Preparation of Zinc Oxide/Graphite Composite Using Solid-State Method as an Anode Material for Lithium-Ion Battery

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Abstract

Lithium-ion batteries using zinc oxide (ZnO) as anode material had a high theoretical capacity of about 987 mAh/g. Unfortunately, ZnO capacity can drop below 200 mAh/g after only a few cycles. For this reason, graphite was added in this study due to its stable theoretical capacity of around 348–374 mAh/g to maintain the stability of lithium-ion battery capacity. Zinc oxide/graphite (ZnO/Graphite) was prepared using a solid-state method, in which ZnO and graphite were mortared until homogeneous with the mass ratio of (1:1), (1:2), and (2:1). The SEM images of all samples showed the agglomerate morphology between ZnO and graphite which affect the results of the battery performance test. The final result of the ZnO/Graphite anode can be considered a continuous anode material due to the stable cycle performance obtained in the range of 219.72–371.27 mAh/g with a decreased value of 40% after 55 cycles.

1. Introduction

Lithium-ion batteries are energy storage in great demand nowadays because of their outstanding performance, high power density, high energy, and long cycle life. Therefore, this is the key to the rapid development and improvement of portable electronic devices and their applications on a large scale [1]. The performance of lithium-ion batteries is highly dependent on the active materials used in the anode and cathode of lithium-ion batteries. Since the anode determines the lithium-ion battery’s output voltage range [2], it is essential to research and modify the active materials used in anodes for lithium-ion batteries as they will eventually be employed in high-power applications such as electric vehicles.

The active materials that are in great demand for use as anodes in lithium-ion batteries are metal oxides. This is because the metal oxide employed will experience a redox reaction during the charge–discharge process [3]. In addition, metal oxides have prominent advantages compared to conventional carbon materials, such as high theoretical capacity, good safety performance, and wide availability [4]. Metal oxides that have been studied in previous studies were Fe₂O₃, CuO [5, 6, 7] and CuO [8, 9, 10, 11].

The metal oxide that will be used is ZnO with a graphite composite since it has various advantages such as easy preparation, strong chemical stability, and inexpensive cost [12]. In addition, ZnO itself has a high theoretical capacity of 987 mAh/g [13, 14, 15, 16]. However, the zinc oxide capacity can only drop below 200 mAh/g after a few cycles [17]. For this reason, graphite composites are used because it has a stable theoretical capacity in the range of 348–374 mAh/g [18, 19]. This is expected to maintain the stability of cycle performance of ZnO for lithium-ion batteries.

The sample in this study was prepared using ZnO and graphite commercial, in which the mixing was conducted using a simple solid-state method. The solid-state
method is one of the most commonly used for lithium-ion batteries because of its cost-effectiveness and ease of synthesis [20]. Therefore, this present study aimed to synthesize ZnO/Graphite as the anode for lithium-ion batteries using the solid-state method.

2. Methodology

2.1. Materials

The active ingredients used as anodes for lithium-ion batteries were zinc oxide (ZnO) (Loba Chemie, 99%) and graphite (Graphite, 99%) without further purification. The active ingredients used as the cathode for the lithium-ion battery were technical NMC-811 (Nickel Manganese Cobalt-811), produced by the Centre of Excellence for Electrical Energy Storage Technology, Sebelas Maret University.

2.2. Sample Preparation of Zinc Oxide/Graphite (ZnO/Graphite)

This research consisted of three main stages of work procedures: material synthesis, battery assembly, and battery performance test, as shown in the flow chart in Figure 1. The material synthesis stage involved making ZnO/Graphite composites as the battery anode using the solid-state method. In the battery assembly stage, ZnO/Graphite that had passed sample characterization were assembled to become lithium-ion batteries. The battery performance test was the stage to determine the performance of the lithium-ion batteries that have been made.

- **Mixing**
  - t = 1 hour
- **Sample characterization**
- **Battery assembly**
  - cylinder full cell 18650
- **Battery testing**
- **Data analyzing**

Figure 1. Research Flow of ZnO/Graphite anode

ZnO/Graphite was prepared using the simple solid-state method by varying the graphite and ZnO mass ratio. This process was started by mixing ZnO powder and graphite powder with different mass ratios, as shown in Table 1. The sample was ground using a mortar for ± 1 hour to obtain a homogeneous sample. The resulting ZnO/Graphite were then characterized. Samples that pass the characterization stage will be used to prepare battery anodes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO powder (g)</th>
<th>Graphite powder (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-C0.5</td>
<td>9</td>
<td>4.5</td>
</tr>
<tr>
<td>ZnO-C1</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>ZnO-C2</td>
<td>4.5</td>
<td>9</td>
</tr>
<tr>
<td>Graphite</td>
<td>0</td>
<td>9</td>
</tr>
</tbody>
</table>

2.3. Characterization

XRD (X-Ray Diffraction) data were collected from a diffraction angle (2θ) ranging from 17° to 70° at a rate of 0.05 s⁻¹. The crystal structure and size of the sample were determined using XRD data. Furthermore, surface morphology was analyzed using SEM (Scanning Electron Microscopy) (SEM, JEOL JSM-6510LA, Japan) with 2500× magnification, and the chemical components present in the sample were identified using SEM-EDX (Scanning Electron Microscopy-Energy Dispersive X-Ray) (SEM EDX, JEOL JSM-6510LA, Japan).

2.4. Battery Performance Test

Battery assembly testing must be done before performing a battery performance test. At the battery assembly stage, it started by dissolving ZnO/Graphite: AB (Acetylene Black): SBR (Styrene Butadiene Rubber): CMC (Carboxymethyl Cellulose) material in a ratio of 80:10:7:3 with distilled water. The ingredients were mixed using a stirrer to form a paste. The resulting paste was coated with a thin layer on top of Cu foil with a width of ± 5.5 cm and a thickness of ± 0.2 cm for each layer, with the final mass of the anode layer was around 4 g. The formed thin layer was then put in the oven until it dried.

The resulting thin anode layer was used to coat the battery components with a separator–anode–separator–cathode arrangement in the battery winding process (Figure 2). Furthermore, the batteries were arranged in a glovebox with an electrolyte solution. The type of electrolyte used was LiPF₆. Electrolytes containing LiPF₆ usually show good conductivity and electrochemical stability and do not promote aluminum corrosion, a material commonly used as a positive electrode current collector [21].

Figure 2. Lithium-ion configuration
In testing battery performance, the test equipment used was an eight-channel battery analyzer (BT5-SPX6A, China), which obtained the results of the battery charge-discharge capacity. The performance test is the formation test by running the charge-discharge performance at C/20 and then continuing with the C-rates to see the capacity's performance when discharge values were set at different stages. C-rate testing was carried out with charge set at 0.5C and discharge rate at 0.1C, 0.2C, 1C, and 2C. The settings 0.1C and 0.2C aimed to determine the slow charge-discharge capacity, 1C for the standard of charge-discharge, and 2C for the fast charge-discharge.

The EIS (Electrochemical Impedance Spectroscopy) (EZstat Pro Nuvant) test analyzed the electrochemical properties of lithium-ion batteries with the frequency range of 0.01 Hz to 10 kHz and the amplitude of 5 mV. The impedance data obtained would be plotted into Nyquist plot using software Origin 2018 version and fit in data using software ZsimDemo 3.2 to acquire the resistance value.

3. Results and Discussion
3.1. Crystal Structure and Morphological Analysis

Figure 3 shows the XRD results of ZnO/Graphite composites. XRD results from samples that had been stacked were compared with XRD ZnO pure (commercial) and graphite (commercial) results to obtain a data match. Based on the XRD results, the ZnO-C.0.5 revealed the two highest peaks at $2\theta = 26.8^\circ$ and $36.59^\circ$ with a crystal size of 18.27 nm. Then, the ZnO-C1 obtained the two highest peaks at $2\theta = 26.71^\circ$ and $36.49^\circ$ with a crystal size of 17.31 nm. The ZnO-C2 produced the two highest peaks at $2\theta = 26.68^\circ$ and $36.47^\circ$ with a crystal size of 14.75 nm.

![Figure 3. XRD Result](image)

XRD results of ZnO/Graphite composites were compared with JCPDS (Joint Committee on Powder Diffraction Standards) data. In the analysis of the diffraction peaks, all samples of ZnO/Graphite had similar data with JCPDS No. 36-1451, which showed that ZnO crystals had the first three highest peaks, indicating the diffraction planes of (100), (002), and (101). This peak pattern suggested that the observed ZnO phase had the hexagonal Wurtzite [22]. Meanwhile, the results of the graphite analysis had the same data as JCPDS data No. 00-012-0212, which showed that the crystal system was also hexagonal. Furthermore, sample characterization was conducted using SEM to determine the surface morphology of ZnO/Graphite, and the results are shown in Figure 4.

Figure 4 shows the SEM images of ZnO/Graphite and pure graphite. Graphite morphology is in the form of coarse grains with an average diameter of 35.38 $\mu$m (Figure 4(a)). The ZnO morphology in Figure 4(b) has a fine structure, even though mainly ZnO is reported to have a spherical and less homogeneous morphology. Figure 4(c-d) shows the morphology of the ZnO/Graphite composite that has been ground with a mortar for an hour. It is evident that the ZnO particles adhered to the graphite surface and that the produced particles tended to agglomerate into one more significant piece. Based on Figure 4(b–d), it can be said that the mortar process for ZnO and graphite samples with their mass ratio (Table 1) still requires a longer time, causing uneven agglomeration and less homogeneous morphology. The more homogenous the ZnO/Graphite composites, the more ZnO crystal growth can be increased, which is helpful for the charge-discharge process.

Table 2. SEM–EDX result of ZnO/Graphite composites

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>Atom</td>
</tr>
<tr>
<td>C</td>
<td>77.23±0.56</td>
</tr>
<tr>
<td>O</td>
<td>7.18±0.45</td>
</tr>
<tr>
<td>Na</td>
<td>0.72±0.11</td>
</tr>
<tr>
<td>Zn</td>
<td>9.92±0.46</td>
</tr>
<tr>
<td>Au</td>
<td>4.95±0.43</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The size of ZnO nanoparticles also has a different effect because the smaller particle size will also cause an increase in surface area, which is directly proportional to the number of reactions that occur so that the reaction results will be better [23]. Incorporating ZnO particles serves as a conductive band and network to allow ZnO particles to combine, significantly reducing the transfer resistance between these particles [24]. This highly affects the intercalation of Li+ ions so that it can facilitate the transfer between Li+ ions during the battery charge-discharge process.

The elemental composition of the samples was characterized by SEM–EDX, as shown in Table 2. Table 2 demonstrated the presence of C, Zn, and O on the surface of ZnO/Graphite nanoparticles with a ratio of 1:1, along with Au impurities obtained from the samples during SEM preparation.
3.2. Impedance Test Results and Charge–Discharge Battery

Figure 5 shows the results of the Nyquist plot data tested by Electrochemical Impedance Spectroscopy (EIS). EIS analysis was performed to investigate the electrodes’ charge transfer resistance and ion diffusion performance [25]. The data obtained from the EIS test were in the form of Nyquist plots and linear plots of 4 variations of anode samples. Wang et al. [26] said that the Nyquist plot is associated with the charge transfer impedance of the electrode, and the linear plot is associated with the Warburg impedance reflecting the diffusion of solid-state Li⁺ to most of the active materials of the materials used. The Nyquist plot or semi-circle radius directly demonstrates the magnitude of the charge transfer resistance [27].

<table>
<thead>
<tr>
<th>Table 3. Resistance Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>Graphite</td>
</tr>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>ZnO-Co.5</td>
</tr>
<tr>
<td>ZnO-C1</td>
</tr>
<tr>
<td>ZnO-C2</td>
</tr>
</tbody>
</table>

Based on the EIS results (Figure 5 and Table 3), the graphite plot in Figure 5(a) had the most significant resistance, whereas the ZnO-Co.5 plot in Figure 5(c) had the least resistance. This can be seen from the semi-circle that intersects the x-axis. Therefore, the smaller the semicircular plot, the smaller the resistance and the better or greater the conductivity of the battery because the conductivity value is inversely proportional to the resistance value and confirmed by the resistance value obtained from fitting the data through the equivalent circuit using a Nyquist plot (Table 3).
chemistry aspect, which produces good surface contact to composites had a large surface area due to the capacity depends on the active material type and the structure of the large ZnO particles can increase the active zinc electrode ensure the intercalation and deintercalation processes electrochemical reaction rate during charging and active materials will also increase the battery capacity. during discharging. The broader surface contact between the homogeneity of the mortared ZnO ingredient of the four anode samples, all zinc oxide graphite al.

Figure 6 displays graphs of the charge and discharge process for the four anode modifications performed with performance of battery cells also lies in the surface phase, to determine the precise lithium-ion battery Columbia efficiency (CE) values in Table 4. CE is the ratio of discharge capacity value divided by the charge capacity value [31]. This suggests that ZnO can be considered a material that can improve the charge transfer efficiency and electron transfer rate of the electrodes, which will help enhance stability and good capacity during battery discharge.

As seen from all variations of the battery anode samples, the four variations have specific capacity values in the range of 150–350 mAh/g. Yang et al. [24] added that a full battery of ZnO/Graphite shows a capacity of around 280–400 mAh/g, and has a superior speed capability. In Figure 6, all ZnO/Graphite batteries have a specific discharge capacity stabilizing in the second cycle. This is because, during the first charge–discharge process, the lithium–ion battery undergoes surface electrochemical interphase (SEI), which is electrolyte decomposition that produces a high irreversible capacity during the first discharge process and starts to stabilize in the second and subsequent cycles. The active material of SEI is derived from the positive electrode material and is responsible for the irreversible capacity, which suffers significant losses in the first cycle of most Li-ion batteries [30].

This has been demonstrated by the calculated Coulombic efficiency (CE) values in Table 4. CE is the ratio of discharge capacity value divided by the charge capacity value [31]. This suggests that ZnO can be considered a material that can improve the charge transfer efficiency and electron transfer rate of the electrodes, which will help enhance stability and good capacity during battery discharge.

Figure 7 shows the performance value of the specific discharge capacity rate of the battery (the C-rate). The C-rate testing was carried out under three charge–discharge cycles, with charge setting at 0.5C and discharge rate at 0.1, 0.2, 1, and 2C. ZnO-C1 anode and graphite have the most stable specific discharge capacity. As can be observed, the particular capacity value did not

Table 4. Coulombic efficiency at the first three cycles

<table>
<thead>
<tr>
<th>Cycle Number</th>
<th>Graphite</th>
<th>ZnO–C0.5</th>
<th>ZnO–C1</th>
<th>ZnO–C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle 1</td>
<td>76%</td>
<td>23%</td>
<td>79%</td>
<td>33%</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>95%</td>
<td>73%</td>
<td>96%</td>
<td>81%</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>95%</td>
<td>81%</td>
<td>97%</td>
<td>89%</td>
</tr>
</tbody>
</table>
significantly decrease even when it was configured with different C-rates. Figure 7 shows that the higher the C-rate, the smaller the specific capacity for discharging the battery.

![Figure 7](image)

**Figure 7.** Rate ability of ZnO/Graphite’s lithium-ion battery

The specific discharge capacity decreases towards the next cycle, and the capacity decrease during the discharging and charging processes due to the volume expansion of the ZnO particles. The results showed that morphological control could overcome problems using ZnO material as an anode of lithium-ion batteries, such as volume expansion and battery shutdown in just a few cycles [22]. This phenomenon can also be attributed to the enlarged interplanar distance and reduced activation barrier for using Li$^+$ with the active materials [32]. Zhang et al. [28] also added that the charge–discharge capacity for the second cycle, both ZnO and graphene, showed good electrode stability and consistent cycle performance.

![Figure 8](image)

**Figure 8.** Cycle performance of ZnO/Graphite’s lithium-ion battery

Figure 8 shows ZnO/Graphite stability after charge-discharge with several cycles. It can be seen that the ZnO/Graphite anode displayed a better cycle performance, which resulted in a constant significant capacity decrease from the initial cycle to cycle 55th with a specific capacity discharge range of 219.72–371.27 mAh/g and decreased value of 40%. Compared to the graphite sample, the specific capacity discharge range from 72.62 to 416.9 mAh/g, with a decrease value of more than 80%. This result is in line with the research conducted by Wang et al. [33], which reported that a stable cycle was achieved after several cycles. According to the EIS results, the ZnO/Graphite anode also showed a lower charge transfer resistance than the commercial graphite electrode, meaning that the ZnO/Graphite anode can produce better electrode reaction kinetic characteristics (charge transfer and polarization). It also could be ascribed to better electron availability and possibly Li$. A better type of crystal is also a fast pathway for mass transport and electron transfer, increasing Li$^+$’s storage capacity [34].

All variations of ZnO/Graphite anodes had sufficient specific capacity rate stability, which can be concluded that ZnO/Graphite may be considered a continuous anode material for lithium-ion batteries. Apart from the high specific capacity and stability of ZnO, the active material ZnO contained in the anode can also act as a continuous anode material because it has a stable structure [29]. However, some considerations are still required in producing anode material from ZnO/Graphite, such as the homogeneity of the sample. The homogeneity of the samples must be taken into account since the shape of the sample has a significant influence on its chemical properties for the cycle performance of the charge-discharge process for lithium-ion batteries.

### 4. Conclusion

ZnO/Graphite composites were prepared using a solid-state method with different ratio mass of graphite and ZnO. XRD results showed the ZnO/Graphite composites had crystal peaks that matched the JCPDS database with an agglomerate morphology where the ZnO adhered to the graphite according to the SEM images. The characterization led to the results of the battery performance testing data. As a result, the ZnO-C1 for the lithium-ion battery was fabricated and had a specific value of stable capacity at 219.72–371.27 mAh/g with a decreased value of 40%. This result showed that the ZnO-C1 had better stability than pure graphite. The EIS impedance graph confirmed that the ZnO-C1 had a lower resistance value than graphite, allowing it to store more electrons. Therefore, the ZnO-C1 can be a candidate for active material additives at the lithium-ion battery anode.

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