

**Title:** Polymeric nanocomposites for solid electrolytes

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**Time Span:** Two years

**Number of Graduate Students:** 2

The objective of this project is to develop improved polymer nanocomposite solid electrolytes for lithium ion batteries and potentially for lithium metal anode batteries through controlled emergent hierarchical structure. We seek to take advantage of our recent studies of the milling of nanoparticle aggregates with polymers which involves competition between incompatibility and kinetic dispersion. On the nanoscale, local clusters form since kinetic mixing cannot impact the nanoscales. These clusters percolate on the macroscopic scale mitigated by the accumulated strain in the mixing process. We have found that this complex multi-hierarchical structure can impact physical properties such as optical appearance and dynamic mechanical properties. We hope to demonstrate that tuning of this multi-hierarchical structure, composed of primary particles, aggregates, clusters of aggregates and percolated micron scale to macroscopic networks of clusters can lead to improved ion conduction through the ceramic phase and interphase regions of polymer nanocomposite solid electrolytes for lithium ion batteries. A team of experts in polymer processing and structural characterization of dispersion in nanocomposites; experts in simulation of mixing processes for nanocomposites; and scientists with expertise in lithium ion battery fabrication are assembled to address this task. The project couples' facilities at the University of Cincinnati, University of Dayton and the Dayton Research Institute as well as taking advantage of the APS USAXS facility. Expertise in synthesis of flame made nanoparticles at the University of Cincinnati will play an important role in new polymer nanocomposites. If successful the team hopes to open a new paradigm for understanding and development of polymer nanocomposite solid electrolytes in lithium ion batteries with the hope for dramatic improvement in battery performance, lifetime, and safety.

A major problem with future rechargeable lithium metal anode batteries as well as for existing lithium ion batteries lies in the electrolyte. [1-3] Lithium metal batteries are composed of an anode (lithium metal replacing heavier graphite), a cathode (mixed lithium oxide), a porous polymer separator, and a lithium ion electrolyte. Oxidation and reduction of lithium at the cathode and anode lead to the production of current that is offset by lithium ion conduction through the electrolyte. Problems can occur with dendritic growth of lithium crystals across the electrolyte leading to a short in the battery. Rapid overheating can occur under these conditions. Further, lithium metal is pyrophoric and if the battery encapsulation is broken a fire can result. One proposed solution to this problem is to replace the liquid electrolyte with a solid electrolyte such as solid lithium salts which prevent dendrite formation. [4,5] Such a battery can be completely encapsulated and provides a more robust structure in addition to removing the possibility of dendrite formation. However, such oxide solid electrolytes are fragile and subject to cracking which can lead to battery failure and even fire hazards. Ion conductivity is much lower in solid electrolytes compared to polymer gel electrolytes. This means that rapid discharge for acceleration in a car is hindered. A flexible, robust, melt processible material such as a polymer would be ideal as the solid electrolyte but materials such as polyethylene oxide (PEO) or polydivinylfluoride (PVDF or PVF2) have lithium ion conductivities three orders of magnitude lower than lithium salts.

A composite material might provide the best of both worlds if the conduction pathway through a lithium salt/PEO or PVDF matrix can be manipulated through processing, surface treatment, and through production of optimal nanoparticles and nanoaggregates of lithium salt. [3-5] Production of lithium salt is generally done using a ball milling followed by sintering at about 1300°C. This leads to rather coarse, micron-size particles. Composites made with these particles have conductivities about 2 orders lower than that of the pure lithium salt solid electrolyte even at high concentrations. Some have predicted and observed an enhancement in ion conduction for polymer nanocomposites since it is postulated that low polymer crystallinity and special ionic environments near the surface of nano-scale ceramic oxides enhances lithium ion transport. Several mechanisms have been proposed. Both non-ion conducting oxides, such as silica and titania, as well as oxides that are known to conduct lithium ions have been investigated.

We plan to investigate 10 different lithium oxides produced by flame synthesis at the University of Cincinnati. The samples will be milled into two matrix polymers, PEO and PVDF. Samples of variable processing history will be produced in collaboration with Krauss Maffie in Cincinnati.

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