Heteroatomic dopants derived from coal fly-ash for the synthesis of nickel-rich Li-ion battery cathode material

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Abstract... -...-....

1 Introduction

Increasing energy consumption, energy demand is also growing. The Net Zero Emissions (NZE) program became popular after the Paris Climate Agreement was held in 2015. The NZE program aims to reduce environmental pollution that has the potential to cause global warming. Energy is one of the sectors focused on achieving the NZE program. The primary energy source currently comes from fossil energy; the existence of this energy is continuously decreasing because the source is non-renewable. Therefore, renewable energy storage sources are needed to meet the ever-increasing demand for energy storage supplies [1].

The supply of energy storage is required to meet the energy storage needs of electronic equipment, industry, and long-term transportation. Batteries are electrochemical cells that convert chemical energy into electrical energy. One type of battery that is currently being developed is the Lithium-Ion battery. Lithium-ion battery is a type of battery with a rechargeable secondary current source. The essential parts of a Lithium-Ion battery are the negative electrode (anode), positive electrode (cathode), electrolyte, and separator. Lithium-ion batteries are batteries that can store electrical energy for a long time. One factor affecting its properties is the quality of the electrode material (anode/cathode). One effort to improve the battery’s performance is to improve the electrodes’ quality [2].

Increasing demand for environmentally friendly and sustainable battery raw materials is an important issue in the battery industry. Fly ash is a waste product of coal combustion. Fly ash waste is often a big environmental problem and is difficult to process. Utilizing coal fly ash waste into a product is one way to deal with the waste produced. Until now, no other trials have specifically discussed the process of taking Al2O3 from coal fly ash for battery manufacture [4].

Responding to the problem of fly ash, Al2O3 and Fe2O3 can be applied as dopants on the nickel-rich cathode material such as LiNi0.8Co0.15Al0.05O2 (NCA) which is a modified form of LiNi0.8Co0.15Al0.05O2 (NCA) which already successfully commercialized by major EV Industries[5-7]. Making cathode material derived from fly ash has several objectives, including overcoming the environmental problems caused by fly ash waste and improving the efficiency and longevity of NCA batteries [8, 9].
addition, other advantages of NCAF batteries are coulombic capacity, gravimetric energy density, and high-power density. In addition, adding nickel to NCAF batteries can make these batteries less toxic and relatively inexpensive.

This study obtained Fe and Al materials from the leaching and recovery process (Co-precipitation). The advantages of the Co-precipitation method compared to other methods such as sol-gel, solid state, hydrothermal synthesis, and spray pyrolysis are the relatively inexpensive price, easy manufacturing method, environmentally friendly, and the most advantageous because it can produce a homogeneous material composition and shape [10–12]. Fe/Al precursors, Ni/Co precursors, and Li sources were mixed and reacted using a solid-state high-temperature method to become NCAF batteries. The physical, chemical, and electrochemical properties of the NCAF samples were analyzed using X-ray diffractometer (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR), Differential Thermal Analysis/Thermal Gravimetry (DTA/TG), and battery capacity tests. Overall, NCAF product development is essential because it can reduce fly ash waste and increase the sustainability of lithium-ion battery technology.

2 Materials And Methods

2.1 Materials
Fly ash waste was obtained from PT Paiton Energi. Fly ash waste was in the form of fine powder. Sulfuric acid (Merck, Germany) was used as a leaching agent to extract Al₂O₃ and Fe₂O₃ from other metals, and NaOH (Asahi, Indonesia) was used as a precipitation agent.

2.2 Recovery of valuable Metals (Al and Fe) from Fly Ash
Coal fly ash was dispersed in 20%v/v sulfuric acid solution at a solid-to-liquid ratio of 1:10. Next, the solution was heated at 80°C for 3 hours. After that, the filtrate was obtained using filtration, and by adding NaOH until the pH reached 12-13, a reddish precipitate was formed. The precipitate is a mixture of hydroxides (Fe(OH)₃ and Al(OH)₃) denoted as AFH.

2.3 Preparation of Ni₀.₅Co₀.₅(OH)₂ Precursors
The Ni₀.₅Co₀.₅(OH)₂ precursor was prepared by dissolving NiSO₄·6H₂O (Zenith, Brazil) and CoSO₄·7H₂O (Rubamin, India) at Ni: Co molar ratio of 4:1 using distilled water. The solution was stirred, and the temperature was kept at 60°C using an electric heater. 25% NH₄OH was added to the solution until the pH reached 10. 4 M NaOH solution maintained the pH level at 11-12. The stirring and heating were performed for 120 minutes, followed by the aging process for 24 hours. The precipitate, denoted as NC, was filtered and washed with distilled water using a vacuum filter.

2.4 Formation of NCAF cathode material
The NCAF precursor was prepared by mixing Ni₀.₅Co₀.₅(OH)₂ precursor with AFH precipitate with a mass ratio of 90:10. The calcination process was carried out to achieve heteratomic oxides of NCAF precursor. The calcination process was carried out at 500°C for 300 minutes. Finely ground NCAF precursors were mixed with LiOH·H₂O (Leverton, India) at a ratio of 1:1.05. The sintering process was carried out at 750°C for 720 minutes with O₂ gas flow.

2.5 NCAF electrode and battery Manufacturing Process
The manufacture of NCAF electrodes requires NCAF active materials, and other additional materials such as Acetylene Black (AB), Carboxymethyl Cellulose (CMC), Styrene-Butadiene Rubber (SBR) (AB, CMC, and SBR were obtained from Gelon, China), and oxalic acid (Merck, Germany). The formulae for the electrode were at the mass ratio of NCAF: AB: CMC: SBR: Oxalic Acid = 90: 3: 2: 3: 2. All of the materials were dispersed in distilled water until a homogenous slurry was formed, which is coated on aluminum foil.

The NCAF cathode sheets are pressed using a pressing machine and then cut into several sections with a width of 5.6 cm each using a slitting machine. Then, on the top of the cathode sheet, it is welded with aluminum tabs and isolated with a capton tape. The following process uses a winding machine to make a jelly roll consisting of an NCAF cathode, separator, and anode (meso-carbon microbeads from Gelon China). The cell was inserted into the battery cylinder casing. Furthermore, the electrolyte LiPF6 was inserted into the cell in the Ar-filled glove box.

2.6 NCAF Material Characterization
The physical, chemical and electrochemical properties of NCAF materials were analyzed using X-ray diffractometer (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR), Differential Thermal Analysis/Thermal Gravimetry (DTA/TG), and capacity tests. Battery.

3 Results And Discussion

3.1 AFH precipitate analysis on fly ash waste
The chemical reactions that occur during the leaching and precipitation of fly ash waste are as follows:

\[ \text{Al}_2\text{O}_3(aq) + 3\text{H}_2\text{SO}_4(aq) \rightarrow 2\text{Al}(\text{SO}_4)_3(aq) + 3\text{H}_2\text{O}(l) \]  
(1)

\[ \text{Al}_2(\text{SO}_4)_3(aq) + 6\text{NaOH}(aq) \rightarrow 2\text{Al(OH)}_3(s) + 3\text{Na}_2\text{SO}_4(aq) \]  
(2)

\[ \text{Fe}_2(\text{SO}_4)_3(aq) + 3\text{H}_2\text{SO}_4(aq) \rightarrow 2\text{Fe}(\text{SO}_4)_3(aq) + 3\text{H}_2\text{O}(l) \]  
(3)

\[ \text{Fe}_2(\text{SO}_4)_3(aq) + 6\text{NaOH}(aq) \rightarrow 2\text{Fe(OH)}_3(s) + 3\text{Na}_2\text{SO}_4(aq) \]  
(4)

The results of APF precipitation in fly ash waste in the form of Al and Fe were then analyzed for their characteristics by FTIR, SEM, and TG-DTA tests.
It can be seen in Fig. 1. The FTIR spectra can identify the sample's chemical bonds and functional groups. The peak at wavenumber 3270/cm is associated with the hydroxyl group bonds and describes the –OH group of water molecules still trapped in the precipitate. Another absorption peak is at wave number 2400/cm, which is a C-O group; besides that, the absorption peak at 1644/cm is a C=O vibrational bond [10]. The wave number 1000/cm is assigned to the Al-O group, and anything below 700/cm is defined as the stretching of the Fe-O group [13].

Fig. 2. shows the Thermal Gravimetry /Differential Thermal Analysis (TG/DTA) curve. The DTA curve from the results of the AFH precipitate made at pH 13 shows the first slight endothermic peak at 67°C with a mass loss of 14% due to the removal of physically adsorbed water. In addition, it is known that water is quickly absorbed on the surface of fine grains as the following reaction is formed (5) and (6) [14]. The second endothermic peak at 208°C saw a gradual decrease in mass, and a mass loss of 15% was caused by the loss of the hydroxyl groups Al(OH)₃ and Fe(OH)₃, which changed to Al₂O₃ and Fe₂O₃. The mass reduction continues as much as 20% occurs at 332°C.

2Al(OH)₃(s) → Al₂O₃(s) + 3H₂O(l)  
2Fe(OH)₃(s) → Fe₂O₃(s) + 3H₂O(l)  

SEM (Scanning Electron Microscopy) analysis was used to analyze the surface morphology structure and particle size or diameter of the AFH precipitate. After investigation with the SEM tool, it can be seen that the characteristics are not uniform in size and shape but have finer and smaller particle distribution, as shown in (Fig. 3.) with magnifications of 500×, 1000×, 2500×, and 5000×. Based on the identification of the distribution of Fe and Al grains using ImageJ software with a sampling point of 15 sampling points at 1000× magnification, an average particle size of 170 nm was obtained.

The EDX test was carried out in the Spc_003 sampling area Fig. 4a. The X-rays dispersed by the material will show an energy dispersion pattern as shown in Fig. 4b., namely Fe, Al, S, and O metals, which are further qualified in terms of composition percentage in the leached material.

In TABLE I, the material resulting from the leaching of fly ash waste that you want to isolate contains Al and Fe, 15.68% Al, 10.74% Fe, and the remaining S is residue from the leaching process.
Table 1. Atomic Composition Of Afh Precipitate From Fly Ash Waste

<table>
<thead>
<tr>
<th>Element</th>
<th>%mass</th>
<th>%atom</th>
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<tbody>
<tr>
<td>O</td>
<td>49.70±2.97</td>
<td>70.08±4.18</td>
</tr>
<tr>
<td>Al</td>
<td>18.75±1.70</td>
<td>15.68±1.42</td>
</tr>
<tr>
<td>Fe</td>
<td>4.98±0.85</td>
<td>3.50±0.60</td>
</tr>
<tr>
<td>S</td>
<td>26.58±4.03</td>
<td>10.74±1.63</td>
</tr>
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3.2 Analysis of NCAF Precursors

The reaction during NC precursor coprecipitation is in the following equation:

\[0.2\text{CoSO}_4(s) + 0.8\text{NiSO}_4(s) + 2\text{NaOH(aq)} \rightarrow \text{Ni}_{0.8}\text{Co}_{0.2}(OH)_2(s) + \text{Na}_2\text{(SO}_4)_2(aq)\] (7)

The results of the precursors made using the co-precipitation method are then analyzed using the DTA/TG test to determine changes in temperature and energy in the material due to the heating treatment.

3.3 Result Analysis of NCAF Cathode Materials

The fabrication of NCAF material begins with adding NCAF precursors with lithium hydroxide (LiOH.H2O) as a lithium source. Structural analysis is performed to ensure the complete formation of nickel-rich cathode material.
Fig. 8. (a) SEM image of NCAF at 2500× magnifications, (b) EDX Test Sampling Area of NCAF, and (c) X-Ray Dispersion Patterns on NCAF

Table 2. Atomic Composition NCAF

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition</th>
<th>Line</th>
<th>%mass</th>
<th>%atom</th>
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<tr>
<td>C</td>
<td>K</td>
<td>1.94±0.17</td>
<td>6.43±0.57</td>
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<tr>
<td>O</td>
<td>K</td>
<td>14.73±0.58</td>
<td>36.76±1.4</td>
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<tr>
<td>Al</td>
<td>K</td>
<td>0.16±0.09</td>
<td>0.24±0.14</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>K</td>
<td>0.87±0.65</td>
<td>0.62±0.46</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>K</td>
<td>17.94±3.67</td>
<td>12.16±2.4</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>K</td>
<td>64.36±9.58</td>
<td>43.78±6.5</td>
<td></td>
</tr>
</tbody>
</table>

The EDX test has also been carried out on NCAF material in which the area is selected as in Fig. 8b. The dispersed X-rays will show an energy dispersion pattern in (Fig. 8c), so that the atomic composition in (TABLE II) where the atomic content is in accordance with the process that has been carried out, namely Ni as much as 43.78%, Co as much as 12.16%, Fe as much as 0.62%, Al as much as 0.24%.

The electrochemical performance of NCAF was conducted in a cylindrical full cell, utilizing graphite or mesocarbon microbeads as the anode material. NC, a material without doping, was also analyzed as a comparison to NCAF. Based on Fig. 9a, a nine-cycle with current of 0.05C (10 mA/g) electrochemical cell tests shows NC material has charge and discharge capacity of around 98 mAh/g and 91 mAh/g, respectively. Meanwhile, NCAF material exhibits a specific charge and discharge capacity of approximately 172 mAh/g and 144 mAh/g, respectively. In Fig. 9b, after nine cycles, there is no significant capacity drop. It can be concluded that the performance of NCAF batteries shows an increase in capacity compared to NC batteries due to the addition of Al and Fe, which can stabilize the cathode and increase battery capacity [5], [7], [16].

4 Conclusion

Fly ash's leaching and precipitation processes produce Al and Fe deposits, which can be used as natural raw materials for NCAF cathode materials made into NCAF batteries using graphite anodes. In the electrochemical cell test of a Li-Ion battery with an NCAF cathode, the charge capacity was 172 mAh/g with a discharge capacity of around 144 mAh/g. Thus, utilizing Al2O3 and Fe2O3 as heteroatomic dopants from fly ash can improve the performance of Ni-rich cathode materials and reduce the potential hazard of fly ash disposal.
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References


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