Printed Electrodes for Flexible, Light-weight Solid-state Supercapacitors – A Feasibility Study

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Abstract

Purpose - It has been shown previously that offset lithography, a common printing technique, can be used to make electrodes for energy storage devices such as primary cells [1,2]. This paper reports on the feasibility of the manufacture of printed rechargeable power sources incorporating, in the first instance, electrode structures from the previous study, and moving on to improved electrode structures fabricated, via flexographic printing, using commercially available inks.

Design/methodology/approach – A pair of the original Ag/C electrodes, printed via offset lithography, were sandwiched together with a PVA-KOH gel electrolyte and then sealed. The resultant structures were characterised using electrochemical techniques and the performance as supercapacitors assessed. Following these studies, electrode structures of the same dimensions, consisting of two layers, a silver based current collector covered with a high surface area carbon layer, were printed flexographically, using inks, on a melinex substrate. The characterisation and assessment of these structures, as supercapacitors, was determined.

Findings - It was found that the supercapacitors constructed using the offset lithographic electrodes exhibited a capacitance of 0.72 mF/cm^2 and had an equivalent series resistance of 3.96 Ω. The structures fabricated via flexography exhibited a capacitance of 4 mF/cm^2 and had an equivalent series resistance of 1.25 Ω. The supercapacitor structures were subjected to bending and rolling tests to determine device performance under deformation and stress. It was found that supercapacitor performance was not significantly reduced by bending or rolling.

Originality/value - This paper provides insight into the use of printed silver/carbon electrodes within supercapacitor structures and compares the performance of devices fabricated using inks for offset lithographic printing presses and those made using commercially available inks for flexographic printing. The potential viability of such structures for low-end and cheap energy storage devices is demonstrated.

Keywords - Conductive inks, Printed electronics, Offset lithography, Flexography, Supercapacitors

Classification - Research paper

Introduction

Energy is increasingly becoming one of the great challenges for society, industry and the world in general. Energy storage, an intermediate step to the versatile, clean and efficient use of energy, has received worldwide concern and increasing research interest [3]. A supercapacitor is an energy storage device which stores charge as electrostatic energy, as opposed to electrochemical energy in batteries. In supercapacitors, there are typically four main components, the current collector/substrate, high surface area active material, electrolyte and insulating separating material. In the presence of a potential difference across the electrodes, the electrostatically charged ions in the electrolyte migrate towards the electrodes of opposite polarity due to the electric field created by the applied voltage. Charges are stored this way until the supercapacitor is discharged.

The main advantages of supercapacitors, over secondary cells or batteries, are that they have very long cycling life (>10,000 cycles), rapid charging and discharging (on the order of seconds) and have high power output. They have many diverse applications ranging from large scale to small scale uses. On the large scale, supercapacitors can be used alongside batteries to provide the power needed for fast acceleration in hybrid electric vehicles. This eases the work load on the battery and extends its life-time. Smaller scale applications include small gadgets and toys in which only a small energy density is required. They can also be used in memory backup systems, GPS devices, modem cards etc.

As the capacitance of a supercapacitor is directly proportional to the electrode surface area, it is of interest to develop stable conducting high surface area materials. Carbon based electrodes are ideal as it is a cheap and widely available material, which is highly stable in a range of electrolytes (acidic and basic) and it is stable at a range of potentials. In this paper we use silver and carbon inks to produce electrodes by offset lithography and flexographic (flexo) printing and study the performance of the electrodes in supercapacitors.

As flexographic printing is a high throughput method with high excellent reproducibility, this research offers insights into the mass production of low-cost supercapacitor electrodes using printing. Flexographic printing involves a rubber or polymer printing plate. The image areas on the plate are raised. Distances range from a fraction of a millimetre to a few millimetres. Ink is applied to the plate cylinder by an anilox roller. This roller is engraved with a fine cell pattern covering the surface (typically 80-200 cells/cm). Flexo inks are very liquid, and often the anilox roller sits in an ink bath, with excess ink removed by a reverse angle doctor blade. The printing plate transfers ink to the substrate, which is supported by a metal impression cylinder, using slight pressure (Fig 1). Inks may be water or solvent based. The raised image on the plate is covered in a uniform layer of ink using an anilox roll, which is an ink-metering device, its surface made up of millions of small wells or cells to carry a precise volume of ink used to transfer the ink to the flexographic plate. The inked plate then is pressed against the substrate using an impression roll. Fine pitch adjustment screws are used to control the pressure of the print mechanically through all stages of the process.

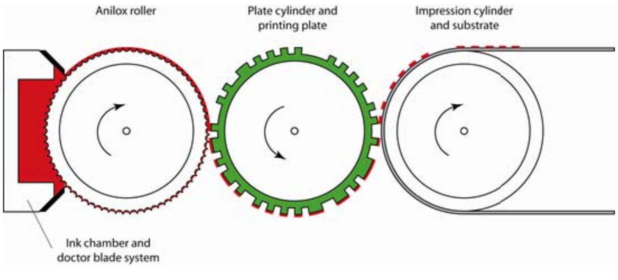

Figure 1 The Flexographic printing process

Flexo is a process capable of producing fine lines with plates manufactured using modern techniques, but as a letterpress-type process it is liable to produce an ‘ink-squash’ pattern especially around solid areas and lines [4]. Flexo used to make electrodes for electrochemical devices has not been fully explored; therefore the aim of the present paper is to study their performance in supercapacitors and compare such electrode performance with those deposited using offset lithography.

Discussion 1 Supercapacitors via Offset Lithography

The electrodes used to fabricate primary voltaic cells previously were made via offset lithography. The electrodes consisted of two layers, silver and carbon, on a polymeric substrate. The silver layer is used as the current collector and the carbon is used as the high surface area active material. The carbon layer must fully cover the silver layer to mask any electrochemistry of the silver layer. For the present study, the use of these electrodes for a rechargeable energy storage device, a supercapacitor, was designed, fabricated and characterised to determine its feasibility for such an application. For supercapacitors, the capacitance is directly proportional to the surface area of the active material, the carbon layer in this case. Therefore the surface morphology of the carbon layer is an important aspect of the electrode. The surface morphology of the substrate, silver and carbon layer is shown in the scanning electron microscope (SEM) images in Figure 2. The substrate was treated in order to increase surface roughness to ensure good adhesion of the lithographically printed silver layer. The surface of the substrate can be seen in Figure 2a and 2d, it confirms that the surface is roughened on the micrometre scale. Figure 2b and 2e show the surface of the silver layer, and figure 2c and 2f shows the surface of the carbon layer. It is evident that the carbon layer is very smooth and consisted of large platelets ranging from 4 to 10 μm. Figure 3 shows the interface between the substrate, silver and carbon layer. The interfaces are very diffuse and are not very well defined.

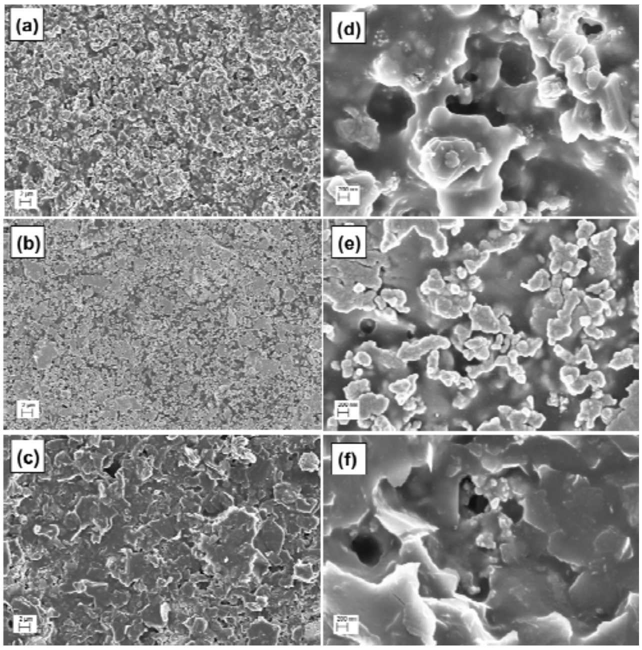

Figure 2. SEM images of the Melinex substrate (a), and lithographically printed silver layer (b) and carbon layer (c) at 5 kX magnification. (d), (e) and (f) and (h) are the respective images at 50 kX magnification.

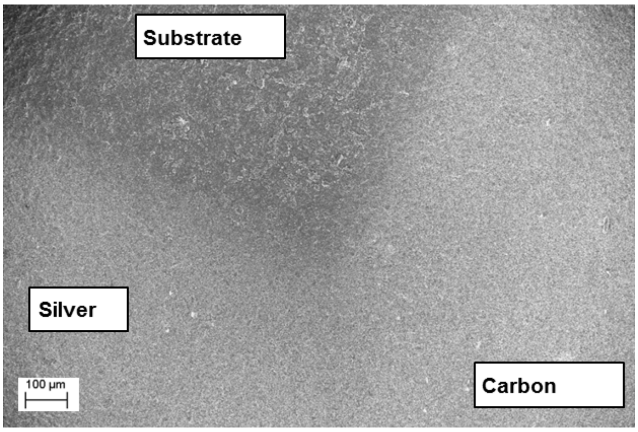

Figure 3. SEM images of the interface between the substrate, and lithographically printed silver and carbon layers at a magnification of 200 x.

Discussion 2 Supercapacitors via Flexography

The SEM images of the flexographically printed silver and carbon layer on an untreated Melinex substrate are shown in figure 4. Figure 4a and 4d show that the surface of the untreated Melinex substrate is very smooth and uniform. Figure 4b and 4e shows the surface morphology of the silver layer. It can be seen that it consists of micrometre sized particles which form a porous structure. The surface of the carbon layer on top of the silver layer can be seen in figure 4c and 4f. The carbon layer consists of very small particles which range from 50 – 100 nm in size. The outline of the silver layer underneath can be seen and it is apparent that the carbon layer has not fully covered the silver layer, as the larger silver particles can be clearly seen in figure 4f. The interface between the substrate, silver and carbon layers are shown at two magnifications in figure 5. It is evident from these SEM images that the interface is very well defined, compared to the interface of lithographically printed layers.

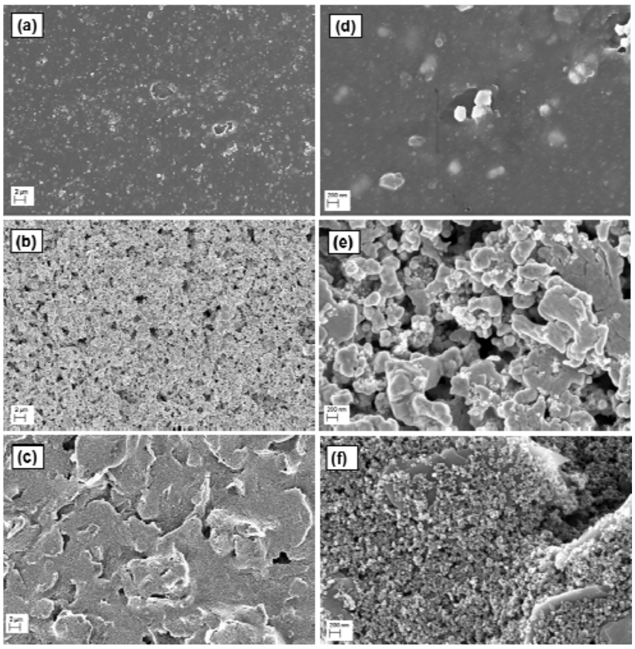

Figure 4. SEM images of the Melinex substrate (a), and flexographically printed silver layer (b) and carbon layer (c) at 5 kX magnification. (d), (e) and (f) and (h) are the respective images at 50 kX magnification.

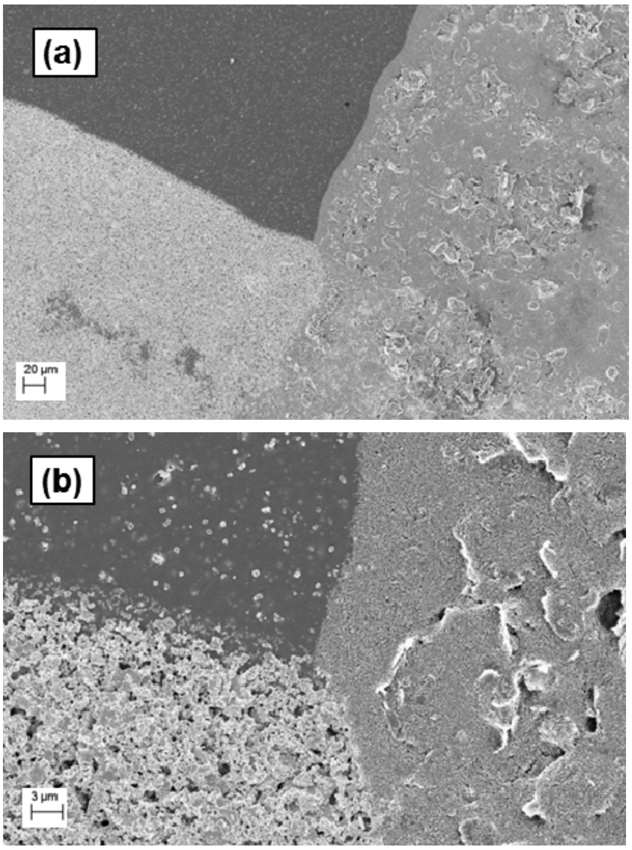

Figure 5. SEM images of the interface between the Melinex substrate and flexographically printed silver and carbon layers at magnifications of (a) 500 kX and (b) 5 kX.

Discussion 3 Performance – Comparisons and Applications

The performance of both lithographically and flexographically printed electrodes were tested and compared in supercapacitors. The structure of the supercapacitor is illustrated in figure 6. For these supercapacitors, a solid state electrolyte was used to eradicate problems with electrolyte leakage and sealing. The electrolyte was PVA-KOH, which was prepared by dissolving PVA (6 g) in water (60 ml) while heating at 80°C, and then adding a solution of KOH (3 g) dissolved in water (20 ml). This formed a clear gel, which was then spread evenly over both electrodes, which were then allowed to partially dry in air for 10 mins before they were sandwiched together. The PVA-KOH electrolyte was then allowed to set for another 60 mins, and then the device was sealed using adhesive laminate.

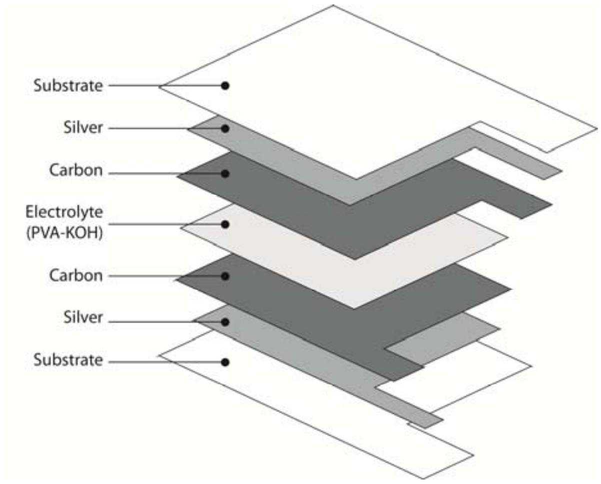

Figure 6. Structure of the supercapacitor configuration.

The supercapacitors based on both lithographically and flexographically printed electrodes were characterised by cyclic voltammetry. Figure 7 shows a comparison of the cyclic voltammograms at a scan rate of 500 mV/s. It is immediately apparent that the flexographically printed electrodes show higher capacitance than the lithographically printed electrodes. Both electrodes exhibit characteristic quasi-rectangular behaviour, even at a very fast scan rate of 500 mV/s, which demonstrates a high rate capability of the supercapacitors. The supercapacitor based on the flexographically printed electrodes shows an increase in anodic current which can be seen from 0.5 V, and a cathodic peak is seen on the reverse scan at the same potential. It is unlikely that the anodic current is due to electrolyte degradation, as this behaviour is not observed for the lithographically printed supercapacitor. The most likely cause of this behaviour is from the silver redox chemistry. From the SEM images, it was visually apparent that the carbon layer did not fully cover the silver layer – there were some gaps and potensial pin-holes in the carbon layer where the electrolyte could have been in direct contact with silver. The CV of the lithographically printed supercapacitor shows no sign of redox behaviour, illustrating complete and efficient coverage of the silver layer.

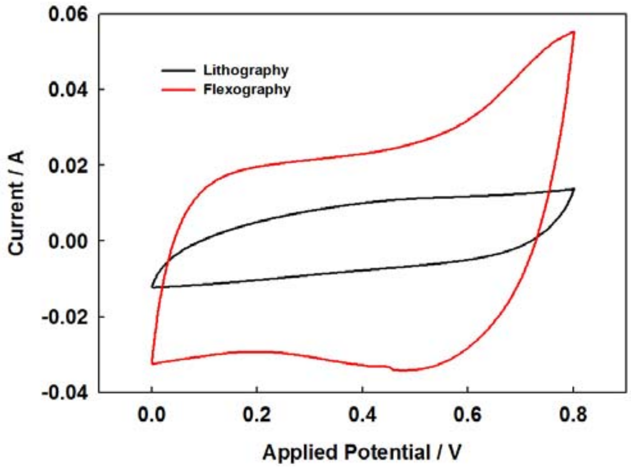

Figure 7. Cyclic voltammograms of a supercapacitor employing lithographically (black line) and flexographically (red line) printed electrodes in a PVA-KOH electrolyte at a scan rate of 500 mV/s.

Figure 8 shows the galvanostatic charge-discharge profiles of both supercapacitors using a charging current of 5 mA. The capacitance was calculated from the gradient of the discharge curve after the initial potential drop (due to internal resistance), according to a recommended literature reported method.[5] The capacitance was 0.10 F and 0.018 F for the flexographically and lithographically printed supercapacitors, respectively. This corresponded to areal capacitances of 4 mF/cm^2 and 0.72 mF/cm^2, respectively.

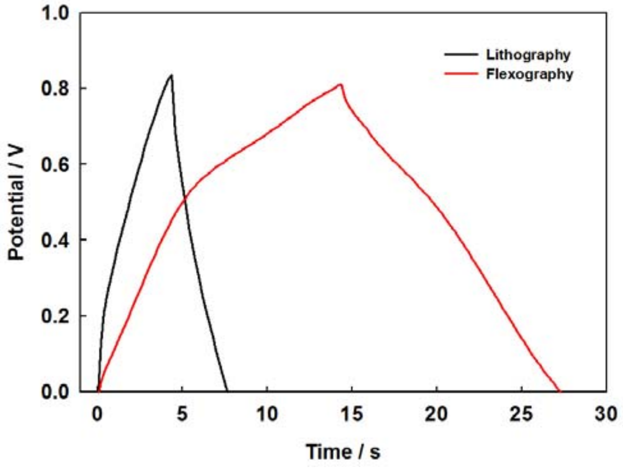

Figure 8. Galvanostatic charge-discharge curves of a supercapacitor employing lithographically (black line) and flexographically (red line) printed electrodes in a PVA-KOH electrolyte under a charging current of 0.005 A.

Nyquist plots for both supercapacitors are shown in figure 9. From the real axis intercept, it can be seen that the series resistance is lower for the flexographically printed supercapacitor compared with the lithographically printed supercapacitor, with resistances of 1.25 and 3.96 Ω, respectively. This is most likely due to the differences in ink formulation and thicknesses of the silver and carbon layers.

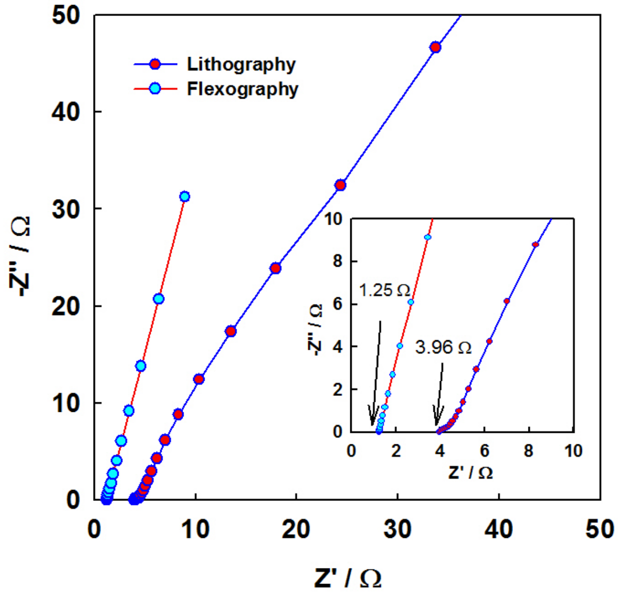

Figure 9. Nyquist plots of the supercapacitors employing lithographically (blue line) and flexographically (red line) printed electrodes. The inset shows an expanded view of the high frequency region.

Discussion 4 Physical durability and flexibility of the flexible supercapacitors.

The flexibility and durability of the solid state supercapacitor based on the flexographically printed electrodes was tested. Figure 10 shows the cyclic voltammograms of the supercapacitor before and after rolling. The measurement was conducted whilst the supercapacitor was rolled as shown in the inset of Fig 10. It shows that there was no significant change in performance upon rolling the device. In fact, it was found that any degree of bending in any direction had no significant adverse effect on its performance. The only thing to stop the supercapacitor from working was folding it in half and forming a crease by applying pressure along the fold line. This can be seen in the cyclic voltammograms shown in figure 11. The rectangular shape of the working supercapacitor changes to a typical ohmic response after folding, possibly due to a short-circuit between the two electrodes along the fold line. However, it was found that by compressing the supercapacitor using a 10 ton press, some of the capacitance could be recovered, as shown in figure 11. This recovery in performance is most likely due to redistribution of the gel electrolyte over the electrode surface. These results demonstrate the excellent robustness of the flexible solid state supercapacitors.

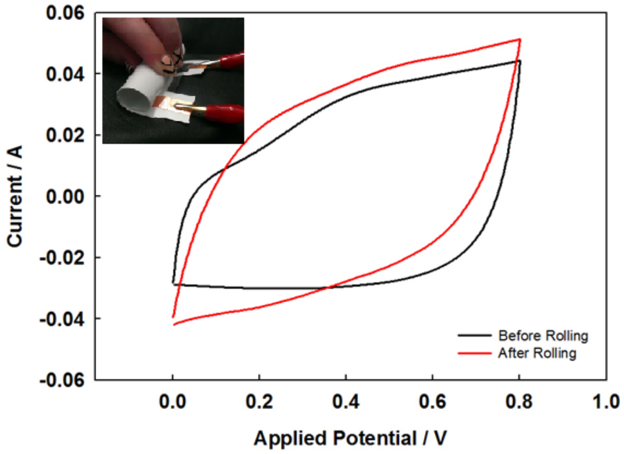

Figure 10. Cyclic voltammograms of the flexographically printed solid state supercapacitor before and after rolling. The inset shows an image of the supercapacitor in its rolled state.

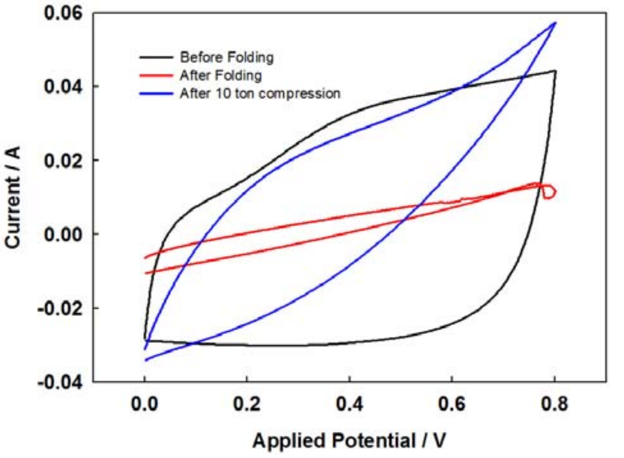

Figure 11. Cyclic voltammograms of the flexo printed solid state supercapacitor before and after folding, and after applying 10 ton pressure.

Discussion 5 Demonstration

To demonstrate the performance of the flexographically printed supercapacitors, they were used to illuminate a 1.6 V yellow LED. Three supercapacitors were connected in series to build up the voltage capability to 2.4 V, and another two sets of these were connected in parallel to increase the overall energy storage of the stack; the circuit diagram is shown in figure 12(a). The supercapacitor stack was charged to 2.4 V, and then was used to power the LED as shown in figure 12. The stack of supercapacitors powered the LED for around 90 seconds, with gradual decay of the LED brightness overtime, until the voltage of the stack fell below 1.6 V, which was the rated operating voltage for the yellow LED.

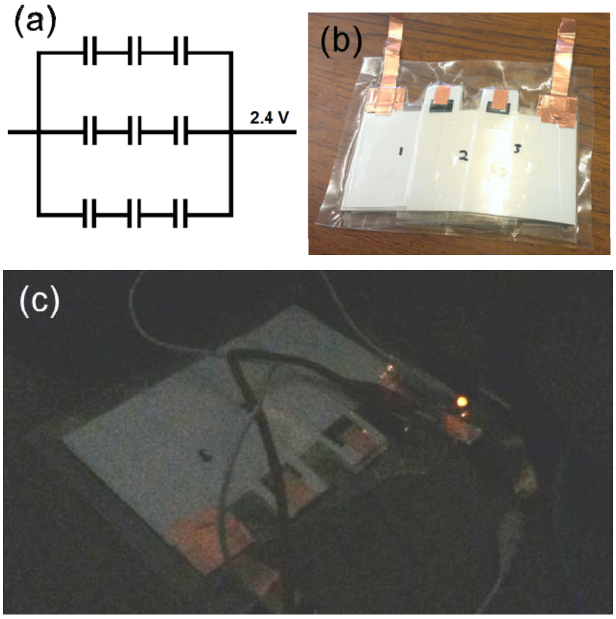

Figure 12. Showing the design and structure of the supercapacitor stack and showing it powering a 1.6 V yellow LED.

Conclusions

This paper describes a process of using offset lithographic and flexographic printing to form electrode structures suitable for supercapacitor fabrication. The supercapacitor performances of electrodes produced from each printing method were compared in a solid state supercapacitor. It was found that the flexographically printed electrodes showed a higher capacitance of 4 mF/cm^2 compared with 0.72 mF/cm^2 for the offset lithography produced electrodes. The higher capacitance for the flexographically printed electrodes was attributed to a higher surface area. However, a potential issue of the flexographically produced electrodes was the incomplete coverage of the carbon layer, which resulted in exposing the silver layer evident by the silver redox chemistry. This issue is required to be resolved as it could lead to cell degradation in long term. This issue was not seen for the offset lithography produced electrodes as the silver layer was completely masked. The robustness of the solid state supercapacitors was excellent based on performance testing after bending and rolling. It was found that only folding the device resulted in device performance failure, which could be easily recovered by simply compressing the device in order to evenly redistribute the gel electrolyte.

Future work

The present study has shown that the flexographic printing process can be used to produce high surface area porous electrodes for use in viable supercapacitors and these might be used to power printed displays [6,7]; however, several challenges still remain. The first challenge is to achieve complete coverage of the silver layer, and the second is to improve the capacitance. To mask the silver layer, printing of multiple carbon layers may have to be utilized; this would also be beneficial as it would result in higher surface area and hence capacitance. The next challenge would be to create printed interconnects to enable easier supercapacitor stacking to allow building up of higher voltages and energy storage. The complete printing of a conventional capacitor has already been achieved, using both conductive and insulating inks; but, these have less capacitance than might be desired. The ultimate challenge is to create a fully printable solid state supercapacitor, however, successful formulation and printing of the electrolyte layer and printing of subsequent layers on top of that remains to be a great material, chemical and electronics challenge.

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