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STRUCTURAL, ELECTRONIC, MAGNETIC AND OPTICAL PROPERTIES OF Zn-Ni-Co TERNARY SPINEL OXIDE BASED Co_3O_4 BY USING DENSITY FUNCTIONAL THEORY WITH HUBBARD U (DFT+U) FOR SUPERCAPACITORS ELECTRODE

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ABSTRACT

Cobalt oxide, Co_3O_4 is a magnetic semiconductor containing cobalt ions, Co^{2+} and Co^{3+} at tetrahedral and octahedral sites respectively. It is considered a good electrode material for supercapacitors due to possessing of redox reversible behaviour. Unfortunately, Co_3O_4 is suffering from inferior ion transport kinetics and poor electrical conductivity, which can affect the rate capability and cycling stability of the electrodes. Modifying the spinel Co_3O_4 via doping with other 3*d* transition metals could offer a rich redox reaction, hence can improve the performance of the electrode. This thesis presents the theoretical work for zinc-nickel-cobalt (Zn-Ni-Co) ternary oxide from metal (*M*)- doped Co_3O_4 (*M*=Ni, Zn) by using density functional theory (DFT) that has been implemented in Cambridge Serial Total Energy Package (CASTEP) software code to calculate the structural, electronic, magnetic and optical properties. It is started with the cubic spinel Co_3O_4 where the findings on structural parameters show Co_3O_4 is calculated to be in antiferromagnetic (AFM) with cation (Co^{2+}) magnetic moment of 2.37μ. The band gap of Co_3O_4 obtained (0.11eV) is severely underestimated with respect to the experimental value. Thus, the inclusion of the Hubbard U (DFT+U) method can give a better description of the cobalt localized *d* states. From optical properties, it is predicted that the electron transition occurs between *p-d* and *d-d* orbital. The second part involves is Ni-doped Co_3O_4 ($NiCo_2O_4$) and Zn-doped Co_3O_4 ($ZnCo_2O_4$) to form binary metal oxide. Due to spinel structure exhibiting two sites, the cation distribution namely *x*=0 (normal spinel) and *x*=1 (inverse spinel) of doped metal among tetrahedral and octahedral must be considered first. It is important due to the cation distribution greatly influences the properties of the material, especially the electronic properties. The findings show the $NiCo_2O_4$ is energetically favourable in inverse spinel meanwhile $ZnCo_2O_4$ is a normal spinel structure. From band gap and density of states analysis, $NiCo_2O_4$ has transformed from semiconductor to half-metallic behaviour meanwhile $ZnCo_2O_4$ remains as a semiconductor. Among these two metal-doped, the $NiCo_2O_4$ are greatly improved the electrical conductivity due to the occurrence of the exchange interaction between Ni 3*d* states with Co 3*d* states. To form the ternary oxide, the co-doped Zn into $NiCo_2O_4$ with different doping ratios (x=0.25,0.50 and 0.75) were calculated. The introduction of Zn has provoked atomic bonding and structure. From the density of states analysis, the value near the Fermi level at higher doping ratio x=0.75, namely $Ni_{1.0}Zn_{0.75}Co_{1.25}O_4$ (16.13electron/eV) has increased from binary oxide, $NiCo_2O_4$ (12.30electron/eV). Such an increase of this value leads to enhancement the electrical conductivity. It can reasonably explain its low resistance consequently enhancing the supercapacitive performances. Overall, the first-principles study in this work from the deepest level of atomic-scale scope can describe the properties of materials and may improve the understanding of supercapacitors.

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CHAPTER ONE
INTRODUCTION

1.1 Research Background

The huge capital costs of managing inflated demands from renewable energy sources have offered the introduction of high-efficiency electrical energy storage (EES) capabilities. The role of EES devices is to store maximum energy at off-peak rates and release it when needed in consequence can lowering the electricity supply costs. The supercapacitors have been appointed as EES and categorized as power quality and reliability EES due to some energy parameters ie: rapid charge/discharging time, very high cycle efficiency >90%, high power density, greater lifetime and high cycling stability (>10,000 cycles) [1]. The scientific community is striving to develop and design the electrode material in supercapacitors to improve its energy and power density for use in a broad range application like automobiles, power backup systems, wind turbine and many more.

In recent times, transition metal oxides (TMOs) have attracted vast attention as electrode material for use in supercapacitors due to its high electron storage capability and emissivity through a chemical redox reaction. Various metal oxides have been devoted as electrode materials like RuO_2, MnO_2, SnO_2, Co_3O_4 and etc [2]–[4]. They exhibited high theoretical specific capacitance in the range of (~1000-3900 Fg^{-1}) depending on the material with excellent electrochemical behaviour. Despite their benefits, intensive studies were conducted on cost-effective metal oxide for commercialization planning including the spinel cobaltite material of cobalt oxide, Co_3O_4. The excellent chemical behaviour and controllable nanostructures of Co_3O_4 are the interesting features therefore suitable for use in supercapacitors [5]–[7]. Nevertheless, Co_3O_4 is suffer from slow electrochemical reaction kinetics and poor electrical conductivity which affected to electrochemical performance of rate capabilities and cycling stability [8]. These drawbacks are also causing greatly hinder in reaching the high theoretical specific capacitance of Co_3O_4 (3000-3900 Fg^{-1}).