

## Surface modification of positive current collector for lithium slurry battery

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**Abstract:** Lithium slurry battery (LSB) is a new energy storage technology suitable for the application in low-speed electric vehicles, base stations, household cases and power grid. Contact resistance between the current collector and the electrode slurry is critical for the electrochemical performance of this technique. In the present work, Al matrixes were decorated with different ratios of carbon black (CB) and polyvinylidene fluoride (PVDF) to investigate the influence of current collector surface treatment on LiFePO<sub>4</sub> half slurry cells. Results showed that the ratio of CB and PVDF affected the homogeneity, the microcrack formation, the surface area, the porosity and the adhesion of the coating layer, leading to different electronic and ionic resistances. When the content of CB is too high, the insufficient adhesion agent was not able to accommodate the high surface tension of the CB nanoparticles during drying process, forming cracks and increasing contact resistance. The specific surface area and pore volume of the coating layer was found to first increase and then decrease as the ratio of CB : PVDF increased from 1 : 1 to 5 : 1, with a maximum around 3 : 1. This phenomenon was consistent with the measured ohmic resistance and charge/discharge profiles. Larger porosity and surface area of the coating layer were beneficial for the transfer of lithium ions in the electrolyte and the electrochemical reactions. Finally, a specific capacity of 149.2 (mA·h)/g at 0.2 mA/cm<sup>2</sup> was obtained for LiFePO<sub>4</sub> half slurry cell using the optimized Al mesh current collector with a coating ratio of 3 : 1 (CB : PVDF).

**Key words:** lithium slurry battery; current collector; surface modification; interface; electrochemical performance

### 1 Introduction

Due to the environmental pollution caused by the consumption of fossil fuel, the renewable energy has gained great development in recent decades<sup>[1,2]</sup>. The capricious nature of renewable power implies a great demand for the low cost energy storage techniques<sup>[3,4]</sup>. Y. C. Chen' group proposed a new type of energy stor-

age battery technology and named it as lithium slurry battery (LSB) firstly in 2015<sup>[5]</sup>. The LSB directly uses the mixed slurry of lithium storage particles, conductive additives and liquid electrolyte as the electrode<sup>[6,7]</sup>. The extra-thick electrode (1 ~ 10mm) and being maintainable to get regeneration are two remarkable features of this technique<sup>[8,9]</sup>. The extra-thick slurry electrode makes it more suitable for providing large

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capacity of energy storage power output. When the performance of the battery declines after a period of time, the internal interface of the electrode can be repaired through regeneration technology to improve the battery vitality and achieve an extremely long calendar service life. When the battery has an inner short circuit accident, the electrolyte will be extracted quickly and safety agent will be injected into the battery reactor. The slurry state makes the manufacture process of the electrode highly simplified and can be easily expanded for scalable cases compared to conventional lithium-ion batteries. Thus, this technique is considered to have good application prospect in the energy storage fields of low-speed electric vehicles, base stations, household cases and power grid.

So far, most reports are focused on the optimization of the electrode with structure of slurry state<sup>[10-14]</sup>. However, the contact resistance between the current collector and the electrode slurry also has a critical impact on the performance of the battery, but such an investigation is still limited. Hamelet et al.<sup>[11]</sup> compared the electrochemical properties of  $\text{LiFePO}_4$  (LFP) slurry using Al foam and Al metal plate as the current collector for slurry thickness of 6mm and 1mm respectively, and found that the resistance increase involved in the thicker catholyte compartment can be partially compensated by the presence of the Al foam. Madec et al.<sup>[12]</sup> found that if the current collector is polished by silicon carbide papers with smaller grain size, the contact resistance between the current collector and the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based anolyte is also smaller. Biendicho et al.<sup>[13]</sup> found that when the current collector is changing from Al to Ti, the impedance of the semicircle in the measured electrochemical impedance spectroscopy (EIS) increases from 150 to 300 $\Omega$ . It can be seen from the above investigations that the material, surface treatment and morphology of the current collector are essential for the decrease of contact resistance.

Al foil is a widely used positive current collector in commercial lithium-ion battery, since it can meet most practical requirements including material cost, density, conductivity, malleability and corrosion stability<sup>[15]</sup>. Coating a layer of carbon black (CB) on

Al foil before coating the electrode materials can effectively reduce the contact resistance in traditional lithium-ion battery<sup>[16]</sup>. However, the detailed morphology was not studied, and it has not been investigated for the case of LSB. Hence, in the present work, Al foil and surface modified Al foil with different mass ratios of CB and polyvinylidene fluoride (PVDF) were studied as the positive current collector for LFP half slurry cells. LFP was chosen as the positive material since it has a long, high and stable voltage plateau vs.  $\text{Li}/\text{Li}^+$ , which is convenient for the analysis of polarization<sup>[17,18]</sup>. The surface morphology of the coatings, the impedance responses and the electrochemical performance of the corresponding LSBs were characterized and discussed. Finally, an optimized design of the positive current collector based on Al mesh was proposed and tested based on the discussion.

## 2 Experimental procedures

### 2.1 Preparation of the electrode slurry

The following materials were used to prepare the electrode slurry: LFP from Tianjin STL Energy Technology Co., Ltd with D50 of 2.0 $\mu\text{m}$ ; CB from Hefei Kejing materials technology Co., Ltd; Electrolyte from Xianghe Kunlun Chemicals Co., Ltd containing 1M  $\text{LiPF}_6$  dissolved in EC:DMC:EMC of 1:1:1 in volume. The ball-milling method was used in the present work to prepare the electrode slurry (LFP:CB:electrolyte = 6.8:0.8:92.4, wt%). Firstly, powders of LFP and CB were weighed and mixed in the ball-milling tank after being dried at 100 $^\circ\text{C}$  for 12h. Zirconia balls were added with the mass ratio of 10:1 to the solid particles. After that, the liquid electrolyte was added into the tank in the argon-filled glove box with oxygen and water levels maintained below 5 and 0.1ppm, 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 ball-milling parameters were set as 500r/min and 8h. After milling, the electrode slurry was poured into a reagent bottle in the glove box and sealed up for the following steps.

### 2.2 Preparation of the current collector

The starting materials of the current collector are

Al foil with a thickness of 20 $\mu\text{m}$  and Al mesh with a thickness of 50 $\mu\text{m}$  and diamond holes of 1mm  $\times$  0.5mm. The coating slurry was made by mixing CB with PVDF at certain mass ratio after adding moderate 1-Methyl-2-pyrrolidinone (NMP) solvent. For a comparison, three mass ratios of CB and PVDF were designed which are 1 : 1, 3 : 1 and 5 : 1. The coated Al foil and Al mesh were dried at 120 $^{\circ}\text{C}$  for 8h in the oven. The thickness of the coating layer on the Al foil is controlled within 100 $\mu\text{m}$  by doctor blade height and the coating areal density is about 1mg/cm $^2$ . The surface modified Al foils coated with CB and PVDF mass ratios of 1 : 1, 3 : 1 and 5 : 1 are called Al11 foil, Al31 foil and Al51 respectively in this paper.

### 2.3 Characterization of microstructures and electrochemical properties

The surface structure of the coated current collector was characterized by scanning electron microscope (SEM) (Zeiss Sigma) under an accelerating potential of 5kV. The specific surface area and pore volume were measured by a Micromeritics ASAP 2020 surface area and porosity analyzer.

The batteries were assembled and tested in a half cell using a 0.4mm thick Li metal foil (99.9%, China Energy Lithium Co., Ltd.) as the counter electrode. Fig.1 shows the construction of the battery. The separator (Celgard 2325) is placed between the lithium anode and the cathode suspension, here the cathode suspension is LFP electrode slurry. During the assembling process, the weight of the LFP electrode slurry was controlled as the same for all batteries. The negative current collector is copper foil and contacts with the lithium anode. The positive current collector is on the cathode suspension side. All the procedures were conducted in the glove box under argon atmosphere.

Before the galvanostatic charge-discharge test, electrochemical impedance spectroscopy (EIS) was firstly conducted for each battery by the ZENNIUM electrochemical Workstation (ZAHNER-Elektrik GmbH & Co. KG, Germany) with voltage amplitude of 5mV and frequency range of  $3 \times 10^{-3} \sim 4 \times 10^6$ Hz. Then, the galvanostatic charge-discharge (GCD) test was carried out with a LAND-CT2001A battery test system.

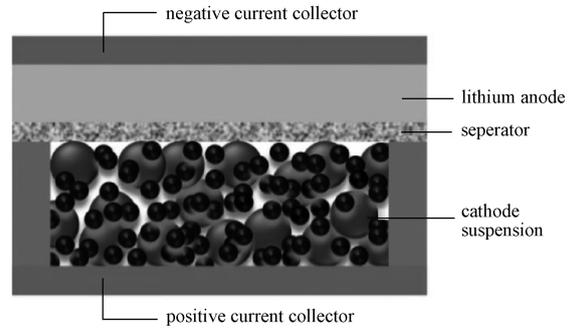


Fig.1 Construction of LSB tested in present work

The voltage range of the charge-discharge process was set as 2~4.5V, while the current density range is 0.2~5mA/cm $^2$ .

### 3 Results and discussion

Fig.2 shows the SEM images of the Al foil, Al11 foil, Al31 foil and Al51 foil. It can be seen from the figure that the coatings of Al11 foil and Al31 foil have continuous surface morphology, but for coating ratio of 5 : 1, visible microcracks were observed. It is known that nanoparticles tend to form clusters due to the high surface energy, which can also be seen from the magnified view in the upper right of each figure. However, when the content of CB is too high, cracks may form due to the high interface energy inside the coating, like the 5 : 1 ratio in the present work. Besides, a porous and rough structure was seen for the coating surface.

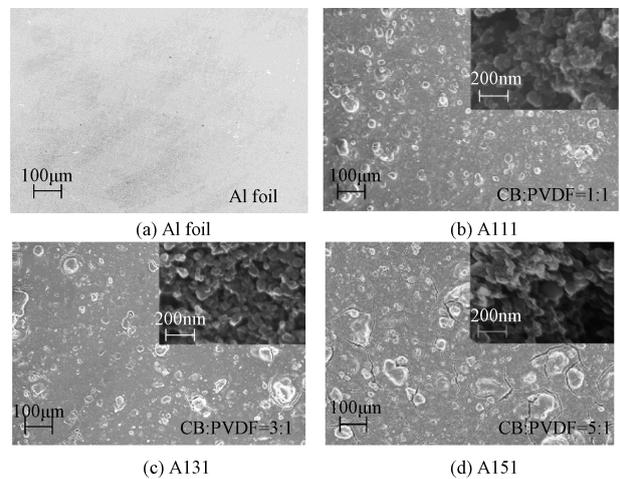


Fig.2 SEM images of Al foil and Al foil coated with different ratios of CB and PVDF

Tab. 1 gives the data of specific surface area, pore volume and average pore sizes for different coating

ratios of CB and PVDF measured by the micromeritics surface area and porosity analyzer. It can be seen from the table that the surface area and pore volume of 3 : 1 coating ratio of CB and PVDF are much higher than the rest two ratios. In order to investigate the effect of coating ratio and morphology of the current collector on the electrochemical performance of the corresponding LSBs, EIS and GCD tests were performed.

Tab.1 Measured parameters for coatings with different ratios of CB and PVDF by micromeritics surface area and porosity analyzer

CB: PVDF	BET surface area / (m <sup>2</sup> /g)	Pore volume / (cm <sup>3</sup> /g)	Average pore width/nm
1:1	42.3	0.60	57.10
3:1	263.3	5.25	79.82
5:1	79.3	0.45	22.93

Fig.3(a) gives the  $Z'$ - $Z''$  plots for LSBs using Al foil current collectors coated with different ratios of CB and PVDF. Two resistances were marked in the EIS profile,  $R_0$  and  $R_c$ . The resistance  $R_0$  in the high-frequency region is ascribed to the sum of electrolyte resistance and other so-called "ohmic contributions". The resistance  $R_c$  at the end of the semicircle principally originates from the contact resistance between the current collector and the electrode slurry, as investigated by Madec et al.<sup>[11]</sup> in the study of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based anolyte. This explanation is supported by the fact that the current collector is the only changing element in the batteries for EIS measurement. It can be seen from Fig.3(b) that  $R_0$  has the lowest value when the ratio of CB and PVDF is 3 : 1, while  $R_c$  increases as the ratio of CB and PVDF increases. However, when the ratio of CB of PVDF is larger than 3 : 1,  $R_c$  increases dramatically.

Fig. 4 shows the galvanostatic charge-discharge curves at the current densities of 0.2 to 5mA/cm<sup>2</sup> for the batteries using different current collectors. It can be seen from Fig.4 (a) that although Al foil has been a successfully used current collector in traditional lithium-ion batteries, it cannot be directly used in LSBs since serious polarization was observed. Fig.4 (b) ~ Fig.4(d) shows that the coating of CB on Al foil can significantly improve the rate performance of LSB, and coating ratio of 3 : 1 (CB:PVDF) illustrates the best

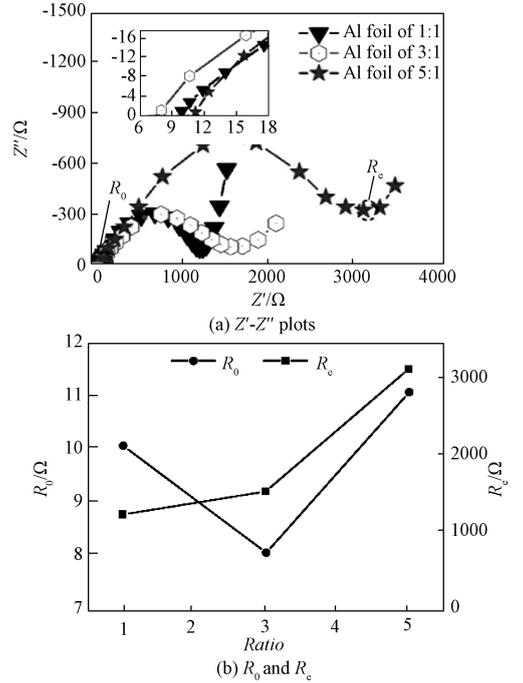


Fig.3  $Z'$ - $Z''$  plots and  $R_0$  and  $R_c$  as a function of ratio of CB to PVDF

performance, which has a specific capacity of 135(mA · h)/g at 0.2mA/cm<sup>2</sup> and 61(mA · h)/g at 5mA/cm<sup>2</sup>. In Fig.4 the voltage is indicated by  $U$  and the specific capacity of LFP is indicated by  $SC$ .

The comparison of the over potentials in the batteries using different current collectors is given in Tab. 2. The over potential is calculated by 3.45V minus the medium voltage of the discharge curve. It can be seen from Tab. 2 that the overpotential increases rapidly with the increase of the current density for all the batteries. But the battery using Al31 foil has the smallest over potential among all the ratios.

In order to analyze the influence of coating morphology, conductivity and porosity of the current collector on the electrochemical performance of the LSB, the scheme in Fig.5 was proposed. Here, one line denotes the current transferred by electrons (namely the electronic current  $I_{e^-}$ ), while another line represents that by lithium ions (namely the ionic current  $I_{\text{Li}^+}$ ). From Faraday's law, the current in a closed circuit should be equal everywhere throughout the circuit. Hence, we have:

$$I_0 = I_{e^-} + I_{\text{Li}^+} \quad (1)$$

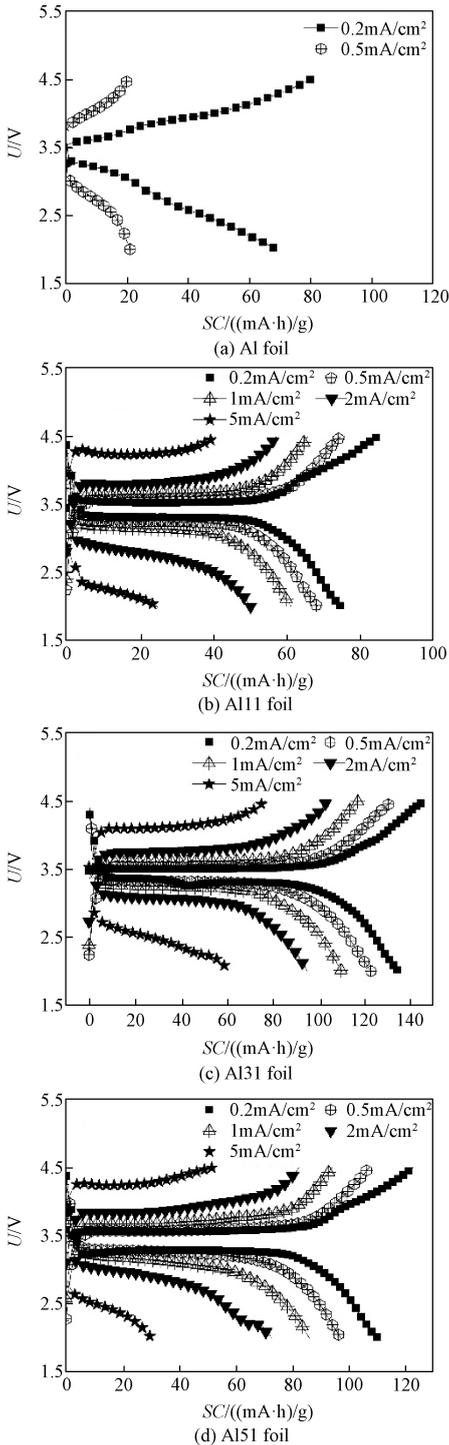


Fig.4 Galvanostatic charge-discharge curves of batteries using different current collectors

Tab.2 Over potentials of batteries using different current collectors

Current collector	Over potential/V				
	0.2 mA/cm <sup>2</sup>	0.5 mA/cm <sup>2</sup>	1 mA/cm <sup>2</sup>	2 mA/cm <sup>2</sup>	5 mA/cm <sup>2</sup>
Al11	0.14	0.21	0.32	0.70	1.21
Al31	0.15	0.15	0.24	0.41	0.99
Al51	0.18	0.22	0.36	0.60	1.02

where  $I_0$  is the constant current in the circuit. From the electrochemical models developed by Newman and co-workers we have:

$$I_{e-} = -\sigma \nabla \Phi_1 \tag{2}$$

$$I_{Li+} = -\kappa \nabla \Phi_2 + \frac{\kappa RT}{F} \left(1 + \frac{\partial \ln a}{\partial \ln c}\right) (1 - t_+^0) \nabla \ln c \tag{3}$$

$$\kappa = \varepsilon^p \kappa_0 \tag{4}$$

where  $\sigma$  and  $\kappa$  are the electronic and ionic conductivity respectively.  $\Phi_1$  and  $\Phi_2$  are the corresponding potentials.  $\kappa_0$  is the ionic conductivity of the pure electrolyte.  $a$  is activity.  $c$  is concentration of Li ions.  $R$  is the gas constant.  $T$  is temperature.  $F$  is the Faraday constant.  $t_+^0$  is the transport number of the positive ion.  $p$  is an adjusted parameter.  $\varepsilon$  is the porosity of the composite layer.

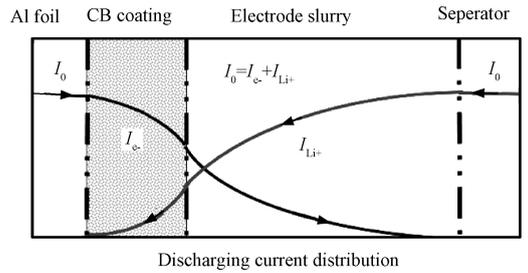


Fig.5 Scheme of current distribution in each component of present LSB

It can be seen from Eqs. (1) ~ Eqs. (3) that the conductivity ( $\sigma$  and  $\kappa$ ) should be inversely proportional to the gradient of potential ( $\Phi_1$  and  $\Phi_2$ ) in order to ensure the constant value of total current  $I_0$ . This means increasing the electronic or ionic conductivity can be an approach to reduce the decrease of potential. The empirical relationship in Eqs. (4) shows that the ionic conductivity is proportional to the porosity of the layer, like the coating layer or the electrode slurry for example. Considering the similar areal coating density in the present work, the porosity should be proportional to pore volume measured for unit mass. Results in Tab. 1 and Fig.3 present that the coating of Al31 foil corresponds to the largest pore volume, lowest electrolyte resistance and not high electronic resistance. Hence, the potential decrease due to the coating layer should be the lowest and the corresponding battery has the

best electrochemical performance among all the ratios tested in the present work. Besides, when the CB layer is coated onto the Al foil, the contact area between the current collector and the electrode slurry is greatly increased due to the porous and rough surface structure of the coating layer, as shown by Fig.1 and Tab.1. It can be deduced from the Ohm's law that in this case the interface resistance is largely decreased.

The adhesion area between the coating layer and the current collector is also considered to be a factor that influences the interface resistance. As a result, Al mesh and Al mesh coated with 3 : 1 ratio of CB and PVDF were further tested in present work and are expected to have better electrochemical behaviors than Al foil in the same cases. This deduction was certified by the galvanostatic charge-discharge test results given in Fig.6. The specific capacity of LFP for the battery using Al mesh with 3 : 1 coating ratio of CB and PVDF reaches  $149.2(\text{mA}\cdot\text{h})/\text{g}$  at  $0.2\text{mA}/\text{cm}^2$  and  $65(\text{mA}\cdot\text{h})/\text{g}$  at  $5\text{mA}/\text{cm}^2$ , which is better than the case using Al foil with the same coating (as shown by Fig.4(c)).

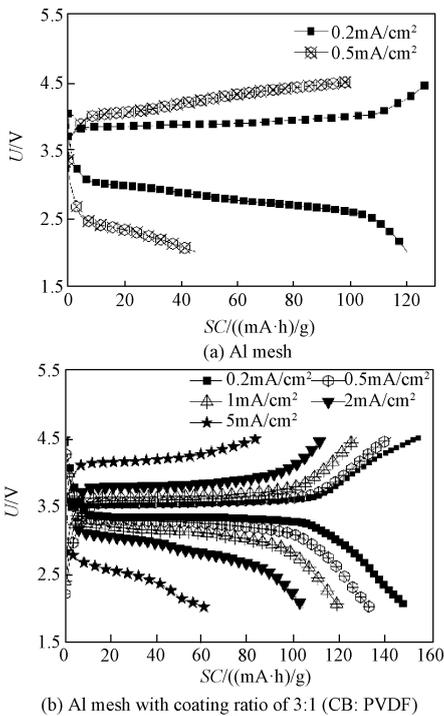


Fig.6 Galvanostatic charge-discharge curves of batteries using different current collectors

## 4 Conclusions

The contact resistance between the current collector and the electrode slurry has been found to have a significant influence on the electrochemical performance of LSB. In the present work, Al foil and Al foil coated with different mass ratios of CB and PVDF are characterized and tested as the positive current collector for LFP half slurry cells. Results show that coatings with ratio of 1 : 1 and 3 : 1 have continuous surface morphology, but when the ratio is increased to 5 : 1, visible microcracks are observed. The nitrogen adsorption surface area analysis presents that the coating with 3 : 1 ratio of CB and PVDF has the highest specific surface area and pore volume, and the LSB using the corresponding current collector behaves small impedance response and best rate performance. The internal scheme is analyzed based on an electrochemical model and shows that a coating layer with larger surface area, higher electronic and ionic conductivity is beneficial for reducing the resistance between the current collector and the electrode slurry. Besides, increasing the adhesion area between the coating layer and the current collector can further improve the performance of the battery, and this deduction is verified by the comparison of the LSBs using Al mesh and Al foil current collectors coated with the same 3 : 1 ratio of CB and PVDF. It can be seen from above analysis that the selection of current collector plays an important role in the design of LSB. Therefore, we will continue to carry out a series of studies of the relevant factors affecting current transport effect between the electrode slurry and the current collector. Rational surface modification technique will be adopted on the basis of micro mechanism research work to improve the comprehensive performance of LSB.

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## 锂浆液电池正极集流体表面改性研究

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**摘要:** 锂浆料电池(LSB)是一种新型储能技术,适用于低速电动汽车、基站、家用机箱、电网等领域。集流体与电极浆料之间的接触电阻是影响锂浆料电池电化学性能的重要因素。本研究采用不同比例的炭黑(CB)和聚偏氟乙烯(PVDF)对铝集流体进行表面处理,研究正极集流体表面处理对 $\text{LiFePO}_4$ 浆料半电池的影响。试验结果表明,CB与PVDF的比例对集流体表面涂层的均匀性、微裂纹的形成、比表面积、孔隙率、涂层附着力等都有一定的影响,进而使集流体产生不同的电子电阻和离子电阻。当炭黑含量过高时,表面涂层与集流体表面的黏附性不足,无法适应炭黑纳米颗粒在干燥过程中产生的高表面张力,因此表面形成裂纹,导致接触电阻增大。随着CB:PVDF的比例由1:1增加到5:1,涂层的比表面积和孔隙体积先增大后减小,最大值在3:1左右,与集流体的欧姆电阻和半电池的充放电测试结果一致。较大的涂层孔隙率和表面积有利于锂离子在电解液中的迁移和电化学反应的发生。 $\text{LiFePO}_4$ 浆料电池采用涂层比为3:1(CB:PVDF)的铝网集流体可实现良好的充放电功能,在 $0.2\text{mA}/\text{cm}^2$ 的条件下比容量达到 $149.2(\text{mA}\cdot\text{h})/\text{g}$ 。

**关键词:** 锂浆料电池;集流体;表面改性;界面;电化学性能

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