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REVIEW ON THE PHD THESIS

"*Highly concentrated electrolytes for Lithium-Sulfur Batteries*"

by Aginmariya Kottarathil, M. Sc.

The thesis is written in English and the presentation is accurate. The initial sections deal with acknowledgements, abstracts (in English and Polish) and a list of publications that resulted from the research carried out in the course of the PhD. Four publications are listed, three of them dealing with original research, with the PhD candidate being the first author in two of them (one already published) and the second in the third, and an additional review paper to which she contributed.

The subject of this PhD falls nicely within the research tradition at Warsaw University of Technology dealing with new electrolyte salts for diverse battery technologies while at the same time embracing a new "hot" topic in the field, that of highly concentrated electrolytes, in collaboration with Chalmers University of Technology in Sweden.

The research carried out focuses in Lithium/Sulfur batteries, which are appealing for the prospects of high energy density at an affordable cost, but suffer from bottlenecks related to polysulfide dissolution that have to date hampered commercialization.

Within this landscape, the objective of the PhD is the mitigation of polysulfide dissolution through the use of new electrolytes and, aside experimental research (preparation of diverse electrolytes, characterization using a wide spectrum of techniques, and testing in Li/S cells) also covers modelling aspects, which is a quite uncommon and remarkable aspect.

The main text follows overall a logical flow of ideas illustrated with pertinent figures. It is structured in a general introduction section to Li/S batteries and the concept of highly concentrated electrolytes, a chapter describing the experimental and computational techniques and four main chapters describing the research carried out with a useful recapitulative partial conclusion at the end, a final section with a general summary, and two annexes describing some specific technical aspects in more detail, and a final bibliography section.

The introduction chapter it describes the state of the art of research in Li/S batteries and the concept of highly concentrated electrolytes to place the thesis in the current research context, enabling to rationalize the scope of the thesis. The chapter devoted to experimental and computational protocols evidences the wide spectrum of techniques to which the PhD candidate has been exposed, including modelling with COSMO-RS, which highlights the interdisciplinary nature of the work carried out.

Chapter 3 describes the results of investigating different electrolytes, some of them with commercial salts (LiTFSI, LiTf) and others with new salts developed at WUT (LiTf). The influence of the electrolyte salt anion on the speciation is assessed by combining Raman spectroscopy with ionic conductivity and viscosity measurements, and its influence on the electrochemical performance in Li/S cells discussed considering

polysulfide solubility deduced from HPLC experiments and COSMO-RS modelling. The overall outcome indicates that solubility is reduced with salt concentrations for all three anions, with minor differences between anions, likely resulting from the different amount of free solvent molecules, and best capacities achieved for LiTDI.

Given the best results achieved for LiTDI, the approach is extended in Chapter 4 to the study of other Hückel anions, namely LiPDI and LiHDI, in order to assess the influence of the length of the perfluoro chain, which seems to result in reduced polysulfide solubility. In view of the results achieved, the study with LiHDI was completed with the addition of $LiNO_3$ to the electrolyte, which is well known to improve performance of Li/S cells using conventional electrolytes, and is also found to be beneficial for LiHDI, with significant improvement of the coulombic efficiency.

After Chapter 3 and Chapter 4 describing exploratory research to compare new salts with conventional ones in highly concentrated electrolytes for Li/S, the following two chapters describe more in depth methodological developed. Along this line, Chapter 5 describes machine learning approaches for polysulfide solubility prediction using COSMO-RS software, while Chapter 6 describes mechanistic insights achieved through *operando* Raman spectroscopy. Despite the complexity of this technique, the results enabled to get a semi-quantitative assessment of the impact of the salt concentration for different Hückel salts (LiTDI, LiPDI and LiHDI) and concentrations on the solubility and diffusion behaviour of polysulfides in Li/S cells.

The final section summarizes all the results reported highlighting potential research avenues to extend the research carried out.

In summary, the work reported by Aginmariya Kottarathil (M. Sc) is a piece of nice fundamental research work involving both experimental and computational approaches to shed some light on the complex nature of highly concentrated electrolytes while at the same time investigating their potential benefit to solve current bottlenecks in the development of Li/S batteries.

In view of all the above considerations, I believe that the thesis fulfils all the requisites for the defence to be awarded the Doctroral degree at Warsaw University of Technology.

Sincerely yours,

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