Flexible energy storage devices based on nanocomposite paper

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There is strong recent interest in ultrathin, flexible, safe energy storage devices to meet the various design and power needs of modern gadgets. To build such fully flexible and robust electrochemical devices, multiple components with specific electrochemical and interfacial properties need to be integrated into single units. Here we show that these basic components, the electrode, separator, and electrolyte, can all be integrated into single contiguous nanocomposite units that can serve as building blocks for a variety of thin mechanically flexible energy storage devices. Nanoporous cellulose paper embedded with aligned carbon nanotube electrode and electrolyte constitutes the basic unit. The units are used to build various flexible supercapacitor, battery, hybrid, and dual-storage battery-in-supercapacitor devices. The thin free-standing nanocomposite paper devices offer complete mechanical flexibility during operation. The supercapacitors operate with electrolytes including aqueous solvents, room temperature ionic liquids, and bioelectrolytes and over record temperature ranges. These easy-to-assemble integrated nanocomposite energy-storage systems could provide unprecedented design ingenuity for a variety of devices operating over a wide range of temperature and environmental conditions.

batteries | carbon nanotubes | supercapacitor

There has been recent interest in flexible safe energy devices, based on supercapacitors and batteries, to meet the various requirements of modern gadgets (1–3). Electrochemical energy can be stored in two fundamentally different ways. In a battery, the charge storage is achieved by electron transfer that produces a redox reaction in the electroactive materials (3). In an electric double-layer capacitor, namely the supercapacitor, the charge-storage process is nonFaradic, that is, ideally no electron transfer takes place across the electrode interface, and the storage of electric charge and energy is electrostatic. Because the charging and discharging of such supercapacitors involve no chemical phase and composition changes, such capacitors have a high degree of cyclability. However, in certain supercapacitors based on pseudocapacitance, the essential process can be Faradic, similar to that in a battery. However, an essential fundamental difference from battery behavior arises because, in such systems, the chemical and associated electrode potentials are a continuous function of degree of charge, unlike the thermodynamic behavior of single-phase battery reactants (3). Now, with the demand for efficient power devices to meet the high-power and -energy applications, there seems to be the possibility of an ideal compromise, which combines some of the storage capabilities of batteries and some of the power-discharge characteristics of capacitors in devices capable of storing useful quantities of electricity that can be discharged very quickly. We address here this need to develop new integrated hybrid devices with adaptability in various thin-film as well as bulk applications by using engineered electrode nanostructures.

The performance characteristics of energy devices are fundamentally determined by the structural and electrochemical properties of electrode materials (4–7). Electrolyte choice (aqueous vs.

nonaqueous), limiting high-power capability and packaging designs, is the other important factor in supercapacitors and batteries (8, 9). If integrated structures containing the three essential components (electrodes, spacer, and electrolyte) of the electrochemical device can be made mechanically flexible, it would enable these to be embedded into various functional devices in a wide range of innovative products such as smart cards, displays, and implantable medical devices. Previous designs of flexible energy-storage devices (1) have been based on separated thin-electrode and spacer layers, proving less-than-optimum in performance and handling because of the existence of multiple interfaces between the layers. Here we demonstrate the fabrication of electrode-spacer-electrolyte-integrated nanocomposite units to build a variety of thin flexible energy-storage devices. We combine two essential materials, cellulose and carbon nanotubes (CNTs), that fit the characteristics of spacer and electrode and provide inherent flexibility as well as porosity to the system. Cellulose, the main constituent of paper and an inexpensive insulating separator structure with excellent biocompatibility, can be made with adjustable porosity. CNTs, a structure with extreme flexibility, have already been widely used as electrodes in electrochemical devices (10–16). The major challenge in fabricating CNT-integrated cellulose composites is the insolubility of cellulose in most common solvents. This issue is solved here by using a room temperature ionic liquid (RTIL) (17) 1-butyl,3-methylimidazolium chloride ([bmIm][Cl]) (17), which dissolves up to 25% (wt/wt) of unmodified cellulose by using microwave irradiation (18). Interestingly, the ionic nature of RTIL (19) permits it to be used as an electrolyte in supercapacitors (20), allowing the assembly of all three components (Fig. 1) via a simple scalable process.

Uniform films of vertically aligned thin-walled multiwalled nanotubes (MWNT) are grown on silicon substrates by using a thermal-chemical vapor-deposition method [supporting information (SI)]. Unmodified plant cellulose dissolved in RTIL ([bmIm][Cl]) (17) is infiltrated into the MWNT to form a uniform film of cellulose and [bmIm][Cl], embedding the MWNT (Fig. 1a). After solidification on dry ice, this nanocomposite is immersed in ethanol to partially or completely extract excess RTIL and dried *in vacuo* to remove residual ethanol. The resulting nanocomposite paper (Fig. 1b), which forms the basic building unit in our devices, is peeled from the substrate for use as the supercapacitor. The excellent mechanical flexibility of the nanocomposite paper (CNT cellulose–RTIL) is shown in Fig. 1b.

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Abbreviations: CNT, carbon nanotube; [bmIm][Cl], 1-butyl,3-methylimidazolium chloride; MWNT, multiwalled nanotubes; RTIL, room temperature ionic liquid.

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Fig. 3. Electrochemical measurements of nanocomposite paper battery. (a) First charge–discharge curves of the nanocomposite thin-film battery cycled between 3.6 and 0.1 V at a constant current of 10 mA/g. (b) Charge capacity vs. number of cycles of the nanocomposite thin-film battery. (c) The flexible nanocomposite film battery used to glow a red light-emitting diode (LED). The flexible battery consists of an individual nanocomposite thin film with the Li thin film present on one side as one of the electrodes. The LED glows even when the battery device is rolled up, and the demonstration could be repeated over several tens of cycles at an initial operating voltage of 2.1 V.

The fabrication of the flexible Li-ion battery based on the nanocomposite paper consists of RTIL-free nanocomposite as cathode and a thin evaporated Li-metal layer as anode (Fig. 1a), with Al foil on both sides as current collectors. Aqueous 1 M LiPF_6 in ethylene carbonate and dimethyl carbonate (1:1 vol/vol) is used as the electrolyte. As with the supercapacitor, the battery also uses the excess cellulose layer in the nanocomposite cathode

as the spacer, without the use of any stand-alone spacer. The charge–discharge cycles of the battery were measured between 3.6 and 0.1 V, at a constant current of 10 mA/g. A large irreversible-capacity (≈ 430 mAh/g) is observed during the first charge–discharge cycle (Fig. 3a), and further charge–discharge cycles resulted in a reversible capacity of 110 mAh/g (Fig. 3b; see SI). The battery device operates under full mechanical flexibility. The laminated Li-ion-based battery device was used to light up a red light-emitting diode (Fig. 3c), showing its discharge behavior. The demonstration could be repeated over several tens of cycles of charging and discharging.

In recent years, supercapacitors coupled with batteries have been considered as promising hybrid devices (25, 26) to combine the best features of a battery and a supercapacitor. We show that our battery and supercapacitor devices could be integrated in parallel to build hybrids, as reported for conventional hybrids (Fig. 4a). In this case, the battery segment of the hybrid is used to charge the adjoining supercapacitor. In addition to this traditional hybrid, the nanocomposite units also allow for building new kinds of merged hybrid devices (27) (with three terminals; Fig. 4b, see legend for the definition of the terminals), which would act as both battery and supercapacitor (a dual-storage device). The Li metal layer (anode; terminal 2) and RTIL-free nanocomposite film (cathode; terminal 3) with a drop of aqueous electrolyte (1 M LiPF_6) forms the battery part of the hybrid, whereas the nanocomposite unit [MWNT (terminal 1)–cellulose–RTIL] assembled adjacent to the battery on the side of the Li layer forms the supercapacitor between terminals 1 and 3. During the operation of the device, the Li electrode (terminal 2) and the supercapacitor electrode (terminal 1) are shorted, and the discharge of the battery is used to charge the supercapacitor. The charging of the supercapacitor takes place because of intercalation at terminal 2; a PF_6^- double layer forms on the surface of the battery cathode (terminal 3), in addition to the electric double layer formed at the supercapacitor electrode

Fig. 4. Supercapacitor-battery hybrid energy devices based on nanocomposite units. (a) Schematic of a four-terminal hybrid-energy device showing the arrangement of supercapacitor and battery in parallel configuration. (b) The discharge curve of battery and supercapacitor is plotted as a function of time. The discharge of battery charges the supercapacitor, and subsequently the supercapacitor is discharged. (c) Schematic of a three-terminal hybrid energy device that can act as both supercapacitor and battery. The three terminals are defined, and the battery and supercapacitor segments of the device are shown. (d) The discharge behavior of the battery and subsequent discharge of supercapacitor are shown. The battery is discharged with terminals 1 and 2 shorted. This simultaneously charges the supercapacitor following the double-layer formation at the electrode interface. Subsequently, the supercapacitor is discharged across terminals 1 and 3. An additional separator (glass fibers) is normally added along with the excess cellulose spacer to improve behavior.