Evaluation of Anode Composition in Lithium-Ion Batteries

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Abstract. A lithium-ion battery is a rechargeable battery with excellent energy, high power, high theoretical capacity, economics, reasonable cycle rate, good stability, high-temperature resistance, and environmentally friendly. An anode is one of the main components of a lithium-ion battery. The most frequently used as an anode material is graphite. Graphite has good structure stability, excellent electrical conductivity, good cycle life and economics, high intercalation-deintercalation, high voltage, and energy efficiency. Another material that can be used as the anode component is SiO$_2$. In this study, we evaluate the anode composition with the dependent variables of active material and binder. Moreover, the structures of samples were characterized by X-Ray diffraction measurement, and the electrochemical performances were tested by galvanostatic charge-discharge. The anode material was applied directly in a 18650 cylindrical cell and graphite with a mass composition of 90% exhibit the best performance with a specific discharge capacity of 367.44 mAh/g (at 0.1C) and coulombic efficiency of 92%.

1. Introduction

The need for a battery is currently increasing. The battery is a device used for energy storage. The most advanced secondary or rechargeable battery is the lithium-ion batteries (LIB). LIB can be applied to handphones, laptops, and cameras and the transportation sector such as electronic vehicles, electric trains, and other sectors. LIB has tremendous energy, high power, and high theoretical capacity (372 mAh/g) [1]. Moreover, LIB has a good cycle rate, good stability, high-temperature resistance, and environmentally friendly [2].

Generally, LIB has four main components, namely cathode, anode, separator, and electrolyte. LiFePO$_4$ is one of the cathodes that is widely used in LIB. LiFePO$_4$ is claimed to provide adequate capacity, cycle life, and higher voltage [3]. Furthermore, there are many types of anode for LIB, such as carbon nanotubes [4], graphene nanosheets [5], expanded graphite [6], and others. Graphite has been extensively used in LIB. Graphite has good structural stability [14–16], excellent electric conductivity, good cycle life, economics [7, 8], high intercalation-deintercalation [9], high voltage, and energy efficiency [10]. On the other hand, graphite has a low voltage rate and specific capacity [9].

Another type that can be used as an anode component is SiO$_2$. SiO$_2$ has a high theoretical capacity of about 1965 mAh/g and interior hollow space nanoparticles. Also, which can gather large volume expansion between lithium-ion and electrode material [11]. The benefits of
using SiO2 material are the ease of separating the electrodes and reducing the reaction to the appearance of high surfaces [12]. However, SiO2 has low initial coulombic efficiency (ICE), low cycling performance [12], and low electronic conductivity [11].

In the anode assembly process, complementary components are required. The binder used is PVDF or Polyvinylidene Fluoride. This component is an effective dispersing agent for connecting and adhering the electrodes to the current collector [13]. AB or Acetylene Black is conductive materials that improve the electric conductivity to adequate contact between the active materials and its current collector [17]. In this report, we investigate the composition of the anode composites. Also, we compare graphite and SiO2, which will be an innovative strategy for superior LIB performance.

2. Experimental
2.1. Materials
The active material of anode is commercial graphite from BTR New Energy Materials Inc., while SiO2 is technical grade SiO2 with a particle size of 11 µm. Polyvinylidene fluoride (PVDF) was as the binder material, Acetylene Black (AB) was as a conductive material, and N-Methyl-2-Pyrrolidone (NMP) as a solvent. The active material of the cathode is LiFePO4 (LFP).

2.2. Preparation of composite
Graphite and SiO2 were crushed using mortar with a pestle so that the powder was homogenous. In this study, five samples were investigated with variations in the composition of Graphite and SiO2 as an active material, AB, and PVDF, as shown in Table 1.

| Sample | Composition (% wt) |
|--------|-------------------|
|        | Graphite | SiO2 | PVDF | AB |
| A      | 90       | 0    | 6    | 4  |
| B      | 92       | 0    | 4    | 4  |
| C      | 94       | 0    | 2    | 4  |
| D      | 96       | 0    | 0    | 4  |
| E      | 0        | 94   | 2    | 4  |

2.3. Battery Manufacturing
The anode composite was dissolved in NMP solvent with a mass ratio of 1:1.5 to form a slurry with good consistency. The slurry was superimposed on Cu foil with a thickness of 150 µm using doctor blade type MSK-AFA-III Automatic Thick Film Coater. The coated Cu foil was dried in the oven at 80°C followed by coating the other side of the Cu foil. Afterward, the anode was kept in the oven at 60°C for 24 hours. To assembly 18650 cylindrical cell fabrication, the anode was cut using GN-SM-110A Slitting Machine. Cathode fabrication used the same process as anode fabrication by dissolving LFP, PVDF, KS6, and AB with a mass ratio of 90%: 3.6%: 4.5%: 1.9%, respectively NMP solvent and superimposing on Al foil. The cutting electrode (anode and cathode) was welded with the electrode terminal with Al and Ni tab. Both electrode and separator were rolled using a winding machine (MSK-112A, MTI) and assembled in a 18650 cylinder case. Furthermore, electrolyte filling was carried out in a glove box under Argon gas. After one day, the cells were created, then the electrochemical performance was tested. 2.4. Characterization of Composite The material structure of graphite and SiO2 were analyzed using
X-Ray Diffraction (XRD) type Mini diffractometer MD-10 with Cu Kα radiation ($\lambda = 1.54178$). These five samples viscosity was tested using Viscometer Brand Gelon Model GN-VM-1 with rotor type 4, velocity 12, and range 500 ms.

2.4. Electrochemical Measurement

The galvanostatic charge and discharge profiles were tested using a Neware battery analyzer and BTS-610 software of voltage window 2.5 V at 0.1 - 5C (with $1C_{\text{theoretical}} = 372 \text{ mAh/g}$ for graphite and $1C_{\text{theoretical}} = 1965 \text{ mAh/g}$ for SiO$_2$).

3. Result and Discussion

3.1. XRD Analysis

The XRD analysis was carried out to determine graphite, SiO$_2$, and anode composites’ structural properties. The XRD results are shown in Figure 1. Figure 1a shows that graphite has a sharp peak of around 26.63° (002). Also, graphite has a soft peak around 44.26° (101) and 54° (004). SiO$_2$ has a broad peak at 23.16° (101) in Figure 1b. The peaks are in good agreement with JCPDS No. 65-6212 and JCPDS No. 29-0085 for graphite and amorphous SiO$_2$, respectively.

The crystallite size was calculated using Debye-Scherrer’s equation (1), and d-spacing was calculated using Bragg’s Law (2). The results for the XRD parameter for graphite and SiO$_2$ were summarized in Table 2.

$$D_x = \frac{k \lambda}{\beta \cos \theta}, \tag{1}$$

with $k =$ shape factor, or Scherer constant (0.9), $\lambda =$ X-ray wavelength (1.54178), $\beta =$ Full Width at half maximum (FWHM), $\theta =$ the angle of diffraction.

$$n \lambda = 2d \sin \theta, \tag{2}$$

with $n =$ order (1), $\lambda =$ X-ray wavelength (1.54178), $\theta =$ the angle of diffraction.

| Sample | Lattice Volume (Å$^3$) | d-spacing | Average crystallite size D (Å) |
|--------|------------------------|-----------|-----------------------------|
| Graphite | 2.698 | 35.643 | 3.923 | 10.608 |
| SiO$_2$ | 0.916 | 168.046 | 3.838 | 7.884 |

The crystal graphite is hexagonal, and the amorphous SiO$_2$ is tetragonal. The crystallinity of the material is indicated by the lattice parameter value, which graphite has a higher value than SiO$_2$ so that graphite has more of a crystalline structure.

Figure 1c displays the XRD spectra of composites at the various components of graphite and SiO$_2$. It can be seen that samples A, B, C, and D have diffraction peaks attributed to graphite. Simultaneously, sample E is related to the XRD spectra of SiO$_2$ because its main composition is SiO$_2$.

Table 3 shows that sample A has the highest lattice parameter value, which indicates the highest crystallinity. Furthermore, the volume increases with the increase in the composition of graphite.

3.2. Electrochemical Properties

The slurry was made by mixing the composite with NMP solvent. The viscosity of mixtures is present in Table 4. The density of varieties increases with an increasing amount of graphite and SiO$_2$. Sample A has the lowest thickness so that the homogeneity of sample A is uniform [18].
Figure 1. X-Ray diffraction patterns of graphite (a) SiO$_2$ (b) graphite (c) SiO$_2$ composite

Table 3. X-ray diffraction parameter of graphite and SiO$_2$ composite

| Sample | a (Å)  | c (Å)  | Lattice Volume (Å$^3$) | d-spacing | Average crystallite size D (Å) |
|--------|--------|--------|------------------------|-----------|--------------------------------|
| A      | 2.503  | 6.819  | 2.724                  | 37.012    | 6.636                          |
| B      | 2.498  | 6.806  | 2.723                  | 36.818    | 6.221                          |
| C      | 2.494  | 6.782  | 2.718                  | 36.559    | 6.749                          |
| D      | 2.499  | 6.803  | 2.721                  | 36.822    | 6.311                          |
| E      | 4.951  | 5.949  | 1.201                  | 145.837   | 0.408                          |

Figure 2 exhibits the initial charge-discharge curve of samples. The specific discharge capacity of samples at composition variations of 90%, 92%, 94% and 96% is 367.44, 303.058, 250.437, and 67 mAh/g, respectively. Based on Figure 2, sample A has the highest coulombic efficiency of 92%. Afterward, sample A was tested at 5°C rate with a specific discharge of 280 mAh/g.

Table 4. The viscosity of graphite and SiO$_2$ composite

| Sample | Viscosity |
|--------|-----------|
| A      | 2         |
| B      | 2.2       |
| C      | 2.5       |
| D      | 2.6       |
| E      | 27        |

The composites’ cycle performance was analyzed using 1/10 C rate for 5 cycles, which can be seen in Figure 3. After charging and discharging for 5 cycles, the discharge capacity decreases. The discharge capacity of sample A decreased from 374.704 to 363.279 mAh/g. Sample B decreased from 341.585 to 230.799 mAh/g, sample C decreased from 258.738 to 166.99 mAh/g, while sample D decreased from 86.722 to 51.814 mAh/g. From this result, capacity retention can be calculated. The capacity retention of samples A, B, C, and D is 96.95%, 67.56%, 64.54%, and 59.74%. Sample D has the lowest discharge capacity because there is no PVDF content in sample D. PVDF is used as a binder of the composite on the foil. Thus, sample D has a weak bond between composite and foil, which results in easy damage.

Furthermore, sample A has the highest discharge capacity and good cyclability. Increasing of discharge capacity as a result of electrochemical stability due to increasing PVDF [19].
PVDF also had better charge carrier mobility along its polymer chain so that it increases the electric conductivity [20], high dielectric constant, viscosity, bonding with NMP solvent of PVDF [13], and lithium-ion diffusion [21]. This indicates that sample A has a strong bond between composites and foil. Besides, the excellent performance of sample A related to the highest crystallinity of sample A.

Compared with sample C with the same AB and PVDF ratio, pure SiO2 has a better discharge capacity of 556.85 mAh/g with a coulombic efficiency of 74.46% and capacity retention of 54.94%. The presence of SiO2 has a good impact on the battery’s electrochemical performance, which is indicated by its high initial discharge capacity. However, the cycle performance of SiO2 is lower than graphite.

4. Conclusion
The variation composition of graphite and SiO2 as anode materials for the lithium-ion battery was successfully investigated. Sample A with the graphite composition of 90% exhibit the highest electrochemical performance with a specific discharge capacity of 367.44 mAh/g at 0.1C and a
coulombic efficiency of 92%. This result is agreed with the theoretical graphite capacity of 372 mAh/g. The highest electrochemical performance is due to the PVDF ratio influence of charge carrier mobility and bonding between composite and foil. Compared with sample E (pure SiO$_2$), it has better electrochemical performance than graphite with 556.85 mAh/g.

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