Opinion

on the Doctoral Thesis of PhD student Hristo Georgiev Rasheev for awarding the educational and scientific degree "Doctor" in the Professional field 4.2 Chemical Sciences, doctoral program "Theoretical Chemistry (Computational Chemistry)" on the topic:
"Molecular modeling of components for post-lithium-ion batteries"

Supervisors: Prof. Dr. Alia Tadjer
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from Prof. Dr. Hristiyan Aleksandrov Aleksandrov,
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The dissertation of PhD student Rasheev is devoted to the theoretical modeling of the processes of solvation and desolvation in electrolytes containing two types of cations (Li^+, Na^+, or Mg^{2+}) in order to clarify whether there is competition or synergy between ions. The topic is very timely, as for several decades lithium-ion batteries have been the main source of energy in portable and mobile devices, backup power supplies, electric vehicles, etc., while limited lithium supplies lead to the need for new technologies where it can be replaced by more abundant and cheaper alternatives such as sodium, magnesium, aluminum, etc.

The dissertation is written on 137 pages and contains 37 figures and 39 tables, while the cited references are 188. It is structured as follows: Introduction (2 pages), Goals and tasks (1 page), Literature review (20 pages), Theoretical methods (15 pages), Results and discussion (86 pages), Conclusions (1 page), Contributions (1 page), and Bibliography (11 pages). For the theoretical study have been provided reasons in the first two parts where the main goals of the dissertation are clearly formulated. The literature review is divided into three chapters and is based on 74 references. In the first chapter are discussed the electrochemical stability of electrolytes for metal-ion batteries, as well as theoretical aspects of the ion-solvent interactions and the diffusion

of ions in the electrolyte. In the second part the author focuses his attention on the processes taking place at the electrode/electrolyte interface, as well as to the decay products that can be deposited on the electrodes. The types of electrode materials used in modern lithium- and post-lithium-ion batteries are discussed in the third chapter of the literature review, and it is emphasized that the processes of intercalation are crucial in them. In "Theoretical Methods" part are described the methods used to obtain the results in the dissertation. At the beginning of the chapter "Results and discussion" the oxidative and reductive stability of four solvents used experimentally in rechargeable batteries was evaluated: ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diglyme (G2). The processes of solvation and desolvation in pristine and mixed electrolytes are further investigated theoretically. For this purpose, homo- (Li^+/Li^+, Na^+/Na^+ and Mg^{2+}/Mg^{2+}) and hetero- (Li^+/Na^+, Li^+/Mg^{2+} and Na^+/Mg^{2+}) cationic pairs interacting with different number of ethylene carbonate molecules were modeled. Interestingly, the binuclear Li^+-Na^+ complexes become preferred only in the absence of solvent molecules, while other mixed electrolytes with the participation of Mg^{2+} cations dominate over mononuclear ones even when interacting with a significant number of solvent molecules. The electrode-electrolyte interactions have also been studied very carefully and in detail. The conclusions made at the end of the dissertation summarize and reflect correctly the results obtained. The synopsis fully and correctly reflects the results of the theoretical study.

Part of the results of the dissertation were published in two publications in journals with impact factor from first quartile (Q1): ChemPhysChem (IF(2020) = 3.102) and ACS Omega (IF(2020) = 3.512) and were presented in six (two oral presentations and four posters) international and three (three oral presentations) national conferences. Mr. Rasheev is a co-author of three more publications in journals from Q1 (The Journal of Physical Chemistry C, Molecules, and Journal of Materials Chemistry A) and he is a participant in seven research projects (three projects for PhD students at SF-SU and four national projects, two of which with European co-financing).

I know Mr. Rasheev as a student in my course "Modeling of Periodic Systems and Nanostructures" within the master's program "Computational Chemistry"; I have attended some of his oral presentations. My impressions of him as a student and young scientist are excellent.

In conclusion, the dissertation of Mr. Hristo Georgiev Rasheev fully meets all the requirements stipulated in the Act for the Development of the Academic Staff in the Republic of Bulgaria. The obtained results and the way of their presentation in the dissertation show that Mr.

Rasheev is a young scientist with high scientific competence and I strongly recommend that he be awarded the educational and scientific degree "Doctor" in professional field 4.2 Chemical Sciences, doctoral program "Theoretical Chemistry (Computational Chemistry)".

01.04.2022,

Sofia / Prof. Dr. Hristiyan Aleksandrov /