Synthesis and Characterization Complex Compound of $K_3[Fe(SCN)_6]$ and Copper(II) Chloride as K-Ion Battery Electrode

Wiwin Dwi Jayanti, Subakti, I Wayan Dasna

1 Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia.
2 Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia.

*Corresponding author’s email: idasna@um.ac.id

Abstract: Besides lithium-ion battery (LIB), potassium-ion battery is also potentially developed as an alternative battery with cheaper and more secure battery. The synthesis of complex compounds of KCu[Fe(SCN)$_6$] was conducted using a direct reaction method. The characterization of complex compounds was conducted through melting point, SEM-EDX and FTIR instrumentation, electrical conductivity, and cyclic voltammetry. The complex of $K_3[Fe(SCN)_6]$ has melting point 92-95 °C, electrical conductivity of 714 µS, and indicated an ionic compound. The characterization with SEM-EDX and FT-IR instruments showed the empirical formula of complex compounds was KCu[Fe(SCN)$_6$]. The cyclic voltammetry analysis shows the complex as potassium-ion battery cathode material.

Keywords: Potassium-ion battery, complex compounds, cathode material, KCu[Fe(SCN)$_6$]

1. Introduction
The demand for energy storage material increases along with the development of electronic devices, electric vehicles, and large-scale energy storage systems. International Energy Outlook 2016 has been released by the US Energy Information Administration estimates that world energy use will grow by 48% between 2016 to 2040 [1]. Along with the development of technology, the storage of electrical energy that is Lithium-ion Battery (LIB) is increasing. However, the problem is whether the global Li reserves 16 million tons can meet the increased demand for large-scale application [2]. This raises concerns about the availability of Li in the future because the Li element is a limited element on earth. Its limitation becomes one of the causes that makes production cost of LIB is high due to the price of material that is expensive [3].

Another alternative of LIB is Potassium-ion Battery. This secondary battery is known as K-ion Battery (KIB) [4]. The abundance of potassium resources in ocean and crust is higher than lithium, which is in the earth's crust is 1.5: 1.7x10$^{-3}$ % and in the ocean is 4.2x10$^{-2}$: 1.8x10$^{-5}$ %.
Besides that, potassium has a standard reduction potential that approaching lithium, which is only a difference of 0.12 V [5].

The research results indicate that complex compound of Prussian Blue can be used cathode material for lithium-ion battery [6-9]. KIB successfully made by using complex compounds based on Prussian Blue that was KFe[Fe(CN)₆] [4], KCr[Fe(CN)₆] [10], KCu[Fe(CN)₆] [11] and KNi[Fe(CN)₆] [12]. The complex compound had a cubic structure with K⁺ ion within the cavity cube [13]. KIB was composed of several main components. First, the KIB anode used KC₈ compound (potassium graphite). Second, the KIB electrolyte used a molten compound of KBF₄. Third, the KIB cathode used a complex compound of KFe[Fe(CN)₆] [14].

This study used two metals that were Fe(III) and Cu(II) reacted with the ligand of thiocyanate ion (SCN⁻). Based on the theory of HSAB [15], metal ion Fe³⁺ could be synthesized with SCN⁻ ion then integrated with Cu²⁺ metal ion. Integration of metal ion Cu²⁺ intended that the electrical capacitance owned by the larger complex compound. The innovation in this study was replacing the ligand of cyanide ion (CN⁻) with a ligand of thiocyanate ion (SCN⁻), so that resulted complex compounds based “Prussian Blue Like” that was KCu[Fe(SCN)₆]. The use of ligand of thiocyanate ion was based on the bond that was longer than the cyanide ion lattice so that pores were formed to be larger. The larger the lattice pores, the greater the mobility of K⁺ ion, consequently, the resulting complex became more stable.

2. Methods
The complex compounds of KCu[Fe(SCN)₆] was synthesized by heating the KSCN salt (18 mmol; 1.7492 g) on 175 °C to melt then added FeCl₃.6H₂O (3 mmol; 0.8254 g) and then heated at 175 °C for 30 minutes. Eerie black solids obtained. This solid dissolved in 40 mL methanol and filtered with a fine filter paper. The residue in the form of a white solid was then tested with an AgNO₃ solution [16]. The test results showed that the solids were KCl. While the red filtrate was collected in a beaker and evaporated at a temperature of 70 °C with stirred on 600. The results showed that the red filtrate was KCu[Fe(SCN)₆]. CuCl₂.2H₂O (3 mmol; 0.5116 g) added to K₃[Fe(SCN)₆] solution and heated at 64 °C with the reflux method [13] for 8 hours. The red-purple solution was obtained. The solution was filtered with a fine filter paper. The resulting residue in the form of a white solid was then tested with an AgNO₃ solution. The test results showed that the solids were KCl. While the resulting red-purple filtrate was collected in a beaker and evaporated at a temperature of 70 °C with 700 rpm stirring with a magnetic stirrer. The results of evaporation are in the form of a Light black solid.

The complex compounds characterized included the melting point test, SEM-EDX analysis, XRD analysis, FT-IR analysis, test electrical conductivity, and cyclic voltammetry test. Melting point test was conducted by placing the crystals synthesized above hotplate Fischer Scientific. The crystals then heated by raising the temperature gradually with 10 °C temperature range. The eest of electrical conductivity (EC) was conducted by measuring the conductivity solution of complex compounds synthesized, methanol, KSCN solution, FeCl₃ solution, and CuCl₂ solution. The SEM-EDX analysis was conducted by placing the crystal of the complex compound on pin coated with silver liquid and then dried. After that, the sample was inserted into the vacuum sputter coater air and sprayed with gold plasma sample order more conductive to the electron radiation of SEM-EDX instruments. The FT-IR analysis aimed to determine the functional groups of the ligand in the complex compounds synthesized. The FT-IR analysis was conducted by synthesizing and crushing the KBr crystals, then the powder was placed on top of the pellets and analyzed.

3. Results and Discussion
The synthesis of complex compounds of KCu[Fe(SCN)₆] from K₃[Fe(SCN)₆] and CuCl₂.2H₂O with reflux method resulting light black solid are shown in Figure 1. The characterization of KCu[Fe(SCN)₆] included the melting point test, analysis of SEM-EDX, FT-IR analysis, test
electrical conductivity, and cyclic voltammetry test. The results of melting point measurement reactants and the complex compound of KCu[Fe(SCN)₆] are shown in Table 1.

Table 1. The Result of Melting Point Test

| Compound                      | Melting Point (°C) |
|-------------------------------|-------------------|
| KSCN                          | 175-177           |
| FeCl₃.6H₂O                    | 39-40             |
| CuCl₂.6H₂O                    | 102               |
| K₃[Fe(SCN)₆]                  | 72-75             |
| The complex compound KCu[Fe(SCN)₆] | 92-95            |

The melting point of a complex compound of KCu[Fe(SCN)₆] is 92-95 °C, these data demonstrated that the complex compound synthesized was a new compound because it was different from the melting point of the reactant. The melting point of KSCN, CuCl₂.2H₂O, FeCl₃.6H₂O are 173, 37, and 100 °C [17]. The results of the SEM analysis of the solid surface morphology of complex compounds K₃[Fe(SCN)₆] is shown in Figure 3. The results of the SEM analysis of the solid surface morphology of complex compounds KCu[Fe(SCN)₆] are shown in Figure 4.

![Figure 1. The complex compounds of KCu[Fe(SCN)₆] prepared by the direct reaction method](image1)

![Figure 2. The morphology of complex compounds K₃[Fe(SCN)₆]](image2)
Figure 3. Morphology of complex compounds $\text{KCu}[\text{Fe(SCN)}_6]$.

Table 2. The Content of Complex Compound Element that Resulted from EDX Analysis and Theoretically

| Element | % Mass (% Wt) | % Atom (% At) |
|---------|---------------|---------------|
|         | EDX           | Theoretical   | EDX           | Theoretical   |
| K       | 25.46         | 22.46         | 14.85         | 13.64         |
| Fe      | 11.19         | 10.75         | 04.57         | 04.54         |
| N       | 15.81         | 16.12         | 25.75         | 27.27         |
| S       | 29.83         | 36.85         | 21.22         | 27.27         |
| C       | 17.71         | 13.82         | 33.62         | 27.27         |

The percentage of mass and atomic percentage of K, Fe, and S obtained from EDX analysis were almost equal to the theoretical percentage. The atomic percentages of K, Fe, and S were respectively 14.85%; 4.57%; 21.22%. These percentages could be determined the atomic ratio with the smallest atomic percentage that was equal to 3: 1: 6. Comparison to the nitrogen atom is rounded up for EDX instrument was only sensitive to many-electron atoms, so EDX less sensitive to electron atoms or atomic mass slightly less than 12 amu [17]. The empirical formula for this complex compound is $\text{K}_3[\text{Fe(SCN)}_6]$.

The EDX analysis of complex compound with mole ratio reactant $\text{K}_3[\text{Fe(SCN)}_6]$; $\text{CuCl}_2$.2$\text{H}_2\text{O}$ = 1:1 resulted in mass percentage (%Wt) and the atomic percentage (%At) of composer complex elements. The mass percentages stated comparison of the total number of complex composer atom. While the atomic percentage was the ratio of the number atom in states of complex compounds that could be used to determine the empirical formula. The results of EDX and theoretically consecutive are displayed in Table 3.

The percentage of mass and the atomic percentage of K, Fe, Cu, and S obtained from EDX analysis were almost equal to the theoretical percentage. The atomic percentage of K, Fe, Cu, and S were respectively 4.16%; 4.08%; 3.88%; 23.98%. These percentages could be determined the atomic ratio with the smallest atomic percentage that was equal to 1: 1: 1: 6. The comparison to the nitrogen atom is rounded up for EDX instrument was only sensitive to many-electron atoms, so EDX is less sensitive to electron atoms or atomic mass is slightly less than 12 amu [17]. The empirical formula for this complex compound is $\text{KCu}[\text{Fe(SCN)}_6]$. 

Table 3. The Content of Complex Compound Element that Resulted from EDX Analysis and Theoretically

| Element | % Mass (% Wt) | % Atom (% At) |
|---------|---------------|---------------|
|         | EDX           | Theoretical   | EDX           | Theoretical |
| K       | 07.31         | 7.71          | 04.16         | 4.76        |
| Fe      | 10.36         | 11.02         | 04.08         | 4.76        |
| Cu      | 11.08         | 12.53         | 03.88         | 4.76        |
| N       | 11.53         | 16.58         | 18.32         | 28.57       |
| S       | 34.56         | 37.95         | 23.98         | 28.57       |
| C       | 24.28         | 14.21         | 44.97         | 28.57       |
| Cl      | 00.98         | -             | 00.61         | -           |

The FT-IR analysis aimed to determine the donor atom and the functional group on the ligand. The results of the analysis in the form of the spectrum provide information about the number of waves and the typical absorption bands for each functional group. The IR spectrum of complex compounds synthesized is shown in Figure 5.

The FT-IR showed a C-N stretching vibration (M-NCS) on wavenumber of 2086.19 cm⁻¹ [18,19], C-N stretching vibration (KSCN) on wavenumber of 945.12 cm⁻¹ [20]. H-O-H bending vibration of water on wavenumber of 1610.56 cm⁻¹ and O-H stretching vibration on wavenumber of 3178-3500 cm⁻¹ [21]. Based on these data, the thiocyanate ligand coordinates with metal ion through N donor atom and shows the presence of H₂O bonds in the complex compound of KCu[Fe(SCN)]₆.

Test the electrical conductivity (EC) was conducted to determine ionic or molecular complex compounds of KCu[Fe(SCN)]₆. EC measurement results are shown in Table 4. EC of complex compounds KCu[Fe(SCN)]₆ is 714 µS. EC value of the complex compound is higher than the solvent. Based on this data, the complex compound of KCu[Fe(SCN)]₆ is ionic compounds because EC of KCu[Fe(SCN)]₆ is higher than solvent.
Table 4. The Electrical Conductivity Test Results

| Compound            | Electrical conductivity (µS) |
|---------------------|-----------------------------|
| FeCl₃.6H₂O          | 336                         |
| CuCl₂.2H₂O         | 243                         |
| KSCN                | 567                         |
| K₂[Fe(SCN)₆]       | 1418                        |
| KCu[Fe(SCN)₆]      | 714                         |
| Methanol            | 3                           |

The cyclic voltammetry test aimed to determine the potential of complex compounds synthesized as K-ion battery. The electrochemical measurements were performed in flooded three-electrode cells containing an electrolyte of aqueous 1 M KNO₃ and 0.01 M HNO₃, a working electrode containing KCu[Fe(SCN)₆], an Ag/AgCl reference electrode, and counter electrode [11]. The voltammogram complex compounds of KCu[Fe(SCN)₆] synthesized are shown in Figure 5.

Figure 5. The voltammogram complex compounds of KCu[Fe(SCN)₆]

Based on the voltammogram, the complex compound of KCu[Fe(SCN)₆] experienced oxidation reaction characterized by anodic peak. The oxidation reaction which occurs at 1.42 volt. The potential oxidation reaction of KFe[Fe(CN)₆] is 0.86 volt [4], KCu[Fe(CN)₆] is 0.95 volt [11], KCr[Fe(CN)₆] is -0.56 volt [10]. This data shows the complex compound of KCu[Fe(SCN)₆] has the highest oxidation potential.

4. Conclusion

Synthesis of complex compounds from K₂[Fe(SCN)₆] and CuCl₂.2H₂O with ratio 1:1 produced light black solid and has melting point 92-95 °C. The complex compound was an ionic compound with the empirical formula KCu[Fe(SCN)₆]. Cyclic voltammetry shows that the oxidation reaction of KCu[Fe(SCN)₆] occurs at 1.42 volt.
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