Structural and electronic properties of nickel doped cobalt oxide electrode for supercapacitors: A first principle study

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Abstract. On the basis of ab initio calculation, we reported the structural and electronic properties of the nickel (Ni) substitution on the cobalt oxide (Co3O4) to produce nickel cobaltite (NiCo2O4) using generalized gradient approximation + U parameter (GGA + U) calculation method. The spinel NiCo2O4 with half-metallic behaviour has a relatively small band gap ~0.64eV which is spotted decreased from pure Co3O4 band gap 1.26eV. This is due to nickel doping decreased the band gap which also implies that an increase in electrical conductivity. Owing to good electrical conductivity, NiCo2O4 thus enables to be considered for application in supercapacitor. Analysis of the partial density of states (PDOS) shows the differences contributions of cobalt (Co) at the tetrahedral site (Td) and Ni at the conduction bands: Co(Td) ions not affected the majority spin which is in contrast with Ni ions.

1. Introduction
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 supercapacitor has appointed as EES and categorized as power quality and reliability EES due to some energy parameters i.e. rapid charge/discharging time, very high cycle efficiency (>90%), high power density, greater lifetime and cycle life [1,2]. Supercapacitor are considered as candidates to bridge the power performance gap between capacitors and batteries. It is differed by ways of storing energy which is fast surface redox reactions (pseudocapacitance) or ion adsorption at the double layer. The main role takes place in supercapacitor mechanism whereby can achieve great energy parameters is electrode material. Thus, develop and designing the electrodes is an urge to meet the requirement. Metal oxide has extensively studied for supercapacitor electrode materials due to its higher specific capacitance from surface redox reaction. Various metal oxides have been devoted as electrode material in supercapacitor like ruthenium(IV) oxide (RuO2), manganese(IV) oxide (MnO2), tin(IV) oxide (SnO2), cobalt oxide (Co3O4) and etc [3–6]. Among the metal oxides, RuO2 has found to be an excellent...
electrode owing to superior supercapacitive performance with high specific capacitance (1580 F g\(^{-1}\)) and high conductivity. Despite these advantages, for commercial extensive occurs the limitation because of the high cost of RuO\(_2\). Thus, the cost-effective metal oxide, Co\(_2\)O\(_4\) offer excellent chemical behaviour and environmentally friendly were exploited as the alternative [7]. Somehow, Co\(_2\)O\(_4\) suffer from poor electronic conduction and have no capacitive feature as good as RuO\(_2\).

By modifying the single-component metal oxide into ternary metal oxide exhibited in a formula A\(_x\)B\(_{3-x}\)O\(_4\) represent (A: tetrahedral, B: octahedral) where A and B is signified by two different transition metals occur in one structure provide a rich redox reaction consequently to enhance the electrical conductivity. Single crystal of cobalt oxide doped with nickel resulting in a significant increase of electrical conductivity while maintaining the spinel structure. Nickel cobaltite (NiCo\(_2\)O\(_4\)) is such a worthy material with fascinated features of greater conductivity (0.12 S cm\(^{-1}\)) [8], great rate capability and cycling stability [9,10], low toxicity and low cost. The various method has been adopted in the synthesis of NiCo\(_2\)O\(_4\) like chemical precipitation [11], sol-gel [12] and hydrothermal [13]. In details, NiCo\(_2\)O\(_4\) is a mixed-valence oxide derivable by nickel (Ni) doping into normal spinel Co\(_2\)O\(_4\) that Ni occupies exclusively in octahedral site while cobalt (Co) ions are distributed over both octahedral and tetrahedral sites. NiCo\(_2\)O\(_4\) is considered an inverse spinel structure with the cation distribution in mixed-valent expressed as Co\(_{x_2}^{2+}\)Co\(_{3-x_2}^{3+}\)[Co\(_{3}^{2+}\)Ni\(_{1-x_2}^{3+}\)Ni\(_{3}^{2+}\)]O\(_4\). In this work, the theoretical works have done in order to have a better understanding of the structural and electronic properties for Co\(_2\)O\(_4\) as parent metal oxide and NiCo\(_2\)O\(_4\) based on first-principle calculation.

2. Computational details

First principle calculation was performed with the Cambridge Serial Total Energy Package (CASTEP) implemented in Material Studio 2016 using pseudopotential method which is based on density functional theory (DFT). The NiCo\(_2\)O\(_4\) crystal structure was built by substituting Ni with Co atom in Co\(_2\)O\(_4\) crystal structure. Thus, Co\(_2\)O\(_4\) need to optimize first. For geometry optimizations are calculated using exchange-correlation functional by Ceperley and Alder [14] as parameterized by Perdew and Zunger [15] for local density approximation (LDA-CAPZ) and semi-local generalized gradient approximation (GGA) exchange-correlation functional of the Perdew-Wang91 [16] (PW91), Perdew-Burke-Ernzerh [17] (PBE) and for solids [18] (PBEsol). The calculation was carried out on a spinel cubic cell containing 56 atoms (8A, 16B and 32O). The plane wave cut off was chosen to be 380eV to ensure acceptable precision and 4x4x4 k-point grids were used in the geometry optimization of the bulk structure. The density mixing parameters of charge density mixing amplitude, cut off energy for mixing and charge density mixing g-vector were 0.5000, 300.0eV and 1.5001 Å\(^{-1}\), respectively. From the parent Co\(_2\)O\(_4\) then appropriate substitution of Co by Ni atom are made. The inclusion of Hubbard (U\(_{eff}\) = Co (2.5eV) and Ni (4.6eV)) is included in calculation to corrected highly 3d orbital.

3. Result and discussion

3.1 Structural properties

Co\(_2\)O\(_4\) is normal cubic spinel crystallizes structure with space group of (227 Fd\(_{3}\)m). Two oxidations stated occurs in Co\(_2\)O\(_4\) which are divalent (Co\(_{2+}\)) and trivalent (Co\(_{3+}\)) exhibit at the tetrahedral AO\(_2\) and octahedral BO\(_6\) coordination. The percentage difference of lattice parameters optimized with the experimental values using different functional is compared as shown in figure 1(a). As resulting of Co\(_2\)O\(_4\) calculated using the LDA-CAPZ functional differ with calculated using the GGA functional: lattice parameters using LDA-CAPZ functional are underestimates while GGA functional overestimates. Hence, among the tested functional, GGA-PBEsol shows the best agreement with the crystallographic parameters with the percentage difference is less than \(\sim\)1%. XRD pattern from calculated Co\(_2\)O\(_4\) is shown in figure 1(b) displays all diffraction peaks are consistent with the experimental standard. The crystal structure of Ni substituted over the octahedral site to obtain NiCo\(_2\)O\(_4\) is shown in figure 2. As the comparison, the lattice constant of Co\(_2\)O\(_4\) obtained is 8.088 Å while the computed lattice constant of NiCo\(_2\)O\(_4\) is 8.192 Å, which is detected increase by 1.2%. Table
1 displays the result obtained in this work is consistent with other reports by experimental and theoretical study.

Figure 1. (a) Percentage difference of lattice parameters $\text{Co}_3\text{O}_4$ using different local functional with respected to the experimental values Ref.[19]$^a$, Ref.[20]$^b$, Ref.[21]$^c$ , (b) calculated XRD patterns of $\text{Co}_3\text{O}_4$
Figure 2. Crystal structure of NiCo$_2$O$_4$ with Co atom (green) and nickel atom (orange) substitute on octahedral site, Co(Oh).

Table 1. Details on lattice parameter and volume of NiCo$_2$O$_4$.

|                      | Calculated (this study) | Experimental Ref. [22] | Theoretical Ref. [23] |
|----------------------|-------------------------|------------------------|-----------------------|
| Lattice constant (Å) | 8.192                   | 8.114                  | 8.152                 |
| Volume ($Å^3$)       | 538.61                  | -                      | -                     |

3.2 Electronic properties

The band diagram with certain symmetry direction applied in a crystal structure within Brillouin zone at the point W (0.500, 0.250, 0.750), L(0.500, 0.500, 0.500), G(0.000, 0.000, 0.000), X(0.500, 0.000, 0.500), and K(0.375, 0.375, 0.750) has explicitly demonstrates in figure 3 and 4 for Co$_3$O$_4$ and NiCo$_2$O$_4$ respectively. It is seen that the band structure of NiCo$_2$O$_4$ is slimmer and flatter along the symmetry points compared to Co$_3$O$_4$. It is feasible for thermal excitations to raise electrons to the conduction band hence responsible to the electrical conduction. The detailed of the band structure of NiCo$_2$O$_4$ is shown in figure 4(a) and (b). It is perceived at the Γ-Γ direction, the band gap obtained about ~0.64eV for the majority spins states. Meanwhile, the appearance of strong dispersion at minority spin bands especially across the Fermi level displayed.

Figure 3. Calculated total band structures for Co$_3$O$_4$ obtained by PBEsol+U functional. Fermi energy is set to 0.
The total density of states (DOS) of Co$_3$O$_4$ and NiCo$_2$O$_4$ structure with different spin states for a majority and minority or known as spin up and spin down, shown in figure 5(a) and (b) respectively. For Co$_3$O$_4$, the peaks attributed to Co 3$d$ state clearly show the differences of the valence band and conduction band. Meanwhile, for NiCo$_2$O$_4$, the valence bands for spin up channels shifted towards the Fermi level and in spin-down channel seem crossed the Fermi level. The calculated band gap of Co$_3$O$_4$ is 1.26 eV. At spin-up channel of NiCo$_2$O$_4$ resulting in a relatively small energy gap 0.64 eV. Therefore, the decrease of the band gap implying the higher electrical conductivity of NiCo$_2$O$_4$ achieved than Co$_3$O$_4$ via substitution of Co(oct) with Ni in Co$_3$O$_4$. It is in agreement with the fact that the band gap is inverse with electrical conductivity [24]. In addition, it is found that at spin up channel, the NiCo$_2$O$_4$ remains unchanged semiconductor contrary to spin down channel becomes conducting specify that the Ni doping has affected Co$_3$O$_4$ transform from semiconductor material to semi-metallic. The partial densities of states PDOS of NiCo$_2$O$_4$ (figure 6) may provide a further understanding of Ni(oct) and Co(Td) contribution into the conductivity.

![Figure 4. Band structure at spin state (a) majority and (b) minority of NiCo$_2$O$_4$ calculated using functional PBEsol+U](image)

![Figure 5. Electronic density of states (DOS) of Co$_3$O$_4$ (a) and NiCo$_2$O$_4$ (b) with references valence band maximum set at 0eV.](image)
It is observed only spin down electron of Ni on octahedral site and Co on tetrahedral site crossed the Fermi level. This strongly agrees the presence of Ni (B sites) cause to electron hopping to the Co (A site) or called as exchange interaction greatly influence the conductivity. In short, the main influence of the changes in minority spin channel after doping Ni is originated from Ni and Co(Td) as well as O ions. This result also consistent with appearance of a significant hybridization between 3$d$ metal and oxygen 2$p$ orbitals. It is believed that NiCo$_2$O$_4$ exhibit the ferrimagnetic properties of this material.

![Graph showing partial density of states (PDOS) of NiCo$_2$O$_4$ with shaded region represent Co at the tetrahedral site, blue (spin up) and green (spin down) line represent Ni at octahedral site.](image)

Figure 6. Partial density of states (PDOS) of NiCo$_2$O$_4$ with shaded region represent Co at the tetrahedral site, blue (spin up) and green (spin down) line represent Ni at octahedral site.

4. Conclusions
The present approach by first principle calculation has shown a great method to understand the material of Co$_3$O$_4$ and NiCo$_2$O$_4$. The substitution of Ni atom at the octahedral site with Co atom which has almost similar size causes the change in lattice parameter and electronic properties. Hence, this effect could improve the electrochemical performance of supercapacitor. Our results show that Ni dopant in Co$_3$O$_4$ turns the material into half-metallic. DOS results show that the lower band gap ~0.64eV for NiCo$_2$O$_4$ subsequently increasing the electrical conductivity. This is reasonably explained for NiCo$_2$O$_4$ to be exploited for supercapacitor application.

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