Study Performance of LiFePO₄/Graphite Cylindrical Pouch Cell

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Abstract. Cylindrical cell Lithium ion battery with a pouch casing has been made at the Integrated Battery Laboratory, BATAN. LiFePO₄ double sided coated aluminum foil with a thickness of 180 μm is used as a cathode sheet. The anode sheet is made from two-sided artificial graphite coated on copper foil with a thickness of 197 μm. The composition, crystal structure, of the coated LiFePO₄ was measured by XRD. Battery cells are built by rolling thin layers of cathode, separator, and anode material into cylindrical shape using a rolling machine. The cylindrical cell is inserted into an aluminum bag and then sealed at 175°C. Cylindrical cell-bag inserted into the Glove Box then filled with ~ 2.5 ml of LiPF₆ electrolyte liquid. A vacuum sealing machine is used to seal the remainder of the bag set at 175 oC. The performance of lithium ion batteries is characterized by using a battery analyzer. LiFePO₄ shows a release capacity of 250.00 mAh, with a specific capacity of 124.10 mAh/g in the 1st cycle and 100.20 mAh/g after 100th cycle, at a rate of 0.3C. The cell shows good performance after 100 cycles with 80.74% retention.

Keywords: LiFePO₄; Graphite, Lithium ion batteries, cylinder cell, pouch cell

1. Introduction
One of the most important power sources worldwide is the rechargeable lithium-ion batteries, since their variety applications such as in mobile phones, laptop computers, digital cameras, electrical vehicles and hybrid electrical vehicles. One cell of rechargeable lithium-ion battery contains several components, namely cathode, anode, separator, electrolyte, current collector and connector. The most important components is the cathode material because relating to the performance of the batteries. The most well-known cathode materials, layered LiCoO₂ and LiNiO₂, spinel LiMn₂O₄, have been studied extensively [1-3]. LiCoO₂ is being used as the cathode material for commercial lithium-ion batteries, but it is toxic and expensive.

The cathode materials of lithium transition metal phosphates LiMPO₄ (M = Mn, Fe, Ni, and Co) with an ordered olivine-type structure, has a high theoretical specific capacity (170 mAh/g) [4-7]. However, it is difficult to attain its full capacity because its electronic conductivity is very low, which leads to an initial capacity loss and poor rate capability, and diffusion of Li⁺ ion across the LiFePO₄/FePO₄ boundary is slow due to its intrinsic character. The electronic conductivity of LiFePO₄ is ~10⁻⁹ S cm⁻¹, which is much lower than those of LiCoO₂ (~10⁻³ S cm⁻¹) and LiMn₂O₄ (2 × 10⁻⁵-5 × 10⁻⁵ S cm⁻¹). There are two methods to improve the electronic conductivity. One method is to introduce
conductive additives including a carbon coating [8] and supervalent cation doping [3]. Another method is to control the particle size by optimizing the synthesis conditions [6]. LiFePO$_4$ can be synthesized by different methods such as a solid-state reaction [9], a sol-gel method [10], a co-precipitation method, and a hydrothermal method [11,12], and so forth. Most of the studies are related to the improvement of the cathode materials, and performance of the battery, but only in half cell or coin cell.

In 2012, the Science and Technology Center for Advanced Materials, National Nuclear Energy Agency, with the support from the Ministry Research and Technology, Indonesia opened an Integrated Battery Laboratory (miniature pilot plant for battery line production) located in Serpong, Indonesia [13-15]. In this laboratory, the scientists have the opportunity to study all relevant process steps of line production of batteries in form of coin, cylinder or pouch cells [16,17].

The aim this study is to analyst cyclic performance of LiFePO$_4$/graphite occurred in cylindrical pouch cell by using Battery analyser [18,19].

2. Experimental method

2.1. Electrode manufacturing

The first step of battery production line was the electrode manufacturing. The raw materials for electrode processing are commercial powders LiFePO$_4$ as cathode materials, and artificial graphite as anode materials. All cathode and anode powder are commercial from MTI Co. Aluminum foil and copper-foil are used as current collectors. To form slurry, the cathode LiFePO$_4$ powders were mixed with artificial carbon and polyvinylidene fluoride (PVDF) that dissolved in N-methyl-2-pyrrolidinone (NMP). The weight ratio of active materials with artificial carbon and PVDF was 80:15:5. About 10 ml slurry was mixed in stainless crucible attached to vacuum mixing equipment. It was mixed for about 30 minutes with a certain speed. Mixing time and energy input are process parameters by means of which particle stability and degree of dispersion can be defined. Similar processes were done for the artificial graphite slurry, but without carbon black.

2.2. Electrode characterization

In order to quantify these electrode sheets in early stage of production, the Al-foil coated with LiFePO$_4$/C (LFP/C) and Cu-foil coated with artificial graphite were characterized by x-ray diffraction. The crystal structure of the LiFePO$_4$/C sheet and artificial graphite sheet were characterized by X-ray diffraction (XRD) using a PANalytical EMPYREAN Series-2, with Cu Kα, scan range from 10°to 80°. All those characterizations were done at the Integrated Battery Laboratory, BATAN [8,14].

2.3. Assembly of cylinder pouch cell

LiFePO$_4$ double sided coated aluminum foil with a thickness of 180 μm is used as a cathode sheet. The anode sheet is made from artificial two-sided graphite coated on copper foil with a thickness of 197 μm. Both aluminum and copper foil each function as a collector of positive and negative currents, respectively. Battery cells are built by rolling thin layers of cathode, separator, and anode material into cylindrical shape using a rolling machine. The cylindrical cell is inserted into an aluminum bag and then sealed at 175°C. Negative and positive connectors made of nickel and aluminum are each welded at the top of aluminum and copper. Cylindrical cell-bag inserted into the Glove Box then filled with ~2.5 ml of LiPF$_6$ electrolyte liquid. A vacuum sealing machine is used to seal the remainder of the bag set at 175 °C. The c-pouch cell was left for 12 hours in glove box, before taken out for testing its electrochemical cell performance.

In the present work, aluminum case was chosen, since it was simpler, lighter and the dimension could be customized. The product was named as a cylinder pouch cell or C-pouch cell, a new form of battery cell.
3. Results and Discussions

3.1. X-ray diffraction of LiFePO₄ and graphite sheet

The performance of cathode LiFePO₄ after coating, drying and calendaring are analysed by using the x-ray diffraction, as shown in Figure 1.

Figure 1. X-ray diffraction pattern of LiFePO₄/coated on Al-foil.

Figure 1 shows the x-ray diffraction data of LiFePO₄/coated on Al-foil that has been refined using the High-score plus program [14]. The major phase of ~71.9% was from the Lithium Iron Phosphate, LiFePO₄, with the olivine structure and space group (No.) P n m a (62). The lattice parameters a, b, and c are 10.322(3) Å, 6.003(2) Å, and 4.691(2) Å, respectively. Another peaks observed were corresponding to graphite, iron phosphate and aluminum phases. To form slurry, 85% LiFePO₄, 10% PVDF and 5% carbon black were mixed together in the vacuum mixer. It is known that the LiFePO₄ has low ionic conductivity (~10⁻⁹ S/cm), therefore in order, to increase its electronic conductivity, the addition of carbon black was needed as carbonaceous sources. Due to this reasons the graphite peaks were observed in the x-ray data [16]. The iron phosphate might appear from the dissociation of lithium hydroxide from LiFePO₄ during vacuum mixing or coating. Another Al peaks related to aluminum foil current collector, where LiFePO₄ was coated on it.

Figure 2. X-ray diffraction pattern of Graphite-coated on Cu-foil.

Figure 2 showed x-ray diffraction pattern of the artificial graphite-coated on Cu foil. The data was compared to the standard graphite material. It was clear that the diffraction peaks corresponding
to the graphite ~57.9% and copper 42.1%. The composition of graphite was rather similar with copper caused by the overlapping peak at 2θ~ 26.2559°. The graphite had a space group (No.) P 63/m m c (194), with the lattice parameters a, b, and c are 2.4603(3) Å, 2.4603(3) Å, and 6.726(1) Å, respectively. From crystal structure refinement, the reliability factors Rwp, Re, and X2 are 19.65156, 0.50427 and 1518.70400, respectively. It should be mentioned here that all the preparation was done open air, not in glove box. This was due to larger production of electrode sheets for cylinder cells. Similar refinements have been performed to the electrolyte material Li3PO4 [14,16].

3.2. Electrochemical testing

Performance of C-pouch cell was analyzed by using a BTS-8 MTI Battery analyzer. The step setting is shown in table 1. It is important to perform initial charging before doing all the charge discharge cycling. After rest for 1 minute, it was charged with a constant current (CC_Chg) 100 mA until the voltage reached 4 Volt. Then it was kept in this charge at contact voltage (CV_Chg) until the current decreased to 5mA, then it was discharged with a constant current (CC-DChg) 100 mA until the voltage reached 2 Volt and rest for 5 minutes. These steps were cycled for hundred times to determine its capacities, stability and Coulombic efficiency. The electrochemical performance was also performed for other types of coin and cylinder cells [15,20]. Figure 3 shows the Volt-Current-Time curve during the cycling.

Table 1. Step setting for electrochemical performance of cylinder pouch cell.

| StepNum | StepType  | Time(mm:ss) | Vol(V) | Cur(mA) |
|---------|-----------|-------------|--------|---------|
| 1       | Rest      | 1:00        | 4      | 100     |
| 2       | CC-Chg    |             |        |         |
| 3       | CV-Chg    |             |        |         |
| 4       | CC-DChg   |             | 2      | 100     |
| 5       | Rest      | 5:00        |        |         |
| 6       | Cycle     |             |        |         |
| 7       | Stop      |             |        |         |

Figure 3. Charge-discharge curve, voltage and current versus time of C-pouch cell LiFePO4/Graphite.
Figure 4 shows the charge discharge curves of LFP/Graphite cylindrical pouch cell with various cycles from 1st to 100th cycles. The discharge capacities for the first and 100th cycles were ~124.10 mAh/g and 100.20 mAh/g, respectively. The cycling performance of LFP/Graphite cylinder pouch cell showed the best capacity of all samples at 0.3C-rates, about 124.10 mAh/g with small decreasing after 100th cycles as shown in Figure 4. The results showed that the cylinder pouch showed good performance and a better stability after 100th cycles. The results are comparable to the LFP/C using cylinder 18650 [9].

4. Conclusions
The electrochemical properties of LFP/Graphite cylindrical pouch cell lithium ion battery (c-pouch cell) exhibited a discharge capacity of 250 mAh, with the specific capacity capacities for the first and 100th cycles were ~124.10 mAh/g and 100.20 mAh/g, respectively. The battery showed good performance after 100 cycles at rate 0.3C with retention of 80.74%. The c-pouch cell can be used as an alternate casing product of lithium ion rechargeable battery.

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