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Re: PhD Thesis Report – Piotr Jankowski

This doctoral thesis describes computational and experimental studies on solid electrolyte interphase (SEI) forming additives for applications in rechargeable lithium-ion batteries.

First, the introductory chapter (1) presents an overview of the context of the work, including the principles behind the lithium-ion battery, a nice review of the SEI and SEI-forming additives, and the scope and general objectives of the PhD thesis.

Chapter 2 describes the fundamentals of the computational and experimental techniques that were used in this project. The quantum mechanical modelling section outlines the key elements of the simulation methods, which is 3.5 pages in length with 3 equations; not essential, but it would have been good to have more details and equations on energy minimization methods, DFT functionals and basis sets, which are used extensively in this thesis work (e.g. chapter 3, part 1). The experimental techniques include cyclic voltammetry, electrochemical impedance spectroscopy, FT infrared spectroscopy and SEM.

Following this chapter on Techniques & Methods, the thesis consists of the Results & Discussion chapter (3) separated into five parts.

Part 1 deals with benchmarking of DFT methodology for the prediction of reduction properties. Various basis sets, DFT functionals and solvation models were tested by correlating against experiments for several well-known SEI-forming additives. Some interesting results were discussed: the application of an implicit solvent was shown to be necessary for accurate predictions; the chemical hardness was found to be a useful property for predicting kinetics and initial stages of the electrode process.

Part 2 covers an examination of a new class of anions as potential SEI-forming agents. The overall aim here was to design new anions able to form a stable SEI-layer and thus provide kinetic stability against solvent reduction. Computational screening was applied to a concept combining two current leading ideas: a tetrahedral boron atom as the anion core and a conjugated system as the anion ligands. Interesting trends were found: all the systems have extensive delocalization of the negative charge with very small lithium-ion interaction energies; the tetrahedral boron centre salts with conjugated ligands could have improved oxidation stabilities, which opens up possible application with high voltage cathodes.

Part 3 is a brief one (5 pages) and extends the work in part 2 by dealing with ionic liquid cations as SEI-formers. Here, an attempt is made to modify standard ionic liquid cations focusing on the reduction potential and the chemical hardness. The computational results suggest these two properties can be tuned by the introduction of a fluorine atom, a nitrile group or a double bond, and warrants experimental investigation.

Part 4 covers a study on pseudo-carbonates –dicyanoketene alkylene acetals as additives for SEI formation. The computational results are compared with experimental data (reduction potentials, FTIR spectra, cycling performance of full cells) from the group of S. Laruelle (LCRS, Amiens, France). The use of pseudo-carbonates was found to be beneficial for SEI-forming additives by lowering the LUMO energy and increasing the softness of the molecules. The simulation results compare well with the FTIR spectroscopy data.

The final part (5) largely deals with experimental and computational studies of structural modifications of sulphur-containing additives including five-membered ring or aromatic-ring-containing additives in standard electrolyte, and additives in a new LiTDI based electrolyte. The range of results indicate that the behaviour of the functional electrolytes are highly dependent on small changes in their chemical structure. Finally, PSOPh, DTDPh and DTD provide cyclability for LiTDI based electrolytes, which nicely conclude the thesis results.

In general, the results and discussion in chapter 3 (parts 1 to 5) are logically presented with figures and tables, and a good number of papers are cited (including recent references). Appropriate conclusions are drawn at the end of each part.

At the end of the thesis, a short one-page chapter (4) summarises conclusions on the major findings of this original work; finally, aspects of possible future work are mentioned, although it would have been good to see more detail than two sentences.

In my view, all of these chapters present quality results in a well-structured manner; the thesis provides an understanding of the various methods employed and the interpretation of a range of results for potential applications in rechargeable lithium batteries. Indeed, this body of research in this thesis has led to five publications (with PJ as first author in three) within high impact journals, which indicate the quality of the work. In addition, the student is co-author on a further 13 publications on studies related to this thesis again in strong journals (e.g., *J. Phys. Chem*. C).

In conclusion, the work presented in this thesis is of sufficient merit to be awarded a PhD degree (distinction Summa Cum Laude).

Professor Saiful Islam FRSC