



Temperature effects on performance of graphite anodes in carbonate based electrolytes for lithium ion batteries

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ABSTRACT

The performance of graphite electrodes in various electrolytes containing ethylene carbonate (EC) and mixtures of EC and propylene carbonate (PC) was studied at temperatures between 0 and 40 °C. Included in the study was also the addition of ethyl acetate (EA). Differential scanning calorimetry (DSC) was employed to investigate phase transitions at low temperature (down to –80 °C) and decomposition at elevated temperatures. Capacity loss was compared for graphite electrodes cycled at varying temperatures between 0 and 40 °C for these electrolytes. Based on the results, suitable electrolytes able to work in a wide temperature range could be identified. Addition of EA improved the low temperature properties of the electrolyte and the graphite electrode, but the electrodes failed upon cycling at +40 °C. Addition of PC to a multi-component system, making the total amount of cyclic carbonates 40% (i.e. 20% EC and 20% PC), increased the liquid temperature range of the electrolyte. However, the addition of PC, led to very high initial irreversible capacity loss of the graphite electrode, and reduced the capacity considerably at 0 °C, most likely related to a higher resistance of the solid electrolyte interphase. Thus, mixtures of EC and linear carbonates like dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) were found to perform best in this temperature range.

1. Introduction

In order for Li-ion batteries (LIB) to be a competitive alternative to the internal combustion engine in vehicles, significant improvements in cost, cycle life, power density and safety are required. In addition, stable operation in a wide temperature window is a vital factor. Graphite is the dominating choice as anode material, due to low cost and availability, combined with high capacity and reasonably stable performance. State of the art electrolyte for LIB is a mixture of linear carbonates, such as diethylene carbonate (DEC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC), and cyclic carbonates, such as ethylene carbonate (EC) and propylene carbonate (PC). Ethylene carbonate is always added due to its unique ability to form a protective film during the initial cycle, commonly known as the solid electrolyte interphase (SEI) [1]. The SEI layer is crucial for the stable operation of graphite anodes, as the intercalation potential lies below the electrochemical stability window of the electrolyte. In fact, the replacement of PC with EC was one key to success for the first commercialization of LIBs, despite of the high melting temperature of EC (+36 °C), as PC causes exfoliation of the graphite, leading to significant capacity loss during cycling. In addition, additives might improve the stability of the

graphite, among the most frequently applied is vinylene carbonate (VC).

The main factors affecting the electrochemical performance of graphite are: i) migration of the Li cation through the SEI [2,3] ii) reduced electrolyte conductivity limiting the mass transfer of lithium ions inside the pores [4,5] iii) reduced lithium ion diffusion in the solid graphite [6], and iv) the desolvation of the Li cation from its solvation sheath at the electrolyte-graphite interface [7,2,3]. The SEI layer generated on the graphite electrodes depends strongly on the electrolyte composition as well as operating conditions, and is a complex mixture of organic (i.e. lithium ethylene carbonate, LEC ((CH₂OCO₂Li)₂), the reduction product of EC), and inorganic compounds, like LiF, Li₂CO₃ and Li₂O [8]. A study on the effect of formation conditions for the SEI showed that good ionic conductivity resulted in poor SEI stability, and vice versa [9], which was attributed to formation of a more porous SEI at high current densities and relatively high temperatures. This SEI was however less passivating than the SEI formed at lower current densities (10–20 mA/g) and moderate temperatures (20–30 °C) [9].

It is of vital importance that the temperature window of LIB is increased, ensuring good performance of the LIB in electric vehicles (EV) in cold and warm climates. While the electrolyte will decompose above

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a certain temperature, extensive capacity fading is observed at low temperatures, eventually leaving the battery useless. There are different interpretations in the literature with respect to the reduced performance of graphite electrodes at low temperatures, as basically all processes mentioned above are affected when the temperature is lowered: i) the interfacial charge transfer resistance/SEI layer resistance [10], ii) electrolyte conductivity [5,11] iii) solid state diffusion of Li between graphene layers [11,12]. The limiting process will depend of the type of graphite and electrolyte, as well as the loading and the thickness of the electrodes.

As pointed out by Jansen et al. [13], who studied performance of full LIB cells at reduced temperatures, the processes responsible for the capacity fade appears to be almost independent of the active material, and related to an electrolyte-interface effect. It has later been established that the desolvation energy [14–17] is the major energy-consuming step and the largest contributor to the overall charge transfer resistance [3] for graphite anodes, and thus also one of the main contributors to the capacity loss at low temperatures. In a recent study, the activation energies for diffusion of Li^+ ions in graphite anodes was found to be around 20 kJ/mol [18], significantly lower than the typical activation energies for the desolvation process at the graphite-electrolyte interface, around 60 kJ/mol [15,19].

The high affinity of EC towards the lithium ion contributes to a higher desolvation energy, which would cause increased electrode resistance and poorer transport properties of Li-ions through the SEI. Hence, decreasing the amount of EC in the solution would force more linear carbonates (which have lower affinity) to solvate the lithium. This would presumably result in lower charge transfer resistance and higher diffusion through the SEI, giving a battery with high performance and rate capability. However, this come at the expense of long term stability as EC is very important for the formation of a stable SEI film. A high EC content is known to cause a higher anodic polarization, which also makes the system more susceptible towards lithium plating [20].

Mixing of EC with PC, whose molecular structure is similar to EC, would presumably result in a significant decrease of the melting point and consequently improve the low temperature properties. However, neither pure EC nor pure PC can be used as solvent, as EC is solid at room temperature, and pure PC will hinder reversible Li^+ intercalation. In the latter case only reductive decomposition of the PC takes place at the graphite surface, and the potential becomes constant around 0.9 V. The addition of linear carbonates is necessary to improve properties like viscosity, wettability and conductivity. The dielectric constant of EC is slightly higher than that of PC (90 vs. 65). Mixtures of cyclic and acyclic alkylcarbonates lead to an optimum relative permittivity of ca. 30–40. For further improvements of the low temperature properties, ternary and quaternary mixtures should be used [12,21].

A few weight% of PC might be added to the electrolyte in order to improve the low temperature performance. In a study comparing 3:7 EC:EMC and 1:1:3 EC:PC:EMC in full cells, the cell with PC containing electrolyte was found to have a lower capacity at room temperature, but a lower relative loss in the temperature range 0 to -20°C . This was attributed to a higher ionic conductivity of the SEI film at low temperatures, as determined by impedance spectroscopy, compared to EC based electrolytes [22]. When attempting to decrease the overall melting point of a binary electrolyte system, it was found that the best results were achieved by mixing species with similar melting points and molecular structure [23].

Many studies have tried to improve the capacity fading at lower temperatures by developing electrolytes with high conductivity and good SEI formation properties [12,21,24,25]. Here, the EC content is important, as electrolytes with a high content of EC have been reported to have a negligible conductivity at -10°C [26]. This was attributed to the solidification of the EC component. Bulk conductivity measurements for multi-component (ternary/quaternary) systems containing several alkyl carbonates showed an increased conductivity at low

temperatures compared to binary solutions [27] when DEC and esters were used in a multi-component system. Some esters have shown reactivity towards the anode (causing degradation) [25], while others in fact showed promising results during very low temperature operation down to -60°C , which was primarily achieved by fixing the EC-content to 20% and the ester co-solvent to 20% [24].

In this study the effect of EC and the addition of PC to a multi-component system have been investigated. The electrolyte compositions investigated were selected from those typically found in the literature, including PC and ethyl acetate (EA) as substitutes for EC, well known for their superior low temperature performance [22,24,27–29]. In addition, one commonly applied (in laboratory experiments) binary electrolyte was included for comparison (LiPF_6 in 1:1 EC:DEC). The thermal stability of all electrolytes was evaluated by differential scanning calorimetry (DSC) over a wide temperature range. Graphite electrodes were studied together with all the electrolytes in order to determine reversible and irreversible capacity in the temperature range 0 to 40°C (considered as a practical temperature range for portable applications, electrical vehicles etc.), capacity fade after repeated cycles, as well as differential capacity curves providing the shifts of intercalation potentials. Thermal stability of cycled electrodes was determined by DSC. The DSC analysis performed at high temperatures for the graphite anodes, after the SEI is formed, can provide important information about the safety of the different electrolytes as it is often the heat developed on the anode that initiates further (and more energetic) exothermic reactions on the cathode, leading to thermal runaway [30]. The aim of this study is thus to: i) compare electrolytes with 20 and 40 wt% EC at reduced temperatures (i.e. whether a thicker, but more stable SEI is beneficial); ii) Investigate the effect (electrochemically and thermally) of adding PC and EA, and find out whether the improved low temperature properties of PC will outweigh the expected exfoliation and inferior SEI formation properties; iii) Determine if any additional degradation is occurring during cycling of graphite at various temperatures compared to cells cycled at constant room temperature.

2. Experimental

Graphite SLP30 was used as received from TIMCAL™. The graphite electrodes were prepared by tape casting a slurry consisting of 37 g SLP30, 2 g poly-vinylidene fluoride (PVDF) (Kynar, reagent grade), 1 g Super P carbon black (TIMCAL™), and 60 g 1-methyl-2-Pyrrolidinone (NMP) (Sigma-Aldrich, > 99%) onto a $10\ \mu\text{m}$ thick Cu-foil current collector from Circuit foil Luxembourg. The tape caster was a “K Control Coater” from Printcoat instruments. The casts were dried in a vacuum oven at 120°C overnight.

The electrolytes were made using varying amounts (in weight%) of ethylene carbonate (EC, Sigma-Aldrich, > 99%), diethyl carbonate (DEC, Aldrich, > 99%), vinylene carbonate (VC (Sigma-Aldrich, 97%)), ethyl methyl carbonate (EMC, Merck, > 99%), ethyl acetate (EA, Sigma-Aldrich, 99,8%), dimethyl carbonate (DMC, Sigma-Aldrich, > 99%) and propylene carbonate (PC, Sigma-Aldrich, 99,7%) as presented in Table 1. All the electrolytes contain 0.9 M LiPF_6 (Sigma-Aldrich, > 99.99%) unless otherwise specified.

Graphite/Lithium half cells were assembled in coin cells (Hohsen)

Table 1
Electrolyte mixtures.

Electrolyte composition (wt%)
1:1 EC:DEC, 0.9 M LiPF_6 + 1% VC
1:1:3 EC:PC:EMC, 0.9 M LiPF_6
1:1:3 EC:EA:EMC, 0.9 M LiPF_6
2:2:3:3 EC:PC:DMC:EMC, 0.9 M LiPF_6
1:2:2 EC:DMC:EMC, 0.9 M LiPF_6
4:3:3 EC:DMC:EMC, 0.9 M LiPF_6

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