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$LiCoO_2$ Cathode Material Prepared through Two Step Sintering Process

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ABSTRACT: $LiCoO_2$ cathode material has been continuously applied in commercial LIBs cells. It has high gravimetric and volumetric density. In this research, an economical approach to obtain $LiCoO_2$ is proposed. Pure cobalt oxide (Co_3O_4) precursor was obtained via atmospheric precipitation of cobalt sulfate and thermal decomposition of the as-obtained hydroxide precursor. The next heat treatment was performed to obtain $LiCoO_2$ powder. To investigate the characteristic of the precursor and the final product, XRD, FTIR, and SEM analysis were conducted. The final product has hexagonal structure and quasi spherical morphology. The size of the particle is in micron. The charge-discharge analysis of $LiCoO_2$ was conducted in $LiCoO_2$/Graphite system where the initial capacity of $LiCoO_2$ is 120 mAh/g at the current density of 0.1 C (20 mA/g). Overall, this method can be used for large scale $LiCoO_2$ cell production.

Keywords: Cathode, $LiCoO_2$, Lithium ion batteries, Synthesis, Sintering.

1. Introduction

Li-ion battery is an energy storage device that able to store and discharge electrical energy with high efficiency, high energy density and high-power density. It also has a relatively long-life cycle and at its end of life, it can be recycled and reused as a fresh Li-ion battery. Today, Li-ion batteries have been widely used as energy storage in both light duty and heavy-duty application. As a matter of fact, Li-ion batteries has been found highly efficient as an energy storage in new and renewable energy based-power plant. This proved that LIBs are highly dependable secondary energy storage compare to its predecessor such as: lead acid battery, nickel cadmium battery, and nickel-metal hydride battery [1].

There are several types of LIBs. It can be categorized based on its shape, size, and active materials. Commercially, LIBs are often categorized based on its working voltage, which is highly dependent on the type of the active material used inside the batteries. It is well known that there are two types of active materials in a LIBs, i.e., cathode and anode. The cathode material is the one with Li-ion source, which will act as the charge carrier during its usage; thus, in the majority, Li-ion batteries often classified based on the cathode material [2].

There are several types of cathode materials. Olivine structured cathode material such as $LiFePO_4$ has high safety and relatively high specific capacity but low conductivity and low working voltage. Spinel structured cathode material such as $LiMn_2O_4$ has high working voltage but low specific capacity and low volumetric density. Layer structured type of material benefits from the combination of high energy density, high conductivity and high volumetric capacity. $LiCoO_2$, a layer structured cathode material, is highly used for auxiliary applications such as smartphones and gadgets. It has high dependability and is still consistently used due to its long cycle life and high volumetric density. However, $LiCoO_2$ is considered expensive due to its high cobalt content, which is an expensive material. However, overall cathode material production cost can be reduced by modification of the production or synthesis process [3–5].

Extensive efforts have been conducted to obtain $LiCoO_2$ cathode material. Mizushima et.al. developed $LiCoO_2$ by electrochemical extraction from rock-salt structured $LiCoO_2$ [6]. Shlyakhtin et. al. produced $LiCoO_2$ via freeze drying [7]. Gan et. al. successfully synthesized $LiCoO_2$ via carbon combustion [8]. These techniques delivered considerably good quality $LiCoO_2$ with good electrochemical performance. However, a more simple and facile method is highly necessary which result in reduced production cost; thus, the cost of $LiCoO_2$ can be significantly reduced [9]. Precipitation process is considered as the most promising technique due to its simplicity and involve low-cost materials. In this research, we develop an approach to obtain high performance $LiCoO_2$ via atmospheric hydroxide precipitation followed by two step high temperature sintering process. The first sintering process was conducted to obtain Co_3O_4 while the second sintering process was applied to obtain $LiCoO_2$ via HT lithiation or Li insertion.

2. Experimental Method

Cobalt sulfate heptahydrate (Rubamin, India) was dissolved in deionized water to obtain 1 M concentration and placed in a reactor. 25% of ammonia (Merck, Germany) solution was introduce into the reactor until a blue solution was obtained. 2 M of NaOH (Asahi, Indonesia) was added dropwise into the reactor until a pH of 12 was reached. The temperature was maintained at 50 °Cand stirred at 500 rpm for 2 hours. After the reaction was completed, the precipitate was allowed to settle for the next 24 hours. The precipitate was then separated from the liquor via gravity filtration and drying. The dried precipitate was calcined at 500 °Cunder air. the calcined powder (cobalt oxide/Co_3O_4) was washed using deionized water to remove the residual sodium sulfate salt from previous precipitation reaction. the powder was dried and mixed with Li_2CO_3 (Brivo, China) with Li:Co molar ratio of 1.05:1. The extra 5% was added to compensate the Li loss during the high-temperature sintering. The mixed precursor was then sintered at 900 °Cfor 10 h. The as-obtained $LiCoO_2$ (LCO) was ground and sieved to a fine powder and ready to be used as a cathode material in an Li-ion battery.

The cathode sheet was prepared by coating a slurry composed of LCO as the active material, AB as the conductive agent and PVDF as binder with a composition of LCO:AB:PVDF=90:5:5 in a 2-methyl n pyrrolidone solvent (NMP). The slurry was laminated on the surface of Al foil, front and back, and dried in a vacuum oven. The dried cathode sheet was pressed and slitted to obtain a sheet with 5.6 cm width. Al tab was welded in the tip of the cathode.

the cathode, celgard separator and graphite anode was rolled and placed in a cylindrical case. The cell was welded and a cap was installed to the Al tab. Into the cell, $LiPF_6$ electrolyte was added. The electrolyte filling was performed in an Ar filled glove box. The cell was punched and ready to be analyzed in the battery testing analyzer (Neware, China). A current of 0.1C (20 mA/g) was employed in the formation phase. The cell was charged and discharged for 5 cycles.

The precipitate powder, cobalt oxide and LCO were characterized. XRD analysis using MD-10 diffractometer (MTI, USA) was performed to investigate the structural properties of each sample. Scanning electron microscope (Jeol JCM 7000) was used to examine the morphological feature of the samples. Meanwhile, FTIR (Shimadzu IR Spirit, Japan) analysis was conducted to understand the surface chemistry of the sample

3. Result and Discussion

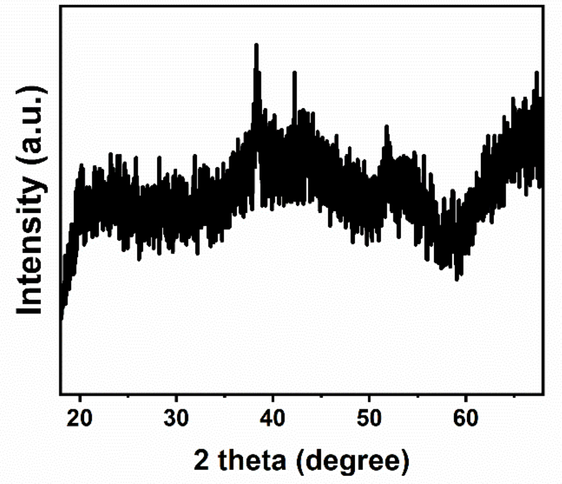
3.1. *Cobalt Precipitate Characterization*

Since sodium hydroxide was utilized as the precipitant, the precipitate was expected to be cobalt hydroxide. However, the precipitation process was conducted in an atmospheric condition, therefore, it is expected that some cobalt is oxidized from Co^{2+} to Co^{3+}. This phenomenon is the reason why it was important to characterize the precipitate sample in order to assure whether the Co^{3+} species exist. Figure 1 displays the X-ray diffraction patterns, FTIR spectra and SEM image of as obtained cobalt hydroxide. Based on Figure 1a, the diffraction peaks can be indexed to cobalt hydroxide ($Co(OH)_2$) with hexagonal structure and categorized in P-3ml space group (JCPDS card no. 45-0031) [10]. However, another phase that has similar structure is CoO(OH) (JCPDS no.72-2280). FTIR spectra presented in figure 1b shows a strong hydroxide peak detected at wavenumber of around ~3500/cm [11][12]. Therefore, it can be estimated that two reactions occurred during the precipitation as presented in equation 1 and equation 2.

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2 \text{ ....(1)}$$

$$Co^{2+} + +1/2\ O_2 + OH^- \rightarrow CoOOH \text{ ....(2)}$$

The exact composition of cobalt hydroxide and cobalt oxyhydroxide (CoOOH) is not being analyzed, but as expected, it can be readily calcined to obtain cobalt oxide powder. The SEM image of the precipitate can be seen in figure 1c. The particle consists of submicron primary particle with irregular agglomeration.



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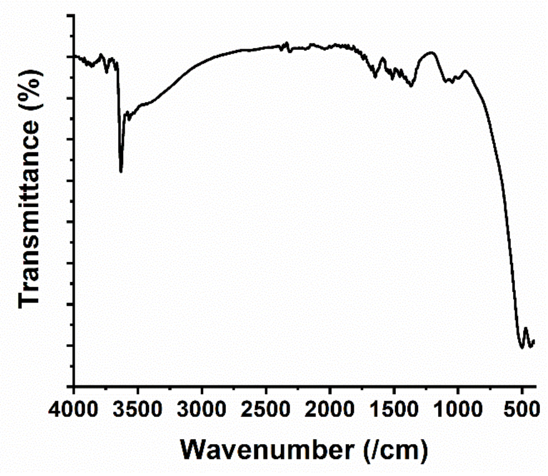

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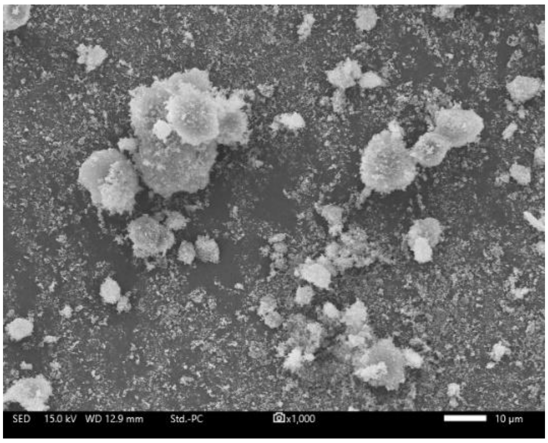

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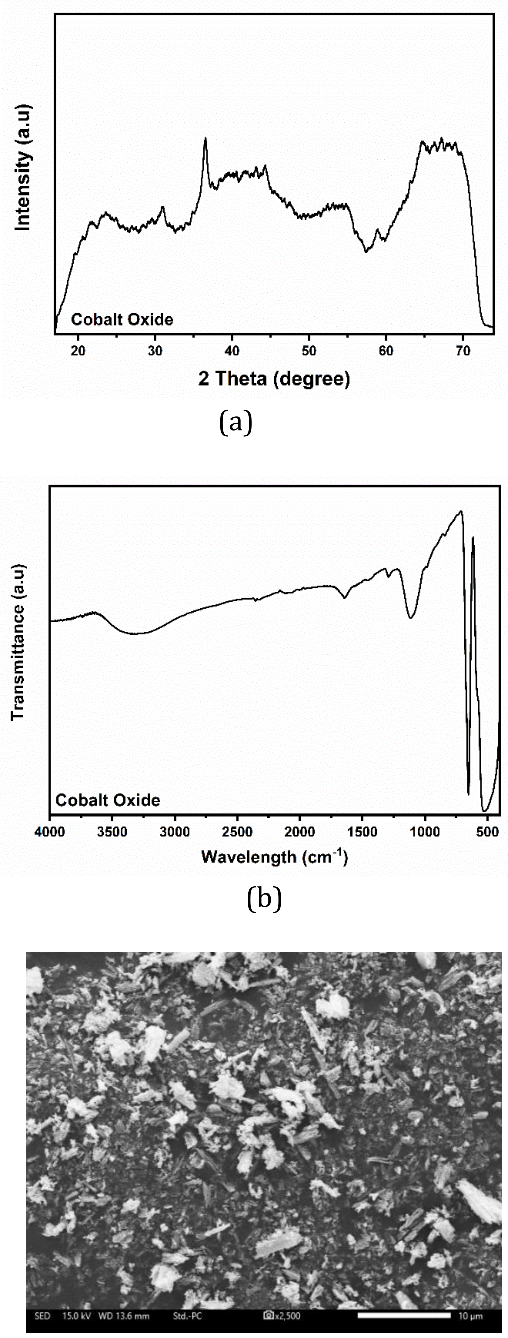
Figure 1. (a) X-ray diffraction patterns, (b) FTIR spectra, and (c) SEM image of the as obtained cobalt precipitate

3.2. Electrochemical Performance Analysis

Since the lithiation process requires an exact Li amount, it is necessary that the powder composition and weight molecule of cobalt precursors is determined. To do so, the precipitate that composed of cobalt hydroxide and oxyhydroxide was calcined to obtain cobalt oxide powder. Figure 2 shows the characterization of cobalt oxide powder using XRD, FTIR, and SEM. Based on the XRD patterns depicted in figure 2a, all peaks are in accordance to JCPDS card no. 78-1970; thus, the sample is indeed a cubic structured cobalt oxide (Co_3O_4) [10,13]and considered pure due to unobservable impurity phase in the XRD pattern. The FTIR spectra in figure 2b indicates a total decomposition of hydroxides. SEM image (figure 2c) shows a particle with cubical morphology and size range of 2-4 µm. The cobalt oxide powder can be readily converted to $LiCoO_2$ material through solid-state high temperature sintering (equation 3)

$$3Li_2CO_3 + 2Co_3O_4 + 1/2\ O_2 \rightarrow 6LiCoO_2 + 3CO_2 \quad \text{...} \quad (3)$$



(a)

(b)

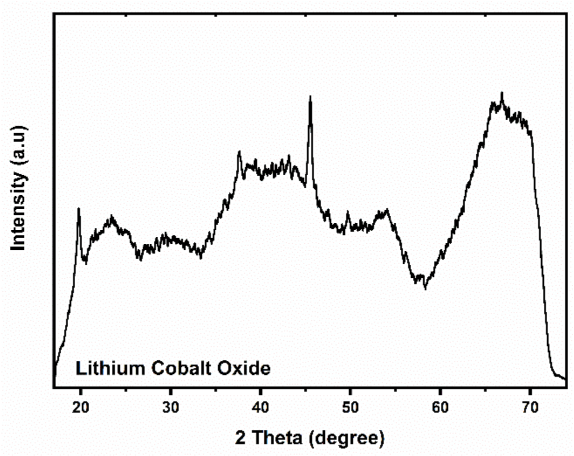
(c)

Figure 2. (a) X-ray diffraction patterns, (b) FTIR spectra, and (c) SEM image of the as obtained cobalt oxide

3.3. *$LiCoO_2$ characterization and electrochemical performance analysis*

Figure 3 shows the X-ray diffraction pattern, FTIR spectra, SEM images of as-prepared $LiCoO_2$ which provide better understanding on the structural, chemical, and morphological properties of the

$LiCoO_2$, respectively. Based on Figure 2a, the as-obtained $LiCoO_2$ has a layered structure and hexagonal phase. FTIR spectra of $LiCoO_2$ shows similar pattern to that of metal oxide, while SEM image of $LiCoO_2$ shows an agglomerated and better size distribution of particle. During the HT lithiation, the submicron particles agglomerated which mediated by the molten Li_2CO_3; thus, secondary particles are formed with larger size (>4 micrometer). Based on the characteristics, $LiCoO_2$ with good structural, chemical, and morphology feature is successfully synthesized and readily used as the cathode material in a Li-ion batteries[9,14].



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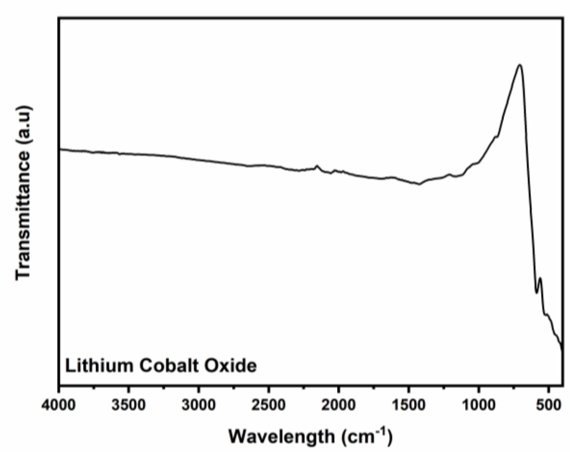

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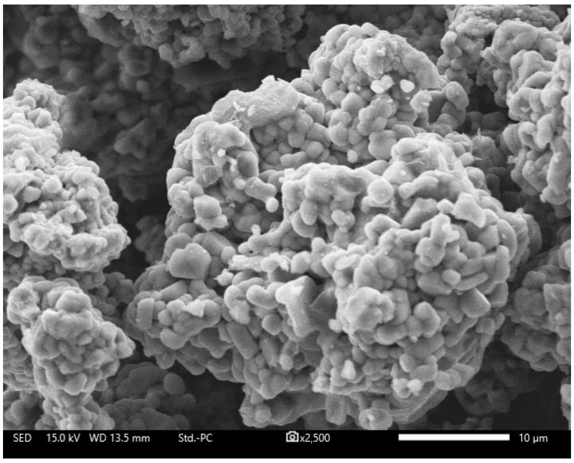

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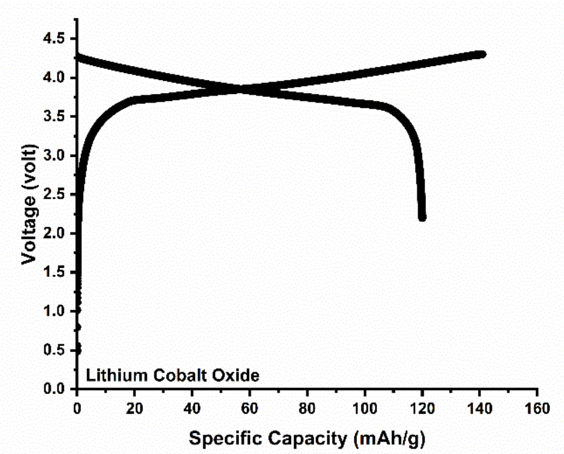
Figure 3. (a) X-ray diffraction patterns, (b) FTIR spectra, and (c) SEM image of the as obtained lithium cobalt oxide

Figure 4a presents the initial charge and discharge performance of $LiCoO_2$/Graphite cells under working voltage of 2.2-4.3 V and current density of 14 mA/g. During the charging process, the voltage increased significantly until a voltage of 3.5 V reached. At that point, the voltage curve has a lower gradient and constantly increased to 4.3V. At this stage, Li from cathode was transferred to the anode. In the cathode side, oxidation of cobalt occurs while in the anode, 6 atoms of carbon forming a hexagonal structure whereas the Li-ion reduced into a lithiated Li. During the discharge process, the Li ion was transferred back to the cathode material, and the voltage was reduced gradually as more Li removed from the graphite anode. Based on the figure, $LiCoO_2$ has a specific discharge capacity of 121 mAh/g where the theoretical capacity of $LiCoO_2$ is 140 mAh. the slight difference of 19 mAh/g occurred due to the cells were used in a commercial cell with graphitic anode, where usually $LiCoO_2$ is tested in half cells. The non-existing Li reservoir or Li metal in commercial cells usually reduce the capacity of the cathode. Some of the Li was consumed during solid electrolyte (SEI) formation and cathodic electrolyte interphase (CEI) formation. The consumed Li during SEI and CEI formation is not being compensated due to non-existing Li reservoir in the anode. However, the value of 121 mAh/g is considered high enough to be developed for large scale production of LiCoO$_2$[15,16]. Figure 4b shows the cycle performance of LiCoO$_2$ at elevated current rate of 2C. The specific discharge capacity after 50 cycles is 99 mAh/g; thus 84.6% capacity retention is obtained.



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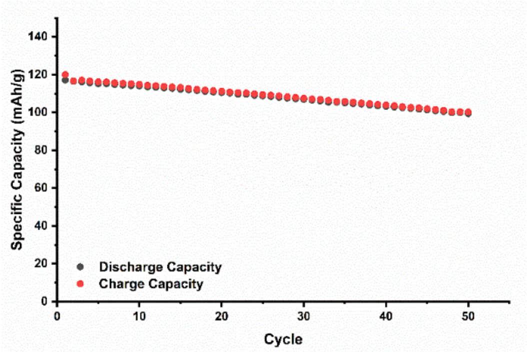

(b)

Figure 4. (a) Charge-discharge curve of LiCoO$_2$/Graphite cell and (b) Cycle performance of LiCoO$_2$/Graphite cell at 2C

4. Conclusions

The synthesis of LiCoO$_2$ cathode material via two stepped sintering process is successfully conducted. The process is highly economical and feasible to be scaled up since the reaction does not require inert atmosphere and complex apparatus. XRD, FTIR spectra and SEM analysis were employed to assure the quality of the precursors and the final product. The final LiCoO$_2$ product has a layer-hexagonal structure with quasi-spherical morphology. The initial specific discharge capacity of LiCoO$_2$ is 121 mAh/g with capacity retention of 84% after 50 cycles at 2 C.

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