Synthesis of Modified Graphite with High Crystalline Na-LTO by Simple Doping Method.

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Abstract. Graphite doped with Na-Li₄Ti₅O₁₂ (Na-LTO) for lithium-ion batteries with stable rateability were prepared in a short time by simple grounding which followed with the short calcination time. High crystalline Na-LTO improved the diffusivity of the Li-ion kinetics and stability. Therefore, Graphite/Na-LTO (G-NaLTO) was compared with the pure graphite to find out the differences in terms of XRD pattern and electrochemical performance. XRD analysis showed there was no significant differences pattern from G-NaLTO with commercial graphite. In terms of electrochemical performance, G-NaLTO which was doped by 1 wt% Na-LTO, presented a high initial charge capacity 356.69 mAh g⁻¹ at 0.1C and stable discharge rate-capability at 0.2C and 1C were 264.64 mAh g⁻¹ and 220.65 mAh g⁻¹, respectively, after 15 cycles. G-NaLTO with a composition of 3 wt% Na-LTO shows a decreasing electrochemical performance so it can be concluded that the addition of 1 wt% LTO by the doping method is the most optimal.

1. Introduction

Due to its high thermal stability, high chemical stability, low cost, and high theoretical capacity, graphite is the most commonly used among the different anode materials [1]. Graphite has a limitation which is that it can't work at high currents. This is caused by dendrites growing on the graphite surface while working at high currents. Dendrite formation has an effect on lowering the charge/discharge output and increase the temperatures operating that was become another problem, such as the safety of battery use. In addition, dendrites forming are the cause of the formation of a thick layer of SEI that decreases battery efficiency. [2]. Many efforts have been made to solve this issue, including surface modification to avoid cracking or expansion [3], decreasing the thickness of the electrode to decrease the limitation of lithium diffusion [4], mesoporous structures leading to high-rate capability of Li insertion/extraction [5], and Carbon Nano Tubes (CNT) for ion transport channels [6].

Among various metal oxides, Li₄Ti₅O₁₂ (LTO), a promising candidate for anode content to ensure battery protection by avoiding lithium dendrites problems [7]. LTO has a high operating voltage value (1.55V vs Li / Li⁺) where the dendrite is less formed due to the property of LTO that no structural change occurs just like with graphite in the charge/discharge cycle [8]. The addition of LTO to graphite in our previous research has provided with the highest capacity of 130.66 mAh g⁻¹ [9]. Further research is developed to enhance electrochemical performance by modifying LTO. The enhancement of crystallinity can improve electrochemical performance of LTO material [10].
alternative way to enhance a material’s crystallinity is by adding a small amount of salt during synthesis, called salt-assisted. The addition of salt (NaCl, KCl) has been succeeded to assist in the crystal formation of materials such as ZnO, ZnFe$_2$O$_4$, and Strontium Ferrite [11]. Thus, high LTO crystallinity by salt addition NaCl was expected to be sufficient for graphite anode material modification to overcome the SEI and rateability problem.

In this study, for the negative electrode of lithium-ion batteries, we used a simple solid-state reaction to dope a high crystalline Na-LTO onto the graphite particles. X-Ray Diffraction (XRD) studied the composite material’s Na-LTO and G-NaLTO crystalline structures. Furthermore, the electrochemical performance will be studied to understand the effect of high crystalline Na-LTO addition on graphitic carbon.

2. Experimental

2.1. Preparation of Graphite/Na-LTO

The Li$_4$Ti$_5$O$_{12}$ (LTO) powders were prepared via solid-state reaction with the addition of NaCl 4% wt [12]. In order to investigate the effect of Na-LTO addition, two different amounts of Na-LTO 1 and 3 wt% were added to the commercial graphite (MTI, America) by grounding the Na-LTO and graphite. Each composition named by G-NaLTO1 for graphite with addition LTO 1 wt% and G-NaLTO3 for graphite with addition LTO 3 wt%. Furthermore, the mixture calcined 600°C under N$_2$ for 1 hour to obtain graphite/Na-LTO.

2.2. Material Characterization

Pure graphite data were analyzed to obtain Brunauer-Emmett-Teller (BET) surface by N2 adsorption and desorption and shown in Table 1. The crystal structure of the LTO and G-NaLTO powders has been examined by X-ray diffractometer / XRD (D2 Phaser Bruker, Germany) using Cu-K-alpha radiation (\(\lambda=1.5418\ \text{\AA}\)) with a frequency of 10°-80° of two theta (2 theta).

2.3. Electrochemical Measurements

The electrochemical characteristics were studied using a full-cell (18650-type cylindrical battery), LiFePO$_4$/LFP as a cathode (GELON LIB CO., China). G-NaLTO powder was combined with conductive carbon (acetylene black / AB, MTI, Richmond, CA, USA) and water-based binder (CMC and SBR) at a weight ratio of 80:10:2:8 in water to form slurry that coated on both sides of copper foil. The assembly of cylindrical cells was performed in Li-ion batteries manufacturing plant located in Surakarta. 1 M LiPF$_6$ dissolved in EC:DMC (3:7) was used as electrolyte. The cells were tested on the NEWARE Battery Device Analyzer, battery performance analysis is performed with the voltage range of 2.5-3.6V with an initial charge/discharge cycle current of 0.1C (37.5 mA/g).
3. Result

Figure 1. XRD pattern of pure LTO (LTO 0%), Na-LTO (NaCl 4%), pure graphite (Na-LTO 0%), graphite/Na-LTO (Na-LTO 1% and Na-LTO 3%)

According to JCPDS File No. 49-0207 all peaks of as prepared Na-LTO can be indexed well as spinel LTO and no impurity peaks of NaCl can be found. Based on the figure, XRD pattern of G-NaLTO samples shows all peak from G-NaLTO related with the pure graphite because low amount of addition Na-LTO.

Table 1. Physical Data of Graphite by Adsorption and Desorption N\textsubscript{2} Analysis

| Graphite                      | Value   |
|-------------------------------|---------|
| BET Surface Area (m\textsuperscript{2}/g) | 12.009  |
| Tot. Pore Volume (cm\textsuperscript{3}/g) | 0.1065  |
| Average Pore Radius (Å)       | 177.32  |
Figure 2. Initial discharge-charge curves of (A) G-NaLTO1 (B) G-NaLTO3 at 0.1C; (C) specific charge-discharge rate performance (0.1C, 0.2C, 1C) of G-NaLTO1; (D) cycle performance of G-NaLTO1.

Figure 2A. and Fig. 2B. exhibits the initial charge/discharge curves of the sample G-NaLTO1 and G-NaLTO3, respectively, with 0.1C rate. The initial specific charge capacities at 0.1C rate of graphite with doping 1% and 3% wt were 356.69 mAh g⁻¹ and 339.89 mAh g⁻¹, respectively. The G-NaLTO1 shows the highest initial charge capacity which is close to the theoretical value (372 mAh g⁻¹). The sample of G-NaLTO3 exhibits the lowest initial charge capacities which means the addition of Na-LTO 3% wt. altering the electrochemical properties of the graphite. The result indicates that higher than 1% wt LTO content will decreases the reversible capacity of the composite. Fig. 3C. shows an analysis of the sample G-NaLTO1 by enhancing the rate charge/discharge to 0.2C and 1C which produces specific discharge capacities 258.75 mAh g⁻¹ and 220.65 mAh g⁻¹, respectively. These results can be compared to another previous studies listed on Table 2. that was showing graphite/Na-LTO by doping method have a similar result with another method.
Table 2. Summary of Graphite Modification Performances from Previous Studies

| Material          | Method           | Rate | Initial Charge Capacity (mAh g⁻¹) | Ref  |
|-------------------|------------------|------|----------------------------------|------|
| NG-2wt% LTO       | Surface Coating  | 1C   | 200.9                            | [3]  |
| Graphite-LTO      | Surface Coating  | 1C   | 171                              | [13] |
| Graphite-5% LTO   | Surface Coating  | 0.2C | 324                              | [14] |
| Graphite-1wt% LTO | Doping           | 1C   | 220                              | This work |

Figure 2D shows the charging plot (lithium-ion insertion) potential as a cycle life function. With the increasing charge/discharge rate, the power slow decreased even at 1C rate, the initial specific charge power still being 220.65 mAh g⁻¹ which can occur because the LTO properties resist lithium dendrites problems which occur in high ratability performance [15]. Thus, the Na-LTO doping had close initial capacity result with another research. It shows that this method can apply as one of the potential development to enhance electrochemical performance.

4. Conclusion
Graphite/Na-LTO was prepared with success using a doping process followed by calcination. The chemical properties on the graphite were strengthened by a Na-LTO. Unlike previous research, the graphite's rate-capability was enhanced by LTO doping. The performance of cycling improvements is poor because the properties of the graphite material were affected by the calcination process during graphite/Na-LTO receiving. Alternatively, for lithium ion batteries, the graphite/Na-LTO could be potential for high-rate and stable rateability anode material.

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