Improving Batteries Using Nothing but a Laptop

Molecular dynamics (MD) simulations of mikto-arm stars in polyethylene oxide (PEO) – a promising gel/solid polymer electrolyte (GPE/SPE) for Li-S and Li ion batteries.

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Abstract

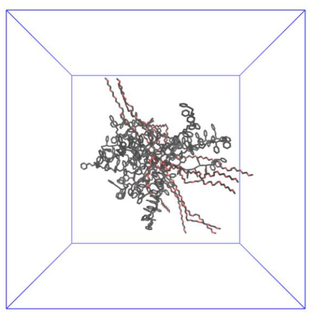
The goal of this project was to employ MD to create a representative model of a real **polymer system** and assess it as **solid electrolyte for Li-S and Li ion batteries**. MD is based on classical physics. Atoms are treated as balls connected with springs. The computer estimates the repulsive and attractive **forces** acting on the atoms, from this **accelerations** are computed, which leads to the atoms' **displacement**. This process is repeated at regular time intervals, often **every 1 fs**. The result is an animation showing how molecules behave in a particular environment. In this study, MD simulations of a range of **mikto-arm stars in PEO** were carried out. More importantly, the materials' properties – **Li^+ diffusion coefficient (D), adiabatic bulk modulus (K), and viscosity (η)** – were calculated.

Motivation

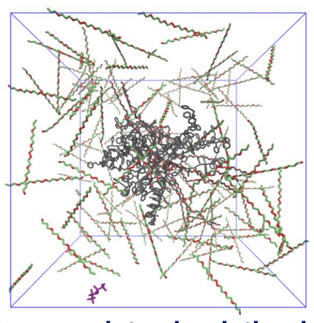
Li-S (lithium-sulfur) batteries have a theoretical gravimetric energy density of **2,567 Wh kg^{-1}** compared with **387 Wh kg^{-1}** for lithium ion batteries (LIBs).[1] The theoretical volumetric energies are **2,199 Wh L^{-1}** and **1,015 Wh L^{-1}** respectively.[1] Li-S batteries could be smaller and lighter while delivering more energy. Moreover, the price of Li-S cells in the future is estimated to fall below **150 USD per kW h^{-1}**, while the price of current LIBs is **600 USD per kW h^{-1}**.[1] Li-S batteries could pave the way to a sustainable future. However, before this happens, some hurdles need to be overcome. **The Shuttle Effect:** Upon reduction of sulfur at the cathode, the formed **polysulfides (PSs) – Li_2S_8, Li_2S_6, Li_2S_4 and Li_2S_2** – migrate to the Li anode through the organic electrolyte solvent, leading to a loss of efficiency.[2] **Safety:** Li metal is extremely reactive, combining it with flammable liquid electrolyte raises the risks of accidents.[3] A proper GPE or SPE (with high diffusivity of Li^+ ions) can solve both issues – stop the polysulfide migration and decrease the likelihood of accidents.

Methods

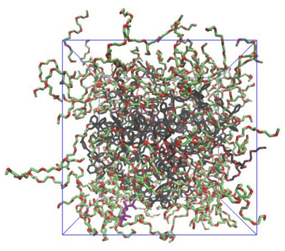
- The molecule models were constructed in **Avogadro** and saved in pdb format.[5]
- The files were converted to a **GROMACS**-compatible format. **GROMACS** is a package for performing MD simulations used in this study.[6]
- Each simulation box contained: **a star polymer molecule** (36% wt.), **10-monomer-unit-long PEO** (which was chosen based on parametric MD simulations of PEO chains of different lengths assessing their viscosities and Li^+ ion diffusivities), and a molecule of **lithium salt** – lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).
- The topology – a file describing atoms, bonds, angles, and dihedral angles in a molecule – was generated using parameters from the **TRAPPE-UA** force field (ff), supplemented with **OPLS-AA** ff parameters.[7,8]
- Each system was equilibrated, compressed to a normal density under 1 bar pressure, re-equilibrated, subjected to thermal annealing using Langevin dynamics, and underwent a short pre-production run under the NPT ensemble.
- Finally, the results – **D**, **K**, **η** – were obtained from **10 ns** simulations under the NPT or NVT ensembles.
- The simulations were visualized with **VMD** software.[9]



The 32/10 star in a box.



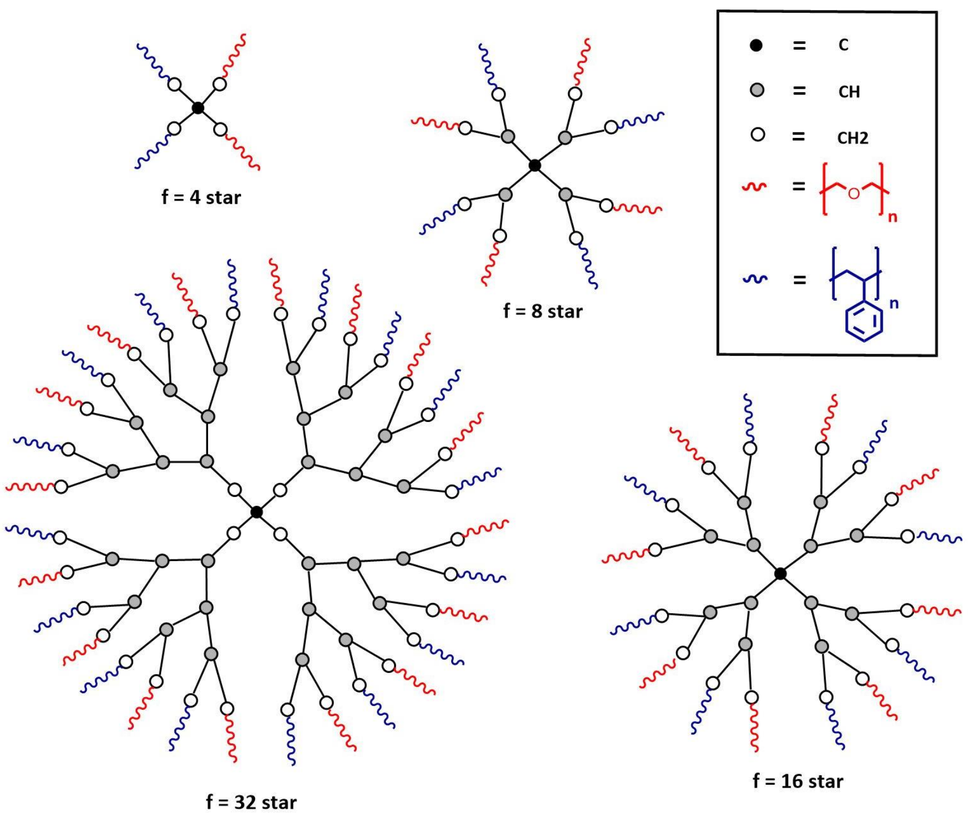
The complete simulation box



The box after compression and equilibration.

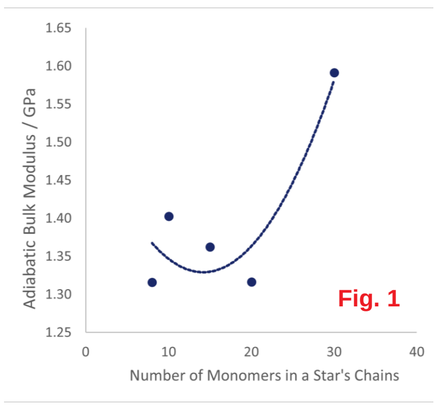
The Materials

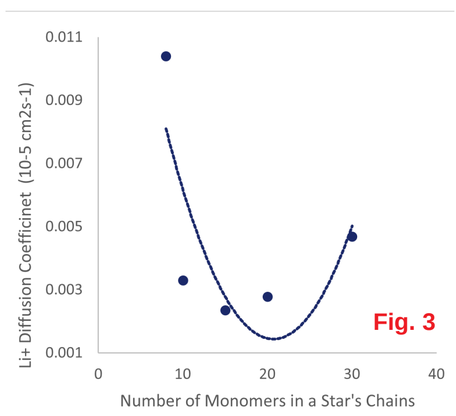
Mikto-arm stars are a class of copolymers with an unusual shape. They consist of a core with **f polymer chains** branching away from it, each chain is composed of **n monomer units**; they are often described with an **f/n label**. The stars in this study consist of **polystyrene (PS) and PEO chains** attached to a carbon core in an alternating fashion. When submerged in viscous PEO, the two polymers form two distinct phases. The PS chains clump together and give the material **rigidity**, while the PEO chains interact with the continuous PEO phase forming a mesh with **good ionic conductivity**; the result is a material which could be employed as a GPE.[4] This study explored the properties of stars with 4 branches of varied lengths – **4/8, 4/10, 4/15, 4/20, and 4/30 stars**; and of stars with 10-monomer-unit-long arms but with varied number of branches – **4/10, 8/10, 16/10, 32/10 stars**.

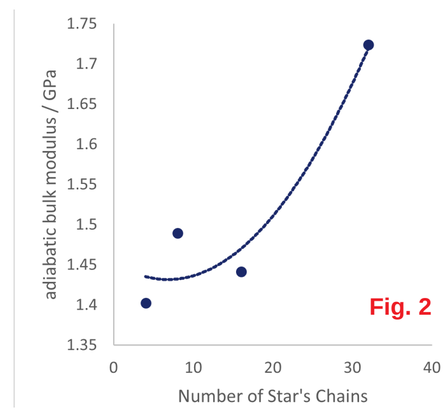


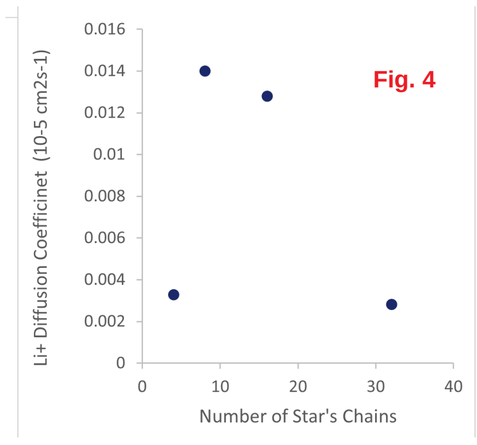
Conclusions

The bulk modulus describes how materials behave when compressed.[10] **K** of rubber and of polymer melts is of the order of 1 GPa.[4] However, many liquids have a similar value of K of around 1 GPa; for methyl alcohol K = 0.97 GPa, for benzene K = 1.10 GPa. The studied systems had a value of K in the range of 1 to 2 GPa. The values are consistent with the materials being gel-like. Additionally, the figures below show that **K** increases with increasing star's chain length (Fig. 1) and with increasing star's number of chains (Fig. 2). **The lithium diffusion coefficient**. **D** is relatively high for all the systems. However, its dependence on the stars' structures is less clear (Fig. 3 & 4). **The shear viscosity** values for the best systems (with the greatest Li^+ ion diffusivity) indicate gel-like state.









Impact / Next steps

- From the calculated Li^+ ion diffusivity values for the best mikto-arm star / PEO systems, the thickness of the GPE or SPE layer can be predicted to realise Li^+ transport at a reasonable rate.
- The next step is for PhD researcher Mr Mathew Matt to synthesise these mikto-arm star composite SPEs and try them experimentally.

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Intern bio

Szymon Kosc is from Poland, he moved to the UK in 2018 to pursue a degree in chemistry. He is a fifth-year MChem student at the University of Edinburgh. Szymon's interests include molecular modelling and organic synthesis.

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