Università Degli Studi di Modena e Reggio Emilia

Dipartimento di Scienze Fisiche, Informatiche e Matematiche (FIM)

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

Michele A. Salvador*, Rita Maji, Elena Degoli, Alice Ruini, Rita Magri

(*michelesalvador@gmail.com)

Outline:

1. Introduction
    a. BAT4EVER project
2. Objectives
3. Methodology
4. Preliminary Results
5. Summary and Perspectives

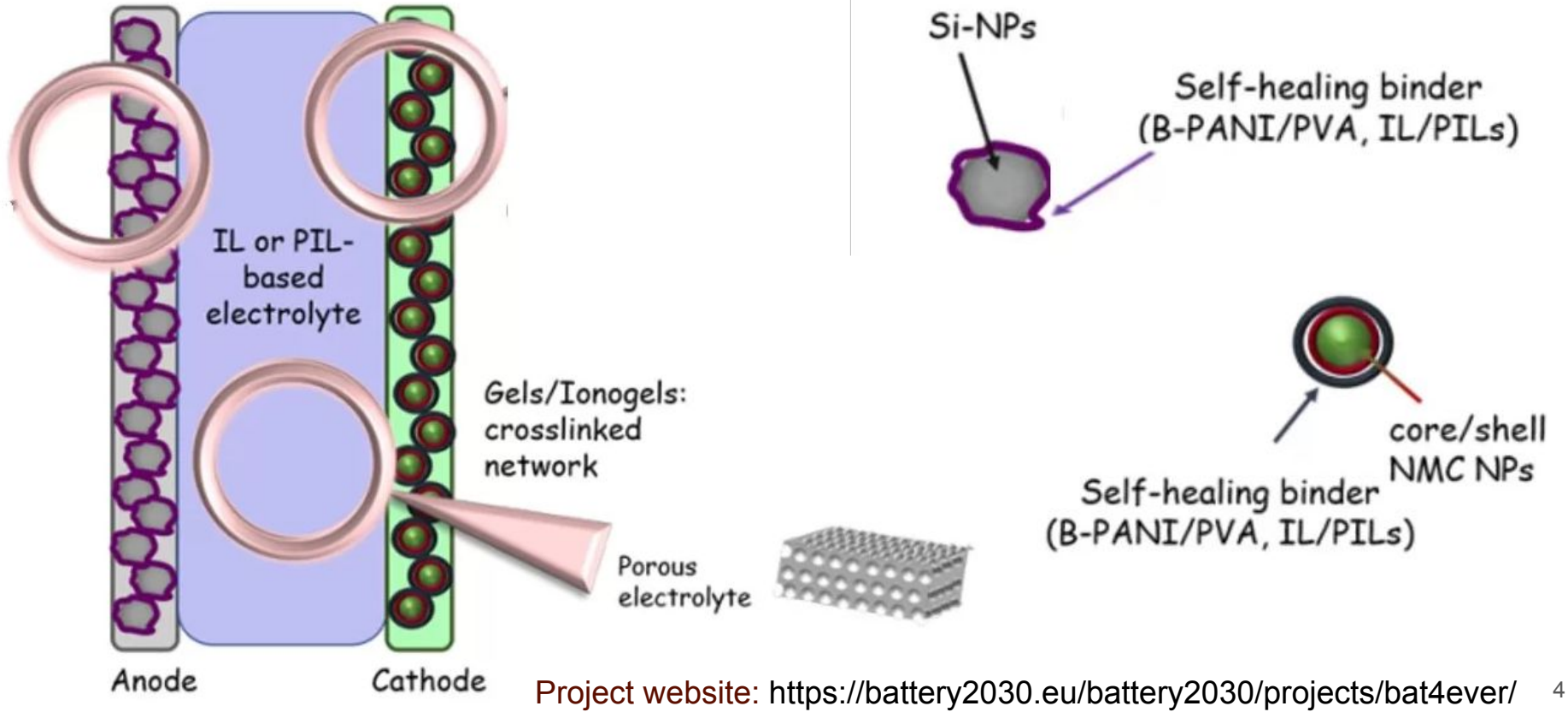
1. Introduction:

BATTERY 2030+

- ➔ To tailor the materials of LIB's;
- ➔ Modifying their state-of-art ancestors;
- ➔ To induce self-healing **functionalities**;
- ➔ To achieve innovative and reliable **Li-ion batteries;**
  - higher **performance**;
  - extended lifetime;
  - safety**.**

Project website: https://battery2030.eu/battery2030/projects/bat4ever/

1. Introduction:



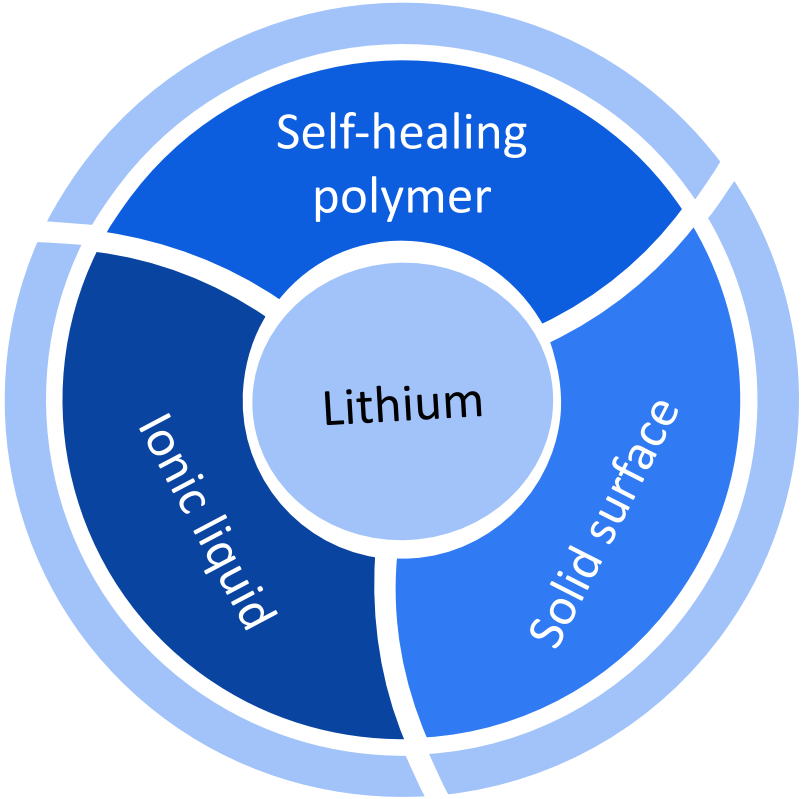
Project website: https://battery2030.eu/battery2030/projects/bat4ever/

2. Objectives:

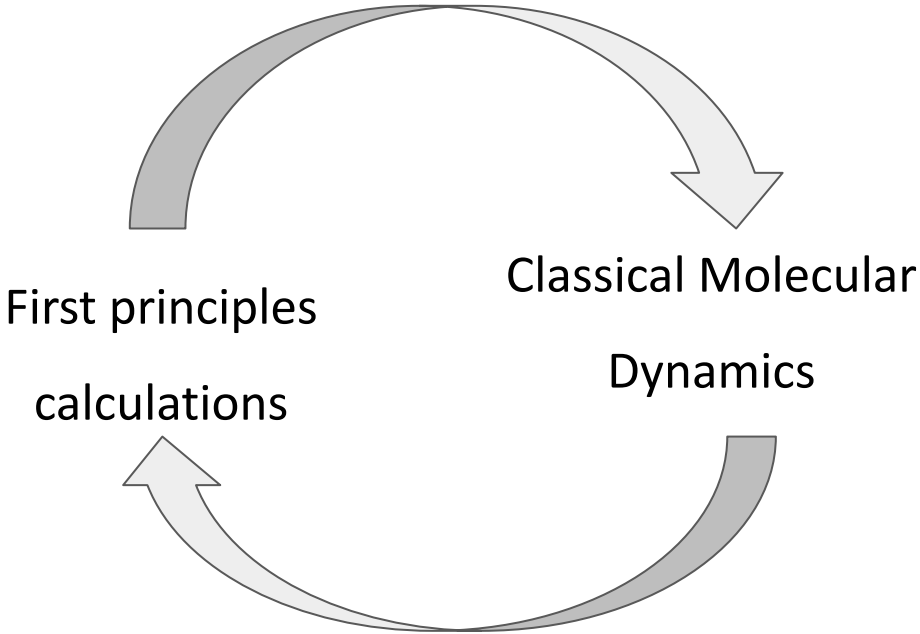
➔ To model the different components of Li-ion batteries and the interfaces:

- electrolyte solution: lithium ions and ionic liquids;
- self-healing polymer;
- electrolyte solution - polymer interface;
- polymer - electrode interface ;

3. Methodology:



Molecular Modeling techniques



4. Results

4.1 Classical Molecular Dynamics: Electrolyte solution: ionic liquid + lithium:

Pyrrolidinium-based ionic liquids; *(1,N-alkyl-pyrrolidinium, N=2 … 6)*

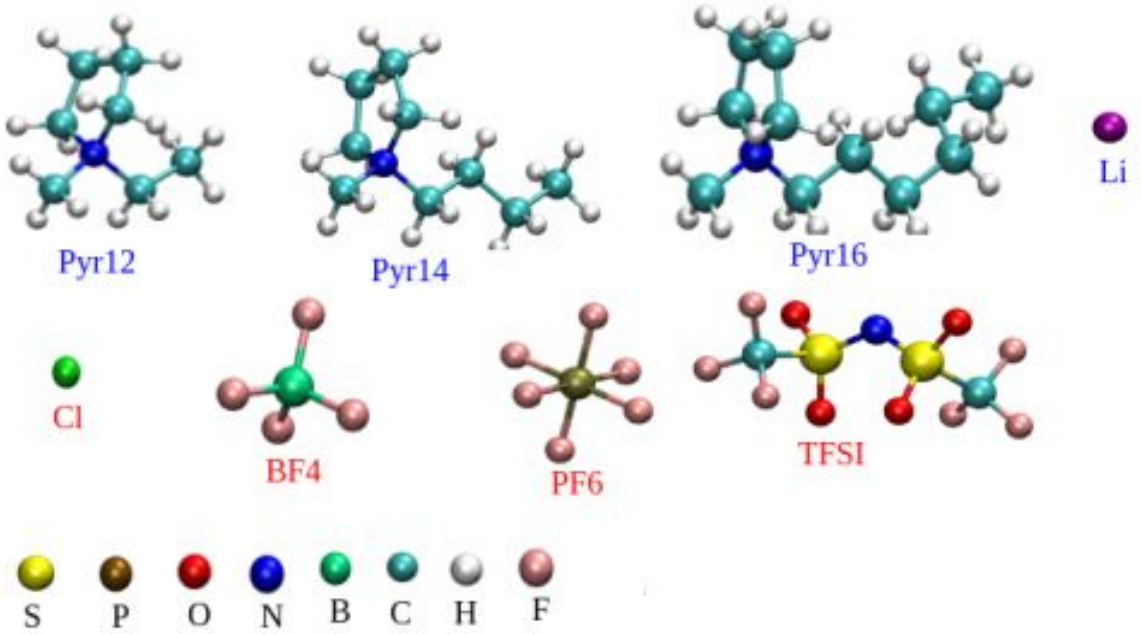
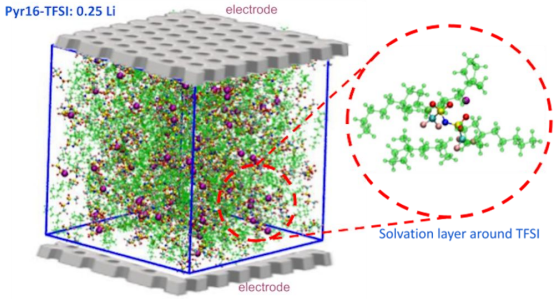


Figure 1. Top row: three of the pyrrolidinium cations (Pyr12, Pyr14, and Pyr16) and the Li-ion; bottom row: anions Cl, BF4, PF6, and TFSI.

4. Results
4.1 Classical Molecular Dynamics:



batteries

MDPI

Article

Structural and Dynamic Characterization of Li–Ionic Liquid Electrolyte Solutions for Application in Li-Ion Batteries: A Molecular Dynamics Approach

Michele A. Salvador [1,*], Rita Maji [2], Francesco Rossella [1,3], Elena Degoli [3,4,5], Alice Ruini [1,3,5] and Rita Magri [1,3,5,*]

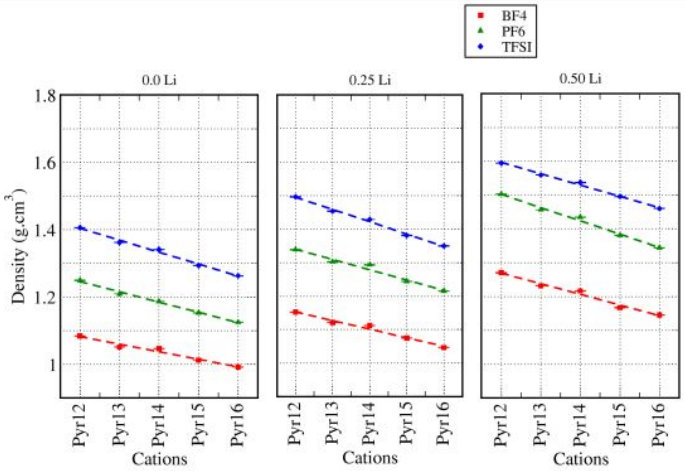


Figure 7. Densities for all systems with different amounts of lithium.

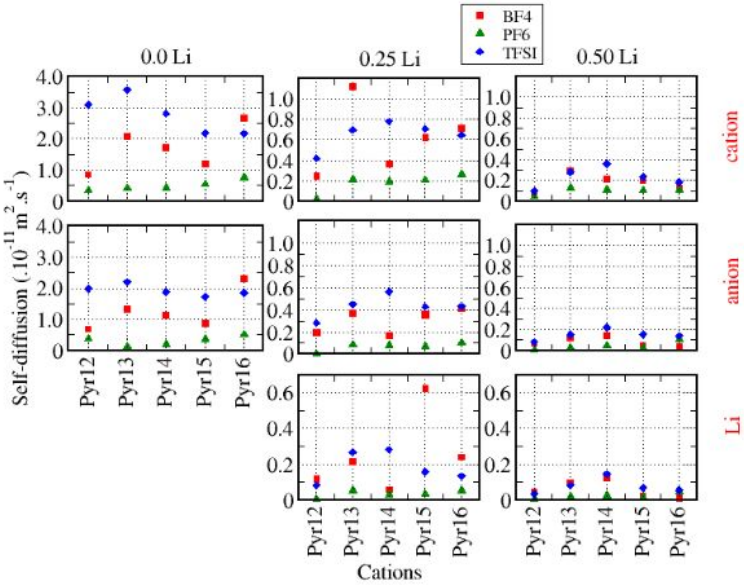


Figure 13. Self–diffusion of all species in the systems considered.

Salvador *et al.*, Batteries 2023, 9, 234.

4. Results
4.2. DFT Silicon surface + polymers:

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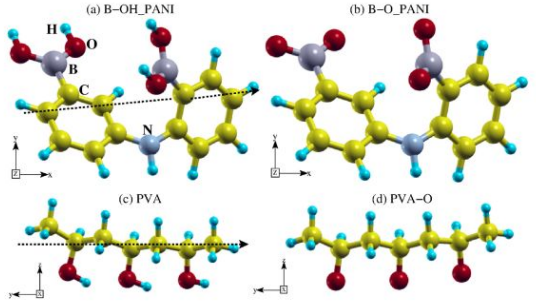


Fig. 1. Molecular structure of the monomers used in this study: (a) B–OH_PANI, (b) B–O_PANI (H removed from $-BO_2H_2$ group), (c) PVA, (d) PVA-O (H removed from –OH group). The dotted arrow represents the molecular axis. B–OH_PANI, boronic acid-doped polyaniline; PVA, polyvinyl alcohol.

A first-principles study of self-healing binders for next-generation Si-based lithium-ion batteries

R. Maji [a, *], M.A. Salvador [b], A. Ruini [b, d, e], R. Magri [b, d, e], E. Degoli [c, d, e]

Table 1
Adsorption energy (eV) of PVA and B–OH_PANI on the Si (110) and Si (111) slabs. The values are reported only for the lowest energy structures.

X	Si(110) (eV)	Si(111) (eV)
One PVA	−1.587	−5.073
Two PVA	−3.160	−6.429
One B–OH_PANI	−1.554	−5.849
Two B–OH_PANI	−2.468	−7.241
One PVA + One B–OH_PANI	−3.478	−7.523

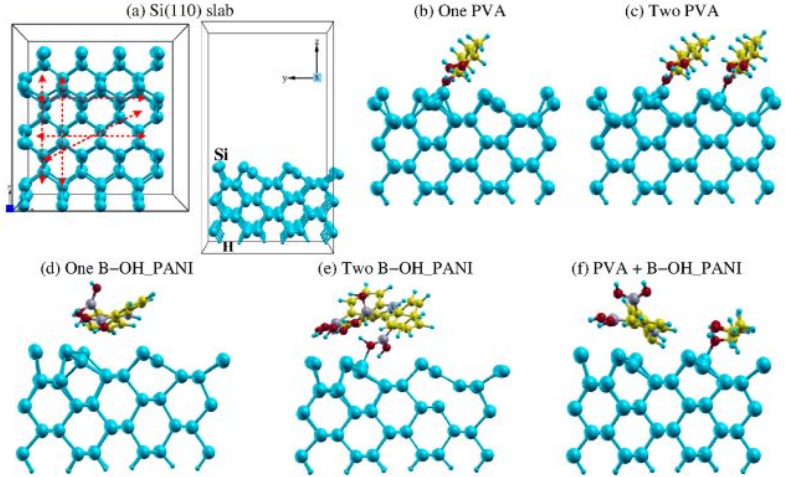
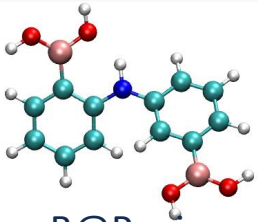


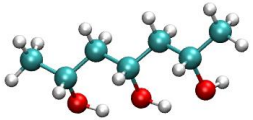
Fig. 2. Si (110) slab (a) optimized surface with x-y, y-z planar view, and along with binders: (b) one PVA, (c) two PVA, (d) one B–OH_PANI, (e) two B–OH_PANI, (f) one PVA and B–OH_PANI together. For all the systems, final optimized structures are presented. Red arrows in (a) schematically represent different initial positions of the binder.

Maji *et al.*, Materials Today Chemistry 29 (2023) 101474

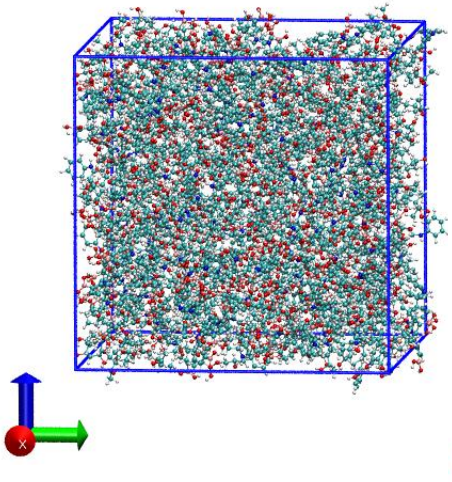
4. Results
4.3 Classical Molecular Dynamics: electrolyte solution + polymer



B@Pani

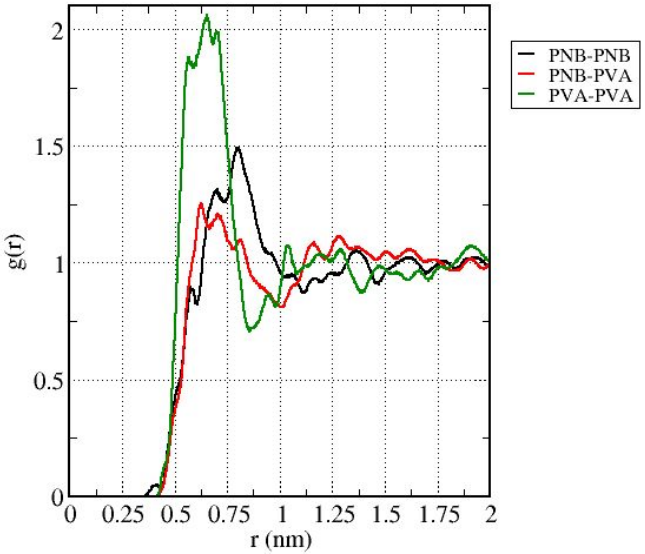


PVA



green: B@Pani
purple: PVA

200 B@Pani + 200 PVA

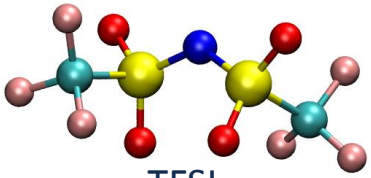


- formation of regions with more B@Pani and more PVA;
- *g(r)* shows PVA-PVA close to each other then the other pairs.

4. Results
4.3 Classical Molecular Dynamics: electrolyte solution + polymer

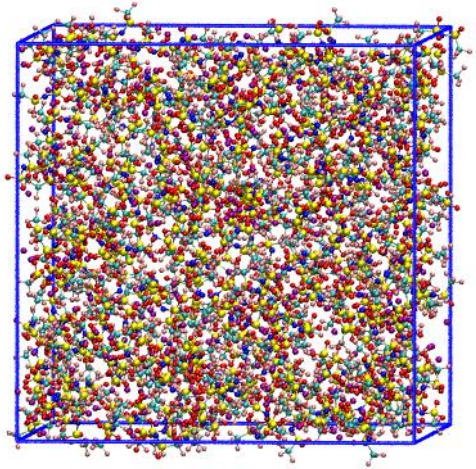
Li

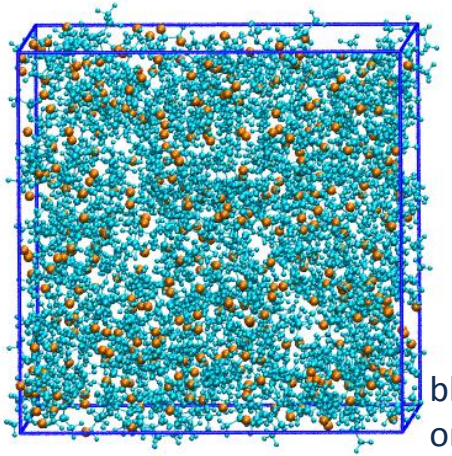
lithium



TFSI

(*bis(trifluoromethylsufonyl)imide*)

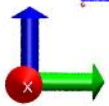


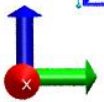


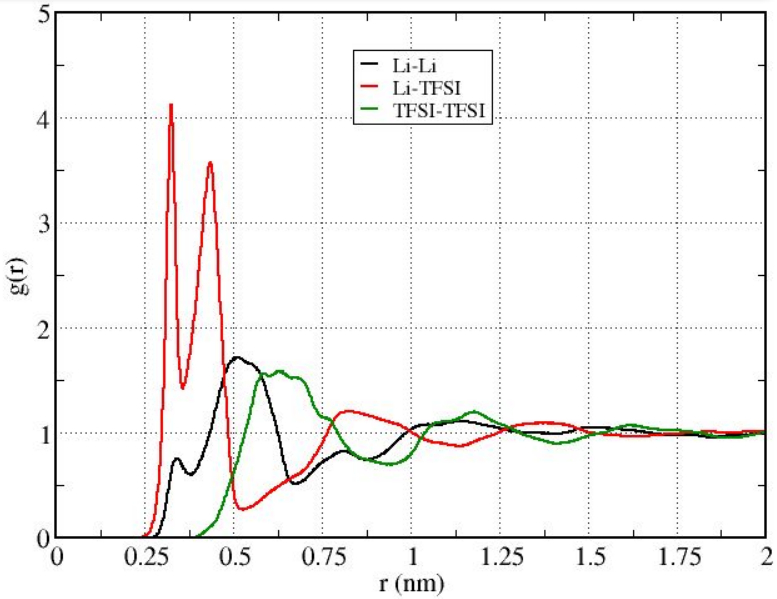
blue: TFSI

orange: Li

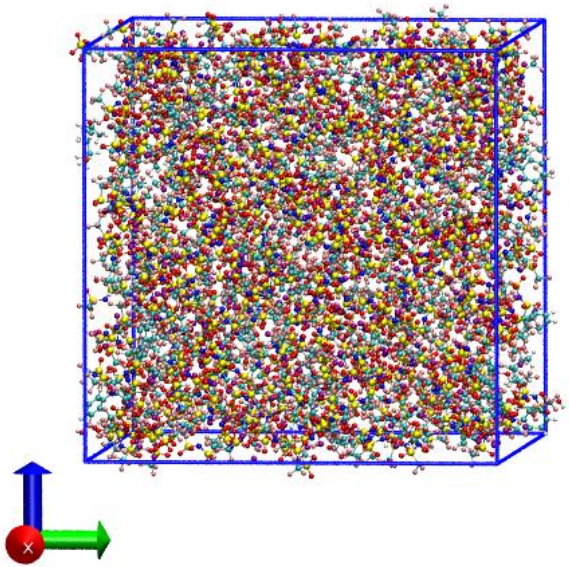
500 Li + 500 TSFI



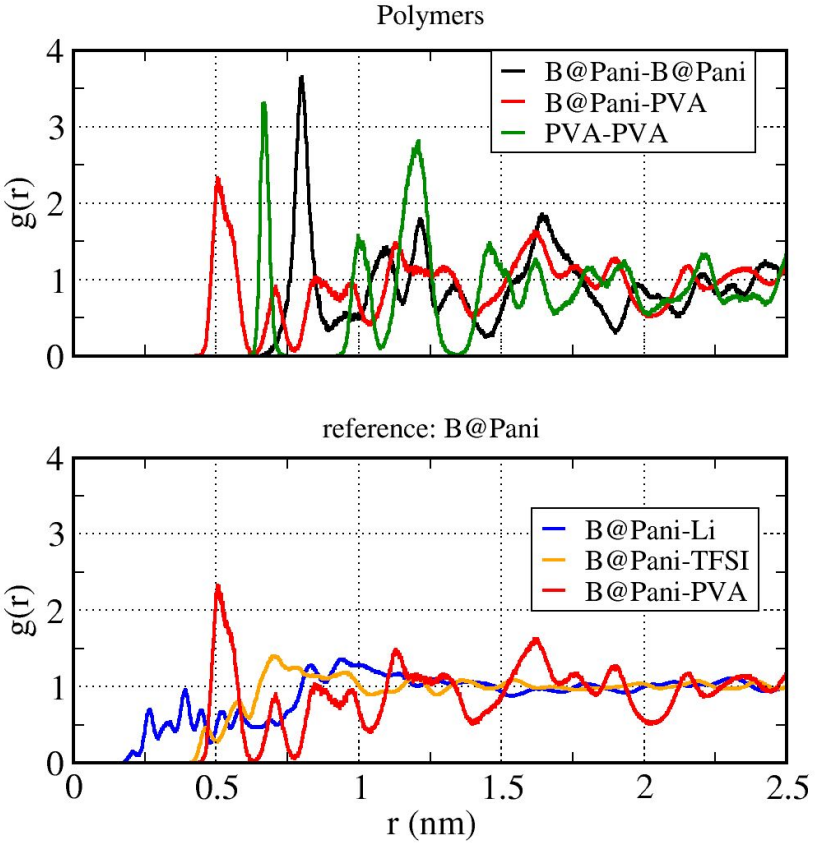




4. Results
4.3 Classical Molecular Dynamics: electrolyte solution + polymer



400 Li + 400 TSFI + 20 B@Pani + 20 PVA



5. Summary and Perspectives

- ➔ The combination of different molecular modeling tools allows us to understand the role of the components of Li-ion batteries and other complex systems;
- ➔ Classical MD calculations were used to systematically study electrolyte solutions composed by the combinations of different anions with cations of various chain sizes. We also considered different amounts of lithium;
- ➔ First principles calculations were used to locally understand the interactions between the polymers and the electrode surface;
- ➔ Classical MD calculations were also used to model the polymer and to study the polymer - electrolyte interfaces.

Next step: to build a model that includes the electrode, the electrolyte solution and the polymer.

Acknowledgements

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UNIMORE