

Study of SEI Layer Formed on Graphite Anodes in PC/LiBOB Electrolyte Using IR Spectroscopy

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The lithium bis(oxalato)borate (LiBOB) based electrolyte has been shown to be effectively stabilizing graphene structure against propylene carbonate (PC).¹⁻² The SEI layer formed by LiBOB based electrolyte on carbon anodes were investigated by X-ray photoelectron spectroscopy³, which indicated that more semicarbonate type species from the SEI in PC/LiBOB vs. EC:EMC/LiPF₆. Analysis for B-containing species was inconclusive. A complimentary analytical method is needed to elucidate further the chemical nature of the SEI layer, and the mechanistic role of LiBOB in the formation of this layer. Ex-situ Fourier Transform Infrared Spectroscopy (FTIR) analysis in the attenuated total reflection (ATR) mode was selected in this case due to its ability to distinguish C-O compounds that are all nominally semi-carbonates by XPS).⁴

Graphite anode coated on Cu substrate were assembled into Li/graphite half-cells PC/LiBOB and EC:EMC/LiPF₆ electrolytes, and subject to several galvanostatic charge/discharge formation/conditioning cycles between 1.6 V and 0.01 V vs. Li at C/25.¹ Upon completion of the cycling, the fully delithiated anodes (discharged to 1V) were disassembled from the cell in the glove box, rinsed initially with a solvent mixture of γ -butyrolactone (GBL)/dimethyl carbonate (DMC) followed by rinsing with neat DMC. The BOB anion vibrational modes were extracted from spectra PC/LiBOB electrolyte (Fig.1) and assigned based on ab-initio molecular orbital calculation. The agreement between experimentally measured vibrational modes and the calculation suggested that BOB anion is weakly solvated in PC electrolyte.

The FTIR spectra of SEI layer on anode cycled in PC/LiBOB and EC:EMC/LiPF₆ are shown in Fig.2. The results provide a more refined description of the composition than earlier analyses with (XPS).³ The vibrational spectra clearly show that electrochemical reduction of the BOB anion is a part of the SEI layer formation chemistry. Carboxylate and/or oxalate functional groups derived from reduction of the BOB anion are probably the components assigned as the "semicarbonate" species in the C 1s XPS spectra of the SEI layer formed in LiBOB electrolyte. Reduction of the BOB anion changes the oxygen coordination around the B atom from tetrahedral BO₄ to trigonal BO₃, e.g. esters of boric acid, and changes the symmetry of the O-C-O bonding closer to that in esters of oxalic acid. Based on the combination of electrochemical and FTIR data, we conclude that products from the electrochemical reduction of the BOB anion are essential components of the SEI layer formed in this electrolyte. We conclude that reduction of the BOB anion at potentials above ca. 0.8 V prevents solvent co-intercalation.

References

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Acknowledgement

This work was supported by the DOE Office of FreedomCAR and Vehicle Technologies Advanced Automotive Technologies of the U. S. Department of Energy. We also thank SAFT America for providing electrode materials.

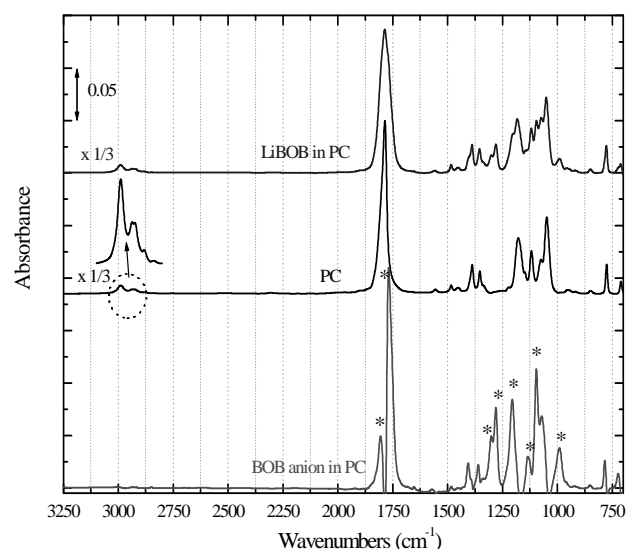


Fig.1 FTIR spectra of LiBOB (upper curve) in propylene carbonate (PC) and pure PC (middle curve), where the CH₃ and CH₂ stretching mode of PC was zoomed for clarity. The IR spectrum of BOB anion (lower curve) was obtained by subtraction of PC from electrolyte (LiBOB/PC), in which features originating from BOB anion were marked in asterisks. Comparison between calculation and experiment reveals that BOB anion is weakly solvated in PC.

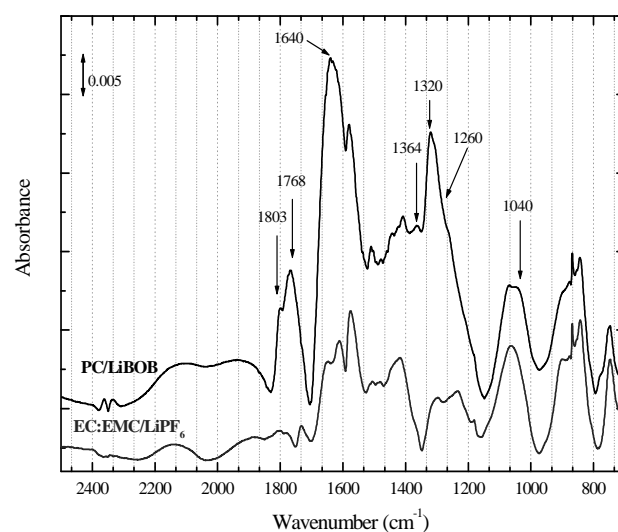


Figure 2. FTIR spectra of anode samples cycled in PC/LiBOB and in EC:EMC/LiPF₆ electrolytes differ significantly. Features denoted by arrows are unique to anode cycled in PC/LiBOB.