Preliminary Investigation of NiO Anode for NCA/NiO Battery from Spent Catalyst Recovery

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Abstract. Spent nickel catalyst is the catalyst residue that has lost its catalytic function. Spent nickel catalyst contains Ni metal which is already high and environmentally hazardous. This problem can be solved by recovering the spent nickel catalyst as an anode and combined with lithium nickel cobalt oxide (NCA) as a cathode for lithium ion batteries. A study about it has never been conducted. The method used to treat the spent catalyst was acid leaching using 1 M citric acid and 4 M hydrochloric acid at 70-80°C for 2 hours, then continued with precipitation and thermal decomposition. Another method employed was direct sintering at 800°C for 12 hours. Material characterisation was carried out by X-Ray Diffraction (XRD), Atomic Absorption Spectrophotometry (AAS), Fourier Transform Infra-Red (FTIR), and X-Ray Fluorescence (XRF), while electrochemical performance was carried out by NEWARE Battery Analyzer and BTS software. The results of this study indicate that Ni can be recovered with hydrochloric acid as much as 15.387 gr higher than citric acid as much as 11.831 gr from 20 gr sample. The XRD pattern also indicates the presence of crystals NiO I and NiO II in the leached and sintered material. The results of acid leaching in the form of NiO I was perfectly formed, but NiO still has a little impurity. Electrochemical performance was tested with a cylindrical battery resulting in a discharge capacity of 37.210 mAh g$^{-1}$.

1. Introduction

Spent nickel catalysts are nickel catalysts that are less active and lose their catalytic function due to repeated use and contamination of chemical processes. Chemical processes used for nickel catalysts are hydrogenation, desulphurization, and dehydrogenation. Hydrogenation contributes the largest spent nickel catalyst from the chemical and petrochemical industries [1]. Spent nickel catalyst can be recovered through the use of nickel metal (Ni) in the spent catalyst. The main reason for recovering Ni are environmental safety, reducing nickel ore mining and energy supply [2]. Environmental safety is problem due to the catalyst regeneration limit has been exceeded, it will become solid waste [3].

The method most widely used for recovering nickel from spent catalysts is acid leaching. Ramos-Cano et al, 2016, recovered nickel from Ni / Al$_2$O$_3$ spent catalyst. This catalyst contains 11.2% Ni and 88% Al$_2$O$_3$ which was treated in 50% nitric acid solution. Ni can recover about 85% at a particle size of 75 μm and operating conditions of 65°C for 2 hours with stirring speed of 600 rpm [3]. Le et al, 2017...
did the same thing using 2.1-2.5 M nitric acid solution at 100°C for 75 minutes. Spent nickel catalyst recovered from fertilizer plants that produce 90% nickel recovery [4]. Another nickel recovery was carried out by Khalid and Athraa, 2017, using 40% nitric acid solution. Recovery from spent NiMo / Al₂O₃ catalysts produces 94% Ni at 80°C, particle size 200 μm, stirring speed of 600 rpm for 4 hours [5]. Other acids such as sulfuric acid, hydrochloric acid, and citric acid can also be used as leaching agents [6], [7]. Another leaching process, i.e. bioleaching, can also be used to recover Ni. Bioleaching using *A. thiooxidans* DSM 11478 conducted by Sharma et al, 2014 which took place at 32°C resulted in a Ni recovery of 89% of the spent petroleum catalyst [8].

Recovery spent nickel catalyst can be used as lithium ion battery anode. There have been many studies on the use of NiO as anode, but NiO derived from spent nickel catalysts does not yet exist. Moreover, NiO as anode and *nickel cobalt oxide* (NCA) as cathode have never been done. Thi et al, 2015 and Feng et al, 2016 using Co-doped NiO and NiO / C as anode produced specific capacities of 1017.6 mAh g⁻¹ vs. Li at 0.1 C and 1458 mAh g⁻¹ vs. Li at 500 mA g⁻¹ [9], [10]. Another study was conducted by Spinner with a capacity of >700 mAh g⁻¹ vs. Li at 1 C using NiO nanostructure [11]. Bell et al, 2015 produced a gravimetric capacity of 1054 mAh g⁻¹ vs. Li at 3 C using Ni-NiO [12]. Wang et al, 2017 using NiO octahedron aggregates mAh g⁻¹ vs. Li at 0.2 C [13]. Lithium nickel cobalt aluminium oxide (NCA) was used as a cathode in this study. The electrochemical performance of NCA which reaches 200 mAh g⁻¹ is expected to be a support for NiO-NCA batteries. The study of NCA as a cathode has been successfully carried out with various types of anodes as well. However, studies using NiO as a cathode have never been done, so it is important to conduct this research, plus the source of the anode comes from the spent catalyst.

Finally, we handled the spent nickel catalyst to be used as battery anode and NCA for the counter electrode. The process for recovery spent catalysts carried out were leaching and sintering. The results were characterized by X-Ray Diffraction (XRD), Atomic Absorption Spectrophotometry (AAS), Fourier Transform Infra-Red (FTIR) and X-Ray Fluorescence (XRF). Battery performance test also conducted to determine the battery electrochemistry.

### 2. Material and Methods

#### 2.1 Material

Spent nickel catalyst was obtained from PT Petro Oxo Nusantara. The extrudate-shaped spent nickel catalyst was treated by crushing and sieving through 100 mesh screen. Citric acid (local vendor) and hydrochloric acid (local vendor) were used as leaching agent to separate Ni from other metal, and oxalic acid (local vendor) was used for precipitation agents.

#### 2.2 Acid leaching with citric acid and hydrochloric acid

20 grams of spent nickel catalyst powder was leached in 1 L of 1 M citric acid and 1 L of 4 M hydrochloric acid in different beaker glass. These two acids will be compared. The leaching process takes place at temperature of 70-80°C under stirring for 180 minutes. Leaching results were separated between filtrate and residue. To obtain NiC₆H₇O₆·2H₂O, the filtrate was precipitated with oxalic acid at 60°C under stirring for 120 minutes. Precipitation results were allowed to settle, washed to neutral pH and then dried in an oven. The next step, the powder formed was reacted with oxygen and sintered. Furthermore this sample was called NiO I.

#### 2.3 Direct sintering from spent nickel catalyst

The sintering process was done by heating the spent nickel catalyst powder in a muffle furnace at 800°C for 12 hours. The results of this direct sintering were NiO II.

#### 2.4 Characterization and electrochemical testing

Characterization was done to find out the material properties. The structure of the crystal was investigated by X-Ray Diffraction (EQ-MD-10-LD Precision Mini XRD, MTI), metal ion concentration
was analysed by Atomic Absorption Spectrophotometry (PinAAcle 900T Perkin Elmer, Waltham, MA, USA), organic and inorganic materials was identified by Fourier Transform Infra-Red (FTIR), and elemental composition was investigated by X-Ray Fluorescence (Bruker XRF Spectrometer, Germany).

Electrochemical performance was carried out using cylindrical batteries. Cathodes, separators, and electrolytes used are NCA sheet, cellgard, and LiPF₆. NiO as anode was mixed with NMP to form slurry then coated on Cu foil. Then, the anode sheet was dried in vacuum oven at 80°C overnight until it was ready to assembly. The performance test was analysed using NEWARE Battery Analyzer and BTS software.

3. Results and Discussion

The recovery spent nickel catalyst in this study specifically aims to utilize Ni metal to be used as an anode of lithium ion batteries combined with NCA as a counter electrode. The tests were carried out to determine elemental composition, structure of the crystal and metal ion concentration of the material, as well as the electrochemical performance of the battery.

Before proceeding further with the spent nickel catalyst, it is necessary to know the elemental composition in it. FTIR test showed the presence of Ni-O in the absorption band 430-490 cm⁻¹ [14]. Therefore, the spent nickel catalyst proved the existence of NiO because there was an absorption band at 430.144 cm⁻¹ as shown in Figure 1. As explained by Chithambararaj et al, 2012, at the peak between 900-1000 cm⁻¹ there was the Mo = O group [15]. Figure 1 also shows the presence of Mo = O at the peak of 1002.06 cm⁻¹. The Mo-O group is in the range of 500-600 cm⁻¹, the spent nickel catalyst was shown at 560.345 cm⁻¹. In addition, there were also -OH groups at 3482.83 cm⁻¹ and 1628.95 cm⁻¹. The XRF test showed that the most dominant compound in the spent catalyst was NiO with a concentration reaching 90.57% followed by MoO₃ of 6.45%. Quantitative analysis showed that Ni and Mo metals are seen at energy levels of 7.5 and 17.5 KeV on Kα1. The high concentration of NiO can prove that if it is not utilized it will suffer losses and if it is disposed it can pollute the environment. The quantitative and qualitative analysis as shown in Table 1 and Figure 2.

Figure 1. FTIR analysis of spent nickel catalyst
Figure 2. Qualitative and quantitative analysis of spent nickel catalyst

The first process in handling spent nickel catalyst was acid leaching. Leaching was carried out in two variations of acid i.e. citric acid and hydrochloric acid with the same operating conditions, but the concentration of the solution was different. Citric acid was used as leaching agent because of its ability to dissolve nickel, as well as hydrochloric acid [16]. 20 grams of treated samples recovered 11.831 grams Ni in 1 M citric acid and 15.387 grams Ni in 4 M hydrochloric acid as shown in Figure 3. Ni recovery using hydrochloric acid gives a higher yield because the Cl\(^-\) ion has high reactivity to the metal and the concentration used is also higher [6]. Some studies show that the higher the concentration of hydrochloric acid, the higher the recovered Ni [17], [18]. The 4 M hydrochloric acid concentration was used based on Joulie et al, 2012 who conducted research using variations of the 1-4 M hydrochloric acid concentration. The results showed that at the 4 M concentration, Ni was leached out properly and the leaching efficiency reached >80% [19].
Figure 3. Ni recovery results in two various acids

The results of precipitation leaching in the form of NiC$_2$O$_4$·2H$_2$O were analyzed by XRD. Figure 4. shows that the material in this study can be indexed to a pure cubic phase NiC$_2$O$_4$·2H$_2$O consistent with JCPDS Card 14-0742 [20]. However, there were other peaks that appear so that there is still impurity in the product.

After acid leaching and precipitation, the next step was to change NiC$_2$O$_4$·2H$_2$O to NiO I with thermal decomposition. The reactions that occur are as follows:

$$2\text{NiC}_2\text{O}_4\cdot\text{2H}_2\text{O} + \text{O}_2 \rightarrow 2\text{NiO} + 4\text{CO}_2 + 2\text{H}_2\text{O} \quad (1)$$

The XRD NiO I shown in Figure 5. that all peaks are compatible with JCPDS Card 47-1049. That means there is no impurity in NiO I. The process with acid leaching can react with MoO$_3$. Whereas in NiO II, MoO$_3$ impurities were still detected because the treatment was only sintering.

In addition to acid leaching, Ni can be recovered by sintering spent nickel catalyst at 800°C for 12 hours. The resulting NiO XRD pattern as shown in Figure 4. It can be seen that all peaks can be consistent with JCPDS Card 47-1049 which is reflected at 37.060º, 43.095º, and 62.620º 2θ in (111), (200) and (220) [21]. Material crystallinity in the pattern showed well. Another peak at 29.9º 2θ shows the presence of MoO$_3$ crystals consistent with JCPDS Card 05-0508 which is still impurities [22]. Further treatment is needed to eliminate this impurity by increasing the temperature and the time of sintering process.
Electrochemical performance was tested with a cylindrical battery consisting of NiO II as an anode and NCA as a cathode. This test used galvanostatic charge discharge and discharge capacity obtained in this study was still low at 37.210 mAh g$^{-1}$ as shown in Figure 6. The presence of by side reactions during the process of charge-discharge and poor battery fabrication can cause low discharge capacity [7].
Spent nickel catalyst consists of dominant components 90.57% NiO and 6.45% MoO$_3$ based on XRD quantitative tests. In the XRF qualitative test also can be seen the presence of Ni and Mo metals. Recovery spent nickel catalyst has been done with acid leaching and sintering processes. In the acid leaching process, 11.832 gr recovered Ni using 1 M citric acid and 15.387 gr 4 M hydrochloric acid.

4. Conclusion
Spent nickel catalyst consists of dominant components 90.57% NiO and 6.45% MoO$_3$ based on XRD quantitative tests. In the XRF qualitative test also can be seen the presence of Ni and Mo metals. Recovery spent nickel catalyst has been done with acid leaching and sintering processes. In the acid leaching process, 11.832 gr recovered Ni using 1 M citric acid and 15.387 gr 4 M hydrochloric acid.
from 20 gr sample. So, the use of hydrochloric acid is better than citric acid. XRD tests have been carried out to determine the crystals due to the above process. For both acid leaching and sintering, the XRD patterns produced by NiO I and NiO II are compatible with JCPDS. However, NiO II still has MoO3 impurity because it was not decomposed, while NiO I was perfectly decomposed. Battery performance testing was also carried out and the discharge capacity of 37.210 mAh g⁻¹ was obtained. The current study is still preliminary study, so further studies are needed so that the spent nickel catalyst can be utilized properly as an anode of lithium ion batteries and as a material that can be combined with NCA.

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