycle life of lithium ion cells [1–3]. Electrolytes with high conductivity and low viscosity can help enhance the charging rate capability of LIBs.

Esters with low freezing points and low viscosity can yield electrolytes with high ionic conductivity when used as co-solvents. Esters have been used in low temperature Li-ion cells to improve their performance, and the most interesting include methyl acetate (MA), methyl propionate (MP), ethyl acetate (EA), methyl butyrate (MB), ethyl butyrate (EB), ethyl propionate (EP), etc [4–12]. Unfortunately the improved low temperature performance is normally accompanied by degraded capacity retention during long-term cycling because esters with low molecular weight (e.g. EA)

are thought to react slowly with negative electrodes [4,5]. EA, MP and MB used as a sole electrolyte solvent along with appropriate electrolyte additives or as a co-solvent have been studied in Li [Ni_{0.33}Mn_{0.33}Co_{0.33}]O₂/graphite, Li[Ni_{0.42}Mn_{0.42}Co_{0.16}]O₂/graphite, LiCoO₂/graphite and Li[Ni_{1-x-y}Co_xAl_y]O₂/Graphite-SiO pouch cells [13–15]. In this work, the effect of two typical esters, MA and MP, on rate capability as well as lifetime of Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O₂/graphite pouch cells were studied.

Ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) are two common linear carbonate co-solvents used in commercial lithium ion cells. Considering the different melting points and viscosities of DMC (4 °C and 0.59 cP at 20 °C) and EMC (–53 °C and 0.65 cP at 20 °C), their effects on the rate capability of Li [Ni_{0.5}Mn_{0.3}Co_{0.2}]O₂/graphite pouch cells were also investigated in this work.

2. Experimental section

2.1. Preparation and formation of pouch cells

All the chemicals were used as received from BASF: LiPF₆ (99.94% purity, water content 14 ppm), ethylene carbonate (EC):

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ethyl methyl carbonate (EMC) (30:70 wt%, water content 12.1 ppm), ethylene carbonate (EC): ethyl methyl carbonate (EMC): dimethyl carbonate (DMC) (25:5:70 vol%, water content 19.7 ppm), vinylene carbonate (VC), fluoroethylene carbonate (FEC), methyl acetate (MA, 99.9% purity, water content 5.2 ppm) methyl propionate (MP, 99.9% purity, water content 19.9 ppm).

Dry and sealed single crystal $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}]\text{O}_2/\text{graphite}$ pouch cells (230 mAh at 4.3 V) that were balanced for 4.5 V operation and do not contain electrolyte were obtained from Li-FUN Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, China, 412000). The single side coating active material electrode loadings were 21.1 mg/cm^2 for the positive electrode and 12.4 mg/cm^2 for the graphite negative electrode. The positive electrode consisted of 94 wt % active material and the negative electrode had 95.4 wt % active material. The positive electrode was compressed to a density of 3.5 g/cm^3 and negative electrode was compressed to 1.55 g/cm^3 . Prior to filing with the desired electrolyte, pouch cells were cut open and dried at 100°C under vacuum for 14 h to remove any residual moisture. Afterwards, pouch cells were filled with 0.85 mL electrolyte in an Ar-filled glove box and sealed with a pouch sealer (MSK-115 A Vacuum Sealing Machine) under vacuum at a pressure of -90 kPa (relative to atmospheric pressure). Six electrolyte blends studied in this work included 1.2 M LiPF_6 in EC:EMC, EC:EMC:DMC, 80 wt% EC:EMC:DMC +20 wt% MA, 60 wt% EC:EMC:DMC +40 wt% MA, 80 wt% EC:EMC:DMC +20 wt% MP, and 60 wt% EC:EMC:DMC +40 wt% MP. For each electrolyte blend, either 2 wt% VC or 2 wt% FEC were used as additives.

After filling, cells were held at 1.5 V for 24 h to promote wetting and subsequently moved to a 40°C box connected to a Maccor 4000 series charger. Pouch cells were charged to 4.3 V at a current corresponding to C/20, held at 4.3 V for 1 h and then discharged to 3.8 V at C/20. In order to remove the gas formed during the charging and discharging process, the pouch cells were cut open and resealed under vacuum in the glove box. Cells were moved for electrochemical impedance spectroscopy measurements.

2.2. Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectra of the pouch cells were collected after formation, using a BioLogic VMP3 equipped with 2 EIS boards. All the measurements were performed at $10.0 \pm 0.1^\circ\text{C}$ from 100. kHz to 10. mHz (10. mV input). A temperature of 10°C was selected to amplify the differences between cells with different ester and additive content.

2.3. Gas volume measurement

The gas production in pouch cells during formation and cycling was measured using Archimedes' principle. Each cell was suspended underneath a Shimadzu analytical balance (AUW200D) and weighed while submerged in nano-purified deionized (DI) water ($18 \text{ M}\Omega\cdot\text{cm}$). The produced gas (Δv) in each cell is proportional to the change in apparent cell weight (Δm) that was caused by the buoyant force, as Equation (1):

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

where ρ is the density of DI water.

2.4. High rate cycling, long-term cycling and the ultra high precision coulometry (UHPC) cycling

High rate cycling was performed at $20. \pm 1^\circ\text{C}$. The cells were charged and discharged between 3.0 and 4.3 V and the voltage was

held at 4.3 V at the top of charge until the current dropped below C/20. Each cell was first charged and discharged at C/5 ($C = 210 \text{ mA}$) for 3 cycles. Subsequently, cells were cycled with sequentially increasing charge rates of 1C, 1.5C, 2C, 2.5C and 3C, respectively. The discharging rate was constantly set at C/3.30 cycles at each charging rate were applied. Cycling ended as unwanted lithium plating occurred. After each period of the high charge rate cycles, cells were charged and discharged at C/5 three times to determine the capacity retention and the existence of unwanted lithium plating using the methods in Ref. [2].

Long term cycling was performed at $40.0 \pm 0.1^\circ\text{C}$ with an upper cut off potential of 4.3 V on a Neware testing system (Shenzhen, China). The cells were charged and discharged with a current corresponding to C/3 between 3.0 and 4.3 V and the voltage was held at 4.3 V at the top of charge until the current dropped below C/20.

The UHPC cycling was performed at $40.0 \pm 0.1^\circ\text{C}$ using the UHPC charger at Dalhousie University and detailed descriptions of the method can be found in Ref. [16]. Cells were charged and discharged with a current corresponding to C/20 between 3.0 and 4.3 V.

2.5. Conductivity measurement

Electrolytic conductivity was measured using a Mettler Toledo FG3 conductivity meter. Before the measurement, the conductivity probe was calibrated using a conductivity standard (RICCA, 12.88 mS/cm at 25°C). 10 mL of electrolyte was added to a Teflon holder under a fume hood. The probe was then sealed to the holder by an O-ring. The sealed Teflon holder with the electrolyte and conductivity probe was then placed in a temperature controlled bath (VWR Scientific model 1151) filled with a water/ethylene glycol mixture. Conductivity was measured at -20°C , 0°C , 20°C , 40°C and 60°C . At each temperature step, a constant temperature was maintained for at least 1 h to allow for the electrolyte temperature to equilibrate with the bath. Data was only considered valid after the temperature of the electrolyte was stable.

2.6. Isothermal microcalorimetry

The average parasitic heat flow of cells containing different amounts of EMC, DMC and MA co-solvents was measured using a TAM III Microcalorimeter at $40. \pm 0.0001^\circ\text{C}$ (TA Instruments: stability $\pm 0.0001^\circ\text{C}$, accuracy $\pm 1 \mu\text{W}$, precision $\pm 1 \text{ nW}$). The baseline drift over the course of the experiments did not exceed $\pm 0.5 \mu\text{W}$. All information regarding microcalorimetry calibration, cell connections, and operation procedures can be found in previous literature [17,18]. After formation, cells were connected to a Maccor 4000 series charger to be charged and discharged between 4.0 V and different upper cut-off potentials: 4.2 V, 4.3 V (twice) and again 4.2 V (twice) at 1 mA investigate the parasitic heat flow occurring in different voltage ranges.

2.7. Open-circuit voltage (OCV) storage

After formation, cells containing 0% MA or 20% MA in EC:EMC were discharged to 3 V and charged to 3.5, 4.0, 4.2 or 4.4 V two times with a current corresponding to C/10. Cells were then held at 3.5, 4.0, 4.2 or 4.4 V, respectively, for 24 h and afterwards transferred to storage boxes at 30, 40, or $50.^\circ\text{C}$, respectively. The open-circuit voltage was recorded automatically every 6 h for 500 h.

3. Results and discussion

Fig. 1a and b shows the calculated conductivity and viscosity versus the molality of LiPF_6 in solvents with different EC:EMC:DMC

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