The Effect of Modified LTO Synthesis using Salt Assisted Method with Various of Salt Metal Materials

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Abstract. This study aims to determine the effect of modified LTO synthesis using salt assisted method with various related materials. Salt assisted Li₄Ti₅O₁₂ for lithium-ion batteries with stable rate-capacity were prepared by simple solid state-mixing, followed by high temperature calcination. This process effected the performance of Li-ion kinetics and stability. Therefore, the salt assisted LTO, which was doped with 1wt% CaCl₂, MgCl₂, and NaCl presented various discharge capacity, and the highest was shown by LTO-Ca (82.41 mAh g⁻¹, at 0.1C). While the stable rate-capability at 0.5C and 1C were 59.28 mAh g⁻¹ and 58.72 mAh g⁻¹, respectively.

1. Introduction

Li₄Ti₅O₁₂ (LTO) is an anode material with an outstanding behaviour, because of its specifications in using high-current electronic devices. At 1.5V vs. Li + / Li, LTO work stably by avoiding electrolyte decomposition, and exhibit safety concerns by the use of carbon that produces a film of surface passivation [1], [2]. The surface passivation cause capacity loss and decreased battery life cycle [3], [4]. Also, LTO has superior structural stability where there is no change in its structure or volume during the lithiation / de-lithiation process [5]–[7].

There are many methods of synthesizing LTO materials, such as sol gel [8], [9], spray pyrolysis [10], hydrothermal [11], microwave-assisted synthesis [12], [13], and solid state reactions [5]–[7]. The studies of Yin et al. (2015) and Bai et al. (2008) stated that the application of molten salt method improved the crystallinity of the LTO material [14], [15]. In several reports, the addition of other metals, such as Ca, Mg, and Na were carried out. The research by Sattar et al (2020) found that, the addition of Mg through high temperature solid state technique, resulted in superior discharge ability and improved electrochemical efficiency [16]. In the Zhang et al (2020) report, the addition of Ca through the co-precipitation method showed that, Ca increased electrochemical stability, capacity, and reversibility [17]. Furthermore the addition of NaCl increased the crystal formation of ZnO, ZnFe₂O₄, and strontium ferrite [18]–[20]. Meanwhile, the increased material crystallinity boosted the electrochemical performance [21].

In this study, the salt-assisted method was adopted with 1wt% CaCl₂, MgCl₂, and NaCl, and it was known that this technique has not been used in the development of LTO materials. Using a CR2032 coin cell and LiFePO₄ as the cathode, electrochemical performance was evaluated.
2. Material and Methods

2.1 Materials Li₄Ti₅O₁₂
The material used for the synthesis of Li₄Ti₅O₁₂ (LTO) were LiOH (Merck, Darmstadt, Germany) and TiO₂ (Merck, Darmstadt, Germany) used as sources of Li and Ti in the Li₄Ti₅O₁₂ material. Analytical grades of MgCl₂, NaCl, and CaCl₂ (Merck, Darmstadt, Germany) were used as salt addition, while methanol or CH₃OH (Merck, Darmstadt, Germany) were used as dispersants in the solid-state mixing process.

2.2 Li₄Ti₅O₁₂ Preparation
LTO powders were synthesized via solid-state reaction. TiO₂ and LiOH were mixed with a Li:Ti molar ratio of 4:5. The investigation carried out in this study was to compare the effects of adding LTO-Na, LTO-Ca, and LTO-Mg, to determine the electrochemical performance, as well as the addition of NaCl, CaCl₂ and MgCl₂ (1% wt). LiOH, TiO₂, CaCl₂/MgCl₂/NaCl, and methanol were mixed in a ball mill for 4 hours. The purpose of using methanol as a material solvent. After the mixing process was complete, the precursor was dried in the oven to evaporate the methanol and sintered at 800°C for 12 hours with O₂ flow (Samator, Jakarta, Indonesia). After this, the material was pounded and sieved using 100 mesh.

2.3 Li₄Ti₅O₁₂ Characterization
The crystalline structure of the LTO powder was analyzed using X-Ray Diffraction/XRD (D2 Phaser Bruker, Germany) and Cu-K-alpha radiation (= 1.5418 Å) with two theta in the range 10° to 80°. The morphological identification of LTO powder was carried out using scanning electron microscopy/SEM (Jeoul JSM-6510LA, Tokyo, Japan).

2.4 Li₄Ti₅O₁₂/LiFePO₄ Cylindrical Cell Assembly
The analysis of electrochemical performance characteristics was carried out using a CR2032 coin cell, and the cathode used was Nickel Mangan Cobalt/NMC (MTI, Richmond, CA, USA). LTO powder was mixed with carbon (acetylene black / AB, MTI, Richmond, CA, USA), and binders (carboxymethyl cellulose (CMC), as well as styrene butadiene rubber (SBR) with a weight ratio of 80: 10 : 2:8 in water. This was carried out to make slurry coated onto copper foil using doctor's blade technique, followed by drying to evaporate the water. Then, the coin cell was fabricated in the glove box with Ar. LiPF₆ (1:1 v/v of EC / DMC) and cellgard (MTI, Richmond, CA, USA) were used as electrolytes and separators, respectively. The charge and discharge test was performed using the MTI BST-CH8-3A battery analyzer (1.0 V to 3.5 V potential range).

3. Results and Discussion

3.1 XRD Characterization

| Sample | Lattice Constant (Å) | FWHM (°) | Crystallite Size (nm) |
|--------|----------------------|----------|-----------------------|
|        | (111)                | (311)    | (440)                 | (111)    | (311)    | (440)    |
| LTO-Ca | 8.36179              | 0.103    | 0.116                 | 0.071    | 81.266   | 84.218   | 244.9    |
| LTO-Na | 8.35483              | 0.120    | 0.132                 | 0.075    | 68.783   | 74.076   | 232.2    |
| LTO-Mg | 8.35896              | 0.113    | 0.149                 | 0.076    | 74.089   | 65.600   | 229      |
| LTO    | 8.36698              | 0.188    | 0.192                 | 0.306    | 44.846   | 50.718   | 56.67    |
The characteristics of LTO material structure was carried out using XRD. Figure 1. showed the XRD patterns of the LTO material at various salt additions at 2θ in the 10°-80° range. All samples showed the overall formation of LTO peaks according to JCPDS Card No. 42-0207, with the cubic spinel structure and the space group of F3dm [43-45]. The XRD results of adding CaCl₂ salt showed the formation of CaCl₂ peaks at 2θ at 25°, and 33° (JCPDS No. 49-1092 and 12-0056). The addition of CaCl₂ and MgCl₂ indicated the formation of MgCl₂ peaks at 2θ and 33° respectively (JCPDS No. 25-1156). Table 1 showed that the lattice constant value was approximately 8.36179-8.35483 Å, and the value was close to that of LTO constant lattice from other literature samples (8.395-8.3538 Å) [22]–[24].

**SEM Characterization**

To analyze the material morphology, the material was characterized using SEM. Figure 2 shows SEM images for various LTO materials with variations in the addition of salt metal through a solid state reaction. The size range of all particle sizes of the LTO material was 1.049 µm – 2.377 µm. Figure 2c shows the morphology of the LTO-Ca material with little agglomeration and the smallest crystal size was 1.049 µm.
3.2 Electrochemical Characterization

Figure 2 SEM Image LTO (a) LTO-Na (b) LTO-Mg (c) LTO-Ca (d)

Figure 3 Charge-Discharge Specific Capacity at 0.1C (a) Rateability of Each Sample (b)
To determine the effect of adding salt (MgCl₂, NaCl, CaCl₂), electrochemical testing was carried out using a BTS Analyzer. Figure 3 showed the electrochemical performance of 0.1C formation, where CaCl₂ indicated the best performance with a capacity of 82.18 mAh / gr. While the lowest was obtained in the LTO with the addition of NaCl with a capacity of 47.66 mAh / gr. The analysis was continued by rating the three samples at 0.5C, to ascertain the retention capacity of each sample. The results showed that the obtained retention capacity for each sample was the highest shown in LTO-Ca of 71.4%, while the lowest was shown in LTO-Na of 70.67%. These results indicated that the addition of CaCl₂ has a greater specific capacity, and produced a material with a better rateability compared to LTO-Na and LTO-Mg. To measure the cycleability resistance of the LTO-Ca material, cycle tests were carried out 100 times. The results showed that after 100 cycles the capacity was reduced to 81%. To determine the performance of LTO-Ca, a rate of 0.1C, 0.5C, 1C, 5C, and 10C was carried out, as in Table 2 which was presented as follows.

![Figure 4 Cycle Test LTO-Ca](image)

### Table 2. Table of Charge and Discharge Specific Capacity of LTO-Ca at Various Rates

| Sample  | Charge (mAh/gr) | Discharge (mAh/gr) |
|---------|----------------|--------------------|
|         | 0.1C | 0.5C | 1C  | 5C  | 10C | 0.1C | 0.5C | 1C  | 5C  | 10C |
| LTO-Ca  |   81.47 | 57.62 | 59.72 | 51.6 | 27.48 | 82.18 | 59.28 | 58.72 | 53.3 | 27.54 |

### 4. Conclusion

The addition of salt has a different effect on the electrochemical performance of modified LTO synthesis. LTO-Ca has the highest retention capacity as well as specific discharge and charge capacities with 82.18 mAh / gr at 0.1C rate. Therefore, the addition of CaCl₂ salt was better than NaCl, and MgCl₂ salts.
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