



# A propylene carbonate based gel polymer electrolyte for extended cycle life and improved safety performance of lithium ion batteries

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## HIGHLIGHTS

- High flash point (141 °C) of PC-based liquid electrolyte (PEV).
- High electrolyte uptake ratio (480 wt%) in PEV gel polymer electrolyte (GPE).
- Effective interphase formation in NMC532/graphite cells containing PEV-GPE.
- Excellent capacity retention ( $\approx 99\%$ ) after 200 charge/discharge cycles.
- Remarkable thermal stability (250 °C) of NMC532/graphite cells comprising PEV-GPE.

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## ABSTRACT

A poly(vinylidene difluoride-co-hexafluoropropylene) (PVdF-HFP)-based gel polymer electrolyte (GPE) containing propylene carbonate (PC)-based liquid electrolyte was developed to enhance the safety performance of LiNi<sub>0.5</sub>Mn<sub>0.3</sub>Co<sub>0.2</sub>O<sub>2</sub>/graphite (NMC532/graphite) lithium ion batteries. The PC-based liquid electrolyte (PEV-LE) consists of 1 mol L<sup>-1</sup> LiPF<sub>6</sub> as lithium salt, PC as the main solvent and ethylene sulfite (ES, 2% by weight) as well as vinylene carbonate (VC, 2% by weight) as solid electrolyte interphase (SEI) forming additives. Electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) revealed that the combination of ES and VC additives facilitates the formation of effective interphases at the respective electrolyte/electrode interfaces, thus contributing to a remarkable cycle life of NMC532/graphite cell comprising PEV-GPE. Flash point measurements and differential scanning calorimetry (DSC) confirmed significantly improved safety performance of PEV compared to the state-of-the-art electrolyte. PEV-GPE is a promising alternative to state-of-the-art electrolyte as it shows extended cycle life and enhanced thermal stability in NMC532/graphite lithium ion cells.

## 1. Introduction

Owing to high energy and power densities, high energy efficiency and long cycle life, lithium ion batteries (LIBs) dominate the energy storage market for portable electronic devices, stationary electricity storage and electric vehicles [1–3]. However, as the energy density of LIBs increases, their safety performance raises more concern in parallel. State-of-the-art (SOTA) non-aqueous aprotic liquid electrolytes (LEs) are one of the most hazardous components in LIBs [4], as they employ the combination of ethylene carbonate (EC) and linear organic

carbonates as main solvents. Due to its high relative permittivity (89.78 at 40 °C) and good compatibility with the graphitic anode, EC is almost indispensable in non-aqueous aprotic electrolyte formulation [5–7]. However, the high melting point of 36.4 °C constrains the use of EC as a single solvent at room temperature [8]. Therefore, linear carbonates must be introduced to extend the liquid range and reduce the viscosity of the electrolyte [5]. However, the use of volatile and flammable linear carbonates, poses significant threat to safe battery operation [9]. One way to improve the safety performance of LIBs is to use solvents with higher boiling and flash points [10–14]. Propylene

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carbonate (PC) is one of the most promising alternatives to the SOTA solvents as it has a wide liquid range ( $-55\text{ }^{\circ}\text{C}$ – $240\text{ }^{\circ}\text{C}$ ), a high relative permittivity (64.92 at  $25\text{ }^{\circ}\text{C}$ ), a moderate room temperature viscosity (2.53 mPa s at  $25\text{ }^{\circ}\text{C}$ ) and a high flash point ( $133\text{ }^{\circ}\text{C}$ ) [15,16].

The major challenge related to PC is that, when being electrochemically reduced, it cannot form an effective solid electrolyte interphase (SEI) with graphitic anodes in the first charge of the battery [5,17,18]. For this reason, SEI forming additives/co-solvents are indispensable for the application of PC as the main solvent. With this in line, various additives/co-solvents were reported for PC, such as, ethylene sulfite (ES) and propylene sulfite [19–22], vinylene carbonate (VC) [23], vinyl ethylene carbonate (VEC) [24], fluoroethylene carbonate (FEC) [25], methyl tetrafluoro-2-(methoxy) propionate (MTFMP) [15], vinylene and vinyl compounds [26–30], isocyanates [31–33], etc. However, in literature, PC was employed to evaluate the effectiveness of the SEI forming additives on graphite anodes, rather than formulating a PC-based electrolyte that enables long cycle life in LIBs [34]. Therefore, the long-term cycling performance evaluation of aforementioned cell type with PC-based electrolyte is scarce [16,34]. As the operation potential of lithiated graphite is beyond the thermodynamic stability window of most solvents including PC [35,36], the SEI enables the reversible lithiation and delithiation of graphite anode in a kinetic stabilization manner, thus facilitating the very low reaction rate between the graphite electrode and the electrolyte and with this enabling repeated charge/discharge cycles. Effective SEI is vital for the cycle life of LIBs. In the aim of improving the cycle life, multiple SEI additives were simultaneously introduced in state-of-the-art electrolyte to form a more effective SEI, due to the synergetic effects observed [37–39]. Inspired by this, ES and VC are introduced here simultaneously to formulate a PC-based electrolyte that enables excellent safety and cycling performance even when graphite is used as the negative electrode material in LIB cells.

As conventional polyolefin separator suffers from poor wettability with the PC-based electrolyte, PVdF-HFP was selected as polymer matrix, as it is compatible with PC. The formulated electrolyte can be categorized as gel polymer electrolyte (GPE) [40]. Compared to the “standard” combination of a polyolefin separator and LE, the PVdF-HFP-based GPE shows reduced flammability and low hazard of liquid leakage [41]. Porous structure is preferred for the PVdF-HFP polymer matrix as it increases the conductivity of the GPE. In our study, a phase inversion technique was applied to prepare a macro-porous PVdF-HFP membrane, according to the method described in literature [42].

## 2. Experimental

### 2.1. Preparation of the GPE and cell assembly

#### 2.1.1. Preparation of the macro-porous PVdF-HFP membrane

Under stirring, 2 g of PVdF-HFP (Kynar Flex<sup>®</sup> LBG) was dissolved in the mixture containing 16 g of acetone (Fisher Chemical,  $\geq 99.5\%$ ) and 2 g of deionized water in a sealed glass bottle at  $70\text{ }^{\circ}\text{C}$ . The obtained solution was cast on a clean glass plate with a doctor blade (gap width:  $600\text{ }\mu\text{m}$ ). After evaporating acetone and water under ambient temperature overnight, the obtained polymer membrane was punched into  $\phi 16\text{ mm}$  disks and further dried under reduced pressure ( $< 10^{-3}\text{ mbar}$ ) at  $60\text{ }^{\circ}\text{C}$  for 12 h to remove the residue water and acetone.

#### 2.1.2. GPE preparation

A formulation containing  $1\text{ mol L}^{-1}$   $\text{LiPF}_6$  in EC: DMC (1:1, by weight) (abbreviated as LP30, Selectilyte<sup>™</sup>, BASF, battery grade) was selected as benchmark LE. ES ( $\geq 99.0\%$ , Sigma Aldrich) was dried over molecular sieves  $4\text{ \AA}$  for at least 12 h before use.  $1\text{ mol L}^{-1}$   $\text{LiPF}_6$  (Selectilyte<sup>™</sup>, BASF, battery grade) in PC (Selectilyte<sup>™</sup>, BASF, battery grade) + 2 wt % ES + 2 wt % VC (Selectilyte<sup>™</sup>, BASF, battery grade) was prepared in a glove box (MBraun) filled with argon ( $\text{H}_2\text{O}$  and  $\text{O}_2 < 0.5\text{ ppm}$ ). All the materials purchased from BASF was used

without further purification. The water content in the prepared liquid electrolytes determined as  $< 30\text{ ppm}$ , being acceptable for cell application. The GPE was prepared by immersing the porous PdDF-HFP membrane into  $120\text{ }\mu\text{L}$  LE in a sealed polytetrafluorethylene (PTFE) container overnight. The LE uptake ratio was determined by dividing the weight of the polymer matrix after gelled overnight with the weight before gelling.

#### 2.1.3. NMC532/graphite LIB cell assembly

Capacity balanced  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  (NMC532, active material content 86% by weight, average capacity loading:  $2.0\text{ mAh cm}^{-2}$ ) and graphite (active material content 96% by weight, average capacity loading:  $2.2\text{ mAh cm}^{-2}$ ) electrode sheets were purchased from Customcells Itzehoe. The electrode sheets were punched into  $\phi 12\text{ mm}$  disks and dried at  $110\text{ }^{\circ}\text{C}$  under reduced pressure ( $< 10^{-3}\text{ mbar}$ ) for 12 h before use. The anode disk, GPE and cathode disk were assembled into a coin cell (CR2032) in a dry room (dew point  $< -65\text{ }^{\circ}\text{C}$ ).

### 2.2. Morphological characterization

The morphology of the PVdF-HFP membrane was characterized by scanning electron microscope (SEM) (Carl Zeiss SMT AG, Germany). The cross-section sample was prepared by immersing the PVdF-HFP membrane in liquid nitrogen for 2 min, followed by fracturing. Both the surface sample and the cross-section samples were sputtered with gold (Quorum Q150T ES) at a current of 45 mA for 30 s, prior to the SEM measurement.

### 2.3. Electrochemical performance characterization

#### 2.3.1. Conductivity determination

The conductivities of LP30 and PEV LEs were determined in a homemade conductivity cell [10] by means of electrochemical impedance spectroscopy (EIS). The electrodes were made of planar stainless-steel disks. The cell constant was determined with a KCl standard (conductivity standard  $1.413\text{ mS cm}^{-1}$ , VWR analytical). A coin cell setup was used for the conductivity determination of the GPEs. Due to its flexibility, the shape of the GPE changes upon mechanical pressure, leading to a variation of the cell constant. In order to keep the cell constant fixed, a homemade plastic ring (thickness:  $100\text{ }\mu\text{m}$ , inner diameter:  $13\text{ mm}$ ) was introduced into the coin cell as the spacer between 2 stainless steel disks, in which the GPE will be confined.

EIS measurements were controlled by Solartron SI 1287 and Solartron 1260 A impedance gain phase analyzers. The amplitude and the frequency range of the input alternating voltage signal were 5 mV and 100 kHz to 10 Hz, respectively. The temperature was controlled with a Binder MK 53 in the temperature range from  $-15$  to  $60\text{ }^{\circ}\text{C}$ .

#### 2.3.2. C-rate and cycling performance evaluation

The C-rate and cycling performance measurements were conducted with a MACCOR Series 4000 computerized test setup and the temperature was constantly kept at  $20.0\text{ }^{\circ}\text{C}$  using a Binder KB 400 incubator. The cycling performance test included 4 formation cycles (C-rates:  $2 \times 0.1\text{C}$ ,  $2 \times 0.5\text{C}$ , specific currents:  $15\text{ mA g}^{-1}$  for  $0.1\text{C}$ ,  $75\text{ mA g}^{-1}$  for  $0.5\text{C}$ ), followed by 200 charge/discharge cycles at  $1.0\text{C}$  rate (specific current:  $150\text{ mA g}^{-1}$ ). 2 cycles at  $0.1\text{C}$  rate were inserted after every 50 cycles at  $1.0\text{C}$  rate. The voltage range was set between 2.8 and 4.2 V for all investigated cells.

The C-rate performance test consisted of 4 cycles at  $0.1\text{C}$ , followed by 3 cycles each at  $0.2\text{C}$ ,  $0.5\text{C}$ ,  $1.0\text{C}$ ,  $2.0\text{C}$ ,  $5.0\text{C}$ , and  $10.0\text{C}$  and  $0.1\text{C}$  for charge and discharge.

### 2.4. Spectroscopic characterization

#### 2.4.1. In operando EIS upon cycling

Bio-Logic VMP3 was employed for the *in operando* EIS

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