Synthesis and Characterization of Anode for Lithium Ion Battery

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Abstract. Anode sheet manufacturing for lithium batteries coated with Polyvinylidene fluoride polymer (PVDF) has been done. The anode sheet is made using a desktop bubble remover from graphite base material by varying the PVDF content of 10%, 15% and 20%, which is called as G1, G2 and G3 samples. The anode material from the mixture of graphite and PVDF is then coated again using PVDF polymer electrolyte with variations in content as much as 10%, 15% and 20%, respectively called as GL1, GL2 and GL3 samples. Characterization of the anode product was measured using XRD diffraction, scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). The conductivity of the anode sheet was measured using LCR meter. The result shows that the PVDF polymer phase is only observed in GL1, GL2, and GL3 samples. The conductivity value (σ) of the anode sheet in the samples G1, G2 and G3 is obtained in the order of $10^{-3}$ S.cm$^{-1}$ to $10^{-2}$ S.cm$^{-1}$ slightly greater than that of the standard anode sheet ($\approx 10^{-3}$ S.cm$^{-1}$). The conductivity (σ) of the anode sheet tends to decrease with the addition of the PVDF polymer for the GL1, GL2 and GL3 samples to $10^{-4}$ S.cm$^{-1}$. The maximum conductivity in this study was obtained in the G2 sample, with a PVDF polymer content of 15%. SEM / EDS observations show that the fluorine (F) element increases with the addition of the PVDF for GL2 sample.

Keywords: anode sheet, PVDF polymer, conductivity, lithium battery

1. Introduction

Lithium-ion batteries (Li-ion) that can be recharged (rechargeable) become one of the important components for portable electronic equipment such as mobile phones (HP) and computer devices. Li-ion batteries have advantages when compared to Ni-Cd or Ni-MH batteries, namely energy density, higher operating voltage and safer. However, research and development of Li-ion battery materials are still being developed, especially to reduce the thickness and weight of materials and study the improvement of cyclical stability [1–5].

In Li-ion battery systems, the most widely used anode material is graphite. However, graphite has a disadvantage, namely the highest energy density which is still limited to only 372 mAh.g$^{-1}$) [4]. The electrochemical properties of natural graphite anodes, involving initial efficiency, reversible capacity and cycle stability have been improved due to higher graphitization degree, higher purity, more
suitable particle size distribution, and so on. Recently, natural graphite has come to be considered as a promising anode material for lithium ion batteries due to its high reversible capacity, appropriate charge/discharge profile and low cost. However, low first cycle efficiency and poor cycle stability has limited its practical use [3,4,6,7].

In the process of fabricating Li-ion battery, polymer binders are very important ingredients to bind the active ingredients of the electrodes. The properties of adhesives and chemical binders have a major influence on battery performance, especially on battery servicing capabilities. The polymers used to produce anodic coating on the Li-ion battery are polyvinylidene fluoride (PVDF). PVDF is easily obtained material, has high crystallinity that can be used in assembly lithium battery. PVDF interacts with electrolytes and is stable at fairly high temperatures. Furthermore, PVDF shows good chemical resistance in common organic-based carbonate [3,6-9]. The combination of binder PVDF and NMP solvents are used for binders and solvents because PVDF is soluble in NMP and allows preparation of slurry with the right viscosity. Production (solvent-based) process for anodic coatings involves such as mixing powdered active ingredients with carbon, dissolving PVDF with NMP solvent and mixing the powder with a solution to form slurry. The above production processes need to be done carefully because NMPs are heterocyclic, volatile organic compounds (VOCs) and flammable between volume percent 1.3 and 9.5. However, NMP has a high boiling point, which is around 200°C.

The stability and performance of graphite-based anodes with PVDF binders in lithium-ion battery operation has been tested very well for electrode resistance both mechanically and electrochemically [6,11,12]. So PVDF has been used for decades to produce lithium-ion batteries commercially. In this study, the anode material used in Li-ion battery technology is materials, graphite and polymer binders whose main function is to improve the mechanical stability of the anode layer and the conductivity of Li-ion batteries. The purpose of this study was to create and learn PVDF electrolyte addition anodes for lithium battery applications and study the effect of adding coatings on graphite stability and performance, which are closely related to particle size and structure in improving graphite material performance.

2. Methods

2.1. Materials

High purity ingredients used are Polyvinylidene fluoride (PVDF), liquid LiPF$_6$ and solids, graphite, N-methyl pyrrolidone (NMP), carbon and copper sheets (Cu). The tools used in this study include compact tape casting film coater, compact precision disc cutter, large glove box, desktop hydraulic crimping machine, desktop bubble remover, hot rolling press, vacuum oven.

2.1.1. Sample Preparation. In this study, the methods carried out through two stages. First, the synthesis of the anode layer is composed of basic materials of carbon (10 weight %), Graphite (80 weight %) and PVDF polymer electrolyte (10 weight %). The PVDF polymer electrolyte was firstly dissolved with NMP until homogeneous. Carbon powder, graphite and PVDF + NPM with variations in composition 10 weight %, 15 weight% and 20 weight% are mixed together in a desktop bubble remover to form a slurry-shaped anode sheet [2]. The anode layer in the form of slurry is placed above the copper sheet (Cu) using a compact tape casting coater film and then dried in an oven. Furthermore, the resulting anode sheet was as called the G1, G2 and G3 samples, respectively.

Second, the surface of the anode sheet from the G1, G2 and G3 samples coated with PVDF + NPM polymer electrolyte solution again with variations in content of 10 weight %, 15 weight % and 20 weight %. After that the samples were dried in an oven at 90°C and compacted using a hot rolling press. The coated samples were called as GL1, GL2 and GL3 samples. The resulting anode coating product was characterized using X-ray diffractometer, scanning electron microscope and energy dispersive spectroscopy (EDS).
3. Results and Discussion
The XRD pattern of the samples G1, G2 and G3 from the anode before being coated with PVDF and the samples GL1, GL2 and GL3 after being coated with PVDF are shown in Figures 1 and 2. In Figure 1, it is clear that the samples G1, G2 and G3 have formed crystals perfectly. This can be seen from the intensity of samples. The two peaks were observed at \(2\theta = 26.63\) and \(43.49\) with each Miller index of (006) and (002). From open data crystallography (COD) no. 96-901-2705 found that the material is graphite. In Figure 1, the crystalline phase of PVDF was not observed in XRD data even though the addition of PVDF polymer electrolyte content was up to 20 weight% by weight.

![Figure 1](image1.png)

**Figure 1.** XRD diffraction pattern of the uncoated anode from (a) G1, (b) G2 and (c) G3 samples.

Figure 2 shows the XRD pattern of the anode sheet material after being coated with PVDF content as much as 10 weight%, 15 weight%, 20 weight% from GL1, GL2, and GL3 samples, respectively. The analysis results showed that PVDF crystals were observed at \(2\theta = 20.19\). The high peak PVDF phase increases with increasing PVDF polymer content. Data obtained from measurements using XRD then adjusted to JCPDS data. This value is close to the Miller index value (110) in the JCCPDS data base. While the graphite phase peaks were observed at \(2\theta = 26.63\) and 43.49.

![Figure 2](image2.png)

**Figure 2.** XRD diffraction pattern of the coated anode from (a) GL1, (b) GL2 and (c) GL3.
The anode which is coated again with PVDF electrolyte solution makes the anode sheet more elastic. PVDF which covers the top layer of the anode will experience strong inter-particle forces with graphite. In addition, the voltage between the graphite and PVDF molecules increased so that at a PVDF concentration of 15 weight % the anode layer was not strong enough to bind copper sheets. At 15% PVDF concentration is the maximum concentration where the stress between graphite molecules and PVDF reaches the strongest state.

### 3.1. Impedance and Conductivity of Anodes

Anode impedance measurement is carried out using instrument electrochemical impedance spectroscopy (EIS). The measurement results are frequency quantities, real impedance values ($R_\text{real}$), and imaginary impedance values ($X$) which are then plotted curves between the real impedance ($Z_\text{real}$) and the imaginary impedance ($Z_\text{imaginer}$) as shown in Figure 3 and Figure 4 for each sample without and with PVDF coating.

![Figure 3](image-url)

**Figure 3.** Impedance of anode *non-coating* PVDF of (a) G1, (b) G2, (c) G3, (d) standard + LiPF$_6$ (e) Cu sheet and (f) Standard Cu.

Figure 3 show that the anode has a pure resistance value or pure $R$ only. The Cu sheet and the standard anode only have a resistance value so that the shape of the curve is perpendicular to the X axis. The shape of the standard anode curve + liquid LiPF$_6$ indicates that the intrinsic properties of the anode are affected by the number of electrolytes. At the anode with variations in PVDF concentration, a shift in the curve indicates that the anode property is affected by PVDF. PVDF provides resistance to graphite but does not significantly affect the shape of the curve because the distribution is fairly even in the composite and the number is small so that the curve remains straight. This shows that the intrinsic properties of the anode remain dominated by graphite and carbon in the composite.

In Figure 4, an anode sample curve coated with PVDF 10 weight % (GL1), 15 weight % (GL1) and 20 weight % (GL3) show a different curve with the anode curve without being coated from sample G in Figure 3. This is because the PVDF concentration the excess adds barriers between molecules and barriers between PVDF molecules with graphite. PVDF will interact with graphite via a hydrogen bridge. At 10 weight % coated anode (GL3 sample), PVDF has a higher viscosity and density that is difficult to interact with graphite in the lower layer, so that the impedance curve shows the nature of graphite alone.
Figure 4. Impedance of PVDF coated anode (a) 10 weight % (GL1), (b) 15 weight % (GL3) and (c) 20 weight % (GL2).

At 10 weight % coated anode (GL1 sample) and 20 weight % (GL3 sample), PVDF has a high viscosity and density, making it difficult to interact with graphite in the lower layer. Consequently the impedance curve shows the nature of graphite only, as shown in Figure 4 (a) and 4(c). Figure 4(b) shows the impedance curve of a sample of 15% PVDF coated anode (GL2 sample). Interaction between the molecules of PVDF and the interaction of the PVDF molecule with graphite reaches the maximum state level so that the impedance value on the curve shows the intrinsic nature of the PVDF molecule. From the measurement results obtained that the best PVDF polymer electrolyte coating was obtained with a concentration of 15 weight %, namely in the GL2 sample.

Conductivity curves are obtained by plotting the frequency log values with conductivity log values. Conductivity values obtained from the equation:

$$\sigma = \frac{1}{R \times t / A}$$

with $R =$ resistance, $A =$ the surface area of the anode used and $t =$ thickness of the anode layer. From equation (1) it can be seen that the presence of PVDF in the composite affects the conductivity value ($\sigma$) of the anode, where the increase in PVDF concentration is proportional to the increase in conductivity, $\sigma$. Measurable conductivity is ionic conductivity of polymer electrolytes because electrolyte ions move on the surface of the anode.

Figure 5 shows the conductivity curves of standard anode layer samples, G1, G2 and G3. The sample measurement results show that the standard conductivity is obtained around $\sigma = 10^{-3} \text{S.cm}^{-1}$. The addition of 10 weight % PVDF electrolyte (Figure 6a) produces a conductivity value, $\sigma < 10^{-3} \text{S.cm}^{-1}$, as in Figure 5 (b). The value of $\sigma > 10^{-3} \text{S.cm}^{-1}$ slightly increases with the addition of 15 weight % PVDF (Figure 5c), and then decreases to $\sigma < 10^{-3} \text{S.cm}^{-1}$ with an increase in PVDF content up to 20 weight % by weight (Figure 5). In this condition, the sample conductivity reaches a maximum at 15 weight % PVDF addition concentration.
From Figure 5, it can be seen that the conductivity non-coated anode (G3) has slightly higher value to the LiFePO$_4$ standard anode which is liquid LiPF$_6$ electrolyte. This is because the spread of solid electrolytes in PVDF polymer occurs evenly between graphite and carbon molecules. Graphite and carbon have high electronic conductivity values. The presence of electrolyte distribution in the anode also increases electron travel so that its electronic conductivity also increases.

Figure 6 shows the coated anode conductivity curve with PVDF. From the measurement results obtained the conductivity value of GL1 samples in order $\sigma < 10^{-4}$ S.cm$^{-1}$ (Figure 6a). Then the conductivity of the layer increases to $\sigma = 10^{-4}$ S.cm$^{-1}$ with an increase in the PVDF layer by 15 weight % (Figure 6b). The conductivity value of the anode layer drops again to $\sigma < 10^{-4}$ S.cm$^{-1}$ with the addition of PVDF layer concentration up to 20 weight % (Figure 6b). Based on the curve in Figure 6, it can be seen that the overall conductivity value of the anode after coupled with PVDF is 10, 15 and 20 weight % (each sample GL1, GL2, GL3) is obtained in order, $\sigma = 10^{-4}$ S.cm$^{-1}$ in the GL2 sample. The value of $\sigma$ is lower than the value of $\sigma$ in the sample G2. In this sample group, the maximum anode conductivity was obtained at a PVDF concentration of 15 weight %, $\sigma = 10^{-4}$ S.cm$^{-1}$ in the GL2 sample.

3.2. Characterization with SEM-EDS
Observation non-coating anode layer of G2 sample and cross-section of GL2 sample morphology was described in Figure 7. It appears that the surface of the anode layer is composed of granules in the form of a granular plate with varying sizes ranging in size from 3μm to 10μm in length and width. The
granules are composed of elements carbon (C of 92 atomic %) and fluorine (F of 5 atomic %), while the element copper (Cu of 3 atomic %) comes from the base. The white colour distributed almost throughout the surface of the anode layer is an element of F. Figure 7(b) shows the morphology of the cross section of the G2 sample. It can be seen that the sample is composed of Cu layer as a base, graphite + PVDF and PVDF layer with 15 weight % content variation. The results of enumeration with EDS in GL2 samples, which were shot in the Graphite + PVDF layer obtained content of elements C (72.24 atomic %), F (20.60 atomic %), O (5.36 atomic %) and Cu (1.81 atomic %). In the GL2 sample, the estimated thickness of graphite + PVDF above the Cu layer is about 45\(\mu\)m, with the thickness of the PVDF polymer layer having a thickness in a range smaller than 4\(\mu\)m.

![Figure 7. Morphology of (a) Non-coating anode layer (G2 sample) and (b) Cross section of GL2 sample. The thickness of cross section of GL2 sample (graphite + PVDF about 45\(\mu\)m) and the thickness of PVDF polymer less then 4\(\mu\)m.](image)

4. Conclusion
Anode sheet synthesis for applications of lithium-free batteries and coated with Polyvinylidene fluoride polymer (PVDF) has been done. PVDF polymer coating is given with a content of 10, 15 and 20 weight % by weight. The results of the measurement can be concluded that the variation of PVDF electrolyte concentration affects the intrinsic properties of the anode. Conductivity value, \(\sigma\) is obtained in the order between \(10^{-2} - 10^{-3}\) S.cm\(^{-1}\) for variations in PVDF content around 15 weight % in the G2 sample. Adding PVDF polymer coating over the anode layer on the GL2 sample with a content variation of about 15 weight % causes a conductivity value, \(\sigma\) decreases to be in order \(10^{-4}\) S.cm\(^{-1}\).

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