Conductivity and electrochemical performance of LiFePO₄ slurry in the lithium slurry battery

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Abstract. Lithium slurry battery is a new type of energy storage technique which uses the slurry of solid active materials, conductive additions and liquid electrolyte as the electrode. The proportion of conductive addition and the active material has significant influence on the conductivity and electrochemical performance of the slurry electrode. In the present work, slurries with different volume ratios of LiFePO₄ (LFP) and Ketjenblack (KB) were investigated by the electrochemical workstation and charge-discharge testing system (vs. Li/Li+). Results show that the conductivity of the slurry increases linearly with the addition of KB, and the measured specific capacity of the slurry reaches its theoretical value when the volume ratio of KB to LFP is around 0.2. Based on this ratio, a slurry battery with higher loading of LFP (19.1 wt.% in the slurry) was tested, and a specific capacity of 165 mAh/g at 0.2 mA/cm² and 102 mAh/g at 5 mA/cm² was obtained for LFP.

1. Introduction

The concept of lithium slurry battery was proposed based on the semi-solid lithium flow battery, which is characterized by flowable semi-solid suspension and independent design of power and energy density [1, 2]. There has been much research work on the semi-solid lithium flow battery [3-9]. However, the low electrical conductivity, high viscosity of the electrode suspension, and high pumping loss caused by the high viscosity are the critical challenges for the application of the semi-solid lithium flow battery [10-12]. The lithium slurry battery can avoid such limitations since it cancels the external circulating system, and the electrode slurry can be viscous and have high loadings of active materials and conductive additions, which is favorable to improve the energy density and decrease the internal resistance. In the lithium slurry battery, the Li-intercalation active materials are not coated on the current collector but dispersed in the electrolyte, then the problems of electrode materials pulverizing and peeling off from the current collector after long-term cycling can be avoided. Theoretically, the lithium slurry battery will implement the charge and discharge function as long as the crystal structure of the active material is not damaged. Therefore, the lithium slurry battery has the potential advantages of high energy density, good cycling performance and also low manufacture cost in large-scale applications.
In the present work, LiFePO4 (LFP) was chosen as the positive active material since it has a long, high and stable voltage plateau, which is convenient for the analysis of polarization [13, 14]. slurries with different ratios of LFP and Ketjenblack (KB) were assembled as half cells (vs. Li/Li+) to investigate the conductivity and electrochemical performance. Based on the analysis of the experimental results, optimized LFP slurry was prepared and can be used in the lithium slurry battery.

2. Experimental procedures

2.1. Preparation of the electrode slurry
Ball-milling method was used to prepare the electrode slurry. Firstly, powders of LFP (SLFP-ES09, Tianjin STL Energy Technology Co., LTD.) and KB (ECP-600JD, Shanghai Cuikehuagong Technology Co., LTD.) were weighed and mixed in the ball-milling tank after being dried at 100 °C for 12 hours. Zirconia balls were added with the mass ratio of 10:1 to the solid particles. After that, electrolyte (1 M LiPF6 dissolved in EC: DMC: EMC of 1: 1: 1 in volume) was added to the tank in the argon-filled glove box with oxygen and water levels maintained below 5 and 0.1 ppm, respectively. Then, the ball-milling tank was sealed with the lid, moved out of the glove box and fixed on the planetary ball-milling tight. The milling time was 8 hours and the rotate speed was 500 rpm. After milling, the electrode slurry was poured into reagent bottle in the glove box and sealed up for the following steps. To analyze the influence of the ratio of KB to LFP on the conductivity and electrochemical performance, multiple component contents (volume percentage) of the electrode slurry were designed, as shown in Table 1.

| Number | Content of LFP (vol%) | Content of KB (vol%) | R_a (Ω) | σ_a (mS/cm) |
|--------|----------------------|---------------------|--------|-------------|
| 1      | 10.0                 | 0.00                | 45.7   | 2.4         |
| 2      | 5.3                  | 0.16                | 28.4   | 3.8         |
| 3      | 5.3                  | 0.24                | 23.4   | 4.6         |
| 4      | 5.3                  | 0.32                | 22.0   | 4.9         |
| 5      | 2.9                  | 0.44                | 17.1   | 6.3         |
| 6      | 2.4                  | 0.44                | 14.2   | 7.6         |
| 7      | 2.4                  | 0.55                | 12.1   | 8.9         |

2.2. Measurement of the conductivity
The method to evaluate the conductivity of the slurry in semi-solid lithium battery has been discussed in our previous work [15], hence the proposed method of alternating current resistance test at fixed frequency was directly used in the present work. A modified mould was used here with a cylindrical test geometry sandwiched by two stainless steel plates. The electrode slurry was encapsulated between the stainless steel plates which were separated by insulating layer to form two electrode poles. The measurement was conducted on the mould by the ZENNIUM electrochemical workstation (ZAHNER-elektrik GmbH & Co. KG, Germany) at a fixed frequency of 1×10^5 Hz and an alternating current amplitude of 0.01 mA. The apparent conductivity of the slurry, σ_a, can be calculated by the formula below:

\[ \sigma_a = \frac{L}{R_a S} \] (1)

Where L is the thickness of the electrode slurry, S is the cross-sectional area of the electrode slurry and R_a is the measured apparent resistance. In the experiments, it was designed that L is 0.25 cm and S is 2.32 cm².
2.3. Measurement of the electrochemical performance
The batteries were assembled and tested in a half cell using a 0.5 mm thick Li metal foil (99.9%, Sigma-Aldrich) as the counter electrode and Celgard 2325 as separator. A plastic insulating frame with thickness of 1 mm was used to form the cavity of the positive LFP slurry. Stainless steel enclosures were used not only to form lugs but also seal the battery. All the procedures were conducted in the glove box under argon atmosphere.

The charge-discharge tests were carried out with a LAND-CT2001A battery test system. Galvanostatic charge-discharge tests were performed between 2.0 V and 4.5 V versus Li/Li⁺. The lowest current density was set as 0.2 mA/cm² and the highest current density was set as 5 mA/cm².

3. Results and discussion

3.1 Influence of the ratio of KB to LFP on the conductivity
The measured apparent resistance and conductivity for the slurry with different contents of LFP and CB are shown in Table 1. The relationship between the ratios of KB to LFP and the conductivity was plotted in Figure 1. It can be seen that the apparent conductivity of the slurry is almost increases linearly with the addition of KB, and when the ratio of KB to LFP is 0.23, the apparent conductivity reaches 8.9 mS/cm.

Figure 1. Relationship between the conductivity and the volume ratios of KB to LFP in the slurry.

3.2 Influence of the ratio of KB to LFP on the electrochemical performance
Figure 2 shows the charge-discharge curves of batteries using different LFP slurries at 0.2 mA/cm². In Figure 2(a), the slurry without KB illustrates the largest polarization, and no charge/discharge voltage plateau was seen. As the content of KB increases, the polarization moderates slightly. The discharge specific capacity of LFP increases to 92 mAh/g when the KB content is 0.32 vol% along with 5.3 vol% of LFP, which is still far lower that the theoretical value. In Figure 5(b), a long and stable discharge voltage plateau was seen for the 5# and 6# slurry, especially for the 6# slurry, which exhibits the smallest polarization and highest specific capacity of 146 mAh/g for LFP.

Figure 2. Charge-discharge curves of different electrode slurries at 0.2 mA/cm².
performs smaller overpotential and better charge-discharge property, which is consistent with the changing tendency of the conductivity in Figure 1. When the volume ratio of KB to LFP is above 0.2, the overpotential is less than 0.1 V.

Figure 3. The LFP specific capacity and overpotential of the battery with the slurry of different volume ratios of KB to LFP.

Except for the specific capacity of active material LFP, the energy density of the electrode slurry is also important for the battery technology. The theoretical specific capacity of the electrode slurry, $C_c$, can be calculated by the following formula:

$$C_c = m_1 \times C_t / (m_1 + m_2 + m_3)$$  \hspace{1cm} (2)

Where $C_t$ is the theoretical capacity of the active material, $m_1$, $m_2$ and $m_3$ are the mass of active material, conductive agent and electrolyte, respectively. Figure 4(a) compares the theoretical specific capacity of the slurry at different volume percentages of LFP as the volume content of KB is changing from 1% to 10%. It can be seen that the influence of the volume content of KB on the theoretical capacity is almost negligible, while the content of LFP is the dominant factor that determines the theoretical capacity of the slurry. In Figure 4(b), the gap between the theoretical and measured specific capacity shows that when the volume ratio of KB to PVDF is low, only small part of the active materials take part in the electrochemical reaction, while when the proportion of KB to LFP is increased to around 0.2, the actual measured capacity is nearly equal to the theoretical value. Therefore, a relatively high KB ratio can not only maintain a high theoretical capacity, but also form a better conductive network and promote the fully reaction of LFP.

Figure 4. (a) Relationship between the theoretical specific capacity of the slurry and the volume percentage of LFP when the volume content of KB is 1, 5 and 10 vol%. (b) Comparison of the theoretical and measured specific capacity of the slurry at different volume ratios of KB to LFP.

3.3 Optimization of the performance of the LFP slurry

When the content of KB particles in the electrode slurry is small, the particles cannot form continuous conductive network, and result in high internal resistance. Along with the increase of the KB content,
some independent clusters gradually appear but are still not connected in the slurry, which cannot improve the conductivity remarkably. Long-range associativity between particles appears until the content of KB increases to a certain critical value and then consecutive conductive network forms in the electrode slurry. The electrical conductivity of the slurry improves and the velocity of electrochemical reaction increases accordingly. The above experiments shows that there can be an effective conductive structure when the KB content is 0.55 vol%.

When LFP and KB particles are dispersed in the electrolyte uniformly, the electronic transfer path exists among the whole solid particles. Small amount of LFP does not affect the electrical conductivity of electrode slurry in the existed conductive network, but the continuing addition of LFP particles may destroy the consecutive structure. Therefore, the volume fraction of conductive particles in the all solid particles is an important factor. Kirkpatrick [16] calculated the critical volume fraction of spherical particles at different filling ways of such as simple cubic, face-centered cubic, body centered cubic and random accumulation with the classic percolation theory. It was pointed out that the conductive network under different filling ways has the same critical volume fraction. Considering the present experimental results that when the volume ratio of KB to LFP is around 0.2, an effective conductive network can be formed, we designed an optimized slurry with 7.5 vol% of LFP and 1.5 vol% of KB (ratio of KB to LFP is 0.2) which has a higher loading of active material (19.1 wt.% of LFP in the slurry with designed specific capacity of 32.5 Ah/kg) and tested its electrochemical property in the following.

The viscosity of the electrode slurry increases with the increasing content of KB due to its nano-structure and high specific surface area. Thus, a ball milling process with less milling time and slow rotate speed (1 hour and 100 rpm) was applied to this designed slurry. Figure 5 shows the measured charge/discharge curves at different current densities. The measured LFP specific capacity is 165 mAh/g at current density of 0.2 mA/cm², corresponding to 31.4 Ah/kg of the slurry, which means nearly full reaction of LFP. The rate property of the battery is also good, which has a specific capacity of 102 mAh/g at current density of 5 mA/cm², corresponding to 19.4 Ah/kg of the slurry.

4. Conclusion
The influence of the ratios of KB to LFP in the electrode slurry on the conductivity and electrochemical performance of the LFP lithium slurry battery was investigated in the present work. Ball milling method was used to prepare the LFP electrode slurry. The results from electrochemical workstation and charge/discharge test show that the performance of the slurry increases with continuing addition of conductive KB, and a 0.2 volume ratio of KB to LFP was found to be a critical value for the slurry to form an effective conductive network and exhibits good specific capacity. Finally, electrode slurry with 7.5 vol% LFP and 1.5 vol% KB was tested and exhibits excellent performance with specific capacity of 165 mAh/g at 0.2 mA/cm² and 102 mAh/g at 5 mA/cm² for LFP.
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