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Mini Review

Copper Based Materials as Anode and Cathode Materials for Lithium Ion Batteries

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With the increasing demands on energy density and power capacity of lithium ion secondary batteries, people begin to look for electrode materials with better capacity and performance. Copper based materials have been considered as ideal additives to improve the electrochemical properties of lithium ion batteries due to their unique nanostructures, high conductivity and thermal conductivity. The applications of copper-based nanomaterials in electrode materials are reviewed. This article discuss the physical, transport and electrochemical behavior of copper-based nanocomposites. This article also discuss the challenges faced by the applications of copper-based nanocomposites and their future development prospects.

Keywords: Lithium ion battery; Copper based materials; Nanocomposite; Anode; Cathode

1. INTRODUCTION

Natural fossil fuels such as oil, coal and natural gas are the most important energy sources for human survival and production. However, with the rapid development of modern industry and the rapid increase in population, an increasing amount of some traditional non-renewable energy are constantly being consumed; thus, fossil fuels are facing a serious exhaustion problem. Fossil fuels are widely used because they provide high-energy chemical energy, which is convenient for storage and transportation [1–5]. Chemical energy can be easily converted into heat energy by burning fossil fuels, but in the process of combustion, fossil fuels will produce greenhouse gases and smoke, which will be discharged into the air to pollute the environment. This will affect not only human health but also the ecological balance. In addition, fossil fuels are found only in some countries, due to their uneven distribution. Countries with low fossil fuel reserves often need to import them to satisfy energy needs. This is not conducive to a country's long-term development and social stability. Therefore, based on the increasing energy demand, rising fossil fuel consumption, and sharply increasing production of greenhouse gases, along with the consideration of social long-term stability, it is urgent to develop new energy storage and conversion technology to obtain clean energy and renewable energy while reasonably developing and utilizing existing energy [6–21]. Among the various kinds of energy storage and conversion technologies, electrochemical storage and conversion are considered to be one of the most promising and valuable technologies. For this reason, researchers invented a storage device for converting chemical energy into electric energy, and a battery was produced. With the development of electronic technology, all kinds of electronic products are becoming smaller and lighter, which puts forward certain requirements for the energy storage power supply used in electronic products [22–31]. Therefore, research on lithium battery technology is advancing with the development of science and technology. Lithium-ion batteries have some desired characteristics, such as high energy density and long cycling life, which have great industrial application value. Compared with other traditional batteries (Table 1), lithium-ion batteries have great advantages and high research value.

Table 1. The performance comparison of lithium ion battery and other conventional batteries.

	Lead Acid Battery,	Nickel Cadmium Battery	Nickel Hydrogen Battery	Lithium Ion Battery
mass energy density (Wh/kg)	30-50	45-48	60-120	110-160
Bulk energy density (Wh/L)	80	150	200	270
Unit rated voltage (V)3.6	2.0	1.25	1.25	3.6
Cycle life (80%)	200-300	1500	300-500	500-2000
Monthly self discharge rate (%)	5	25-30	30-50	6-12
Charging time (h)	12	8	8	3
Impact on the environment				

Lithium-ion batteries are composed of a series of electrochemical components, mainly polymer membranes, positive electrodes, negative electrodes and organic electrolytes with dissolved lithium salt. Considering that liquid electrolytes easily leak and can be unsafe, researchers have studied the utilization of solid electrolytes [32–34]. Compared with liquid electrolytes, solid polymer lithium-ion batteries are easier to make into various shapes, such as buttons, cylinders and squares. The function of the electrolyte and separator is to act as the ion conductor of lithium ions and the insulator of electrons in the process of charge and discharge. For lithium-ion batteries, the performance of each component will affect the electrochemical performance of lithium-ion batteries [35–42]. Therefore, the core components of a lithium-ion battery, namely, the positive and negative electrodes and their material composition, have become a major focus of current research [43–48].

Lithium-ion batteries are secondary batteries. An original lithium battery refers to a primary battery, also known as a lithium primary battery [49–52]. The lithium primary battery has been widely used in some small electronic products, such as commonly used calculators and cameras, due to its advantages of high energy density, high working voltage and wide working temperature range; however, their further development is limited due to the existence of the following problems [53–57]. First, the positive material of the lithium primary battery is ferox or thionyl chloride, and lithium is used as the negative material. When the battery is assembled, there is a voltage difference between the positive and negative poles, so it does not need to be charged. If this kind of battery is charged after use, the uneven surface of lithium makes the surface voltage distribution uneven. When it is charged and discharged many times, lithium will deposit unevenly on its surface, and some of the lithium will deposit too fast, thus easily forming internal dendrites on the surface of the lithium anode [58–62]. With continuous charging and discharging, an increasing number of lithium dendrites will pierce the electronic insulating diaphragm between the positive and negative electrodes, which will cause an internal short circuit of the battery. The short circuit generates an instantaneously strong current, which releases a considerable amount of heat and may even cause an explosion. Therefore, in general, lithium primary batteries are not allowed to be charged.

In addition, because lithium metal is very active, it easily reacts with electrolytes, resulting in high pressure and serious danger [63]. In view of these problems with lithium primary batteries, scientists performed considerable research until the concept of "electrochemical embedding" was proposed. This theory has been the key to the success of lithium-ion batteries. After that, with the continuous efforts of research and technological progress, the performance of the lithium-ion battery has been constantly improving. At present, due to its unique performance, lithium-ion batteries have been widely used in some small and portable electronic products. Compared with a traditional lead-acid battery, nickel cadmium battery or nickel hydrogen battery, a rechargeable lithium-ion battery is a potential energy storage device for electric vehicles due to its high mass energy density, volume energy density and long cycling life.

2. OVERVIEW OF Cu-BASED ANODE AND CATHODE MATERIALS

In lithium-ion batteries, the choice of cathode materials determines to a certain extent the level of electrochemical performance [64]. At present, a wide range of research work has been carried out on cathode materials for lithium-ion batteries. In general, cathode materials of lithium-ion batteries should have some basic characteristics [65–67]. The Gibbs free energy of the reaction between the cathode material and lithium should be large so that there is a large potential difference between the positive and negative electrodes; thus, the output voltage of the battery can be high. The charge discharge voltage curve of the material is flat to ensure the stability of the output voltage. In a lithium-ion battery, the cathode material itself needs to have high electronic conductivity and lithium-ion conductivity, which can reduce electrode polarization and internal resistance of the battery [68–70]. Thus, when a battery is charged and discharged with high current, the voltage drop is reduced, and the irreversible capacity loss when the battery is working is reduced. The material should have a large transport tunnel, large interfacial structure and large specific surface area to increase the amount of space for embedding lithium and improve the lithium capacity of the material. The mobility coefficient and diffusion coefficient of lithium ions should be large enough to improve the maximum working current and ensure good reversibility and cycling performance of lithium-ion batteries. Electrode materials should have low solubility in electrolyte solution and good chemical stability to ensure the structural stability of the electrode. Materials and electrolytes should have good thermal stability to ensure the safety of lithium-ion batteries [71–73].

The energy density of lithium-ion batteries depends on the specific capacity of the battery and the working voltage between the positive and negative poles. At present, commercial lithium-ion batteries still cannot meet the needs of high energy density batteries for new electronic equipment and electric vehicles. For this reason, many researchers have developed high-capacity anode materials for lithium-ion batteries, such as titanium and silicon, along with tin oxides, tin alloys and transition metal oxides. They hope to develop anode materials that are different to traditional carbon materials [74–77]. In the past few decades, great efforts have been devoted to the exploration of high capacity anode materials, and the research on materials has expanded from traditional graphite to multi non-carbon anode materials such as alloys and metal oxides [78–81]. An anode material of lithium-ion batteries generally needs to meet some characteristics. The redox potential should be low, as close as possible to the lithium metal, so that there is a large voltage difference between the positive and negative poles, and the battery has a high output voltage. The structure should be stable. In the process of charging and discharging, the repeated insertion and release of lithium ions should not cause serious collapse of the structure. For instance, a large number of electrode materials tend to fall off, and the capacity decline can be serious. The anode material should be beneficial to the reversible insertion and removal of lithium ions, which will provide the battery good reversibility and cycling performance. The material should not only ensure a stable output voltage but also have good electronic conductivity [82–84].

In the past few decades, copper-based transition metal oxides have been widely studied because of their high theoretical specific capacity. There are two common copper oxides, cuprous oxide (Cu_2O) and copper oxide (CuO). All of them are p-type semiconductor materials, which have become potential anode materials for lithium batteries due to their high theoretical specific capacity (372 mAh/g and 674 mAh/g, respectively), nontoxicity, low price, good chemical stability and environmental friendliness [85–87]. However, it has been found that the main problems of copper oxide used as cathode materials are as follows: (1) during a long electrochemical cycle, there is serious capacity decay and (2) the chemical reaction kinetics are poor. The above problems for CuO are mainly due to its low conductivity and large volume change in the charging and discharging process, resulting in serious powdering of the electrode materials; furthermore, some of the material may fall off into the electrolyte. Moreover, the resulting metallic nanoparticles agglomerate to form large particles and lose their original reaction activity, thus resulting in a rapid decline of battery capacity and poor cycling performance [88–92].

At present, there are two typical solutions to the problems of utilizing copper oxide as an anode material of lithium batteries. An effective method is to construct nanosized copper oxides with different morphologies. Currently, various kinds of nanosized copper oxides, including nanosheets, nanospheres, nanotubes, and nanowires have been successfully synthesized, and the anode performance has been improved. Wang et al. [93] synthesized three kinds of copper oxide nanomaterials with different morphologies, namely, flower, thorn and ball, by simple and common methods. The results show that compared with the other two morphologies, copper oxide nanospheres show excellent cycling performance and magnification performance. Thus, it was found that the morphology of the material directly affects the electrochemical performance of lithium batteries. Another method is to select carbon, metal and conductive polymers to modify nanoactive materials to form nanocomposite materials and make full use of the structure and electronic activity of each component to provide an improved electrochemical performance in lithium batteries [94–98].

Many studies have shown that carbon-modified metal oxides are an effective way to improve the electrochemical performance and rate performance of lithium-ion batteries. The introduction of carbon can not only improve the conductivity of the electrode but also inhibit the agglomeration and pulverization of electrochemically active nanomaterials to improve their cycling performance. Huang et al. [99] prepared CuO/C nanocomposites with $CuCl_2$ as the copper source and formaldehyde and resorcinol as the carbon source; the results show that the specific capacities of the CuO/C nanospheres are 470 mAh/g and 440 mAh/g, respectively, after 50 cycles at a current density of 100 mA/g. Furthermore, the capacity retention was 80%. Compared with the original CuO (300 mAh/g), the capacity was significantly improved. Xiang et al. [100] prepared a blade-like CuO/MWCNT composite by a precipitation method. The copper oxide nanoblade was effectively connected by multiwalled carbon nanotubes to modify it. Compared with the original CuO, the capacity was significantly improved. Under a current density of 60 mA/g, the specific discharge capacity remained at 627 mAh/g after 50 cycles. The increase in the capacity can be explained by the improvement of the conductivity between the copper oxide particles, the active material and the collector; the mobility of lithium ions; the effective contact between the electrode material and the electrolyte; and the buffer effect during the volume change that occurs in the charging and discharging process.

The above studies have also laid a theoretical foundation for the research of copper-based lithium-ion battery cathode materials. Copper sulfide (Cu_xS) has been widely used in sensors, optoelectronic devices and solar cells and is expected to become the cathode material of the next generation of high-performance lithium-ion batteries. Cu_xS mainly includes CuS and Cu_2S, which have a high theoretical specific capacity (CuS 560 mAh/g, Cu_2S 337 mAh/g) as the positive material of lithium-ion batteries. However, the polysulfide formed during the charge and discharge process easily dissolves in an organic electrolyte, and the capacity seriously decays in the process of cycling [101]. The electrochemical performance of Cu_xS is greatly affected by the shape and size of the material, so researchers have made some efforts in this regard. However, there are few studies in this field, and a considerable amount of effective work still needs to be done. Without any surfactant or template, a new type of spherical CuS multipolar structure material has been prepared in a stainless steel autoclave with $CuCl_2{\cdot}6H_2O$ and S as raw materials and ethanol as the solvent. The morphology of the material was greatly affected by the amount of $CuCl_2{\cdot}6H_2O$, the reaction temperature and the reaction time. The electrochemical performance test showed that the first discharge capacity was 582 mAh/g, the charge capacity was 350 mAh/g, and the efficiency was 60%. However, the cycling performance of the material was poor, and the capacity retention rate after 10 cycles was only 13.8%. This was mainly due to the dissolution of intermediate products and the structural destruction of the electrode material at low potential. The capacity retention rate could be improved by controlling the minimum discharge voltage and using an appropriate electrolyte composition. A kind of CuS composite was prepared in situ by Wang et al. [102] The prepared CuS electrode was a three-dimensional network structure composed of a large number of nanochips. The results showed that the reversible capacity of the DME/DOL (2:1, v:v) electrolyte with 1 M $LiClO_4$ was 447.4, 414.1, 389.9 and 376.0 mAh/g at 0.2C, 0.5C, 1C and 2C, respectively.

3. PERFORMANCE COMPARISON OF Cu-BASED ANODES IN LITHIUM-ION BATTERIES

Well-organized silicon and copper nanowires have been directly fixed to a collector to improve cycling stability, while also taking advantage of the high performance increase of silicon to produce as an excellent anode for lithium-ion batteries [103]. Xue et al. [104] prepared a three-dimensional porous Cu_6Sn_5 anode. They deposited tin on the surface of a copper foam. By optimizing the process, a Cu6Sn5 alloy with a thickness of 1.2 µm was formed on the surface of the copper foam. Electrochemical tests showed that the new anode had excellent electrochemical performance in terms of specific capacitance and cycling. Banerjee et al. [105] reported on the synthesis of CuO nanostructures using an MOF. They used controlled pyrolysis to prepare CuO nanoparticles. The CuO synthesized with an MOF retained 90% of its initial reversible capacity after 40 cycles. Rate performance studies showed that at a high current rate of 2 A/g, the reversible capacity of 210 mAh/g could be transported. Applestone et al. [106] prepared a Cu_2Sb-Al_2O_3-C nanocomposite alloy material.

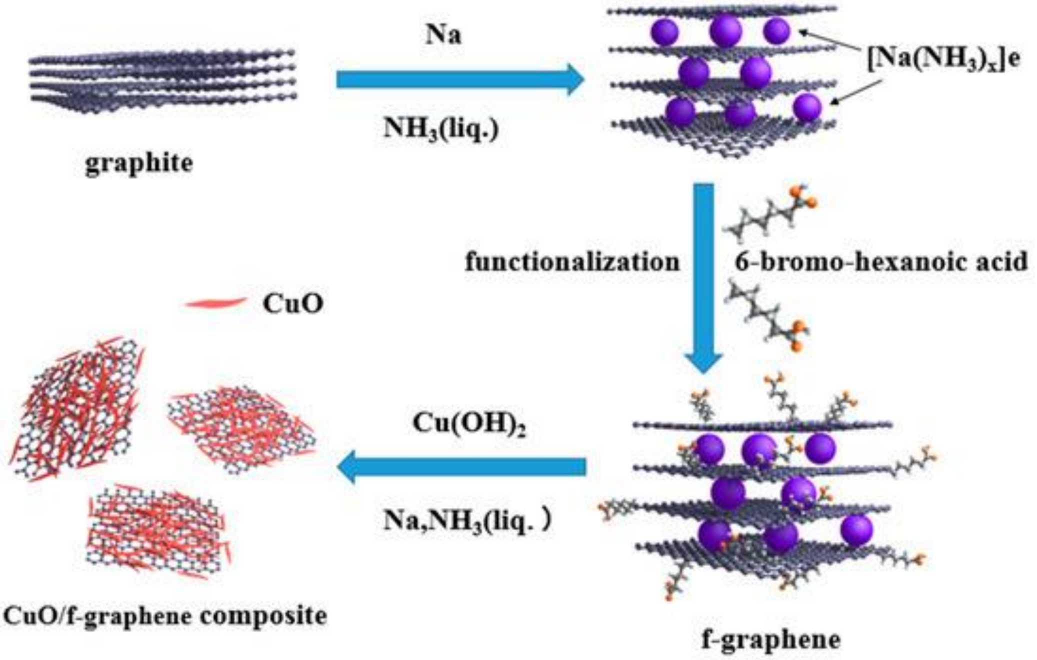

Figure 1. Schematic of the synthesis procedure of the CuO/f-graphene composite. Copyright obtained from MDPI [107].

The characterization technique showed that the nanocomposite was composed of nano-Cu_2Sb particles in an amorphous Al_2O_3 structure and a conductive carbon matrix. The presence of alumina in nanocomposites increases the cycling life of the materials. Cu_2sb-Al_2O_3-C has a higher capacity than that of a commonly used graphite anode. The conductive Cu framework supports the electrochemical activity of Sb and results in a low impedance and a good increase in performance, while the ceramic oxide and conductive carbon matrix reduce the agglomeration of nanocrystalline Cu_2Sb particles and buffer the volume expansion/contraction that occurs during cycling. Zhang et al. [107] synthesized copper oxide nanowires/functionalized graphene composites using a pot method (Figure 1). The composite material was well dispersed. When utilized as a cathode material in a lithium-ion battery, the composite material demonstrated good cycling stability after 50 cycles. Table 2 shows lithium-ion battery performance comparisons when using Cu-based anodes.

Table 2. Comparison of the lithium-ion battery performance using Cu-based anode.

Materials	Performance	Reference
3D porous Sn–Cu_6Sn_5	404 mAh/g over 100 cycles	[104]
CuO/Cu_2O hollow polyhedrons	740 mAh/g after 250 cycles	[108]
Cu_2SnS_3	600 mAh/g after 50 cycles	[109]
SnO_2/Cu hybrid nanosheets	470 mAh/g after 150 cycles	[110]
Cu–Ge core–shell nanowire array	734 mAh/g after 80 cycles	[111]
Oxidized Cu foil	-	[112]
CuO-MOF-199	210 mAh/g after 40 cycles	[105]
$LiFePO_4$/Cu-Sn	400 mAh/g after 50 cycles	[113]
Cu_xS/Cu Nanotubes	282 mAh/g after 50 cycles	[114]
3D nanoporous copper-supported cuprous oxide	145 mAh/g after 120 cycles	[115]
CuO nanoflake arrays coated Cu foam	193.5 mAh/g after 400 cycles	[116]
Cu/TiO_2	-	[117]
Cu_2O–graphene	252 mAh/g after 50 cycles	[118]
Cu–Si core–shell nanowire	310 mAh/g after 100 cycles	[119]
Cu_2Sb–Al_2O_3–C	330 mAh/g after 500 cycles	[106]
Fe–Cu–Si	-	[120]
Si–Cu	1620 mAh/g after 500 cycles	[121]
Cu_2ZnSnS_4	680 mAh/g after 40 cycles	[122]
Cu_2SnS_3	621 mAh/g after 50 cycles	[123]
CuO-f-graphene	677 mAh/g after 50 cycles	[107]

4. PERFORMANCE COMPARISON OF Cu-BASED CATHODES IN LITHIUM-ION BATTERIES

Lee et al. [124] improved the conductivity of the cathode by adding a copper sheet to $LiFePO_4$. The evenly dispersed copper sheet was converted into CuO during calcination. The Cu-doped cathode had a high capacity of 161 mAh/g. Meng et al. [125] used an atomic layer deposition method to deposit nanometer-sized copper sulfide on a network of single-walled carbon nanotubes. The resulting core-shell composite structure ensured close contact between the two components while maintaining high porosity for efficient charge transfer. Electrochemical tests showed that the nanocomposites exhibited excellent stability over 200 discharge and charge cycles in lithium-ion batteries. Zhao et al. [126] proposed a simple bubble template synthesis for the preparation of copper and mesitylene hollow balls. They used glutathione as a template agent, sulfur source and assembler. By changing the volume ratio of water/methanol in the solvent system, the hollow-ball nanomorphology could be obtained. The above material was used as an anode material in a lithium-ion battery and exhibited a high specific capacity. Chen et al. [127] prepared CuS with a thickness of approximately 25 nm by a hydrothermal method. At the same time, they studied the possibility of CuS as a cathode material for lithium-ion batteries. The electrochemical test results showed that the CuS had excellent cycling stability. Table 3 shows lithium-ion battery performance comparisons when using Cu-based cathodes.

Table 3. Comparison of the lithium-ion battery performance using Cu-based cathode.

Materials	Performance	Reference
$Cu_{0.02}V_{1.98}O_5$	97 mAh/g	[128]
Copper sulfidenanowire array	244 mAh/g after 100 cycles	[129]
$LiFePO_4$-Cu flake	161 mAh/g after 50 cycles	[124]
ε-$Cu_{0.95}V_2O_5$	-	[130]
CuS nanowire	-	[131]
Single-walled carbon nanotube-Cu_2S	260 mAh/g after 200 cycles	[125]
Copper-stabilized sulfur-microporous carbon	200 mAh/g	[132]
Cu-doped $LiFePO_4$	-	[133]
$LiFePO_4$/Cu	147 mAh/g	[134]
Copper vanadate	100 mAh/g	[135]
CuS	-	[126]
CuS	463 mAh/g	[136]
$Li[NiCo_{1-x}Cu_xM_n]_{1/3}O_2$	160 mAh/g	[137]
Aligned lithiophilic CuO nanosheets	170 mAh/g	[138]
CuS	180 mAh/g	[127]

5. CONCLUSION

As lithium-ion batteries expand into a wide variety of new applications, they must exhibit superior rate-charge and discharge performance, as well as providing high energy and power density. To achieve this ultimate goal, a considerable amount of research has been carried out to improve lithium battery technology, especially in electrode performance. Nanoscale materials represent a rapidly developing field in lithium batteries due to their great advantages in mass transportation. In this review, Cu-based materials have been used for the construction of electrodes to be used in lithium-ion battery applications.

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