공학석사학위논문

Design Current Collector of Different Cell Size Metal Foam for Lithium-ion Batteries

리튬이온전지를 위한 다양한 셀 사이즈 발포금속인 집전체의 설계

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이 논문을 공학석사학위논문으로 제출함

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JIN TAO의 석사학위논문을 인준함

2016년 12월

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Abstract

Design Current Collector of Different cell size Metal Foam Cathode for Lithium-ion Batteries

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In the last two decades, Lithium-ion batteries could be considered to be the most impressive success story of modern electrochemistry. Among rechargeable batteries, because Lithium-ion batteries have high energy density and high power performance, they are key components of the portable, entertainment, computing and telecommunication equipment. However, the energy density and electrochemical performance are still required to be further improved for more applications. The most important problem is that there are 50-100 ㎛ thick active materials on the foil-type current collector, and to sustain high power performance, the thickness of active materials is only 20-60 ㎛. In this way, to obtain large-scale capacity, the batteries become heavy and large. It is also caused by increased inactive materials, such as separator, current collector and so on. Moreover, one of the big issues for application is high production cost due to the increasing of materials and workload. To solve these problems, three- dimensional structure material – metal foams have been used

for Lithium-ion battery electrodes instead of commercial foil-type current collectors in this study.

In the condition of same volume, the cathodes using 450 ㎛ cell size metal foam and 3000 ㎛ cell size metal foam are compared in electrochemical performances. According to the charge-discharge test, cyclic voltammetric (CV) analysis, better kinetic performance is obtained for the 450 ㎛ cell size metal foam cathode due to the more triple junctions (junction of active material, metal frame, and electrolyte). But the electrode density of 3000 ㎛ metal foam cathode is higher than 450 ㎛ metal foam cathode, because the weight of active materials of 3000 ㎛ cell size metal foam cathode is more than 450 ㎛ metal foam cathode. It causes 3000 ㎛ metal foam cathode to have high energy density. So it is in need of a cathode which has both high performance of 450 ㎛ metal foam cathode and high capacity of 3000 ㎛ metal foam cathode.

Two kinds of metal foam cathode are prepared: one kind of cathodes is sandwiched structure metal foam cathode that is combined with different cell size metal foam cathode as sandwich. The side metal foams(300 ㎛ thickness) which are the same cell size, are different from mid metal foam(1000 ㎛ thickness). And the other kind of cathodes is dual structure metal foam cathode which is combined 450 ㎛ metal foam cathode (600 ㎛ thickness) with 3000 ㎛ metal foam cathode (1000 ㎛ thickness). For the sandwiched structure, mid metal foam cell size is 450 ㎛, the AC Impedance analysis shows that charge transfer resistance is 11.22 Ω, which is less than other cathodes. And the specific currents at positon of peaks of sandwiched structure metal foam cathode whose cell size of mid metal foam is 450 ㎛ shows higher than other cathodes, because there are more triple junction than other cathodes. According

to the charge-discharge test, the columbic efficiency of dual structure metal foam cathode is higher than other cathodes. The energy density of dual structure metal foam cathode is higher than sandwiched structure metal foam cathode whose mid metal foam cell size is 450 ㎛, and is equal to the energy density of sandwiched structure metal foam cathode that mid metal foam cell size is 3000 ㎛. And dual structure metal foam cathode exhibited the same proportion of reactiveness of active materials with the 450 ㎛ metal foam cathode in high current density according to the charge-discharge test.

Considering the power performance and capacity performance in unit volume, dual structure metal foam cathode is very promising for the high power and high capacity cathode structure for Lithium-ion batteries. It not only almost has the same energy density with 3000 ㎛ cell size metal foam cathode but has superior kinetic performance as 450 ㎛ cell size metal foam cathode as well in unit volume.

Based on the study, metal foam cathode which has the dual structure is one of the promising current collectors for high power and high capacity for Lithium-ion batteries.

Keywords: metal foam cathode, Lithium-ion batteries, triple junction, electrode density, current collectors

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Chapter 1. Introduction

1.1 Li-ion battery

Modern civilization has become dependent on fossil fuels of finite supply and uneven global distribution, which has two problematic consequences: (1) vulnerability of nation states to fossil-fuel imports and (2) CO_2 emissions that are acidifying our oceans and creating global warming.[1-2] In order to solve such problems, the rechargeable batteries is necessary to develop to care of our environment. So far, so many rechargeable batteries have been investigated, such as lead-acid, Ni-Cd, Ni-MH and Li-ion batteries.[3] Li-ion batteries not only have excellent energy density but also have outstanding power density. The specific energy density of Li-ion batteries is 150-250 Wh kg^{-1}, and volumetric energy density of Li-ion batteries is 250-530 Wh L^{-1}, therefore, the power density is also superior , about 300-1500 W kg^{-1}.[4-7] Li-ion batteries are expected with the increase of energy consumption and people's needs because of their high energy density and high power density. However, the large-scale applications have not been solved yet, the volumetric energy density and power performance of Li-ion batteries are still waiting to be improved.

For Li-ion batteries, $LiCoO_2$(LCO), $LiMn_2O_4$(LMO), $LiFeO_4$(LFP), $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) as active materials are usually applied in commercial market. And each of active materials has its own characters, such as high voltage for LCO, low cost and high voltage for LMO, cheaper than LCO for NCM, high capacity for NCA, excellent cycle life, low cost, high capacity, high thermal stability and low toxicity for LFP. But the electronic conductivity of LFP is very low, using carbon black coating to LFP power can greatly improve electronic conductivity of LFP.[8, 9-20]

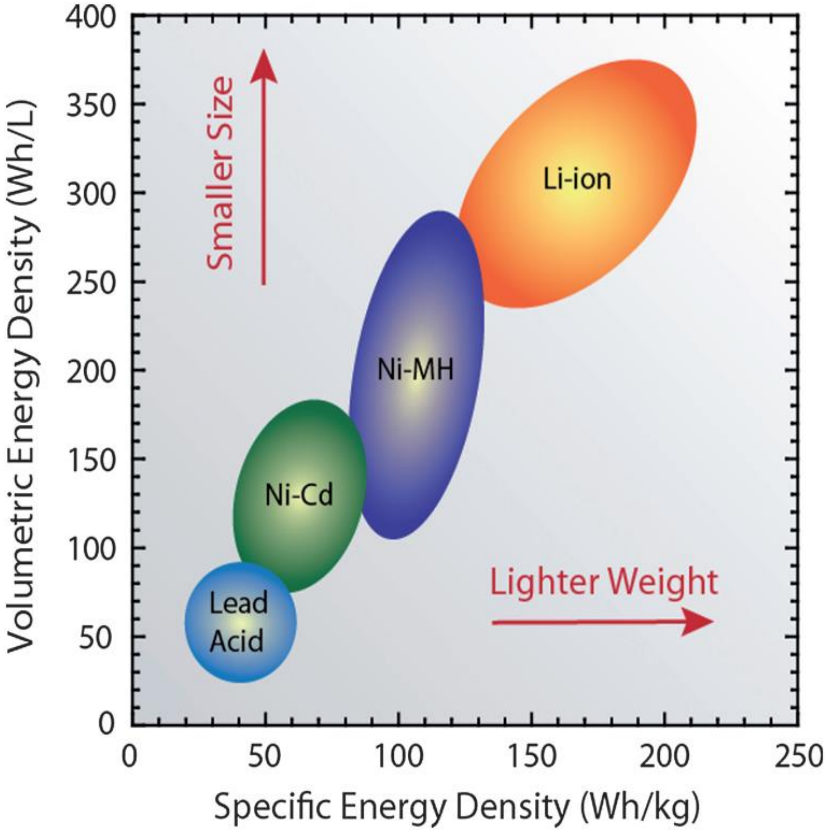

Figure 1.1 Energy densities for types of rechargeable batteries.

1.2 Commercial Li-ion battery

The process of commercial Li-ion battery is that coating active material on the two sides of aluminum foil for cathode and coating graphite on the two sides of copper foil for anode are rolling pressed after heat treatment. Putting the separator between cathode and anode, they are rolled before packaging the cell[21-31].

Generally, the thickness of active material on the current collector of aluminum foil is about 50-100 ㎛ for low current density discharge devices, and when using high current density discharge, the thickness of active material is only for 20-60 ㎛.[32-34] The first issue is thickness of active material cannot be thick.

Figure 1.2 Structure of Lithium-ion battery in commercial production.

The another major issue is the high production cost with increasing the amount of inactive materials such as Al foil, Cu foil and separator and increase of workload. Additionally, formation of cracks and peeling phenomena is existed after heat treatment when too thick active material on the current collector.[35-40]

1.3 Metal foam cathode

Metal foam is three-dimensional structure with Ni-Cr-Al alloy as shown in Figure 1.3.1. Because of three-dimensional structure, the active materials loading in metal foam can avoid the formation of cracks and peeling phenomena after heat treatment. And for the thick cathode a sheet of metal foam is sufficient, according to metal foam cathode, it can economize production cost and workload, such as cutting, stacking and so on. Using metal foam cathode, the volume of inactive material in metal foam cell is lower than foil-type cell.

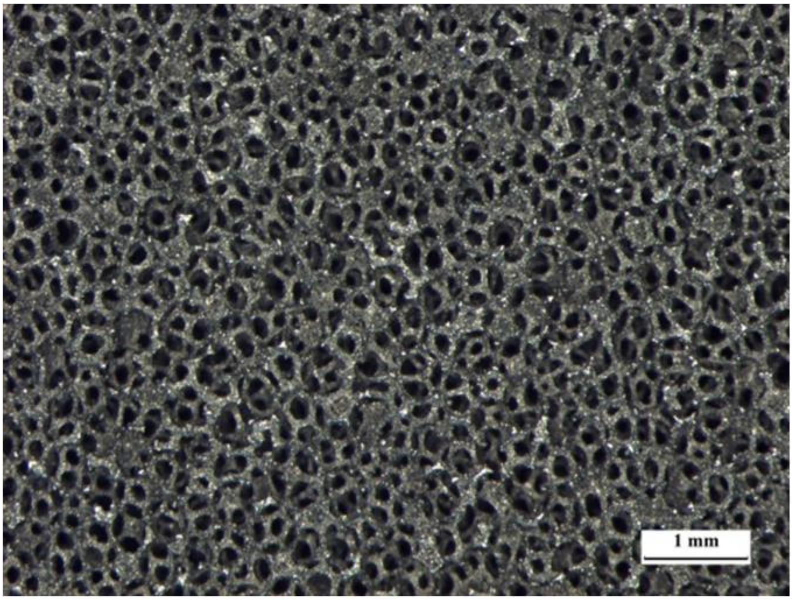

Figure 1.3 SEM image of the NiCrAl alloy metal foam.

The most important parameter of metal foam is cell size for the Li-ion battery cathodes. The maximum cell size of metal foam is 3000 μm and the minimum cell size of metal foam is 450 μm are supported by Alantum Corporation. So the large cell size metal foam is more suitable for the ultra-thick electrode, and the 450 μm cell size metal foam cathode is promising for the high rate application.

There are another advantage in applying metal foam cathode in Li-ion batteries. The triple junction (junction of active material, metal frame and electrolyte)[41] exists in metal foam cathode. As shown in Figure 1.3.2, it is comparisons of the charge-discharge curves for the cathodes using metal foam and foil-type at 0.2 mA and 2 mA.

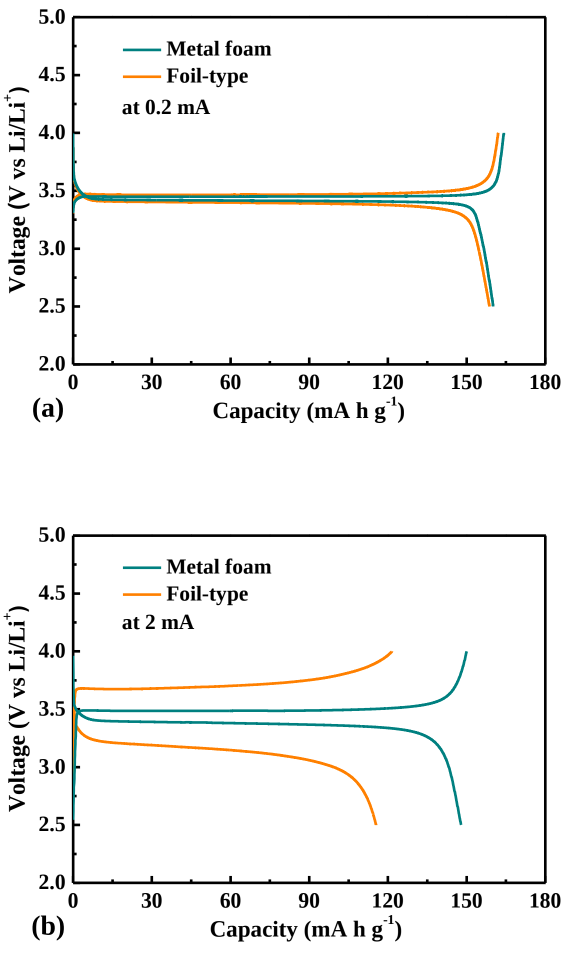

Figure 1.4 Comparisons of the charge-discharge curves for the cathodes using metal foam and foil type at 0.2 mA (a) and 2 mA (b).

1.4 Motivation

The minimum cell size metal foam is 450 μm, and it has the large area of triple junction, so 450 μm cell size metal foam cathode has superior kinetic and power performance. The maximum cell size metal foam is 3000 μm, and it can load the large amount of active material in the same volume, so 3000 μm cell size metal foam cathode has higher volumetric capacity. Designing the 450 and 3000 μm cell size metal foam cathode obtains optimization electrochemical performances.

According to the position of 450 and 3000 μm cell size metal foam cathode, three kinds of cathodes are prepared by combining 450 and 3000 μm cell size metal foam cathode. Two kinds of Sandwiched structures and one kind of Dual structure are researched in this study.

Chapter 2. Experiment

2.1 Fabrication methods of metal foam cathode

The commercial Ni foam substrate is manufactured by Ni plating on a three dimensional polyurethane and then the inner polyurethane is removed by heating. After the metallic NiCrAl alloy powder is adsorbed onto the resultant Ni foam, the substrate is reheated to obtain the NiCrAl alloy foam. All the manufacture processes are carried out by Alantum Corporation. The largest cell size of metal foam is 3000 μm and the smallest cell size of metal foam is 450μm. The thickness of metal foam is controlled via process which is combined by mechanical polishing and pressing before loading the slurry of active materials. Firstly, the slurry for metal foam cathode is mixed $LiFePO_4$/C (Hanwha Chemical Co., Korea) and carbon black (TIMCAL Ltd., Switzerland), and the weight ratio of $LiFePO_4$/C to carbon black is 5. Then, the mixture of $LiFePO_4$/C and carbon black is dissolved in a weight ratio with an N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) solution dissolved with polyniny lidene fluoride (PVdF, Sigma-Aldrich) as shown in Figure 2.1. Cutting metal foam for 1*3 cm^2, the slurry is loaded into it for 1*1cm^2 area to obtain the metal foam cathode. Then, metal foam cathode is firing for 10 hours at 120°C in vacuum.

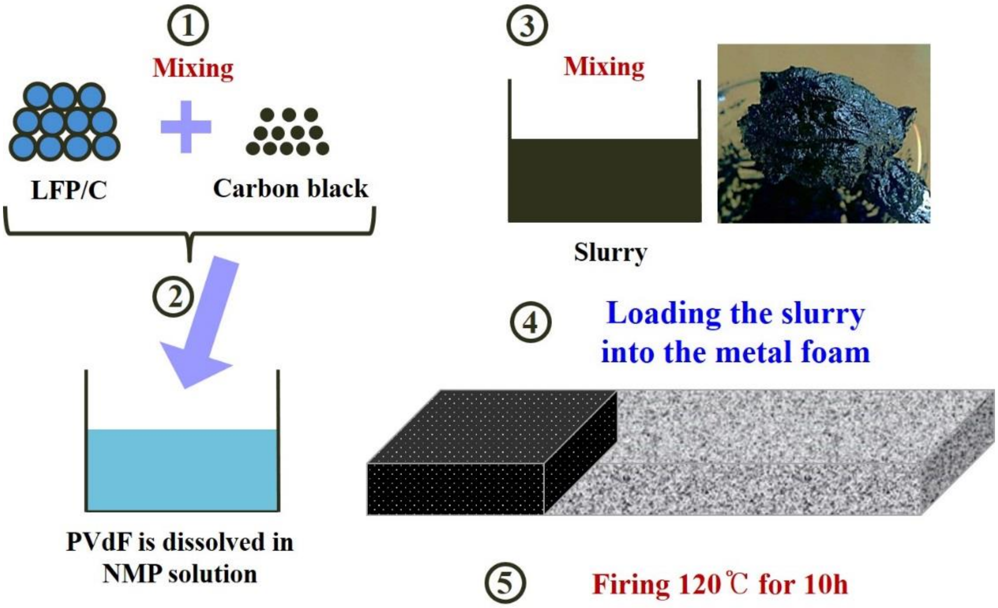

Figure 2.1 Manufacture process of metal foam cathode.

2.2 Design of cathode and preparation of Li-ion battery cell

Three kinds of metal foam cathodes are prepared as shown in Figure 2.2. Type 1 cathode is a whole metal foam cathode whose thickness is 1600㎛ circled by separator and Li metal in turn. Type 2 cathode is designed by one kind of cell size metal foam cathode whose thickness is 1000㎛ is between two metal foam cathodes that the cell size is different from previous metal foam cathode and the thickness is 300㎛. They are circled by separator and Li metal successively. The cell size of middle metal foam cathode is 3000㎛, named "Sandwiched-A Structure". The cell size of middle metal foam cathode is 450㎛, named "Sandwiched-B Structure". Type 3 cathode named "Dual Structure" is combined by 3000㎛ cell size metal foam cathode and 450㎛ cell size metal foam cathode, and the thickness of 3000㎛ cell size metal foam cathode is 1000㎛ and the thickness of 450㎛ cell size metal foam cathode is 600㎛. They are also circled by separator and Li metal in proper sequence.

Putting such battery cell into the pouch with appropriate electrolyte after sealing three sides of pouch, the part of metal foam unloaded slurry is connected with aluminum foil and Li metal is related to copper foil to outside. Final process is sealing the part of opening side of pouch. Aluminum and Copper foil outside is convenient for testing electrochemical performances.

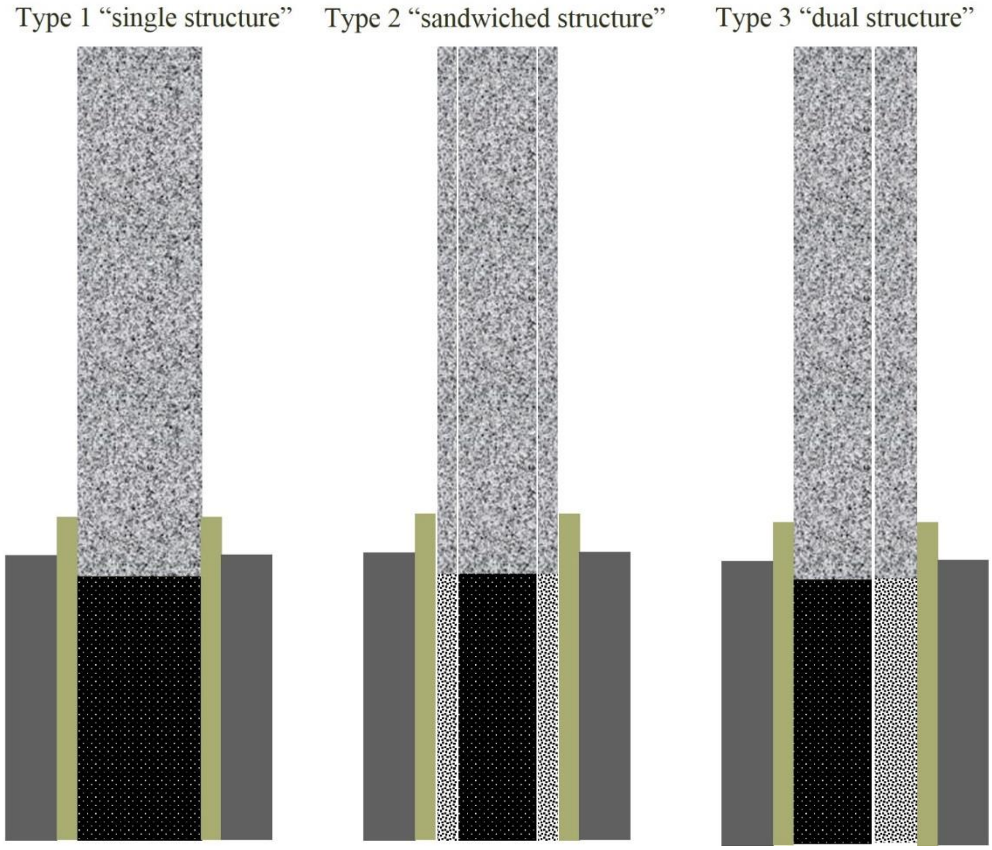

Figure 2.2 Design of different cell size metal foam for cathode.

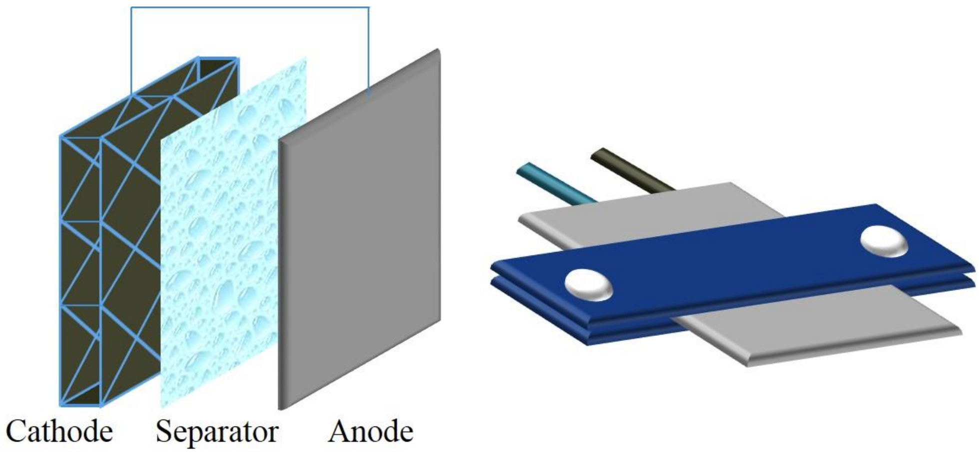

Figure 2.3 Schematic of metal foam cell.

2.3 Measurements for characterization of Li-ion battery cell

Galvanostatic charge-discharge test is that using 2mA constant current density charges the cell until voltage is 4.0V and using 2mA, 5mA, 10mA currents discharge the cell when voltage is dropped to 2.5V, every discharge-current for three times. Charge-rate test for columbic efficiency is that using 0.2c-rate (n (c-rate) * t (charge-discharge hours) =1) current charges the cell until voltage is 4.0V and after using 0.2c-rate, 0.5c-rate, 1.0c-rate, 1.5c-rate currents discharge the cell for three times until voltage is 2.5V, using 0.2c-rate current discharges the cell for three times when voltage of the cell dropped to 2.5V. Cyclic voltammetric (CV) analysis is performed using constant voltage scanning rate 0.1mV/s from 2.5V to 4.3V. Both galvanostatic charge-discharge test, charge-rate test and cyclic voltammetric analysis is evaluated by WBCS3000 battery cycler system at room temperature. The AC Impedance is analyzed using two-electrode system after the cell discharges completely at 2mA current density. The frequency range is from 10^5 to 0.01-0.02 Hz with a signal of 5mV amplitude by Electrochemical Analyzer (CHI608A).

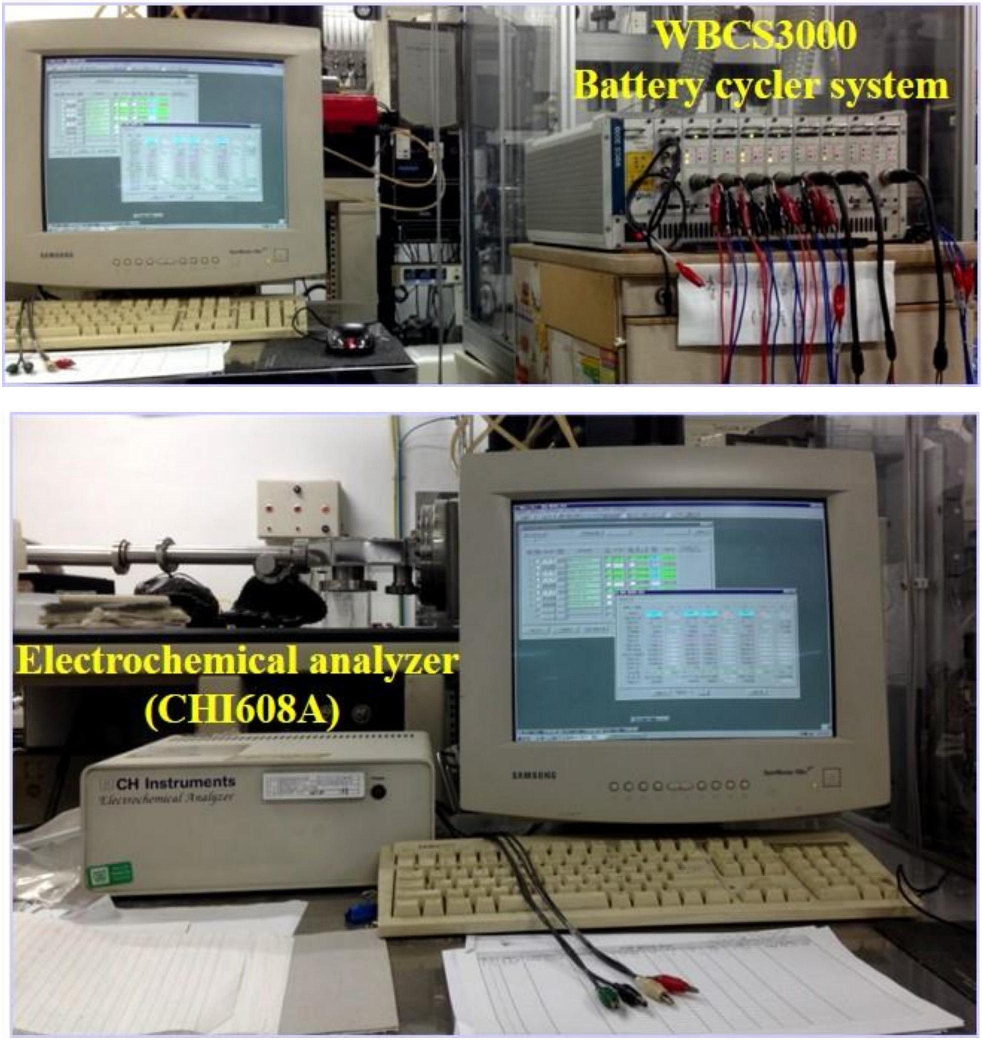

Figure 2.4 WBCS3000 Battery Cycler System and Electrochemical Analyzer (CHI608A).

Chapter. 3 Results and Discussion

3.1 450 ㎛ and 3000 ㎛ cell size metal foam cathode

Two kinds of current collectors are prepared with 450 ㎛ and 3000 ㎛ cell size metal foam for comparison of the electrochemical performances of cathodes. The slurry is prepared by mixing $LiFePO_4/C$ active materials, carbon black and PVdF at a weight ratio of 75:15:10 with an NMP solution. The thickness of 450 ㎛ cell size metal foam is 1600 ㎛ and the thickness of 3000 ㎛ cell size metal foam is 5000 ㎛ by manufacture processes of Alantum Corporation. The thickness of 3000 ㎛ cell size metal foam is reduced from 5000 ㎛ to 1600 ㎛ by via mechanical polishing to 3000 ㎛ and pressing to 1600 ㎛ before loading the slurry. As a result of the cell size of 450 ㎛ cell size metal foam is less than 3000 ㎛ cell size metal foam, the metal frame of 450 ㎛ cell size metal foam is more than 3000 ㎛ cell size metal foam in unit volume. So the amount of active material loading into 3000 ㎛ metal foam is more than loading into 450 ㎛ metal foam. The electrode density is 0.375g cm^{-3} for 450 ㎛ metal foam cathode and 0.6125g cm^{-3} for 3000 ㎛ metal foam cathode as shown in Table 3.1.1.

Table 3.1.1 Analytical data of cathodes using 450 and 3000 ㎛ metal foam.

Types of cathode	Electrode Thickness(μm)	Amount of active material(mg cm $^{-2}$)	Electrode density(g cm $^{-3}$)
450㎛	1600 μm	60 mg cm $^{-2}$	0.375
3000㎛		98 mg cm $^{-2}$	0.6125

Figure 3.1.1 shows a comparison of the charge-discharge curves at 2mA for the 450 ㎛ cell size metal foam cathode and 3000 ㎛ cell size metal foam cathode. The cell voltage remains constantly until the $LiFePO_4$ phase and $FePO_4$ phase become a single phase at the surface of the active material. In a word, because of the diffusion of Li in the $LiFePO_4$ phase and $FePO_4$ phase, the voltage of cell can keep constantly

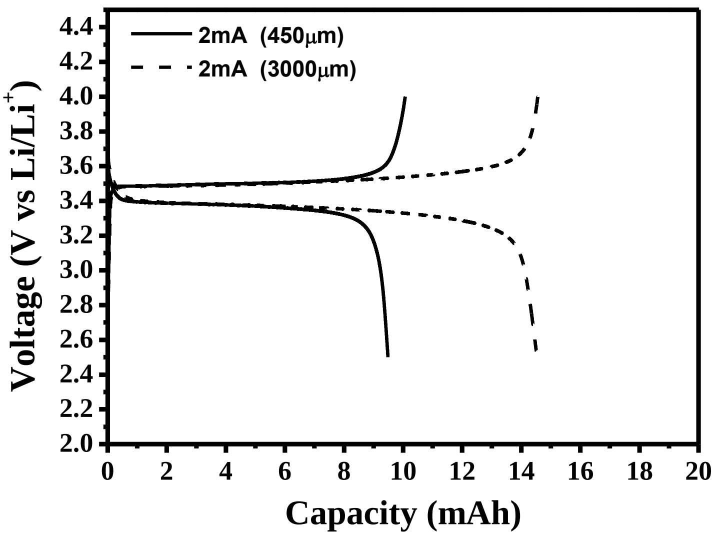

Figure 3.1.1 Comparison of the charge-discharge curves for the cathodes using 450 ㎛ and 3000 ㎛ cell size metal foam at 2mA.

when charging and discharging the cell. At 2mA current density, the discharge capacity of 450 ㎛ cell size metal foam cathode is 9.487 mAh and the discharge capacity of 3000 ㎛ cell size metal foam cathode is 14.533 mAh in the same volume.

Figure 3.1.2 shows a comparison of the charge-discharge curves at 5mA for the 450 ㎛ cell size metal foam cathode and 3000 ㎛ cell size metal foam cathode. At 5mA for high current density, the discharge capacity of 450 ㎛ cell size metal foam cathode is 9.2667 mAh and the discharge capacity of 3000 ㎛ cell size metal foam cathode is 11.337 mAh in the same volume.

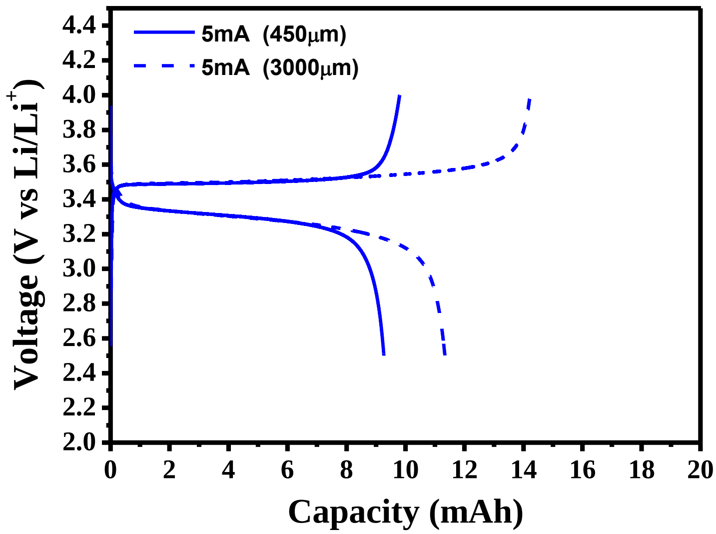

Figure 3.1.2 Comparison of the charge-discharge curves for the cathodes using 450 ㎛ and 3000 ㎛ cell size metal foam at 5mA.

Figure 3.1.3 shows a comparison of the charge-discharge curves at 10mA for the 450 ㎛ cell size metal foam cathode and 3000 ㎛ cell size metal foam cathode. At 5mA for extra-high current density, the discharge capacity of 450 ㎛ cell size metal foam cathode is 8.5751 mAh and the discharge capacity of 3000 ㎛ cell size metal foam cathode is 8.1592 mAh in the same volume.

It shows 3000 ㎛ cell size metal foam cathode has more capacity than 450 ㎛ cell size metal foam cathode in the same volume at 2mA current density. However, with increasing current density, the volumetric capacity of 3000 ㎛ cell size metal foam cathode decreases more rapidly than 450 ㎛ cell size metal foam cathode.

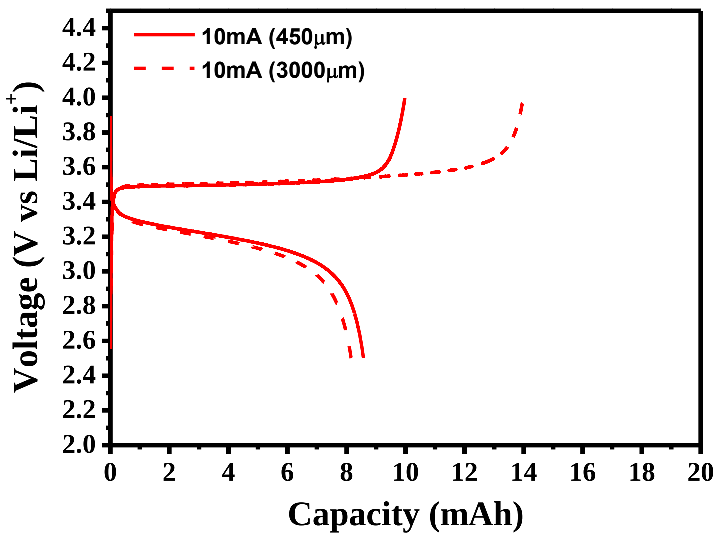

Figure 3.1.3 Comparison of the charge-discharge curves for the cathodes using 450 ㎛ and 3000 ㎛ cell size metal foam at 10mA.

Figure 3.1.4 shows a comparison of the charge-discharge curves for specific capacity at 2mA for the 450 μm cell size metal foam cathode and 3000 μm cell size metal foam cathode. At 2 mA current density, the specific discharge capacity of 450 μm cell size metal foam cathode is 143.7424 mAh g^{-1} and the specific discharge capacity of 3000 μm cell size metal foam cathode is 148.2959 mAh g^{-1}. The IR drop of 3000 μm cell size metal foam cathode is a little higher than 450 μm cell size metal foam cathode. And the gradient of plateau curve of 450 μm cell size metal foam cathode is less than 3000 μm cell size metal foam cathode.

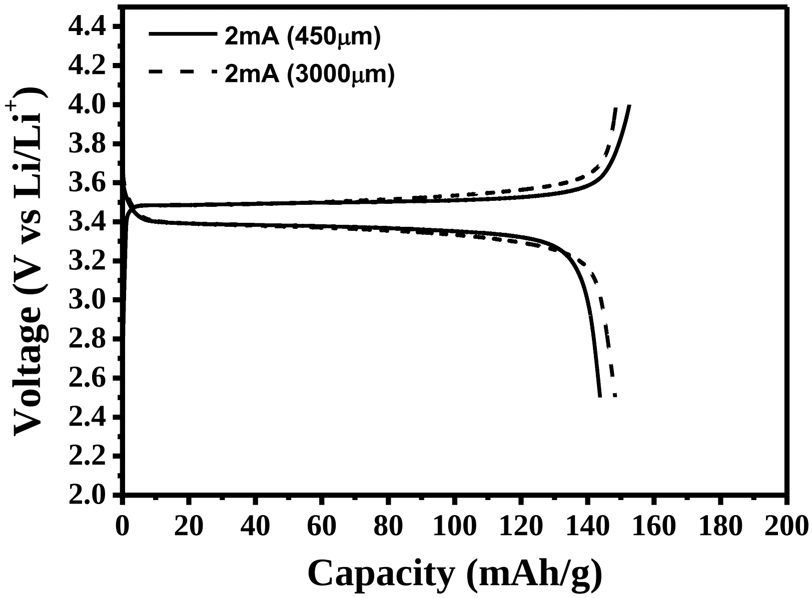

Figure 3.1.4 Comparison of the charge-discharge curves for specific capacity for the cathodes using 450 μm and 3000 μm cell size metal foam at 2mA.

Figure 3.1.5 shows a comparison of the charge-discharge curves for specific capacity at 5mA for the 450 μm cell size metal foam cathode and 3000 μm cell size metal foam cathode. At 5mA for high current density, the specific discharge capacity of 450 μm cell size metal foam cathode is 140.4045 mAh g^{-1} and the specific discharge capacity of 3000 μm cell size metal foam cathode is 115.6836 mAh g^{-1}. The gradient of plateau curve of 450 μm cell size metal foam cathode is also less than 3000 μm cell size metal foam cathode.

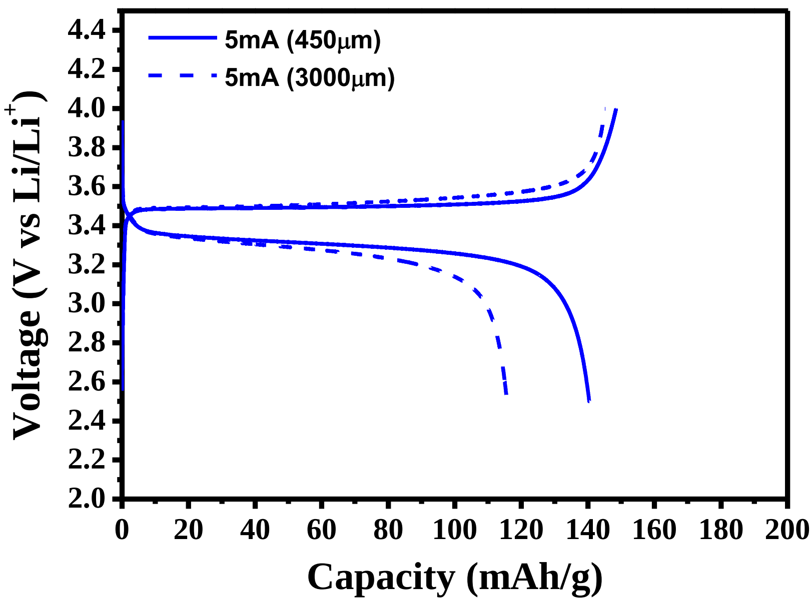

Figure 3.1.5 Comparison of the charge-discharge curves for specific capacity for the cathodes using 450 μm and 3000 μm cell size metal foam at 5mA.

Figure 3.1.6 shows a comparison of the charge-discharge curves for specific capacity at 5mA for the 450 ㎛ cell size metal foam cathode and 3000 ㎛ cell size metal foam cathode. At 10mA for extra-high current density, the specific discharge capacity of 450 ㎛ cell size metal foam cathode is 129.9257 mAh g^{-1} and the specific discharge capacity of 3000 ㎛ cell size metal foam cathode is 83.2571 mAh g^{-1}. At extra-high current density, the specific discharge capacity of 3000 ㎛ cell size metal foam cathode is almost half less than 450 ㎛ cell size metal foam cathode. And the gradient of plateau curve of 3000 ㎛ cell size metal foam cathode is higher than 450 ㎛ cell size metal foam cathode.

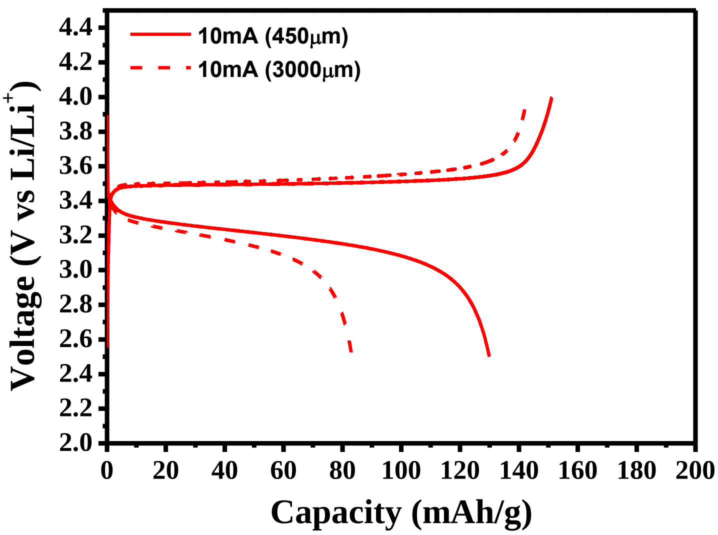

Figure 3.1.6 Comparison of the charge-discharge curves for specific capacity for the cathodes using 450 ㎛ and 3000 ㎛ cell size metal foam at 10mA.

It implies that increasing discharge current density, the proportion of reactiveness of active materials in 3000 ㎛ cell size metal foam cathode decreases more rapidly than 450 ㎛ cell size metal foam cathode.

The limitation of reaction includes electron transfer limitation and mass transfer limitation. As shown in Figure 3.1.7, charge transfer resistance of 450 ㎛ cell size metal foam cathode is about 2.56 Ω and the bulk resistance is 4.33 Ω. For 3000 ㎛ cell size metal foam cathode, the charge transfer resistance is about 20.39 Ω and the bulk resistance is 5.41 Ω. According to Figure 3.1.7, it shows diffusion of Li-ion is more quick in 450 ㎛ cell size metal foam cathode. It implies that not only the velocity of charge transfer in 450 ㎛ cell size metal foam cathode is higher than 3000 ㎛ cell size metal foam cathode but also the velocity of mass transfer in 450 ㎛ cell size metal foam cathode is more quick than 3000 ㎛ cell size metal foam cathode. The kinetic performance of 450 ㎛ cell size metal foam cathode is better than 3000 ㎛ cell size metal foam cathode.

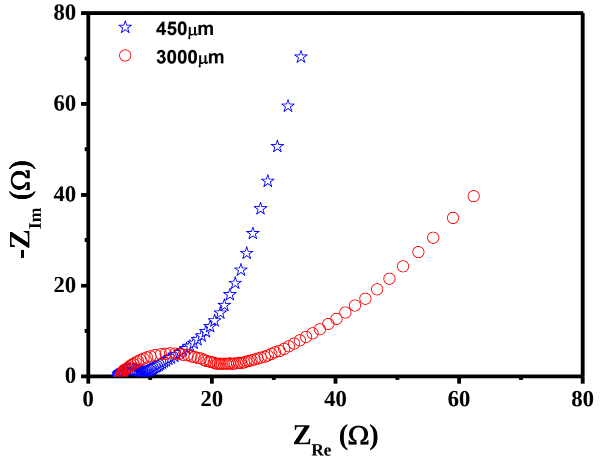

Figure 3.1.7 Comparison of the AC impedance curves for the 450 μm cell size metal foam cathode and 3000 μm cell size metal foam cathode.

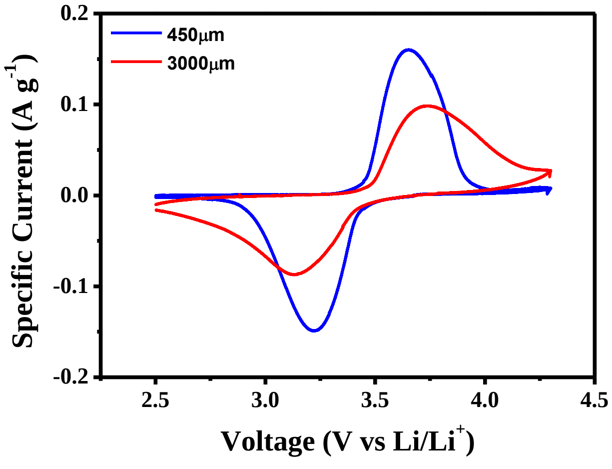

Figure 3.1.8 Comparison of the Cyclic voltammetric (CV) curves at 0.1mV s^{-1} for the 450 μm cell size metal foam cathode and 3000 μm cell size metal foam cathode.

Figure 3.1.8 shows the cyclic voltammetric (CV) curves for the 450 ㎛ cell size metal foam cathode and 3000 ㎛ cell size metal foam cathode at scan rate of 0.1mV s^{-1}. As shown in Figure 3.1.8, the redox peaks appear much earlier and the specific currents are higher at the peaks for the 450 ㎛ cell size metal foam cathode. The redox peaks of 450 ㎛ cell size metal foam cathode are 3.65 V and 3.22 V and the specific currents at position of peaks are 0.160 A g^{-1} and -0.149 A g^{-1}. However, the redox peaks of 3000 ㎛ cell size metal foam cathode occur 3.74 V and 3.13 V and the specific currents at positon of peaks are 0.098 A g^{-1} and -0.087 A g^{-1}. It shows that the kinetic performance and the power performance of 450 ㎛ cell size metal foam cathode are much more superior than 3000 ㎛ cell size metal foam cathode as a result in there are more triple junctions in 450 ㎛ cell size metal foam cathode.

As shown in Figure 3.1.9, it shows that schematic of reaction in metal foam cathode, and the reaction occurs in the triple junctions (junction of active material, metal frame, and electrolyte)99. Li-ion attending reaction is in the electrolyte and electron can transfer from metal frame and in the triple junctions they are provided to reaction site as quickly as possible. When charging the metal foam cathode, Li-ion deinserts from LFP/C active materials to electrolyte in the triple junction. When discharging the metal foam cathode, Li-ion inserts in to LFP/C active materials from electrolyte. According to the Fick's 1st Law, Li diffuses from surface to mid of LFP/C active materials or diffuses from mid of LFP/C active materials to surface until two phases become single phase. Owing to more triple junction in the 450 ㎛ cell size metal foam cathode, the kinetic performance and the power performance is much more better than 3000 ㎛ cell size metal foam cathode.

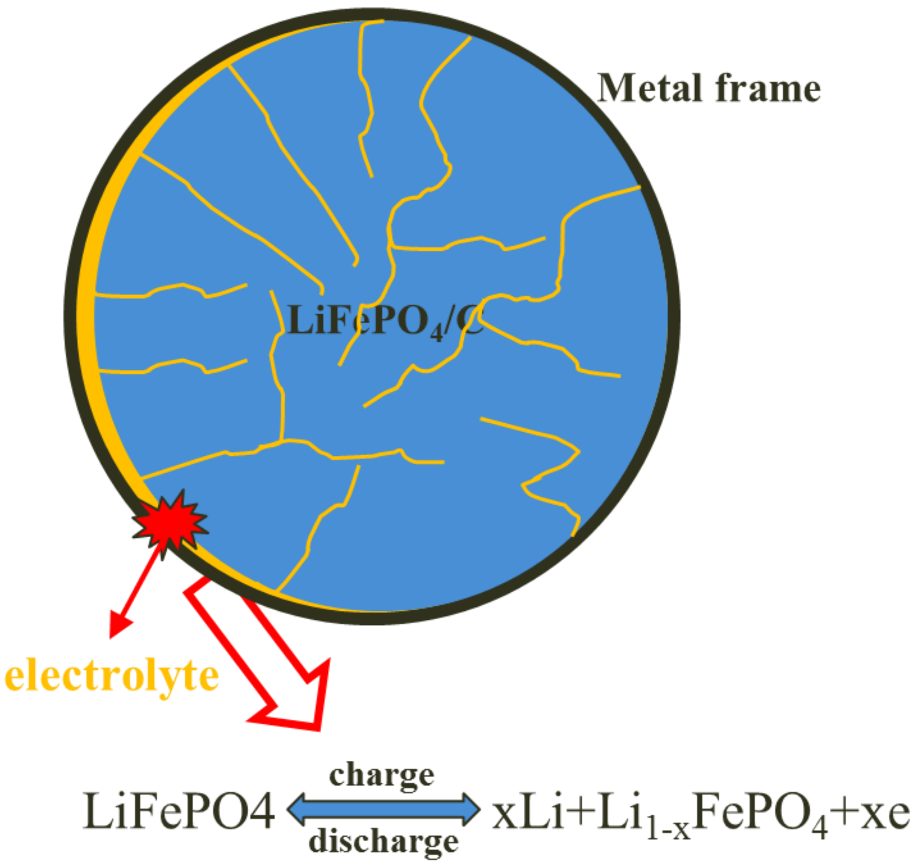

Figure 3.1.9 Schematic of reaction in metal foam cathode.

3.2 Sandwiched-A structure metal foam cathode

Sandwiched-A structure is that 3000 ㎛ cell size metal foam in the mid of cathode and its thickness is 1000 ㎛ made by via mechanical polishing from 5000 ㎛ to 3000 ㎛ then pressing to 1000 ㎛ before loading mixture of active materials, carbon black and PVdF with an NMP solution. And two 450 ㎛ cell size metal foams whose thickness is 300 ㎛ made by via mechanical polishing from 1600 ㎛ to 500 ㎛ and pressing to 300 ㎛ before loading mixture, are in the side of 3000 ㎛ cell size metal foam. So 450 and 3000 ㎛ cell size metal foam and Sandwiched-A structure metal foam cathode has the same thickness. Most of volume of Sandwiched-A structure is 3000 ㎛ cell size metal foam, so the amount of active materials in Sandwiched-A structure is nearly equal to 3000 ㎛ cell size metal foam cathode and the electrode density is 0.5718 g cm^{-3} as shown in Table 3.2.1.

Table 3.2.1 Analytical data of 450 ㎛ and 3000 ㎛ cell size metal foam cathode and Sandwiched-A structure metal foam cathode.

Types of cathode	Electrode Thickness(µm)	Amount of active material(mg cm^{-2})	Electrode density(g cm^{-3})
450㎛	1600 µm	60 mg cm^{-2}	0.3750
3000㎛		98 mg cm^{-2}	0.6125
Sandwiched-A type		91.5 mg cm^{-2}	0.5718

Figure 3.2.1 shows that Sandwiched-A structure has a little less capacity than 3000 μm cell size metal foam cathode but has more capacity than 450 μm cell size metal foam cathode in the same volume at 2 mA current density discharge. At 5 mA high current density discharge, Sandwiched-A structure metal foam cathode has more capacity than 3000 μm cell size metal foam cathode and almost has no volumetric capacity loss compared with 2 mA current density discharge. As shown in Figure 3.2.3, at 10 mA extra-high current density discharge, although Sandwiched-A structure metal foam cathode has more capacity loss than 450 μm cell size metal foam cathode compared with 5 mA current density discharge, it always has more volumetric capacity than 450 μm cell size metal foam.

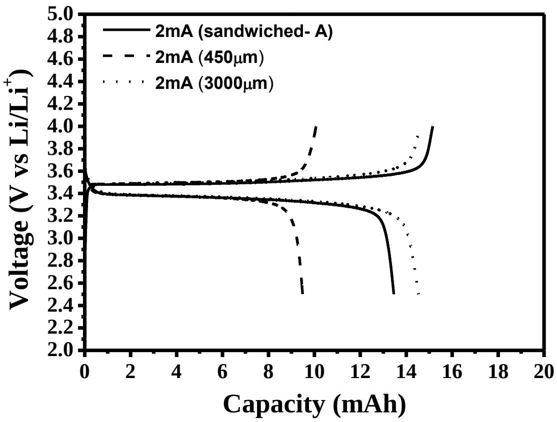

Figure 3.2.1 Comparison of the charge-discharge curves for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-A structure metal foam cathode at 2mA.

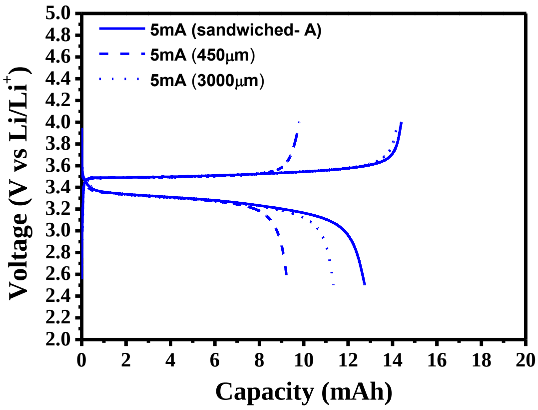

Figure 3.2.2 Comparison of the charge-discharge curves for the 450 ㎛ and 3000 ㎛ cell size metal foam cathode and Sandwiched-A structure metal foam cathode at 5mA.

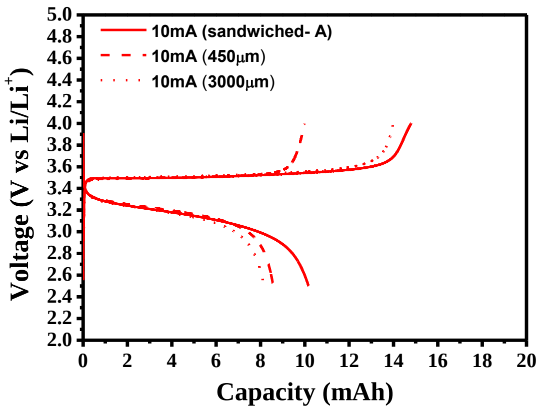

Figure 3.2.3 Comparison of the charge-discharge curves for the 450 ㎛ and 3000 ㎛ cell size metal foam cathode and Sandwiched-A structure metal foam cathode at 10mA.

Figure 3.2.4 shows that charge-discharge curves for the specific capacity, at 2 mA current density discharge, the specific discharge capacity of Sandwiched-A structure metal foam cathode is 147.1038 mAh g^{-1}, and the proportion of reactiveness of Sandwiched-A structure metal foam cathode is equal to 3000 μm cell size metal foam cathode and they are a little more than 450 μm cell size metal foam cathode. The gradient of plateau curve is similar to 3000 μm cell size metal foam cathode. At 5 mA high current density, the proportion of reactiveness of Sandwiched-A structure metal foam cathode reduces much less than 3000 μm cell size metal foam cathode and the specific discharge capacity is about 139.3114 mAh g^{-1}. But the gradient of plateau curve of Sandwiched-A structure metal foam cathode is higher than 450 μm cell size metal foam cathode. At 10 mA extra-high current density, the specific discharge capacity of the Sandwiched-A structure metal foam cathode is 111.1315 mAh g^{-1} as shown in Figure 3.2.6, and the proportion of reactiveness of Sandwiched-A structure metal foam cathode decreases a little more than 450 μm cell size metal foam cathode. It implies that 450 μm cell size metal foam cathode being side part of 3000 μm cell size metal foam cathode causes less specific discharge capacity loss than 3000 μm cell size metal foam cathode with increasing discharge current density.

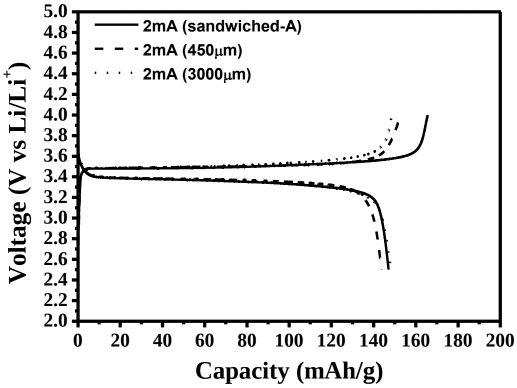

Figure 3.2.4 Comparison of the charge-discharge curves for specific capacity for the 450 ㎛ and 3000 ㎛ cell size metal foam cathode and Sandwiched-A structure metal foam cathode at 2mA.

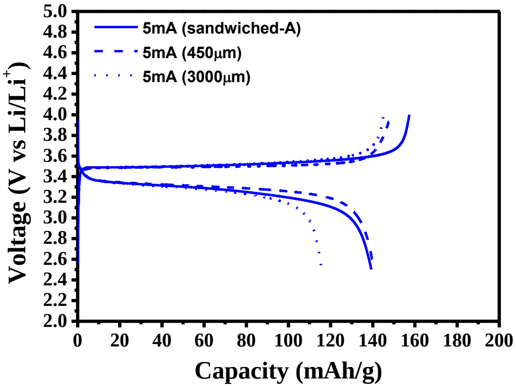

Figure 3.2.5 Comparison of the charge-discharge curves for specific capacity for the 450 ㎛ and 3000 ㎛ cell size metal foam cathode and Sandwiched-A structure metal foam cathode at 5mA.

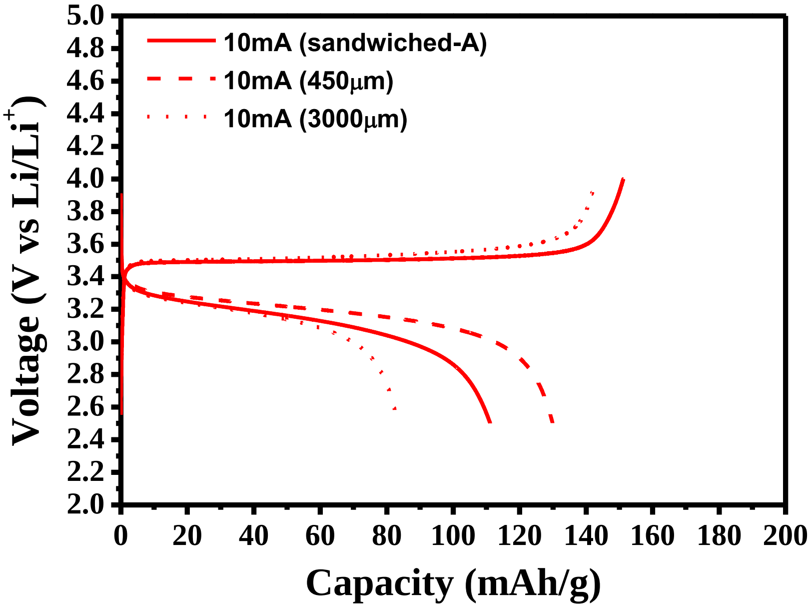

Figure 3.2.6 Comparison of the charge-discharge curves for specific capacity for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-A structure metal foam cathode at 10mA.

Figure 3.2.7 shows that the charge transfer resistance of Sandwiched-A structure metal foam cathode is 29.22 Ω and the bulk resistance is 4.09 Ω. According to the Figure 3.2.7, it shows that diffusion of Li-ion of Sandwiched-A structure metal foam cathode is almost equal to 450 μm cell size metal foam cathode. And it implies the limitation of Sandwiched-A structure metal foam cathode is mass transfer limitation, not charge transfer limitation. Because charge transfer resistance of Sandwiched-A structure metal foam cathode is higher than 3000 μm cell size metal foam cathode, the proportion of reactiveness of active materials is much higher than 3000 μm cell size metal foam cathode.

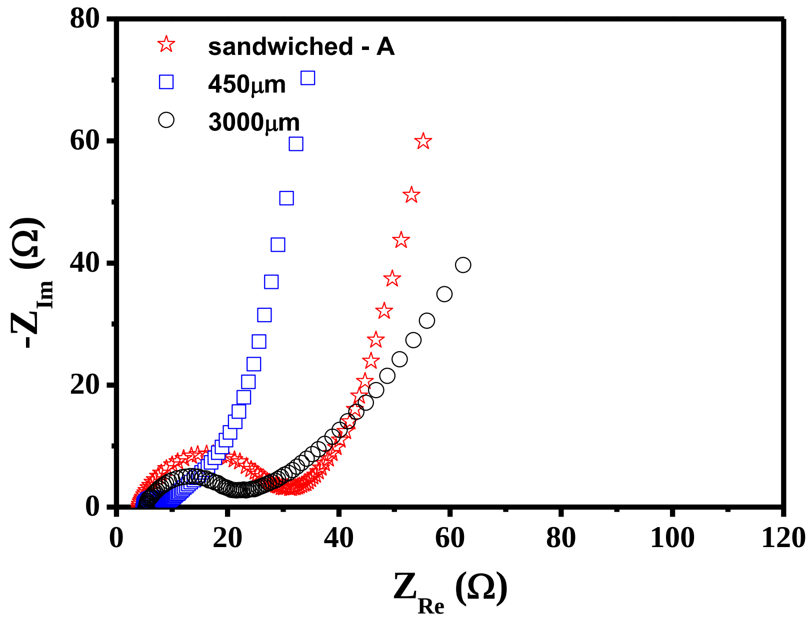

Figure 3.2.7 Comparison of the AC impedance curves for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-A structure metal foam cathode.

Figure 3.2.8 shows the CV curves for the 450 and 3000 μm cell size metal foam cathode and Sandwiched-A structure metal foam cathode at scan rate of 0.1 mV s^{-1}. As shown in Figure 3.2.6, at 10 mA extra-high current density, the plateau curve is shifted from 2.9 V to 3.3 V. In this region, the reduction of Sandwiched-A structure metal foam cathode occurs more easily than 3000 μm cell size metal foam cathode, although reduction specific current of position of peak of Sandwiched-A structure metal foam cathode is a little lower than 3000 μm cell size metal foam cathode. So the kinetic performance and the power performance of Sandwiched-A structure metal foam cathode is more superior than 3000 μm cell size metal foam cathode.

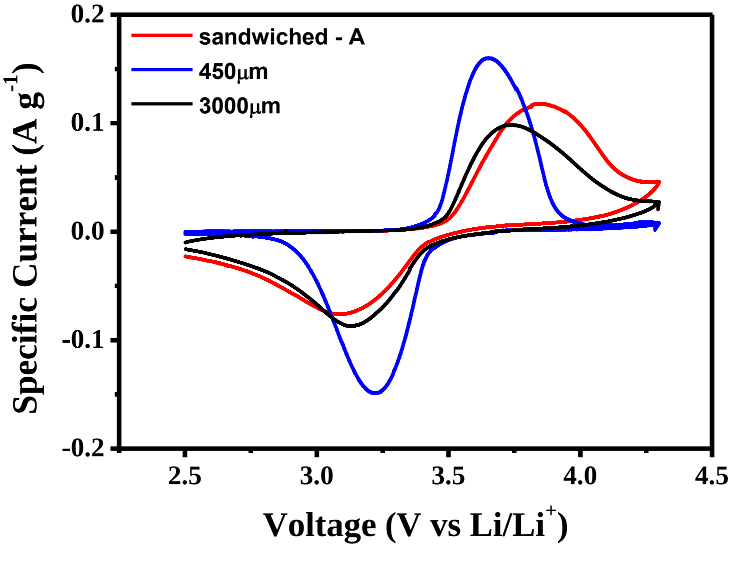

Figure 3.2.8 Comparison of the CV curves at 0.1mV s^{-1} for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-A structure metal foam cathode.

3.3 Sandwiched-B structure metal foam cathode

Sandwiched-B structure is that 450 μm cell size metal foam in the mid of cathode and its thickness is 1000 μm made by via mechanical polishing from 1600 μm to 1000 μm before loading mixture. And two 3000 μm cell size metal foams whose thickness is 300 μm made by via mechanical polishing from 5000 μm to 3000 μm and pressing to 300 μm before loading mixture, are in the side of 450 μm cell size metal foam. So 450 and 3000 μm cell size metal foam and Sandwiched-B structure metal foam cathode has the same thickness. Most of volume of Sandwiched-B structure is 450 μm cell size metal foam, so the amount of active materials in Sandwiched-A structure is the average of the amount of active materials in 450 and 3000 μm cell size metal foam cathode and the electrode density is 0.4875 g cm^{-3} as shown in Table 3.3.1.

Table 3.3.1 Analytical data of 450 μm and 3000 μm metal foam cathode and Sandwiched-B structure metal foam cathode.

Types of cathode	Electrode Thickness(μm)	Amount of active material(mg cm^{-2})	Electrode density(g cm^{-3})
450μm	1600 μm	60 mg cm^{-2}	0.3750
3000μm		98 mg cm^{-2}	0.6125
Sandwiched-B type		78 mg cm^{-2}	0.4875

Figure 3.3.1-3 shows that charge-discharge curves for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-B structure metal foam cathode at 2 mA, 5 mA high and 10 mA extra-high current density discharge. The loss of volumetric capacity of Sandwiched-B structure metal foam cathode is nearly equal to 450 μm cell size metal foam cathode from 2 mA to 5 mA current density discharge. At 10 mA extra-high current density discharge, the capacity of Sandwiched-B structure metal foam cathode is equal to 450 μm cell size metal foam cathode and they are a little more than 3000 μm cell size metal foam cathode in the same volume. It implies that 3000 μm cell size metal foam cathode being side part of 450 μm cell size metal foam cathode causes more volumetric capacity than 450 μm cell size metal foam cathode until discharging at 5 mA high current density.

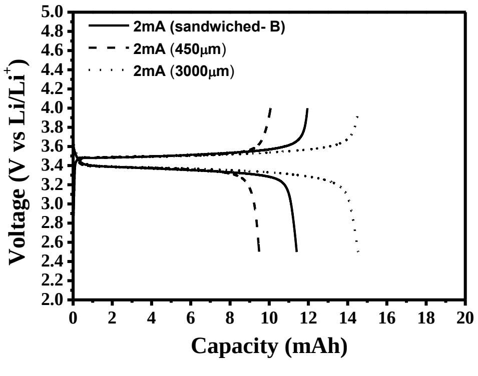

Figure 3.3.1 Comparison of the charge-discharge curves for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-B structure metal foam cathode at 2mA.

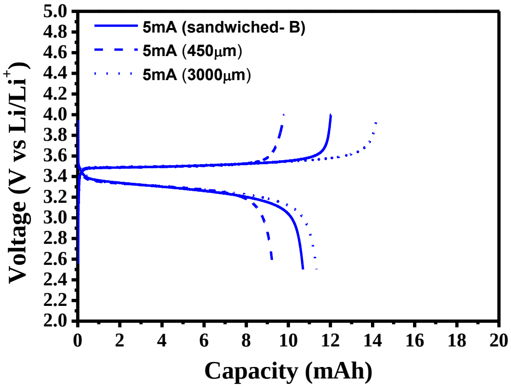

Figure 3.3.2 Comparison of the charge-discharge curves for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-B structure metal foam cathode at 5mA.

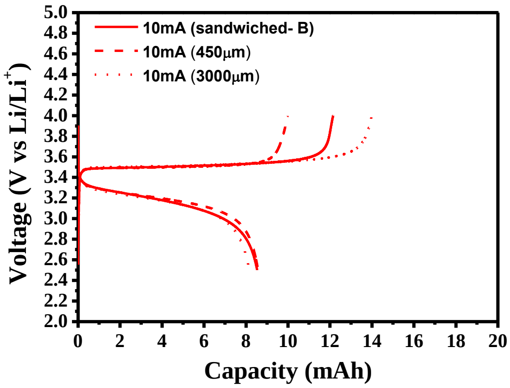

Figure 3.3.3 Comparison of the charge-discharge curves for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-B structure metal foam cathode at 10mA.

Figure 3.3.4 shows that charge-discharge curves for the specific capacity, at 2 mA current density discharge, the specific discharge capacity of Sandwiched-B structure metal foam cathode is 146.1794 mAh g^{-1}, and the proportion of reactiveness of Sandwiched-B structure metal foam cathode is a little more than 450 ㎛ cell size metal foam cathode. The gradient of plateau curve is similar to 3000 ㎛ cell size metal foam cathode. At 5 mA high current density, the proportion of reactiveness of Sandwiched-B structure metal foam cathode reduces a little more than 450 ㎛ cell size metal foam cathode and the specific discharge capacity is about 137.1282 mAh g^{-1} as shown in Figure 3.3.5. But the gradient of plateau curve of Sandwiched-B structure metal foam cathode is much less than 3000 ㎛ cell size metal foam cathode. At 10 mA extra-high current density, the specific discharge capacity of the Sandwiched-B structure metal foam cathode is 109.3615 mAh g^{-1} as shown in Figure 3.2.6, and the proportion of reactiveness of Sandwiched-B structure metal foam cathode decreases more than 450 ㎛ cell size metal foam cathode.

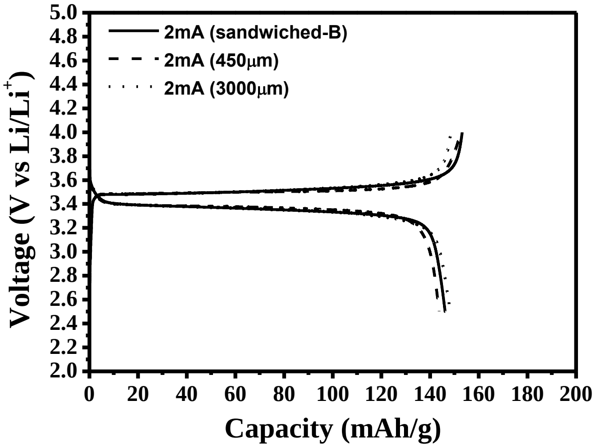

Figure 3.3.4 Comparison of the charge-discharge curves for specific capacity for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-B structure metal foam cathode at 2mA.

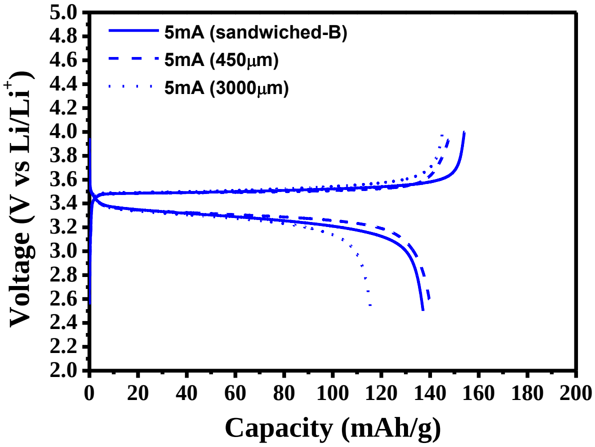

Figure 3.3.5 Comparison of the charge-discharge curves for specific capacity for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-B structure metal foam cathode at 5mA.

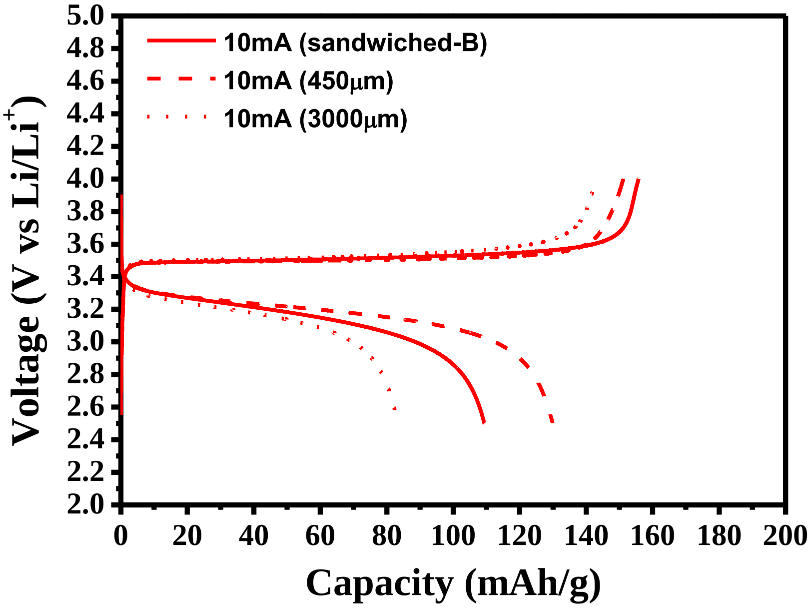

Figure 3.3.6 Comparison of the charge-discharge curves for specific capacity for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-B structure metal foam cathode at 10mA.

Figure 3.3.7 shows that the charge transfer resistance of Sandwiched-B structure metal foam cathode is 11.12 Ω and the bulk resistance is 4.13 Ω. According to the Figure 3.3.7, it shows that diffusion of Li-ion of Sandwiched-B structure metal foam cathode is higher than 3000 ㎛ cell size metal foam cathode. And it implies the limitation of Sandwiched-B structure metal foam cathode is combined mass transfer limitation with charge transfer limitation. Because charge transfer resistance of Sandwiched-B structure metal foam cathode is higher than 450 ㎛ cell size metal foam cathode, and the mass transfer resistance of Sandwiched-B structure metal foam cathode is also higher than 450 ㎛ cell size metal foam cathode. And the charge transfer resistance and the mass transfer resistance of Sandwiched-B structure metal foam cathode is lower than 3000 ㎛ cell size metal foam cathode.

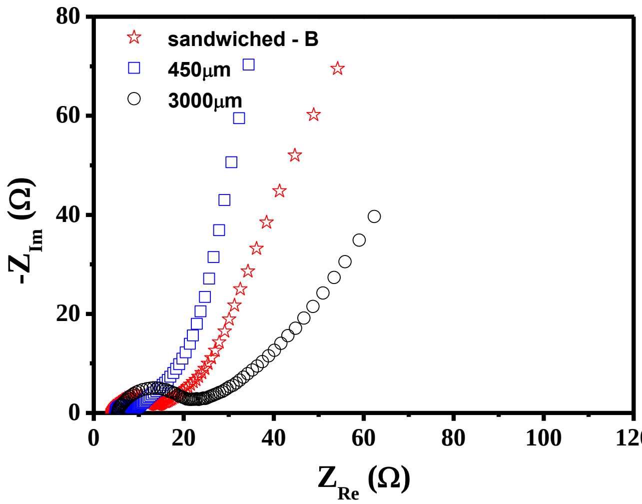

Figure 3.3.7 Comparison of the AC impedance curves for the 450 ㎛ and 3000 ㎛ cell size metal foam cathode and Sandwiched-B structure metal foam cathode.

Figure 3.3.8 shows the CV curves for the 450 and 3000 μm cell size metal foam cathode and Sandwiched-B structure metal foam cathode at scan rate of 0.1 mV s^{-1}. As shown in Figure 3.3.6, at 10 mA extra-high current density, the plateau curve is shifted from 2.9 V to 3.3 V. In this region, the reduction of Sandwiched-B structure metal foam cathode occurs more easily than 3000 μm cell size metal foam cathode, and reduction specific current of position of peak of Sandwiched-B structure metal foam cathode is a little higher than 3000 μm cell size metal foam cathode. And with the voltage of plateau region lower, the kinetic performance and the power performance is more superior than 3000 μm cell size metal foam cathode.

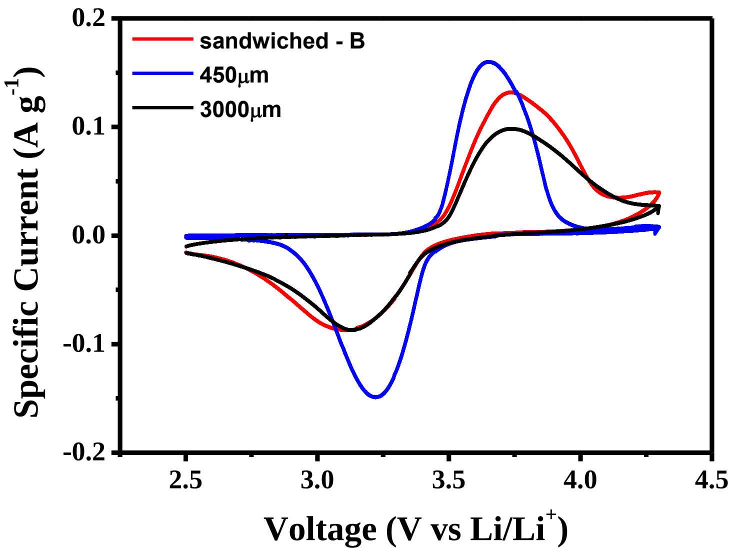

Figure 3.3.8 Comparison of the CV curves at 0.1mV s^{-1} for the 450 μm and 3000 μm cell size metal foam cathode and Sandwiched-B structure metal foam cathode.

3.4 Dual structure metal foam cathode

Dual structure is that 3000 μm cell size metal foam in the one side of cathode and its thickness is 1000 μm made by via mechanical polishing from 5000 μm to 3000 μm then pressing to 1000 μm before loading mixture. And 450 μm cell size metal foam whose thickness is 600 μm made by via mechanical polishing from 1600 μm to 600 μm before loading mixture, is in the other side of cathode. So 450 and 3000 μm cell size metal foam and Dual structure metal foam cathode has the same thickness. Most of volume of Dual structure is 3000 μm cell size metal foam, so the amount of active materials in Dual structure is nearly equal to 3000 μm cell size metal foam cathode and the electrode density is 0.5718 g cm^{-3} which is equal to Sandwiched-A structure metal foam cathode as shown in Table 3.4.1.

Table 3.4.1 Analytical data of 450 μm and 3000 μm metal foam cathode and Dual structure metal foam cathode.

Types of cathode	Electrode Thickness(μm)	Amount of active material(mg cm^{-2})	Electrode density(g cm^{-3})
450μm	1600 μm	60 mg cm^{-2}	0.3750
3000μm		98 mg cm^{-2}	0.6125
Dual structure		91.5 mg cm^{-2}	0.5718

Figure 3.4.1 shows that charge-discharge curves for the 450 μm and 3000 μm cell size metal foam cathode and Dual structure metal foam cathode at 2mA current density discharge. The volumetric capacity of Dual structure metal foam cathode is a little less than 3000 μm cell size metal foam cathode. But at 5 mA high current density discharge, the capacity of Dual structure metal foam cathode decreases less than 3000 μm cell size metal foam cathode and extent of loss capacity is equal to 450 μm cell size metal foam cathode about 0.25 mAh. And increasing the discharge current density to 10 mA for extra-high current density discharge, the volumetric capacity of Dual structure metal foam cathode is the highest between 450 and 3000 μm cell size metal foam cathode and is 1.5 times larger than others.

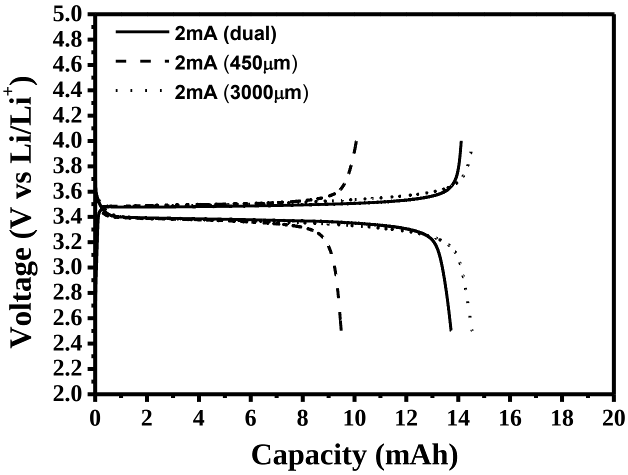

Figure 3.4.1 Comparison of the charge-discharge curves for the 450 μm and 3000 μm cell size metal foam cathode and Dual structure metal foam cathode at 2mA.

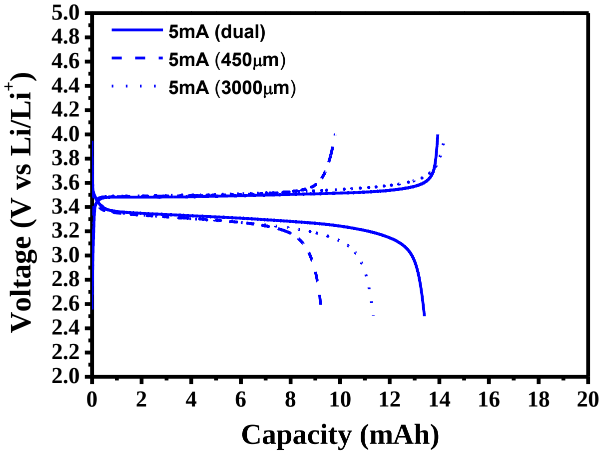

Figure 3.4.2 Comparison of the charge-discharge curves for the 450 ㎛ and 3000 ㎛ cell size metal foam cathode and Dual structure metal foam cathode at 5mA.

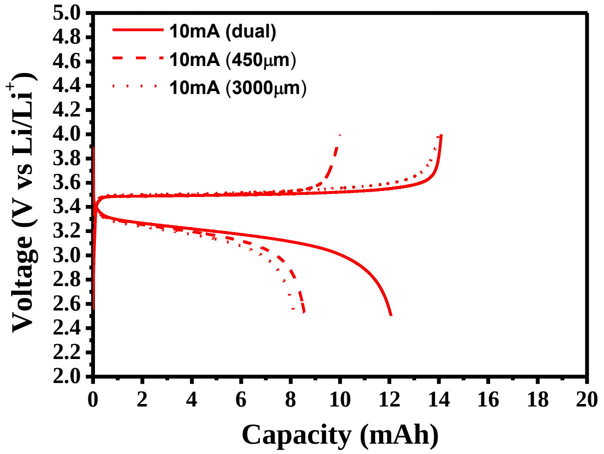

Figure 3.4.3 Comparison of the charge-discharge curves for the 450 ㎛ and 3000 ㎛ cell size metal foam cathode and Dual structure metal foam cathode at 10mA.

Figure 3.4.4 shows that charge-discharge curves for the specific capacity, at 2 mA current density discharge, the specific discharge capacity of Dual structure metal foam cathode is 149.9781 mAh g^{-1}, and the proportion of reactiveness of Sandwiched-A structure metal foam cathode is a little more than 3000 ㎛ cell size metal foam cathode and is 6 mAh g^{-1} more than 450 ㎛ cell size metal foam cathode. The gradient of plateau curve is lower than 3000 ㎛ cell size metal foam cathode and similar to 450 ㎛ cell size metal foam cathode. At 5 mA high current density, the proportion of reactiveness of Dual structure metal foam cathode decreases much less than 3000 ㎛ cell size metal foam cathode and the specific discharge capacity is about 146.4481 mAh g^{-1}, and is more than 450 ㎛ cell size metal foam cathode. And the gradient of plateau curve of Dual structure metal foam cathode is equal to 450 ㎛ cell size metal foam cathode. At 10 mA extra-high current density, the specific discharge capacity of the Dual structure metal foam cathode is 131.9016 mAh g^{-1} as shown in Figure 3.2.6, and the proportion of reactiveness of Dual structure metal foam cathode is also more than 450 ㎛ cell size metal foam cathode. It implies that, at low current density discharge, the part of 3000 ㎛ cell size metal foam cathode in which have more active materials than 450 ㎛ cell size metal foam cathode is main reaction site, and at high or extra-high current density discharge, the part of 450 ㎛ cell size metal foam cathode in which have more triple junctions than 3000 ㎛ cell size metal foam cathode is important role in reaction.

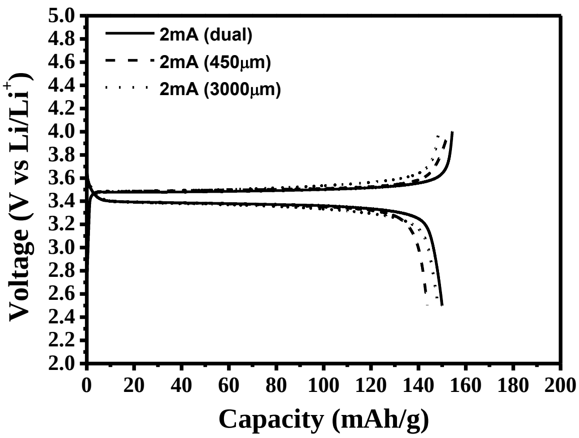

Figure 3.4.4 Comparison of the charge-discharge curves for specific capacity for the 450 μm and 3000 μm cell size metal foam cathode and Dual structure metal foam cathode at 2mA.

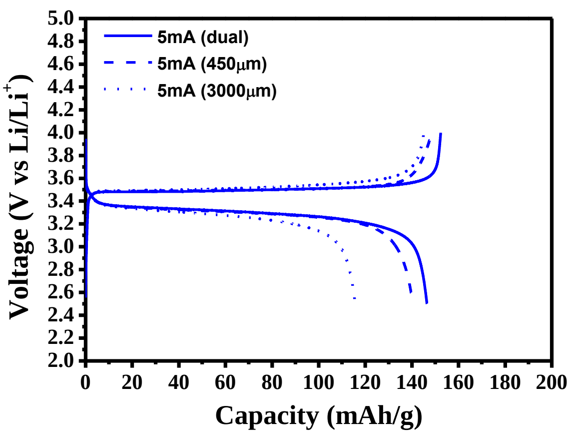

Figure 3.4.5 Comparison of the charge-discharge curves for specific capacity for the 450 μm and 3000 μm cell size metal foam cathode and Dual structure metal foam cathode at 5mA.

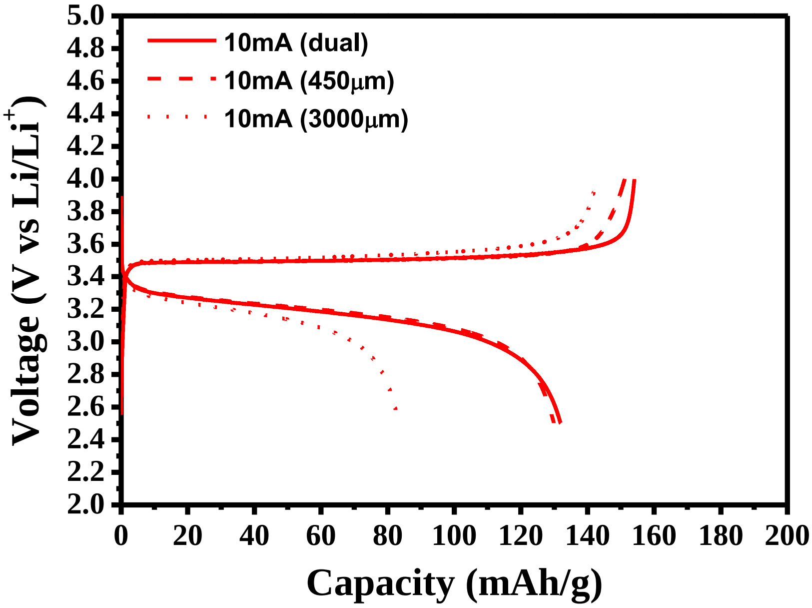

Figure 3.4.6 Comparison of the charge-discharge curves for specific capacity for the 450 μm and 3000 μm cell size metal foam cathode and Dual structure metal foam cathode at 10mA.

Figure 3.4.7 shows that the charge transfer resistance of Dual structure metal foam cathode is 14.22 Ω and the bulk resistance is 11.56 Ω. According to the Figure 3.4.7, it shows that diffusion of Li-ion of Dual structure metal foam cathode is a little less than 450 ㎛ cell size metal foam cathode, however, is higher than 3000 ㎛ cell size metal foam cathode.

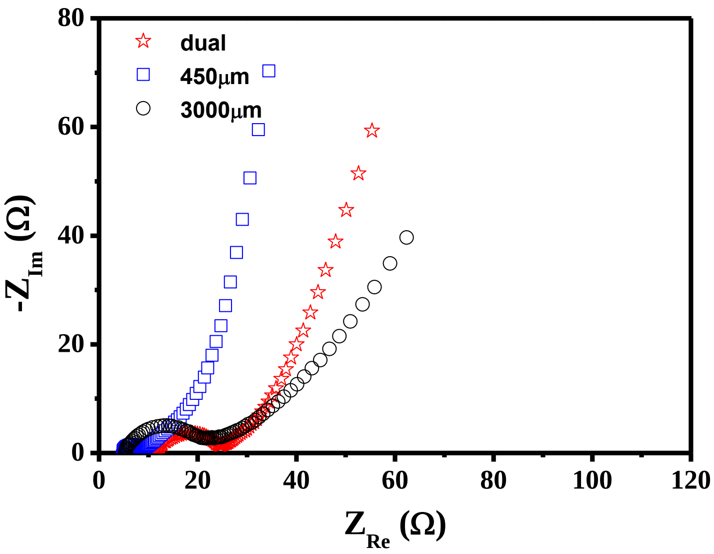

Figure 3.4.7 Comparison of the AC impedance curves for the 450 ㎛ and 3000 ㎛ cell size metal foam cathode and Dual structure metal foam cathode.

Figure 3.4.8 shows the CV curves for the 450 and 3000 μm cell size metal foam cathode and Dual structure metal foam cathode at scan rate of 0.1 mV s^{-1}. As shown in Figure 3.4.6, at 10 mA extra-high current density, the plateau curve is shifted from 2.9 V to 3.3 V. In this region, the reduction of Dual structure metal foam cathode occurs more easily than 3000 μm cell size metal foam cathode. The reduction specific current of position of peak of Dual structure metal foam cathode is -0.095 A g^{-1}, and it higher than 3000 μm cell size metal foam cathode. So the kinetic performance and the power performance of Sandwiched-A structure metal foam cathode is more superior than 3000 μm cell size metal foam cathode. For 450 μm cell size metal foam cathode, the amount of active materials in 450 μm cell size metal foam cathode is less than Dual structure metal foam cathode, so at the same current density discharge, current density of unit active material mass is higher than Dual structure metal foam cathode. It actually causes Dual structure metal foam cathode has the same superior power performance and kinetic performance as 450 μm cell size metal foam cathode when discharging at the same current density.

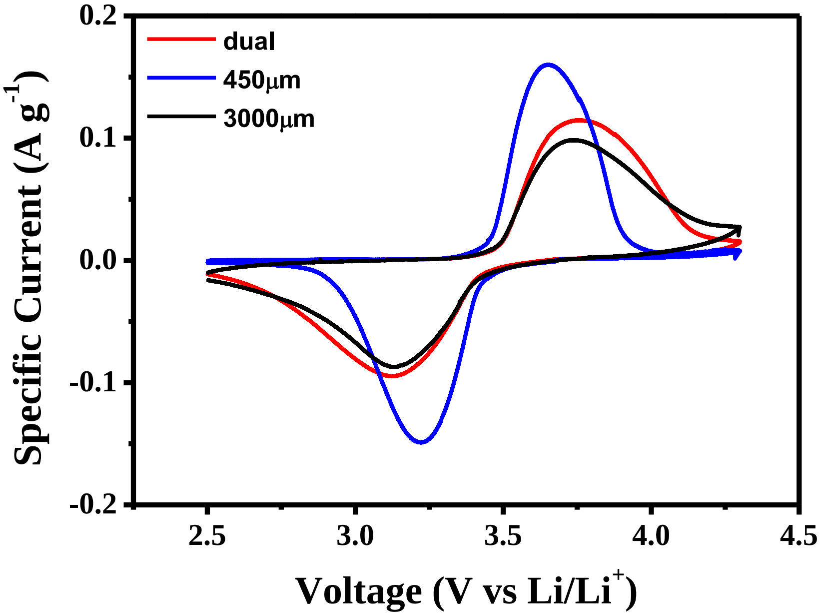

Figure 3.4.8 Comparison of the CV curves at 0.1mV s^{-1} for the 450 ㎛ and 3000 ㎛ cell size metal foam cathode and Dual structure metal foam cathode.

Chapter 4. Conclusions

The electrochemical performances are compared between 450 ㎛ and 3000 ㎛ cell size metal foam cathode. At the condition of same volume, the volumetric capacity of 3000 ㎛ cell size metal foam cathode is larger than 450 ㎛ and cell size metal foam cathode, and the proportion of reactiveness of active materials in 450 ㎛ and cell size metal foam cathode is much more than 3000 ㎛ cell size metal foam cathode at high current density discharge, because of more triple junctions in 450 ㎛ and cell size metal foam cathode. Additionally, the charge transfer resistance and mass transfer resistance of 450 ㎛ cell size metal foam cathode is much less than 3000 ㎛ cell size metal foam cathode and the specific current peak of reduction of 450 ㎛ cell size metal foam cathode is higher than 3000 ㎛ cell size metal foam cathode.

Considering the both advantages of 450 ㎛ and 3000 ㎛ cell size metal foam cathode, three kinds of metal foam cathodes are prepared by combined 450 ㎛ and 3000 ㎛ cell size metal foam cathode. Added 450 ㎛ cell size metal foam cathode to the side of 3000 ㎛ cell size metal foam cathode, it obviously shows with increasing current density of discharging the volumetric capacity of Sandwiched-A structure metal foam cathode decreases less than 3000 ㎛ cell size metal foam cathode, and it also has less mass transfer resistance, so the limitation of Sandwiched-A structure metal foam cathode is mass transfer limitation. For adding two 3000 μm cell size metal foam cathodes to the side of 450 μm cell size metal foam cathode, the volumetric capacity of Sandwiched-B structure metal foam cathode is larger than 450 μm cell size metal foam cathode due to more the amount of active materials in Sandwiched-B structure metal foam cathode. Dual structure has the same amount of active materials with Sandwiched-A structure metal foam cathode volumetric capacity of Dual structure metal foam cathode is much more than 450 μm and 3000 μm cell size metal foam cathode. And the proportion of reactiveness of Dual structure metal foam cathode is higher than 450 μm cell size metal foam cathode.

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국문초록

리튬이온전지를 위한 다양한 셀 사이즈 발포금속인 집전체의 설계

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지난 20 년 동안 리튬 이온 전지는 현대 전기 화학의 가장 인상적인 성공 사례로 간주 될 수 있다. 재충전 가능한 전지 중 리튬 이온 전지는 높은 에너지 밀도와 높은 전력 성능을 가지고 있기 때문에 휴대용, 엔터테인먼트, 컴퓨터 및 통신 장비의 주요 구성 요소이다. 그러나, 에너지 밀도 및 전기 화학적 성능은 더 많은 응용 분야에 대해 여전히 개선 되야 하는 것이다. 가장 중요한 문제점은 일반적으로 포일 형 집전체 위에 50 ~ 100 ㎛ 두께의 활물질이 있고, 고출력 성능을 유지하기 위해서는 활물질의 두께가 단지 20 ~ 60 ㎛ 밖에 되지 않는다는 것이다. 이러한 방식으로 대용량을 얻으려면 전지가 무겁고 커지게 된다. 이것은 분리 막, 집전체 등과 같은 반응에 참가하지 않은 물질들이 많기 때문이다. 또한, 적용의 큰 문제점 중 하나는 재료 및 작업량의 증가로 인해 높은 생산 원가가 발생한다. 이러한 문제를 해결하기 위해 본 연구에서는 포일 형 집전체 대신에 3 차원 구조의 금속 - 발포 금속을 사용 한다.

같은 부피의 조건에서 450 ㎛ 셀 크기의 발포금속과 3000 ㎛ 셀 크기의 발포금속을 사용하는 양극을 전기 화학적 성능에서 비교된다. 충전 - 방전 시험에 따르면, 순환 형 전압 전류 (CV) 분석 결과, 삼 중 교차점 (활물질, 금속 프레임 및 전해질의 접합부)으로 인해 450 μm 셀 크기의 발포금속 양극에서 더 좋은 성능이 얻어진다. 그러나 3000 ㎛ 발포금속 양극에 있는 활물질 양이 450 ㎛ 금속 발포 양극보다 많기 때문에 3000 ㎛ 발포금속 양극의 전극 밀도가 450 ㎛ 발포금속 양극보다 높다. 따라서 450 ㎛ 금속 발포 양극의 고성능과 3000 ㎛ 발포금속 양극의 고용량을 갖춘 양극이 필요한다.

두 종류의 발포금속의 양극이 준비되었다. 한 종류의 양극은 양 쪽에 있는 셀 크기와 가운데 있는 셀 크기가 서로 다른 샌드위치 모양으로 결합 된 발포금속의 양극이다. 측면 발포금속(300㎛ 두께)은 중간 금속 폼 (1000㎛ 두께)과 다르다. 그리고 다른 종류의 양극은 450 ㎛ 발포금속 양극 (600 ㎛ 두께)과 3000 ㎛ 발포금속 양극 (1000 ㎛ 두께)이 결합 된 듀얼 구조로 만든 양극이다. 중간 발포금속의 셀 크기가 450㎛인 샌드위치 구조 양극은 AC 임피던스 분석 결과 전하 이동 저항이 11.22Ω으로 다른 양극보다 작다. 그리고 특정 전류는 다른 양극보다 삼 중 교차점이 많기 때문에 다른 양극보다 높다. 충 방전 시험에 따르면 듀얼 구조 발포금속 양극의 효율은 다른 양극보다 높은 것으로 알고 있다. 듀얼 구조 발포금속 양극의 에너지 밀도는 중간 발포금속의 셀 크기가 450㎛ 인 샌드위치 구조 발포금속의 양극보다 높으며, 중간 발포금속 셀 크기가 3000㎛ 인 샌드위치 구조의 에너지 밀도와 동일하다. 듀얼 구조 발포금속의 양극은 충 방전 시험에 따라

높은 전류 밀도에서 450 ㎛ 발포금속 양극과 같은 우수한 고전력 성능이 나타냈다.

단위 부피에서 전력 성능 및 용량 성능을 고려할 때, 듀얼 구조 발포금속 양극은 리튬 이온 전지의 고전력 및 고용량 양극 구조에 대해 매우 유망하다. 3000 ㎛ 셀 크기의 발포금속 양극과 거의 동일한 에너지 밀도를 가질 뿐 만 아니라 450 ㎛ 셀 크기의 발포금속 양극과 같은 고전력 성능을 가지고 있다.

연구 결과에 따르면 듀얼 구조를 갖는 발포금속의 양극은 리튬 이온 전지의 고전력 및 고용량을 위한 유망한 집전체 중 하나이다.

주요어: 활물질이 발포금속에 채워진 양극, 리튬 이온 전지, 삼중 교차점, 전극 밀도, 집전체

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