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Flexible Electrodes and Electrolytes for Energy Storage

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ABSTRACT

The advent of flexible, wearable electronics has placed new demands on energy storage systems. The demands for high energy density achieved through the use of highly conducting materials with high surface area that enable facile electrochemical processes must now be coupled with the need for robustness and flexibility in each of the components: electrodes and electrolytes. This perspective provides an overview of materials and fabrication protocols used to produce flexible electrodes and electrolytes. We also discuss the key challenges in the development of high performance flexible energy storage devices. Only selected references are used to illustrate the myriad of developments in the field.

Contents

1. Introduction

It is now hard to imagine a world without portable electronic devices, and wherein wearable componentary is on the increase. Devices, such as smart phones coupled to wearable sensors to monitor vital physiological signs are part of a growing trend towards the seamless integration of electronic devices and humankind. More sophisticated implantable electronic systems already allow the deaf to hear, parkinsons disease symptoms to be controlled and epileptic seizure to be monitored. The performance of these wearable implantable devices is critically dependent on the realization of appropriately configured energy supply systems. At present, such systems are predominantly energy storage devices: batteries or supercapacitors. All-solid-state power sources are preferred, not just for safety in that liquid electrolyte leakage can be avoided, but also due to the flexibility available in shaping

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and forming. An ever-increasing demand for portable electrical devices will remain a driving force for the continuing development of new inexpensive, flexible/wearable, light-weight and environmentally benign energy storage devices [1] and a number of excellent reviews have appeared [2–8].

Flexible batteries/supercapacitors consist of three main components: electrode, electrolyte and separator (Fig. 1) [9]. These components can be assembled as flat or fiber. In the flat film configuration, solid electrolyte is sandwiched between the flexible cathode and anode. They typically show a five-layer structure, for the cathode and anode with an integrated current collector. They are commonly assembled into a prismatic cell for use. They may be packaged into a flexible polymer-based case (pouch cell). Fiber batteries contain the same essential elements. With fibers the omni-directional flexibility facilitates integration into different forms and structures including knitting or weaving into textiles [10,11]. Flexible electrodes need to meet the requirements of high capacity/capacitance, high rate capability, low self-discharge, excellent cycling stability, and robust flexibility. Solid electrolytes should possess high ionic conductivity, negligible electronic conductivity, and a wide electrochemical window, coupled with thermal and mechanical stability.

2. Flexible Electrodes

2.1. Planar Thin Film

Flat flexible batteries originated from all solid-state thin film batteries. They may be constructed by sequential vapor deposition of cathodes ($LixMn_2O_4$ or V_2O_5), solid electrolyte ($Li_{2.9}PO_{3.3}N_{0.46}$) and anodes (Li), and subsequently encapsulated with a protective coating [12]. The use of thin metal foils as the deposition substrate facilitated development of flexible batteries [13]. The use of elastomeric materials as the substrates results in a battery that is not just flexible but bendable [14] or even stretchable [15,16]. Most recently, the use of low cost cellulose-based or textile-based materials as substrate has accelerated the application of flexible electrodes and devices [5,7,17,18].

Flexible, mechanically strong, free-standing papers or films, such as bucky paper [19], graphene paper [20] and conducting polymer papers [21] offer an alternative approach. They can be used directly as battery or supercapacitor electrodes without the use of low capacity conducting additives and insulating binder (Fig. 2). Also they can be easily engineered into the desired shapes or structures by conventional mechanical techniques.

2.1.1. Free Standing Planar Films

Free-standing flexible thin film electrodes based on carbon materials (carbon nanotubes(CNTs) or graphene) can be produced from dispersions using evaporative casting or filtration to remove the solvent media [22–25]. The stable dispersion containing those individual tubes or sheets (colloid) is formed by breaking up large bundles of CNTs or graphene oxide/graphene particles with an ultrasonic energy with or without the assistantance of amphiphilic molecules (dispersants). During the filtration process, CNTs or graphene oxide/graphene were held together *via* strong π-π stacking and van der Waals forces, along with the interdigitation of CNTs tubes or interlocked/tiled graphene sheets due to their large aspect ratio.

CNTs based thin film electrodes consist of randomly entangled and cross-linked carbon nanotubes. The open space between the entangled fibrils creates a porous structure, offering high accessible surface area. These structures provide a highly conductive network. These papers possess the advantage of high power and cycling stability as an energy storage electrode [19,26]. They can also be used as high surface area substrate for the deposition of conducting polymer/metal oxides, forming composites [27]. In these composites, CNTs function as a three-dimensional robust conductive network, facilitating effective charge transport and efficient ion diffusion. The CNT network also provides mechanical robustness, thus improving the cycling stability, energy and power density [28,29].

Graphene papers possess a unique layered structure, in which graphene sheets are interlocked/tiled together in a near-parallel fashion. However, the aggregation or restacking of the graphene nanosheets (GNs) due to the strong π-π stacking and van der Waals forces limits the available surface area and charge storage capacity. The unique properties available from the individual sheets, such as high surface area and extraordinary electronic transport, cannot be delivered. The strategies to inhibit the restacking of graphene sheets mainly include incorporation of spacers separating the graphene sheets, and creation of three-dimensional porous networks [30]. Hydrothermal and freeze drying are two common techniques used to construct a three-dimensional porous graphene assembly [31,32]. It is generally believed that the addition of spacers (such as CNTs, conducting polymers or metal oxides) in-between the graphene sheets can effectively inhibit restacking to maximize the available surface area, and thus improve the charge storage capacity. The incorporation of these active components induces much higher charge storage capability too. Highly conductive GNs also act as a conducting matrix in such hybrid structures, which has a direct impact on improving the coulombic efficiency, rate capability and cycle life. A synergistic effect can be driven from both components in the graphene-based composite materials [33–37].

Flexible free standing films of inherently conducting polymers (ICPs) with controlled thickness and morphology can be produced using electropolymerisation [38]. A free-standing film can be peeled from the conductive substrate where it is electrodeposited. These films can be shaped into the desired structures and used

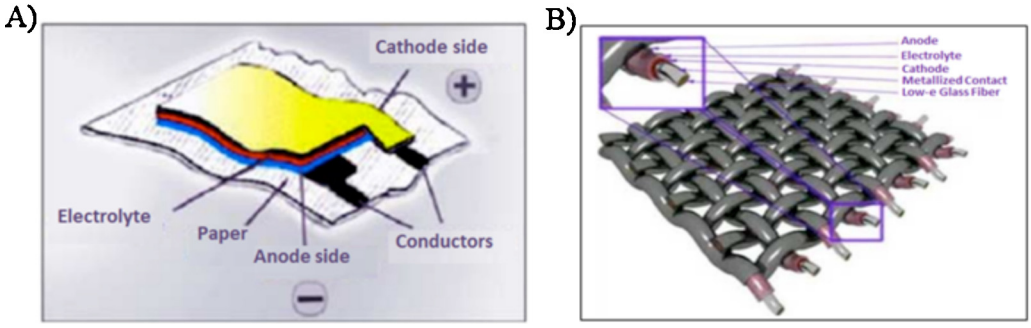

Fig.1. Scheme of a flat flexible battery (A), a fiber battery and a demonstration of fiber batteries weaved into textile (B) (adapted from Ref. [9] with permission).