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Paper-based batteries: A review

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ABSTRACT

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Keywords: Paper battery Paper-like battery Electrochemical battery Biofuel cell Lithium-ion battery Supercapacitor Nanogenerator There is an extensively growing interest in using paper or paper-like substrates for batteries and other energy storage devices. Due to their intrinsic characteristics, paper (or paper-like) batteries show outstanding performance while retaining low cost, multifunctionality, versatility, flexibility and disposability. In this overview, we review recent achievements in paper (or paper-like) batteries as well as their applications. Various types of paper power devices are discussed including electrochemical batteries, biofuel cells, lithium-ion batteries, supercapacitors, and nanogenerators. Further scientific and technological challenges in this field are also discussed.

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1. Introduction

In recent years, paper has been used as a substrate for electronics instead of conventional rigid materials such as glass and silicon (Metters et al., 2013; Maxwell et al., 2013; Rolland and Mourey, 2013; Lo et al., 2013). The motivation is very clear: (i) Paper is extremely cheap and ubiquitously available; (ii) paper is combustible, so the paper-related devices can be economically

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disposed of by an incinerator; (iii) paper is thin, lightweight and flexible; (iv) paper is biocompatible and biodegradable and (v) paper provides high surface area for reagents to be stored (Steckl, 2013; Zhang et al., (2012); Yetisen et al., 2013; Martinez et al., 2010). Moreover, paper is attractive because it has the ability to wick fluids via capillary action. Therefore, microfluidic paper devices have a distinct advantage in that no external pumps and tubings are required to move liquid through the patterned fluidic pathways within the paper. Recently, advanced nanomaterials and nanotechnologies have been incorporated into paper, forming "paper-like" flexible films with enhanced performance (Chen et al., 2013; Jabbour et al., 2010). The normal paper can be





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applied as a skeleton for formation of paper-like nanocomposite films, which easily scale-up for commercial applications (Zhao and Shao, 2012).

Several patterning processes on paper have also been accomplished in a programmed manner, such as photolithography (Martinez et al., 2008), wax printing (Carrilho et al., 2009) and laser micromachining (Chitnis et al., 2011). The main objective of those patterning methods is to create hydrophobic barriers on paper that constitute the walls of capillary channels. One successful approach to patterning paper is based on photolithography (Martinez et al., 2008). An entire sheet of paper is impregnated with photoresist and selectively polymerized by exposing it to UV light through a transparent mask. The unexposed portion of the paper is then washed away. Another patterning method uses a commercial solid wax printer which rapidly deposits wax on paper (Carrilho et al., 2009). The paper is then heated to re-melt the wax which penetrates the paper to generate complete hydrophobic barriers. Another patterning method is based on laser treatment (Chitnis et al., 2011). Any paper with a hydrophobic surface coating, such as parchment paper, can be used for this purpose. The selective surface modification can be made by using a CO₂ laser to create hydrophilic patterns on those hydrophobic papers.

Equipped with a variety of techniques to pattern paper, paper electronics have also been successfully demonstrated by many groups. Whitesides et al. first demonstrated a novel biosensing system using patterned paper as a substrate, named microfluidic paper-based analytical devices (μ PADs) (Martinez et al., 2007). This device was used for glucose and protein sensing in urine. Fortunato et al. fabricated flexible film field-effect transistors (FETs) using cellulose fiber paper-like materials as a dielectric layer (Fortunato et al., 2008), and (Steckl (2013) developed the electronic displays on polymer-coated paper called "e-paper". A wide range of other electronic devices using paper substrates have been developed as well, including organic diodes (Zhang et al., 2012), MEMS sensors (Liu et al., 2011), RF antennas (Rida et al., 2007), circuit boards (Siegal et al., 2010) and capacitive touch pads (Mazzeo et al., 2012).

Along with the advancement in paper electronics, paper or paper-like batteries and energy storage devices have attracted more and more interest because (i) a power source directly integrated onto paper would be preferable for easy system integration with paper electronics (Lee, 2006), and (ii) the intrinsic rough and porous surface of paper is beneficial for manipulation of electrons and ion transport across the entire structure, especially inside the electrode, for achieving high-power performance (Hu and Cui, 2012). To date, several types of paper (or paper-like) batteries and energy storage devices have been developed for various applications, such as a fluidic battery in paper-based microfluidic devices for the on-chip fluorescence assay (Thom et al., 2012), a urine-activated paper battery for biosystems (Lee, 2005), a supercapacitor integrated into photoelectrochemical lab-on-paper device (Ge et al., 2013), a paper-based microbial fuel cell for disposable diagnostic devices (Fraiwan et al., 2013a, 2013b, 2013c) and a lithium-ion paper-like battery with a high energy density (Leijonmarc,k et al., 2013).

As paper (or paper-like) batteries are on the verge of entering the commercial realm, the scarcity of review articles regarding this topic creates an opportune time to summarize and examine this broad field. This review will cover the full scope of paper-based and paper-like-batteries and energy storage devices. We hope that this review will be helpful to readers who are interested in initiating work in this area as well as to researchers already working in this field who wish to learn of the progress achieved to date.

2. Paper-based batteries and energy storage devices

According to the basic operating principles, we categorized the paper-based and paper-like batteries and energy storage devices as the following: (i) electrochemical batteries, (ii) biofuel cells, (iii) lithium-ion batteries, (iv) supercapacitors, and (v) nanogenerators. Table 1 summarizes their powers, electrode materials and potential applications. For high-power paper electronics applications, lithium-ion batteries or supercapacitors are good power sources while mechanical nanogenerators are attractive for wearable electronics, such as with sport clothing and military uniforms. Biofuel cells or electrochemical batteries might be good candidates for paper-based μ PADs or other types of small-power electronics (e.g. biosensors) which require only a couple minutes of power. In the following sections, we will discuss each type of battery in detail.

2.1. Electrochemical battery

An electrochemical battery derives electrical energy from spontaneous redox reactions, and generally consists of two metals connected by a salt bridge or an ion exchange membrane. In the electrochemical batteries, species from one half-chamber lose electrons to their electrode while species from the other halfchamber obtain electrons from their electrode. The salt bridge or an ion exchange membrane is employed to provide ionic contact between two half-chambers with different electrolytes, preventing the solutions from mixing and causing unwanted side reactions. Electrochemical batteries can be fabricated on paper substrates (i) by depositing electrodes on the paper and/or (ii) by introducing electrolytes into a whole paper or hydrophilic regions patterned within the paper.

One method is to use paper as an electrode. Hilder et al. (2009) reported a flexible paper-based zinc-air battery generating an

Table	1
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Summary of the paper-based batteries and energy storage devices.

	Electrochemical battery	Biofuel cell	Lithium-ion battery	Supercapacitor	Nanogenerator
Operating principle	Redox reaction	Bio-redox reaction	Li ⁺ ion reaction	Redox reaction	Conversion of mechanical energy
Application of paper	Reservoir, electrode and/or supporter	Reservoir, ion exchange membrane, electrode and/or supporter	electrode and/or supporter	electrode and/or supporter	electrode and/or supporter
Power generation	μW–mW	μW	mW	mW	μW
Electrode	Metallic catalysts	Biocatalysts (e.g. bacteria)	Lithium based metal oxide materials	Metal oxides or other carbon- based materials	Piezoelectric or metallic materials
Potential application	Low power biosensors	Low power biosensors	High power electronics	High power electronics	Wearable electronics
Remarks	Common standard battery, rechargeable	Self-sustainable, clean energy	Rechargeable	Rechargeable	Energy harvesting from vibrations

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