Paper Batteries: Paper Thin Power

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Abstract: ***Traditionally, electronics have been designed around their batteries. In recent years, however, a new battery, known as the paper battery, has been developed that can easily conform to the size and shape of various electronics. The paper battery is becoming increasingly significant as technology tends towards thinner and more paper-like devices. This paper will include a technical discussion of how the paper battery works. It will assess the efficiency and explore the advantages of recent developments in the fabrication of paper batteries. Several applications of the paper battery will then be described, and ethical issues that arise with it will be explored. This paper will illustrate how the paper battery utilizes carbon nanotubes and cellulose in its design to create a flexible battery while maintaining electrical efficiency. Further discussion will detail how the paper battery integrates the components of a typical batteryinto a cohesive design that is paper thin. The advantages of this design include an increased range of applicability and a simpler, more efficient fabrication process. Applications that will be explored include smart cards, medical devices and solar panels. This description will be followed by a discussion on ethical issues surrounding the paper battery, such as nanotoxicology; since paper batteries use nanotechnology, any health risks must be evaluated, especially for medical applications. However, the paper battery is a promising innovation whose efficient use of space will open up thousands of possibilities for electronic and mechanical design.***

Keywords: Carbon nanotubes, Microelectronics, Nanotechnology, Paper battery, Paper electronics

1. Paper Batteries: Paving the Way for Thinner Electronics

Electronic devices have evolved from large desktop computers to compact pocket-sized smart phones capable of running numerous applications; as technology slims down, engineers must find a way to pack more power into smaller spaces. One innovative solution is the paper battery. The recent development of the paper battery utilizes carbon nanotubes as electrodes and an integrated design of layers of electrolytes to create a thin and flexible battery [1]. The paper battery is extremely significant as it could open up possibilities for smart labels, medical devices, and electronic displays in advertising [2, 3, 4]. The paper battery distinguishes itself from other batteries in its use of carbon nanotubes, which allow for electrical efficiency and effective use of space, the details of which will be discussed in the following sections.

2. Nanotechnology Allows for Innovative Design: A Technical Discussion

In order to understand the novelty of the paper battery, it is important to first look at the design of traditional batteries. Then, through comparison, it will be possible to see the advantages that the slight changes from battery to paper battery bring.

3. Back to the Basics: A Review of the Traditional Battery

Traditionally, batteries are made up of a negative electrode, called an anode, and a positive electrode, called a cathode. These electrodes take up the majority of the space in the battery. They are separated by an electrolyte, which in traditional batteries is usually a liquid solution. This is embedded in a separator. The separator prevents the anode and cathode from touching, but still allows electrons to be transferred between the two [4]. Charge collectors made of metal sheets, meshes, or films provide charge transport to the battery's terminals, thus allowing the electrical energy to be transported to whatever device is attached to the battery [2]. Electrochemical charge-transfer reactions occur in the electrodes, converting chemical energy into electric energy that can be used. The amount of energy created depends on the type and amount of materials used [4].Lastly, all of these components are contained inside a metal or plastic case [5].

4. The Mechanics of Paper Batteries

Like traditional batteries, paper batteries also consist of two electrodes, an electrolyte, a separator, and charge collectors. However, unlike traditional batteries, paper batteries have one electrode made of conductive carbon nano tubes, the separator is made from plant cellulose (the main ingredient in paper), and the second electrode is made by coating the opposite side of the paper separator with lithium oxide. To provide the electrolyte, the paper is saturated with an ionic liquid – that is, an organic salt that is liquid at room temperature. Since the ionic liquid does not contain water, the batteries do not contain anything that will freeze or evaporate, enabling them to withstand extreme temperatures, ranging from -78°C to 177°C [1]. Also, since the battery is dry, it does not need a sealed case, as do traditional batteries [5]. It is also possible to make a super capacitor from the carbon electrode and paper separator by folding it in half so that the paper is in the middle and both the top and bottom electrodes are carbon. One such postage-stamp-sized super capacitor has a voltage of almost 2.5 volts, which is comparable to other standard super capacitors that are much larger[1].

5. The Secret Ingredient: Paper

The use of a paper separator has several key advantages over traditional mediums used. First, because of the intrinsic porous structure of paper, it not only serves well as a separator with lower impedance than commercial separators, but it also has good cyclability. Researchers at Stanford

University found no degradation after 300 cycles of recharging. Furthermore, a paper separator can also function as the mechanical support for the battery, making the battery cheaper and easier to manufacture since no additional materials are needed to provide the support [3].

The advantages of using a paper separator are also clear when considering its low resistivity in the electrolyte. Researchers at Stanford University built a paper battery and found the resistance of the electrolyte in the pores of the separator, R_{SL}, for varying thicknesses of the separator. The value of R_{SL} is given by the following expression:

$$R_{SL} = \frac{\rho_s L}{A}\left(\frac{\tau}{f}\right) \quad (1)\ [3]$$

where ρ_s is the resistivity of the electrolyte, L is the thickness of the separator, A is the area of the separator perpendicular to the axis of the electrode, τ is the ratio between the path length of the ions and the thickness of the electrode, and f is the ratio between the pore volume and the total volume of the electrode. The ratio τ/f indicates how easily the electrolyte can go through the separator. So a smaller ratio indicates less resistivity, and thus better conductivity. The researchers at Stanford found that commercial paper has a ratio of approximately 9.1, while standard separators have a ratio of approximately 28.8. This clearly indicates that paper, which is much cheaper than the standard separator, has a much better conductivity at the same thickness, making it much more suitable as a separator [3].

6. Variations on Structure

While the materials described above cover the basic structure and design of the paper battery, there also exist variations on the types of materials used. One particular type of paper battery is the zinc carbon battery. In this battery, zinc is used for the anode and manganese dioxide is used for the cathode. The electrolyte is comprised of an aqueous solution of ammonium chloride and zinc chloride. Since manganese dioxide is not a good conductor, carbon black must be added as a cathode conductor. This results in the following reaction:

$$Zn + 2MnO_2 + 2NH_4Cl \rightarrow Zn(NH_3)_2Cl_2 + 2MnOOH \quad (2)\ [2]$$

In this reaction, zinc from the anode combines with manganese dioxide from the cathode and ammonium chloride from the electrolyte to form diammine dichlorozinc and manganite. As this occurs, there is an exchange of electrons. In other words, as the current is drained, zinc is oxidized (loses electrons) at the anode and manganese dioxide is reduced (gains electrons) at the cathode. This movement of electrons from the anode to the cathode is what creates the electrical energy that can be used [2].

An alternative battery design proposes the use of carbon nanotubes in the charge collectors and the cathode conductor, which provides the conductance to the charge collector. The metal in the charge collectors is replaced by random networks of nanotubes, and the carbon black used for the cathode is also replaced by nanotubes. This structure could lead to a device consisting of only one layer per electrode, as depicted in Figure 1 below. This layer would contain a mixture of active material and nanotubes, and it would both replace the cathode conductor and provide conduction paths for current collection [2].

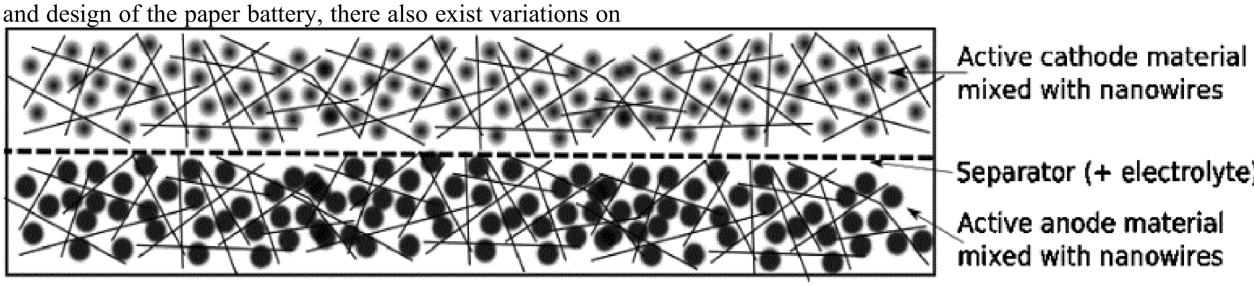

Figure 1: Proposed single-layer battery structure [2]

Recently, yet another change to the structure of the paper battery has been proposed. Yi Cui, assistant professor of materials science and engineering at Stanford University, found that using a chemical vapor deposition technique, silicon nanowires can be synthesized and used in place of the carbon nanotubes at the anode. Another option could be coating the carbon fibers with the silicon. Cui found that, theoretically, batteries with silicon nanowire anodes could store ten times as much energy as traditional graphite anode batteries.Cui is also conducting research to find a replacement for the traditional lithium metal oxide at the cathode. The substitute would, like the silicon, improve the efficiency and power of the battery, making it more useful as a battery and, thus, more marketable. One possibility that he is currently looking at as a substitute is lithium sulfide, but further research must be done before anyone can truly know its full potential [6].

7. Printing Batteries: A Review of Manufacturing Processes

The slight changes proposed to the structure of the paper battery allow for different manufacturing processes as well. However, not all processes are equally efficient or cost effective. Thus, in commercializing the paper battery, it will be necessary to consider which manufacturing process will be the most effective.

The original design of carbon-based supercapacitors and battery devices includes metal charge collectors. To make these devices, vacuum and metal thin film deposition methods are used. Essentially, deposition techniques consist of showering the substrate – in this case, the paper separator – with atoms or molecules – in this case, the metal. This metal coating expands molecule by molecule until a thin film is formed [7]. However, these fabrication processes are not compatible with printing, which would be a much more

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efficient process, as will be explained later. Thus, the use of metal charge collectors requires the use of less efficient methods to make the devices.

Another method currently being used to produce paper batteries takes carbon nanotubes suspended in water, making an ink-like substance, and dips the paper separator into the ink. Then the paper is heated in an oven to get rid of the water. However, this method is still not as efficient as a printing method, since time must be spent waiting for the paper to be dehydrated in the oven [8].

The design shown in Figure 1 replaces the metal charge collectors with random networks of nanotubes and consists of only one layer per electrode, thus eliminating the need for vacuum and metal thin film deposition and allowing for the use of a printing method or roll-to-roll fabrication. This would allow paper batteries to be produced in much the same way as newspapers [2].With the implementation of a printing method, it would be possible to cut down tremendously on the cost of the fabrication of the batteries and increase greatly the efficiency and speed of the process.

One company in particular has already started printing paper batteries. At Paper Battery Co. sheets of paper batteries are printed using roll to roll printing methods. However, rather than building the battery around a starting web or paper sheet as is done in most printing, the battery is print-formed from particles. This method is illustrated below in Figure 2. This printing allows the mechanical and storage properties of the sheet to be fit to the needs of the desired application. Furthermore, the sheets can be 'cut to fit' to accommodate any shape or size required [9]. So not only can the batteries be manufactured very efficiently, but they can also be easily fit to the specific design needs of their application.

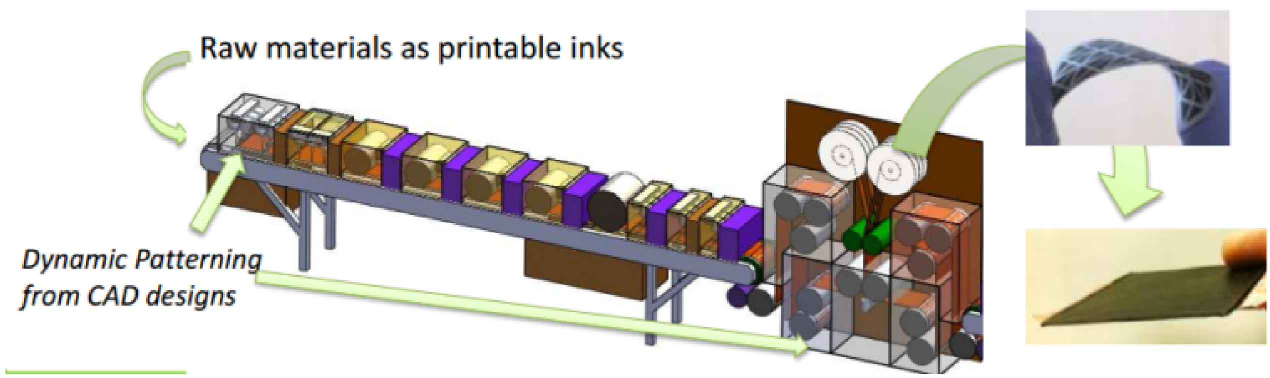

Figure 2: Roll to roll Printing [10]

8. Batteries Required: Applications of the Paper Battery

The paper battery has many applications ranging from greeting cards to medical devices; its flexibility and paper thin thickness allow it to be utilized in a wide array of products. Additionally, its biocompatibility allows for potential use in medical products and artificial organs. Moreover, stacking sheets of paper batteries could increase the overall power and lead to potential applications in larger electronics.

8.1 Radio Frequency Identification Device

One important application of the paper battery is its use in powering radio frequency identification devices or RFID [2,3]. In the past, RFID tags have been used to keep track of cattle and livestock [11]. However, paper batteries could allow companies to place RFID tags and smart labels on almost all products. For instance, in a grocery store using these RFID tags, the shopping cart could automatically process which items are placed in the cart, charge the customer's credit card and keep track of the store's inventories [11]. Although many supermarkets do not have this technology in store now, with the help of the paper battery to power these RFID tags and labels, this sort of technology could appear in the near future. RFID electronics also appear in road toll collection, animal tracking, passports and airline baggage management; all these potential uses could benefit by having a more powerful and light weight battery, allowing for a longer lasting tag and better data storage [11].

8.2 Media and Advertising

Besides tracking devices, paper batteries could also play a large role in media and advertising. For instance, researchers from Rensselaer Polytechnic Institute suggested that the paper battery "has enough power to light a small light emitting diode" [1]. Therefore, paper batteries could be used in greeting cards to power electronic displays or lights embedded in the card; they could also power any sort of audio device that would play a song or recording upon opening of the card. Other potential applications include using paper batteries to power electronic displays on packaging for items such as cereal boxes [3, 12]. The lightweight and compactness of a paper battery would allow the device to be easily fit into the cardboard design of a cereal box and display videos and play music, attracting more attention, and thus providing better advertising. .

8.3 Medical Devices

In addition to packaging and greeting cards, the size and flexibility of the paper battery also make it an advantageous power source for medical devices. For instance, the paper battery can be fit to the shape of a pacemaker, and because it is very light, it will not weigh down the devices, making it easier for the patient to hold inside them. Moreover, the paper battery is biocompatible. According to Victor

Pushparaj, senior researcher at Rensselaer Polytechnic Institute, the paper battery's "high paper contentand lack of toxic chemicals" make it safer than other batteries, even or use in body [13]. So the paper battery would be an optimal solution for powering devices that work inside the body such as artificial organs. In fact, the paper battery can even use blood, sweat, or urine as the electrolyte [1, 4]. This would be an ideal power source for artificial organs where bodily fluids are abundant and can recharge the device. Another application is temperature monitors on blood bags [11]. Since they are lightweight and flexible, it would be an efficient way to monitor the temperature of blood throughout transportation and storage.

8.4 Large Scale Electronics

Although the compactness of the paper battery is one of its major benefits, the paper battery is not limited to small devices; in
fact, it has many potential applications in larger devices such as cars, laptops and wind farms [14]. Because the paper battery has the ability to be recharged, it could be used in a typical car battery. By integrating the paper battery into the design of a traditional battery, it is possible to decrease the weight of the battery by up to twenty percent; this would be especially relevant for electric and hybrid cars, since a reduction in weight could potentially increase efficiency [14]. It has also been suggested that the paper battery could power car doors since the paper battery can be formed to fit the curved shape of a vehicle [13]. Additionally, researchers from Rensselaer Polytechnic Institute have proposed that the "paper batteries' light weight could make them ideal for use in automobiles, aircraft, and even boats" [13]. By stacking large sheetsof paper batterieson topof each other, it would be possible to increase the voltage and increase the power, thus making the paper battery capable of providing energy for larger machines. Furthermore, according to Yi Cui of Stanford University, this pile of paper batteries "could also inexpensively help solar and wind farms store what energy they generate" [14]. For instance, the flexibility of the paper battery could allow it to be used in solar panels of varying shapes and its ability endure numerous recharge cycles would make it an ideal device to capture the energy from solar power or wind power.

8.5 Endless Possibilities

The paper battery has numerous applications, a few of which are detailed previously. There exist many potential applications of the paper battery that have not yet been fully explored; such applications include smarts cards where debit cards which could electronically display the amount of money left on the card, thus eliminating the need to check one's balance online or go to a kiosk [12]. Others include possibilities include wearable electronics and flexible solar panels and [2, 15].With such a wide range of applications from greeting cards to medical devices to cars, it becomes evident that paper battery will have an extensive impact on daily life.

9. Nanotoxicology: Ethical Concerns Regarding the Use of Nanotechnology

Before encouraging the widespread use of a new technology, one must always consider the possible ethical concerns surrounding that technology. One of the major ethical issues regarding paper batteries is the potential adverse health effects of carbon nanotubes on the human body and the environment. Nanotoxicology studies have shown that the surfaces of certain nanoparticles have many sharp points, much like asbestos. These sharp points make it difficult for macrophages, or immune cells, to clear foreign particles from the body [16]. Moreover, as the size of these particles decreases, the surface area increases, allowing for better transport across cell barriers and increased ability to react with important cell structures, such as microtubules and DNA [17]. As a result, nanoparticles can have potential harmful health effects, especially in the lungs [18]. Although direct exposure with nanoparticles or fibers is unlikely in many of these applications, as it will be stored away in part of the electronic, it is important to consider, for instance, any possible damage to the electronic that would perhaps break the case and expose the nanoparticles to air and the user. More importantly, any adverse health effects create occupational hazards for those manufacturing the paper batteries.

10. Results of Nanotoxicological Research

Because of the size of nanoparticles, imaging the nanoparticle in tissue has been a challenge in nanotoxicologic studies. However, many of the studies, which will be explained shortly, use cellular responses to assess the effects of carbon nanotubes. A study presented at the American Chemical society national Meeting in 2004 showed that exposing single wall carbon nanotubes to *in vitro* keratinocytes and bronchial epithelial cells "resulted in oxidative stress, as evidenced by the formation of free radicals, accumulation of peroxidative products, and depletion of cell antioxidants" [18]. These free radicals are molecules that can react with chemicals in the body and induce cellular damage; since the exposure displayed decreased levels of antioxidants, which work against free radicals, it is clear that the carbon nanotubes had a negative effect on cells. A study using live mice showed similar adverse effects; after exposure to single walled carbon nanotubes, the mice developed fibrosis in their lungs, as early as one day following exposure [17]. In other words, when the lungs of mice were directly exposed to carbon nanotubes, the mice showed significantly increased formation of connective tissue; since this sort of overgrowth can block fluids from bringing nutrients to cells, it shows that the nanotubes can have harmful.

These studies performed with rodents are consistent with research using human subjects. For instance, scientists have found high rates of deposition of ultrafine particles in the respiratory tract of human subjects in addition to showing "effects on the cardiovascular system, including blood markers of coagulation and systemic inflammation and pulmonary diffusion capacity" [18]. These results demonstrate that it is not only possible for nanoparticles to become lodged in the linings of the lung and trachea but also for nanoparticles to induce significant cellular stress. In addition, studies performed with in vitro human lung fibroblasts also increased cell proliferation, collagen production and increased expression of matrix metalloproteinase-9, a protein involved with cell death [17]. Any up regulation or down regulation of biomarkers such as these can indicate stresses on the cell. Therefore, it becomes clear that nanoparticles can have adverse health effects.

10.1 Environmental Effects

Additionally, the carbon nanotubes could potentially end up in the environment, as paper batteries from smart cards and used temperature monitors are disposed, causing damage to the soil and plants [17]. Ecological studies have shown that the exposure of nanoparticles to largemouth bass fish resulted in lipid damage in the brain. Also, other studies have demonstrated an up regulation of immune system and tissue repair proteins in fish exposed to nanoparticles [17]. Because nanoparticles have been found to have these negative effects on animals in the environment, the use of nanotechnology also raises environmental concerns. For instance, is it ethical to continue using nanotechnology when products like the battery could potentially harm the wildlife? Another important aspect to consider is whether mass production of nanotechnology will result in nanotubes appearing in the environment, and thus our food and water supply. Furthermore, even if the nanoparticles are manufactured to be biocompatible, it is possible that upon disposal, the environmental factors, such as the air and ultraviolet radiation, could cause the coatings to deteriorate, exposing the perhaps harmful material [17].

11. How Nanotoxicology Affects the Paper Battery

In spite of these risk factors associated with nanotechnology, we still support the production and development of paper batteries. With the paper battery, it is unlikely that such direct and concentrated exposure will occur as it modeled in these studies. Also, the battery would be encased and in many applications, such as solar panels, boats, wind farms, there would be little human contact with these devices. The paper battery is relatively safe compared to other nanotechnology products such as sunscreen and various medical diagnostic tests where nanoparticles are directly exposed to the body and where absorption of nanomaterials is more likely.

Therefore, we suggest that researchers and engineers address these health concerns rather than eliminating the paper battery as a potential power source. Scientists should take into account any health effects by further testing the toxicity of manmade nanoparticles and carbon nanotubes prior to commercializing paper batteries. Since nanotechnology has appeared in a variety of products besides the paper battery, such as cosmetics, tires, and filters, an effort to study nanotoxicology would be a valuable use of time and money. Once researchers can define safety proceduresfor carbon nanotubes used in paper batteries, it would be possible to better protect manufacturing workers from carbon nanotube exposure and then commercialize the paper battery.

12. An Investment for the Future

Keeping ethical concerns in mind, it is important to be reminded of the significance of the paper battery in today's society. Not only does it have numerous advantages over traditional batteries, but it also has the potential to revolutionize both electronics and everyday shopping.

Changing the Way We Design Electronics

One of the most remarkable aspects of the paper battery is its ability to be rolled and folded without any loss of efficiency. According to chemical and biological engineering professor Robert J. Linhardt at Rensselaer Polytechnic Institute, "Being able to mold the battery to any shape that corresponds to the space available is a real advantage" [1]. This is clear when one considers the dependency of electronics today on their batteries. With more flexible batteries, electronics will be able to take on any shape or form. Along the same lines, the paper battery's capacity is proportional to its area. So as Baruch Levanon, chief executive of Power Paper, the company that developed the paper battery, said, "The more area, the more energy, so you adjust the battery to the needs of the product, not vice versa" [12]. So if a product requires more or less energy, onecan simply change the size of the battery, rather than having to design the product around set amounts of power that a given battery can supply. This opens doors for new electronics to take on any shape or form imaginable. They no longer have to be held back by the constraints of their batteries.

13. The Importance of Being Paper

In addition to expanding the world of electronics, the paper battery has several important advantages over traditional batteries. As Yi Cui of Stanford University points out, nanomaterials – such as the carbon nanotubes in paper batteries – are better conductors than traditional materials because they are able to move electricity more efficiently[19]. In other words, paper batteries will lose less electricity due to inefficient conductors than traditional batteries lose.

Another advantage that paper batteries have over traditional batteries is the materials they are made up of. Since paper batteries are dry they require no casing while traditional batteries must be encased and sealed in metal or plastic. Not having a case eliminates a step in the manufacturing process and cuts down on the cost of manufacturing the battery. In addition, the paper substrate and the electrolytes used in paper batteries are environmentally safe and nontoxic. Therefore, paper batteries would have less of an impact on the environment than traditional batteries, which contain harmful acids [5].

Perhaps the most obvious advantage of paper batteries over traditional batteries is their size. One square-inch of a Power Paper battery can provide a voltage of 1.5 V – as much as common consumer batteries – and hold its power for over two years [5]. So, in a time when electronics are shrinking to paper-thin dimensions, a battery as thin as a paper battery is almost necessary, and it has already been developed enough to have comparable outputs to traditional batteries. Further research into the types of materials best suited for paper batteries can only lead to more breakthroughs in the field of paper electronics.

As an example of the advantages of a paper battery over more traditional batteries, researchers at Stanford University compared a paper battery that they made toa soft battery developed by Enfucell Inc. and Blue Spark Inc. The Enfucell battery, which is printed on a plastic substrate, is neither rechargeable nor flexible, while Stanford's paper battery is both. In addition, Stanford's battery has an energy density of 108 mWh/g and is only about 300 μm thick. Enfucell's battery, on the other hand, is more than twice as thick and has less than half the energy density of Stanford's battery, as shown in Figure 3, where the arrow indicates the improvement direction [3].

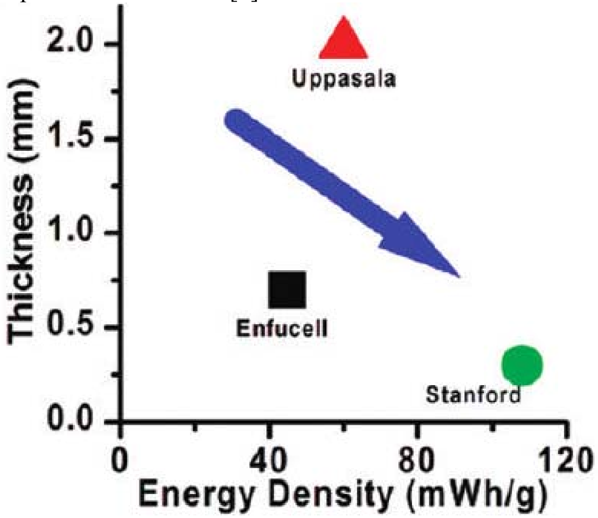

Figure 3: Energy density comparison graph [3]

14. Additional Advantages

Besides having obvious advantages over traditional batteries and having the potential to accelerate technology forward, the paper battery also has encouraging economical benefits. A common concern is that paper batteries would be too expensive to commercialize since carbon nanotubes, which are fairly expensive, are an essential component of the paper battery. However, while carbon nanotubes currently cost around $200 per gram, paper batteries only need less than 0.2 milligrams of carbon nanotubes per square centimeter of battery. Therefore, the cost is only about two cents per square centimeter. This means that the cost of the carbon nanotubes for paper batteries is essentially negligible, making them a promising investment [3].

Finally, the paper battery is a significant technology because it has the potential to revolutionize the way we shop. Its aforementioned potential applications in cereal boxes and other food products and packaging could make even grocery shopping an exciting and interactive experience. Furthermore, the new method of purchase with the use of RFID tags would make shopping more time efficient by eliminating the need for a checkout counter, and the use of smart cards would give any shopper the ability to check their balance at any time.

15. Paper Batteries: Thin, Flexible Power

Because the paper battery offers an integrated design of the electrode and the electrolyte, the paper battery has many advantages over other batteries, including electrical efficiency and compactness. The flexibility gives the paper battery a mechanical advantage in that the battery can be fit to the electronic, instead of having to build the electronic around the battery. Such advantages make the paper battery a good option for many applications such as smart cards and temperature monitors. As technology trends towards thinner electronics and electronic displays, the paper battery will play a larger role in small electronics. While the paper battery is still in a stage of research and development, it is clear that the paper battery will have significant impact on powering portable electronics in the future.

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