Interfacial and structural characterization of polymer - electrolyte systems using classical Molecular Dynamics

M.A. Salvador, Elena Degoli*, Alice Ruini, Rita Magri

Dipartimento di Scienze Fisiche, Informatiche e Matematiche, Università di Modena e Reggio Emilia, MO, Italy

*Dipartimento di Scienze e Metodi dell'Ingegneria, Università di Modena e Reggio Emilia, RE, Italy

e-mail: msalvado@unimore.it

ABSTRACT SUBMISSION

In this work we studied the interactions of a self-healing polymer, a combination of boronated polyaniline (B@Pani) monomers and polyvinyl acetate (PVA) trimers, and an electrolyte solution formed by a pyrrolidinium-based ionic liquid, with composition $(Pyr16)_{0.5}(Li)_{0.5}$-TFSI, using molecular dynamics calculations.

INTRODUCTION

The combination of ionic liquids and polymers are considered to be a promising alternative to improve the performance of Lithium-ion batteries, due to the association of chemical-physical properties such as the polymer mechanical stability, and the ionic liquid conductivity. However, limitations are related to the poor conductivity at room temperature, which depends upon the ion/salt concentration and polymers structure. To understand the properties of these mixtures, and, in particular, the polymer-electrolyte solution interface is of the outmost importance.

MODEL

The Boronated Pani (B@Pani) model was built from the leucoemeraldine base form of Pani monomer functionalized with -B(OH)$_2$. For the PVA model, we built a chain with 3 monomers, so that the size of B@Pani and PVA are similar. Neat ionic liquid (Pyr16-TFSI), ionic liquid plus Li electrolyte solutions (Pyr16-Li-TFSI), with half of Pyr16 replaced by lithium in a 1:1 proportion, were studied in previous works [3]. Our calculations were performed using the Gromacs software [1], with OPLS-AA force-field parameters for carbon, hydrogen and nitrogen, and the parameters for boron and oxygen of the boronated moiety were taken from the literature [2]. All results presented here were produced at 300 K temperature and 1 bar pressure.

SAMPLE SECTION

Once we had the electrolyte solution and polymer systems separately characterized, we modeled the mixture between electrolyte solutions and polymer, by (i) considering as solute either the polymers or the electrolyte, and (b) by building polymer/electrolyte well-defined interfaces and allowing the systems to relax. Results showed that when we have Pyr16-TFSI as solvent and B@Pani as solute, the Pyr16 cations are closer to the B@Pani monomers than the anions. We also obtained the density and pair correlation functions of the polymer phase and the electrolyte solutions. In the interface studies, we can see formation of a mixed phase 1 nm thick.

CONCLUSION

This work allowed us to understand the interactions between the constituents of the electrolyte solution (Pyr16, TFSI, Li) and the self-healing polymer (B@Pani-PVA), both in mixture and in interface models.

REFERENCES

[1] van der Spoel, et al., GROMACS: Fast, Flexible and Free. J. Comp. Chem., 26, 2005, 1701–1719

[2] Kurt, B., et al., Development of AMBER parameters for molecular dynamics simulations of boron compounds containing aromatic structure. Chemical Physics Letters 775 (2021) 138656

[3] Salvador et al. Structural and dynamic characterization of Li–ionic liquid electrolyte solutions application in Li-ion batteries: a Molecular Dynamics Approach, to be submitted.
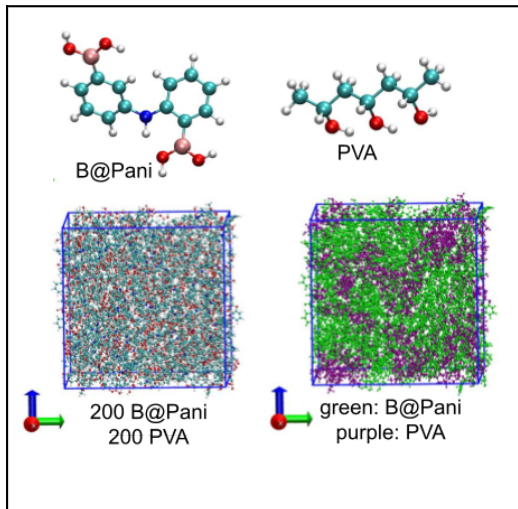
Figure 1: top: B@Pani and PVA models; bottom: box with 200 B@Pani and 200 PVA, ball-and-stick atomic representation and labelling by molecule.
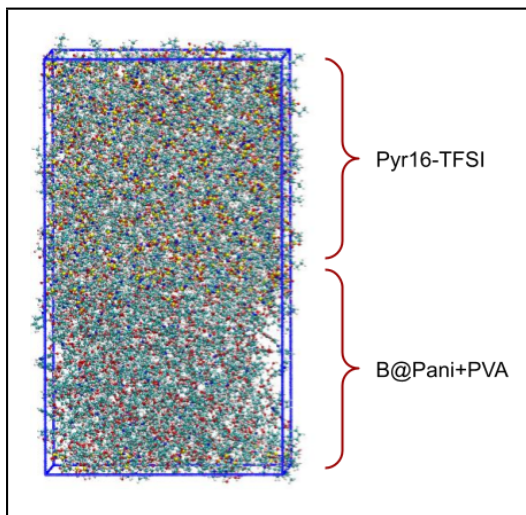

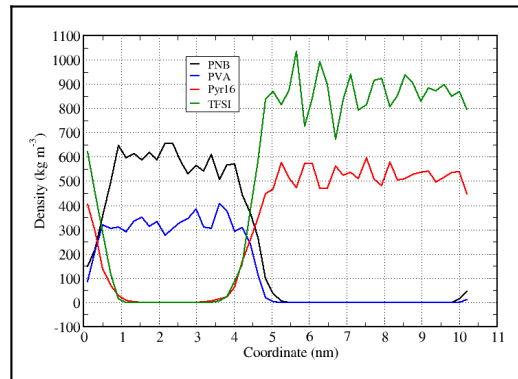Figure 2: model of the polymer - electrolyte solution interface.

Figure 3: Number density of the system represented in Figure 2. X-axis in the graph represents the z direction in the box.