1	Recycling supercapacitors based on shredding and mild thermal treatment
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8	ABSTRACT
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10	Supercapacitors are widely used in electric and hybrid vehicles, wind farm and low-power
11	equipment due to their high specific power density and huge number of charge-discharge cycles. Waste
12	supercapacitors should be recycled according to EU directive 2002/96/EC on waste electric and
13	electronic equipment. This paper describes a recycling approach for end-of-life supercapacitors based
14	on shredding and mild thermal treatment.
15	At first, supercapacitors are shredded using a Retsch cutting mill. The shredded mixture is then
16	undergone thermal treatment at 200°C to recycle the organic solvent contained in the activated carbon
17	electrodes. After the thermal treatment, the mixture is roughly separated using a fluidized bed method
18	to remove the aluminium foil particles and paper particles from the activated carbon particles, which is
19	subsequently put into water for a wet shredding into fine particles that can be re-used. The recycled
20	activated carbon has a BET surface area of up to 1200 m ² /g and the recycled acetonitrile has a high
21	purity.
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23	Keywords: supercapacitors, activated carbon, recycling
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- 1 1. Introduction
- 2

3 Supercapacitors are electrochemical devices for energy storage with very fast power delivery or uptake due to the physical nature of the Helmholtz double-layer formed at the interface between the 4 high surface area carbon electrode and the electrolyte solution. A typical fully charging or discharging 5 6 time is in seconds with up to a million cycles, and the power density can be up to 15 kW/kg (Beguin et 7 al., 2014). These characteristics make supercapacitors ideal for applications in complementing or 8 replacing batteries for electric and hybrid vehicles, smart grids, and consumer electronics. Global sales 9 of supercapacitors amounted to \$470 million in 2010 and will rise to around \$1.2 billion in 2015 10 (Munchgesang et al., 2014).

With an increasing numbers of supercapacitors in use, disposal of end-of-life components and manufacturing scraps will become an important issue. Moreover, waste supercapacitors are classified as hazardous products and require a special treatment facility according to EU directive 2002/96/EC on waste electric and electronic equipment. Therefore, a viable recycling technology is desirable from a point of view of sustainability and legislation on recycling.

Supercapacitors are comprised of two electrodes separated by a porous non-electric conductive separator housed in a metallic casing (Budde-Meiwes et al., 2013). Currently available electrodes are made of activated carbon deposited on a metallic foil, which works as the support of the electrode and current collector. A polymer binder is used to provide cohesion between the activated carbon particles and adhesion of the carbon particles to the metallic foil. The electrodes are then soaked in an electrolyte solution of organic solvent and dissolved salt.

22 Recycling supercapacitors has not yet attracted attention so far, although recycling other 23 electrochemical devices such as electrolytic capacitors and batteries has already been in commercial 24 operations in many countries. The primary objective in recycling those devices is the recovery of 25 precious metals contained in the electrodes (Bernardes et al., 2004). A pyrolysis or incineration process 26 is often adopted to remove the organic matter in gas form, leaving the precious metals for metallurgical 27 refining (Gratz et al., 2014; Horai et al., 2014; Joo et al., 2015). Chemical or electrochemical precipation 28 is also used for recovery of the previous metals by using a suitable solvent to dissolve the metal salts in 29 the electrodes (Cai et al., 2014; Renault et al., 2014; Zhang et al., 2015). However, thermal processes are 30 frequently used in commercial operations due to its simplicity and robustness (Bernardes et al., 2004; 31 Chagnes and Pospiech, 2013; Zeng et al., 2014). Supercapacitors do not contain precious metals, but contain much more electrolyte solution dispersed in activated carbon electrodes. Alternative 32 33 procedures must be developed to recycle the hazardous electrolyte solution instead of combustion.

Although activated carbon is relatively cheap, a feasible reuse of the activated carbon would partly
 compensate the recycling cost.

3 Several hazards are needed to be considered in the development of the recycling technologies. (1) 4 Hazards associated with the solvents. The most widely used solvents for dissolving electrolytes are propylene carbonate (PC) and acetonitrile (AN) (Beguin et al., 2014). (2) Hazards associated with the 5 6 electrolytes. The electrolytes used in supercapacitors are organic salts. Tetraethylammonium 7 tetrafluoroborate (TEA-BF₄) is the most widely used in commercial supercapacitors (Beguin et al., 2014). 8 (3) Hazards associated with the polymer binder. The most commonly used binders are fluropolymers 9 such as polytetrafluroethylene (PTFE) or poly(vinylidene fluoride) (PVDF) due to their inert nature. 10 A straightforward method to recycle the organic solvent is via evaporation after disintegration of 11 the waste supercapacitors. The actual temperature for removing the organic solvent needs to be 12 determined since it is absorbed into the porous carbon, not on the surface. After removing the organic solvent, the polymer binder and organic salt will be left in the activated carbon. Further separation of 13 14 the salt and fluoropolymer binder is problematic. The salt is soluble in water and most organic solvent. It can be recycled by leaching using a suitable solvent. However, recycling such small amount of organic 15

16 salt would be expensive. The fluoropolymer binders are not soluble in normal organic solvents.

17 If the electrolyte salt and the polymer binder are removed by thermal treatment to produce clean 18 activated carbon, further environmental concerns will arise due to the nasty decomposition products. 19 TEA-BF₄ is decomposed into toxic compounds, triethylamine $(C_2H_5)_3N$, ethylfluoride C_2H_5F and boron 20 trifluoride BF₃ (Prasad and Sudhakarbabu, 2014). The decomposition products of fluoropolymers in 21 nitrogen are mainly tetrafluoroethylene, cyclo-perfluorobutane, hexafluoropropene (HFP), and other 22 fluorocarbons (Arito and Soda, 1977; Bhadury et al., 2007; Conesa and Font, 2001; Simon and Kaminsky, 23 1998). Most of these substances are toxic, but highly toxic substances like perfluoroisobutene or 24 fluorophosgene can be formed under some reaction conditions (Simon and Kaminsky, 1998).

25 On the other hand, the presence of the polymer binder will be an advantage to prevent dust 26 formation during handling the recycled activated carbon. Also, the organic salt used in supercapacitors 27 is thermally stable and chemically inert. When the above characteristics of the polymer binder and the 28 salt, together with the difficulties in separation, are taken into account, there lacks the necessity for 29 separating the binder and the salt from the activated carbon. However, an upper temperature limit 30 should be placed for the re-use of the recycled activated carbon to prevent the decomposition of the 31 organic matter. Therefore, after the solvent is recycled, the major recycling task is to develop a proper method to strip off the large activated carbon agglomerates from the metallic foil and then disintegrate 32 33 the large activated carbon agglomerate into usable fine granules.

In this paper, we describe a principle of concept recycling method for supercapacitors based on
 shredding and mild thermal treatment to recycle the solvent and the activated carbon into fine particles
 ready for use. Subsequently, the surface area and pore structure of the recycled activated carbon is
 characterised, and the upper limit temperature is defined for the recycled activated carbon. Finally, a
 conceptual recycling process is proposed from the results of the proof of concept work.

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2. Materials and Methods

8

9 2.1. Materials.

10 The supercapacitors were purchased from Mouser Electronics (UK) model Boostcap [®]25F-2.7V, 11 which was manufactured by Maxwell Technologies. The electrodes were made of activated carbon 12 deposited on aluminium foil, and the electrolyte solution was tetraethylammonium tetrafluoroborate 13 (TEABF₄) dissolved in acetonitrile. Paper was used as the non-electric conductive separator for the 14 electrodes.

15

16 **2.2. Recycling procedure.**

17 A Restch cutting mill (SM300) is used to disintegrate the supercapacitors at a rotation speed of 18 1200rpm for 5 minutes. The sieve below the three-disc rotor had 4mm square holes. During the 19 mechanical treatments, extraction fan were used to prevent formation of mixtures of air-organic vapour 20 (Lain, 2001). Due to proof of concept nature of the work, condensation of the small amount of organic vapour was not conducted. About 60% of solvent was lost. The other 40% was still retained inside the 21 22 pores of the activated carbon, which was recycled by evaporation. The shredded mixture was then 23 placed in a 500 mL round bottom flask at an elevated temperature of 200°C to recycle the solvent for 30 24 minutes. After the solvent was removed, the dried mixture was placed in a fluidized bed (ϕ 70 x 400mm) 25 to separate the particles from the paper insulator, plastic packaging, metal pins, rubber sealing and 26 aluminium foil particles from the activated carbon particles. The air velocity was 0.5 m/s to remove 27 paper particles, and increased gradually to 0.8 m/s to blow out the activated carbon agglomerates (less 28 than 4 mm diameter). The aluminium foil particles, metal pins and rubber disc were left in the bed. A 29 standard cyclone was used with the fluidized bed to separate the solid particles from the fluidizing air 30 that carried the particles. In the cyclone, the entrained particles in the carrier air spiral down the barrel 31 and cone region and exit through the dipleg into a collection flask. The carrier gas reverses its flow and exit through the outlet as clean air. The separated large agglomerates of activated carbon were then put 32 33 into 300 mL water in a plastic beaker. A Waring heavy duty blender (WSB50E) was used to shred the raw 34 activated carbon particles into fine particles at a speed of 18000 rpm for 5 minutes. After the wetshredding, the mixture was filtered first using a fine metal screen to remove the aluminium particles
that were blown out together with the activated carbon. The filtrate was filtered again on a filter paper
under vacuum to remove water. The obtained activated carbon was dried at 120°C for 2 days for later
analysis. A diagram in Figure 1 shows the whole recycling process and the product.

5 The reason for use a wet-shredding step rather than shredding further in the Retsch cutting mill is 6 to prevent the lost of carbon during shredding under extraction fan. Also energy consumption of the 7 Retsch cutting mill for size reduction into fine sizes is large. Our experimental work indicates that 8 shredding in water can reduce the size of activated carbon agglomerates effectively, but it is not 9 effective to reduce the aluminium particles and the plastic packaging material, which facilitates later 10 separation by filtration of the fine activated carbon particles from the residual aluminium and plastics 11 that was not separated by the fluidized bed.

12

13 **2.3.** Materials characterisation.

The conditions of the evaporation of acetonitrile and the decomposition temperatures of the polymer binder and the electrolyte salt were determined using thermogravimetric analysis (TGA). The TGA experiment was conducted using a Q600 Simultaneous DSC-TGA (TA Instruments). About 10 mg of the electrode was cut into small pieces and then placed into a platinum crucible. The sample was heated from room temperature to 750°C under nitrogen gas flow with a heating rate of 20, 50, and 100°C/min.

20 The surface area and the pore size of the recycled activated carbon were determined by nitrogen 21 adsorption at 77 K using a Quantachrome Autosorb-1 sorptometer. The samples were outgassed at 22 300°C in vacuo overnight before the adsorption / desorption measurements were made. The surface 23 area was calculated respectively using multi-point BET method in the partial pressure (P/P₀) range 0.05 to 0.2, and Langmuir method in the partial pressure (P/P_0) range 0.05 to 0.4 from the adsorption 24 25 isotherm branch. The mesopore size was calculated using the BJH method from the desorption isotherm 26 branch, and the micropore size was calculated using the DA method from the adsorption isotherm 27 branch.

In order to investigate the effect of thermal treatment temperature on the surface area of recycled activated carbon, some of the recycled activated carbon was heat treated at 350°C for 60 minutes or 600°C for 5 minutes to remove the polymer binder and the organic salt, and BET surface area was measured after the treatments.

32

33 3. Results and discussion

1 **3.1.** Thermal analysis

2 Figure 2 shows the TG traces of the activated carbon electrode at various heating rates. The 3 temperature for each peak is listed in Table 1. At a heating rate of 20°C/min, there are four peaks at 4 around 25°C, 75°C, 375°C and 560°C. At higher heating rates, the four peaks shift to the right gradually. 5 The first two peaks at 25°C and 75°C can be attributed to the evaporation of the acetonitrile on the 6 surface and in the pores respectively. The peaks at 375°C and 560°C are attributed to the decomposition 7 of the polymer binder and the electrolyte salt respectively. The designation was verified by TG analysis 8 of activated carbon adsorbed with acetonitrile only, where peaks appeared at 25, 75 and 375°C, but the 9 peak at around 560°C did not appear.

The kinetic equations for the evaporation of acetonitrile in the pores, decomposition of the
binder and decomposition of the electrolyte can be expressed using Eq. 1.

12

13
$$\frac{d\alpha}{dT} = \frac{A}{\beta} exp\left(-\frac{E}{RT}\right)(1-\alpha)^n$$

14

Where α is the fractional conversion, T is the temperature, β is the heating rate, A is the pre-exponential
factor, E is the activation energy, n is the order of reaction and R is the universal gas constant.
Kessinger's method (Kissinger, 1957) was used to derive the kinetic parameters A, E, and n, as given in

(1)

Table 1. Eq. 1 was then solved numerically using the 4th order of Runge-Kutta method for the time to
evaporate acetonitrile (Figure 3) and the decomposition profile of the binder and electrolyte at various
temperatures (Figures 4 and 5 respectively).

21 As can be seen from Fig. 3, the time for complete evaporation of the acetonitile in the electrodes 22 is about 15 seconds at 120°C. In practice, when the evaporation was conducted at 120°C, it took about 23 10 minutes for complete evaporation, which may be due to the diffusion control because the activated 24 carbon is in a large agglomerate form after shredding using the Retsch cutting mill. Considering that the 25 evaporation of the acetonitrile is mainly controlled by diffusion rather than kinetic control, we adopted 26 200°C to evaporate the acetontrile to shorten the time, which needs about 5 minutes to evaporate all 27 the acetonitrile contained in the activated carbon. Another advantage for processing at higher 28 temperature is to facilitate the separation of paper in fluidized bed, which becomes fragile at this 29 temperature. Also at this temperature, the extent of decomposition of the polymer binder and the 30 elecytrolyte can be neglected, as shown in Figures 4 and 5. According to the decomposition kinetics of acetonitrile in nitrogen (Asmus and Houser, 1969; Britt, 2002), acetonitrile is stable at a temperature up 31 32 to 300°C for evaporation.

1 From Figures 4 and 5, it can be seen that below 250°C, the binder is quite stable, and the salt is 2 stable below 400°C. Therefore, the recycled activated carbon fibre can be used below 250°C, which is 3 far beyond the normal using temperature of fresh activated carbon.

4 5

3.2. Qualities of the recycled components

6 Before starting recycling, we wondered if the activated carbon can be stripped off the aluminium 7 foil by shredding in the Retsch cutting mill. It is surprised to find later that the activated carbon can be 8 stripped off just by shredding. The activated carbon left on the aluminium foil support is less than 1 % 9 (wt) after examination using ashing method. Since this work is a proof of concept, the acetonitrile 10 vapour generated during the shredding was not condensed, but only recycled by evaporation of the shredded mixture after the shredding. In this situation, about 40% (wt) of the acetonitrile was recycled. 11 12 In a large scale recycling facility, a vacuum line and condenser can be connected with the cutting 13 chamber to collect the volatile solvent. In a fluidized bed separator, the aluminium particles are left in 14 the bed, while the paper is blown out at first and the activated carbon particles are blown out subsequently by increasing air velocity. A picture of the recycled acetonitrile, activated carbon and 15 aluminium particles are shown in Figure 1. The recycled acetonitrile is very clear. No impurities can be 16 17 detected using GC-MS.

Figure 6 shows the SEM images of activated carbon before and after wet shredding at 200°C. 18 19 Before wet shredding, activated carbon is in a large agglomeration form held together by the polymer 20 binder. After wet-shredding, the recycled carbon has a granular shape, indicating that wet-shredding is 21 sufficient to break the binder cohesion.

22 Figure 7 shows the nitrogen adsorption and desorption curves for the recycled activated carbon. 23 The adsorption isotherms correspond to type IV of the referred IUPAC classification, while the 24 adsorption/desorption shows type B hysteresis (de Boer, 1958). The shape of the isotherm indicates 25 that the recycled carbons contain both micropores and well developed mesopore.

26 The results for nitrogen adsorption measurements are given in Table 2. The surface area of the 27 recycled activated carbon decreases with an increase in heat treatment temperature. When the temperature increases from 200°C after removal of acetonitrile to 350°C for 60 minutes, the surface 28 29 area has a slight decrease. However, when the heat treatment temperature increases from 200°C to 600° C for 5 minutes, the surface area has a significant drop from 1204.6 m²/g to 569.3 m²/g. The 30 31 Langmuir surface area has a similar trend. The diameter and volume of the micropores and mesopores also varies with the heat treatment temperature. With an increase in heat treatment temperature, the 32 diameter of micropores increases and the volume of the micropores decreases steadily. This indicates 33

that some of the micropores have coalesced at high temperatures. However, the diameter and volume
 of the mesopores does not have distinct change with temperature.

3 It should also be noted from Table 2 that the presence of the polymer binder and electrolyte salt
4 do not affect the surface area of the recycled activated carbon. The most important factor is the
5 thermal treatment temperature.

6

7

3.3. Proposed recycling process based on the proof-of-concept work

8 Based on the results of this proof of concept work, a schematic diagram for supercapacitor 9 recycling is shown in Figure 8. In this conceptual recycling scheme, end-of-life supercapacitors are 10 collected and shredded using a cutting mill connected with a vacuum line and a condenser. The solvent vapour generated during shredding is condensed in the condenser. The shredded mixture goes to a 11 12 dryer where the residue solvent in the activated carbon is evaporated at an elevated temperature and then condensed in the same condenser. The dried shredded mixture is fed into a fluidized bed 13 14 separator by means of a belt conveyer. The lightest component paper particles are removed first at a low air velocity, and then the second lightest component activated carbon particles are removed at a 15 higher air velocity and collected via the cyclone attached to the fluidized bed. The collected activated 16 17 carbon is fed into a wet shredder containing water medium by means of an airlock valve fitted under 18 the dipleg of the cyclone. The activated carbon is shredded into fine particles in the wet-shredder using 19 a high speed stirrer. The suspension of the shredded fine activated carbon particles is first filtered using 20 a screen filter to remove the small amount of residual aluminium foil particles and the activated carbon 21 is separated from the water using a centrifuge. The separated activated carbon is then dried in a dryer 22 and collected. The separated aluminium particle may go to a metallurgical recycling plant as raw 23 materials.

In this recycling process, energy is mainly consumed in the cutting mill for size reduction of waste supercapacitors and the wet-shredding process. In the following, estimations of the energy consumption and the main output of the recycled materials are made based on a recycling capacity of 100 kg/h. The supercapacitors are assumed to consist of 40% (wt) aluminium housing and aluminium electrode support, 30% (wt) of activated carbon electrode and 25% (wt) of actonitrile, which are typical composition for commercial supercapacitors. The fine grain size of the cutting mill is assumed to be 4 mm.

For an average grain size of 4mm, energy consumption of the cutting mill is about 100 KWh/t (Macko, 2012). Since shear force is mainly responsible for the wet shredding process, the energy demand in a large scale operation can be scaled-up based on power drawn per volume of liquid with similar loading of coarse activated carbon particles, and many types of shredding machine may be used (Cui and Forssberg, 2003). In the experimental study, the high speed immersion blender has a power of
 0.65 kW in a 300 mL water containing 12 g dried coarse activated carbon particles for 5 minutes. The
 energy density is 0.65 kW x (5/60) h/0.3 L = 0.054 KWh/L, and the loading of dried shredded mixture is
 12g/300mL = 0.04 kg/L.

According to the above assumption and experimental wet shredding power drawn and loading, the energy consumption and major material output are as follows: The energy consumption for cutting mill is 100 kg/h x 40% /1000 kg/t x 100 KWh/t = 4 KWh. The energy consumption for wet shredding is 100 kg/h x 30% / 0.04 kg/L x 0.054 KWh/L = 41 KWh. If the energy demand for other parts accounts for 30% (Macko, 2012), the total energy demand will be (41 + 4) x (1+30%) = 58.5 KWh. Approximately 100 kg/h x 23% = 23 kg/h acetonitrile, 100 kg/h x 30% = 30 kg/h activated carbon, and 100 kg/h x 40% = 40 kg/h aluminium particles are recycled.

The operations such as size reduction by a cutting mill, fluidized bed separation, evaporation, conveyer transport, centrifugation and wet shredding are traditional unit operations in chemical engineering. Therefore, the maintainability of the recycling process is high and energy demand can be reduced after process optimisation. The size of the supercapacitors that can be recycled using this process is dependent on the size of the cutting mill. For recycling large size supercapacitors, a disassembly process has to be taken into account, which is well developed in the waste treatment of waste electric and electronic equipment (WEEE).

19

20 4. CONCLUSIONS

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A recycling process for supercapacitors is developed based on shredding and mild thermal treatment. The three main component, activated carbon, solvent and aluminium can be recycled, while the polymer binder and electrolyte salt are left in the recycled activated carbon. The presence of polymer binder is beneficial to maintain the recycled carbon in a granular form. Due to the presence of electrolyte salt and binder, the upper limit use temperature of the recycled carbon should be below the 250°C.

The shredding in Retsch cutting mill is sufficient to strip the activated carbon off the aluminium foil. After shredding, a mild thermal treatment at 200°C can evaporate all the solvent in 5 minutes. At this temperature, the extent of decomposition of the polymer binder and electrolyte salt can be neglected. After removal of the solvent, the activated carbon agglomerates can be separated from the shredded mixture using a fluidized bed. The separated activated carbon can be broken down into fine particles by the wet-shredding in water with a surface area up to 1200 m²/g.

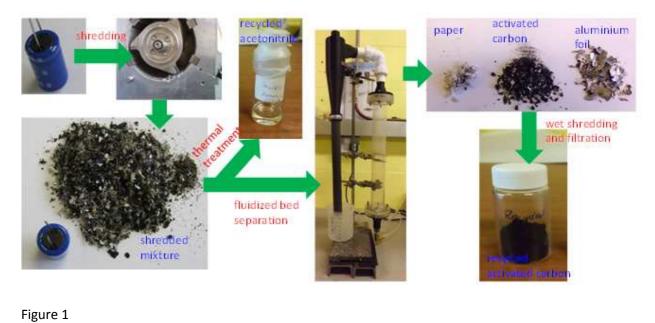
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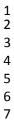
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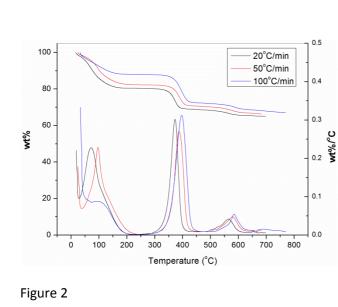
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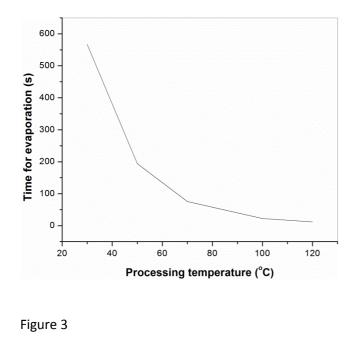
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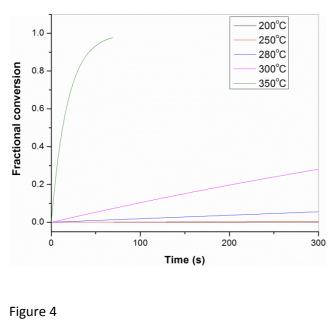












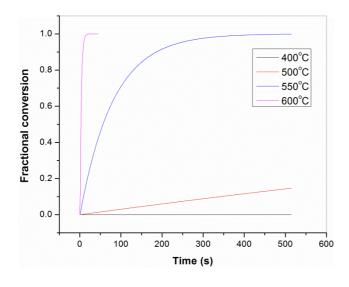
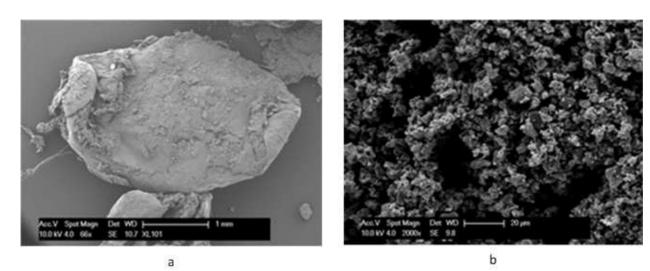


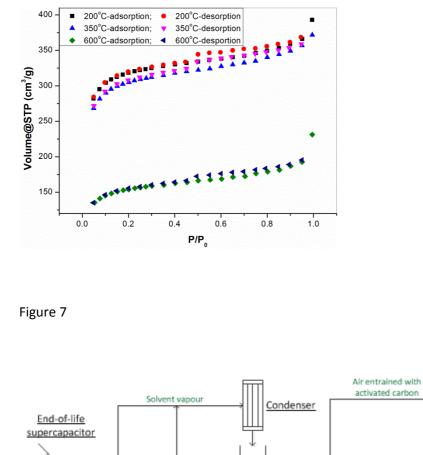


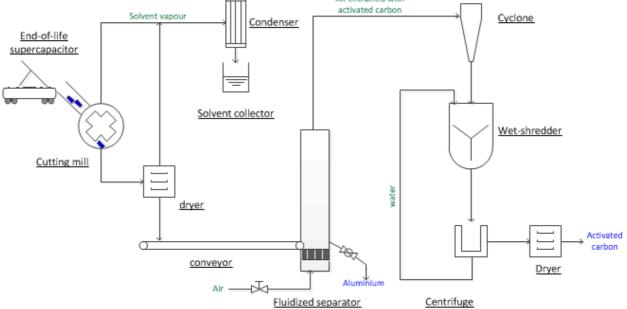
Figure 5



- Figure 6

- 16





- 13 Figure 8

- 2 Table 1. Evaporation and decomposition temperatures of acetonitrile, binder and electrolyte

3 determined using thermogravimetric analysis.

Heating rate	2 nd Acetonitrile	Binder decomposition	Electrolyte decomposition					
(°C/min)	evaporation (°C)	(°C)	(°C)					
20	71	374	562					
50	95	387	579					
100	104	398	584					
Kinetic constants								
E (KJ/mol)	43.8	231.5	391.0					
n	1.2	1.1	1.0					
A (min⁻¹)	4.5 x 10 ⁷	8.3 x 10 ¹⁹	4.8 x 10 ²⁴					

11 Table 2 The surface area and pore size characterisation of the recycled activated carbons

Recycling	BET Langmuir		DA micropore		BJH mesopore	
Temperature	m²/g	m²/g	Vol.	diameter	Vol.	diameter
(°C)			(cm ³)	(nm)	(cm³)	(nm)
200	1204.6	1464.9	0.555	1.26	0.130	3.81
350	1135.7	1426.6	0.534	1.30	0.112	3.81
600	569.3	718.7	0.281	1.42	0.128	3.80