Porous biochar purification method from coconut shell by alkali roasting followed by leaching and its application as a lithium primary battery

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Abstract. The electrochemical performance of coconut shells biochar can be improved as a Lithium primary battery by increasing its purity. Biochar was synthesized by pyrolysis under N₂ atmospheric conditions at a temperature of 500°C for 5 hours. The methods to purify biochar were the alkaline roasting method to reduce silica content and the leaching method at room temperature using 10% w/w H₂SO₄ to reduce metal oxide content. The used alkaline substance was 45% w/w NaOH solution under process temperature, which varied between 200-350°C with increasing the pressure. Energy-dispersive X-ray results show that biochar's carbon purity increased from 90.18% w/w to 97.41% w/w at the alkaline roasting temperature of 300°C. The surface area of biochar is also increased from 782,112 m²/gram to 1218,646 m²/gram at the same temperature. Electro Impedance Spectroscopy test shows charge transfer and semi-infinite diffusion, which can be explained by the diffusion of Li⁺ ions from LiClO₄ solution to purified biochar at the cathode. The charge transfer resistance value in purified biochar is less than in biochar that has not been purified. The discharge performance test shows that lithium primary batteries' capacity increases along with biochar purity. The highest capacity of biochar is 126.21 mAh/gram at 300°C.

1. Introduction

One of the developing biochar usage methods is as raw material for making cathode in lithium primary battery. Battery cathode is widely used in electronic devices such as wristwatch, remote, and laser pointer because biochar has a high specific storage capacity (372 mAh/g) to produce battery cells with high energy density [1]. Biochar from coconut shells has a good pore structure with a high surface area and good conductive material [2]. Biochar from coconut shells is also easy to find in nature, and it is available in large quantities [3].

Biochar from coconut shells requires a purification process to have high use value as battery anode [4]. The other biochar component from coconut shell besides carbon is silica [5]. In general, biochar purification is similar to graphite refining because the aim is equally to get high carbon content. The method commonly used in purifying graphite is physical purification by flotation. However, this method still produces a low purity of graphite, which is below 80%. It is quite difficult to increase its purity by flotation. In fact, as a raw material for making battery cathode, graphite with higher purity is needed so that the flotation graphite still requires further refining processes [4]. Other purification methods that already exist that can provide high purity are using thermal and chemical methods. This thermal purification graphite method requires a very high temperature of 2300°C to
produce graphite with sulfur content <0.5% [6]. While purification of graphite using HF chemistry with a concentration of 10%-70% to produce biochar with a purity of 99.9% [7]. However, HF is a very reactive and dangerous compound, so other methods need to be developed. Between the two methods, graphite's chemical purification is more valuable and easier due to using the thermal method requires higher energy. Lu and Forssberg (2002) [8] examined graphite's chemical purification with the alkali roasting method using NaOH to produce graphite purity of 99.4%. Biochar sources from coconut shells have different compositions and higher purity than the raw materials used by [8].

Therefore, the chemical method of alkaline roasting is used in purifying biochar from coconut shells to obtain pure graphite. This alkaline roasting method uses alkali in the form of a base is NaOH. It will be mixed with biochar from coconut shell then roasted in the furnace at a specific temperature. This method was chosen because biochar from coconut shell has the most impurities in the form of silica. Silica can react with base NaOH becomes Sodium silicate that is soluble in water [9]. Impurities will be removed from biochar. Besides silica, another pollutant is the metal oxide compound. Silica and other impurities are not desirable on biochar because they can close the surface pores and reduce conductivity. The choice of purification method by alkaline roasting followed by leaching using H₂SO₄ is appropriate because impurities have dissolved easily in acids [10]. The acid which is commonly used in the process of dissolving metal oxides is H₂SO₄. This process is also called leaching. Dissolved metal oxides open pores in the carbon. The target values of the specific surface area of the biochar were (>782,112 m²/g) with a specific storage capacity (372 mAh/g) as its conductivity.

A good lithium primary battery has a high electrical capacity and high conductivity [11]. The alkaline roasting method using NaOH is expected to reduce silica content, which has insulator properties. High carbon content and good microstructure are expected to facilitate the intercalation of Li⁺ ions [12]. It can increase the electrical storage capacity and conductivity. These are parameters that are desired in battery design. Battery performance test results are discussed systematically.

2. Methodology

2.1. Carbonization of Coconut Shell into Biochar

A schematic diagram of the carbonization equipment is presented in Figure 1. The pyrolyzer consists of a ceramic cylinder with a 35 mm diameter, 5 mm thickness, and 400 mm length. It was covered by a band heater that has inlet and outlet ports. Before the carbonization, the reactor's oxygen content needs to be reduced so that the coconut shell does not react with oxygen then turns into CO₂ and H₂O. Purging means expelling oxygen and replacing it with other gases. N₂ gas was carried out for 20 minutes with a gas flow rate of 40 mL/minute. The pressure setting of N₂ in the exit tube was maintained at 120 kPa. After that, the next process was carbonization. The carbonization was carried out at a temperature of 500°C. Carbonization was carried out for 5 hours when the carbonization reactor reaches a steady-state condition. After that, the band heater was turned off. The pyrolysis reactor was cooled to room temperature. Biochar product was removed from the pyrolysis reactor.

Figure 1. schematic diagram of the carbonization equipment
2.2. **Biochar Purification**

Flowchart of Biochar Purification Process by Alkali Roasting Method is shown in figure 2. Biochar powder mixed with 45% w/w NaOH (Supplied by Merck) solution with a solid-liquid weight ratio was 2:1. Then, the mixture of materials (slurry form) was put into a pressurized reactor. The reactor was placed in a furnace with temperature variations of 200, 250, 300, and 350°C for 3 hours. Next, the alkaline roasting slurry was filtered using a vacuum filter. Then, it washed with aquadest. Washing aims to remove dissolved excess alkali. The cake produced from the filtration was carried out by leaching. It was mixed with 10% w/w H₂SO₄ (Supplied by Merck) solution at room temperature with a liquid-solid weight ratio of 4:1 for 15 minutes to remove insoluble components, especially hydroxides and metal oxides. Then, it was filtered with a vacuum filter. It was washed with aquadest to remove the acid solvent. In the last step, the cake was dried in an oven at 110°C. It became purified biochar. Furthermore, product characterization and battery testing were carried out on purified biochar. EDX (Energy Dispersive X-ray) analysis was used to determine the purity of biochar particles produced from the alkaline roasting method. Meanwhile, the Quantachrome NOVA 1200 instrument was used to determine the surface area of biochar. The electrochemical performance test was carried out using Electro Impedance Spectroscopy (EIS) method to determine reaction phenomenon and its impedance values. The tool used for the EIS test was Potentiostat/galvanostat (Autolab PG STAT 302, Methrom). Test battery performance used the BST8 series battery analyzer.
2.3. Preparation of Biochar as Electrode

Purified biochar was weighed as many as 20 mg. It was then added with 2 mg of Polyvinylidene difluoride (PVDF) (Supplied by Merck). PVDF functioned as a binder to attach biochar particles to an aluminum plate. Furthermore, biochar-PVDF was mixed. This mixture was added with 20 microliters (about 2-3 drops) N-Methylpyrrolidone (NMP) (Supplied by Merck), which functions as PVDF solvent. It was stirred evenly. It was then glued on one side of a circular aluminum plate with a diameter of 1.5 cm. With the same mass and mass ratio, LiFePO₄ was mixed with PVDF and NMP. It was also coated with a copper plate. Next, aluminum and copper plates were coated with slurry are put into a furnace at 150°C for 2 hours to evaporate the solvent.

2.4 Battery Discharge Performance Test
The battery discharge performance test used a three-electrodes split cell device as the contact point for electrodes and electrolytes shown in Figure 3. The anode in the form of LiFePO₄ powder was glued to an aluminum plate with a diameter of 1.5 cm placed at the top three-electrodes split cell device. The microfiber filter was placed under the separator. It was dipped with LiClO₄ 2 M electrolyte solution.

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**Figure 2.** Flowchart of Biochar Purification Process by Alkali Roasting Method
The cathode was biochar glued to a copper plate with a diameter of 1.5 cm. Furthermore, as shown in Figure 3, the three-electrodes split cells were connected to one of the battery analyzer's channels. The discharge current was constant at 0.1 mA for all variables to obtain data related to battery discharge ability.

![Diagram of electrode arrangement](image)

**Figure 3.** Electrodes and electrolyte arrangement in three-electrodes split cell device

### 3. Results and Discussion

#### 3.1. Effects of Alkaline Roasting Temperature on Biochar Purity

The analysis result of biochar using EDX (Energy Dispersive X-ray) is shown in Table 1. EDX analysis results show that non-purified biochar has a carbon content of 90.18% w/w, with the most impurity is silica (6.43 w/w). Besides, other impurities are metal oxide compounds. The alkaline roasting method using NaOH has proven to dissolve silica in biochar successfully. The carbon content was increasing when the alkaline roasting temperature increases. This can be explained by the solubility of silica in NaOH [9]. Silica dissolves more easily into NaOH at higher temperatures. Table 1 shows that the optimum temperature of alkaline roasting is at 300°C. Silica solubility value at 350°C tends was not much different from the temperature of 300°C. The content of other impurities is that metal oxide compounds also decrease after going through the leaching stage using H₂SO₄. Soluble silica and metal oxide compounds will open the pores. Pores that open can make the purified biochar have a higher surface area. This is supported by the results of surface area analysis presented in Table 2.

| Elements | Non purified biochar | Purified biochar |
|----------|----------------------|------------------|
|          | T=200°C  | T=250°C  | T=300°C  | T=350°C  |
| C        | 90.18    | 92.31    | 93.76    | 97.41    | 97.29    |
| O        | 2.13     | 0.91     | 0.85     | 0.75     | 0.77     |
| Na       | 0.31     | 0.22     | 0.28     | 0.19     | 0.21     |
| Mg       | 0.03     | 0.03     | 0.02     | 0.01     | 0.02     |
| Al       | 0.56     | 0.54     | 0.63     | 0.41     | 0.36     |
| Si       | 6.43     | 5.76     | 4.92     | 0.98     | 1.02     |
| K        | 0.12     | 0.02     | 0.08     | 0.03     | 0.05     |
| Fe       | 0.11     | 0.14     | 0.18     | 0.14     | 0.17     |
| Ca       | 0.13     | 0.07     | 0.13     | 0.08     | 0.11     |
3.2. Effect of Alkaline Roasting Temperature on Surface Area

Table 2 data shows the effect of alkaline roasting temperature used on the purified biochar surface area. It is known that the surface area of purified biochar tends to be larger (>782,112 m²/g) with increasing temperature. It happened because the biochar to be purified by alkali roasting contains silica. After roasting with NaOH, the silica was extracted with NaOH. The biochar pores will be open, so it becomes larger, as shown in Figure 4. The higher temperature used, the more silica extracted so that the surface area of biochar is larger [13]. The pattern of increasing surface area (table 2) has similarities with the pattern of increase in purity in the EDX analysis (3.1). The larger surface area (1218,646 m²/g) is achieved on biochar purified at 300°C. This temperature is the optimum temperature of alkaline roasting. Alkaline roasting above 350°C is not much different from 300°C.

| Temperature (°C) | Surface Area (m²/g) |
|------------------|----------------------|
| Without Alkali Roasting | 782,112 |
| 200              | 923,713              |
| 250              | 955,672              |
| 300              | 1218,646             |
| 350              | 1187,871             |

Table 2. Surface Area test result of biochar

Figure 4. Illustration of biochar pores formation by the alkali roasting method

3.3. Electrochemical Performance Test of Biochar by the EIS method

Figure 5 shows the electrochemical performance test of purified and non-purified biochar. Values of the EIS test are presented in table 3. In figure 5, the semicircle diameter width shows the resistance value [14]. The resistance value of purified biochar is lower than non-purified biochar. It also shows that there are two phenomena. The two phenomena are charge transfer, which is indicated by semicircles' presence, and ion diffusion shown by linear lines [14]. The solution resistance (Rs) value was not much different because it uses the same solution during the test. Electrolyte solution test is LiClO₄ with 2 M concentration. Purified biochar has charge transfer resistance and ion diffusion resistance, lower than non-purified biochar. The lower ion transfer resistance value indicates that Li⁺ ions more easily move from the anode to the cathode during the discharge. The lower diffusion resistance value indicates that Li⁺ ions easy to intercalation into the biochar at the cathode. Purified biochar with low silica content causes Li⁺ ions to move with less passive barriers. Figure 6 shows the equivalent circuit model of purified biochar and non-purified biochar. Figure 6 shows that purified biochar EIS test have Warburg resistance, while non-purified biochar does not have Warburg resistance. Warburg resistance in purified biochar indicates a semi-infinite linear diffusion type [14]. This shows that the phenomenon of Li⁺ ion diffusion in purified biochar is relatively faster than the finite-length diffusion pattern. A finite-length diffusion pattern is mostly avoided for battery materials. This phenomenon causes the purified biochar electrochemical performance to be better than the non-purified biochar supported by the battery performance test graph in Figure 7.
Figure 5. EIS test result of purified and non-purified biochar

![Figure 5](image_url)

Figure 6. Equivalent circuit model from EIS test results for non-purified biochar a), and purified biochar b)

![Figure 6](image_url)

Table 3. EIS test parameters for a) Non-purified biochar, b) Purified biochar

| Elements | Parameter | Unit  | Purified Biochar | Non-purified Biochar |
|----------|-----------|-------|------------------|----------------------|
| Rs       | R         | Ω     | 8.321            | 6.5                  |
| Rp-1     | R         | Ω     | 126.33           | 317.88               |
| CPE-1    | Y₀        | Mho   | 0.0047           | 0.00002              |
|          | N         |       | 0.61288          | 0.8937               |
| Rp-2     | R         | Ω     | 1851.8           | 8763.8               |
| CPE-2    | Y₀        | Mho   | 0.01509          | 0.00072              |
|          | N         |       | 0.5168           | 0.57143              |
| W1       | Y₀        | Mho   | 0.0181           | -                    |
3.4. Battery Performance Test of Biochar as Cathode in Primary Lithium Battery

Figure 7 shows the results of battery performance tests for non-purified biochar and purified biochar with temperature variations. Battery discharge test performance charts for purified biochar and non-purified biochar show similar patterns but different in voltage and capacity values. The discharge pattern decreases, then remains constant at stable voltage until the voltage drops suddenly and runs out. This pattern is the desired pattern of battery, which shows voltage stability [15]. In practice, this stability pattern maintains the performance of electrical devices to optimal. Non-purified biochar has the least stable voltage (± 2.54 Volts) than purified biochar. In purified biochar, the higher alkali roasting temperature causing higher stable voltage produced. The highest stable voltage produced by purified biochar at a temperature of 300°C (±2.79 Volts). While biochar purified at 200°C, 250°C, and 350°C have stable voltages of ± 2.61 Volts, ± 2.64 Volts, and ± 2.66 Volts, respectively. The same pattern also occurs at specific discharge capacities. Biochar purified at 300°C has the highest specific discharge capacity (126.21 mAh/g) than non-purified biochar (99.81 mAh/g) and biochar purified at 200°C (110.50 mAh/g), 250°C (116.66 mAh/g), and 350°C (119.10 mAh/g).

![Figure 7. Battery performance test result for non-purified biochar and purified biochars with temperature variations](image)

4. Conclusion

Biochar purification from coconut shells was successfully carried out with an alkaline roasting method using NaOH, followed by leaching using H₂SO₄. Purified biochar at an alkaline roasting temperature of 300°C has the highest purity with a carbon content of 97.41% w/w. The largest surface area of 1218,646 m²/g is achieved by biochar, which is purified at an alkaline roasting temperature of 300°C. Purified biochar has two discharge phenomena, namely charge transfer and ion diffusion. Purified biochar can transfer mass and diffusion of Li⁺ ions, which is easier than non-purified biochar. Purified biochar at an alkaline roasting temperature of 300°C has the highest stable voltage (±2.79 Volts) and specific storage capacity (126.21 mAh/g).
5. References

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