THIN FLEXIBLE POLYMER-BASED ENERGY SYSTEMS FOR LOW-POWER WIRELESS MONITORING DEVICES

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Abstract: In this work we present the novel design for a polymer based energy harvesting and storage system for thin flexible wearable biomedical devices. The energy system employs novel long lasting polymer solar cells and polymer hybrid sodium-ion super capacitors capable of both immediately storing harvested photo energy and slowly discharging power for micro to milli-watt devices. The polymer nature of this platform system makes its suitable for roll-to-roll print manufacturing, supporting applications requiring high volume and low cost. We present performance results for the two energy system components along with results for an integrated single cell energy system.

1 INTRODUCTION

One the most important challenges in sensors and systems deployed in wireless, portable or wearable applications will be in selecting the energy source. For most electronics, the energy required to power its microprocessor is negligible, however, its' sensor and actuator elements may consume significant amounts of power. In medical applications as in remote hospitals or home-monitoring, ultra-lightweight systems with small footprints operating autonomously are required. Often the primary energy source for such applications is a battery, which must be substantially larger than the system it powers in order to meet the requirements for wireless use. In wearable systems the battery footprint becomes a very important issue.

Recent efforts to reduce this battery footprint along with increasing device lifetimes and reliability have included supplementary power sources using solar or mechanical energy harvesting. Integrated solar cells on outdoors wireless sensor nodes, and vibration energy harvesters used on automotive sensor units are some commonly found examples. Assisted powering of autonomous electronic devices with energy harvesting is a non-trivial challenge that requires the matching of function and environment, and hence, there is no universal solution (e.g., photovoltaic energy harvesting is not suitable with a subcutaneous implantable bio-sensor).

Solar energy is attractive as it is arguably the most accessible energy source found on Earth. Silicon-based solar cells can achieve 20% in power conversion efficiency (PCE), but their high material and manufacturing costs along with rigid and fragile structures discourage greater use. Unlike silicon-based solar cells, polymer solar cells (PSC) cost much less to manufacture due to roll-to-roll processing and the extremely low quantities of active material required. The polymer inks used for the active layers can be printed onto thin, flexible substrates using a variety of print-based manufacturing such as roll-to-roll, or ink-jet printing. Recent advances in polymer solar cell technology have increased its PCE to higher than 8% (Green et al, 2011) and efficiencies could reach as high as 17% in the near future (Park et al, 2009). PSCs have comparable PCEs to silicon-alternatives such as Cadmium-Telluride (CdTe) and Copper-Indium-Gallium-Selenide (CIGS) solar cells without the toxicity concerns. Combined with a low cost of manufacturing, PSCs can offer a very attractive sub-dollar-per-watt figure, and are anticipated to greatly surpass silicon-based solar cells in both use and application range.

Despite their exciting outlook, a few challenges hinder the widespread use of flexible PSCs. First,

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their lifetime is limited when they are fabricated in air. A controlled fabrication chamber is needed to completely eliminate oxygen and moisture in order to produce long-lasting PSCs; however, such specialized equipment greatly increases the fabrication costs. Second, to provide a complete energy solution, the PSCs must be integrated with an efficient energy storage reservoir. This reservoir system should exhibit both high power and energy densities, and must be similarly thin, flexible, and lightweight to take advantage of all the PSC characteristics.

Recent studies have shown that ionic polymer metal composites (IPMC) as energy storage films exhibit supercapacitor and rechargeable battery like characteristics (Landrock and Kaminska, 2011). Polymer ion-exchange membranes based on perfluorosulfonic acid (PSFA) based films such as Nafion™ (DuPont) and Aquivion™ (Solvay Solexis) are low cost and widely available. Without hydration these ion exchange membranes can be used in the construction of polymer energy storage (PES) devices, which can be conveniently shaped and scaled into nearly any dimension or geometry, and operated at high-temperature conditions (Landrock and Kaminska, 2010). Furthermore, the ions can be tailored within the polymers for specific applications. Here we present on a sodium-ion (Na+) hybrid super-capacitor. Sodium-ions have the distinction of being very stable, low in toxicity and high in energy density, making them an ideal choice for use in biomedical devices.

Many recently developed biomedical devices consume power measured in the mW and even nW range. Marzencki et al (2010), have presented a wearable wireless sensor system requiring 2.1V operating voltage with 1.86mW to 16.6mW power used in conjunction with a mobile phone for data collection; while Xiaodan et al (2009) have reported on a 1V sensor interface chip requiring a mere 450nW of power. However in order to take advantage of these devices small footprint and flexible nature a powering system that is comparably small and flexible.

This paper presents a fully flexible polymer-based powering system with a footprint of 1cm^2 and less than 50um thick, capable of supplying an operating voltage of 2.7V and 100uA continuously during day light hours.

2 DEVICE COMPONENT ARCHITECTURE

Several methods in improving the lifetime of polymer/organic solar cells have been reported in the recent past. Inverted solar cell structures were demonstrated to have better stability in air by (Krebs, 2008), while allowing for better roll-to-roll processing. The stability of the enhanced, inverted PSCs is up to a few weeks, however, with a low power-conversion efficiency (PCE) of ~0.08% (Manceau, 2010). A new interfacial layer containing chromium-oxide was inserted between the cathode and active polymer to improve performance and stability of polymer solar cells (Wang, 2010). The improved interfacial layer provided stability up to one week holding a PCE of 3.5% in an inert environment, but decreased by half within 12 days (Wang, 2010).

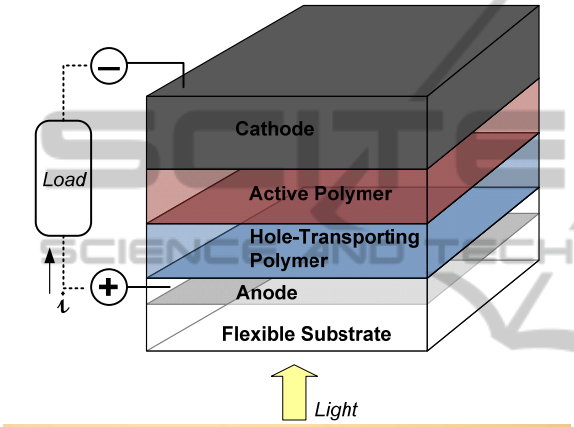
Thin, flexible, disposable batteries have been demonstrated and are available (in limited quantities) off-the-shelf from niche companies that provide “soft” batteries such as Enfucell, PowerPaper and BlueSpark. The batteries are primarily based on zinc/manganese-dioxide technology. Typically a zinc anode and manganese dioxide cathode surround a polymer electrolyte. Most devices range from 0.3mm to 1mm thick, and provide energy capacities between 2 to 5mAh/cm^2. The nominal cell voltage is configured to 1.5V, a requirement for aqueous electrolytes as water electrolyzes above 2V. The internal resistances of the devices are typically high, around 300Ω. The energy sources also only provide low nominal continuous current (0.03mA to 1.5mA). It is common for the devices to have a limited operating temperature range between -20°C to 60°C. These devices are not applicable tor solar energy harvesting applications, where cells can easily be heated under the sun to temperatures above 70°C.

Here we present the latest performance results of novel PSC and PES devices as well as a combined system for energy harvesting and storage in operation.

2.1 Stable Polymer Solar Cells

It is well known that polymer solar cells are subject to oxygen and moisture degradation. Figure 1 illustrates the typical structure of a solar cell comprised of a bulk heterojunction (active layer) such as poly(3-hexlthiophene) and [6,6]-phenyl C61 butyruc-acud-nethyk-ester (P3HT:PCBM blend). The active layer degrades due to oxidation of sulfur

atoms in the P3HT thiophene ring (Krebs, 2008). Oxygen and moisture in the active layer are generated by two known mechanisms. The first is due to oxidation of the cathode (typically Aluminum) that allows for Oxygen diffusion directly into the active layer. The second is oxygen diffusion into the active layer from the transparent anode, typically Indium-Tin-Oxide (ITO) via the hole-transporting layer, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) commonly known as PEDOT:PSS. This degradation leads rapidly to dramatic drops in PCE and failure of the device.



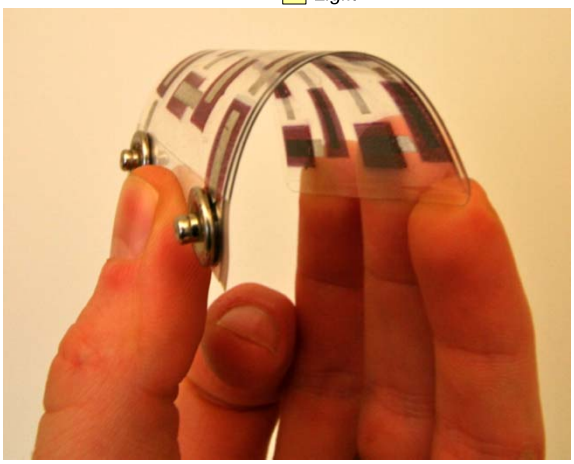


Figure 1: Structure of a generic polymer solar cell and photograph of a working polymer solar panel. The panel consists of 12 cells connected in series and can generate 5Vin outside light.

Photooxidation due to exposure to UV rays acts as a catalyst in the degradation process. PSC device life times typically run from several hours to several days (Manceau, 2010; Wang, 2010). The high-quality polymer solar cells that are achieved typically are done so in controlled fabrication chambers filled with inert gas (e.g. nitrogen) or under high vacuum. The additional costs associated with the use of specialized air-controlled and high vacuum chambers conflicts with the cost effectiveness of roll-to-roll (R2R) or print-types of manufacturing.

Our group has recently shown a polymer solar cell with a PCE around 2% that has lasted for over one year and shows little evidence of degradation using a novel cathode (Hohertz et al. 2011). The novel cathode design allows diffusion of Indium ions into the active layer, which attract oxygen atoms creating a non-reactive Indium-oxide compound (In2O3) before degradation can occur. Evidence of this diffusion has recently been shown using X-ray photoelectric spectroscopy (XPS), a sensitive technique that probes the chemical composition within a sample (Hohertz et al., 2011). Figure 2 shows XPS results (Kratos Axis Ultra DLD XPS) of active layers from newly prepared and six month old novel PSCs in comparison to a standard PSC fabricated with an Al cathode. It can be clearly seen from the energy peaks that In, InO-, and In_2O_3 are present in the novel PSC sample after 6months, and appears to be just forming in the newly fabricated samples. The Al-cathode device however does not show this behavior. This result strongly suggests that Indium diffuses into the active layer and forms a strong oxide bond, preventing the oxygen atoms from destroying the Sulfur bonds.

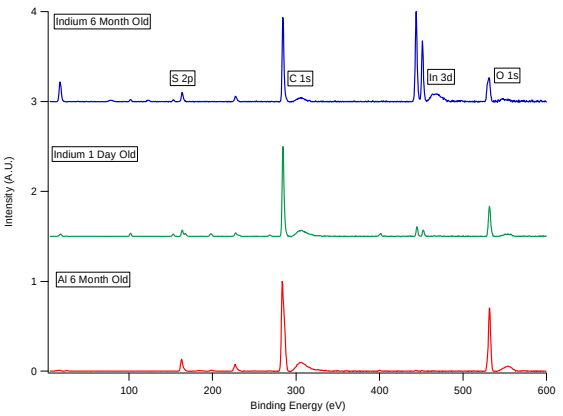


Figure 2: Broad-spectrum scans of Aluminium Cathode vs. Indium Cathode based PSCs.

2.2 Hybrid Polymer Energy Storage

We have recently demonstrated a novel hybrid energy storage film, which exhibits high temperature resistance, good chemical resistance, and good durability, an ion-transport/electrolyte medium (Landrock and Kaminska, 2011; Landrock, 2010).

The traditional fabrication processes for PFSA-based ionic polymer metal composites involve tedious electrode compositing steps to ensure good electrode implantation; however, we have shown that simplified fabrication techniques can results in devices (Figure 3) with reasonable power and energy storage capacity (Landrock, 2010) ranging from 40F/g to 332F/g and 31mAh/cm^2 respectively with a working voltage of 2.7V for a single sodium-ion cell.

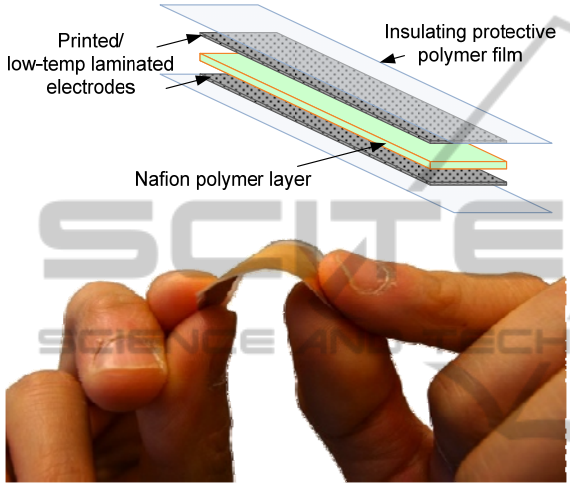


Figure 3: Schematic of a IPMC-based Na-ion hybrid energy storage film and photograph of a basic device.

2.3 Architecture of Energy System

For an energy-harvesting device to be useful a storage reservoir is necessary for that energy unless it can be consumed immediately through a matching load. Energy harvesting devices are usually independent from the energy storage reservoir, which is inefficient, inconvenient, and as an incomplete system is a major deterrent when considering energy harvesting solutions. Here we show an integrated powering system that combines PSCs along with PES in a thin, compact configuration. Figure 4 illustrates the flexible energy stack, as a printed film roll, composed of an PSC functional layer and a PES layer disposed on the two opposing surfaces of a flexible carrier substrate. The carrier substrate acts as the structural backbone of the flexible energy stack, and can range from 10 to several 100s of microns thick, largely depending on the carrier substrate requirements. The electrical connections and circuit routing between the PSC, PES, and other application specific system components are also made within the carrier substrate layer. This is similar in construction to flexible circuit board functions. The stack is further protected on both sides by UV-shielding plastic films that transmit only the visible light within the primary, non-damaging, absorbing wavelengths of the PSC. The percentage of the light intensity transmitted through the protective film is dependent on the thickness and composition of the polymer where 70-90% transmission of the incident light can be expected when the film is in the range of 100µm to 200µm thick.

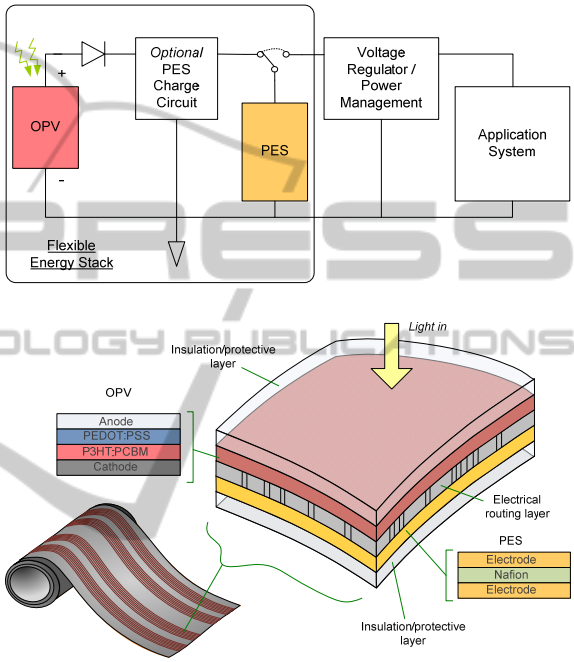


Figure 4: Architecture of integrated energy harvesting/storage system along with the system blocks for the integration configured to power a device.

3 EXPERIMENTAL RESULTS & SYSTEM PERFORMANCE

The operational performance of the PSCs was studied under ambient conditions using a calibrated solar simulator (AM1.5G 100mW/cm2, Newport Solar Simulator) as well as in direct sunlight outdoors (latitude 52°25'N, Vancouver CANADA). Results for a single cell are summarized in Table 1 in comparison to short-lifetime conventional Al-cathode based PSCs. The stability of the device was evaluated based on the percentage drop in performance over time. The conventional Al-based PSC showed a decrease in all categories of performance by more than 50% within 24 hours, and fully fails within 2 days; whereas the novel-cathode

PSC show less than 5% decrease in open-circuit voltage (VOC), short-circuit current (JSC), Fill Factor (F.F), and PCE even after one year. I-V characteristics are shown in Figure 5. It can be expected that with improvement in active polymer blend formulation, substitution with higher efficiency photoactive polymers, more conductive anode materials, more efficient electrical interconnects, even higher PCE values can be achieved.

Table 1: Polymer Solar Cell Performance.

Measurement	PSC Novel Cathode	Conventional PSC with Al Cathode
V_{OC} (V)	0.55 / 0.52	0.6 / 0
J_{SC} (mA/cm2)	8.5 / 6.2	8.5 / 0
F.F. (%)	65 / 60	70 / 0
PCE (%)	3.03 / 2.05	3.6 / 0
Stability (days)	**>365**	**1**

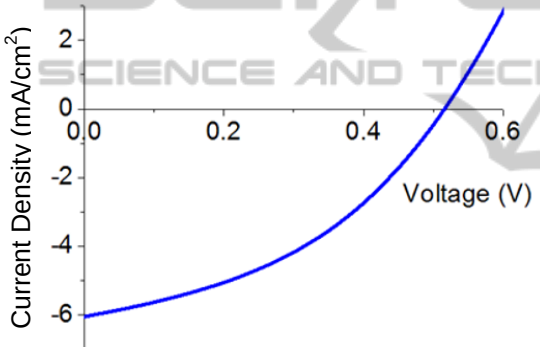


Figure 5: I-V curve for a single PSC after 1 year of operation.

The energy storage films have a nominal capacitance of approximately 3mF/cm^2, or 300F/g. The methods of measurement and characterization are reported in further detail under another article (Aristizabal, 2011). The PES films also show very stable energy storage attributes in the range of 20°C to 100°C, with less than 10% drop in capacitance at 110°C compared to room temperature. The breakdown voltage of a 1cm^2 device is approximately 10V. The PES film is also fast charging, and is suitably charged with input sources anywhere from 0.5mA up to 1000mA. Figure 6 shows the typical discharge curve of a 1cm^2 PES cell. It is charged for 2min at constant voltage of 4V, 10mA current limited (e.g. equivalent of what a small array PSCs connected in series can provide). The PES cell is discharged through a constant 100uA load until the voltage falls below 50% of its initial value. The plot shows the full 2.7V potential from the sodium-ions.

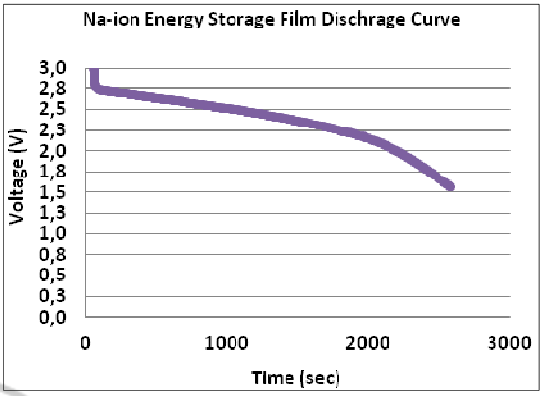


Figure 6: Discharge profile for a single PES cell with a constant current load of 100uA charged with 5V.

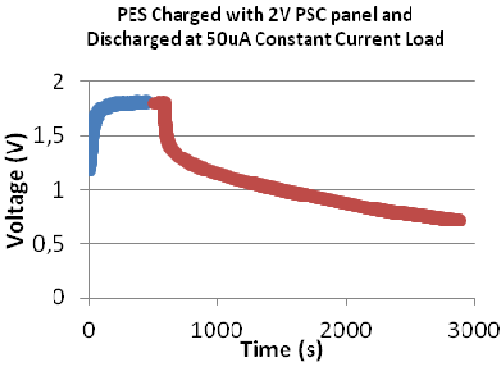


Figure 7: Energy system test results: top photograph shows the actual energy system with PSC panel and PES cell that is just viewable behind the solar cells (gold coloured cell); the bottom plot shows charge/discharge curve of a PSC-PES system in operation.

Testing of the integrated three-dimensional (3D) system was initiated by connecting a PES to a PCS as seen in Figure 7, and ambient indoor low-light conditions of 0.2 W/m^2 were used to radiate the PSC. Measurement of the charge and discharge of the PES was done by connecting a digital acquisition

(DAQ) module to the setup, which allows real-time monitoring. The 3D test layout configuration is however ideal for device performance. In two-dimensional configurations long interconnects between the organic devices and the capacitors result in excessive energy lost reducing the effectiveness of PCSs. This low-light demonstration shows the versatility of the 3D energy harvesting system configuration. With more techniques (such as vias and monolithic fabrication) even more energy efficient 3D configurations can be envisioned and have been previously reported by our group (Landrock et al., 2011), however they are not always convenient for testing purposes.

4 CONCLUSIONS

This work describes an energy harvesting system comprised of polymer solar cells and a hybrid polymer energy storage film. We have shown that this system may be used to generate and store useful amounts of electrical power, up to several milli-watts per cm^2, making it useful for a number of wireless biomedical sensors applications.

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