A Combined Molecular Dynamics and Density Functional Tight Binding Study in Solid State Polyaniline and CN-functionalized Polyaniline as Organic Cathodes for Lithium and Sodium Ion Batteries

National Univ. of Singapore [1], Institute for High Performance Computing, A*STAR [2], Yinqqian Chen[1], Johann Lueder[1], Man-Fai Ng[2], Michael Sullivan[2], ◦Sergei Manzhos[1]

E-mail: mpemanzh@nus.edu.sg

We present multiscale simulations of the discharge process of polyaniline (PANI) based polymeric cathode materials for electrochemical batteries in solid state. To deal with the large required numbers of atoms and structures, a combination of force-field molecular dynamics (MD) and Density Functional Tight Binding (DFTB) is used. Structures were pre-optimized with MD and then DFTB was used for final optimization and oxidation potential calculations, from which voltage-capacity curves are estimated in Li and Na ion batteries. The DFTB is benchmarked to Density Functional Theory (DFT) calculations using different functionals to confirm its accuracy. The oxidation of PANI and of cyano groups (CN) functionalized PANI induced by coordination to the electrolyte anions is computed and voltage curves are estimated. The cyano functionalized PANI is expected to not suffer from irreversible formation of pernigraniline base at high degrees of oxidation, which could nearly double the reversible capacity. The voltages computed with the solid state model are in good agreement with available experimental data and ab initio models based on oligomers. The solid state model also predicts substantially increased voltage with PANI functionalized with cyano groups. The results show that DFTB can be a viable tool for modeling of organic materials for electrochemical power sources where large simulation cells (on the order of 10^3 atoms or more) are required, but benchmarking to DFT is necessary: we also highlight cases of other potential organic electrode materials where a match of DFT and DFTB could not be achieved.

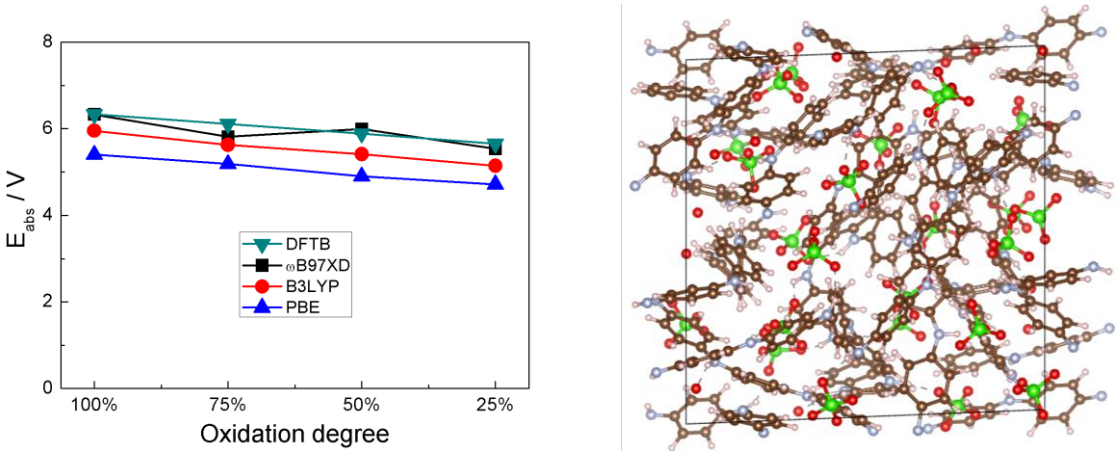

Figure 1. Left: comparison of oxidation potentials of PANI for different degrees of oxidation computed with different methods. Right: an example of a simulation cell containing CN-functionalized PANI and ClO_4 anions.