Applications of MOFs-Derived Materials in Lithium-Ion Batteries and Sodium-Ion Batteries

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Abstract. Recently, the energy storage system is a popular and widely used system all over the world. It has 5 types of energy storage systems in this paper, and the major topic is the battery energy storage system, including lithium-ion battery (LIB) and sodium-ion battery (SIB). Metal-organic frameworks (MOFs) is widely used in many areas, such as battery design. Thus, for better understanding how MOFs-derived materials are synthesized and what area MOFs-derived materials does increase the performance of LIBs and SIBs, three materials are selected, including Co_3O_4 hollow dodecahedrons, $LiCoO_2$@C, and amorphous carbon nitride. Synthetic procedures of both MOFs and MOFs-derived materials are detailly discussed. The performance and development of these three materials is measured by comparing their cycle number, efficiency, and specific energy with traditional LIBs and SIBs. In the end, the capability of being a large power supply system is also evaluated by comparing it with the solid gravitational energy storage system, which has high power rating and energy capacity.

Keywords: metal-organic frameworks, lithium-ion battery, sodium-ion battery.

1. Introduction

Recently, the depletion of the fossil fuels including natural gas, gasoline, and coals and the rising concentration of the CO_2 are two major problems arisen and should be solved for the energy crisis. Sustainable energy comes in many forms, including solar, wind, and other energy sources. These sustainable energy sources could not output the energy continuously and without the fluctuations. Thus, the sustainable energy storage system is created to make sure the energy generated from the solar system and the nature could produce stable and continuous power. There are five different types of energy storage that can be distinguished: mechanical, thermal, electrical, chemical, and electrochemical [1]. In this paper, the sodium-ion battery (SIB) and Lithium-ion battery (LIB) of the electrochemical energy storage and the solid gravitational energy storage are discussed how to improve the energy storage capacity, efficiency, and output stability.

Recently, an innovative type of material known as metal-organic frameworks (MOFs) has found extensive application in medication delivery, catalysis, and gas separation and storage (including H_2, CO_2, CH_4, and so forth) [2]. The number and the kind of the MOFs continue increasing and surpass 20,000 types since 2013 [3]. The reason why MOFs could have these many types are their structures and chemical properties. The MOFs could have different structures when the synthetic precursor and the synthetic conditions are different [3]. Besides, the MOFs is constructed based on the metal-organic structures and synthesized into a cluster of molecules. It has hollow centre, which indicates that the MOFs has large surface area and porosity. Besides, the MOFs also has tunable structures. This property causes the MOFs that could be manufactured to different morphologies, such as thin films, pellets.

It is pliable, diverse, and porous for the MOFs to be a powerful material to apply in the energy storage system. Take the electrochemical energy storage as the example. The electrochemical energy storage is usually based on batteries, such as SIB and LIB. The battery consists of 2 electrodes (cathode and anode) and the electrolyte, which allows the ions and electrical blocks that could flow and complete the circuit [3]. These means the performance of the battery is majorly dependent on the quality and the performance of two electrodes and the electrolyte conductivity [3]. Thus, the MOFs

could be a potential material for both electrodes and the electrolyte based on its storage, porosity, and redox-active metal sites.

However, the pristine MOFs is prone to be an insulator and semiconductor. To make sure the MOFs could have conductivity; the MOFs should be tuned by using the redox-active conjugated guest molecules to obtain different extent of electrical conductivity. The MOFs used as the electrodes could have many types of morphologies. Thus, this paper will focus on the structure and synthetic mechanisms of the MOFs; how could the MOFs improve the performance of the electrochemical energy storage; and comparison of the performance among basic batteries, solid gravitational energy storage, and the MOFs based batteries.

2. Synthesis of MOFs and MOFs-derived materials

As mentioned above in the introduction, the MOF is currently manufactured in electrodes for the electrochemical batteries. Two types of MOF and three types of MOF-derived materials are selected to discuss how much performance they could improve by comparing with them with the traditional LIBs and SIBs. Here ZIF-67 and ZIF-8 are selected. In the applications, MOFs are typically the precursors and used to produce the MOF-derived materials, such as the $LiCoO_2$@C and Co_3O_4 hollow dodecahedrons based on ZIF-67 [4-6] and the amorphous carbon nitride based on ZIF-8 [4, 7, 8]. The $LiCoO_2$@C and Co_3O_4 hollow dodecahedrons are the cathode and anode for LIBs. The amorphous carbon nitride is the anode for SIBs. Before analyzing the improvement brought to the LIB and the SIB by MOFs and its derived materials, the synthesis procedures will be discussed.

2.1. Synthesis procedures for ZIF-67 and ZIF-8

All MOF-derived materials need to synthesize the MOF first as the precursor for synthesizing the final product. Thus, ZIF-67 and ZIF-8 should be synthesized first. As shown in Fig. 1, for ZIF-67 used for $LiCoO_2$@C, it is synthesized raw materials, including Co^{2+} and 2-methylimidazole (2-Mim), to ZIF-67 powders by the microwave-assisted methods [5]. For ZIF-67 used for Co_3O_4 hollow dodecahedrons, 2-Mim is mixed under the methanol reaction condition with the cobalt salt with continuous stirring in the room temperature [6]. ZIF-67 is formed and precipitated when the reaction mixture stops stirring and cools down in the ambient temperature for 24 hours [6]. With different reaction conditions, sizes of the ZIF-67 rhombic dodecahedrons are different. The average particle size for small-sized, middle-sized, and large-sized are 100 nm, 800 nm, and 2 μm [6].

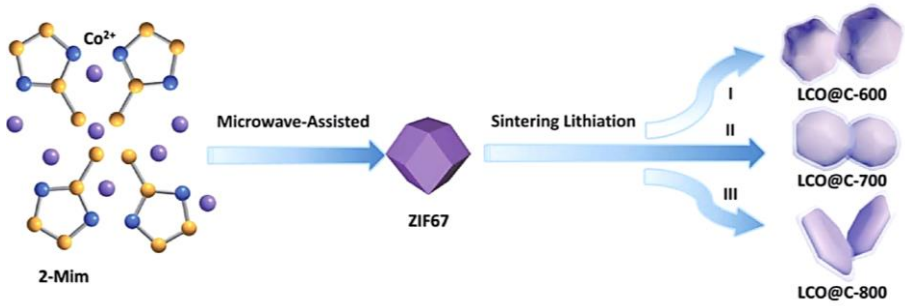

Fig. 1 Synthesis of ZIF-67 and LCO [5].

For ZIF-8 used for amorphous carbon nitride, the synthesizing mechanism is using the $Zn(NO_3)_2{\cdot}6H_2O$, 98% and 2-Mim [8]. Mix the reactants in the methanol solution with continuous stirring [8]. Place the solution at the room temperature for 24 h, and ZIF-8 product precipitates [8]. The reaction equation of the ZIF-8 is presented below [8]. There are several side-products during this reaction, including water, hydrogen ions, and nitrate ions.

2.2. Synthesis procedures for MOFs-derived materials

Different MOF-derived materials have different synthesis procedures for their own materials. As shown in Fig. 1, The general idea of the synthetic mechanism of $LiCoO_2$@C is to mix the lithium

carbonate with ZIF-67 powder to convert ZIF-67 nanopolyhedron into N-doped $LiCoO_2$ particles coated by carbon through sintering lithiation in high temperature and annealing in elevated-temperature solid-state method with nitrogen atmosphere [5]. To avoid the framework destruction and abrupt weight loss of the precursor ZIF-67 around 375 °C, the precursor ZIF-67 should be preheated to 400 °C, and then the reaction should be proceeded in the condition with full of nitrogen, to form $LiCoO_2$@C crystalline [5]. And the reaction temperature could influence the morphology of the $LiCoO_2$@C crystalline.

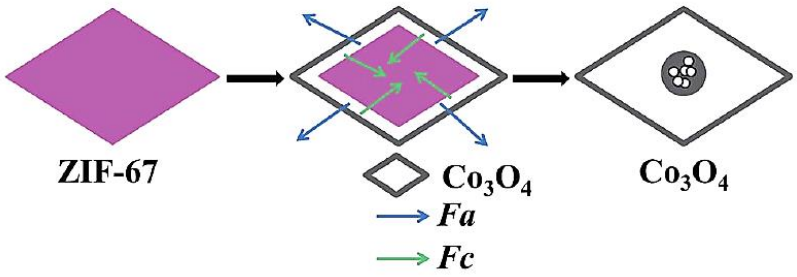

Fig. 2 Formation of ball-in-dodecahedron Co_3O_4 [6].

For the Co_3O_4 hollow dodecahedrons, there are two different synthetic mechanisms. One produces ball-in-dodecahedron Co_3O_4, and the other produces concave-dodecahedron Co_3O_4 [6]. The mechanism of this material is due to the self-decomposition by the adhesive force (Fa) and the contraction force (Fc) [6]. As shown in Fig. 2, the adhesive force, associated with the Co_3O_4 crystalline formation, has the opposite direction of the contraction force, which causes the structure of the ZIF-67 to collapse and shrink inside and form the ball-in-dodecahedron Co_3O_4 [6]. In a large void the ball-in-dodecahedrons Co3O4 form. To produce concave-dodecahedron Co_3O_4, the ZIF-67 should be decomposed under 500 °C in the nitrogen atmosphere for the protection, and then be annealed in the flowing air in 350 °C [6]. Steps are shown in Fig. 3.

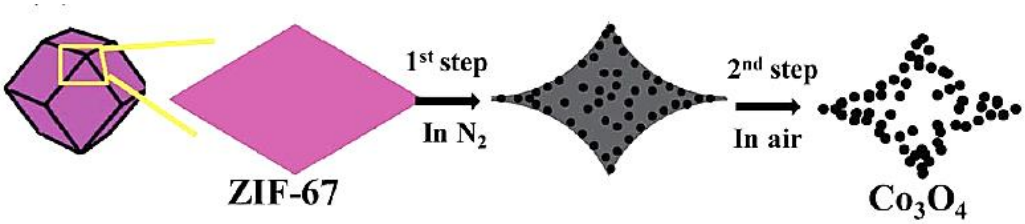

Fig. 3 Formation of concave-dodecahedron Co_3O_4 [6]

The synthesis of the amorphous carbon nitride is based on the ZIF-8 powders. ZIF-8 powder could be obtained by centrifuge the solution after the reaction, including zinc nitrate and 2-methylimidazole in methanol solution [7]. ZIF-8 should be washed by methanol for several times and dry out at 80 °C over night [7]. The final step is to directly heat ZIF-8 powders under the condition with full of nitrogen at certain temperature for 2 hours and the amorphous carbon nitride is formed [7].

3. Comparison among MOFs-derived and traditional LIBs and SIBs

To quantitatively evaluate the performance of MOFs-derived traditional LIBs and SIBs, there are several metrics selected for comparison, including cycle number, efficiency, capacity after cycles/reversible capacity, and specific energy [4, 9-11]. The cycle number determines the duration of the battery system. The efficiency determines how much energy of the battery could be output and used. The reversible capacity means that the available capacity in mAh/g could be utilized after the electrode is formed. This term could approximately equal to the capacity after cycles, if assume the electrode is properly formed after several cycles. The specific energy determines how much energy could be stored per mass. The reversible capacity could be transformed into the specific energy when the voltage of the battery is provided.

There is no general data of the traditional SIBs. Thus, the data of the sodium-sulfur battery and the $NaNiCl_2$ battery could be applied for comparison because they have similar working principles as the SIB, which utilize the sodium ion (Na^+) as the charge carrier. Besides, the efficiency of LIBS and SIBs could be considered as the Coulombic efficiency, which describes the capacity the battery could release. The Coulombic efficiency could be determined by using the charge capacity divided by the discharge capacity because all data show that the charge capacity is smaller than the discharge capacity and the Coulombic efficiency must be smaller than the 1.

Table 1. The metrics of MOFs-derived and traditional LIBs and SIBs [4-7, 9-11].

Type of Batteries	Cycle numbers	Efficiency (%)	Reversible capacity (mAh/g)	Specific energy (Wh/kg)
Co_3O_4 hollow dodecahedrons (LIBs' anodes)	140	62.4	1265	12.65-3795
$LiCoO_2$@C (LIBs' cathodes)	200	92.5	171.1	513.3-769.95
Amorphous Carbon Nitride (SIBs' anodes)	2000	67.2	175	70
Traditional LIBs	600-1200	65-88	N/A	75-200
Traditional SIBs	4500 (NaS), 1500-3000 ($NaNiCl_2$)	89 (NaS), 85-95 ($NaNiCl_2$)	N/A	100-240 (NaS)

Based on the Table 1, it shows that LIBs have large development in the specific energy. Both Co_3O_4 hollow dodecahedrons and $LiCoO_2$@C have higher specific energy than the traditional LIBs, even when the working voltage is relatively low, lower than 4.5 voltage. Co_3O_4 hollow dodecahedrons could have 19 times higher specific energy and $LiCoO_2$@C could have 3.8 times higher specific energy than traditional LIBs. The efficiency of Co_3O_4 hollow dodecahedrons is lower than traditional LIBs, but the $LiCoO_2$@C has higher efficiency. Although they have higher specific energy and relatively good efficiency, the cycle number is much smaller than traditional LIBs. Thus, in the future, some better electrodes should be developed to have high cycle numbers, high efficiency, and specific energy at the same time.

In addition, the amorphous carbon nitride does not have great performance compared to traditional SIBs. Only the cycle number is in the expected region. The other data are all lower than traditional SIBs' data. However, the low specific energy could attribute to the low operational voltage. 0.4 V is not a typical working voltage for most SIBs.

Overall, MOFs-derived LIBs have great performance and almost exceed the traditional LIBs in efficiency and specific energy. These 2 factors indicate that MOFs materials help LIBs could store more energy and release the energy more effectively and loss less energy during the discharge process. MOFs-derived SIBs should improve the specific energy and the working efficiency. However, MOFs-derived SIBs could not be drawn the conclusion that it must have lower performance than traditional SIBs because of the operational conditions. This type of material needs more research and be tested in diverse working operation conditions to determine the performance.

Table 2. The working voltage of MOFs-derived and traditional LIBs and SIBs [5-7].

MOFs-derived materials	Co_3O_4 hollow dodecahedrons (LIBs' anodes)	$LiCoO_2$@C (LIBs' cathodes)	Amorphous carbon nitride (SIBs' anodes)
Voltage (V)	0.01-3.0	3.0-4.5	0.4

4. Comparison among MOFs-derived LIBs and SIBs and solid gravitational energy storage system

Based on the Table 2, the working voltage is between 0.01-4.5 voltage. Compared with the normal power supply of the home use, around 220 V in China, this voltage is too small. The voltage around 5 V is used for smartphones, USB-powered devices, and other small electronic devices [12]. Thus, after evaluating the capability, development, and performance of the MOFs-derived LIBs and SIBs in small voltage supply, the application in high voltage or large power supply should also be evaluated. To better understand the potential of MOFs-derived LIBs and SIBs as a large power supply, the solid gravitational energy storage system could be selected for comparison because the power supply could be at least 1 MWh and up to 20 GWh [13]. For a better comparison, MOFs-derived LIBs with $LiCoO_2$@C will be selected because this technology has the best performance among 3 MOFs-derived LIBs and SIBs, including cycle number, specific energy, and efficiency.

The technology of the solid gravitational energy storage chosen for comparison is the Piston-based solid gravitational energy storage system (PSGES). This technology utilizes the piston and liquid medium to store the gravitational energy by changing the height of the piston. The energy is stored by driving the motor or pump to press the liquid from the bottom to elevate the piston and sealing the piston at a certain position to prevent the energy loss. The PSGES will also be evaluated based on the efficiency, lifetime (no cycles), and specific energy or energy density. The data are presented in Table 3.

Table 3. the metrics of $LiCoO_2$@C and PSGES [1, 9, 11, 13, 14].

Type of Batteries	Cycle numbers or lifetime	Efficiency (%)	Specific energy (Wh/L)	Power Rating
$LiCoO_2$ @C (LIBs' cathodes)	200, 14-16 years (Li-ion)	92.5	150-200 ($LiCoO_2$)	0.1-50 MW (Li-ion)
PSGES	40-60 years	75-80	0.2-3.1 (GES)	40-1600 MW

$LiCoO_2$@C technology has advantages in efficiency and specific energy but does not have good performance in lifetime and power rating. To carefully determine the capability of the $LiCoO_2$@C as a large power supply, the Pugh method is good choice. Table 4 presents the criteria for the evaluation of the $LiCoO_2$@C as a large power supply.

Table 4. The metrics of $LiCoO_2$@C and PSGES.

Criteria	Importance Weight	$LiCoO_2$@C	PSGES
Cycle numbers or lifetime (years)	3	-1	1
Efficiency	3	0	0
Specific energy	1	1	-1
Power Rating	4	-1	1
Total	-	-6	6

The energy storage system won't be able to supply energy to the entire region if the power rating is too low, so it has the highest weight of importance. The lifetime should be long enough because the energy storage system could be considered as the infrastructure device. It will cost too much for replacement and may cause energy shortages once it fails. The efficiency is also important as the lifetime. Higher the efficiency, more energy could be used, and less energy could be dispersed. The specific energy is not important once the facility is large enough if the cost of the facility is ignored.

As shown in Table 4, the $LiCoO_2$@C is not capable to be a large power station. Although it has high efficiency and specific energy, the lifetime and the power rating are relatively low to be a power station for large use. If MOFs-derived LIBs and SIBs want to develop in the large power supply area, the lifetime and power rating must be increased.

5. Conclusion

As synthesis procedures of these electrodes of MOFs-derived LIBs and SIBs shows, it is relatively easy to manufacture MOFs-derived LIBs and SIBs in a large amount. Besides, compared with the traditional LIBs and SIBs, MOFs-derived LIBs, such as $LiCoO_2$@C and Co_3O_4 dodecahedrons, almost exceed and have better performance, especially $LiCoO_2$@C technology. However, MOFs-derived SIBs (amorphous carbon nitride) do not have the same achievement as the $LiCoO_2$@C. For both MOFs-derived SIBs and LIBs, it should continue to develop to increase the cycle number, lifetime, and specific energy in low voltage working conditions. If MOFs-derived LIBs and SIBs want to apply in the large power supply, the power rating and lifetime should be significantly increased, or the cost of the infrastructure will be too large to be accepted. All things considered, the MOFs greatly advances the development of the battery energy storage system and improves system performance.

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