Synthesis and Characterization of ZnO from Thermal Decomposition of Precipitated Zinc Oxalate Dihydrate as an Anode Material of Li-Ion Batteries

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Abstract: Zinc oxide (ZnO) is one of the most promising materials applied in Li-ion batteries. In this research, ZnO was synthesized by the thermal decomposition of zinc oxalate dihydrate. This precursor was obtained from the precipitation process of zinc sulfate with oxalic acid. In-depth studies were carried out on the effect of various heating temperatures of zinc oxalate dihydrate precursors on ZnO synthesis. The as-prepared materials were characterized by XRD, SEM, and FTIR. Based on the XRD analysis, the presence of the ZnO-wurtzite phase can be confirmed in samples heated at temperatures above 400 °C. Meanwhile, SEM-EDX results showed that the ZnO particles have a micron size. Cells with ZnO samples as anodes have low columbic efficiency. In contrast, cells with ZnO/Graphite composite anodes have a relatively large capacity compared to pure graphite anodes. Overall, based on the consideration of the characterization results and electrochemical performance, the optimal sintering temperature to obtain ZnO is 600 °C with a cell discharge capacity of ZnO anode and in the form of graphite composites is 356 mAh/g and 450 mAh/g, respectively. This suggests that ZnO can be used as an anode material and an additive component to improve commercial graphite anodes' electrochemical performance.

Keywords: Li-ion battery; ZnO; anode; precipitation; sintering

1. Introduction

The increasing demand for reliable and superior energy storage, such as Li-ion batteries (LIB), has significantly influenced the rapid development of electronic devices and electric vehicle technology globally. Li-ion batteries are an essential part of smartphones, power tools, wind power plants, solar power plants, and electric cars with impressive characteristics. Since the beginning of the 21st century, the LIB price has continuously declined, and this decrease is expected to occur until in the next decade. Therefore, cheaper LIB components, such as separators, cathodes, electrolytes, and anodes, need to be continuously explored, studied, and adapted to achieve good energy storage that is economically competitive and sustainable [1–3].

Zinc oxide or ZnO is likely to be the next new anode material for energy storages such as LIBs due to its abundant availability on the market, eco-friendliness, high theoretical capacity, and low lithiation and de-lithiation potential values, thereby causing high overall
voltage output and an increased energy density of the LIB [4]. However, there are several disadvantages associated with the use of this oxide as an anode, such as large volume expansion, low electrical conductivity, and high-capacity loss due to the immutable alloy discharge mechanism of Li-ion. These drawbacks eventually reduce its shelf life and make it unfavorable for high-power applications [5,6].

There are several techniques to improve ZnO properties, such as adapting the structural design with nanostructures. Unfortunately, this approach requires intensive effort [6–8]. In contrast, merely mixing ZnO with conductive carbonaceous materials [8,9], such as commercially available artificial graphite, can be considered the easiest and simplest method to overcome these disadvantages, thereby providing satisfactory performance. Based on synthesis perspective, homogeneous ZnO particles are easily obtained by simple deposition of a solution containing zinc ions followed by precipitate thermal decomposition. Several precipitating agents can be used directly, such as sodium hydroxide, which forms zinc hydroxide [10,11], carbonate salts that produce zinc carbonate, and oxalic acid or other oxalic salts that produce zinc oxalate [12,13]. Based on these chemicals, precipitants containing oxalate are preferred because the precipitation process takes a short time, with high crystalline properties, which is easily separated from the solution and requires less energy to be thermally decomposed to ZnO. In this research, ZnO powder was synthesized by thermal decomposition of dehydrated zinc oxalate obtained by the deposition of low-cost zinc sulfate oxalate fertilizer at various temperatures. Since the application of ZnO in a full Li-ion battery cell is rarely reported, here, ZnO and ZnO/C composites are studied as anode material for NMC batteries. ZnO/C composites are prepared by simple solid-state milling of ZnO and graphite powder. Overall, this study provides strong evidence of the potential of ZnO application in commercial Li-ion batteries.

2. Materials and Methods

Zinc sulfate heptahydrate (ZnSO₄·7H₂O) (New Sunshine Ltd., Xiangtan, China) was used as a Zn source, where oxalic acid (H₂C₂O₄·2H₂O) (Yuanping Chemicals Co., Shanxi, China) was used as a precipitant. This research was carried out by dissolving 1 mole of ZnSO₄·7H₂O in demineralized water to obtain 1 M ZnSO₄ using a beaker glass. In addition, 1 mole of oxalic acid was separately dissolved to obtain a 1 M solution. The zinc sulfate solution was stirred continuously at a speed of 300 rpm using a magnetic stirrer. After one hour, the oxalic acid solution was poured into it and allowed to settle. The precipitate was filtered and washed three times using demineralized water to ensure the removal of dissolved waste. It was further dried in the oven for one night. Dry zinc oxalate precursor was sintered in a muffle furnace at 200 °C, 400 °C, 500 °C, 600 °C, and 800 °C for 4 h under atmospheric air to obtain ZnO powder. The as-prepared samples were labeled as ZnO 200 °C, ZnO 400 °C, ZnO 500 °C, ZnO 600 °C, and ZnO 800 °C, respectively. Zinc oxalate precipitate was characterized using Fourier transform infrared spectroscopy (Shimadzu, Kyoto, Japan). Meanwhile, ZnO samples were characterized using an X-ray diffractometer (MD-10 mini diffractometer, CA, USA) at a diffraction angle of 17 < θ < 71° and a wavelength of CuK-α 1.5418 Å. The morphology of the ZnO powder was investigated by scanning electron microscopy (SEM JEOL, Kyoto, Japan). Zinc oxide battery samples were applied as Li-ion battery anodes in two ways. In the first, ZnO was used directly as the anode material for the LiNi₀.₆Mn₀.₂Co₀.₂O₂ (NMC622) battery, while in the second, the ZnO/graphite composite was used as the anode for the NMC622 battery. The composite was prepared by solid milling between ZnO and graphite powder with a weight ratio of 1:4. ZnO electrodes were made by dispersing ZnO powder, acetylene black (AB), carboxymethyl cellulose (CMC), and styrene-butadiene rubber (SBR) with a weight ratio of 80:10:3:7 into demineralized water to obtain a homogeneous slurry. CMC, AB, SBR, NMC622, and graphite were obtained from MTI, CA, USA. The slurry was then cast sequentially on two sides of the copper foil, followed by vacuum drying at 100 °C. Correspondingly, the previously blended ZnO/graphite composites, CMC, and SBR with a weight ratio of 90:3:7 were cast and dried to obtain the composite electrode. All coated
electrodes were dried in an an oven and stored in a vacuum for 24 h before the LIBs cell assembly process. The cells were carefully designed in order to obtain a mass loading of anode sheet and cathode sheet of 8 mg/cm² and 35 mg/cm², respectively. These values were deduced from the theoretical capacity of ZnO (978 mAh/g) and NMC622 estimated capacity (200 mAh/g) to a \( n/p \) value of ~1.2, thus in ZnO||NMC622 cell, the cathode became the limiting electrode. The mass loading of ZnO/graphite||NMC622 was identical to the ZnO||NMC622, which resulted in \( n/p \) value of 0.58; thus, the anode became the limiting electrode. The detailed procedure of cylinder cell assembly and electrolyte filling was performed, as described in previous research [14]. Before the electrochemical analysis, all cells were aged for one day. The electrochemical measurement was achieved using a battery analyzer (Neware, China), where fully charged cells were cycled over a potential window of 2.0–4.3 V at a current density of 100 mA/g under room conditions.

3. Results and Discussion

3.1. Zinc Oxalate Dihydrate Characterization

Figure 1a shows the FTIR spectrum of the ZnO precursor through the oxalate precipitation pathway, while Figure 1b shows the XRD pattern of the ZnO precursor. Figure 1a shows the presence of several functional groups, such as O-H, C=O, O-C=O, and O-C=O. The OH bonds, C=O, O-C=O, and O-C=O groups appear in the symmetrical, antisymmetric, symmetric, symmetric bending mode ranges of 3300 cm⁻¹, 1600 cm⁻¹, 1300 cm⁻¹, and 800 cm⁻¹, respectively. On the other hand, XRD data (Figure 1b) showing that all diffraction peaks were indexed as ZnC₂O₄·2H₂O orthorhombic phases with lattice parameters \( a \), \( b \), and \( c \) of 27.7; 5.9; 8.7, respectively. Therefore, based on XRD and FTIR data analysis, it can be concluded that the material used as ZnO precursor is ZnC₂O₄·2H₂O [12,13,15].

![Figure 1. (a) FTIR Spectra and (b) X-ray diffraction spectra of ZnO precursor (zinc oxalate).](image)

3.2. Zinc Oxide Characterization

Figure 2a shows the diffractogram of ZnO powder derived from various sintering temperatures. All samples had a diffraction pattern identical to the Wurtzite hexagonal phase (JCPDS no. 36-1451) except for ZnO-200 [16,17]. Furthermore, it can be seen that ZnO samples obtained from sintering above 200 °C, showing high intensity, sharp peaks, and a fine baseline, indicating that the powder has high crystallinity. However, in ZnO samples with a sintering temperature of 200 °C, the peaks formed did not match the JCPDS reference, which indicates that the ZnO structure was not formed completely. The peaks observed in ZnO 200 °C may relate to the dehydration result from the ZnC₂O₄·2H₂O precursor. The crystal sizes of ZnO powder samples are listed in Table 1 and calculated using the Debye–Scherer method. Table 1 and Figure 2b show that the higher the sintering temperature, the larger the ZnO crystal diameter. This suggests that the sintering temperature has a
significant effect on the crystallite size of ZnO. The activation energy for the growth of ZnO crystal lattice at different temperatures can be deduced from the following Arrhenius equation

\[ d_{101} = d_{101,0} e^{\frac{E_a}{kT}} \]  

(1)

where \( k \) is the Boltzmann constant \( (8.617 \times 10^{-2} \text{ meV/K}) \) and the temperature in absolute form (Kelvin). By plotting \( 1/T \) vs. ln particle diameter \( (101) \), as shown in Figure 2c, we could derive linear regression calculations, resulting in the activation energy value of the ZnO particle growth was 71.43 meV \([18,19]\).

\[ \text{Figure 2.} \quad (a) \text{ X-ray diffraction spectra of ZnO from various sintering temperatures,} \quad (b) \text{ particle size curve plot (101) towards T sintering, and} \quad (c) \text{ Arrhenius plot to determine activation energy.} \]

\[ \text{Table 1. The crystallite size of ZnO powder samples.} \]

| Samples      | Peak Location (°) | FWHM (°) | Crystallite Size (nm) |
|--------------|-------------------|----------|-----------------------|
| ZnO 800 °C   | 36.01             | 0.488    | 17.89                 |
| ZnO 600 °C   | 36.18             | 0.723    | 15.11                 |
| ZnO 500 °C   | 35.94             | 1.202    | 13.16                 |
| ZnO 400 °C   | 36.46             | 0.77     | 11.35                 |

The calculated structural parameters for various samples are shown in Table 2. The value of the lattice parameter ratio \( c/a \) increases when the sintering temperature rise from...
400 to 600 °C and decreases at 800 °C. Therefore, the highest value obtained is 1.651, which showed that the best hexagonal structure among all samples is ZnO 600 °C. The Zn-O (L) bond length is determined for all samples using the following equation [20,21].

\[ L = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \]  

(2)

where the position ‘u’ parameter in the wurtzite structure is defined as:

\[ u = \frac{a^2}{3c^2} + 0.25 \]  

(3)

Table 2. Structural parameters of ZnO powders.

| Samples       | a (Å) | c (Å) | c/a | V      | L      | APF   |
|---------------|-------|-------|-----|--------|--------|-------|
| ZnO 400 °C    | 3.235 | 5.170 | 1.598 | 140.614 | 1.967  | 75.617 |
| ZnO 500 °C    | 3.275 | 5.191 | 1.584 | 144.726 | 1.986  | 76.252 |
| ZnO 600 °C    | 3.297 | 5.254 | 1.651 | 148.444 | 2.003  | 75.848 |
| ZnO 800 °C    | 3.274 | 5.229 | 1.597 | 145.646 | 1.990  | 75.673 |

The variation in bond lengths for ZnO powders are shown in Table 2. They were found to be 1967, 1986, 2003, and 1990 Å for ZnO 400 °C, ZnO 500 °C, ZnO 600 °C, and ZnO 800 °C, respectively. ZnO 600 °C has the largest L value. However, the atomic packing fraction (APF) value, as calculated from the equation below, is not significantly different with the increase in sintering temperature.

\[ APF = \frac{2\pi}{3\sqrt{3}} \frac{a}{c} \]  

(4)

Figure 3 shows the test results of the ZnO sample using FTIR spectroscopy. This is consistent with the XRD results, with the ZnO sample successfully obtained when the zinc oxalate dihydrate precursor was heated at 400–800 °C. This is evidenced by the absence of the compound’s absorbance peaks in the wavelength range above 500 cm\(^{-1}\). In the ZnO 200 °C sample, there is an infra-red absorption peak at ~3400 cm\(^{-1}\), while the absorption peak at an infrared wavelength between 400–1700 cm\(^{-1}\) indicates an oxalate phase. This proves that the precursor zinc oxalate dihydrate only has a dehydration process of 2 hydrate molecules from its crystals when heated at 200 °C [21].
3.3. ZnO SEM Analysis

Figure 4a–e shows an electron microscope scan (SEM) image of a ZnO sample obtained by heating zinc (II) oxalate dihydrate at temperatures of 200, 400, 500, 600, and 800 °C. As explained in the previous XRD analysis, ZnO 200 °C is a ZnC₂O₄ sample that has been dehydrated; therefore, morphologically, it is estimated to have similarities with ZnC₂O₄·2H₂O. ZnO 200 °C has polyhedral morphology with relatively fine sides and large agglomeration size, thereby forming larger particles (>5 µm). The sharp particle edges showed high crystalline properties consistent with the XRD test results. ZnO has smaller primary particles than ZnO 200 °C because, at 400 °C, the oxalate group of Zn-oxalate decomposes to form CO₂ gas, which is predicted to cause cavities with particles less than <5 µm. In ZnO 500 °C and ZnO 600 °C samples, smaller particles tend to form agglomerations due to the increase in sintering temperature. Figure 4d shows that ZnO 600 °C is surrounded by a submicron-sized aggregate collection of primary particles, which increased secondary particles’ area. It is predicted that a large particle size can increase the sample conductivity. Figure 4e indicates that the agglomeration forms larger secondary ZnO particles. Therefore, based on these findings, it can be concluded that as the sintering temperature increases, the ZnO particle morphology tends to form large secondary particles. Figure 4f shows the qualitative analysis with the EDX ZnO sample, while the EDX quantitative data for the ZnO sample are presented in Table 3. However, it is important to note that the presence of Au (Figure 4f and Table 3) in the sample are caused by the addition of the Au layer during the SEM-EDX testing. Besides the Zn and O components, the substance also contains Fe impurities from the raw material of ZnSO₄·7H₂O obtained from Zn fertilizer. Nevertheless, the Fe content is relatively small, while in previous studies, the range was more significant [20].

![Figure 4a](image1.png) ![Figure 4b](image2.png)

Figure 4. Cont.
Figure 4. SEM images of ZnO samples heat treated at (a) 200 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C and (e) 800 °C and (f) EDX test results for ZnO samples at a temperature of 600 °C.

Table 3. Results of the SEM-EDX quantitative analysis of the ZnO 600 °C sample composition.

| Component | % Mass (%) | % Atom (%) |
|-----------|------------|------------|
| Zn        | 43.7       | 16.5       |
| O         | 30.9       | 47.4       |
| C         | 16.8       | 34.3       |
| Fe        | 2.5        | 1.1        |

3.4. Electrochemical Performance of ZnO Samples

The ZnO samples’ electrochemical performance was evaluated by combining ZnO with LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2 as the anode and cathode of the Li-ion battery cells, respectively. Figure 5 shows the charge–discharge formation curve of various ZnO samples vs. LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2 counter cathode at a current rate of 100 mA/g anode. As depicted in Figure 5, at the beginning of the charging process, the cell was at a voltage of ~0 V, and the lithium at the cathode was deintercalated and moved to the anode through an electrolyte medium. At the anode, lithium is stored up to a voltage of 4.3V, and in the discharge process, it moves from the anode to the cathode, as indicated by a decrease in cell voltage. The ZnO material’s Li storage capacity ranges from 750 mAh/g to 860 mAh/g, while the theoretical ZnO capacity is 978 mAh/g. Table 4 shows that the cell’s charge capacity is greater than the discharge, consistent with previous studies. The discharge capacity of ZnO vs. Li is 792 mAh/g which can be seen in Figure S1. Xiao et al. reported the nanostructured ZnO initial lithiation capacity of 2958.2 mAh/g (vs. Li/Li⁺), however the de-lithiation capacity was only 906.7 mA (vs. Li/Li⁺) which showed 30.7% coulombic
Another study by Zhang also confirmed an initial coulombic efficiency of 38% (489 mAh/g/1273 mAh/g) [22]. In our study, the initial coulombic efficiency during formation of the various ZnO samples and their specific energy can be seen in Table 4.

Table 4. The charge–discharge capacity and energy density of NMC/Pure ZnO cells.

| Anode          | Cathode | Specific Charge Capacity (mAh/g) | Specific Discharge Capacity (mAh/g) | Initial Columbic Efficiency | Specific Discharge Energy (mWh/g) |
|----------------|---------|----------------------------------|-------------------------------------|-----------------------------|----------------------------------|
| ZnO 400 °C     | NMC622  | 751.2                            | 289.7                               | 38%                         | 932.7                            |
| ZnO 500 °C     | NMC622  | 858.3                            | 309.0                               | 36.0%                       | 989.8                            |
| ZnO 600 °C     | NMC622  | 792.3                            | 356.7                               | 45.0%                       | 1034.1                           |
| ZnO 800 °C     | NMC622  | 790.8                            | 318.7                               | 40.3%                       | 1009.6                           |

In the process of charging a full cell, the cathode releases Li-ions through the deintercalation mechanism of Li ions from the NMC 622 material network with the following Equation (5):

$$\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2 \rightarrow \text{Li}_{1-x}\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2 + x\text{Li}$$

(5)
There are two stages of the Li-ion storage mechanism when charging the process in NMC/ZnO cells at the ZnO electrode, namely the conversion and the alloying process, as shown in the following equation:

\[
2\text{Li}^+ + \text{ZnO} + 2e^- \rightarrow \text{Li}_2\text{O} + \text{Zn} \\
\text{Li}^+ + \text{Zn} + e^- \rightarrow \text{LiZn}
\]

These two stages have an impact on the high storage capacity of Li ions in ZnO. However, in this reaction, some of the Li atoms are inseparable. Therefore, only a portion is returned to the cathode during the discharging process, causing low cell coulombic system efficiency of cells. However, the largest discharge capacity and efficiency were produced by the ZnO 600 °C sample, as shown in Figure 5. Using cathode material weight as the basis for calculation, the discharge capacity of NMC622/ZnO cell is 56 mAh/g. This value is a direct proof that pure ZnO powders are not promising to be implemented directly as an anode active material for LIB cells [14,23]. Several attempts such as Li incorporation or the pre-lithiation of material can be considered to improve the Li-ion reversibility; however, the use of sacrificial Li metal reduce the economic attractiveness of ZnO anode [24,25].

3.5. Zinc Oxide/Graphite Composite Characterization

The diffraction pattern of ZnO and Graphite mixture with the ratio of ZnO:graphite = 1:4 is shown in Figure 6. The diffraction pattern indicates the presence of graphite and zinc oxide phases in each sample, with no significant differences between each sample. This phenomenon occurred due to the high graphite content in the sample [14,26]. However, when compared to pure graphite, the ZnO phase was clearly visible. The crystallite diameter of the ZnO–graphite composite sample is shown in Table 5. When viewed on the graphite peak at two thetas of 27°, the particle diameter value becomes consistent with the results of the pure ZnO diameter.

Figure 6. X-ray diffraction pattern of ZnO/graphite from various temperatures.

| Samples                | Peak Location (°) | FWHM (°) | Crystallite Size (nm) |
|------------------------|-------------------|----------|-----------------------|
| ZnO 800 °C/Graphite    | 31.68             | 0.657    | 13.13                 |
| ZnO 600 °C/Graphite    | 31.06             | 0.879    | 11.64                 |
| ZnO 500 °C/Graphite    | 31.49             | 0.972    | 8.87                  |
| ZnO 400 °C/Graphite    | 32.52             | 1.067    | 9.39                  |

Table 5. The crystallite size of ZnO graphite/powder samples.
Figure 7 shows the electrochemical performance of the formation curve of ZnO/graphite composites from various sintering temperature variations in a NMC622 battery. Cells were analyzed by measuring the charge-discharge capacity of ZnO/graphite applied as the anode. ZnO 600 °C shows the highest initial specific discharge capacity of 450.2 mAh/g. Compared to pure ZnO anode, the addition of ZnO 600 °C to the graphite anodes significantly increased the coulombic efficiencies, thus less irreversible Li was stored during the charged state. Therefore, it can be concluded that the use of ZnO as a composite in commercial graphite can significantly improve its cell and electrochemical performances as an anode material [5,14]. Based on Table 6, the cell capacity and energy density are consistent with the predictions on the crystal structure expressed in the XRD. The discharge capacity of ZnO 600 °C/graphite composite compared to graphite can be seen in Figure S1. The ZnO sample by heating at 600 °C has good structural characteristics. The many primary particle agglomerations and large surface area facilitate the Li-ion transfer and better storage reaction processes. Figure 7f shows that the ZnO graphite sample in all variations had a significant decrease in capacity from the initial to 20th cycle. However, after reaching the next cycle, it was no longer too significant. These results are consistent with reports provided by Zhang et al. [22] and Xiao et al. [6] which claimed that a stable cycle was achieved after several cycles. In contrast, pure graphite has a constant capacity decrease. The retention capacity of NMC cells with graphite anode after 40 cycles, ZnO 400 °C/graphite, ZnO 500 °C/graphite, ZnO 600 °C/graphite and ZnO 800 °C/graphite were 68%, 70%, 71%, 79% and 72%, respectively. Therefore, based on the cycle testing results, the stability value of ZnO/graphite composite-based anodes is less consistent. The decrease in capacity may be related to the n/p ratio used in the cell design. The actual n/p capacity ratios of NMC622/ZnO–graphite cells are higher compare to n/p capacity of NMC622/pure graphite cell. The low n/p capacity value may cause uncontrolled SEI growth and Li plating or deposit on the anode material, which result in irreversibility of Li-ion movement and capacity fading [27–29]. This phenomenon could be one of reasons why the cycling stability of ZnO 600 °C/graphite cell is superior compared to a cell with pure graphite anodes. In other words, with consistent n/p, ZnO/graphite material can provide better results than commercial graphite anodes. These promising results provide space for future research improvement.
Figure 7. (a–e) Charge–discharge curve of NMC622 | ZnO/Graphite and NMC622 | graphite cells with various ZnO samples and (f) the cycle performance of all samples.

Table 6. The charge–discharge capacity and energy density of NMC/ZnO/graphite cells.

| Samples               | Specific Discharge Capacity (mAh/g) | Specific Discharge Energy (mWh/g) |
|-----------------------|------------------------------------|----------------------------------|
| ZnO 400 °C/Graphite   | 327.3                              | 1162.8                           |
| ZnO 500 °C/Graphite   | 397.4                              | 1443.9                           |
| ZnO 600 °C/Graphite   | 450.2                              | 1668.9                           |
| ZnO 800 °C/Graphite   | 447.2                              | 1648.0                           |
| Graphite              | 307.85                             | 889.83                           |

4. Conclusions

ZnO material was successfully prepared from high-temperature sintering of zinc oxalic obtained from the precipitation reaction between ZnSO₄ with oxalic acid. All ZnO samples derived from precursor sintering at 400–800 °C had good crystalline properties and wurtzite structure. Furthermore, the SEM analysis indicates the growth of primary particle agglomeration into secondary with large sizes. Therefore, based on charge–discharge analysis, cells with ZnO-based anodes obtained the highest specific cell capacity using sintering treatment at a temperature of 600 °C. ZnO material composite in graphite material...
has succeeded in increasing the anode capacity of commercial graphite. Therefore, the use of ZnO as anode material in NMC battery cell is considered promising and can be developed in future research.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/en14189980/s1, Figure S1: Initial Discharge Curve of ZnO-600 °C, ZnO 600 °C/Graphite and Graphite anode material.

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