Novel Electrolytes for Lithium Ion Batteries

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Accomplishments

While commercial lithium-ion batteries (LIBs) perform well for most home electronic applications, currently available LIB technology does not satisfy some of the performance goals for Plug-in Hybrid Electric Vehicles (PHEV). In particular, currently available LIB technology does not meet the 10-15 year calendar life requirement set by the United States Advanced Battery Consortium (USABC). The most extensively used LIB electrolytes are composed of $LiPF_6$ dissolved in organic carbonates or esters. However, $LiPF_6$ electrolytes have poor thermal stability and the required use of ethylene carbonate (EC) limits low temperature performance. Significant energy fading occurs after several years at room temperature and over only a few months at moderately elevated temperatures (>55 °C). While there are several different factors that limit the thermal stability and calendar life of LIBs, the reactions of the electrolyte with the surface of the electrode materials is frequently reported to be the most important.

We have been investigating three primary areas related to lithium ion battery electrolytes. First, we have been investigating the thermal stability of novel electrolytes for lithium ion batteries, in particular borate based salts. Second, we have been investigating novel additives to improve the calendar life of lithium ion batteries. Third, we have been investigating the thermal decomposition reactions of electrolytes for lithium-oxygen batteries. The primary focus areas of research are listed below.

Thermal Dissociation of Lithium difluoro(oxalato) borate (LiDFOB)

Lithium difluoro(oxalato) borate (LiDFOB) is a promising alternative lithium salt for lithium ion battery electrolytes. The ligand exchange reaction of LiDFOB to generate Lithium tetrafluoroborate ($LiBF_4$) and lithium bis(oxalato)borate (LiBOB) was investigated by Nuclear Magnetic Resonance (NMR) spectroscopy. A thermally induced equilibrium exists between LiDFOB, $LiBF_4$ and LiBOB. The activation barrier for conversion of LiDFOB to $LiBF_4$ and LiBOB is 137 KJ mol^{-1} and the equilibrium favors LiDOFB by 14 KJ mol^{-1}.

Methylene-Ethylene Carbonate: A Novel Additive to Improve the thermal stability of Lithium Ion Batteries

The preparation of methylene ethylene carbonate (MEC) and the incorporation of MEC into lithium ion batteries as an electrolyte additive were investigated. MEC is prepared in good yield by mercury catalyzed cyclization. Addition of low concentrations of MEC (1-2 %) to 1 M $LiPF_6$ in 3:7 ethylene carbonate/ethyl methyl carbonate improves the capacity retention of lithium ion batteries cycled at elevated temperature (60 ^{o}C). Ex-situ surface analysis (XPS and FT-IR) of the electrodes supports the presence of poly(methylene ethylene carbonate) on the anode surface. Modification of the anode solid electrolyte interphase (SEI) correlates with significant improvements in the cycling performance at 60 ^{o}C.

Lithium Difluoro(oxalato)borate (LIDFOB) as an Alternative Salt for Propylene Carbonate Based Electrolytes

Propylene carbonate (PC) has illustrated high level of interest as an electrolyte solvent due to have greater physical properties when compared to that of traditional ethylene carbonate (EC). Additionally, lithium difluoro(oxalate)borate (LiDFOB) has shown promise as an alternative to lithium hexafluorophosphate ($LiPF_6$) as a primary electrolyte salt. Coin cells of 1.2M LiDFOB in 3:7 PC/EMC were constructed using natural graphite/$LiCoO_2$ electrodes and cycled in order to obtain discharge capacities. *Ex situ* surface analysis of the electrodes was conducted via the use of x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FT-IR). The corresponding results showed that PC and LiDFOB with the addition of 1.5% vinylene carbonate cycled comparably to that of standard 1.2M LiPF6 in 3:7 EC/EMC showing that LiDFOB is a good alternative salt to use in PC based electrolytes for lithium-ion batteries.

Reactivity of Electrolytes for Lithium Oxygen Batteries

The stability of electrolytes is a significant limitation for cycle life performance in Li-O2 batteries. Since Li2O2 is generated at the cathode surface during cycling, an investigation of the thermal stability of common electrolytes with Li2O2 was conducted. All of the solvents investigated, including ethylene carbonate (EC), propylene carbonate (PC), dialkyl carbonates, dimethoxyethane (DME), tetraethylene glycol dimethyl ether, and acetonitrile, have good thermal stability in the presence of Li2O2. Many salts, including LiBF4, lithium bis(oxalaoto)borate (LiBOB), and lithium Bis(trifluoromethanesulfonyl)imide (LiTFSI), also have good stability in the presence of Li_2O_2. However, $LiPF_6$ reacts rapidly with Li_2O_2 to generate OPF_2OLi and LiF.

Publications

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Students and Post-Doc that worked Project

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