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Current collectors for low resistance aqueous flexible printed supercapacitors

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ABSTRACT

In this paper we propose various current collector alternatives to be used in flexible supercapacitors with aqueous electrolyte when low equivalent series resistance (ESR) is required. The current collector material should be corrosion resistant when in contact with the saline electrolyte. Simultaneously it should have high electrical conductivity. In addition, environmental and cost aspects must be taken into account. We report supercapacitors with current collectors made of two different thicknesses of graphite foil (25 µm and 150 µm) and aluminium coated with graphite inks. These disposable and non-toxic supercapacitors show remarkable improvements in ESR compared with values obtained for similar components with current collectors made of graphite ink. When graphite foil or aluminium is used as current collector, the ESR can be decreased by more than 80 % compared to using graphite ink alone. Supercapacitors using a dense graphite protective layer on top of aluminium showed no sign of corrosion and their performance was not significantly reduced after ageing for 950 days. With graphite foils, comparable ESR values can be obtained as with aluminium. The graphite foil is an interesting alternative if metal materials should be avoided, e.g. to facilitate incineration of the supercapacitors together with regular household waste. Especially with non-porous graphite foil, we obtained properties suitable for practical applications.

1. Introduction

Soon, the Internet of things (IoT) will connect more than 50 billion smart devices helping to engineer novel solutions for different problems such as healthcare, automation, wearable electronics, security and maintenance of public infrastructure. [1] Such smart technology is not sustainable without proper energy harvesting systems which could help in avoiding the massive waste problem caused by an enormous number of batteries

In many applications, energy harvesting systems need energy storage device as a back up to provide energy when the primary energy source is not available. Therefore, energy storage systems attract much interest. [2] Batteries and supercapacitors can keep smart object working when the primary energy sources are not usable. Both of them rely on electrochemical principles, although the different electrochemical mechanisms in batteries and supercapacitors result in differences in their energy and power density values. Supercapacitors (also called electrochemical capacitors [5], ultracapacitors or electric double-layer capacitors [6]) can provide an excellent energy-power-cost-life balance, and can be made entirely from non-toxic, low-cost, abundant materials. [3]

During the past decade, the energy storage field had a dramatic expansion in scientific research. [4] In many cases, supercapacitors are a better choice for energy storage than batteries due to their longer cycle life [5], disposability and safety. Printed supercapacitors are typically manufactured by a stacked assembly method where the electrodes are fabricated separately. Then a separator is laminated between the electrodes and electrolyte is added. The final step is sealing the supercapacitors to prevent electrolyte leakage and evaporation. [6,7]

The equivalent series resistance (ESR) measured for a supercapacitor results from the non-ideal phenomena and resistance in supercapacitors. ESR is caused by electrode resistance, current collector resistance, electrolyte resistance and the contact resistance between different layers of the supercapacitors. ESR results in wasting power for heating during charging or discharging and in a voltage drop over the supercapacitor. [8] Earlier a wide range of material has been examined to be used as supercapacitor electrolytes, electrodes, separators and current collectors. [3,9–16] This work is on materials and methods that

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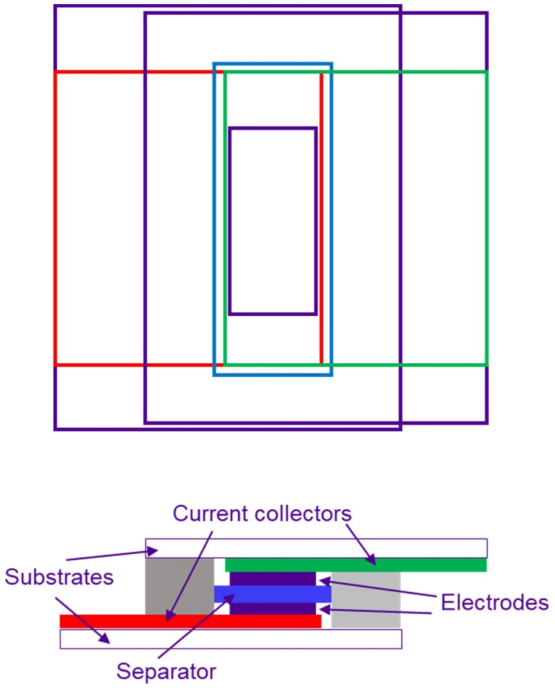

Fig. 1. Schematic cross-section and layout of the supercapacitors.

can enhance the performance of the current collectors and make the supercapacitors work stably for a longer time while still focussing on low-cost, non-toxic materials. We report materials and architectures that reduce the ESR of environmentally friendly, disposable printed supercapacitors.

2. Experimental

Supercapacitors were prepared on polyethylene terephthalate (PET film, Melinex ST506 from DuPont Teijin Films, thickness 125 µm). Graphite ink, Acheson PF407C, was used as a current collector in the reference supercapacitor. The other materials used to improve the current collector were the thick graphite foil Sigraflex from SGL Carbon and the thin graphite foil T68A from T-Global Technology Co., Ltd. On PET/aluminium laminate (from Walki, thicknesses of the layers 50 and 9 µm, respectively) the supercapacitor electrodes were manufactured on the Al side, so the aluminium layer acted as current collector. The protective graphite ink applied to Al was Acheson Electrodag 965SS.

The printed PF407C graphite ink was cured at 95 °C for 1 h and the 965SS graphite ink at 120 °C for 15 min. The electrodes were fabricated from activated carbon (AC), Kuraray YP-80F made from coconut shells. [15] Chitosan (Sigma-Aldrich, Chitosan from shrimp shells, 50494) was used as a binder. The recipe of the ink has been reported previously. [7]

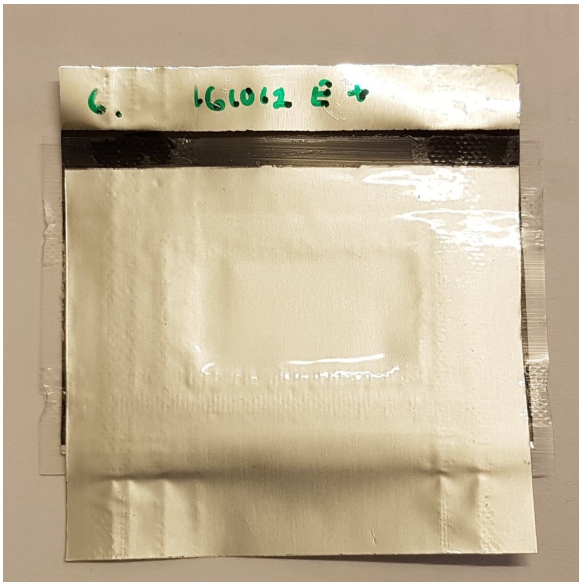

Fig. 3. The protected Al current collector supercapacitor.

The separators were made of 40 µm thick Dreamweaver Silver AR40 cellulose paper. The electrolyte was diluted NaCl (Fluka 38979) to deionized water in 1:5 mass ratio. When assembling face-to-face, the current collectors were insulated from each other using a polyethylene (PE) frame, thickness 150 µm. Adhesive tape (468MP-200MP from 3M) was used for sealing the supercapacitors. The graphite inks were applied by stencil printing (doctor blade applicator using mtv Messtechnik Film Applicator). Screen printing was used to apply AC to graphite films due to the low cost and reliability of the technique for depositing uniform thick films. [15,17–19]

The capacitance, leakage current and ESR were determined according to the IEC 62391-1 standard [20] using a Maccor 4300 test system. The devices were charged and discharged with constant current (10, 30 and 100 mA) between 0 V and 1.2 V three times, then for 30 min the voltage was kept at 1.2 V and capacitance was measured during the constant current discharge step between 0.96 V and 0.48 V potentials. The leakage current was defined by keeping the supercapacitor for 1 h at constant voltage. The ESR was calculated from the IR drop in the measurement with discharge current 10 mA.

3. Results and discussion

3.1. Manufacturing process development

Fig. 1 shows the schematic cross-section and layout of the supercapacitors. [16]. The electrode dimensions were 10 mm × 18 mm and

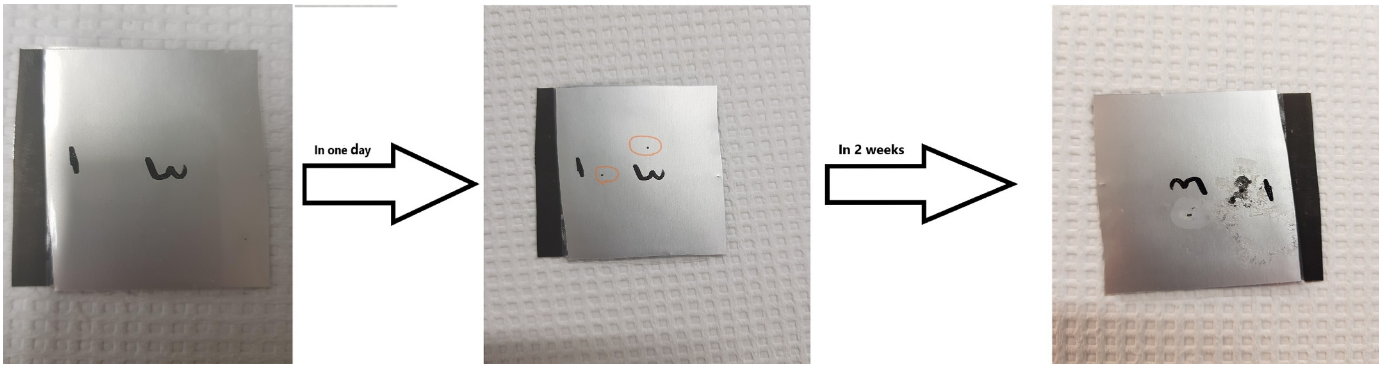

Fig. 2. Aluminium current collector supercapacitor corrosion in 1 day and two weeks.

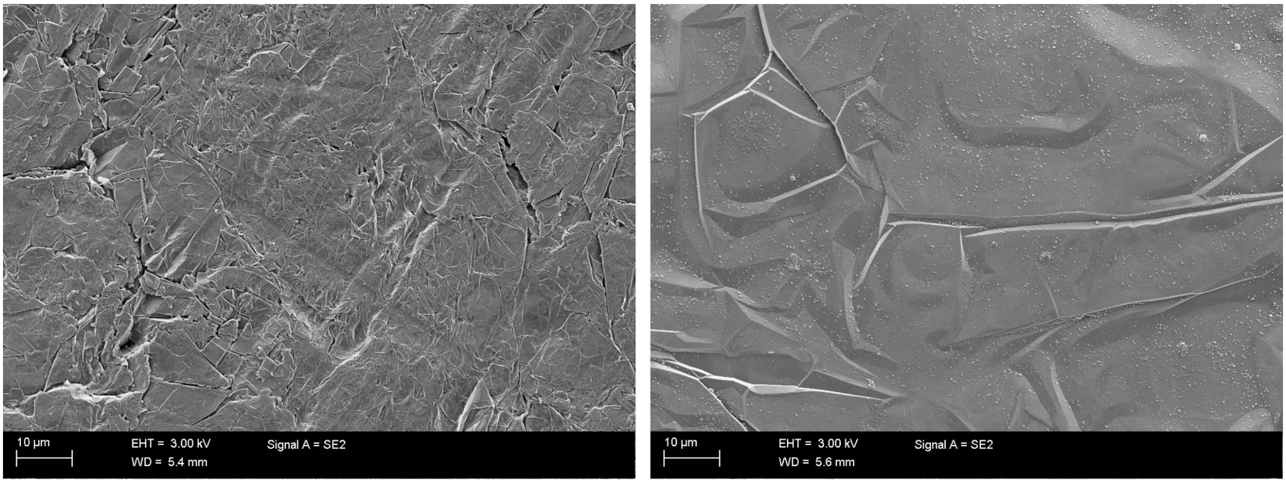

Fig. 4. SEM imaging of thick graphite foil (Left) and thin graphite foil (Right).

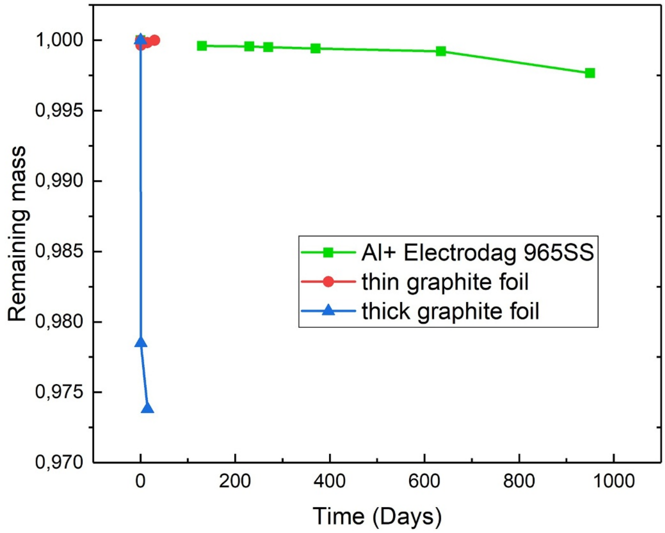

Fig. 5. Normalized mass change of the supercapacitors versus time.

are shown purple in the Fig., printed on a 39 mm × 48 mm current collector that is shown in green and red in Fig. 1. The electrodes were separated by a 24 mm × 13 mm separator paper, shown in blue in the Fig.. The current collectors were insulated from each other using PE, grey part in Fig. 1. The device was sealed by adhesive tape.

The Al current collector supercapacitor coated only with PF407C graphite did not work after one day because of corrosion. Fig. 2 shows the corroded aluminium current collector 1 day after assembling and after two weeks. Thus, the PF407C graphite ink alone is not sufficient to prevent the electrolyte from reaching the aluminium surface and corroding it. Different materials can be coated on Al for corrosion protection. [21-24]

In this work, a layer of protective graphite ink Electrodag 965 SS was applied on top of the Al to protect it against corrosion. The protective graphite film deposited smoothly, and it shows good bonding with Al substrate. Fig. 3 shows a protected Al current collector supercapacitor.

3.2. *Microstructure*

Fig. 4 shows SEM images of the thin and thick graphite foil. The surface of the thick graphite foil shows considerable porosity.

The supercapacitors were weighed after assembling and several times after different time periods. Normalized mass changes versus time are shown in Fig. 5. The weight of the thick graphite foil supercapacitors clearly decreases already in 2 weeks. The weight of the thin graphite foil supercapacitor remained stable in the same period. The pores on the thick graphite foil allow the electrolyte to evaporate more easily than in the case of the thin one. It also affects the performance of the supercapacitors, as will be reported later in this paper.

2.3. *Electrical performance of the supercapacitors*

The performance of the supercapacitors with the different current collectors is presented in Table 1.

The results are for the measurements performed on the same day that the supercapacitors were made. All the supercapacitors with improved current collector structures show dramatically better ESR comparing to the reference supercapacitor, which has only graphite ink PF407C as current collectors. Specific leakage current in the Al supercapacitors is comparable with the reference, while the leakage current is higher in supercapacitors with thick graphite foil. This is due to the porous structure of the graphite foil, which e.g. allows oxygen penetration to the electrolyte [25].

The Al supercapacitors with only PF407C graphite ink layer degrade after one day due to Al corrosion by the salt water electrolyte, but the supercapacitors with a protective graphite thick film on the Al were highly stable. Table 2 shows the electrical properties of the Al supercapacitor with Acheson 965SS layer during 950 days.

As seen in the table, ESR and specific leakage current of the graphite

Table 1
Electrical properties of the supercapacitors.

Current collector Of the Supercapacitors	Capacitance (mF)	ESR (Ω)	Leakage current (µA)	Specific Leakage current (µA/F)
Reference (graphite ink only)	309	9.7	8	26
Thick Graphite foil	361	1.3	13.7	37
Thin Graphite foil	326	1.3	10.8	33
Aluminium + PF407C	357	1.5	10.1	28
Aluminium + Electrodag 965SS + PF407C	272	2.1	7.8	29

Table 2
Electrical properties of the graphite ink 965SS protected Al current collector supercapacitor during 950 days.

Days	Capacitance (mF)	ESR (Ω)	Leakage current (µA)	Specific Leakage current (µA/F)
0	272	2.1	7.8	29
130	273	2.3	6.5	24
230	270	2.4	5.5	20
270	268	2.4	5.2	19
370	264	2.5	5.6	21
635	262	2.6	7.1	27
950	257	2.8	5.8	22

Table 3
Electrical properties of the thick graphite foil current collector supercapacitor versus time.

Days	Capacitance (mF)	ESR (Ω)	Leakage current (µA)	Leakage current/ Capacitance (µA/F)
0	361	1.3	13.7	37
15	354	1.4	15.6	44
30	362	0.9	15.9	43
45	365	0.7	16.7	46

Table 4
Electrical properties of the thin graphite foil current collector supercapacitor versus time.

Days	Capacitance (mF)	ESR (Ω)	Leakage current (µA)	Leakage current/ Capacitance (µA/F)
0	326	1.3	10.8	33
15	326	1.4	10.9	33
30	350	1.0	7.6	21
45	340	0.89	6.3	18

protected Al supercapacitor were stable for at least 950 days. Fig. 5 shows the mass change for the graphite protected Al supercapacitor in 950 days, it was stable and only small mass change was observed. Tables 3 and 4 show the performance of the thick and thin graphite foil supercapacitors over a period of 45 days, respectively.

The device comprising thick graphite foil ages quickly due to the porosity of the graphite foil, as observed in the SEM image. The porous structure lets the electrolyte evaporate quickly, thus both the mass of the supercapacitors and specific leakage current show performance degradation after 45 days. The thin graphite foil supercapacitor has a denser, less porous structure resulting in more stable supercapacitor performance. Obviously, after a longer time period the loss of electrolyte would result in a non-functional supercapacitor. The specific leakage current of the thick graphite supercapacitor is high and does not decrease with time as is the case with thin non-porous graphite current collectors. This may be due to impurities in the thick graphite foil or the penetration of oxygen from air to the electrolyte [7].

The maximum power of a supercapacitor is calculated according to Eq. (1). [26]

$$P = U^2/4R \tag{1}$$

where R is ESR. Therefore, when the ESR is decreased from about 10 Ω to near 1 Ω, with the same mass, dimensions and specific energy, the maximum power would increase accordingly.

4. Conclusions

Disposable, non-toxic, flexible supercapacitors were manufactured using printing processes, using thick and thin graphite foils and dense graphite protected Al as current collectors. The improvement in current collector enhances the performance of the supercapacitors, especially with regard to ESR and thus maximum power.

All the improved supercapacitors show about lower ESR than supercapacitors comprising only printed graphite as current collector. To increase the lifetime of the Al supercapacitors and prevent the early corrosion, a dense layer of graphite ink was applied on top of the Al. This increased the stability in performance up to at least 950 days. The performance of the supercapacitor with thin, less porous graphite foil current collectors was stable. This work opens up the possibility for printed supercapacitors to be implemented when higher peak power densities, e.g. for a Bluetooth low energy (BLE) transmission, are needed.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.est.2020.101384.

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