Electrode capacity and voltage performance of lithium iron phosphate – polyaniline coin cell battery

I Rahayu¹*, A Wijayati¹, A R Noviyanti¹, S Hidayat² and Risdiana²

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran Jl. Raya Bandung Sumedang km 21 Jatinangor, West Java 45363, Indonesia
²Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran Jl. Raya Bandung Sumedang km 21 Jatinangor, West Java 45363, Indonesia

*iman.rahayu@unpad.ac.id

Abstract. Battery is the main component in many portable electronic devices that serves as energy storage. Lithium cobalt oxide (LiCoO₂) is one of the most popular types of lithium-ion battery due to its low self-discharge and high energy density. However, LiCoO₂ is toxic to the environment, thus a safer material is important to be studied. A non-toxic and thermally stable lithium iron phosphate (LiFePO₄) could be a good alternative for battery material. Nevertheless, the low electrical conductivity of LiFePO₄ (10⁻⁹ S.cm⁻¹) should be enhanced by using a conductive polymer, such as polyaniline (PANI), to form a composite. This study aims to investigate the electrode capacity of the coin cell battery composite using galvanostatic cycle and to examine its voltage performance using the cyclic voltammetry methods. The cathode was prepared in powder form. The composite was assembled in the form of coin cell battery. It consists of lithium, lithium hexafluorophosphate-ethylene carbonate-dimethyl carbonate, and lithium iron phosphate-polyaniline-polyvinylidene fluoride as the anode, electrode, and cathode, respectively. It is found that the electrode capacity of [Li|1 M LiPF₆/EC DMC|LiFePO₄-PANI-PVDF] coin cell battery was 38 mA h g⁻¹ with a working voltage of 3.6 – 4.0 V.

1. Introduction

In latest decade, eco-friendly technology and energy storage are the opportunities for technology advancement. Those opportunities have been received great attention from various parties involving research groups, industry, and government. The desire for the better portable energy source increases every year. The consumer needs energy storage that have higher capacity and working voltage to integrate multiple devices into a single product, like digital camera, radio, music player, and GPS in one smart phone. The device requires a source of massive and flexible energy to support these functions [1-4].

From all of the existing battery technologies, lithium-ion batteries have enormous energy storage capacity, for example, LiCoO₂ battery as a cathode which has a storage capacity of 900 mAhg⁻¹ [4-7]. Despite its enormous capacity, LiCoO₂ is not environmentally friendly and unstable at high temperatures. Therefore, battery manufacturers are looking for alternative replacement cathode materials such as LiNiO₂, LiMn₂O₄, and LiFePO₄ [7-10].

Theoretically, specific capacity of LiFePO₄ is 170 mAhg⁻¹ at a voltage 3.45 V, which is well within the window of the polymer as well as the carbonate electrolytes [6-10]. It is, therefore, an inexpensive, environmentally benign, safe cathode capable of thousands of charge/discharge cycles without
degradation. Therefore, LiFePO$_4$ is considered to be a leading candidate material for the cathode of the large-capacity batteries.

Polyaniline (PANI) is one of the most studied conductive polymers because of its high stability in the environment, readily synthesized, and has reversible electrical changes via protonation. PANI is conductive in the form of emeraldine salts (ES) [5-7]. In recent studies, many cathode materials combined with polymers, for example, LiV$_3$O$_8$ / polypyrrole have been successfully synthesized and show better cycling performance in lithium cells [5-10]. Among the various types of conductive polymers, PANI has been used extensively because it is easily produced with the desired morphology and structure. PANI is superior to polypyrrole and polythiophene in energy density and durability. PANI is electrochemically active in the range 2.0 - 3.8 V. Furthermore, PANI is not only useful as a conductive adhesive such as carbon in the electrode, but also participate as an active material [5-7].

From our previous study, it is found that the process of electrode coating with conductive polymers is an effective method to improve the electrical performance of cathode and anode materials in lithium-ion batteries [5-10]. The conductive polymer is an additional material in lithium ion batteries. It has several properties that could facilitate redox reactions in batteries involving lithium ions or anion electrolyte. Conductive polymers also could be isolated crystalline particles, preventing agglomeration on the surface of the electrode. Furthermore, conductive polymers may prevent the dissolution of the active material into the LiPF$_6$ electrolyte. In this work, we attempt to use PANI in LiFePO$_4$ - PANI cell battery and investigate its charge capacity and working voltage with structure [Li | 1 M LiPF$_6$/EC DMC | LiFePO$_4$-PANI-PVDF].

2. Materials and Method

2.1. Materials

The material used are aniline (pro analyst, Merck), lithium iron phosphate, ammonium hydroxide (pro analyst, Merck), ammonium peroxydisulfate (pro analyst, Merck), distilled water, hydrochloric acid (37%, Merck), methanol, 1 methylpyrrolidinone (99.5%, Sigma Aldrich), toluene (pro analyst, JT Baker), polyvinylidene fluoride (pro analyst, Merck), lithium (Kyokuto Metal Co., Japan), Celgard® 25021 polypropylene (Celgard LLC, USA), lithium hexafluoro phosphate (pro analyst, Merck), ethylene carbonate (pro analyst, Merck), and dimethyl carbonate (pro analyst, Merck).

2.2. Method

PANI was synthesized by interfacial method [5-7]. The electrode was prepared by mixing 70% by weight of LiFePO$_4$, 15% by weight of PANI ES, and 15% by weight of polyvinilidene fluoride (PVDF) in a mortar. The powder mixture was then added with N-methylpyrrolidinone (NMP) to become slurry, then molded with a thickness of 20 m and a diameter of 2 cm above the aluminum sheet. Afterwards the sample was dried in the oven for 24 hours at a temperature of 80 °C. The dried sample were compacted using the roll to roll coater. The electrode was re-dried in a vacuum oven for 12 hours at 80 °C. Battery manufacture refers to R2032 Standard coin cell battery. All electrodes which have been vacuumed for 12 hours at 80 °C were included in a pure Argon Humidity Controlled Glove Box and H$_2$O gas concentration <1 ppm and O$_2$ <1 ppm gas. The lithium sheet was used as a negative electrode (anode) and a reference electrode. Celgard® 25021 polypropylene is used as a separator, and 1 M lithium hexafluoro phosphate (LiPF$_6$) in ethylene carbonate (EC) and dimethyl carbonate (DMC) mixture 1:1 (v/v) were used as an electrolyte [5-7]. The battery was characterized using cyclic voltammetry, and Galvanostatic cycle to measure its capacity. The coin-cell making scheme is shown in figure 1.

There are two categories of solvent that can be used: (i) an organic solvent-based system and (ii) a water-based system. The organic solvent is more commonly used to obtain good suspension. The examples of the organic solvent are NMP. If using a water-based system, there will be an agglomeration of the powder in the suspension caused by strong hydrogen bonding and electrostatic forces. One of the keys in the coating process is to control agglomeration, which can improve dispersion and slurry stability.
The method used for the preparation of cathode slurry coatings was the doctor blade method. The cathode slurry was placed in a doctor blade reservoir and printed on an aluminum sheet. The thickness of the cathode is the gap between the doctor blade and the aluminum sheet. The coating is very influential on the electrode results. The addition of excessive NMP causes the slurry to become very dilute (low viscosity) so there is much cracking in the electrode that results in less optimal battery performance. After the cathode was printed, the next step was done to evaporate the solvent in the slurry.

When the coin cell is an assembly at Glove Box, it is important to keep O₂ and H₂ pressures less than 1 ppm to minimize the bursting of lithium metal. In addition, coin cells must be sealed completely during the sealing process to prevent reactions between lithium metal and air. Figure 2 shows an example of a coin cell sealing.

![Figure 2](image_url)

Figure 2. Sealing of (a) coin cells in well-sealed and (b) not well-sealed.

The assembled battery cells were then electrochemically tested with cyclic voltammetry and galvanostatic cycles to identify redox potential and storage capacity.

3. Results and Discussion

Cyclic voltammetry of LiFePO₄ - PANI cell battery is presented in figure 3. The oxidation and reduction peak of the cell is at 2 V - 4 V which indicates good reversible property. The increasing of applied voltage increase current, but when the current is reduced the coin cell battery’s voltage is decreased gradually. It shows the coin cell battery has an internal redox.
Figure 3. Cyclic voltammetry of coin cell battery [Li][1 M LiPF₆/EC DMC|LiFePO₄-PANI-PVDF].

The PANI cyclic voltammogram shows two oxidation peaks at 3.5 and 4.0 V and three reduction peaks at 2.0, 3.2 and 3.6 V. Redox peaks (oxidation/reduction) at 3.5/3.2 V shows benzoquinone, and the last peak at 4.0 / 3.6 V indicates presence of head-to-tail dimer oxidation and conversion of emeraldine structure to pernigraniline. A reduction peak at 2.0 V indicates leukomeraldine formation.

The galvanostatic cycle is used to identify the charging and discharging capacity in a battery system over a given cycle. Figure 4 shows graphs of charging and discharging coin cells [Li | 1 M LiPF₆ / EC DMC | LiFePO₄-PANI-PVDF] at 298 K for 25 cycles. The measurement of the coin cell is carried out at a current density of 30 A cm⁻². LiFePO₄-PANI-PVDF electrode produces maximum voltage at 4.0 V during filling and discharging process. The charging capacity of the electrode was 38 mAhg⁻¹ and was decreased to 3 mAhg⁻¹ for 25 cycles.

Figure 4. Charging and Discharging graphic of coin cell battery [Li][1 M LiPF₆/EC DMC|LiFePO₄-PANI-PVDF].

The processes that occurred during the charging and discharging process take place are [9, 10]:

\[
\text{LiFePO}_4 \rightarrow x\text{FePO}_4 + (1-x)\text{LiFePO}_4 + x\text{Li}^+ + xe^- \quad (1)
\]

\[
\text{FePO}_4 + x\text{Li}^+ + xe^- \rightarrow x\text{LiFePO}_4 + (1-x)\text{FePO}_4 \quad (2)
\]

The reasons why practical capacity is lower than theoretical capacity is, firstly not all the Lithium can be removed from the lattice of the host material. The rest of the Li is removed above the cut off
potential. Therefore, it is not accessible. Secondly, the lithium metal reacts with the electrolyte during the filling process, producing a film. During lithium deposition, the film temperature will be high due to ion transfer in the film itself. The result of heating the film is the film into an electronic conductor, and lithium metal is deposited in the film. If heating does not occur, then isolated lithium becomes electrochemically inactivated [11]. Thirdly, the slurry is too dilute, resulting in the cracked coating and hence decreasing the amount of composite printed on the aluminum sheet.

Besides that, the existence of PVDF is also affect the capacity of cell battery. Excessive percentage of PVDF lowers the value of composite conductivity, and results in low capacity values. The reason was due to PVDF only serves as an adhesive between the composite and aluminum sheet and it has no conductivity value. The presence of PVDF will inhibit the intercalation of lithium ions and the extension of PANI conjugation.

4. Conclusion
The electrode charging capacity of the [Li | 1 M LiPF$_6$ / EC DMC | LiFePO$_4$-PANI-PVDF] coin cell battery is 38 mAh$^{-1}$ and the working voltage at 3.6 – 4.0 V in 25 cycles. The practical capacity (38 mAh$^{-1}$) is lower than theoretical capacity (170 mAh$^{-1}$) due to not all the Lithium can be removed from the lattice of the host material.

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