

Key Contributions of Atomic-Scale Simulations to Design Solid Polymer Electrolytes

Calculations provide performance properties and atomic-scale understanding for multitudes of polymer formulations and combinations of salts

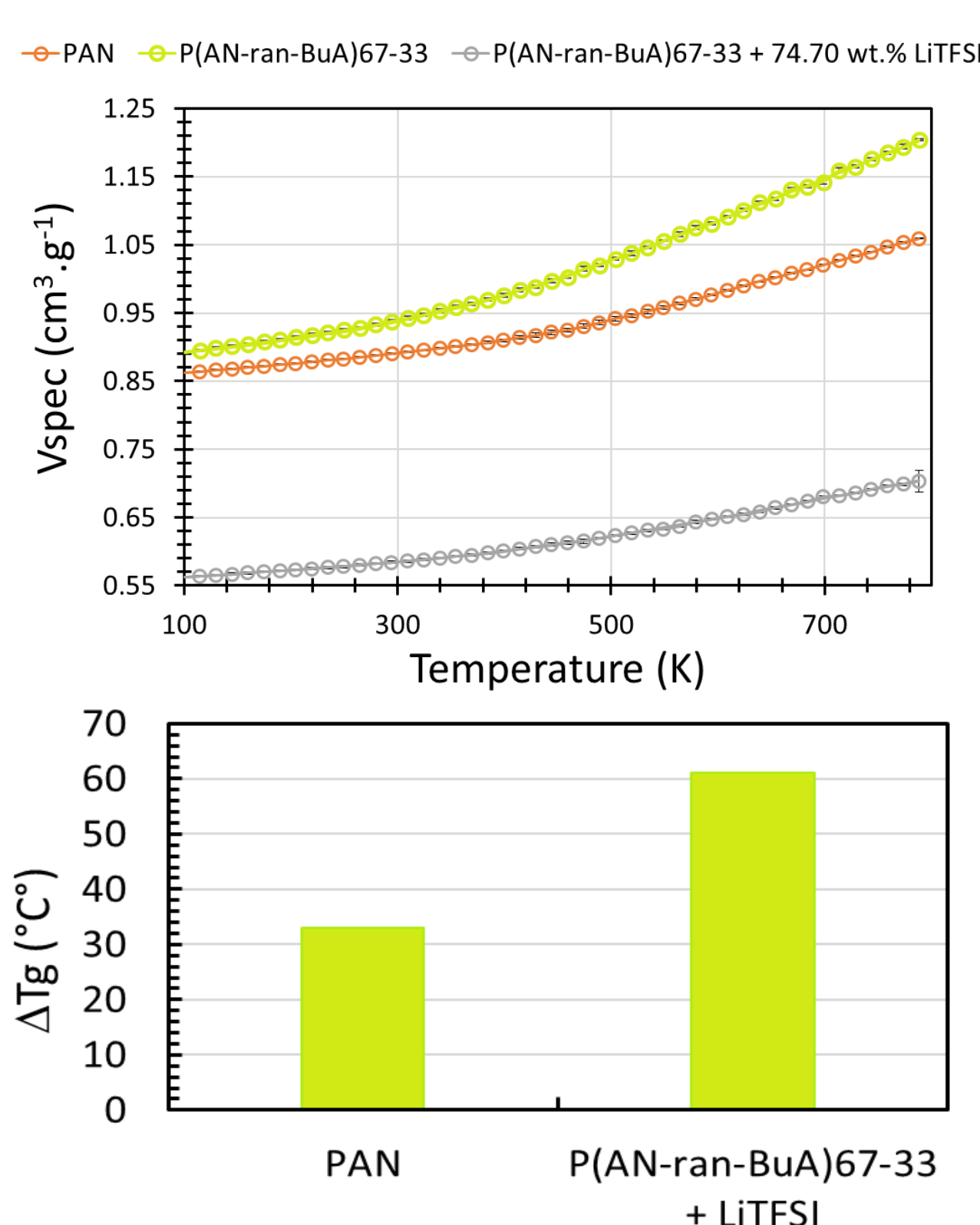
- ▶ Electrochemical stability (ES): Cope with voltages > 5 V
- ▶ Ion conductivity: Desired is $\sigma_{\text{ion}} \geq 10 \text{ mS cm}^{-1}$ at 25°C for fast charging & high power
- ▶ Glass transition temperature (Tg): should be $\leq 25^\circ\text{C}$; depends on polymer formulation and content of Li salt
- ▶ Mechanical properties (MP): Ductility is favored over brittleness

Figure of Merit

Formulation ID	Tg	σ_{ion}	MP	ESR
12_X_W				
13_X_W				
11_Y_Z				
21_Y_Z				
22_Y_W				
11_X_W				



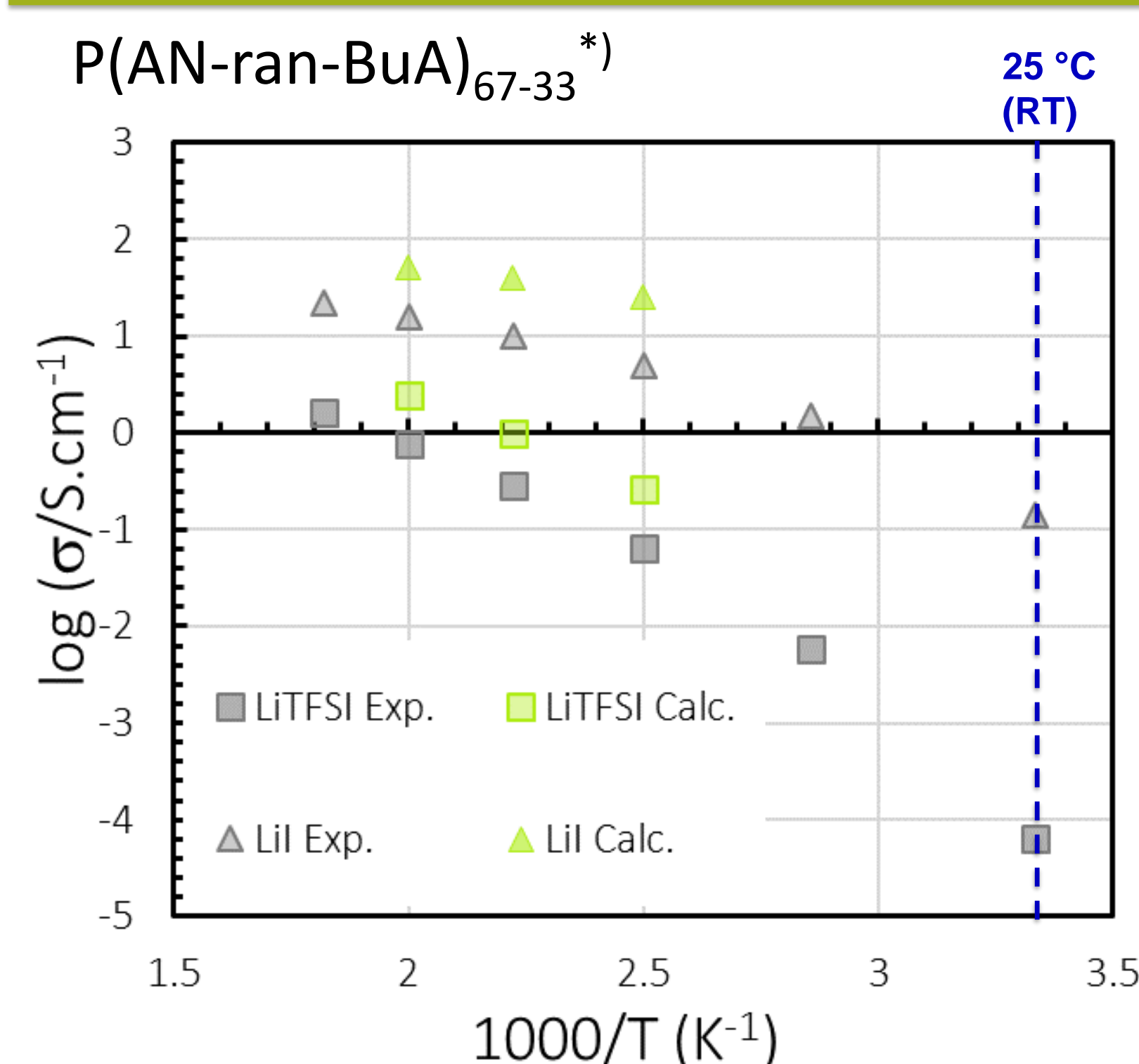
Glass Transition Temperature (Tg)



Polymer-in-Salt electrolytes acrylonitrile(AN)/butyl-acrylate (BuA) - copolymers

- ▶ Effect of LiTFSI (charge carrier salt)
- ▶ Evaluation of Tg by atomistic dilatometry
- ▶ The variation of Tg calculated between PAN and P(AN-ran-BuA)₆₇₋₃₃ agrees with the experimental value of 30 K
- ▶ Compared to the pure copolymer
 - Tg **increases** with increasing LiTFSI content

Ion Conductivity (σ_{ion})



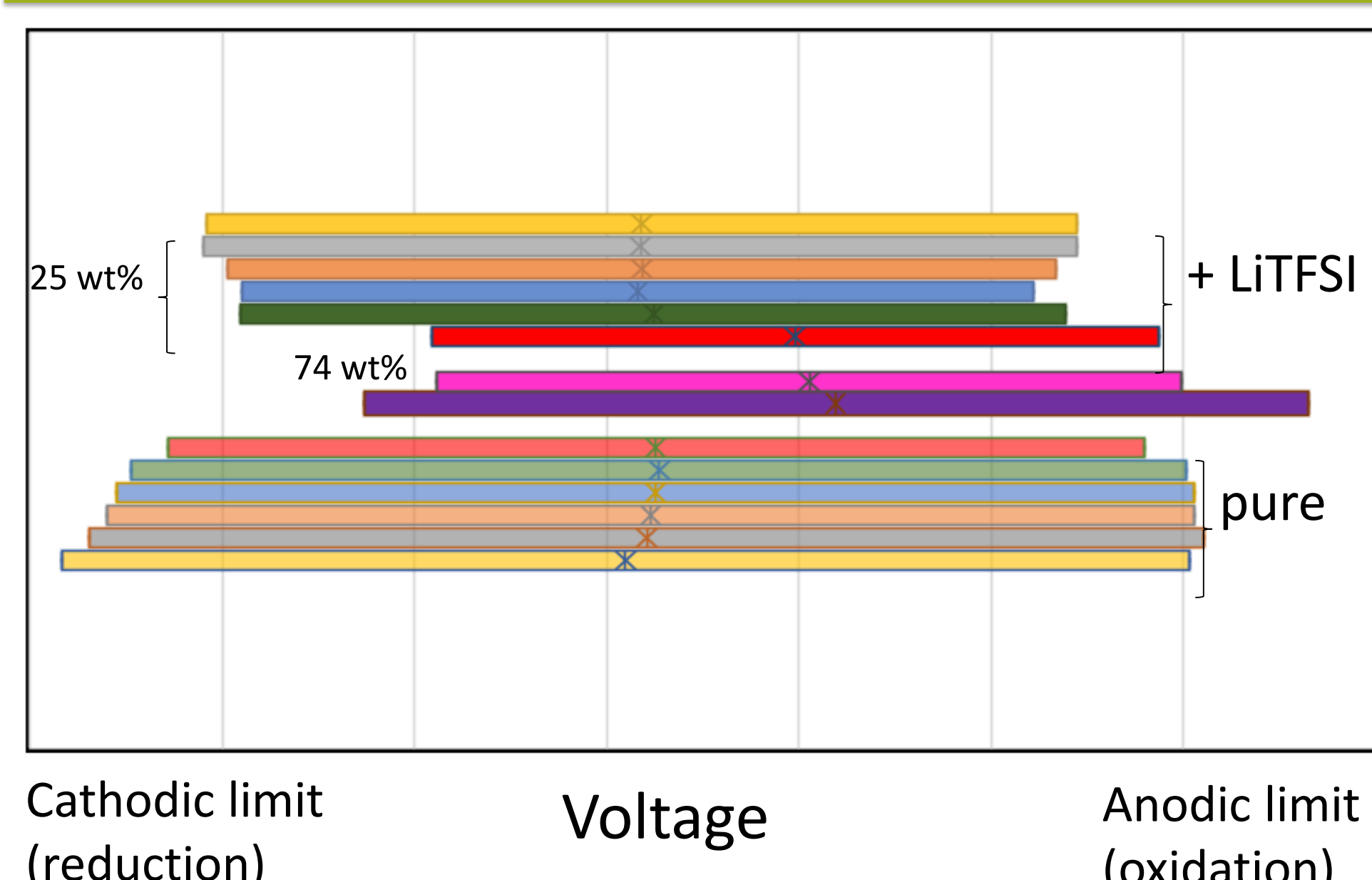
Polymer-in-Salt Electrolytes acrylonitrile(AN)/butyl-acrylate (BuA) -copolymers

- ▶ Effect of **charge carrier salts** LiI and LiTFSI, respectively
- ▶ Semi-quantitative agreement of calculations with measurements
- ▶ RT $\sigma_{\text{ion}} \approx 0.1 \text{ S cm}^{-1}$ with LiI due to salt domains (phase separation) compared to homogeneous morphology and RT $\sigma_{\text{ion}} \approx 0.1 \text{ mS cm}^{-1}$ with LiTFSI

Exp. Z. Florjanczyk et al. Polymer-in-Salt electrolyte based on acrylonitrile/Butyl Acrylate copolymers and lithium salts, J. Phys. Chem. B 2004, 108, 14907-14914

*P(AN-ran-BuA)₆₇₋₃₃: Acrylonitrile/Butyl Acrylate Copolymers with 67 mol% of Acrylonitrile

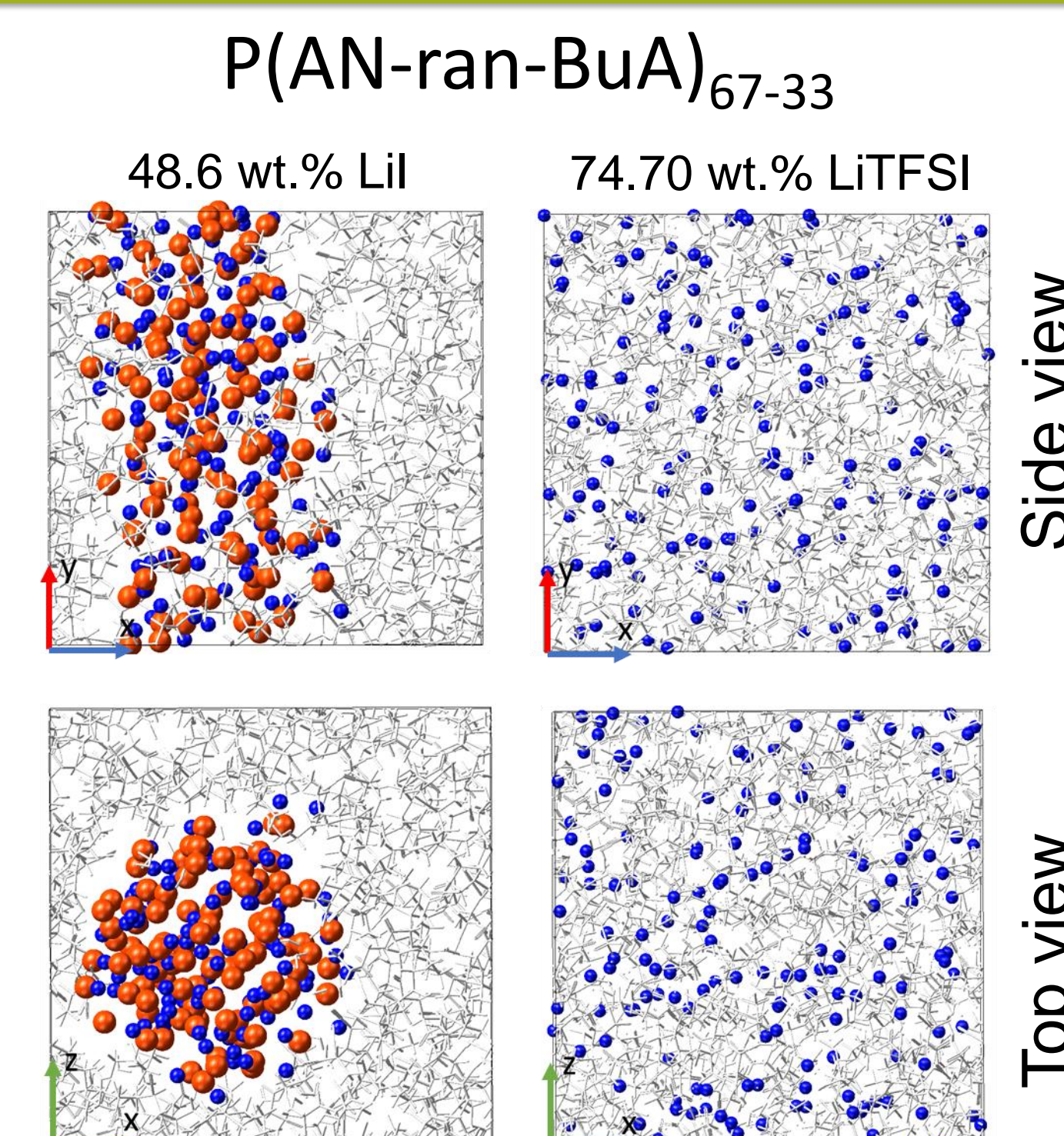
Electrochemical Stability (ES)



- Glutaronitrile
- Adiponitrile
- Pimelonitrile
- Suberonitrile
- Sebaconitrile
- P(AN-ran-BuA)₆₇₋₃₃
- LiTFSI crystal
- LiTFSI glass

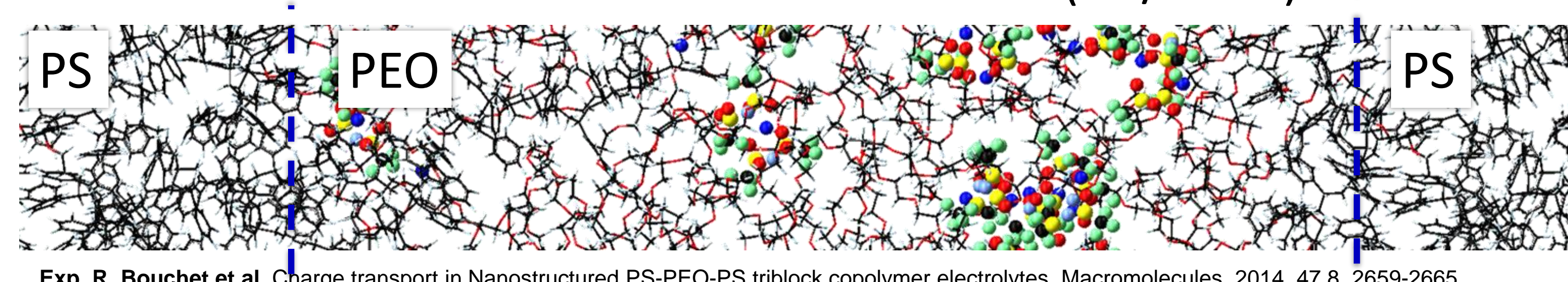
- ▶ ES range of pure acrylonitrile/butyl-acrylate copolymer is narrower compared to pure dinitrile solvents
- ▶ LiTFSI salt considerably reduces the ES range of the polymer
- ▶ With 74 wt% LiTFSI, the ES range of polymer-in-salt electrolytes is very similar to the ES range of pure, amorphous LiTFSI

Electrolyte Morphology



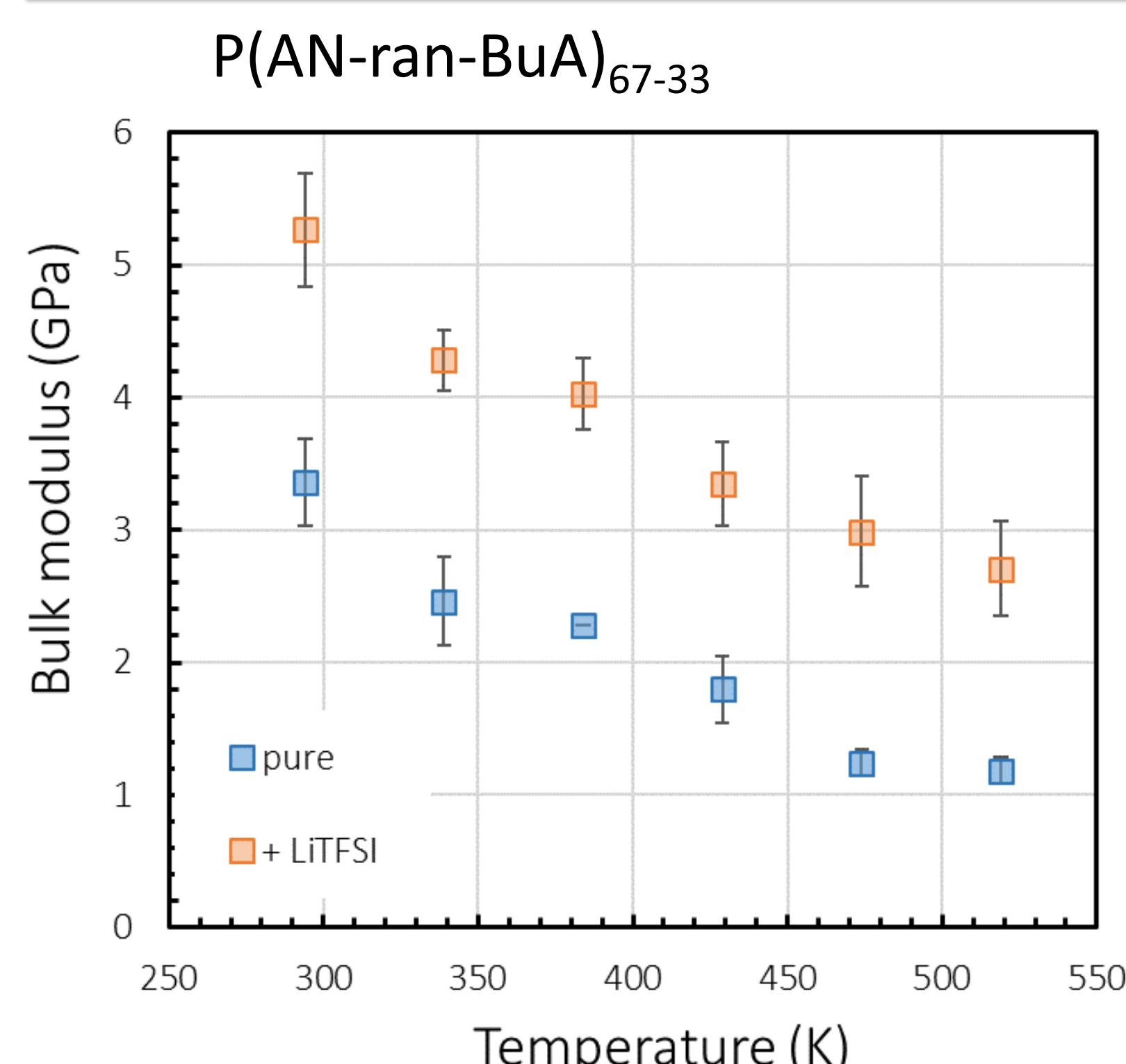
- ▶ Simulations predict charge carrier salt dependent morphology for P(AN-ran-BuA)₆₇₋₃₃
 - Heterogeneous morphology with LiI; the latter forms nano-pipes and nano-lamellas that are enclosed by polymer domains
 - Homogeneous distribution of LiTFSI in a P(AN-ran-BuA)₆₇₋₃₃ matrix
- ▶ **Polystyrol (PS) - polyethylene (PEO) - PS triblock polymer**
 - Both simulations and measurements agree on partially dissociated LiTFSI salt, located in the PEO blocks

Nanostructured PS-PEO-PS Triblock + LiTFSI (EO/Li=20)



Exp. R. Bouchet et al. Charge transport in Nanostructured PS-PEO-PS triblock copolymer electrolytes, Macromolecules, 2014, 47,8, 2659-2665

Elasticity & Mechanical Properties



Polymer-in-Salt electrolytes acrylonitrile(AN)/butyl-acrylate (BuA) -copolymers

- ▶ **Effect of Li salt**

At all temperatures, the polymer-in-salt electrolyte is more brittle than the pure polymer
- ▶ **Effect of temperature**

Softening of polymer-in-salt electrolyte and pure polymer with increasing temperature

Design Approach

