

Reactivity of Li-ion Battery Electrolytes

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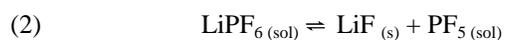
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The typical non-aqueous electrolyte for commercial Li-ion cells is a solution of LiPF₆ in linear and cyclic carbonates such as dimethyl carbonate and ethylene carbonate respectively.^{1, 2} During battery operation, the anion plays a critical role in the formation of the solid electrolyte interphase (SEI) layer, and the stability of the Li salt may be crucial. For example, perchlorate or nitrate salts may be explosive when mixed with organic solvents.³ Hexafluorophosphate (PF₆⁻) salts can produce PF₅ gas,⁴ a strong Lewis Acid.⁵ Similar reactions have been observed for LiAsF₆.⁶ There is evidence to suggest that LiPF₆ solutions in trioxane give cleavage of ether linkages.⁷ Studies of liquid electrolytes have addressed the thermal instability of LiPF₆ solutions,⁸ but the role of PF₅ in the reaction with carbonate electrolytes for Li-ion batteries is as yet unresolved. The purpose of this report is to explore further the reactivity of PF₅ and EC/linear carbonates and to understand the thermal and electrochemical decomposition reactions of LiPF₆ in carbonate solvents. The reactivity of other salts such as LiBF₄ and LiTFSI are also examined.

Solid LiPF₆ is in equilibrium with solid LiF and PF₅ gas



The reaction temperature and the pressure of PF₅ gas determine the equilibrium position. Removal of PF₅ gas consumes LiPF₆ and produces LiF. For a LiPF₆ solution, the analogous equilibrium exists. Because LiF is insoluble, only the concentration of LiPF₆ and PF₅ determine the equilibrium position.



In the electrolyte, the equilibrium can move toward products as PF₅ reacts with the solvents.

The 1M LiPF₆/carbonate solvent mixtures react when heated. After 2 days at 85°C, a brown color, solid precipitate, and gas production are observable. Gas chromatographic analysis of the EC:linear carbonate ratios over time show that the EC concentration decreases faster than the linear carbonate solvent concentration. The same analyses show the formation of transesterification products but the rate of production of these products do not account for the loss of EC. This is observed with EC/DMC, EC/DEC and EC/EMC mixtures and the appropriate transesterification products are observed for each solution. Similar products are observed for LiBF₄ and LiAsF₆ although it is noted that the reactivity of LiPF₆ is considerably greater at temperatures above 50°C. No reactivity is observed with LiTFSI or with no salt present at any temperature up to 85°C.

The discrepancy in material balance may be explained by the production of polymers. The polymerization of ethylene carbonate by treatment with Lewis acid initiators is well known⁹ and can lead to PEO-like polymers. The polymerization is endothermic until 180°C and is driven by CO₂ evolution. Above this temperature the polymerization becomes exothermic and leads to a violent decomposition. The pEO-like polymers also react with the PF₅ to yield further products that may

be soluble in the electrolyte or participate in SEI formation in real cells. GPC analysis of the heated electrolytes indicates the presence of material with M.Wt.'s up to 5,000. Further results on the polymerization reactions and further reactions with PF₅ will be reported.

The transesterification products are observed in the electrolytes of Li-ion cells which have only undergone a single formation cycle and which have not been subjected to any heat treatment. This result indicates that the PF₅ reactions are present in practical cells. Further analysis of the products from cycled cells will be discussed with particular emphasis on how they may affect the formation of protective films on the electrodes and how such reactions affect safety.

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