

# HYBRID ORGANIC-INORGANIC NANO-COMPOSITES FOR SOLID-STATE BATTERY ELECTROLYTES

John Kieffer, University of Michigan, USA  
kieffer@umich.edu  
Vazrik Keshishian, University of Michigan, USA  
Cameran Beg, University of Michigan, USA  
Weimin Wang, University of Michigan, USA

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Desired properties of solid electrolytes are high ionic conductivity and transference number, high shear modulus to prevent dendrite growth, chemical compatibility with electrodes, and ease of fabrication into thin films. Especially, elastic stiffness and ionic mobility are opposing attributes in a homogenous material, and a composite approach towards designing novel electrolytes is therefore advisable. We use a two-step sol-gel method to synthesize silica-based hybrid organic-inorganic materials for this application. First, a continuous porous silica structure is created that provides electrochemical stability and mechanical rigidity. This network also contains unreacted epoxy groups. In step 2, single-sided amine-functionalized polyethene glycol (PEG-NH<sub>2</sub>) infiltrates the pores via fluid exchange. As PEG-NH<sub>2</sub> fills the pores, the amine groups react with the epoxy groups and anchor the polymer to the silica network, which provides highly conductive pathways. IR spectroscopy, Raman and Brillouin light scattering, impedance spectroscopy, small angle x-ray scattering

(SAXS), charge-discharge cell testing is performed to identify the structural and chemical origins that underlie the performance of these hybrid electrolytes. A room temperature ionic conductivity in excess of 10<sup>-5</sup> S/cm is reached (Fig. 1).

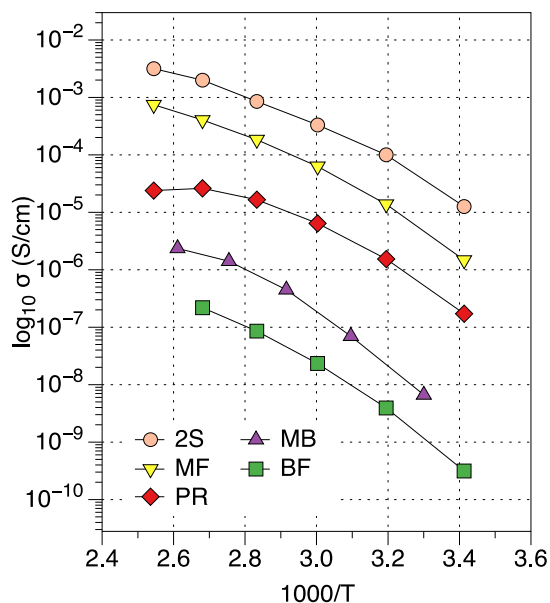


Fig. 1 Conductivity as a function of temperature for: (MB) silica xerogel mechanically blended with PEG, (BF) bi-functional PEG (reactive on both ends) co-polymerized with silica, (PR) bi-functional PEG partially co-polymerized with silica, (MF) mono-functional PEG co-polymerized with silica, and (2S) mono-functional PEG grafted on silica in a two-step process.

The covalent bonding between polymer and silica is essential to enhancing the ionic conductivity without sacrificing mechanical stability. To better understand the reason for this we conducted systematic investigations into the mechanisms of cation transport in amorphous structures, both experimental and computational. We found that, for mixed network former glasses, the adiabatic bulk elastic modulus, measured using Brillouin light scattering (BLS), and the activation energy for the modifier cation conductivity are strictly correlated. Using data from NMR spectroscopy and BLS as input for a reaction equilibrium-based statistical thermodynamic analysis we derived a quantitative account of all possible network building units. The resulting statistical measures for the distribution of cation hopping pathways in these glasses led to the development of an improved transition state theory model for ion conduction in these materials [1]. Our model allows us to assess the spatial extent of this deformation, as well as estimate the relative amounts of configurational and vibrational entropy changes associated with this thermally activated process. Atomistic models of these glasses established using MD simulations based on a reactive force field further substantiate our new kinetic theory, and allow us to derive materials design criteria for materials with simultaneously high ionic conductivity and elastic moduli.

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1 W. Wang, R. Christensen, B. Curtis, S.W. Martin, and J. Kieffer, 'A New Kinetic Model Linking Elastic Properties and Ion Conductivity in Mixed Network Former Glasses,' Phys. Chem. Chem. Phys. 20, 1629 (2018)