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Enabling linear alkyl carbonate electrolytes for high voltage Li-ion cells

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HIGHLIGHTS

- Ethylene carbonate (EC) is actually detrimental for Li-ion cells at high voltages.
- EC-free linear alkyl carbonate electrolytes with various "enablers" were developed.
- Linear alkyl carbonate electrolytes have very good performance at high voltages.

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ABSTRACT

Some of the problems of current electrolytes for high voltage Li-ion cells originate from ethylene carbonate (EC) which is thought to be an essential electrolyte component for Li-ion cells. Ethylene carbonate-free electrolytes containing 1 M $LiPF_6$ in ethylmethyl carbonate (EMC) with small loadings of vinylene carbonate, fluoroethylene carbonate, or (4R,5S)-4,5-Difluoro-1,3-dioxolan-2-one acting as "enablers" were developed. These electrolytes used in $Li(Ni_{0.4}Mn_{0.4}Co_{0.2})O_2$/graphite pouch type Li-ion cells tested at 4.2 V and 4.5 V yielded excellent charge-discharge cycling and storage properties. The results for cells containing linear alkyl carbonate electrolytes with no EC were compared to those of cells with EC-containing electrolytes incorporating additives proven to enhance cyclability of cells. The combination of EMC with appropriate amounts of these enablers yields cells with better performance than cells with EC-containing electrolytes incorporating additives tested to 4.5 V. Further optimizing these linear alkyl carbonate electrolytes with appropriate co-additives may represent a viable path to the successful commercial utilization of NMC/graphite Li-ion cells operated to 4.5 V and above.

1. Introduction

Li-ion batteries (LiBs) with higher energy density as well as longer lifetime are desired for applications such as portable consumer electronics, electric vehicles (EVs) and grid energy storage [1,2]. While the energy density generally relies on the selection of electrode materials, the lifetime depends heavily on the choice of electrolyte. Over the past few decades, a variety of electrode materials have been developed and commercialized [3–10]. However, the commercialization of new electrolyte solvents has been relatively slow. Currently, state-of-the-art electrolytes are very similar to the ones used twenty five years ago. These are based on mixtures containing $LiPF_6$, ethylene carbonate (EC), sometimes propylene carbonate (PC) and linear carbonates selected from ethyl methyl carbonate (EMC), dimethyl carbonate (DMC) and diethyl carbonate (DEC). A wide variety of electrolyte additives, such as vinylene carbonate (VC) [11] and biphenyl [12], are incorporated to improve battery lifetime and response to electrical abuse, respectively. The cycling performance of Li-ion cells with these carbonate based electrolytes has been poor at or above 4.4 V due to increased electrolyte oxidation at the surface of positive electrode as the potential increases. The degradation of these electrolyte components at high voltages results in salt consumption, gas evolution and impedance growth, which reduce the energy density and the lifetime of Li-ion cells [13–16].

New alternative electrolyte formulations with high anodic stability are needed. Several organic compounds with strong electron-withdrawing groups, such as sulfones [17,18], nitriles [19,20], ionic

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liquids [21–24] and fluorinated compounds [25–28] are reported to have excellent anodic stability and have been studied as electrolyte solvents for high voltage Li-ion cells. However, many of these organic compounds which have high oxidation stability do not provide a good passivation at the graphite electrode without EC as a co-solvent. Moreover, problems associated with solubility with salt, toxicity, cost and safety must be addressed before these solvents are widely used in Li-ion cells [29,30].

It is thought that EC is essential for the passivation of the graphite electrodes surface during the first cycle [31,32]. However, left-over EC in the electrolyte may be continuously oxidized at the positive electrode in cells operated to high voltage. This may lead to gas generation and impedance growth. It was recently shown that the removal of EC from carbonate-based electrolytes yielded high voltage Li-ion cells with longer life-time [33]. EC-free-linear alkyl carbonate-based electrolytes with a small amount of “enabler”, namely vinylene carbonate (VC), allowed NMC(442)/graphite cells to be cycled up to 4.4 V with longer cycle and calendar life, compared to cells with a state-of-the-art electrolyte incorporating additives [33]. For instance, NMC(442)/graphite cells filled with 1 M $LiPF_6$ EMC:VC (98:2) + 2% PPF (pyridine phosphorus pentafluoride) were shown to have longer cycle life at both room temperature and 55 °C when cycled up to 4.4 V than cells with EC-based electrolytes incorporating state of the art additive blends [33]. The EMC:VC (98:2) electrolyte system also has acceptable conductivity, wets separators quickly, shows good tolerance to high voltage and provides cells with low polarization growth when cycled up to 4.4 V.

SEI forming additives other than VC, such as fluoroethylene carbonate (FEC), (4R,5S)-4,5-Difluoro-1,3-dioxolan-2-one (DiFEC) [34], methylene-ethylene carbonate (MEC) [35], prop-1-ene-1,3-sultone (PES) [36] and succinic anhydride (SA) [37] are also effective “enablers” for $Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O_2$ (NMC442)/graphite pouch cells containing linear alkyl carbonate-based electrolytes cycled to high voltages. Fig. 1 and Fig. S1 (supporting information) show the structure of various additives and differential capacity (dQ/dV) *vs.* voltage (V) curves for the first charge (formation cycle) of NMC442/graphite pouch cells filled with EMC-based electrolytes to which various additives have been added. Fig. 1 and Fig. S1 show that cells which do not contain any additives have a large reduction peak around 3.2 V. This peak corresponds to the reduction of EMC and is associated with the generation of a large volume of gas (around 2 mL corresponding to 100% cell expansion). Fig. 1 and Fig. S1 clearly show that enablers such as VC, FEC, DiFEC, PES, SA and MEC can greatly suppress the reduction peak of EMC at 3.2 V (graphite around 0.45 V vs. Li/Li^+) while other additives such as vinyl ethylene carbonate (VEC), maleic anhydride (MA) and diphenyl carbonate (DPC) cannot. The amount of enabler is also critical. For instance, Fig. S2a shows that a low concentration of SA such as 0.2% or 0.5% is not enough to suppress the reduction peak of EMC while higher concentrations such as 1% can totally suppress the reduction peak of EMC. However, for additives such as VEC (see Fig. S2b), even with 4%, the reduction peak of EMC cannot be suppressed. Table 1 shows a summary of additives that can successfully passivate the graphite electrode, when used with linear alkyl carbonate solvents alone.

In this paper, four “enablers” including EC, VC, FEC and DiFEC were compared head to head in NMC442/graphite pouch type Li-ion cells. Other enablers such as SA, MEC, PES will not be included in this paper but will be discussed in latter publications. Experiments were made using ultra high precision coulometry (UHPC) [38], a precision storage system [39],electrochemical impedance spectroscopy (EIS) and a gas measurement. Gas evolution during formation and cycling, coulombic efficiency, charge endpoint capacity slippage during cycling and EIS spectra before and after cycling were examined and were compared to EC-based electrolyte with some promising additive blends.

2. Experimental

2.1. Chemicals

1 M $LiPF_6$ in ethylene carbonate (EC):ethyl methyl carbonate (EMC) 3:7 wt% ratio, (BASF - $LiPF_6$, purity 99.94%, water content 14 ppm; EC:EMC, 3:7 by weight, water content < 20 ppm) was used as the control electrolyte. Electrolyte blends based on 1 M $LiPF_6$ in EMC were also studied. To the EMC-based electrolyte, additives

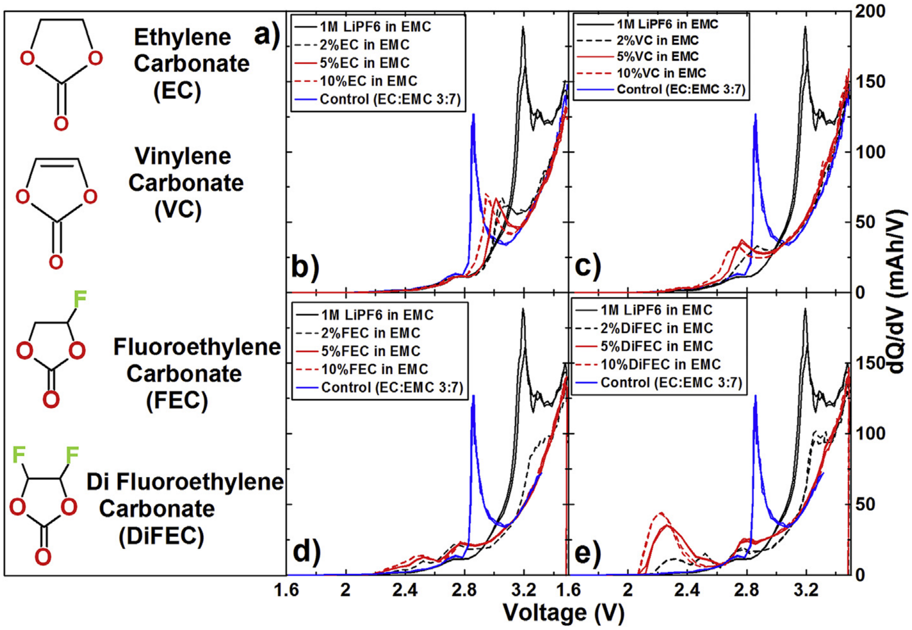

Fig. 1. a) Chemical structure of the four enablers described in this work. Differential capacity (d*Q*/d*V*) versus potential (*V*) during formation step 1 for the 180 mAh NMC442/graphite pouch cells with different enabler concentration: b) EC, c) VC, d) FEC and e) DiFEC.