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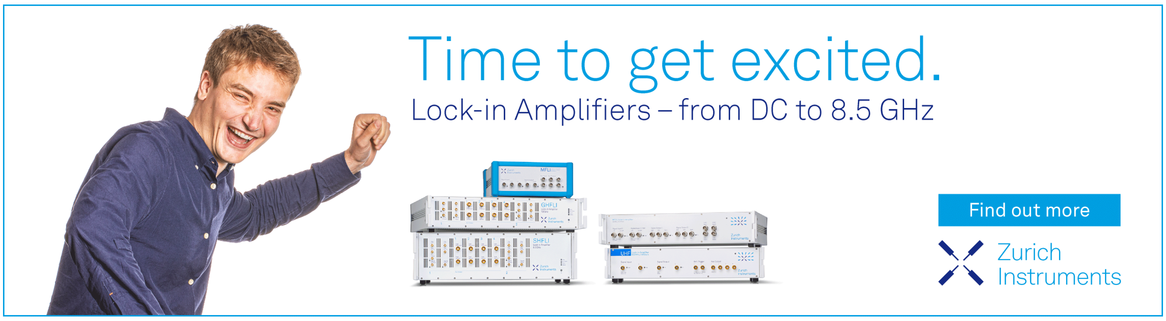

Synthesis of Manganese Carbonate and Manganese Oxalate from Indonesian Manganese Ore as NMC Cathode Precursor

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Abstract. The Li-NMC cathode battery production usually applies carbonate precipitation processes. Manganese compound used is in the form of manganese sulfate ($MnSO_4$) and precipitate using carbonate to produce manganese carbonate. This research has studied the synthesis of manganese carbonate from Indonesian manganese ore as raw material for the manufacture of NMC cathode precursor. Some manganese ores are leached using oxalic acid as a reducing agent in a sulfuric acid atmosphere. This leaching process was conducted using sulfuric acid with a concentration of 6%, leaching temperature 80^{o}C, for 6 hours, oxalic acid used 30 g/liter, with a ratio of ore to the sulfuric acid solution was 52.63 gr/l. Then, the impurities (mainly iron) precipitation from pregnant leached solution was carried out with pH adjustment using various alkalis. The alkalis used in this study were NaOH, Na_2CO_3, and NH_4OH. Manganese carbonate products were characterized using XRF and XRD. The results showed that manganese carbonate with high purity (>95%) can be synthesized from Indonesian manganese ore using leaching and precipitation method.

INTRODUCTION

Li NMC ($LiNiMnCoO_2$) batteries are a type of lithium rechargeable battery. The main difference between such products is the use of a complex alloy that contains nickel, manganese and cobalt [1]. A battery cathode is made from a mixture of these metals, which can significantly increase the power of energy storage. A feature of the Li-NMC oxide battery is that even at the production stage, the characteristics of the battery can be changed by increasing or decreasing the content of the elements that make up the battery [2]. The main scope of Li NMC batteries is electric transport for various purposes. In this case, the power of the device does not matter. Batteries can be successfully used both in electric scooters and in large machines. Li NMC batteries has many advantages such as fireproof products and its high electrical capacity. Accordingly, in any portable devices, this quality reduces the weight of the batteries.

Although manganese is widely used in metallurgy and other needs, manganese still gets little attention from many investors. Manganese is the fourth most used metal in the world – after iron, aluminum, and copper. Today, manganese is increasingly needed in the battery industry especially for electric vehicle batteries and for renewable energy such as grid electricity storage. Manganese is an important link in the lithium-ion battery supply chain that is driving electric vehicle (EV's) adoption. Manganese has been used in nickel-cobalt-aluminum (NCA) and nickel-manganese-cobalt (MNC) batteries for EV's. Therefore, manganese is increasingly being seen as a leading-edge metal for battery production.

The world's largest manganese producing countries are Australia, Gabon, China, South Africa and Brazil [3,4]. Although Indonesia is not major producer of Manganese Ores, Indonesia has manganese ores resources (around 146

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million tons), and are distributed in Sumatera, Java, Nusa Tenggara (West and East), and Kalimantan [5,6]. The manganese ores resources are potential as the raw materials for Li-NMC battery cathode precursor.

One of the synthesis method of manganese compound as the precursor of battery cathode is co-precipitation via oxalate precipitation, carbonate precipitation or hydroxide precipitation [7,8,9,10,11,12,13,14]. The manganese precursor used in the co-precipitation is usually in the form of manganese sulfate [15,16,17]. Manganese sulfate can be obtained from the manganese ores by leaching process. The study aims to synthesis of manganese compounds (manganese oxalate and manganese carbonate) from Indonesian manganese ores by leaching and co-precipitation method for preparation of Li-NMC battery cathode precursor. From this study, it could be prepared the manganese compounds directly from manganese ores leaching for synthesis of NMC precursor.

METHODOLOGY

Characterization of Manganese Ore

The sample of manganese ore used in this study was obtained from Lampung Province of Indonesia. The ore sample was crushed and ground into powder with the particle size smaller than 0.074 mm (-200 mesh). The chemical analysis using X-Ray Fluorescence (XRF, Epsilon 3XLE, PANalytical, Netherland) and Powder X-Ray Diffraction (XRD, X'pert^3 Powder, PANalytical, Netherland).

Leaching of Manganese Ore

All the chemical reagents (sulfuric acid, oxalic acid, and sodium carbonate) used in our experiments were of analytical grade and were used as received without further purification. Leaching tests were performed in jacketed vessels (borosilicate glass) with a cylindrical shape, round bottom and upper opening for sample collection. Each leaching test was carried out under magnetic stirring and at constant temperature. The reductive leaching process was carried out in sulphuric acid media (H_2SO_4 96% ISO for analysis, Merck) using oxalic acid (Merck) as reducing agent in conformity to the global stoichiometry of reaction:

$C_2H_2O_4 + MnO_2 + 2H^+ \rightarrow 2CO_2 + Mn^{2+} + 2H_2O$ …………………………………….. (1)

Leaching tests were performed according to the optimised conditions determined in previous works [5] (Astuti et al, 2019): 52.63 g of ore in 1000 mL of solution containing 6% of sulfuric acid concentration and 30 g/L oxalic acid at 80ºC for 6 h. Concentration of sulfuric acid used in the experiment is 6% v/v. The separation of liquor leach from gangue was obtained by filtration using filter paper Whatman No. 42.

Synthesis of Manganese Product

Synthesis of manganese oxalate and manganese carbonate was conducted using direct co-precipitation of manganese from pregnant leached solution using oxalic acid (1M) to produce manganese oxalate, as well as using sodium carbonate to produce manganese carbonate. The manganese oxalate co-precipitation process was carried out in the room temperature, with the ratio of leaching filtrate to oxalic acid was 1 to 2 v/v. While, the manganese carbonate co-precipitation process was carried out in the room temperature with the amount of sodium carbonate used was depend on the pH adjustment. Final pH used in the process was 10.

RESULTS AND DISCUSSION

Characteristic of Manganese Ore

As listed in Table 1, it showed that manganese ore used contained 36.77% Mn, 4.1% Si, and 6.59% Fe. It can be seen that the manganese was mainly in the form of MnO_2 in manganese ore. XRD pattern of the ore, as depicted in Fig. 1, showed that manganese was mainly in the form of manganese dioxide in pyrolusite (90,3%), and the main gangue minerals included quartz (9,7%).

TABLE 1. Chemical composition of Manganese Ore using XRF

Compound	Al	Si	Fe	S	Mn
Concentration	0.45	4.1	6.59	0.41	36.77
Unit	%	%	%	%	%

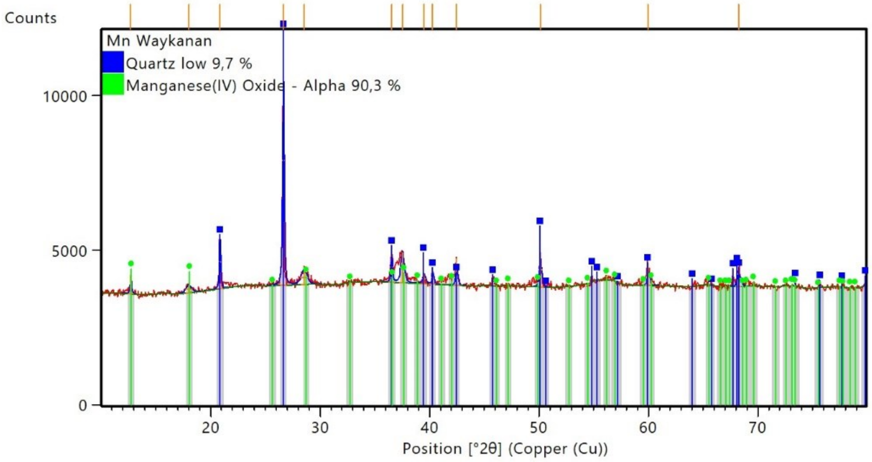

FIGURE 1. XRD Pattern of Manganese Ores from Lampung Province

Recovery of Manganese from Leaching Processes

Manganese in the ores was in the form of MnO_2 (pyrolusite). This mineral is very stable and difficult to be leached directly using any acid [18,19,8,20,21,22,23,24,25,26]. Sulfuric acid is common acid that used in the leaching process of many metals, due to its cheaper and more effective than other reagents. In this leaching experimental, the process need reductant to reduce MnO_2 become MnO that MnO is more effective to be leached by acid. Oxalic acid was used as the reductant. Manganese recovery obtained from the leaching process was 100%. It can be concluded that oxalic acid was very effective as the reductant, as well as, sulfuric acid was also very effective as the leaching reagent.

Synthesis of Manganese Oxalate

Synthesis of manganese oxalate occurred following this reaction.

$$Mn^{2+} + H_2C_2O_4 \rightarrow MnC_2O_4 + 2H^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

Manganese oxalate product was characterized using XRF and XRD. The chemical composition of manganese oxalate (see Table 2) showed that the purity of manganese in this product was 96.139%. The XRD pattern (Fig 2) was also presented that all peaks of the XRD were manganese oxalate.

It can be concluded that manganese from leaching filtrate of manganese ore can be synthesized to be manganese oxalate with high purity by very simple co-precipitation process directly using oxalic acid as the precipitation agent. It was also known that we can use the manganese leaching filtrate directly that contain manganese sulphate in the synthesis of NMC precursor via oxalate co-precipitation. Manganese oxalate produced can also be the manganese precursor due to its high solubility in the sulphuric acid.

TABLE 2. Chemical composition of Manganese Oxalate Product using XRF

Compound	Al	Si	P	Ca	Sc	Mn
Concentration	596.8	215.6	0.185	0.918	196.1	96.139
Unit	ppm	Ppm	%	%	Ppm	%

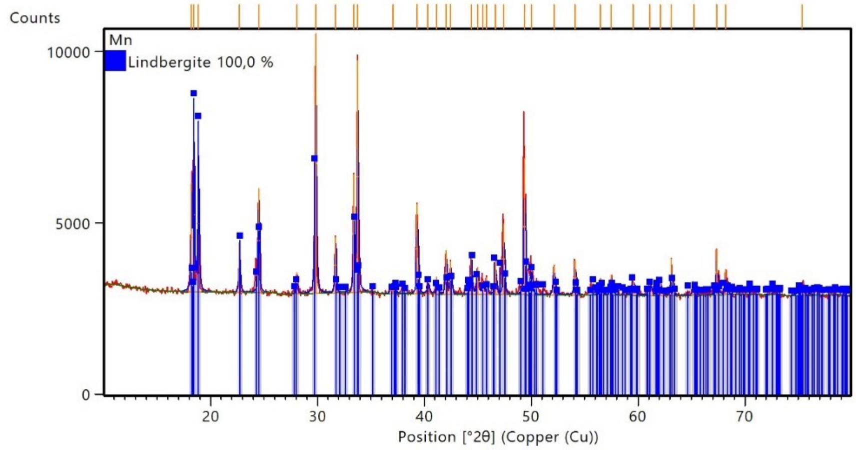

FIGURE 2. XRD Pattern of Manganese Oxalate Product

Synthesis of Manganese Carbonate

Synthesis of manganese carbonate occurred following this reaction.

$$Mn^{2+} + Na_2CO_3 \rightarrow MnCO_3 + 2Na^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

Manganese carbonate product was characterized using XRF and XRD. The chemical composition of manganese carbonate (see Table 3) showed that the purity of manganese in this product was 96.725%. The XRD pattern (Fig. 3) was also presented that all peaks of the XRD were manganese carbonate.

It can be concluded that manganese from leaching filtrate of manganese ore can be synthesized to be manganese carbonate with high purity by very simple co-precipitation process directly using sodium carbonate as the precipitation agent. Similar to the manganese oxalate precipitation, it was also known that we can use the manganese leaching filtrate directly that contain manganese sulphate in the synthesis of NMC precursor via carbonate co-precipitation. This method proposes direct synthesis of manganese precursor from manganese ores.

TABLE 3. Chemical composition of Manganese Carbonate Product using XRF

Compound	K	Si	P	Ca	Sc	Mn
Concentration	583.1	0.135	0.168	0.511	292.0	96.725
Unit	Ppm	%	%	%	ppm	%

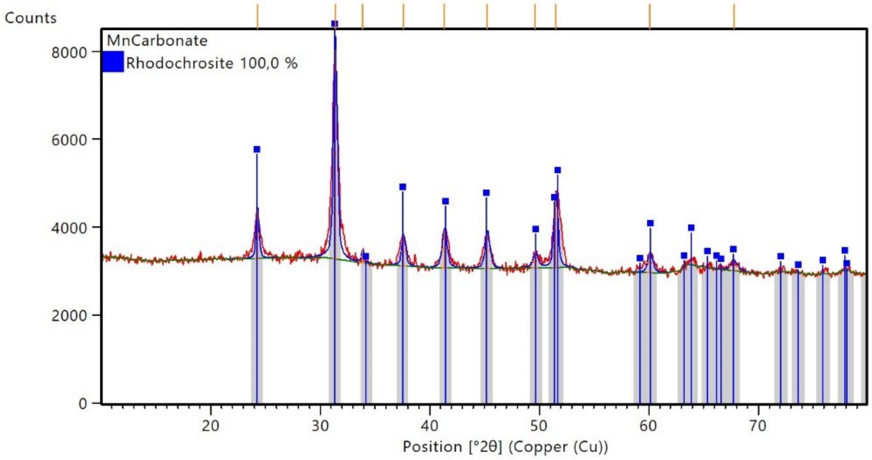

FIGURE 3. XRD Pattern of Manganese Carbonate Product

CONCLUSION

Manganese can be extracted from Indonesian manganese ores using reductive leaching (sulfuric acid as leaching reagent; tannic acid or oxalic acid as reductant). Manganese leaching filtrate (pregnant leached solution) contains manganese sulfate that can be used as manganese precursor for NMC cathode. Manganese carbonate can be synthesized from manganese leaching filtrate via co-precipitation using sodium carbonate, with Mn compound >95%. Manganese oxalate can be synthesized from manganese leaching filtrate via co-precipitation using oxalic acid, with Mn compound >95%. In summary, Manganese precursor for Li-NMC cathode is easily prepared from Indonesian manganese ores using simple and direct method with high purity product.

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Contribution: All authors are main contributors.

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