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Research Progress of Constructing Anode Materials for Potassium Ion Batteries Based on Electrospinning Technology

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Abstract: Potassium offers the benefits of plentiful supplies, widespread availability, and inexpensive cost. Potassium-ion batteries (KIBs) are thought to be one of the best energy storage technologies to take the place of lithium-ion batteries in the future since potassium has a low electrode potential and rapid ion transport kinetics in the electrochemical system. As opposed to lithium-ion batteries, potassium-ion battery research is still in its early stages, and the system has issues with low capacity, inferior rate performance, and short cycle life. As a result, creating safe, dependable, and high-performance charge-discharge potassium-ion batteries still presents several difficulties. One of the main elements promoting the development of potassium-ion batteries is the development of anode materials for these batteries. At present, there are various methods for constructing potassium-ion battery anode materials, including hydrothermal method, solid phase reaction, electrospinning method, etc. The advancement of electrospinning and the creation of potassium-ion battery anode materials based on electrospinning are the main topics of this review article. This report also anticipates the direction of research and development for high-performance, low-cost anode materials.

Keywords: Potassium-ion battery, Anode material, Electrospinning.

1. Introduction

Lithium-ion batteries (LIBs) are widely used in energy storage and drives, such as portable smart devices, electric vehicles or robots [1,2]. Despite playing a significant role in our daily lives, lithium-ion batteries still encounter obstacles in the field of large-scale energy storage because of a paucity of lithium supplies, a relatively high price, and a low energy density [3,4]. Therefore, the development of a rechargeable battery system that can take the role of lithium-ion batteries is essential. The element potassium (K), which is in the same family as lithium, has received a lot of attention. Due to the same charge-discharge mechanism, variety of sources, and inexpensive cost, potassium ion batteries (KIBs) are seen as an effective replacement for lithium-ion batteries (LIBs) [5,6]. As a result, there has been a lot of interest in KIBs research recently. Furthermore, as science and technology have continued to advance, materials, particularly nanomaterials, have emerged as one of the key pillars supporting the growth of modern science and technology. Nanotechnology provides new discoveries and opportunities for ensuring sustainable energy in the future because of its distinctive structure, composition, physical and chemical capabilities. Nanostructured materials can be synthesized by a variety of techniques, including top-down synthesis and bottom-up methods [7-9]. A new innovation in the production of nanofiber materials is electrospinning technology, which is easy to use, effective, and affordable. Electrospinning is used in many different industries and has produced excellent results [10,11]. The use of electrospinning technique in the anode materials of potassium ion batteries has not yet been completely analyzed, despite the fact that several publications on the synthesis of electrospun nanofiber materials and their possible uses have been published over the years. In this review, we cover the investigation and development of electrospun anode materials for KIBs.

2. Research Status of Anode Materials for KIBs

2.1. The advantages of KIBs

As one of the effective alternatives to LIBs, KIBs have the following advantages: 1) the potassium source in the earth's crust is relatively rich (1.5wt %), widely distributed and low price [12,13]. Figure 1a displays the comparison between lithium, sodium, and potassium elements. 2) K^+ has the lowest Stokes′ radius and the weakest Lewis acidity when compared to Li^+ and Na^+. This results in increased mobility, a higher migration number, and a lower desolvation energy in the electrolyte [14,15]. 3) The development of KIBs can benefit from the K^+/K redox couple having the lowest potential in some organic electrolytes, such as propylene carbonate (PC), where K^+/K redox couple has a reduction potential of −2.88 V in PC, lower than Li+/Li (−2.79 V) and Na+/Na (−2.56 V), giving KIBs a high operating voltage and high energy density. [16]. 4) Similar to Li^+, K^+ can be inserted into the graphite layer to form the KC_8 compound with a theoretical capacity of about 279 mAh/g [17]. Figure 1b provides a schematic representation of the "rocking chair" design of KIBs for power batteries. 5) By substituting Al for Cu on the anode side of the substrate, K does not form an alloy when it comes into contact with Al at lower voltages, which can minimize the cost of producing batteries [14]. KIBs are therefore considered one of the most promising alternatives, which has a broad application prospect in the field of large-scale energy storage, the conception of the potential applications of KIBs to better support the future of human life is displayed in Figure 1c.

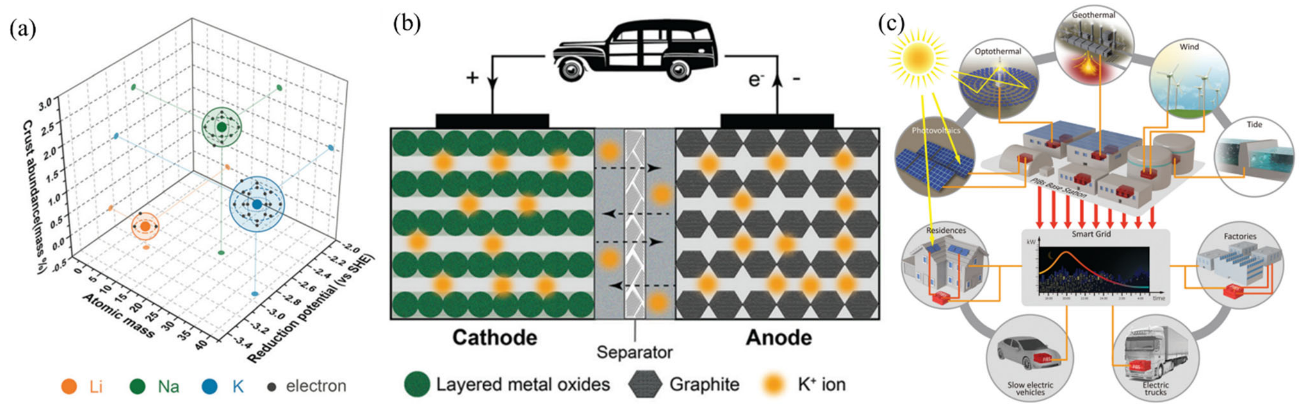

Figure 1. (a) The comparison between lithium, sodium, and potassium elements; (b) the schematic illustration of the "rocking chair" model of KIBs for power batteries; (c) the conception of the potential applications of KIBs to better support the future of human life [12].

2.2. Key problems of anode materials for KIBs

Due to specific safety concerns and the limited cycling efficiency of KIBs caused by K metal's high chemical reactivity to water and electrolyte components, the use of potassium metal in KIBs on a broad scale is constrained [18]. The size of K^+ (2.76 Å) is much larger than that of Li^+ (1.52 Å), which will result in significant volume fluctuations and structural deformation throughout the potassiation/depotassiation process, the energy density will be significantly reduced [19]. Other issues such as weak potassium ion reaction kinetics, harmful side effects, electrolyte consumption, dendrite growth, insufficient energy density, and battery safety risks have emerged as major challenges to the development of potassium ion batteries [20-23]. Finding the electrode materials appropriate for K^+ deintercalation, such as crystal structure and reaction mechanism, is the key to research in potassium ion battery systems. Common anode materials primarily consist of carbon-based, organic, alloy, and conversion materials, etc. [24-27]. Anode materials, a crucial part of KIBs, have undergone much research recently, leading to progressively better mechanisms and enriched systems. As a result, a thorough evaluation of the anode materials research status is required.

3. Research Status of Electrospinning Technology

3.1. Principles of electrospinning technology

The five processes that make up electrospinning devices are fluid charging, Taylor cone generation, jet refining, jet instability, and fiber reception. Electrospinning devices typically contain high-voltage power supplies, solution storage, injection, and receiving devices [28]. Figure 2 displays a schematic of how an electrospinning equipment is set up. High voltage static electricity is used in electrostatic spinning. The polymer solution or branded body is charged and deformed in the high voltage electrostatic field, generating a droplet at the end of the spinning electrode. A high-speed polymer jet will form on the surface of the droplet when the charge repulsive force on the surface of the droplet outweighs the surface tension. High-speed electric field force stretches these jets, which are then volatilized by the solvent, hardened, and eventually deposited to create polymer nanofibers on the receiving electrode plate.

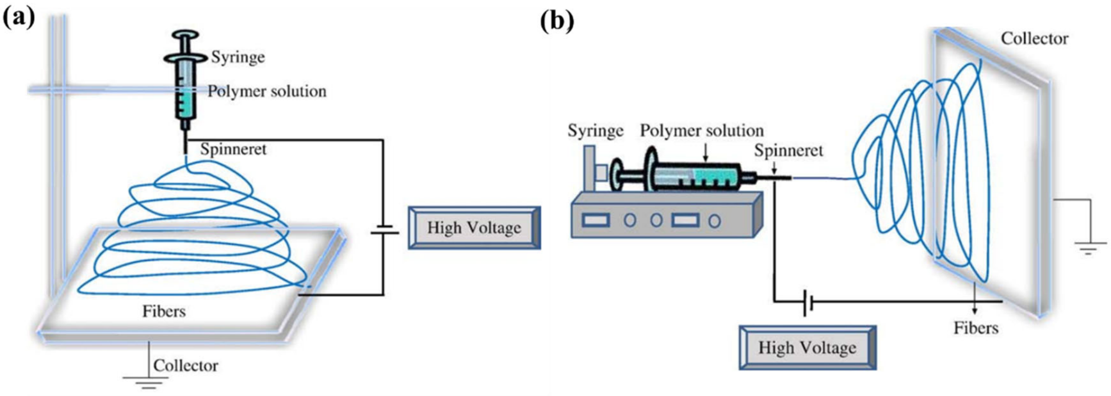

Figure 2. Schematic diagram of set up of electrospinning apparatus (a) typical vertical set up and (b) horizontal set up of electrospinning apparatus [28].

3.2. Advantages and disadvantages of electrospinning

Because of its benefits, including its straightforward manufacturing method, low spinning costs, large range of spinnable materials, and controllable process, electrostatic spinning is widely employed in many different industries [29-31]. Only ultra-fine fibers having a diameter of less than 100 nm are considered nanofibers. It has the characteristics of large specific surface area and high porosity, so it can be widely used in biological materials, high precision instruments, protective materials, nano-composites and other fields [32,33]. However, there are still many problems in the application of electrospinning technology. The completed inorganic nanofiber materials made using electrospinning technique are extremely brittle and lack sufficient flexibility and continuity. As a result, it will cause the specific use process a great deal of inconvenience [34].

4. The Advantages of Electrospinning Technology in Batteries

Today, there is a growing focus on lightweight, flexible, wearable or foldable batteries to drive the development of advanced portable electronic devices [35,36]. Thankfully, the production of 3D flexible carbon-based films based on electrospinning technology with great mechanical stability, excellent conductivity, and good flexibility has become a key technology [37-39]. Model electrospun nanofiber-based freestanding and binder-free electrodes were shown in Figure 3 along with their use in LIBs, NIBs, and KIBs. The traditional way of making mud-based electrode materials for batteries, which calls for binders, conductive agents, and current collectors, significantly reduces total capacity and energy density. Electrospinning technology replaces this method [40]. Binders must be used in the preparation of electrodes since they invariably diminish electrical conductivity and the availability of active materials, leading to kinetic issues [41]. Additionally, carbon-based fibers with varied architectures, such as core-shell, hollow, necklace, etc., can be created using electrospinning processes to fulfill a variety of performance needs. For instance, hollow carbon nanofibers (HCNFs) were prepared by electrospinning method with several coaxial nozzles, in which the level of the inner nozzle-end is adjustable. Core/shell nanofibers were prepared from poly(methyl methacrylate) (PMMA) as a pyrolytic core and polyacrylonitrile (PAN) as a carbon shell with three types of normal (viz. inner and outer nozzle-ends are balanced in the same level), inward, and outward coaxial nozzles [42].

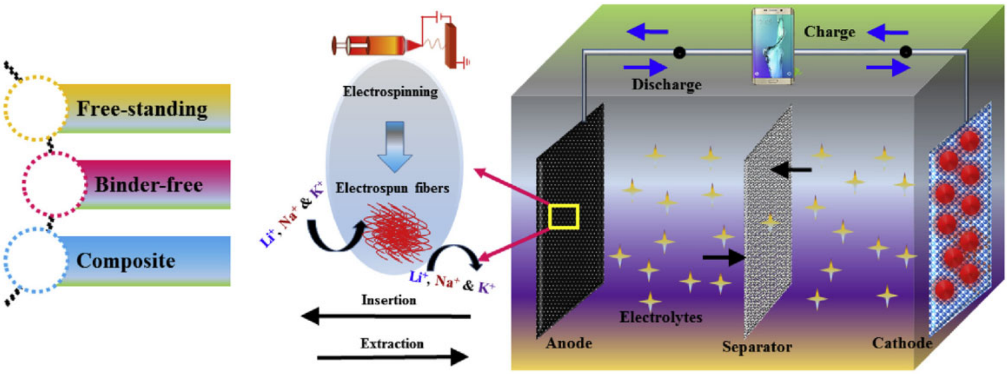

Figure 3. The model electrospun nanofiber-based freestanding and binder-free electrodes and their application in LIBs, NIBs & KIBs [40].

5. Research Progress of Anode Materials for Kibs Based on Electrospinning Technology

After an overall search in Web of Science, the electrospinning technology-based KIBs anode can be divided into carbon-based materials, transition metal compound/carbon composite materials, metal/carbon composite materials. Due to its low cost and great thermal stability, carbon-based material is the most preferred KIBs anode material [43,44]. The first electrochemical potassium insertion in graphite in a non-aqueous electrolyte was described by Ji et al. [45], and it displayed a high reversible capacity of 273 mAh/g. However, the diffusion of K$^+$ into the graphite layer causes a volume expansion of up to 61%, which frequently results in the collapse of the electrode's primary structure and a rapid reduction of cycle capacity. At the same time, the rate performance at high current density needs to be enhanced due to the poor K+ diffusion dynamics. As a result, the creation of non-graphite carbon-based materials, such as hard carbon microspheres, has emerged as a key area of research for KIBs' anode [46,47].

Hard-soft composite carbon [48], graphene aerogel [49], carbon nanofiber [50], et al. Among them, the flexible and free-standing carbon-based nanofibers (CNFs) prepared by electrospinning has gained great attention. Because of their flexibility, capacity to manage their morphology, and high conductivity, the produced CNFs can be employed without binders, carbon-conductive additives, or heavy metal foil as the anode electrode for KIBs [51,52]. By doing so, the total specific capacity can be raised in comparison to electrodes made using the conventional slurry-casting approach [53,54]. Additionally, electrospinning allows for the creation of certain CNF shapes including porous and hollow ones, which is beneficial for enhancing KIBs' electrochemical performance [55-58]. By providing little resistance and promoting ion movement with a reduced diffusion distance, porous structures can enhance electrochemical performance [56]. Multichannel carbon fibers (MCCFs) were created by Zheng et al. [59] by electrospinning an appropriate mixture of poly(methyl methacrylate) and polyacrylonitrile, followed by calcination treatment, to serve as freestanding KIBs anodes. The MCCFs electrode exhibited a reversible capacity of 110.9 mAh/g over 2000 cycles at a higher current density of 2 A/ g and great rate capacity. The exceptional multi-channels in amorphous MCCFs for buffering volume change and allowing electrolyte infiltration, as well as the high conductivity of N-, O-doping in MCCFs, were credited with this great electrochemical performance. Similarly, Xu et al. [60] proved the remarkable rate capability and long cycle life of the free-standing 3D porous CNF paper anodes for KIBs. Pol′s group [51] produced carbon nanofibers as free-standing anode for KIBs by electrospinning of polyacrylonitrile polymer and subsequent carbonization, which exhibited exceptional cycling stability through the amorphous carbon structuring and one-dimensional architecture accommodating significant material expansion upon K^+ intercalation, resulting in a stable capacity of 170 mAh/g after 1900 cycles at 1C rate for N-rich carbon nanofibers. The K-ion surface storage mechanism and the higher K+ solid diffusion coefficient in carbon nanofibers as compared to graphite led to excellent rate performance of 110 mAh/g at 10C rate as opposed to 230 mAh/g at C/10 rate. In Wu et al.′s work [61], they created easy-to-electrospin, high-temperature self-fluid N-doped mesoporous carbon nanofibers (NMCNFs) with internal cross-linked multi-scale pores. Although the prepared material cannot be used directly as a flexible self-supporting electrode, the NMCNFs displayed an impressively reversible capacity of 351.1 mAh/g at a current density of 0.2 A/g after 500 cycles, excellent rate performance of 134 mAh/g under 10 A/g. More interestingly, after extremely long-term 20,000 cycles, an amazing capacity of 122.3 mAh/g has been reached, even at a high rate of 5 A/g. Additionally, there is a ton of research on the superior potassium storage capabilities of carbon fiber based on electrospinning, indicating that this technique is crucial to the study of KIBs. However, since the performance of pure carbon fibers for storing potassium still needs to be improved, many researchers are examining other promising candidates, such as metals and alloys (Sb, Sn, and SnSb), conversion materials (oxides, sulfides, selenides, and phosphides), and carbon-based fibers combined with these materials [62-64].

The metal antimony (Sb) is a promising anode due to its high theoretical capacity, unique puckered-layer structures, small electrode polarization, and a moderate working voltage [65]. The fast diffusion of K ions and the release of structure strain are advantages of the puckered-layer structure, which can increase rate capability and maintain stability. Motivated by these advantages, Zhang at al. [62] prepared Sb nanoparticles finely encapsulated in N, P co-doped mesoporous carbon nanofibers (Sb@NPMC) by electrospinning method followed by a heat treatment, this material was successfully applied it as an anode electrode in KIBs. The Sb@NPMC exhibited ultra-long cycling stability and high specific capacity of 130 mAh/g at 1 A/g after 1500 cylces. The huge active surface of mesoporous carbon nanofibers and the highly conductive connection network for electron transport are primarily responsible for this exceptional performance. Additionally, it is anticipated that Sb nanoparticles dispersed in carbon nanofibers will offer a high theoretical capacity. The electrochemical reactivity and electrical conductivity of mesoporous carbon nanofibers were improved by phosphorus and nitrogen co-doping. Hou et al.′s group [66], successfully prepared nano Sb confined in N-doped carbon fibers (Sb@CN nanofibers) through an electrospinning method, exhibited outstanding electrochemical potassium storage performances. Qian et al. [63] designed sulfur-defective vanadium sulfide/carbon fiber composites (D-V_5S_8/CNFs) by a facile electrospinning method as shown in Figure 4a, and investigated its K ion storage performance. The D-V_5S_8/CNF anode revealed a high capacity of 350 mAh/g at 0.1 A/g (Figure 4b), as well as admirable long-term cycling characteristics as shown in Figure 4c (165 mAh/g after 3000 cycles at 1 A/g). This excellent storage performance and long-term cycling stability are attributed to the two merits below: 1) The carbon fiber's confinement of the V_5S_8 nanoparticles creates short-range channels and a wealth of adsorption sites for ion storage 2) the increased interlayer spacing also mitigated volume changes and provided less resistance to vanderwaals interactions and ion diffusion to store more K ion reversibly. Yang′s group [64] reported a self-supported anode material composed of CuO/Cu clusters distributed in nitrogen-doped carbon microfibers (CuO/Cu-NCNFs electrode) via a simple electrospinning technology. In comparison to nitrogen-doped carbon microfibers (NCNFs), which shown a reversible capacity of 205.9 mAh/g after 100 cycles at 0.1A/g, the generated three-dimensional conductive networks interlaced by CuO/Cu-NCNFs microfibers for KIBs indicated improved electrochemical performance. Besides, in many other research works, the prepared composites also show excellent potassium ion storage properties [67-72]. The anode materials used to build KIBs by electrospinning are listed in Table 1 for convenience.

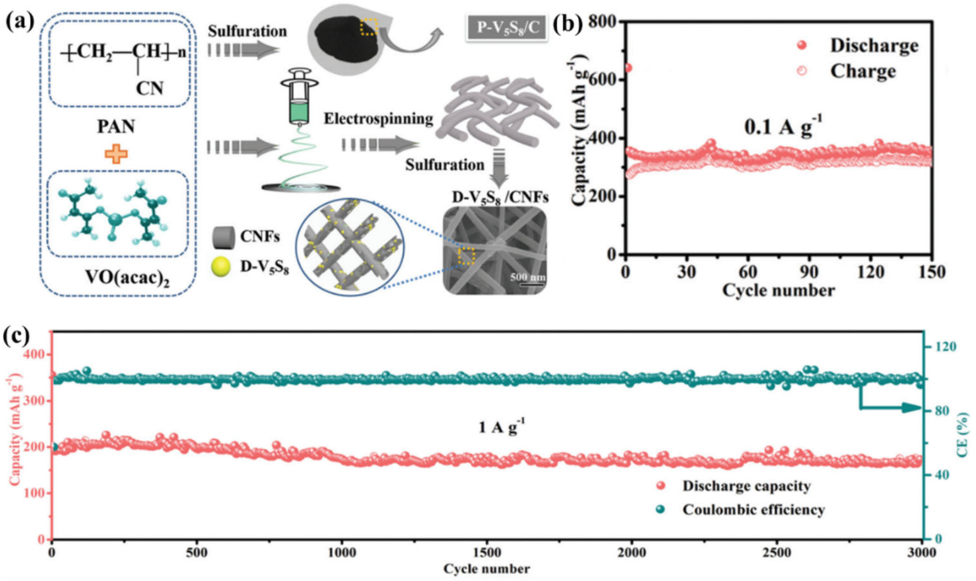

Figure 2. (a) Schematic illustration for synthesizing the D-V_5S_8/CNF and P-V_5S_8/C composites. (b) Cycling performance of the D-V_5S_8/CNF electrode for KIBs at a current density of 0.1 A/g. (c) Long-term cycling performance at a current density of 1 A/g of the D-V_5S_8/CNF electrode for KIBs [63] .

Table 1. The anode materials for KIBs constructed based on electrospinning.

Anode materials	Capacity (mAh/g)	Current density (A/g)	References
multichannel carbon fibers (MCCFs)	~110.9 (2000 cycles)	2	[59]
porous carbon nanofiber (CNF)	~211 (1200 cycles)	0.2	[60]
carbon nanofibers	~170 (1900 cycles)	1C	[51]
mesoporous carbon nanofibers (NMCNFs)	~351.1 (500 cycles) ~122.3 (20000 cycles)	0.2 5	[61]
Sb nanoparticles finely encapsulated in N, P co-doped mesoporous carbon nanofibers (Sb@NPMC)	~266.2 (50 cycles) ~130 (1500 cycles)	0.05 1	[62]
Sb confined in N-doped carbon fibers (Sb@CN)	~360.2 (200 cycles) ~212.7 (1000 cycles)	0.05 5	[66]
vanadium sulfide/carbon fiber composites (D-V_5S_8/CNFs)	~165 (3000 cycles)	1	[63]
CuO/Cu clusters distributed in nitrogen-doped carbon microfibers (CuO/Cu-NCNFs)	~205.9 (100 cycles)	0.1	[64]
iron phosphide nanoparticles-doped CNFs (Fe_2P-CNFs)	~179.6 (2000 cycles)	2	[67]
$Co_{0.85}Se$@carbon nanoboxes ($Co_{0.85}Se$@C)	~299 (400 cycles)	1	[68]
Ta-doped TiO_2/C nanofibers	~148 (800 cycles)	2	[69]
In_2S_3/C nanofibers	~262.8 (50 cycles)	0.05	[70]
MoS_2@Fe_xO_y@CNF	~320 (100 cycles)	0.05	[71]
Sn_4P_3 in N-doped carbon fibers	~160.7 (1000 cycles)	0.5	[72]

6. Summary

The use of electrospinning technology is widespread at the moment. The electrospinning nanofiber membrane has undergone extensive development and has produced outstanding results when modified using techniques such as miscible, cross or coaxial electrospinning, multilayer composite, coating, and electrostatic spray. Electrospinning, however, also has a lot of disadvantages. First off, electrospun nanofiber membranes have inadequate mechanical strength. The fracture strength of electrospinning nanofiber membrane needs to be increased in order to guarantee the mechanical strength necessary for mass production and the battery assembly process. Second, poorly oriented nanofibers produced by electrospinning are another issue. It can only be formed into a fiber network due to the complexity of the electrospinning process and the difficulty in controlling the fiber orientation. Therefore, the preparation of environmental protection and green nanofibers with strong mechanical properties is the focus of future research.

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