Journal of Power Sources 326 (2016) 717–725

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Miniaturized supercapacitors: key materials and structures towards autonomous and sustainable devices and systems

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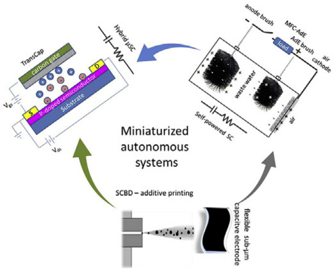
HIGHLIGHTS

- Novel supercapacitor integration approaches for multifunction autonomous devices.
- Flexible supercapacitive electrodes fabricated by Supersonic Cluster Beam Deposition.
- Strategies to miniaturize supercapacitive low-power electrolyte gated transistors.
- Supercapacitors, electrolyte gated transistors and microbial fuel cells integration.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 February 2016
Received in revised form
27 April 2016
Accepted 28 April 2016
Available online 7 May 2016

Keywords:
Flexible micro supercapacitor
Electrochemical double layer
Supersonic cluster beam deposition
Electrolyte gated transistor
Microbial fuel cell

ABSTRACT

Supercapacitors (SCs) are playing a key role for the development of self-powered and self-sustaining integrated systems for different fields ranging from remote sensing, robotics and medical devices. SC miniaturization and integration into more complex systems that include energy harvesters and functional devices are valuable strategies that address system autonomy. Here, we discuss about novel SC fabrication and integration approaches. Specifically, we report about the results of interdisciplinary activities on the development of thin, flexible SCs by an additive technology based on Supersonic Cluster Beam Deposition (SCBD) to be implemented into supercapacitive electrolyte gated transistors and supercapacitive microbial fuel cells. Such systems integrate at materials level the specific functions of devices, like electric switch or energy harvesting with the reversible energy storage capability. These studies might open new frontiers for the development and application of new multifunction-energy storage elements.

1. Introduction

Worldwide electric energy consumption from ICT and home entertainment consumer electronics is fast growing. While each device consumes a small quantity of electricity, power use in stand-by mode and massive widespread use make the cumulative

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http://dx.doi.org/10.1016/j.jpowsour.2016.04.131

consumption considerable. It has been estimated that the global energy demand of network-enabled devices is expected to reach around 1140 TW h by 2025 corresponding to an increase of 6% of current total global electricity consumption [1]. Efforts are required to power down or reduce and minimize energy requirements without losing functionality. On the other hand, energy autonomy is critical for remote sensing, robotics and medical applications like wearable and skin-attachable sensors [2] and implantable devices for in vivo diagnostics [3].

The design of autonomous systems includes a nanogenerator that harvests energy from the environment (photovoltaic, thermoelectrics, mechanical vibration, piezoelectric, bio- or enzymatic fuel cells), an energy storage unit (like a microbattery or a microsupercapacitor) that stores the harvested energy and delivers the power required to switch on function units like sensors and transceivers [2]. The key issue of autonomous systems is that energy harvesters typically provide power and voltage output that can be lower than what is required to charge conventional batteries and supercapacitors (hence for energy storage) and to switch on the function device. Hence, viable strategies are: i) the miniaturization of the energy storage system; ii) the decrease of power demand of the function device; and iii) the integration of different system components. On the other hand, the above reported applications have raised the problem of developing sufficiently compact and/or flexible, multifunctional electronic components by sustainable processes like printing methods [4–15].

Within this context microsupercapacitors (μSCs) are playing a key role. μSCs are high power systems that may outperform μ-batteries in applications having high peak-to-average power demand due to their capability to store/deliver charge in relatively short times [12]. Compared to μ-batteries, μSCs feature much lower energy density but exhibit superior cycling stability, which is of paramount importance for applications (e.g. sensors) where repeated power peaks are required. Several classes of supercapacitors making use of electrodes with different nature and composition have been demonstrated [16,17]. The most common are the electrochemical double layer capacitors (EDLCs) that use high surface area carbon electrodes which store/deliver charge by an electrostatic process. Pseudo-supercapacitors feature battery-like electrodes (electronically conducting polymers and metal oxides) that are charged/discharged by fast and reversible redox processes. Hybrid supercapacitors feature positive and negative electrode materials of different nature that are charged/discharged via different electrostatic and faradic modes. Carbons and polymers are key materials for μSCs since they are easily processable for in-plane or flexible architectures.

A plethora of electrode and electrolyte combinations have been proposed to yield supercapacitors with operating voltages varying from 1 V (aqueous systems) to 3 V and above (organic electrolytes, ionic liquids) and specific energy and power values spanning the 5–40 W h kg^{-1} and 1–6 kW kg^{-1} ranges [17]. This high "electrical response flexibility" of μSCs is crucial for their implementation into autonomous devices. Specifically, carbonaceous materials can store charge within a wide working voltage range which is limited only by the electrochemical stability of the electrolyte that for aqueous electrolyte is constrained below 2 V. For this reason, EDLCs can be successfully combined with a wide range of energy harvesters including those operating at low voltage like photovoltaics (PVs) [18] or enzymatic and microbial fuel cells [19].

Furthermore, a valuable, key aspect of supercapacitor electrodes is that many materials exhibit strategic additional properties that can be exploited for specific applications, along with their capability of reversibly storing charge and, thus, energy. This enables integration of the energy storage capability and of the target function at materials level [20]. Pseudocapacitive polymers, like poly(pyrrole), poly(3,4ethylenedioxythiophene), poly(3-alkylthiophenes) and poly(aniline), have specific mechanical, optical and electronic properties that are exploited in actuators, electrochromic devices, and sensors [21,22]. Metal oxides are also used as mediators for electrocatalytic processes (e.g. MnO_2 and RuO_2) and may feature electrochromic and semiconductive properties (e.g.WO_3 and TiO_2) [23]. The semiconductivity of polymers and inorganic compounds is exploited in transistors. These widely used circuital electronic components are at the basis of several functionalities, from sensors to memories. In particular, electrolyte gated transistors (EGTs) are attractive candidates to be coupled to energy harvester/storage microsystems for their low-voltage operation characteristics [24]. In EGTs, the charge carrier density in the semiconductive channel can be reversibly modulated upon application of a bias (V_{gs}) between the channel and a gate electrode through an electrolyte. Current (I_{ds}) flows through the channel by application of a voltage (V_{ds}) between drain and source (Fig. S1). Coupling pseudocapacitive channels like polymers and metal oxides with high double-layer capacitance carbon gates enables current modulations of several orders of magnitude at relatively low V_{gs} which positively affects power consumption and device stability (Fig. S1).

Sub-1V operation of EGTs has been demonstrated by combining activated carbon gates with polymer or inorganic channels and with both aqueous and organic electrolytes [25–29]. Specifically, p-type EGTs with poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) and poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene (MEH-PPV) p-type polymer channels were considered for their great potential for flexible, low-cost and easily processable electronic devices. PEDOT:PSS is one of the most investigated materials for Organic EGTs (OECTs) to be used in bioelectronic implants, chemical and biological sensors, and lab-on-a-chip systems [26,30]. MEH-PPV is well known for its electroluminescence and for its potential applications to optical and electronic devices such as light-emitting diodes (LEDs) [31]. As it concerns inorganic channels, WO_3 is well investigated for its application in electrochromism, sensing, photocatalysis and photoelectrochemistry [32]. The electric response of the organic and inorganic EGTs making use of high surface area carbon gate and IL-based electrolytes are summarized in Table S1. Table S1 also reports the energy required to drive EGTs (E_{EGT}) that includes the contributions to dope the channel ($E_{gs} = |V_{gs} Q_{ch}|$) and to let the current flowing through the channel (E_{ds}) over a certain time (t). E_{ds} depends on the power dissipated through the channel ($P_{ds} = |I_{ds} V_{ds}|$) (see SI). The doping charges and V_{gs} are in the 100–300 μC and 0.8–1.2 V ranges and the E_{gs} are of 0.03–0.1 μW h. The channel/electrolyte/gate stacking of EGTs can be viewed as a 2-electrode electrochemical cell where the capacitive channel and carbon gate components reversibly store charge at given V_{gs}. Specifically, the channel/electrolyte/carbon gate stacking is analogous to that of a hybrid μSC where channel and gate electrodes are charged/discharged by a faradic and an electrostatic process, respectively. This means that the E_{gs} energy used to dope the channel is stored and, then, deliverable upon the EGT switch OFF. For the different EGTs here considered up to 50% of the energy spent to drive the EGT can be stored ($E_{stored} = 100$ Egs/E_{EGT}), and thus, saved (Table S1). More importantly, these results point to the integration of EGT and μSCs at materials level, which has been demonstrated with TransCap [27]. TransCap featured an MEHPPV channel, a gate based on commercial activated carbon layer deposited on carbon paper and the ionic liquid N_{1113}TFSI. The device could simultaneously work as EGT and μSC. The E_{gs} stored during the potentiostatic (PS) switch on at 0.8 V was ca 0.02 μWh and it was delivered during the following switch OFF (0 V) with an efficiency of 99.5% (Fig. S1) [27]. The energy (E) and power (P) delivered under a conventional