**Interfacial Interactions between Polymers and Particles:**

**Applications in Sensors and All-solid-state Batteries**

Polymer-particle composites are ubiquitous in everyday life. Engineered interactions between these two components facilitate a massive breadth of applications. Herein, we explore in-depth some of the key properties of each constituent and how they affect the structure and properties of bulk composites in two very different systems: (i) magnetic-core/gold-shell nanoparticles (MAuNPs) for surface-enhanced Raman spectroscopy (SERS)-based sensing platforms and (ii) novel argyrodite Li6PS5Cl (LPSCl) sulfide solid electrolyte thin films utilizing poly(isobutylene) (PIB) binder. For the first system, MAuNPs were grafted with methoxy poly(ethylene glycol) thiol (PEG) and/or 4-mercaptobenzoic acid (4-MBA) and examined using a variety of microscopy, spectroscopy, magnetometry, and scattering techniques. The second system focused on sulfide solid-state electrolytes, which possess high room-temperature ionic conductivity. However, slurry casting of the free-standing, sheet-type thin sulfide solid electrolyte (SE) films to enable all-solid-state batteries to deliver high energy and power density remains challenging.

For MAuNPs grafted with both PEG and 4-MBA, the order in which they were grafted impacted not only the graft density of the individual ligands, but also the overall graft density. It was found that the presence of 4-MBA slowed the magnetic mass deposition rate, and it was postulated that the rate disparity originated from differing NP-substrate surface interactions.

A paradigm of solvent and binder selection for solution processing LPSCl solid-state electrolyte particles based on Hansen solubility parameters (HSPs) is introduced. Treatment of the LPSCl in selected solvents results in particle morphological change, but crystallographic structure remains intact. Although solution processing reduced the LPSCl’s ionic conductivity, it promoted interfacial stability by alleviating its reductive decomposition against Li metal.

The HSP theoretical framework was also applied to an anti-perovskite-structured oxide SE, Li2OHBr, and surface energy parameters determined, but on account of Li2OHBr strong dipole moments or hydrogen bonding tendencies, the results require additional stringent validation.

Applying these findings, LPSCl was slurry cast to form free-standing films with low (≤ 5 wt.%) loadings of PIB binder. Nevertheless, increasing polymer binder loading inevitably introduced voids in the thin film SEs, compromising anode/electrolyte interfacial ion transport.

It was demonstrated PIB molecular weight plays a crucial part in determining the properties of the SE thin film separators. Three important trends were observed: (i) increased PIB molecular weight lowered the limit on binder mass loading required to fabricate free-standing films, (ii) increased binder molecular weight resulted in greater grain boundary resistance and decreased critical current density, and (iii) lower molecular weight PIB film surfaces exhibited more even binder distribution than higher molecular weight PIB film surfaces, but the resulting confined PIB chains were less able to provide the elastic recovery required to maintain contact with the active material.

Finally, it was shown that the choice of slurry constituents and relative quantities have a profound effect on SE film quality using LPSCl, Li2OHBr, Li3PS4, and Li3InCl6 SEs.

**Key Words**: SERS, sensors, polymer-grafted nanoparticles, core/shell nanoparticles, solid electrolytes, solid-state batteries, thin films, surface energy, polymer binder