Abstract #1181, 224th ECS Meeting, © 2013 The Electrochemical Society

Oxidation-Induced Decomposition of Electrolytes and Additives from Quantum Chemistry Calculations

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Insight into electrolyte oxidation stability and oxidation-induced decomposition reactions is expected to benefit development of the lithium battery electrolytes that will show an improved compatibility with high voltage cathode materials. A systematic study[1] of the solvent/solvent, solvent/anion and solvent/(lithium salt) complexes using DFT and correlated wave function methods demonstrated the deficiencies of projecting oxidation stability and decomposition reactions from isolated solvents and isolated anions to electrolytes. It was found that the intrinsic oxidation potential of most solvent molecules was higher than experimental values for electrolytes even after the solvation contribution to the oxidation potential was included in the calculations via a polarized continuum model. The presence of anions and other solvent molecules was found to lead to the reduced solvent oxidative stability, changed the order of the solvent decomposition reactions, altered decomposition products and influenced the decomposition kinetics for carbonate (EC,DMC,PC), alkyl phosphate (TMP) and ether-based electrolytes with $LiPF_6$, $LiBF_4$, $LiB(CN)_4$, LiTFSI, LiTFSI salts.[1-4]

Unlike alkyl phosphates and carbonates, oxidation of dimers of linear and cyclic sulfones such as EMS and TMS and their complexes with BF_4^- or PF_6^- anions did not lead to a spontaneous H-transfer, instead, a low barrier for H-transfer was observed in these complexes. We speculate that the absence of a spontaneous H-transfer in many TMS and EMS complexes could be attributed to better performance of these electrolytes with high voltage cathodes when compared to carbonates. In contrast to ubiquitous spontaneous oxidation induced H-transfer or F-transfer reactions observed in carbonates clusters and carbonates in contact with BF_4^-, PF_6^- and $B(CN)_4^-$ anions, the H-transfer reactions were not observed in the oxidized carbonate solvent complexes with $DCTA^-$ or $DFOB^-$ anions or for VC/anion.

This presentation will extend upon previous studies of the initial stages of oxidation-induced decomposition reactions of common electrolyte solvents. The propagation and termination reactions that follow the initial step of the oxidation-induced decomposition reaction will be discussed for the EC-based electrolytes.

Kinetics of the initial oxidation reactions were analyzed using Marcus theory of electron transfer. Preliminary results indicate that the cyclic carbonates and alkyl phosphates have a significantly larger difference between the vertical and adiabatic oxidation energies than linear carbonates (DMC, EMC, VC) indicating lower barrier and faster reaction rates for the electron transfer in the linear carbonates (DMC, EMC, VC) within the context of Marcus theory of electron transfer. A systematic analysis of the reorganization energy and electron transfer rates will be presented for the solvent-anion clusters.

Oxidation stability and initial decomposition reactions calculated using DFT will also be reported for a number of electrolyte additives ranging from fluorinated alkyl phosphates such as tris(hexafluoro-iso-propyl) phosphate (*HFiP*) to boron analogs and trimethylboroxine (TMB). TMB additive was investigated as it was reported by Sharabi et al.[5] to be a promising additive for the $LiCoPO_4$ high voltage cathode-containing cells. In DFT calculations it was found that oxidation of the TMB/PF_6^- complex was immediately followed by the F-transfer from the PF_6^- anion to TMB additive and $CH_3^\bullet$ radical formation.

The intrinsic oxidation potential was calculated for a selected set of additives listed in Table 1 using a polarized continuum model (PCM) (ε=23). Fluorination of trimethyl phosphate $PO(OCH_3)_3 \rightarrow PO(OCF_3)_3$ increases its intrinsic oxidation potential by 1.4 V. HFiP and HFiAl additives have 0.2 -0.3 V lower intrinsic oxidative stability compared to f-TMP, while HFiB has oxidative stability of 8.5 V among additives. Presence of the fluorinated anions such as BF_4^- significantly decreases additive oxidative stability, for example, $HFiB/BF_4^-$ oxidative stability is 1.6 V lower than that of HFiB due to spontaneous fluorine transfer from BF_4^- to HFiB and B-O bond cleavage as shown in Figure 1. Similarly, PF_6^- anion transferred F to HFiP and decreased stability of P-O bond. Thus, fluoro-containing anions and other nucleophilic groups influence oxidation stability of additives and their oxidation induced decomposition reactions.

Table 1. Oxidation ΔG^{ox} potential vs. Li^+/Li calculated with PCM(ε=23) using M05-2X/6-31+G**.

	ΔG^{ox} (V)
$PO(OCH_3)_3$ (TMP)	6.9
$PO(OCF_3)_3$ (f-TMP)	8.3
$PO(OCH(CF_3)_2)_3$ (HFiP)	8.1
$B(OCH(CF_3)_2)_3$ (HFiB)	8.5
$HFiB/Li^+$	
$Al(OCH(CF_3)_2)_3$ (HFiAl)	8.0
$B(OCH(CF_3)_2)_3/BF_4^-$ ($HFiB/BF_4^-$)	6.9

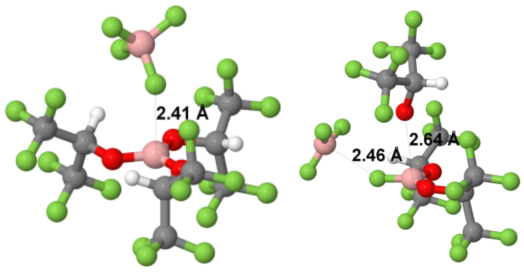

Figure 1. Optimized geometry of $HFiB/BF_4^-$ complex before and after oxidation.

Acknowledgement
This work was supported via an Interagency Agreement between the U.S. Department of Energy and the U. S. Army Research Laboratory under DE-IA01-11EE003413 for the Office of Vehicle Technologies (ABR Program).

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