STATEMENT

on the PhD Thesis of **Hristo Georgiev Rasheev**
for earning the educational and scientific degree "Doctor"
in professional area 4.2. Chemical Sciences,
PhD program "Theoretical Chemistry (Computational Chemistry)"
Title: "Molecular modeling of components for post-lithium ion batteries"

MEMBER OF THE SCIENTIFIC JURY (by order of the Rector of Sofia University "St. Kliment Ohridski № RD-38-86/07.02.2022)**:**
Prof. Dr. Ekaterina Zhecheva from the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences

The PhD thesis of Hristo Rasheev contains 137 pages with 55 figures, 41 tables and 183 references. The thesis fully meets the requirements for obtaining the educational and scientific degree "Doctor" in terms of size, structure and design.

Due to their high performance and reasonable price, lithium-ion batteries appear as the "gold standard" among rechargeable ion batteries. However, the ever-increasing strict economic and environmental requirements impose a need for further improvement of battery life, power, reliability and safety and determine intensive search for new electrode materials, electrolytes and even new types of batteries. One of the research strategies is a complete or partial replacement of the lithium charge carriers with cheaper and more common metals such as Na, Mg, Ca, Al. In case of partial replacement of lithium, the so-called hybrid ion batteries appear, which are expected to combine the advantages of lithium-ion batteries with a lower cost, toxicity, etc. This is a promising and still insufficiently studied research area. Its development requires a deep insight into the interactions between the different charge carriers in the electrolyte and at the electrolyte/electrode interface. The PhD thesis of Hristo Rasheev, which belongs to the computational chemistry, falls in this research area.

The PhD thesis is entitled "Molecular modeling of components for post-lithium ion batteries" and it shows quantum chemistry results on the solvation and de-solvation processes occurring in mixed electrolytes for hybrid ion batteries in order to establish a possible rivalry or synergy between the two types of cations. Combinations of cations, anions, solvents and electrodes corresponding to real batteries were chosen as objects of study, a computational protocol for geometry optimization was elaborated and a scheme was selected that estimates the thermodynamic parameters determining the electrochemical behaviour.

In the thesis a detailed and critical literature overview is made on molecular modeling of the interactions between ions and solvent in the electrolytes of metal-ion batteries as well as of the formation of the passivating layer on the electrode surface. The main types of intercalation compounds and redox-active organic molecules used or have potential to be used as electrode materials in rechargeable ion batteries are summarized. The review suggests that the candidate has well covered the available literature studies from the point of view of both

computational chemistry and electrochemistry. The basics of the theoretical methods used for obtaining the results in the thesis are presented.

The major results are as follows:

●The oxidation and reduction stability of four organic solvents used in rechargeable ion batteries was evaluated: ethylene carbonate, dimethyl carbonate, propylene carbonate and diglyme. Optimizations were performed in an implicit solvent with considering its dielectric constant. The calculation protocol has been refined and it has been found that the electrochemical stability "window" increases as the polarity of the solvent decreases. A novel approach has been proposed to stabilize organic solvents by addition of electrochemically more active substances that undergo oxidation/reduction prior to the solvent.

●Within the DFT method, the properties of mixed Li-Na, Li-Mg and Na- Mg ionic electrolytes were simulated in polar and non-polar medium using model complexes of homo- and hetero-ion pairs with different numbers of ethylene carbonate molecules. Stability, structure, charge distribution and solvation/de-solvation tendency of the complexes were evaluated. It has been found that in mixed Li-Na electrolytes bi-nuclear complexes are preferred for a small number of solvent molecules, while in mixed Li-Mg and Na-Mg electrolytes bi-nuclear complexes dominate over mononuclear ones even at higher degrees of solvation.

●De-solvation occurring during adsorption of Li^+, Na^+ and Mg^{2+} mono- and bi-nuclear complexes on the (111) surface of a $Li_4Ti_5O_{12}$ electrode is simulated by periodic DFT calculations. Due to interactions of the ethylene carbonate solvent with the electrode oxide surface, side reactions of partial electrolyte decomposition also occur. The electrolyte decomposition proceeds to a greater extent in a lithium electrolyte, as well as in the presence of PF^{6-} as counter-ions. Bi-nuclear complexes de-solvate at the electrode-electrolyte interface more easily than mononuclear ones, simultaneously with suppression of solvent decomposition. The role of the counter-ions PF^{6-} or their decomposition products for facilitating the de-solvation of bi-nuclear complexes has been outlined.

The general impression of the thesis is that systematic and large amount of work has been carried out. The combination of the research profiles of the two supervisors has enabled to focus the potential of molecular modeling on real problems in the development of post-lithium ion batteries. A number of data have been obtained that explain experimental facts and would be useful for the selection of new electrolytes. The main contribution of the research is the possibility to conclude that the mixed lithium-magnesium and sodium-magnesium electrolytes are promising for the development of rechargeable ion batteries involving magnesium.

The thesis is written clearly and is well formed with rich illustrative material. The candidate demonstrates a very good knowledge of the research topic, which allowed the obtained results to be comprehensively analyzed. The abstract is in accordance with the requirements and correctly reflects the main content and the main results of the thesis.

The results of the thesis are included in 2 publications, both in Q1 journals (ChemPhysChem and ACS Omega with impact factors of 3.102 and 3.512, respectively), which indicates a high research level. Results were reported at 6 international and 3 national scientific forums. The candidate has participated in 3 projects of the Science Fund of Sofia

University for PhD students. He was also a team-member of 4 projects with national funding, two of which with European co-funding. I will also note that outside of the PhD thesis, Hristo Rasheev is co-author of 3 more papers on energy storage materials

Conclusion. The PhD thesis of Hristo Rasheev fulfills the requirements of the Act on Development of the Academic Staff in the Republic of Bulgaria and the Regulations for the terms and conditions for acquiring academic degrees and occupying academic positions at the Sofia University "St. Kliment Ohridski". The candidate has acquired a high level of scientific competence in the field of theoretical chemistry, which has allowed him to obtain reliable and important scientific results. Based on this, I evaluate the thesis positively and strongly recommend the Scientific jury to award the educational and scientific degree "Doctor" in professional area 4.2 "Chemical Sciences" (Theoretical Chemistry) to Hristo Georgiev Rasheev.

Member of the Scientific juri:

(Prof. Dr. Ekaterina Zhecheva)

03.04.2022.