Lifetime and reliability of flexible aqueous supercapacitors: constant voltage floating and bending experiments

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***Abstract*— We have developed thin and flexible supercapacitors that can be combined with energy harvesting components. The substrate material is a laminate foil made of polyethylene terephthalate and aluminum. Activated carbon is used as the electrode, graphite ink as the current collector and aqueous NaCl or Li_2SO_4 as electrolyte. Constant voltage floating experiments were done to estimate the practical voltage window of aqueous supercapacitors with respect to lifetime. We measured the capacitance, equivalent series resistance, efficiency and leakage current over time at constant voltage between 0.9 and 1.6 V. The results indicate that 1.5-1.6 V is feasible for a short time, *i.e.* about 1-100 hours depending on the materials. Lower voltages are substantially more stable: after 2000 hours at 1.2 V the capacitance decreased by about 10 % and at 0.9 V by only ca. 3 %. Potassium iodide was tested as an additive to the aqueous electrolyte, which clearly increased (up to 3-fold) capacitance but simultaneously shortened the lifetime. The potential for scalable manufacturing of supercapacitor components by printing was demonstrated in an upscaling trial. The supercapacitors were bent to less than 1 cm minimum radius without deterioration of their electrical properties.**

Keywords—supercapacitor, energy storage, aqueous electrolyte, reliability, voltage floating, bending

I. INTRODUCTION

Supercapacitors [1], [2] are able to meet high peak power requirements of energy storage applications. A supercapacitor consists of two electrodes separated by an ionically conductive electrolyte. The electrodes are typically made of activated carbon (AC) powder that is bound using fluorine containing polymers. Organic solvents such as propylene carbonate or acetonitrile are commonly used as electrolytes, but it is also possible to use water based electrolytes [3], [4]. With organic electrolytes a maximum voltage of about 2.5 V can be applied between the electrodes, whereas with water based electrolytes the maximum voltage is theoretically limited to approximately 1.2 V due to water splitting. However, it has been reported that larger potential difference between the electrodes would be feasible in practical components.[5], [6], [7]

Low-price and non-toxic power storage devices can be used in distributed electronics applications, e.g. in wireless sensor networks as well as in wearable and RFID applications. Supercapacitors can be used together with energy harvesting devices [8], [9], [10] and they can enhance the power output of another energy storage device [11], [12]. By making the supercapacitors flexible they find new applications in weareable and portable electronics [13], [14]. Printing can be used to minimize manufacturing costs. It is also possible to use materials that are environmentally friendly and can be disposed of with normal household waste. [15], [16]

We have developed thin and flexible supercapacitors that can be combined with energy harvesting components. In this paper we report experiments to define the life time of the aqueous supercapacitors when floated at constant voltage and when bent.

II. EXPERIMENTAL

A. Supercapacitor fabrication

The schematic structure of a flexible supercapacitor is shown in Fig. 1. The total thickness of the capacitor with packaging was about 0.6 mm, with the length and width being 50 mm. The essential technical requirements for current collectors are that they should have low resistance and the electrolyte should not corrode them. Together with current collectors the substrates form the package of the component. It is also important that the package prevents the evaporation of electrolyte and provides the required mechanical strength also when bent to relatively small radius.

Polyethylene terephtalate/aluminium laminate (PET/Al, Walki, thicknesses of the layers 50 and 9 mm, respectively) was used as substrate. The aluminium layer was used only as barrier layer and the current collectors were fabricated on the PET side of the PET/Al laminate. The manufacturing process

of the supercapacitors started by making two current collectors with graphite ink (Acheson PF407C, red and green in Fig. 1.). The graphite ink was dried at 95 °C in a forced convection oven leading to thickness of 35-40 µm. Electrodes made of activated carbon (Kuraray YP-80F) ink with chitosan binder (Sigma-Aldrich, black) were applied onto them. A laboratory scale doctor blade coater (mtv messtechnik) was used for applying the current collector and AC inks. The AC ink was dried at room temperature resulting in films with thickness of 70-100 µm. Dreamweaver separator was placed between the electrodes, and the electrodes and separator were impregnated with electrolyte. Four different aqueous electrolytes were used: 1 M NaCl, 1 M Li_2SO_4, 1 M NaCl + 0.5 M KI and 1 M Li_2SO_4 + 0.5 M KI. The completed device was heat-sealed with Paramelt Aquaseal X2277 polyolefin dispersion or with 3M 468 MP adhesive (gray).

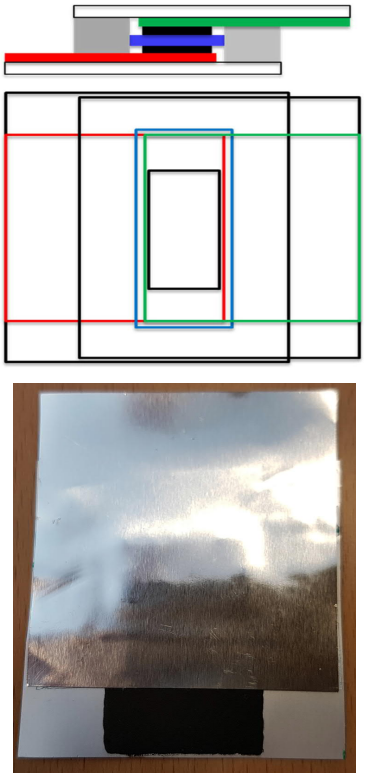

Fig. 1. Schematic structure and photograph of the supercapacitor.

To prove the feasibility of the supercapacitor structure in larger scale production, a rotary screen print machine was used to fabricate supercapacitor electrodes. VTT's ROKO pilot-facility was used for the roll-to-roll printing trials. Same inks, as applied for the doctor blade experiments, were used during the roll-to-roll trials. In order to achieve thick layers, Gallus BY screen, plate thickness 220 µm, 64 meshes/inch, was selected for the experiments. The printing speed during the experiments was 2 m/min. The drying temperature of 120 °C was used during the trials with Walki Al-PET substrate. The total length of the ovens used for the drying was 4 m. The activated carbon ink layers were printed with similar screens on the roll-to-roll line and dried at 90 °C to ensure complete drying before storing as a roll. The thicknesses of the graphite and activated carbon layers were 20-25 µm and 70–100 µm, respectively.

B. Characterization

The electrical properties of the capacitors such as capacitance, equivalent series resistance (ESR), and leakage current were determined according to the IEC 62391-1 standard [17] using a Maccor 4300 instrument. In the measurement procedure, the component was first charged and discharged with constant current three times between 0 V and maximum voltage, then the voltage was kept for 30 min at the maximum, after which the capacitance was defined during the constant current discharge step between 80 % and 40 % of the maximum potential. After keeping the supercapacitor for 1 h at constant voltage, the current required to maintain the potential was measured to get the leakage current value. The efficiency was defined as the ratio of the discharged and charged energy in the voltage range of 0 V – maximum potential. To define their lifetime, the supercapacitors were floated at a constant voltage of 0.9-1.6 V for varying periods of time between the above described measurement procedure to show the effect of floating to electrical properties. The cyclic voltammetry experiments were performed with a Zahner Zennium potentiostat.

Bending tests were done for the supercapacitors made of the electrodes fabricated by rotary screen printing. The electrolyte used in the supercapacitors was 1M NaCl. Two series of ten supercapacitors were prepared, where eight of the supercapacitors were bent and two were used as references. One batch of ten samples was sealed by heat sealing and the other was sealed with the 3M adhesive film. The samples were then subjected to two types of mechanical stress: static and cyclic bending. In the static bending stress, the supercapacitor was measured five times with the Maccor instrument. Measurement was done once before the bending, and then with the sample fastened to a cylinder with diameters of 5 cm, 3.5 cm and 2.3 cm as seen in Fig 2. Finally, the supercapacitors were straightened under a small weight and measured once more after the bending. Each time the supercapacitors were left bent for at least 12 h prior to the electrical characterization. The reference supercapacitors were measured five times next to the bent samples to separate the effect of aging by charge-discharge from the bending.

Fig 2. Supercapacitor statically bent to 2.3 cm cylinder and measured.

In the cyclic bending measurement, the supercapacitors were fatigue stressed while attached between two parallel

plates, where the plate distance varied from 1.5 cm to 4.5 cm. The plate movement was controlled with Instron 4411 Universal Tensile Machine (UTM). The plate speed was set at 500 mm/min and the plates were cycled 500 times. The supercapacitors were characterized before and after the cycling.

III. Results and Discussion

The work can be divided to three parts: aqueous electrolytes with and without potassium iodide, lifetime test at constant potential, and mechanical bending tests. The samples printed in laboratory scale by blade coating were used in the electrolyte and lifetime studies and the roll-to-roll printed samples in the bending experiments.

A. *Electrical properties with various electrolytes*

The electrical properties (average of five devices) of supercapacitors having different electrolytes are shown in Table 1.

TABLE I. Electrical properties

Electrolyte	***Capacitance (F)***	***Specific capacitance (F/g)***	***ESR (Ω)***	***Leakage current at 1.6 V(μA)***	***Energy eff. with 1 mA (%)***
NaCl	0.33	28	11	38	83
NaCl + KI	0.95	85	41	121	63
Li_2SO_4	0.31	28	13	35	80
Li_2SO_4 + KI	0.99	95	47	108	60

The choice between NaCl and Li_2SO_4 electrolytes does not significantly change the electrical properties. Similar results have been reported earlier for supercapacitors with graphite current collectors and aqueous NaCl electrolyte [15]. In this case the majority of ESR originates from graphite current collectors. The reason for using potassium iodide was a report indicating improved electrical properties at elevated potential [7]. The addition of KI completely changes the electrical properties. The specific capacitance increases by more than 200 %. Simultaneously, the leakage current increases by the same factor, which means that the self-discharge rate remains constant. The Faradaic reactions responsible for the higher capacitance [7] are relatively slow, which can be seen as increased ESR. The energy efficiency is also decreased due to the higher ESR.

Figure 3 shows cyclic voltammetry behaviour of the supercapacitors with the four various electrolyte alternatives.

The higher capacitance obtained with potassium iodide addition is clearly visible in accordance with the numerical data shown in Table 1. With potassium iodide electrolyte the slope of the current increases at about 1.3-1.4 V indicating increasing leakage current or possibly the beginning of the electrolysis of water.

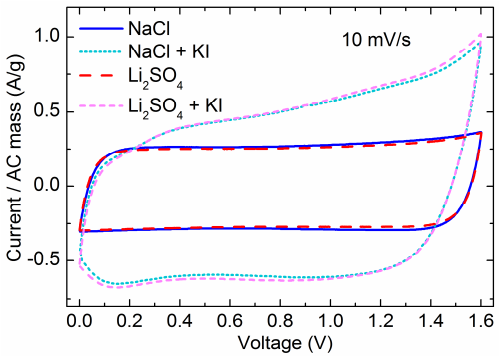

Fig. 3. Cyclic voltammetry with scan rate 10 mV/s for supercapacitors with various electrolytes.

B. *Lifetime: floating tests*

Since the amount of the energy stored in a supercapacitor is proportional to the square of the potential difference between the electrodes, increasing the potential would be beneficial. However, increased voltage is known to shorten supercapacitor lifetime. This would be expected especially with voltage that is high enough to cause the electrolysis of water, since an aqueous solution is used as the electrolyte. It has also been shown that for supercapacitors with neutral aqueous electrolyte 1.0 V can be the optimal choice [18].

The floating tests were first made at 0.9 V and 1.2 V for supercapacitors with 1 M NaCl electrolyte. The capacitance as a function of floating time is presented in Figure 4. As can be seen, in the beginning the capacitance clearly decreased by few percents then the rate of capacitance decrease became lower. After 2000 hours about 97 % of the original capacitance was remaining when floated at 0.9 V and about 89 % when floated at 1.2 V.

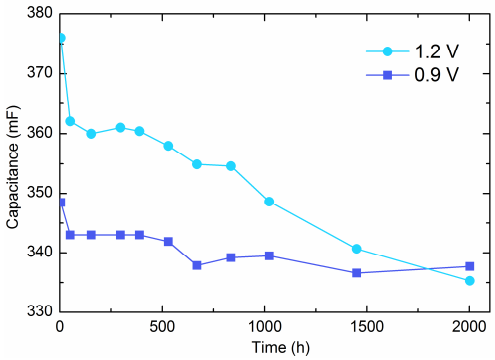

Fig. 4. Capacitance of supercapacitors with 1 M NaCl electrolyte as a function of time when floated at 0.9 V and 1.2 V.

Based on the encouraging cyclic voltammetry results as presented in Figure 2, lifetime tests for the various electrolytes were performed at 1.6 V. The capacitance as a function of floating time is shown in Figure 5.

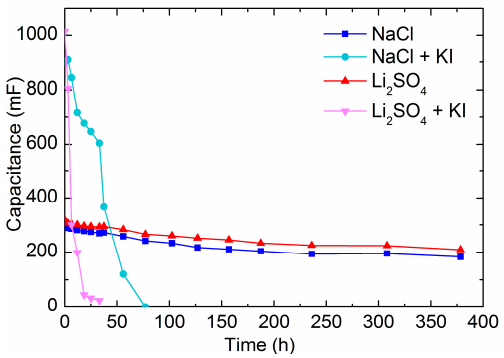

Fig. 5. Capacitance as a function of floating time at 1.6 V.

There is a clear difference in the aging behavior between the supercapacitor with or without potassium iodide addition in the electrolyte. Although KI increases the capacitance, the positive effect is spoiled by the considerably shortened lifetime. If the lifetime is defined to be the point when 80 % of the original capacitance is remaining, without KI the lifetime in this case was 90-120 h and with KI 3-12 h. Compared with Abbas et. al. [7] our lifetime for the supercapacitors with KI containing electrolytes is considerably shorter. The difference could originate from different supercapacitor materials and encapsulation. Possibly the lower oxygen content in the electrolyte due to Swagelok cells, use of glass fiber separator or PTFE electrode binder facilitated longer lifetime.

Beside capacitance during floating we also measured the change in ESR and leakage current. The ESR and leakage current of supercapacitors with NaCl electrolyte as a function of floating time is presented in Figure 6. During 2000 hours the ESR remained almost constant at 8 Ω when floated at 0.9 V and increased to about 10 Ω in the case of floating at 1.2 V. Thus in the same way as with capacitance, the deterioration rate was faster with higher voltage. Still the change in ESR even with 1.2 V is tolerable and does not increase losses considerably. The leakage current is obviously higher when measured at 1.2 V than at 0.9 V. The behavior as a function of time is similar in both cases. When kept at constant voltage, the leakage levels to an almost fixed value and in this cases remains constant for the whole test time of 2000 hours.

The change of ESR and leakage current were defined also at 1.6 V to find out how other properties beside capacitance are affected by the higher potential. From the curves in Figure 7 it is clear that especially with KI addition to the electrolyte the lifetime is limited as already confirmed by the change in capacitance. The deterioration of ESR could be partly explained by the splitting of water, which creates gas bubbles and thus increases the ionic resistance of the electrolyte. The gas bubbles also decrease the capacitance by preventing the contact between electrolyte and electrode surface. The reason for the quick increase of leakage current in the case of NaCl+KI electrolyte is not clear but could also be associated to gas formation resulting in mechanical stress causing an electrically conductive path through the separator.

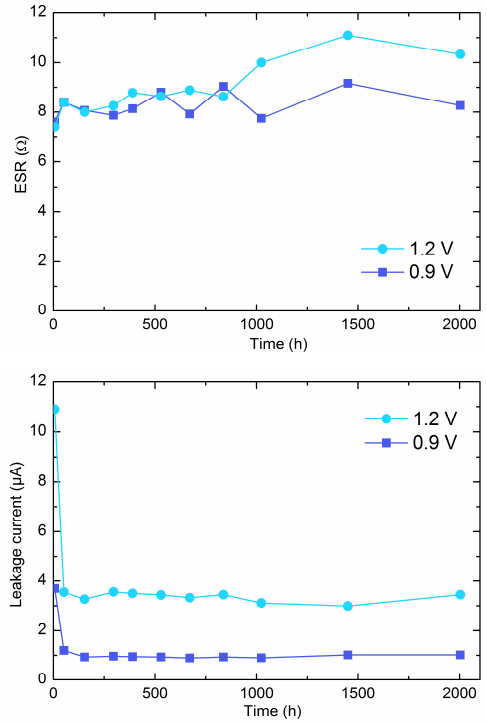

Fig. 6. ESR and leakage current as a function of floating time with 1 M NaCl electrolyte.

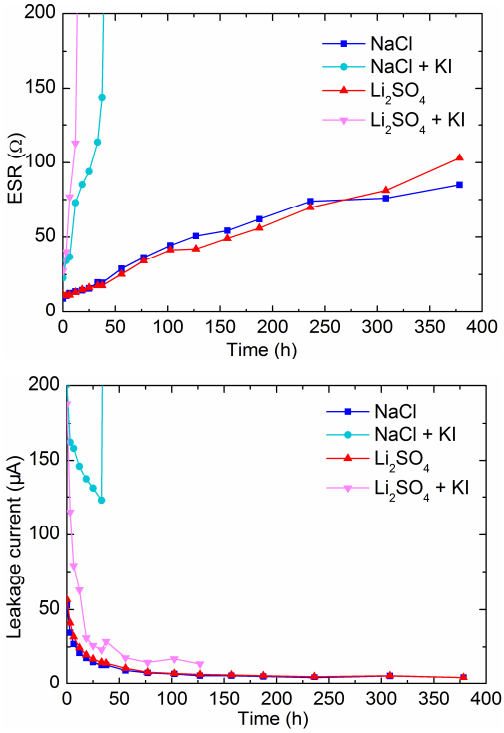

Fig. 7. ESR and leakage current as a function of floating time at 1.6 V.

C. *Bending tests*

Fig 8 shows the charge discharge cycle for the heat sealed supercapacitors after successive static bending tests to the diameters 5, 3.5 and 2.3 cm. The reference and two samples are compared to each other.

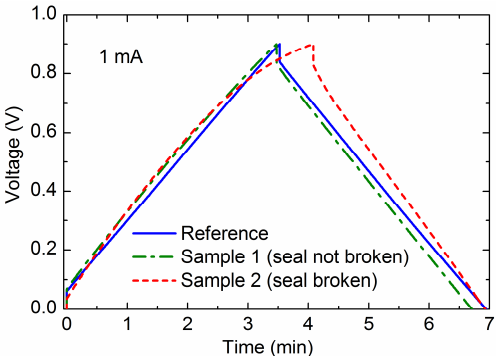

Fig 8. Charge-discharge cycle of two samples after static bent and a reference sample using 1 mA current.

As can be seen in Figure 8, the sample 1 follows the same trend as the reference sample. The rise and fall time of the sample 1 is slightly faster because of smaller capacitance value, which is due to small thickness differences in the printed electrodes. The bending does not affect the electrical properties of supercapacitor in the case of sample 1. However, charging sample 2 takes somewhat longer than sample 1 and reference samples and the end of charging in the case of sample 2 becomes nonlinear. This indicates that the leakage current for sample 2 rises considerably after the bending, which was determined to be due to a broken seal between the electrodes. Broken seal opens up a pathway for oxygen to enter the electrolyte, which immediately increases the leakage current value. The ambient air exposure dries the electrolyte over time and creates an open circuit between the electrodes. The numerical results for the before and after measurement of the samples in Fig. 8 are shown in table II.

Table II. Electrical properties before and after static bending

		Before	**After**
Reference	Capacitance (mF)	239	238
	ESR (Ω)	28.7	30.6
	Leakage current (µA)	6.9	3.0
Sample 1	Capacitance (mF)	235	235
	ESR (Ω)	34.9	34.3
	Leakage current (µA)	7.9	5.1
Sample 2	Capacitance (mF)	227	231
	ESR (Ω)	28.8	54.4
	Leakage current (µA)	6.4	244

The Table II shows that the bending does not effect the electrical properties of the supercapacitor if the seal is not broken.

With the heat sealed samples, the seal broke in seven out of eight samples, which was seen as a rise in the leakage current. However, when using the 3M adhesive as sealant material, all the eight samples survived the static bending test. Another batch of 3M adhesive sealed supercapacitors was then subjected to the cyclic bending test. The 500 cycles did not impact to the electrical properties of the supercapacitor and the seal was not harmed by the bending. The limiting factor of the bending was correct sealing of the supercapacitor.

IV. Conclusions

We have fabricated flexible aqueous supercapacitors and characterized their essential electrical properties and durability regarding lifetime when floated at various potentials as well as when mechanically bent. Aqueous electrolytes with potassium iodide increase the capacitance 3-fold but have negative effect on the lifetime. The electrical properties are almost identical for NaCl and Li_2SO_4 containing electrolytes. Without potassium iodide aqueous NaCl electrolyte shows almost negligible deterioration in electrical properties when floated at 0.9 V and only little deterioration after floating at 1.2 V for 2000 hours. The experiments at 1.6 V proved that the devices should not be used at that voltage continuously but on the other hand occasional short time use at this high voltage does not destroy them. To optimize the durability against bending 3M adhesive is preferred to heat sealing. The bending experiments showed the feasibility of the supercapacitors in applications where flexibility is required.

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