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Thesis evaluation report for work submitted by Anna Bitner-Michalska

Title: Studies on optimization of imidazolate sodium salts based electrolytes for sodium-ion battery applications

The thesis submitted by Anna Bitner-Michalska is an important contribution to the science particularly towards characterisation and evaluation of performance of novel salts, electrolytes and active materials for sodium batteries. During her thesis she used and characterised two new salts based on imidazolium anion (NaTDI and NaPDI) and three fluorine free salts (NaTCP, NaTIM and NaPCPI). The novelty of the approach can be visualized with two patent applications, besides that the quality of work is reflected in the 5 scientific papers in the highly ranked per-reviewed international journals, out of all she is the first author in three papers dealing with application and characterisation of new salts in different electrolyte solutions for Na-ion based batteries. Work presented in the papers is in the scope of the thesis which aim was to develop non-aqueous (liquid and polymer) electrolytes and low voltage, high capacity negative electrode material. Salts were implemented in the liquid and into the polymer type of electrolytes and by using different characterisation techniques she showed that proposed new salts exhibit stability against anode and cathode materials. The list of experimental techniques used in her work is impressive, pointing out a lot of skills that she has to develop during thesis. Use of different types of spectroscopies (NMR, Raman, IR, ...) and techniques for electrolyte characterisation can be applied in the different fields of science, giving her good qualification for the future carrier.

In the first paper where she is a leading author, she showed application of liquid electrolyte containing new tailored salts (NaTDI and NaPDI) for sodium ion batteries. Salts exhibit good electrochemical stability and very good conductivity at concentration of 0.75M NaTDI in EC/DMC. Electrochemical tests with suitable cathode material showed that those electrolytes can be successfully applied in the sodium ion cells. In the second paper where she is a leading author, a microwave plasma chemical vapour deposition of the Sb_xO_y/C negative electrode materials is shown and characterised with lithium and sodium Hückel salts in electrolytes. Good reversibility and capacity have been obtained and the concept of using Hückel anions as electrolytes in both lithium and sodium batteries have been approved. Third paper with Anna

Bitner-Michalska as a leading author shows application of fluorine free electrolytes for all solid state batteries based on percyano-substituted organic salts. New salts used in this work (NaTIM, NaTCP, NaPCPI) have high thermal stability and polymer electrolytes containing those salts have very good ionic conductivities (>1mS at 70°C). Additionally, very good electrochemical stability has been proved and results demonstrate the potential application of percyano Hückel-type anion salts in all-solid and liquid electrolytes for sodium ion batteries.

Needless to say that Anna Bitner-Michalska is a contributing author to two more research papers published in the high quality scientific journals. She has contributed to the review paper where different electrolytes for Li-ion batteries and their properties have been summarized with emphasise on TDI and PDI based electrolytes developed in Warsaw. Those electrolytes were tested in different laboratories and it was shown that they exhibit high thermal stability and high oxidative stability, while conductivity is in the range of PF6 based electrolyte. Another paper where Anna Bitner-Michalska is a contributing author deals with new tailored sodium salts for battery application and this work was published in Chemistry of Materials, journal with very high impact factor. This work shows application of NaTDI and NaPDI salts in carbonate based solvents. Tested electrolytes exhibit excellent conductivity and electrochemical stability which was proven with impedance spectroscopy and cycling voltammetry.

From the above considerations, it is my opinion that this work is perfectly appropriate to be defended to obtain a Ph.D. degree in the Materials Science.

At the end I would like to conclude work performed within this thesis shows high innovation potential and it will have high impact on the research society. Work was very well conducted and many different approaches have been used in characterisation. Five new electrolytes were tested in the combination with some new active electrode materials and the quality of the work can be reflected within 5 research papers where Anna Bitner-Michalska is a first author of three papers including the one published in Scientific Reports which is a journal of the Nature publishing group. Overall, the work presented is of high quality and it deserves the highest ranking among PhD thesis. Definitely this work is between 5% thesis that I have examined and therefore I suggest that to honour it with Summa Cum Laude recognition.

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