The Optimization of CMC Concentration as Graphite Binder on the Anode of LiFePO₄ Battery

S Hidayat¹, T Cahyono¹, J Y Mindara¹, N Riveli¹, W Alamsyah¹ and I Rahayu²

¹ Department of Physics, Faculty Mathematic and Natural Sciences, University of Padjadjaran, Jl. Raya Bandung-Sumedang Km 21 Jatinangor 45363, West Jawa Indonesia
²Department of Chemistry, Faculty Mathematic and Natural Sciences, University of Padjadjaran, Jl. Raya Bandung-Sumedang Km 21 Jatinangor 45363, West Jawa Indonesia

E-mail: sahrul.hidayat@phys.unpad.ac.id

Abstract. Recently, the most dominating power supply on the mobile electronics market are rechargeable Lithium-ion batteries. This is because of a higher energy density and a longer lifetime compared to similar rechargeable battery systems. Graphite is commonly used as anode material in the Lithium-ion batteries, because of its excellent electrochemical characteristics and low cost fabrication. In this paper, we reported the optimization of the concentration of the CMC (carboxymethyl cellulose), that acts as the binder for graphite anode. Based on our experimental results, the best composition of graphite : C : CMC is 90 : 8 : 2 in weight %. Anode with such composition has, based on SEM measurement, a relatively good surface morphology, while it also has relatively high conductivity, about 2.68 S/cm. The result of cyclic voltammogram with a scan rate of 10 mV/s in the voltage range of 0 to 1 Volt, shows the peak of reduction voltage at 0.85 Volts and the peak voltage of oxidation is at −1.5 Volt. The performance of the battery system with LiFePO₄ set as the cathode, shows that the working voltage is about 2.67 Volts at 1 mA current-loading, with the efficiency around 47%.

1. Introduction

Environmental pollution and energy crisis have been severely accumulated due to the excessive utilization of fossil fuel resources. To overcome these problems, novel clean energy resources and its related energy conversion and storage materials and devices are highly demanded. Among the diverse energy storage devices, lithium-ion batteries (LIBs) have been studied overwhelmingly, and certain kinds of LIBs have been commercialized already. LiCoO₂ is one of the main LIB cathode materials that are used in industrial scale. But LiCoO₂ have several drawbacks, such as that it could pollute the environment during production process, overcharge during usage thus causing potential safety hazard, and that cobalt is expensive for its limited storage [1]. Therefore, search for alternative materials is always a research hotspot. Having similar crystal structure as LiCoO₂, LiNiO₂ has the advantage of a lower price, but it also has difficulties in its synthesis, it has poor structure, thermal, and cycling stability [2].

Therefore, the exploits of high-performance electrode materials, electrolytes, and membrane for LIBs have attracted great attention during the last decade. Lithium iron phosphate (LiFePO₄, LFP) with olivine structure is one of the most promising cathode materials for LIBs, owing to its high theoretical capacity (170 mAh g⁻¹), acceptable operating voltage (3.4 V vs. Li⁺/Li⁻), good cycling stability, low toxicity, good thermal stability, and low cost [3].

Lithium ion batteries are made up of one or more generating compartments called cells. Each cell is composed of three components: a positive electrode, a negative electrode, and an electrolyte between them. The positive electrode is made from chemical compound named lithium iron phosphate (LiFePO₄). The negative electrode is made up of carbon (graphite) and the electrolyte varies from one type of battery to another. All lithium ion batteries more or less work in the same manner. During the charging of the battery, lithium based positive electrode expel some of its lithium ions, which move through the electrolyte to reach to the negative electrode and remain there. The battery stores energy during this process. When the battery is
discharging, the lithium ions move back across the electrolyte to the positive electrode, producing the energy that powers the battery. In both cases, electrons flow around the outer circuits in the opposite direction to the ions. Electrons do not flow through the electrolyte as it tends to be an effective insulating barrier. The movement of ions (through the electrolyte) and electrons (around the external circuit, in the opposite direction) are interconnected to each other; if any one of them stops, the other will also stops. If the ions are no longer move through the electrolyte because the battery is completely discharged, the electrons can’t move through the outer circuit either, then the battery is no longer powered.

In commercial Li-ion batteries, PVDF has been widely used as the binder for both the negative and the positive electrodes, because of its good electrochemical stability and high binding power. PVDF binder is expensive, not easy to recycle, and involves the use of volatile organic compounds such as the toxic and environmentally harmful N-methyl-2-pyrrolidone (NMP), in its processing.

As an alternative binder material, we use CMC that are cheaper and environmentally friendlier than PVDF [5]. CMC is a familiar substance in the food industry, used as emulsifiers. We use local produced CMC, ordered from the PUDAC Scientific. CMC, which is produced from the insertion of carboxymethyl groups into natural cellulose, is the commonly used binder for anodes and cathodes of Li-ion batteries. CMC has a strong shear-thinning behavior that adjusts to the slurry rheology.

2. Experiment
The main interest of our experiment is the optimization of CMC as binder for the graphite-Carbon cathode. In the experiment, a layer of CMC-graphite-C is deposited on the glass substrate. Study of characterization is then conducted, that consists of conductivity measurement and photo micro. Several different composition of the cathode are tested. Once we found the composition of best quality, we use it to replace the anode in the commercial LiFePO4 battery. As the electrolyte, we use 1M Lithium hexafluoro phosphate in mix with Ethylene carbonate, Di-methylene Carbonate and Di-ethylene carbonate. Finally, we perform battery performance test, that includes charge-discharge process, energy density and efficiency.

In the fabrication for anode layer, graphite, conductive carbon and the CMC are mixed in distilled water using magnetic stirrer. The layer is the constructed using the Doctor Blade methode. Figure 1 shows the steps of the battery packaging. First, the anode and cathode layer are prepared. Then, components of the battery are stacked as follows: cathode, separator and anode. The battery with ordered components is then placed into the packaging cell. Finally, the electrolyte is filled to the cell via the glove box with argon environment. The battery is then ready for characterizations.

![Figure 1. The steps of battery packaging.](image)

In the battery characterization step, we used voltage/current source for charging process, automatic battery loader for discharging process, and multimeter for measuring the voltage or current of battery. The system is integrated with the personal computer.
3. Results and Discussion

Figure 2. Conductivity of CMC-graphite-C.

Figure 2 shows the conductivity of CMC:graphite:C layer with five different compositions of CMC. The conductivity values are obtained through the four line probe method. As the basis, we start the measurement with the layer when the CMC composition is of 5%. We then reduce the CMC composition and obtained an increasing tendency of the conductivity. Based on our experiment, the maximum conductivity is obtained when the CMC composition is of 2%. The layer with such composition is then used in the battery system.

Cyclic voltammogram is used to studies of oxidation and reduction processes of CMC-graphite-C layer in electrolyte media. In this test, we use CMC-graphite-C deposition on ITO substrate as working electrode and platinum as counter electrode. In Fig. 4 is shown the reduction peak and the oxidation peak. When the scan voltage increased, the lithium ion move intercalation into the graphite layer and the opposite happen when scan is reversed. In Figure 3 we can also observe the reduction and oxidation in CMC-graphite-C layer occurs in reversibly.

Figure 3. Cyclic voltammogram of the CMC-graphite-C layer.

The battery is made in the small cell model, where the area of electrode is 4 cm² only, causing the capacity of battery is limited. When the charging time is less than 20 minute, the working voltage of battery goes below 2.5 Volt. While as the charging time is above 25 minute, the working voltage does not change significantly. We found that 30 minutes is the optimal charging time. Figure 4 shows the optimization of current discharging process. We can observe that the optimal discharge current is about 1 mA, and that corresponds to the maximum battery efficiency of about 47%. We can increase the discharge current by making the battery with wider electrode.
4. Summary

In this study we vary the composition of CMC which act as the binder in CMC-graphite-C cathode in a LIB battery system. We found that the layer with CMC composition of 2 % (%wt) is the one that gives best performance. It produces good surface profile and high conductivity of about 2.68 S/cm. This shows that the use of CMC increases the binding power of the active cathode components. CMC composition of less than 2% produces less binding power, while the composition of higher than 2% will start to slow down the charge movement, does reduce its conductivity. That is due to the fact that CMC is a cellulose with the properties of an isolator. For the use of the cathode layer in the battery system, the optimal charging voltage is at 4 Volt for about 30 minutes, The working voltage is about 2.7 volts and the maximum efficiency is 47%, at a discharge current of 1 mA.

References
[1] Lee J H, Paik U, Hackley V A, Choi Y M 2005 J. of The Electrochemical Society 9 A1763
[2] Hamid N.A., Wennig S., Hardt S., Heinzel A., Schulz C., Wiggers H 2012 Journal of Power Sources 216 76
[3] Pei B, Yao H, Zhang W, Yang Z 2012 Journal of Power Sources 220 317
[4] Hidayat S, Amelia O, Rahayu I, Fitriawati 2015 Materials Science Forum 827 125
[5] Ebrahimzadeh S, Ghanbarzadeh B, Hamishehkar H 2016 International Journal of Biological Macromolecules 84 16