UNIVERSITI TEKNOLOGI MARA

FIRST PRINCIPLES STUDY ON PROPERTIES AND VOLTAGES OF CATHODE MATERIAL NICKEL DOPED PRUSSIAN BLUE FOR SODIUM ION BATTERY

NOOR ATIQAH BINTI MD NASIR

Thesis submitted in fulfillment
of the requirements for the degree of
Master of Science
(Physics)

Faculty of Applied Sciences

April 2022

ABSTRACT

Within this work, first principles techniques have been applied to understand on the fundamental knowledge of cathode material Prussian blue (PB), or iron hexacyanoferrate on structural properties, electronic properties, and voltages for sodium-ion batteries (SIBs). Sodium is an alternative choice in term of large-scale energy storage as it is having similar physical and chemical properties to lithium, other than having abundance resource and cost friendly. All the calculations are performed using density functional theory (DFT) through the computer simulation CASTEP computer code. The pure crystal structures of PB are optimized using different exchange-correlation functional named LDA-CAPZ, GGA-PBE, and GGA-PBEsol. GGA-PBE functional is found to be the best functional as it exhibits the most accurate values for lattice parameter, thus is chosen for further calculations. Moreover, the effects of DFT plus Hubbard U (DFT+U) are explored especially on the electronic properties of PB as the transition metals are shown in the material. The band gap for PB is increases from 0.26 eV o 1.76 eV and is proved that Hubbard U correction improved the electronic band gap close to the experimental result. The effects of different number of Na ion intercalation on PB has also been studied. The open cubic framework structure of PB makes the intercalation/deintercalation of Na ion fast and easy although the radius of Na is bigger than Li. Based on the finding, $NaFeFe(CN)_6$ (Na_1PB) display higher voltage than $Na_2FeFe(CN)_6$ (Na_2PB) with 4.21 V compared to 3.01 V which is compliant with the experimental value. Furthermore, the effects of Ni ion substitution on N-coordinated Fe ion into the Prussian blue analogues (PBAs) with stoichiometry $Na_2Ni_xFe_{1-x}Fe(CN)_6$ at x = 0.01, 0.03, 0.05, 0.10, and 0.15 are investigated. The partial DOS shows the presence of Ni ion among the PBAs atoms. The results of Ni-doped PBA show the increasing in structural stability and producing higher voltage compared to non-doped PBA. The voltages are increase to 3.23 V, 3.27 V, 3.45 V, 4.32 V and 5.65 V with increasing number of Ni substitution. The first-principles study in this work can clarify the doping effects in PBA and may improve understanding of PB as cathode material for SIB.

ACKNOWLEDGEMENT

First and foremost, I wish to thank Allah S.W.T., The Almighty God for the endless blessing and giving me the opportunity to embark on my degree in Universiti Teknologi MARA to complete this long and challenging journey successfully. My gratitude and thanks go to my main supervisor Dr Mohamad Fariz, and my co-supervisor Dr Fadhlul Wafi for their continuous support for my study and for their patience, motivation, and immense knowledge in helping me accomplish this research and the thesis writing.

Special thanks to Nab, Dr Hazrie, Dr Hafiz, Aqeel, Haziq, other colleagues, and friends for helping me with this project. Thank you for the continuous support that you guys providing me and for all the valuable comments and suggestions that I received for my study.

Finally, this thesis is dedicated to my parents especially my mother, Sabiah for believing in me and supporting me spiritually throughout my life together with my father, Md Nasir.

TABLE OF CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 Research Background

Production of energy and storage technologies have attracted huge attention for daily applications from the portable electronic equipment to the hybrid electric vehicles. Fossil fuels such as coal, petroleum and natural gas are most commonly used non-renewable energy resource worldwide. The fact that this energy has led to depletion allow the new combinations of solar, wind, hydraulic, and tidal energy as a trend toward the use of clean energy (Dunn et al., 2011). The best available option to achieve constant electricity output for large electrical energy storages is using battery which can convert the electrical energy to chemical energy. The battery space is currently dominated by lead-acid and lithium technologies and the first known lead–acid cells is developed by Gaston Planté over 150 years ago and lead–acid battery technology saw significant refinement over the subsequent 100 years (McKeon et al., 2014).

Research are done for many years to make better battery which are lighter in weight and higher power density and that is when lithium becomes convenient compared to lead, which is heavier than lithium. Technologies of lithium ion secondary batteries were established by Sony in 1991 (Nishi, 2001) and they have played a significant role in energy storage devices ever since. Up till now, lithium ion batteries (LIBs) hold a great promise in solving the energy and environmental crisis due to their high energy density, long lifespan and environmentally friendliness (Hou et al., 2017). However, the high demand for lithium associated with these new and large-scale applications is expected to increase the price of lithium rapidly, affecting reserves as well, as it is not a naturally abundant element (Hwang et al., 2017).

In recent years, sodium ion batteries (SIBs) have received increasing research attentions as alternative for LIBs in the application of large-scale electric energy storage (Choi & Aurbach, 2016). SIBs have the advantages of high sodium abundance and low cost as well as its safety (Zhao et al., 2017). To enable sodium ion technology, a lot of efforts have been focused on to explore sodium host materials that have adequate electrochemical capacity and reversibility for battery applications.