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Printed environmentally friendly supercapacitors with ionic liquid electrolytes on paper

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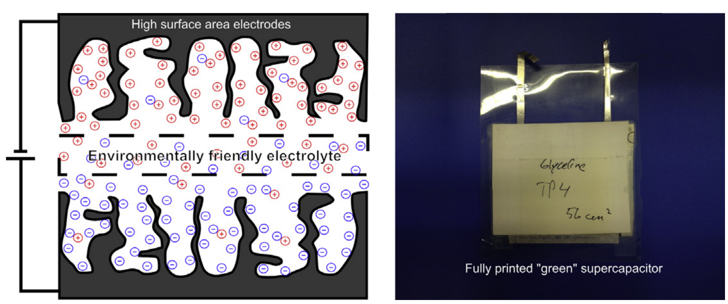
HIGHLIGHTS

- Environmentally friendly supercapacitors are fabricated on a paper substrate.
- Deep eutectic solvents based on chlorine chloride are used as electrolyte.
- The materials used are inexpensive and the entire supercapacitor is printed.
- Electrodes are printed using a screen printer in a pilot scale production line.
- Glyceline™ has the highest capacitance and highest power density.

GRAPHICAL ABSTRACT



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ABSTRACT

Environmentally friendly supercapacitors are fabricated using commercial grade aluminum coated paper as a substrate and symmetrical activated carbon electrodes as large area electrodes. Different choline chloride-based eutectic solvents are used as electrolyte. These are inexpensive, environmentally friendly and have a larger operating window compared to that of water electrolytes. As the entire device is printed and the materials used are inexpensive, both small- and large-area power sources can be fabricated to be used in cheap, disposable and recyclable devices. Supercapacitors with different eutectic solvents are measured using cyclic charge–discharge and impedance spectroscopy measurements and compared to one widely used and one "green" imidazolium ionic liquid; EMIM:TFSI and EcoEng 212™, respectively. A mixture of ethylene glycol and choline chloride, Glyceline™, show the highest capacitance and power densities of the electrolytes being tested, including the imidazolium alternatives.

1. Introduction

Supercapacitors (SC) [1] are used in energy storage applications especially when high power peaks are required to be absorbed (stored) or delivered. A typical SC consists of two large area

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electrodes separated by a porous membrane, i.e. a separator. The electrodes are typically made of activated carbon (AC) powder that is bound using fluorine containing polymers. The ion conductive electrolyte fills the voids in the electrodes and the separator. As electrolytes, aqueous alternatives containing e.g. KOH [2], H_2SO_4 [2], and even NaCl or other salts such as sulfates and carbonates are often used [3]. But also organic solutions such as propylene carbonate or acetonitrile with tetraalkylammonium salts [4–6] or ionic liquids (IL) [7–9] such as EMIM:TFSI [10] are also commonly used. In high power density applications, or when making small SCs, the organic alternatives are advantageous as they can withstand voltages up to 3–5 V (water electrolyte SC degrade around 1.2–1.5 V) giving higher power densities and, hence, higher powers per unit area are reached.

Today's society is increasingly moving towards capturing and transmitting data, i.e. moving towards realizing “the Internet of Things”, where everything is connected. To reach this there is a need for small sized power sources that can be applied in identification and data storage/transfer devices as well as in miniaturized sensors systems. The supercapacitor being a simple power device, both in terms of materials choices as well as in fabrication processes, can be of great use in such applications. Active type tags and sensors require a suitable power source to fully utilize their potential allowing greater memory capacity in the tag and increasing the range from which the tag can be read [11]. These tags are often intended to be used as integrated parts of recyclable or disposable (burnable or biodegradable) products. Hence the materials of choice should be inexpensive and safe, and obviously the manufacturing methods and materials choice should both result in low-cost products as well as having a low carbon footprint. Further, many of the objects/things envisaged of being tagged are by themselves small, or the tag needs to be nonintrusive (or physically small for other reasons). Here, a solution which combines the environmentally friendliness of water electrolytes with the higher voltage capabilities (i.e. higher power per unit area) of the organic salts (IL and/or organic salt solutions) would be attractive. These demands are not easily met using the traditional materials and material combinations mentioned above.

In the above described applications photovoltaic cells or small size primary or secondary batteries can be used as the main power source. On the other hand a combination of any of these with a SC is also a feasible possibility, especially for applications where high current output is required only for short periods of time. For instance environmentally friendly biobatteries – although providing low peak current output on their own – is a “green” alternative that can be used in a wide range of applications when integrated with a printed supercapacitor [12].

The manufacturing of these small sized supercapacitors by printing methods is essential to facilitate inexpensive manufacturing process. The same manufacturing route can be applied when preparing supercapacitors of larger sizes and/or for other applications, as printing processes allow up-scaling by facilitating the manufacturing of either a large number of small components or large area ones. The manufacturing of supercapacitor electrodes using printing techniques has been described in patents [13,14] and scientific reports [12,15–21]. A solution based process that can be modified to screen printing has been reported in the preparation of polyaniline-based supercapacitors [22]. Batteries and supercapacitors of carbon nanotubes and room-temperature ionic liquid electrolytes have been constructed using paper as a substrate material [23].

The supercapacitors presented in this paper are of the non-Faradaic electric double layer capacitor (EDLC) kind. This means that no charge is transferring between the electrode and the ion conductive dielectric when the capacitor is being charged i.e. the charge is being stored electrostatically on the electrodes. As there are no electrochemical processes (ideally) taking place, i.e. no reduction or oxidation of/at the electrodes, the supercapacitors can stand more charging- and discharging cycles (>100,000 switches) than secondary batteries, in which reduction/oxidation processes typically reduce the cycle life to below 5000 cycles.

Environmentally friendly SC have previously been realized using water-based electrolytes with NaCl as the salt. [17] These devices, however, are limited by their operating window as water is electrochemically dissociated above 1.23 V. This severely limits their power storage capabilities and to achieve higher voltages the SC cells need to be serially connected which complicates their manufacturing processes. For these applications where higher voltages/power density is needed, ionic liquids are useful since they have a larger electrochemical window compared to that of water-based electrolytes.

When ILs have been used in SC, the ILs have mostly been based on the imidazolium class of ILs, [7–10] but also others such as phosphonium-based ILs have been used to create SC. [24] Some of these are considered fairly safe and non-toxic, for example 1-ethyl-3-methylimidazolium ethyl sulfate (EcoEng) has been marketed as a greener alternative. But the most used and some of the best imidazolium SCs have been made using fluorinated anions, such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM:TFSI) or BF_4 and PF_4 salts. Organofluoride compounds are not a natural part of our ecosystem; they release toxic fumes when burned and should be avoided in widely spread devices, such as are targeted here.

We have instead investigated and used ionic liquids based on choline chloride (ChoCl). ChoCl is a quaternary ammonium salt and is widely used as chicken food additive to accelerate growth. We have used mixtures of ChoCl and urea, oxalinic acid, ethylene glycol and sorbitol. Blending these create deep eutectic solvents that have similar properties to ILs [25,26]. These solvents are liquids or semi-liquids (syrup/gel) at room temperature. These ILs and EcoEng are here used to create environmentally friendly supercapacitors on paper. The IL EMIM:TFSI is used as a reference to compare the different ILs. To minimize the impact on the environment and create fully recyclable and/or biodegradable devices, the devices are printed on a paper substrate.

The electrodes used, in the laminated large supercapacitors presented in this paper, are printed using a rotary screen printer in a pilot scale production line. Several meters (~30 m) of electrodes were printed and stored on a 10 cm in diameter roll without delamination. The rest of the devices are fabricated on a laboratory scale using roll-to-roll (R2R) compatible technologies. So the final steps, including screen printing the IL, addition of the separator and lamination, could easily be scaled up to pilot scale production as well.

2. Experimental

The deep eutectic solvents (referred to as ILs in this paper) are created by mixing: ChoCl with different hydrogen bond donors. Mixtures with urea, oxalic acid and ethylene glycol were purchased from Scionix Ltd (Reline™, Oxaline™ and Glyceline™ respectively). For the sorbitol variant we mixed ChoCl with sorbitol (1:1 mol%) and heated it at 60 °C for 24 h to create the IL here called CSorb.

To characterize the devices two different supercapacitor structures were used in this paper; one type for measuring on a “standardized” SC and a second type with gold electrodes to clarify the role of the electrolyte/activated carbon interactions in the SC. In the first standardized SC structure the different ionic liquids are sandwiched between two reference activated carbon electrodes printed on PET film. The electrodes are separated using a rubber O-