The effect of addition Ni$^{2+}$ to Cr$_2$O$_3$ and its potential characterization as anode potassium ion battery

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Abstract. Potassium ion battery (PIB) is an alternative to replace Lithium ion battery (LIB). In this study, amount of Ni$^{2+}$ is added to substitute of Cr(III) on Cr$_2$O$_3$. The purpose of this study is to determine the effect of adding Ni$^{2+}$ ions to Cr$_2$O$_3$ and to test its potential as anode of PIB. Synthesis used the coprecipitation method followed by calcination at 700°C for 12 hours. The results showed that the Cr$_2$O$_3$ - NiCr$_2$O$_4$ composites were formed when the addition of Ni$^{2+}$ was 0.25; 0.50; and 0.75 mole with the most dominant amounts of NiCr$_2$O$_4$ in the addition of 0.50 mole Ni$^{2+}$. Cyclic voltammetry analysis of addition of 0.50 mole of Ni$^{2+}$ to the Cr$_2$O$_3$ shows that the material has an reduction potential of +0.0344 V and an oxidation potential of +0.587 V. NiCr$_2$O$_4$/Cr$_2$O$_3$ material has the potential as anode material for PIB.

Keywords: potassium ion battery, anode, Cr$_2$O$_3$, NiCr$_2$O$_4$

1. Introduction

The lithium ion battery (LIB) is a battery that is used widely as battery for cell phones, cameras, and laptops. However there are limitations to this battery, such as the abundant of lithium in earth crust is very small (< 20 ppm) and only spreads in China, South America, and United States of America (USA). This will increase the production cost and the selling price of LIB[1-2]. Because of the limitations of the LIB, the better alternative is needed, such as potassium ion battery (PIB). This PIB has many advantages, the battery can be used in electrolytes instead of water, and has a potential voltage 0.15V higher than LIB. The potential standard of K$^+$/K is quite low compared to Li and Na in non water electrolytes[3]. When the graphite anode is applied to Sodium Ion Battery (NIB) show results low battery capacities. This is can occurred because the sodium ions can’t be intercalated to graphite and formed intercalated graphite. Intercalation is the reversible insertion ions or molecules into a material with layered structure. In other hand, potassium ions has potential standard lower than sodium ion and the potential standard value of potassium ion is close with lithium ion[1,4].
It has been reported regarding the storage of potassium ions in various anodes, such as carbon-based anodes, metal alloys, organic materials, and oxide materials [5].

The electrochemical reaction in PIB anode depends on the ability of the reversible which is closely related to ion diffusion and the rate of electrons. In contrast to the intercalation – deintercalation reaction that occurs in the cathode, the anode material exhibits a variety of storage mechanism, including intercalation – deintercalation process, conversion reaction, precipitation reaction, and a series of intercalation to precipitation reaction [6-7]. Anode doesn’t determine the capacity and potential of PIB, but plays role in determining the life cycle and the safety of battery usage [8].

Chromium oxide is the one of important transition metal oxide. There are several forms of chromium oxide that have been reported, CrO₂, CrO₃, CrO₄, Cr₂O₅, Cr₂O₇, and the most stable is Cr₂O₃. This oxide is very important because this oxide can be applied to many fields, for example as a color pigment, catalyst, coating agent, hydrogen storage material, gas sensor, solar energy applications, and as electrode material for lithium battery [9-10].

Cr₂O₃ is an oxide that has potential as battery anode because it has high theoretical storage capacity (~ 1058 mAhg⁻¹). On the other hand, like the other metal oxide materials, in practical use as anode battery, Cr₂O₃ has the disadvantages of low electronic conductivity and severe crystal volume changes in the battery cycle, which causes periodic capacity fading and the death of battery cycle [11]. This led to the emergence of new ideas to overcome the deficiencies and to improve the electrical performance of Cr₂O₃, which is the doping method.

Doping method can be performed using several transition metal ions, which one is Ni²⁺. This Ni²⁺ ion is an efficient dopant for metal oxide materials, especially for increase the electrical properties [12-13]. The Ni²⁺ that added to metal oxide material will reduce the crystal size of the oxide material. If the crystal size get smaller, it will expand the surface of the crystal and produce strain on the crystal which causes structural disturbance and changes the conductivity and reactivity of the oxide compound. This is suitable with the result of study by Mohanapandian dan Krishnan (2014) that observed the effect of addition Ni²⁺ into Cr₂O₃ materials with variation 0.025, 0.050, and 0.075 mole using the solvothermal method. The researchers observed the addition effect of Ni²⁺ on the electro conductivity at the several temperatures. The study showed that the Ni²⁺ ion that added to Cr₂O₃ will decreased the crystal size and strongly influence on the conductivity and reactivity of oxide compound [14].

In this study, the NiCr₂O₄ compound was synthesized using a simple coprecipitation method and observed the effect of addition Ni²⁺ on the Cr(III) potential as anode of PIB. The addition of Ni²⁺ is expected to increase the electro conductivity of Cr₂O₃ and show its potential as anode material of PIB. Therefore, this study conducted with purpose to determine the effect of adding Ni²⁺ ions to Cr₂O₃ and to test its potential as anode of PIB.

### Table 1. Comparison of lithium, sodium, and potassium ions

|                | Li⁺ | Na⁺ | K⁺ |
|----------------|-----|-----|-----|
| Atom Mass      | 6.94| 22.9| 39.09|
| Atom radius (Å) | 0.76| 1.02| 1.38|
| Melting point (°C) | 180.5| 97.7| 63.4|
| Abundance (% mass) | 0.0017| 2.3| 1.5|
| E° vs. SHE (V)  | -3.04| -2.71| -2.93|
| Desolvation energy in propylene carbonate (kJ mol⁻¹) | 215.8| 158.2| 119.2|
| Graphite capacity in theory (mAh g⁻¹) | 372| 279|
2. Material and Method

2.1. Preparation of oxide compound
Synthesis of NiCr$_2$O$_4$ compounds using a simple coprecipitation method [15] was carried out with variations of Ni = 0.25, 0.50, and 0.75 mole. This synthesis was initiated by dissolving NiCl$_2$·6H$_2$O, CrCl$_3$·6H$_2$O, and KOH into demineralized water with the mol ratio (1:1:6). The mixture was stirred for two hours and thirty minutes. After stirring, the mixture is filtered and the precipitate obtained is washed until it is free from chloride ions using demineralized water then dried at room temperature [16]. When the precipitate is dried, the precipitate is heated at 700°C for 12 hours.

2.2. Characterization
The sample powder was analyzed using SEM-EDX (FEI type INSPECT-S50), FT-IR (Shimadzu Type FT-IR 8400S) at wave numbers 400 – 4000 cm$^{-1}$, dan XRD (Panalytical XPert Pro) at range 2θ 10 - 90° and wavelength 1.54059 nm.

2.3. Electrochemical Performance
The electrochemical performance of the sample was tested using cyclic voltammetry. The oxide compounds are made into working electrode using additives in the form of PVDF and NMP with ratio 8:1:1. Tests were carried out using KOH electrolyte at a voltage of 0 – 3 V.

3. Results and Discussion
The synthesis of oxide compound from precursors NiCl$_2$·6H$_2$O, CrCl$_3$·6H$_2$O, and KOH with ratio 1:1:6 in demineralized water with mole variations of Ni$^{2+}$ produces a greenish-blue solid, the more ion Ni$^{2+}$ is used, the more blue at the solid it can be seen in the figure 1. After heating, the oxide compound will turn to black. Furthermore, this oxide compound will be characterized and tested for its electrochemical performance.

![Figure 1](image)

Figure 1. Oxide Compounds with addition of Ni$^{2+}$ (a) 0.25 mol, (b) 0.50 mol, dan (c) 0.75 mol

3.1. SEM
In the analysis with SEM, the morphology of oxide compound formed can be shown in figure 2 and 3.
Figure 2. Results of analysis by SEM at 50,000x magnification of the sample (a) mole variation of Ni$^{2+}$ 0.25 mole, (b) mole variation Ni$^{2+}$ 0.50 mole, (c) mole variation of Ni$^{2+}$ 0.75 mole.

Figure 3. Results of analysis by SEM at 100,000x magnification of the sample (a) mole variation of Ni$^{2+}$ 0.25 mole, (b) mole variation Ni$^{2+}$ 0.50 mole, (c) mole variation of Ni$^{2+}$ 0.75 mole.

Based on figures 2 and 3, it can be observed the shape of oxide compound is oval. In the figure 3(b), it can be observed that there is no agglomeration because it can be clearly observe the morphology of oxide compound.

3.2. FT-IR

FT-IR analysis is used to identify covalent bonds that occur in the oxide compound. These covalent bonds will vibrate and it will produce distinctive peaks at the certain wavenumbers so that it can produce an FT-IR spectrum. The oxide compound spectrum can be seen at figure 4.

Figure 4. The FT-IR spectrum of oxide compound.

According to Bakar[17], the IR spectrum of NiCr$_2$O$_4$ nanoparticles is in the range 280 – 4000 cm$^{-1}$. In the range, peaks appear at a typical wavenumber indicating a metal-oxygen bond, Ni–O at wavenumber about 470 cm$^{-1}$ and Cr–O at wavenumber about 600 cm$^{-1}$ which is a stretching vibration of metal – oxygen bonds[18]. Absorption wavenumber data can be seen in table 2.

| Table 2. Oxide Compound Cr-O and Ni-O wavenumber |
| No. | Mole of Ni$^{2+}$ added (mol) | Wavenumber (cm$^{-1}$) |
|-----|-----------------------------|------------------------|
|     |                             | Ni–O                  | Cr–O                  |
| 1.  | 0.25                        | 470.19                | 594.23                |
| 2.  | 0.50                        | 441.34                | 558.63                |
| 3.  | 0.75                        | 470.19                | 594.23                |
|     | Theoretic                   | 470                   | 600                   |
Based on these data, it can be seen that the oxide compound synthesized is an oxide that contain of Cr and Ni metals, because in the IR spectrums peaks of Ni-O and Cr-O appear at the wavenumber that close with the reference.

3.3. XRD
XRD analysis is carried out to identify the phases of oxide compounds formed. XRD analysis was carried out in the range 2\(\theta\) at 10 - 90° where the peaks would be adjusted to the peaks in the databases in the COD (Crystal Open Database).

![Figure 5. X-ray diffraction patterns of oxide compound](image)

In the XRD analysis, the diffraction patterns of oxide compound matches with the diffraction patterns of Cr\(_2\)O\(_3\) (COD 969016601) and NiCr\(_2\)O\(_4\) (COD 961011031). The match with the diffraction patterns shows the identity of the oxide compounds because this compatibility is seen from the appearance of typical peaks and peak intensity on the same 2\(\theta\). The suitability of this diffraction patterns can be observed in figure 6.

![Figure 6. Comparison of oxide compound diffraction patterns with the databases](image)

In the analysis using the Rietveld method by MAUD, the phase that formed in the oxide compound can be obtained. This analysis is carried out on phases Cr\(_2\)O\(_3\) (COD 969016610), NiCr\(_2\)O\(_4\) (COD 961011031), and NiO (COD 961526381). The mass percentage of the formed phase can be observed in table 3.
Table 3. The mass percentage that formed in the oxide compound

| No. | Mole of Ni$^{2+}$ is added (mole) | Cr$_2$O$_3$ | NiCr$_2$O$_4$ | NiO |
|-----|----------------------------------|------------|----------------|-----|
| 1.  | 0.25                             | 91.15      | 3.02           | 5.82|
| 2.  | 0.50                             | 14.88      | 76.47          | 8.64|
| 3.  | 0.75                             | 80.93      | 6.42           | 12.65|

Based on table 3, the oxide compounds obtained composed of several phases, Cr$_2$O$_3$, NiCr$_2$O$_4$, and NiO which form a Cr$_2$O$_3$/NiCr$_2$O$_4$ composite and it can be seen that the addition of Ni$^{2+}$ ions of 0.50 mole can form a Cr$_2$O$_3$/NiCr$_2$O$_4$ composite with the largest percentage of mass NiCr$_2$O$_4$ compared to other variations.

3.4. Electrochemical Performance

The resulting voltammogram shows the ability of the oxide compounds to react redox. The oxidation reaction that occurs is indicated by the appearance of the $I_{pa}$ peak and the reduction reaction that occurs is indicated by the appearance of the $I_{pc}$ peak. In addition, the voltammogram shows the cell potential value of the redox reaction experienced by the oxide compound so that it can be determined. The voltammogram of the synthesized oxide compound can be seen in the figure 7.

![Voltammogram of Oxide Compound](image)

Figure 7: Voltammogram of Oxide Compound (Cr$_2$O$_3$/NiCr$_2$O$_4$, Ni$^{2+}$ = 0.5 mol) (E vs. log I) in KOH 0.1 M

Based on the voltammogram of the oxide compound, the addition of 0.50 mole Ni$^{2+}$ ions can undergo an oxidation reaction at +0.578 V and a reduction reaction at +0.0344 V towards the Ag/AgCl reference. So that the possible reaction equations can be written in equation 1–3 [19].

$$\text{NiCr}_2\text{O}_4 + 8\text{K}^+ + 8\text{e}^- \rightarrow \text{Ni} + 2\text{Cr} + 4\text{K}_2\text{O}$$  \hspace{1cm} (1)

$$\text{Ni} + \text{K}_2\text{O} \rightarrow \text{NiO} + 2\text{e}^- + 2\text{K}^+$$  \hspace{1cm} (2)

$$2\text{Cr} + 3\text{K}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + 6\text{e}^- + 6\text{K}^+$$  \hspace{1cm} (3)

4. Conclusion

The addition of Ni$^{2+}$ ions to Cr$_2$O$_3$ formed a Cr$_2$O$_3$/NiCr$_2$O$_4$ composite. In the additions of 0.50 mole Ni$^{2+}$ can formed NiCr$_2$O$_4$ with the highest amount, 76.47%. This compound also has potential as PIB anode with a reduction potential at +0.0344 V and oxidation potential at +0.578 V.
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