Bandgap engineering of polymer electrolytes: A simulations based study

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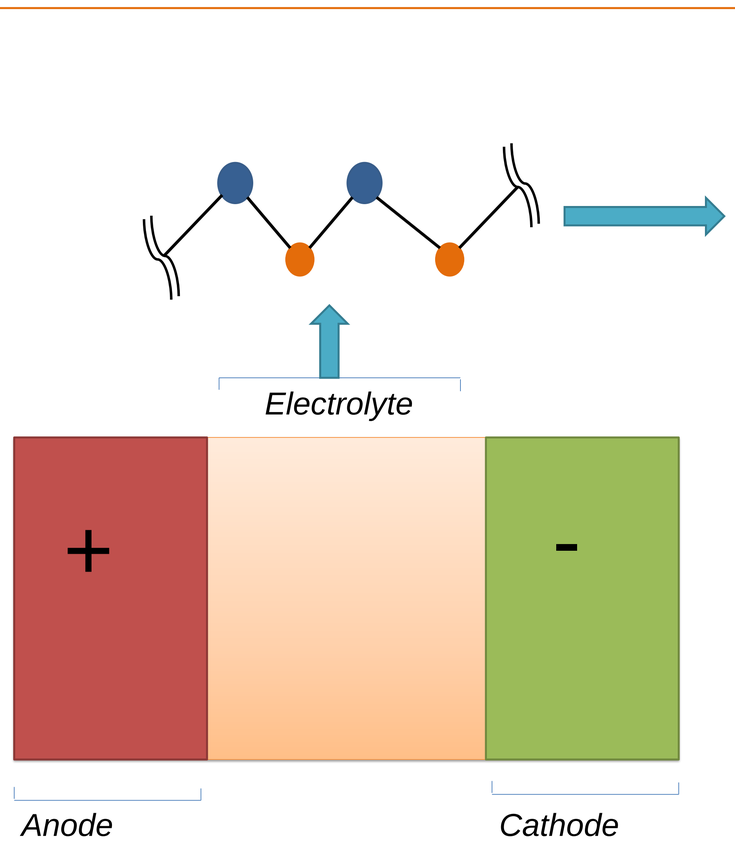
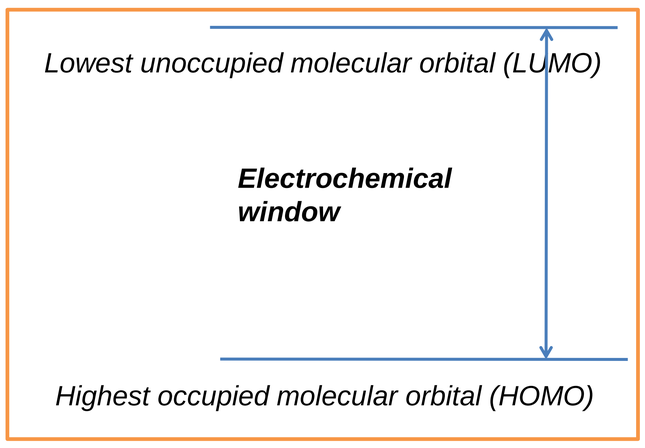
OBJECTIVE

The aim is to study how the bandgap can be varied with different functional groups added to the polymer. The calculations are initially compared with the corresponding experimental values for various sulfone compounds. The method is further extended to PEO functionalized with groups like OH, COOH, NH_2,NP and$(CH_3)_3Si$ to study how the bandgap can be engineered by varying the chemistry of the material.

MOTIVATION



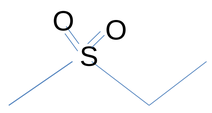


Higher electrochemical window enables high-voltage battery and improved safety.

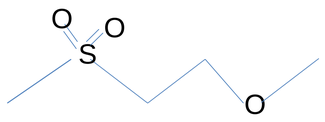
METHODOLOGY

- The initial structural optimization was performed using Hartree-Fock method (using cc-pVDZ basis set). Further calculations using MP2 with the same basis set yielded results with deviation more than one volt.
- The HOMO-LUMO gap calculated (from the density of states) using DFT with Projected-augmented-wave (PAW) method and GGA functional showed close match with experimental values (read below)
- To benchmark the calculations, the HOMO-LUMO gap of sulfone based organic electrolytes were calculated and compared with the corresponding experimental values.
- These values matched closely with the experimental values of sulfone-based electrolytes as well as polyethylene oxide (PEO)
- Hence this methodology was extended to study the effect of different important functional groups on PEO.

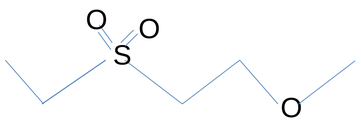
Benchmark calculations (with Sulfones)



Ethyl methyl sulfone (EMS)

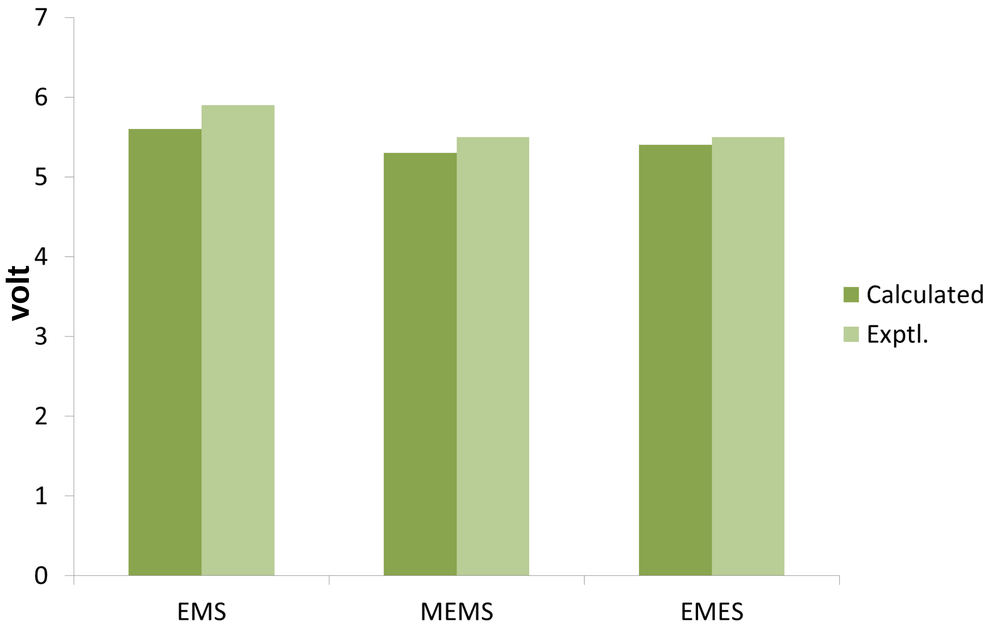


Methoxy ethyl methyl sulfone (MEMS)



Ethyl methoxy ethyl sulfone (EMES)

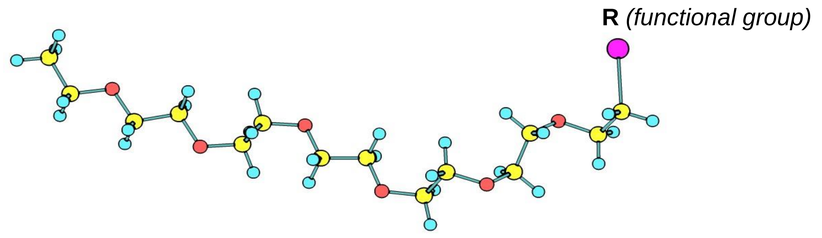
- Sulfone based electrolytes are being studied for high-voltage applications
- HOMO-LUMO gap calculations of the three sulfone electrolytes (shown on left) were carried out for benchmarking
- The calculations found close agreement with corresponding experimental values[1,2], hence the methodology was extended to polyethylene oxide



Comparison of electrochemical window (or bandgap) between experimental and DFT calculated values for ethyl methyl sulfone (EMS), methoxy ethyl methyl sulfone (MEMS) and ethyl methoxy ethyl sulfone (EMES); a class of electrolytes.

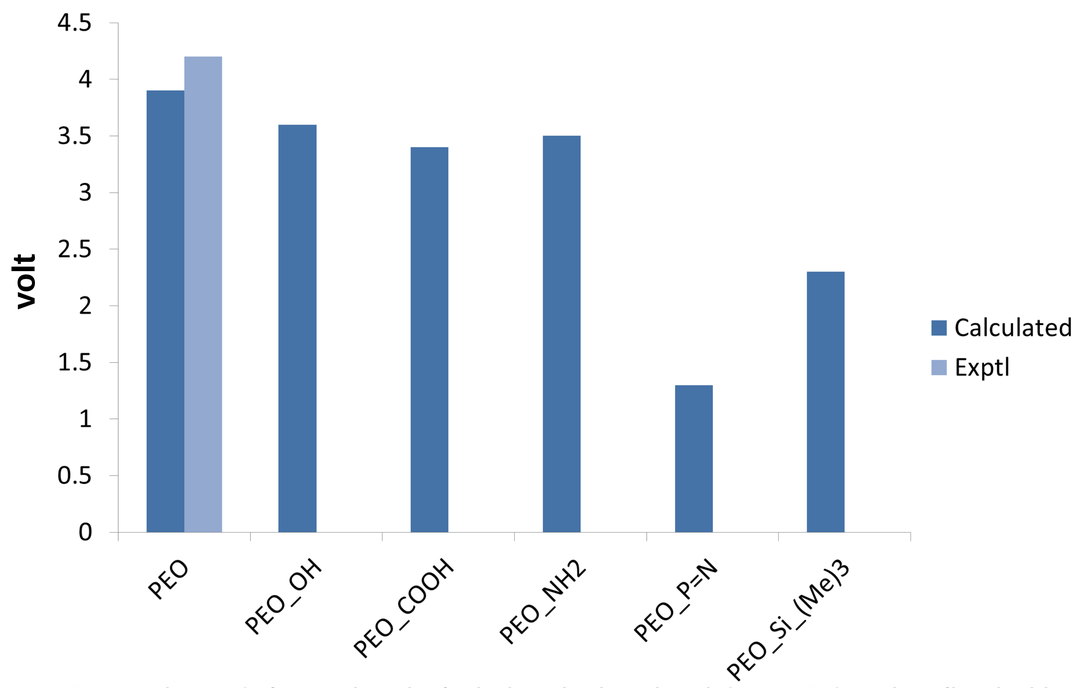
Polyethylene oxide

PEO: CH_3-$(CH_2$-O-$CH_2)_6$-CH_3



R = -COOH, -OH, $-NH_2$, -P=N-, $(CH_3)_3$-Si-

- The electrochemical window calculations were carried out for PEO and PEO with important functional groups (yet to be validated experimentally)
- A close match was found between calculated and experimental[3] value for PEO
- **However, all the functional groups considered showed reduced HOMO-LUMO gap**
- Future work should consider more than one molecule (correlation between neighboring molecules)



Comparison of electrochemical window (or bandgap) for PEO functionalized with various functional groups.

Reference

1. Shao et al, J. Phys. Chem. B 2011, 115, 12120–12125
2. Xu, K.; Angell, C. A. J. Electrochem. Soc. 1998, 145, L70–L72.
3. Sequeira C et al, Polymer electrolytes : Fundamentals and applications, Woodhead Pub., 2010

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