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Report on the PhD thesis manuscript of M Sc Aginmariya Kottarathil, "Highly Concentrated Electrolytes for Lithium-Sulfur Batteries"

The thesis presented by Aginmariya Kottarathil is hereby briefly evaluated. The thesis text discusses the topic of novel electrolytes for lithium-sulfur (Li-S) batteries, which are expected to play an important role in the future energy system due to their reliance on low-cost materials and high specific energy. Li-S battery devices have caused significant interest in the last 10-15 years, due to the need to find alternatives to Li-ion batteries, and commercial systems exists. However, these batteries are plagued by a number of failure mechanisms: side-reactions on the anode, non-uniform deposition of lithium, dissolution of sulfur, self-discharge due to the polysulfide shuttle, poor balancing of the electrodes, etc. Several of these shortcomings could potentially be addressed by exploring novel electrolyte systems. This serves as a background to the thesis.

The electrolytes under study in the thesis are so called high-concentrated electrolytes (HCEs). Such electrolytes have been explored in several different battery chemistries before. Due to the high salt concentration, the solvent molecules become strongly coordinated and thereby less prone to take part in different side-reactions, which can increase the cycling stability of the rechargeable battery. This is in the thesis explored for the archetypical Li-S electrolyte system of DME:DOL, where a range of salts are explored. These include both conventional Li-S battery salts as LiTFSI and LiTf, but also a range of Hückel salts: LiTDI, LiPDI and LiHDI. These have been synthesized and explored by the local group at WUT in recent years, and is a novel materials platform for these HCE systems used in Li-S batteries. In this sense, it is a topic worthy of investigation.

The HCEs provide an interesting category to better understand and explore fundamental electrolyte properties. The coordination chemistry is at clear interplay with the ionic transport and the electrochemical behavior, and the possible side-reactions that can appear when employing reactive and less stable electrodes (as in Li-S). These phenomena are in the thesis explored through spectroscopic techniques (such as FTIR and Raman spectroscopy), viscometry, impedance spectroscopy, and a range of associated techniques. The electrolytes are then tested in prototype Li-S cells, and the cycling behavior analyzed. The thesis also comprises computational studies using DFT-based methods, combined with an outlook into machine-learning approaches. All methods employed in the thesis are relevant to disentangle the scientific questions regarding HCE systems, and all appears employed according to the standards of the scientific field. One would, naturally, be interested in complementary investigations of for example the evolution of the surface chemistry (using XPS), or the microstructure of both the anode and the cathode in the Li-S cells (using microscopy or scattering techniques). This should, on the other hand, likely be too extensive to fit within the time frames of the thesis work.

The thesis itself is 107 pages and written almost entirely in English, while an abstract in Polish is also included. Parts of the text is based on a recent scientific publication in an established and respected peer-reviewed journal: Journal of the Electrochemical Society. Other manuscripts are also planned based on the thesis work. This is a strength: parts of the research work have apparently been scrutinized before by key experts in the field, which have considered it adequate for publication. The level of the scientific English is generally at an appropriate level, and it is understandable for an independent reader who is familiar with the scientific field.

The text is divided into 7 main chapters. Chapter 1 gives brief introduction into Li-S batteries and HCEs as study objects, and ends with more fundamentally addressing the specific thesis topic. The text provides an overview over both these two research areas, and address the main challenges and questions in an appropriate way. If possible, it would be interesting to add more outlook into the shortcomings of both Li-S and HCEs from an industrial perspective – there are clearly reasons why these are not already implemented in commercial devices. It would likewise be interesting with a more profound discussion on how diffusivity and viscosity correlate with the specific coordination chemistry, and limitations of the spectroscopic and computational tools used to characterize these coordination structures and ionic mobility.

Chapter 2 constitutes an overview over the methods used in the thesis, both experimental and modelling techniques. The focus is a description of how the methods were utilized, which make the studies largely reproducible for an independent reader. In parts, especially regarding the spectroscopic tools, a background to the used techniques is provided. Considering how decisive sulfur loadings of the electrodes are for the performance of Li-S batteries, it is a shortcoming that such values are not easily found in the thesis. A more profound discussion of the shortcoming and advantages of the used computational tools would also be commendable.

The main achievements of the thesis work are summarized in Chapter 3, 4, 5 and 6. All contain sound, high-quality and interesting scientific work, relevant for the scope of the thesis. Chapter 3, which is the most extensive and is already published, makes a comparison of LiTFSI-, LiTf-, and LiTDI-based HCEs for a range of concentrations. The amounts of "free" anions is characterized by Raman spectroscopy, correlated to ionic conductivity, and trends are thereafter discussed. It is here observed that LiTDI in many ways constitutes and intermediate between LiTFSI and LiTf in the data. Nevertheless, there were large performance difference seen in the resulting Li-S cells, with LiTDI showing remarkably better capacity and capacity retention. While the better performance than LiTf is explained by the higher ionic conductivity, the better performance as compared to LiTFSI is discussed to be due to the lower polysulfide (PS) dissolution. In Fig. 3.7, however, LiTFSI appears to dissolve less of S_8 than LiTDI. On the other hand, it is far from certain that the solubility of S_8 is a good approximation of PS solubility.

Chapter 4, in turn, makes a systematic comparison of different Hückel salts: LiTDI, LiPDI and LiHDI (which increase in this series in ionic size). Spectroscopic data are again compared with conductivity studies, viscometry and electrochemical data. The PS solubility is assessed with modelling. In Fig. 4.5, the conductivity data is – as expected – inversely correlated to the viscosity. It would be interesting with a discussion on why these trends are

not more clear for the studies in Chapter 3? Moreover, a more clear discussion of the relationship both in theory and in the data regarding the ionic size and the aggregate formation, and how this is correlated to ionic mobility, would have been useful to interpret the observed trends.

Chapter 5 discusses a machine-learning approach to assess and predict PS solubility in these electrolytes. Considering that the PS solubility is a decisive factor to explain the electrochemical data, it is of importance that the methodology is robust. The DFT-based approach COSMO-RS is used to build a regression model for the PS solubility. It would be useful here to better explain the descriptor used in this model. The shortcomings of the model, considering the size of the dataset, and the limited amount of types salts that the model is trained on, are not extensively elaborated.

Chapter 6 entails some state-of-the-art studies of PS dissolution and diffusivity based on Raman spectroscopy. These results are highly interesting, since they give clear indications on phenomena that could explain the electrochemical results obtained. Since these results are obviously correlated and on similar systems as those discussed in Chapter 5, a comparison of these is of scientific interest. This is now made in qualitative terms (which is good), but the quantitative difference in Table 4.1 is small for the 1 m-concentrated electrolytes.

Finally, Chapter 7 provides a summary and outlook, where scale-up studies are specifically targeted. I do question that the overall conclusion that LiTDI-based electrolytes outperforms LiTFSI and LiTf counterparts due to their poor PS solubility is soundly proven. The operando studies have not been performed on the LiFTSI/LiTf systems, and other data are less convincing. An extended discussion of this statement would be useful.

Generally throughout the thesis, I would also argue that some conclusions appears to be made based on limited data – at least data shown in the thesis. While clear trends from sufficient data sets are seen in the spectroscopy data, the Li-S cell testing appears as less rigorously performed. How many cells were fabricated per system? How reproducible are the data from the Li-S cells? There are little error estimations made in these studies, and large differences is seen in cell performance while the electrolyte properties are not as strikingly different.

Nevertheless, my overall assessment is that the scientific work has been performed well according to the standards of the relevant scientific fields (electrochemistry, materials science, modelling), and that the results are novel and scientifically interesting. These are important findings to construct better electrolytes and Li-S batteries chemistries. Some more discussions would be interesting, as pointed out above. The thesis is ready to be defended. I look forward to discuss it further.

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