STANDPOINT

on PhD Thesis "Molecular modeling of components for post-lithium ion batteries"

of Hristo Georgiev Rasheev

presented for obtaining educational and scientific degree "Doctor"

in Professional field 4.2 Chemical sciences

Doctoral program "Theoretical Chemistry (Computational Chemistry)"

by Prof. Dr. Tony Georgiev Spassov

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The presented PhD Thesis contains 137 pages; 45 figures and 39 tables are included. The bibliography includes 188 literature sources. In terms of volume, structure and design, it fully corresponds to a dissertation for an educational and scientific degree "Doctor".

In his PhD work, the PhD student Hristo Rasheev aims to establish whether in the solvation and desolvation processes in electrolytes containing two types of ions there is competition or synergy between the ions. To achieve this goal, an appropriate calculation protocol has been created for optimizing the geometry of objects of finite and infinite size with the participation of neutral and charged particles. A reliable scheme for estimating the thermodynamic quantities characterizing the electrochemical behavior of the studied objects was also chosen. It is also important to note that in the molecular modeling of these processes, cations, anions, solvent and electrode surface are selected, which are close to the real operating conditions of ion batteries.

The study in the Thesis is planned with the aim to achieve the fullest possible thermodynamic and electrochemical characterization of the components of an ion battery. They begin with molecular modeling of solvation and desolvation in single- and dual-cation electrolytes. The tendency to form binuclear complexes was quantified by analyzing the structure of the ion-solvent clusters and the energy of the ion-solvent interaction. The

polarizing effect of the cations was also evaluated. In the second part of the work the modeling of the interactions (cation-electrolyte-electrode) on the electrode/electrolyte interface is performed. The purpose of this study is to bring the obtained energy characteristics closer to those of real ion batteries. Appropriate selection of the electrode surface was performed and the adsorption sites on the electrode surface ($Li_4Ti_5O_{12}$) were specified. The adsorption and desolvation of mononuclear and binuclear complexes "Metal ion/s - ethylene carbonate" and the influence of the counter ion on the adsorption and desolvation of mono- and binuclear complexes were studied.

The results obtained from the very well planned and implemented modeling of the components of ion batteries have allowed important conclusions to be formulated, which are the basis of several significant contributions to the study. First, a strategy is proposed to expand the window of electrochemical stability of solvents used in electrolytes for ion batteries, based on the calculation of the absolute electrochemical potential of oxidation and reduction. Original models for studying the processes of solvation and desolvation of alkali and alkaline earth ions in mixed electrolytes, as well as the influence of the electrode-electrolyte interface on desolvation processes are proposed. Some side effects of decomposition of the electrolyte components due to their interaction with the electrode surface are explained. It has been found that the use of hybrid electrolytes containing magnesium with lithium or sodium could be a successful approach for overcoming some of the limitations of pure magnesium electrolytes.

An important indicator of the value of the results obtained in the presented PhD work are publications in international journals with high impact factor: ChemPhysChem (Q1, Impact Factor: 3.102), ACS Omega (Q1, Impact Factor: 3.512). Parts of the dissertation are presented at 6 international and 3 national scientific forums.

Mr. Hristo Rasheev was my student, who showed in-depth knowledge in the field of physical chemistry of materials and methods for characterizing their structure and properties.

Based on the above, I believe that the presented dissertation has all the necessary qualities and the Hristo Rasheev deserves the award of educational and scientific degree "Doctor".

TONY GEORGIEV SPASSOV
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April 02, 2022 Prof. Tony G. Spassov