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Importance of Reduction and Oxidation Stability of High Voltage Electrolytes and Additives

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ABSTRACT

The electrolyte is a critical component for rechargeable Li-ion batteries, especially batteries containing high voltage cathodes. A series of electrolyte salts, solvents and additives was investigated via cyclic voltammetry (CV) on glassy carbon (GC) electrodes. Quantum chemistry (QC) calculations were used for prediction of oxidation and reduction stability of electrolyte components such as ethylene carbonate (EC), dimethyl carbonate (DMC), fluoroethylene carbonate (FEC), vinylene carbonate (VC), tris (trimethylsilyl) phosphate (TMSP), 1,3-propane sultone (PS), tris(hexafluoroisopropyl) phosphate (HFiPP) and lithium salts such as $LiPF_6$, $LiBF_4$, lithium difluoro(oxalato)borate (LiDFOB), lithium 4,5-dicyano-2-trifluoromethyl-imidazolide (LiTDI), and lithium bis(trifluoromethanesulfonimide) (LiTFSI). QC calculations predicted that defluorination of $LiPF_6$ and LiTFSI aggregates coupled with electron transfer significantly increased their reduction potential, while H-transfer upon oxidation lowered oxidation potential for many solvents. The composition of the Li^+ cation solvation shell was estimated from the binding energies for the Li^+–solvent complexes using cluster-continuum calculations and was used to provide insight into the experimental data on electrolyte reduction. Full coin cell data was acquired using $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cathodes with graphite anodes at 25 °C and 55 °C. Differential capacity plots (dQ/dE vs. E) and electrochemical impedance spectroscopy (EIS) results. The electrolyte with the most desirable performance was 1 M $LiPF_6$ in 3:7 EC:EMC (wt%) with 1 wt% TMSP. Oxidative CV experiments show that the TMSP containing electrolyte has a slightly lower oxidation stability compared to the baseline, which is consistent with the order of oxidation stability of electrolyte components from QC calculations. The EIS measurements showed that the TMSP containing electrolyte had the lowest impedance after cycling and the dQ/dE plots show that the redox reactions retained their peak shape and area more so than an electrolyte without TMSP, indicating a greater capacity retention. Density functional theory calculations of TMSP oxidation on the LNMO surface were performed in order to provide insight into the additive role in improving cell performance.

1. Introduction

One approach for increasing the energy density over that of the state-of-the-art Li-ion batteries is to employ cathodes that operate at higher voltages, such as the spinel structure lithium nickel manganese oxide, {$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) [1], 4.7 V vs. Li/Li^+}, and the olivine structure lithium cobalt phosphate, {$LiCoPO_4$ (LCP) [2], 4.8 V vs. Li/Li^+}. With capacities similar to their lower voltage counterparts, $LiMn_2O_4$ (LMO) at 4.0 V and $LiFePO_4$ (LFP) at 3.4 V, the higher discharge voltages increase the energy density of the cell when used with the same anode. A common question often raised is whether electrolytes exist that would enable the operation of the high voltage cathodes. This uncertainty likely results from the generally accepted belief that the state-of-the-art Li-ion electrolytes can only be operated at voltages less than ~4.5 V with respect to Li/Li^+ [3]. Therefore, the reported high voltage electrolyte developments have taken two main approaches. The first approach is the use of fluorinated versions of the carbonate solvents, taking advantage of their higher oxidation stability compared to the non-fluorinated counterparts [4–8]. Raising the oxidation potential with fluorine addition usually also raises the reduction potential of these solvents. When using a graphite

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anode, forming and maintaining the solid electrolyte interface (SEI) is critical to battery performance. For this reason, changing the bulk properties of the electrolyte may not lead to a suitable solution. The other approach is the use of additives that oxidize at potentials lower than the oxidation potential of the active cathode material (and lower than that of the bulk electrolyte) and thus form a protective layer on the cathode [9,10]. Lucht et al. have shown that the use of additives improve the electrolyte performance in LNMO/Graphite full cells, especially at high temperature [11–13].

Previous molecular modeling studies indicated that oxidation of electrolyte components is often complicated by decomposition or deprotonation reactions [14,15]. For example, quantum chemistry (QC) calculations predicted that the oxidation potential of the commonly used solvent ethylene carbonate (EC) in an isolated state but surrounded by implicit solvent with a dielectric constant $\varepsilon = 20$, which is similar to the dielectric constant of an EC:EMC mixed electrolyte, is ~7 V vs. Li/Li^+. When similar calculations are performed with EC in the presence of an anion such as BF_4^- the oxidation stability lowers to 6.2–6.3 V when the same M05-2X density functional theory (DFT) was used. Even lower oxidation potentials of 6.1 V and 5.2 V were predicted for $EC–BF_4$ and EC_2, respectively, when the more accurate G4MP2 theory was used [16]. The oxidation potential of ethyl methyl carbonate (EMC) in the presence of PF_6^-, (EMC/PF_6^-), is predicted to be 5.9 V, which is also more than one volt lower than the oxidation potential of an isolated EMC molecule [14]. The oxidation stability of the PF_6^- anion was predicted as 8.6 V in an implicit solvent with a dielectric constant $\varepsilon = 20$ [14,17], which is significantly higher than oxidation stability of EC_2, $EC–PF_6$ indicating that the PF_6^- anion is the most oxidatively stable component of EC:DMC/$LiPF_6$ electrolytes. EC and DMC were also found in QC calculations to undergo deprotonation on the surface of charged LNMO spinel [16]. While calculations of oxidation reactions of single molecules do not represent real world situations in which the molecules are in a complex mixture of salts and solvents polarized at the cathode interface, examination of the representative electrolyte clusters provided significant insight into oxidation stability and initial decomposition reactions. In short, these previous computational results suggest that the electrolytes made of 1 M $LiPF_6$ salt in EC:EMC solvent mixtures would undergo oxidation coupled with H-transfer around 5 V vs. Li/Li^+, which is close to the operational voltage of high voltage electrolytes.

The computational results could be validated by experimental results using cyclic voltammetry (CV) on an inert electrode such as glassy carbon (GC) [18], in which a voltage sweep of the GC electrode in either the oxidative or reductive direction is applied, and the current response is observed until a large current increase occurs, indicating the decomposition voltage of the electrolyte. The CV results suggest the oxidative stability of electrolytes composed of $LiPF_6$ in EC:EMC mixtures are >5 V without considering the reactivity with the cathode, with the results being dependent on the scan rate.

When the working electrode is made of active material, the current observed in CV measurements is often complicated by redox or irreversible reaction currents coming from Faradaic reactions by the active material in addition to the oxidative or reductive decomposition current of the electrolyte itself. Therefore, it would be useful to examine the oxidative and reductive responses of the electrolyte on an inert electrode before examination on an active electrode.

One important point to consider for the development of electrolytes for high voltage Li-ion cells is the fact that the full cell is first formed by charging the cell to an upper voltage limit during which time the anode quickly drops in voltage to the lithium intercalation potential of graphite while the cathode remains at relatively low voltage (Fig. 1). The electrolyte undergoes a reduction reaction at the graphite anode first before it is oxidized at the cathode while the full-cell voltage is increased gradually until it reaches the high voltage cutoff. The reduction reaction of the electrolyte decides the ensuing reactions of the cell. While it is important to look for a more oxidatively stable electrolyte, we believe that it is also critical to understand the reduction reactions and how they affect the subsequent oxidation reactions of the electrolyte components both experimentally and in QC calculations.

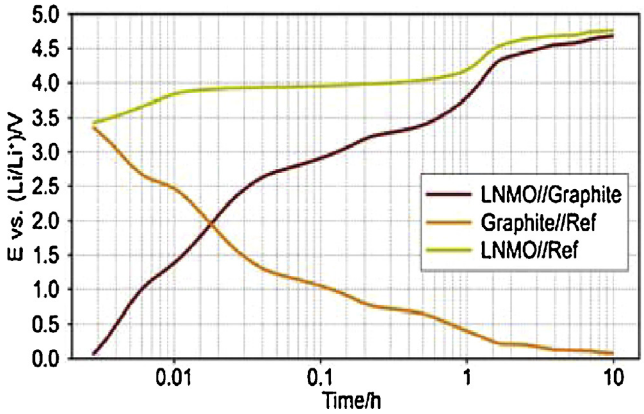

Fig. 1. Voltage vs Time plot for 3-electrode LNMO/Li/Gr (cathode/reference/anode) pouch cell showing observed voltages at cathode and anode relative to full cell voltage (x-axis on log scale for clarity).

This paper will examine the electrochemical redox reactions of the electrolyte components including salts, solvents, and additives (Fig. 2) on an inert electrode (glassy carbon) and how they compare with the computational predictions. We will then explain how additives affect reductive reactions or the oxidative reactions of electrolytes and ultimately the cycling behavior of high voltage Li-ion cells with high voltage cathodes.

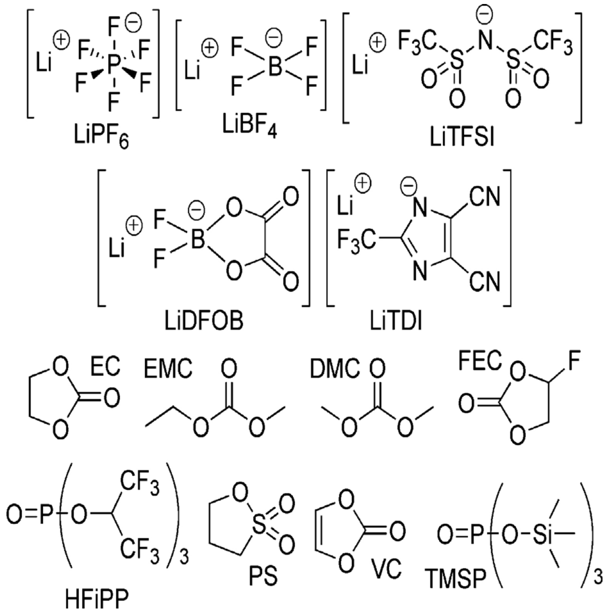

Fig. 2. Electrolyte components used in this study.