UNIVERSITI TEKNOLOGI MARA

FIRST-PRINCIPLES STUDY ON PROPERTIES OF HYDRATED AND PURE PRUSSIAN BLUE WITH POTASSIUM ION INTERCALATION FOR CATHODE MATERIAL OF POTASSIUM ION BATTERY

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MSc

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

Battery is a device that converts chemical energy into electrical energy in a chemical reaction. For rechargeable battery, potassium ion battery (KIB) has been received great interest among researchers due to its low cost and abundance in Earth's crust. The most suitable cathode material for KIB is Prussian blue (PB) ($Fe_4[Fe(CN)_6]_3$). In this work, the structural and electronic properties of hydrated PB, pure PB, KPB and K_2PB were calculated using density functional theory (DFT) within Cambridge Serial Total Energy Package (CASTEP) computer code. From the geometrical optimization of pure PB, the generalized gradient approximation for Perdew-Burke-Ernzerhof Scheme (GGA-PBE) functional shows the most comparable structural properties with experiment data compare to local density approximation by Ceperley and Adler as parameterized by Perdew and Zunger (LDA-CAPZ) and the generalized gradient approximation for Perdew-Burke-Ernzerhof for solids (GGA-PBEsol) functional. From this result, all the calculation of structural properties and electronic properties for hydrated PB, KPB and K_2PB is calculated by GGA-PBE functional. For the PB with the presence of water (hydrated PB), the optimized structure of PB in the cubic structure becomes distorted which changes its lattice. Upon removing $Fe(CN)_6$ and introduction of H_2O into the cavity of Prussian blue, the structure undergoes a slight contraction and is distorted from the ideal cubic cell. Upon the addition, the electronic properties of the pure PB have been calculated with GGA-PBE functional and it is found that the band gap slightly underestimated from the experimental value which is 0.72 eV. Hubbard U was used to broaden the bands crossing the Fermi level. Thus, by using GGA-PBE+U, the band gap produced 1.77 eV with U for Fe^{3+} is 6 eV and Fe^{2+} is 4 eV. So, the value of band gap of pure PB show 1.13% of percentage difference with band gap of the experimental value which is 1.75 eV. With the intercalation of K^+ into PB, the intercalation voltage was calculated and it shows that the voltage for KPB is higher compared to K_2PB which agrees with experimental data. The intercalation voltage with different numbers of K^+ in PB is calculated to be 4.33 V and 1.40 V for KPB and K_2PB which are in good agreement with the reported experiment, 4.20 V and 1.20 V. It is found that the calculated voltage has been improved near to experimental value. Therefore, the first-principles calculation in this work can give more understanding of the behaviour of hydrated PB, pure PB, KPB and K_2PB for its uses as cathode material in KIB.

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TABLE OF CONTENTS