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Synthesis, characterization and electrochemical performance analysis of nanomaterials for high capacity lithium batteries

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The synthesis and electrochemical characteristics of nanomaterials for high-capacity lithium batteries are analyzed. α-CuV_2O_6 nanowires were obtained by the hydrothermal method. The mechanism of lithium intercalation and the electrochemical characteristics of α-CuV_2O_6 nanomaterials have been studied. The results show that α-CuV_2O_6 nanomaterials have the advantages of large surface area and short path of solid-state diffusion of lithium ions, which can greatly improve the electrochemical performance. At a current density of 20 mA/g, the specific discharge capacity of α-CuV_2O_6 nanomaterials can reach 514 mAh/g, and the apparent activation ability of the TV output reaction can reach 39.3 kJ/mol, which is much better than that of submicron wires and micron rods with particles of α-CuV_2O_6 nanomaterials. Therefore, α-CuV_2O_6 nanomaterials exhibit more efficient electrochemical performance in lithium primary batteries and have great development prospects.

Keywords: new energy vehicles, high capacity lithium battery, synthesis and characterization of nano-materials, electrochemical performance.

Синтез та аналіз електрохімічних характеристик наноматеріалів для літієвих акумуляторів великої ємності. *Zhaona Lu, Yang Wang, Junlong Wang, Chuanxing Wang*

Проаналізовано синтез та електрохімічні характеристики наноматеріалів для літієвих батарей великої ємності. Гідротермальним методом були отримані нанодроти α-CuV_2O_6. Досліджено механізм інтеркаляції літію та електрохімічні характеристики наноматеріалів α-CuV_2O_6. Результати показують, що наноматеріали α-CuV_2O_6 мають переваги великої площі поверхні та короткого шляху твердофазної дифузії іонів літію, що може значно покращити електрохімічні характеристики. При щільності струму 20 мА/г питома розрядна ємність наноматеріалів α-CuV_2O_6 може досягати 514 мА·ч/г, а активна здатність TV-вихідної реакції може досягати 39,3 кДж/моль, що значно краще, ніж у субмікронних проводів і мікронних стрижнів з частинками наноматеріалів α-CuV_2O_6. Отже, наноматеріали α-CuV_2O_6 демонструють ефективніші електрохімічні характеристики в літієвих первинних батареях і мають більші перспективи розвитку.

1. Introduction

In order to cope with the energy crisis and environmental pollution, countries all over the world vigorously develop new energy-saving vehicles [1]. As a new energy source, lithium batteries have the advantages of high energy, high working voltage, high specific power, long cycle life and wide service temperature, and are widely used in

Table 1. Performance comparison of different batteries

Project	Lithium battery	NiMH batteries	Nichrome batteries
Operating voltage, V	3.6	1.3	1.3
Weight specific energy, Wh/kg	100 ~ 150	75	60
Volume specific energy, Wh/L	300	200	2000
Charge and discharge life (times)	500 ~ 800 [9]	300 ~ 600	300 ~ 500
Self-discharge rate, %	6 ~ 10	20 ~ 50	10 ~ 40
Battery capacity	high	high	low
High temperature performance	Good	normal	normal
Low temperature performance	Bad	normal	normal
Battery safety	Charge and discharge protection function	Charging protection [10]	Charging protection

new energy sources. However, lithium batteries currently use carbon anode materials [2], which have the disadvantage of low specific capacity. When working at high rate, lithium crystals are prone to precipitate, which seriously threatens the safety of lithium batteries [3]. Therefore, the development of new non-carbon anode materials such as silicon is the hot spot and the main direction of lithium battery research at present. The traditional electrode materials in lithium batteries have some problems, such as low utilization, slow diffusion of lithium ions and large polarization, which restrict the performance of lithium batteries. The properties of electrode materials are related to the methods of their preparation, composition and structure of nano-layers [4], and electrochemical properties. Therefore, the use of nano-materials with high reactivity, high specific surface area and unique structure can obtain excellent electrochemical performance, which is currently an important way to improve lithium batteries. In this paper, the synthesis and electrochemistry of α-CuV_2O_6 nanomaterials are analyzed in order to find ways to improve the performance of lithium batteries.

2. Description of lithium batteries

2.1 Brief introduction to lithium batteries

Lithium battery is a high-performance battery [5], in which Li^+ is embedded and removed from positive and negative materials to complete charging and discharging. Their positive electrode accepts a redox reaction and has a high potential. The transition metal oxides of lithium battery are $LiCoO_2$, $LiNIO_2$ and $LiFePO_4$, etc. The anode materials are closer to the lithium potential [6], such as graphite, silicon and tin. The electrolyte generally uses organic solvents that dissolve lithium salts, such as $LiClO_4$ and $LiPF_6$ [7]. Organic solvents such as propylene carbonate and vinyl carbonate are commonly used. Porous polyolefin resin, single-layer or multi-layer polyethylene are used as separators in lithium batteries [8]. With $LiCoO_2$ as the positive electrode and layered graphite as the negative electrode, the chemical reaction process between the electrode and the battery is shown in formulas (1), (2) and (3).

Positive reaction:

$$LiCoO_2 \underset{discharge}{\overset{charge}{\rightleftarrows}} Li_{1-x}CoO_2 + xLi^+. \quad (1)$$

Negative reaction:

$$C + xLi^+ + xe^- \underset{discharge}{\overset{charge}{\rightleftarrows}} Li_xC. \quad (2)$$

Battery reaction:

$$LiCoO_2 + C \underset{discharge}{\overset{charge}{\rightleftarrows}} Li_{1-x}CoO_2 + CLi^+. \quad (3)$$

Lithium batteries have better performance than nickel-metal hydride and nickel-chromium batteries, and the specific results are shown in Table 1.

Lithium battery is significantly superior to Ni–MH and Ni–Cd batteries in performance, with higher working voltage, higher specific power, longer cycle life and wider working temperature range. At present, lithium batteries are comprehensive batteries and are widely used in new energy vehicles. At the same time, the continuous improvement of new energy vehicle technology and the increasing market demand are open-

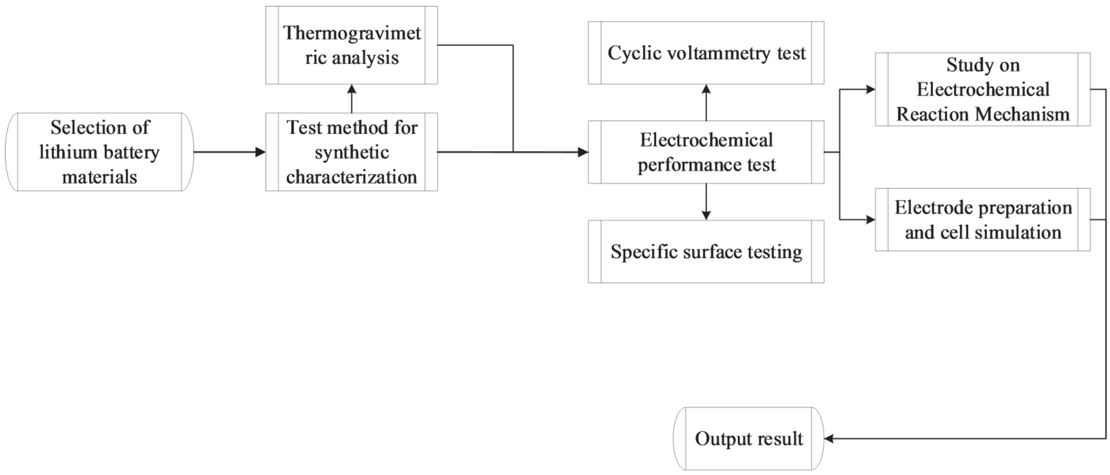

Fig. 1. Test flow of nano-materials for lithium battery.

ing opportunities for the development of lithium batteries.

2.2 Key electrode materials for lithium batteries

A large number of studies have shown that the energy density and cycle life of lithium battery electrode materials are related to the surface area, size and crystallization degree of the materials. Traditional lithium batteries mainly use short-term reactions or ions to propagate electrons through surface diffusion. It is difficult for traditional materials to enter the core of lithium battery [11], which leads to a low utilization rate of activators and limits the capacity and discharge performance of the battery. Nano-materials have a high reactivity and a short ion diffusion path, which allows full use of the physical and chemical properties of electrode materials. Therefore, developing the concept of lithium storage is an important direction and content of lithium battery development. Theoretically, $LiCoO_2$ nanotubes should be used as the positive electrode of the lithium battery, and the specific discharge capacity of this material can reach 185 mAh/g. After 100 times of discharge, its specific discharge capacity is still above 80 % [12]. For another example, CuV_2O_6 has a good reversible lithium deintercalation energy, and the discharge capacity can reach 285 Ah/g at 15 mA/g. Among the anode materials, CuV_2O_6, MO, Co_3O_4 and Fe_3O_4 nanotubes are beneficial to reduce the turn-on resistance of particles [13], which makes the lithium battery have higher discharge capacity and excellent cycle performance. Therefore, nanomaterials have a large proportion of atoms on the surface and interface of bulk materials; and their reactivity is relatively high. Moreover, the materials have a small particle size and a short diffusion path, which ensures good kinetic properties of electrodes in batteries [14]. Under the same external current, nano-materials can reduce the real current density and reduce the polarization phenomenon during the electrochemical process at battery electrodes. At the same time, nano-materials can provide more space for intercalation/detachment, and improve the capacity and energy density of lithium batteries.

2.3 Synthesis, characterization and electrochemical performance test methods

The principle of synthesis. Nanometer controllable equipment is the key to study the structure and activity, and it is the basis for further studying the potential of synthetic materials [15, 16]. The preparation methods of nano-materials include physical method, chemical method and other methods. Under certain limitations, the chemical method makes it possible to measure the properties of the gas phase, the solid phase, the thermodynamic and kinetic characteristics of nanomaterials, and to ensure the controlled growth of nanomaterials. Through hydrothermal and solvothermal reactions, the chemical method can realize operability and adjustable denaturation of nanomaterials, and better understand the properties of nano-materials.

Characterization methods. The main characterization methods of nano-materials are scanning electron microscopy, transmission electron microscopy, X-ray energy spectroscopy, X-ray photoelectron spectroscopy, specific surface area measurements and thermogravimetric analysis.

Electrochemical performance test method. The electrochemical performance test

Table 2. Chemical structure and morphology of products under experimental conditions

Time	Concentration, mol/L	Shape	Chemical structure
0	0.06	grain	$Cu_3(OH)\ 2V_2O_7{\cdot}2H_2O$
1	0.06	Granules, monolithics	$Cu_3(OH)\ 2V_2O_7{\cdot}2H_2O$
3	0.06	Split tablets	$CuV_2O_6\ Cu_3(OH)\ 2V_2O_7{\cdot}2H_2O$
4	0.06	Separate lines	$CuV_2O_6\ Cu_3(OH)\ 2V_2O_7{\cdot}2H_2O$
6	0.06	Nanowires	CuV_2O_6
12	0.06	Nanowires	CuV_2O_6
12	0.03	Sub-nanowires	CuV_2O_6
12	0.1	Submicro-nanowires	CuV_2O_6
12	0.15	Micron wire rods	CuV_2O_6

method realizes cyclic voltammetry testing, constant current charge and discharge testing and AC impedance testing by preparing electrodes and simulating battery assembly.

3. Synthesis, characterization and electrochemical properties of α-CuV_2O_6

3.1 the Synthesis of α-CuV_2O_6

α-CuV_2O_6 has the advantages of high specific discharge capacity and electrochemical stability due to its unique self-passivation characteristics. Therefore, the higher the proportion of α-CuV_2O_6, the more stable the charging and discharging of lithium batteries, and the more power they provide for new energy vehicles. In addition, the preparation stability of α-CuV_2O_6 is low and its own stability is high, and its preparation process is an important part of the rationality of lithium battery nanomaterials. The high capacity lithium battery prepared in this paper is based on α-CuV_2O_6 to realize the innovation of the nano-battery preparation. 8 ml (0.06 mol/L) $CuCL_2$ solution was prepared at 20°C. At the same time, 8 ml (0.12 mol/L) NH_4VO_3 solution was prepared at 80°C. After the solutions were cooled, NH_4VO_3 was injected into the $CuCL_2$ solution, and stirred continuously until yellow precipitation appeared. The suspension was transferred to a 25 ml PVC reactor, lowered to 21°C and heated for 12 hours. After the reaction was completed, the reaction solution was cooled to room temperature, washed with deionized water and absolute ethanol for 4 times, and dried in vacuum at 60°C for 4 hours to finally obtain α-CuV_2O_6 nanowires. Among them, sub-nanowires and micro-nanowires were obtained by changing the concentration of reactants, and the growth mechanism of nanowires was studied by continuously observing the shape and structure of reactants. The specific results are shown in Table 2.

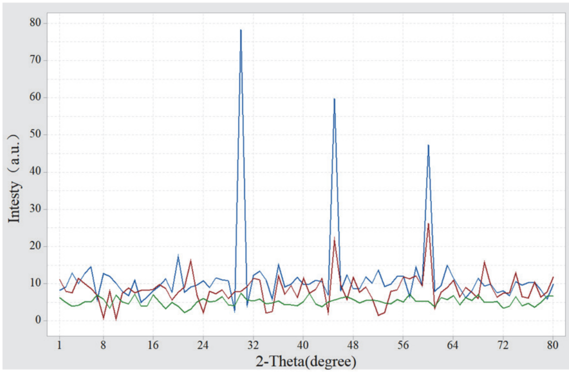

Fig. 2. XRD and Rietveld retouched maps.

3.2 Characterization of αCuV_2O_6

The α-CuV_2O_6 samples were characterized with XRD and the results are shown in Fig. 2.

As can be seen from Fig. 2, the α-CuV_2O_6 samples can be obtained by reaction at the solution concentration of 0.06 mol/L and 210°C temperature for 12 hours. The XRD spectra of α-CuV_2O_6 samples show that all diffraction peaks belong to triclinic α-CuV_2O_6, which is consistent with the peak position in the standard card (No.30-0513), and there is no impurity. Therefore, the concentration of samples is high. After Rietveld full spectrum fitting, it was found that the peak position and peak intensity of α-CuV_2O_6 were consistent with the measured results (fitted degree = 1.126, reliability = 87.5 %). The unit cell parameters of α-CuV_2O_6 (a = 9.12, b = 3.52, c = 6.52, d = 7.25, e = 11.45, f = 5.23) were basically consistent with the standard values of α-CuV_2O_6 (a = 9.13, b = 3.51, c = 6.53, d = 7.24, e = 11.46, f = 5.21). The intensity of

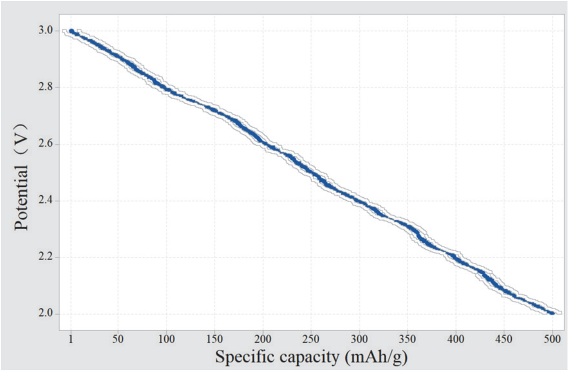

Fig. 3. Changes of the α-CuV_2O_6 constant current discharge curve.

the diffraction peaks is high, and the sharp peaks indicate that the α-CuV_2O_6 product has good crystallinity.

3.3 Electrochemistry of αCuV_2O_6

The characterization of αCuV_2O_6 was tested, and the test results are shown in Fig. 3.

Stability is an important performance parameter for lithium batteries. When α-CuV_2O_6 was stored at 37°C for two months, the constant current discharge test was carried out at 20 mA/g current density, and it was found that the discharge capacity actually reached 510 mAh/g, and the initial discharge capacity reached over 90 %, which indicated that α-CuV_2O_6 nanowires had strong chemical stability and could be stored for a long time. The α-CuV_2O_6 nanowires were compared with other samples, and the results are shown in Table 3.

According to the data of Table 3, the discharge capacity of α-CuV_2O_6 nanowires can reach 520 mA/g. Compared to other materials, the discharge capacity of α-CuV_2O_6 submicron nanowires and micron rods was 450 mA/g and 410 mA/g, respectively; it is greater than the discharge capacity of bulk particles. At the same time, the results show that the discharge capacity ofα-CuV_2O_6 nanowires increases with the decrease in the structure size. When the discharge capacity is greater than 40 mA/g and 80 mA/g, the discharge capacity of α-CuV_2O_6 nanowires can reach 326 mA/g and 234 mA/g of bulk nanowires. Compared with bulk nanowires, linear nanowires have higher electric storage performance and higher discharge performance.

Table 3. Electrochemistry of different samples

Sample	Current density, mA/g	Specific capacity, mAh/g
Nanowires	20	520
	60	460
	80	350
Submicron nanowires	20	450
Micron rods	20	410
Lumpy granules	20	326
	60	234
CuV_2O_6	40	320
	40	340
$Ag_2V_4O_{11}$	32	270

4. Conclusion

$CuCl_2$ and NH_4VO_3 are used as raw materials to prepare α-CuV_2O_6. The method has the advantages of low synthesis temperature, high product purity, uniform particle diameter and easy chemical dosage. It is relatively easy to add any template and surfactant throughout the reaction process. The structure and morphology of α-CuV_2O_6 are relatively good at different reaction time; and different product diameters can be obtained by adjusting the concentration of reactants, thus realizing the controllability of material preparation. Electrochemical performance test shows that, the size and model significantly affect electrochemical properties, and the discharge specific capacity and high rate performance of the "rice noodle" are significantly better than those of sub-nanowires and micron rods. XRD results show that the multi-step reduction reaction occurs in the process of lithium intercalation; the crystallinity of reactants is good, and the discharge performance and electric storage performance meet the requirements of high-capacity batteries for new energy vehicles.

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