



Jiang, Guozhan and Pickering, Stephen J. (2016)
Recycling supercapacitors based on shredding and mild
thermal treatment. *Waste Management*, 48 . pp. 465-
470. ISSN 1879-2456

Access from the University of Nottingham repository:

<http://eprints.nottingham.ac.uk/45473/8/waste%20management%202016.pdf>

Copyright and reuse:

The Nottingham ePrints service makes this work by researchers of the University of Nottingham available open access under the following conditions.

This article is made available under the Creative Commons Attribution Non-commercial No Derivatives licence and may be reused according to the conditions of the licence. For more details see: <http://creativecommons.org/licenses/by-nc-nd/2.5/>

A note on versions:

The version presented here may differ from the published version or from the version of record. If you wish to cite this item you are advised to consult the publisher's version. Please see the repository url above for details on accessing the published version and note that access may require a subscription.

For more information, please contact eprints@nottingham.ac.uk

1 **Recycling supercapacitors based on shredding and mild thermal treatment**

2
3 *Guozhan Jiang¹, Stephen J Pickering*

4 *Division of Materials Mechanics and Structures,*
5 *University of Nottingham, Nottingham NG7 2RD, UK*

6 7 8 **ABSTRACT**

9
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 m²/g and the recycled acetonitrile has a high
21 purity.

22
23 **Keywords:** supercapacitors, activated carbon, recycling

24

¹ Current address: School of Biology Chemistry and Forensic Science, University of Wolverhampton,
Wolverhampton WV1 1LY, UK. Email: Guozhan.jiang@wlv.ac.uk

1 **1. Introduction**

2

3 Supercapacitors are electrochemical devices for energy storage with very fast power delivery or
4 uptake due to the physical nature of the Helmholtz double-layer formed at the interface between the
5 high surface area carbon electrode and the electrolyte solution. A typical fully charging or discharging
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).

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

16 Supercapacitors are comprised of two electrodes separated by a porous non-electric conductive
17 separator housed in a metallic casing (Budde-Meiwes et al., 2013). Currently available electrodes are
18 made of activated carbon deposited on a metallic foil, which works as the support of the electrode and
19 current collector. A polymer binder is used to provide cohesion between the activated carbon particles
20 and adhesion of the carbon particles to the metallic foil. The electrodes are then soaked in an
21 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 precipitation
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
32 contain much more electrolyte solution dispersed in activated carbon electrodes. Alternative
33 procedures must be developed to recycle the hazardous electrolyte solution instead of combustion.

1 Although activated carbon is relatively cheap, a feasible reuse of the activated carbon would partly
2 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
5 propylene carbonate (PC) and acetonitrile (AN) (Beguin et al., 2014). (2) Hazards associated with the
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 fluoropolymers
9 such as polytetrafluoroethylene (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
13 solvent, the polymer binder and organic salt will be left in the activated carbon. Further separation of
14 the salt and fluoropolymer binder is problematic. The salt is soluble in water and most organic solvent.
15 It can be recycled by leaching using a suitable solvent. However, recycling such small amount of organic
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 (C₂H₅)₃N, ethylfluoride C₂H₅F 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
32 method to strip off the large activated carbon agglomerates from the metallic foil and then disintegrate
33 the large activated carbon agglomerate into usable fine granules.

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

6 7 **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
21 vapour was not conducted. About 60% of solvent was lost. The other 40% was still retained inside the
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 (ϕ70 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
32 exit through the outlet as clean air. The separated large agglomerates of activated carbon were then put
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 wet-

1 shredding, the mixture was filtered first using a fine metal screen to remove the aluminium particles
2 that were blown out together with the activated carbon. The filtrate was filtered again on a filter paper
3 under vacuum to remove water. The obtained activated carbon was dried at 120°C for 2 days for later
4 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.**

14 The conditions of the evaporation of acetonitrile and the decomposition temperatures of the
15 polymer binder and the electrolyte salt were determined using thermogravimetric analysis (TGA). The
16 TGA experiment was conducted using a Q600 Simultaneous DSC-TGA (TA Instruments). About 10 mg of
17 the electrode was cut into small pieces and then placed into a platinum crucible. The sample was
18 heated from room temperature to 750°C under nitrogen gas flow with a heating rate of 20, 50, and
19 100°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/P_0) range 0.05
24 to 0.2, and Langmuir method in the partial pressure (P/P_0) range 0.05 to 0.4 from the adsorption
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.

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

32 33 **3. Results and discussion**

34

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.

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

12

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

14

15 Where α is the fractional conversion, T is the temperature, β is the heating rate, A is the pre-exponential
16 factor, E is the activation energy, n is the order of reaction and R is the universal gas constant.

17 Kissinger's method (Kissinger, 1957) was used to derive the kinetic parameters A , E , and n , as given in
18 Table 1. Eq. 1 was then solved numerically using the 4th order of Runge-Kutta method for the time to
19 evaporate acetonitrile (Figure 3) and the decomposition profile of the binder and electrolyte at various
20 temperatures (Figures 4 and 5 respectively).

21 As can be seen from Fig. 3, the time for complete evaporation of the acetonitrile 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 acetonitrile 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 electrolyte can be neglected, as shown in Figures 4 and 5. According to the decomposition kinetics of
31 acetonitrile in nitrogen (Asmus and Houser, 1969; Britt, 2002), acetonitrile is stable at a temperature up
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
11 shredded mixture after the shredding. In this situation, about 40% (wt) of the acetonitrile was recycled.
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
15 subsequently by increasing air velocity. A picture of the recycled acetonitrile, activated carbon and
16 aluminium particles are shown in [Figure 1](#). The recycled acetonitrile is very clear. No impurities can be
17 detected using GC-MS.

18 [Figure 6](#) shows the SEM images of activated carbon before and after wet shredding at 200°C.
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
28 temperature increases from 200°C after removal of acetonitrile to 350°C for 60 minutes, the surface
29 area has a slight decrease. However, when the heat treatment temperature increases from 200°C to
30 600°C for 5 minutes, the surface area has a significant drop from 1204.6 m²/g to 569.3 m²/g. The
31 Langmuir surface area has a similar trend. The diameter and volume of the micropores and mesopores
32 also varies with the heat treatment temperature. With an increase in heat treatment temperature, the
33 diameter of micropores increases and the volume of the micropores decreases steadily. This indicates

1 that some of the micropores have coalesced at high temperatures. However, the diameter and volume
2 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
11 vapour generated during shredding is condensed in the condenser. The shredded mixture goes to a
12 dryer where the residue solvent in the activated carbon is evaporated at an elevated temperature and
13 then condensed in the same condenser. The dried shredded mixture is fed into a fluidized bed
14 separator by means of a belt conveyer. The lightest component paper particles are removed first at a
15 low air velocity, and then the second lightest component activated carbon particles are removed at a
16 higher air velocity and collected via the cyclone attached to the fluidized bed. The collected activated
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.

24 In this recycling process, energy is mainly consumed in the cutting mill for size reduction of waste
25 supercapacitors and the wet-shredding process. In the following, estimations of the energy
26 consumption and the main output of the recycled materials are made based on a recycling capacity of
27 100 kg/h. The supercapacitors are assumed to consist of 40% (wt) aluminium housing and aluminium
28 electrode support, 30% (wt) of activated carbon electrode and 25% (wt) of acetonitrile, which are typical
29 composition for commercial supercapacitors. The fine grain size of the cutting mill is assumed to be 4
30 mm.

31 For an average grain size of 4mm, energy consumption of the cutting mill is about 100 KWh/t
32 (Macko, 2012). Since shear force is mainly responsible for the wet shredding process, the energy
33 demand in a large scale operation can be scaled-up based on power drawn per volume of liquid with
34 similar loading of coarse activated carbon particles, and many types of shredding machine may be used

1 (Cui and Forssberg, 2003). In the experimental study, the high speed immersion blender has a power of
2 0.65 kW in a 300 mL water containing 12 g dried coarse activated carbon particles for 5 minutes. The
3 energy density is $0.65 \text{ kW} \times (5/60) \text{ h} / 0.3 \text{ L} = 0.054 \text{ KWh/L}$, and the loading of dried shredded mixture is
4 $12\text{g}/300\text{mL} = 0.04 \text{ kg/L}$.

5 According to the above assumption and experimental wet shredding power drawn and loading,
6 the energy consumption and major material output are as follows: The energy consumption for cutting
7 mill is $100 \text{ kg/h} \times 40\% / 1000 \text{ kg/t} \times 100 \text{ KWh/t} = 4 \text{ KWh}$. The energy consumption for wet shredding is
8 $100 \text{ kg/h} \times 30\% / 0.04 \text{ kg/L} \times 0.054 \text{ KWh/L} = 41 \text{ KWh}$. If the energy demand for other parts accounts for
9 30% (Macko, 2012), the total energy demand will be $(41 + 4) \times (1+30\%) = 58.5 \text{ KWh}$. Approximately 100
10 $\text{kg/h} \times 23\% = 23 \text{ kg/h}$ acetonitrile, $100 \text{ kg/h} \times 30\% = 30 \text{ kg/h}$ activated carbon, and $100 \text{ kg/h} \times 40\% = 40$
11 kg/h aluminium particles are recycled.

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

19 20 **4. CONCLUSIONS**

21
22 A recycling process for supercapacitors is developed based on shredding and mild thermal
23 treatment. The three main component, activated carbon, solvent and aluminium can be recycled, while
24 the polymer binder and electrolyte salt are left in the recycled activated carbon. The presence of
25 polymer binder is beneficial to maintain the recycled carbon in a granular form. Due to the presence of
26 electrolyte salt and binder, the upper limit use temperature of the recycled carbon should be below the
27 250°C .

28 The shredding in Retsch cutting mill is sufficient to strip the activated carbon off the aluminium
29 foil. After shredding, a mild thermal treatment at 200°C can evaporate all the solvent in 5 minutes. At
30 this temperature, the extent of decomposition of the polymer binder and electrolyte salt can be
31 neglected. After removal of the solvent, the activated carbon agglomerates can be separated from the
32 shredded mixture using a fluidized bed. The separated activated carbon can be broken down into fine
33 particles by the wet-shredding in water with a surface area up to $1200 \text{ m}^2/\text{g}$.

34

1 **Acknowledgements**

2

3 The research leading to these results has received funding from the European Union Seventh
4 Framework Programme (FP7/2007-2013) under grant agreement n°266391.

5

6 **References**

7

8 Arito, H., Soda, R., 1977. Pyrolysis products of polytetrafluoroethylene and polyfluoroethylenepropylene
9 with reference to inhalation toxicity. *Annals of Occupational Hygiene* 20, 247-255.

10 Asmus, T.W., Houser, T.J., 1969. Pyrolysis kinetics of acetonitrile. *Journal of Physical Chemistry* 73, 2555-
11 2558.

12 Beguin, F., Frackowiak, E., Presser, V., Balducci, A., 2014. Carbons and electrolytes for advanced
13 supercapacitors. *Advanced Materials* 26, 2219-2251.

14 Bernardes, A.M., Espinosa, D.C.R., Tenorio, J.A.S., 2004. Recycling of batteries: a review of current
15 processes and technologies. *Journal of Power Sources* 130, 291-298.

16 Bhadury, P., Singh, S., Sharma, M., Palit, M., 2007. Flash pyrolysis of polytetrafluoroethylene (teflon) in a
17 quartz assembly. *Journal of Analytical and Applied Pyrolysis* 78, 288-290.

18 Britt, P.F., 2002. Pyrolysis and combustion of acetonitrile. Oak Ridge National Laboratory.

19 Budde-Meiwes, H., Drillkens, J., Lunz, B., Muennix, J., Rothgang, S., Kowal, J., Sauer, D.U., 2013. A review
20 of current automotive battery technology and future prospects. *Journal of Automobile Engineering*
21 227, 761-776.

22 Cai, G.Q., Fung, K.Y., Ng, K.M., Wibowo, C., 2014. Process development for the recycle of spent lithium
23 ion batteries by chemical precipitation. *Industrial & Engineering Chemistry Research* 53, 18245-
24 18259.

25 Chagnes, A., Pospiech, B., 2013. A brief review on hydrometallurgical technologies for recycling spent
26 lithium-ion batteries. *Journal of Chemical Technology and Biotechnology* 88, 1191-1199.

27 Conesa, J.A., Font, R., 2001. Polytetrafluoroethylene decomposition in air and nitrogen. *Polymer*
28 *Engineering and Science* 41, 2137-2147.

29 Cui, J., Forssberg, E., 2003. Mechanical recycling of waste electric and electronic equipment: a review.
30 *Journal of Hazardous Materials* B99, 243-263.

31 de Boer, J.H., 1958. *The Structure and Properties of Porous Materials*. Butterworths, London.

32 Gratz, E., Sa, Q., Apelian, D., Wang, Y., 2014. A closed loop process for recycling spent lithium ion
33 batteries. *Journal of Power Sources* 262, 255-262.

1 Horai, K., Shibata, J., Murayama, N., Koyanaka, S., Niinae, M., 2014. Recycling technology for lithium ion
2 battery by crushing and classification, and hydrometallurgical process. *Journal of the Japan*
3 *Institute of Metals* 78, 250-257.

4 Joo, S.H., Shin, S.M., Shin, D.J., Wang, J.P., 2015. Development of recycling technology to recover
5 valuable metals from lithium primary and ion batteries. *Proceedings of the Institution of*
6 *Mechanical Engineers Part B-Journal of Engineering Manufacture* 229, 212-220.

7 Kissinger, H.E., 1957 Reaction kinetics in differential thermal analysis. *Analytical Chemistry* 29, 1702-
8 1706.

9 Lain, M., 2001. Recycling of lithium ion cells and batteries. *Journal of Power Sources* 97/98, 736-738.

10 Macko, M., 2012. Size reduction by grinding as an important stage in recycling, in: Damanhuri, E. (Ed.),
11 *Post-Consumer Waste Recycling and Optimal Production*. InTech, pp. 273-294.

12 Munchgesang, W., Meisner, P., Yushin, G., 2014. Supercapacitors specialities - technology review, in:
13 Meyer, D.C., Leisegang, T. (Eds.), *1st International Freiberg Conference on Electrochemical Storage*
14 *Materials*. AIP, Freiberg, Germany, pp. 196-203.

15 Prasad, M.R.R., Sudhakarbabu, K., 2014. Thermal decomposition of tetraethyl ammonium
16 tetrafluoroborate. *Journal of Thermal Analysis and Calorimetry* 115, 1901-1905.

17 Renault, S., Brandell, D., Edstrom, K., 2014. Environmentally-friendly lithium recycling from a spent
18 organic Li-ion battery. *ChemSumChem* 7, 2859-2867.

19 Simon, C.M., Kaminsky, W., 1998. Chemical recycling of polytetrafluoroethylene by pyrolysis. *Polymer*
20 *Degradation and Stability* 62, 1-7.

21 Zeng, X.L., Li, J.H., Singh, N., 2014. Recycling of spent Lithium-ion battery: A critical review. *Critical*
22 *Reviews in Environmental Science and Technology* 44, 1129-1165.

23 Zhang, X.H., Cao, H.B., Xie, Y.B., Ning, P.G., An, h.j., You, H.X., Nawaz, F., 2015. A closed-loop process for
24 recycling $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ from the cathode scraps of lithium-ion batteries: Process
25 optimization and kinetics analysis. *Separation and Purification Technology* 150, 186-195.

26

27

1 **List of Figures**

- 2
- 3 Fig. 1 The recycling process and the separated products from supercapacitors.
- 4 Fig. 2 TG traces for the activated carbon based electrode at various heating rates.
- 5 Fig. 3 Time needed to complete evaporation of the acetonitrile in electrodes calculated from the kinetic
- 6 equation (Eq. 1) and the kinetic constant in Table 1.
- 7 Fig. 4 Decomposition profile of the polymer binder at different temperatures calculated from the kinetic
- 8 equation (Eq. 1) and the kinetic constant in Table 1.
- 9 Fig. 5 Decomposition profile of the electrolyte at different temperatures calculated from the kinetic
- 10 equation (Eq. 1) and the kinetic constant in Table 1.
- 11 Fig. 6 SEM images of activated carbon fibre before wet-shredding (a), after wet-shredding (b).
- 12 Fig. 7 Nitrogen adsorption and desorption of the recycled activated carbon at different heat treatment
- 13 temperatures.
- 14 Fig. 8 A schematic flow diagram of the conceptual recycling of supercapacitors based on the shredding
- 15 and mild thermal treatment process

16
17
18
19

20 **List of Tables**

- 21
- 22 Table 1 Evaporation and decomposition temperatures of acetonitrile, binder and electrolyte determined
- 23 using thermogravimetric analysis.
- 24 Table 2 The surface area and pore size characterisation of the recycled activated carbons

25

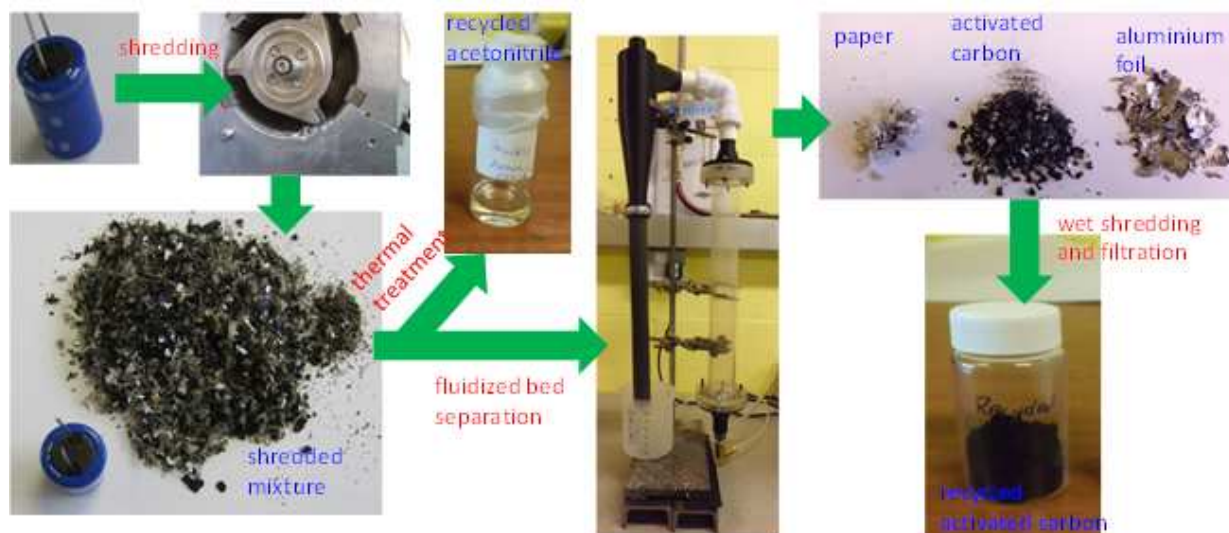


Figure 1

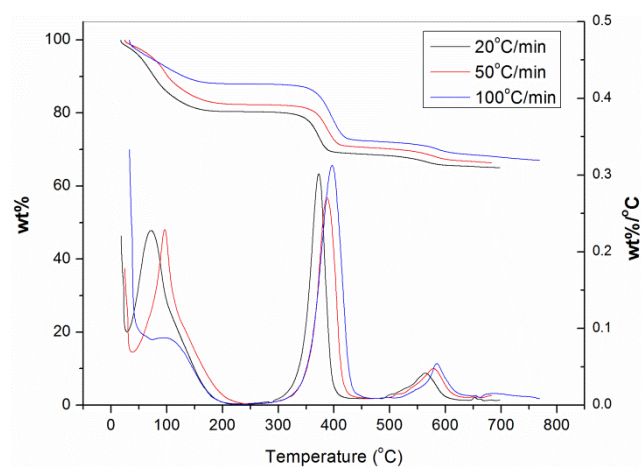
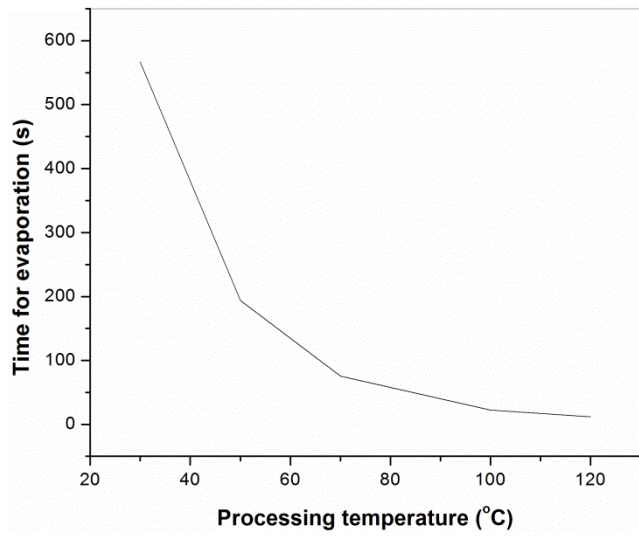
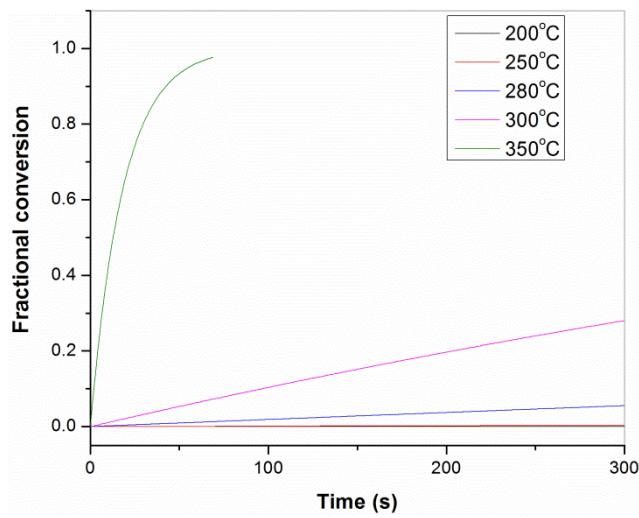


Figure 2



1
2
3
4
5
6

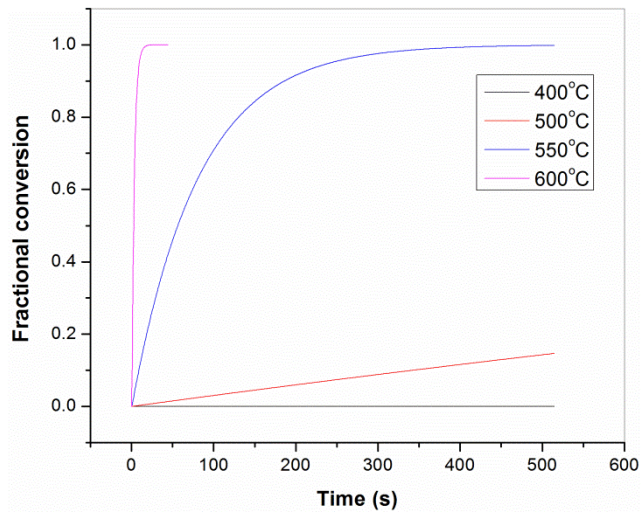
Figure 3



7
8
9

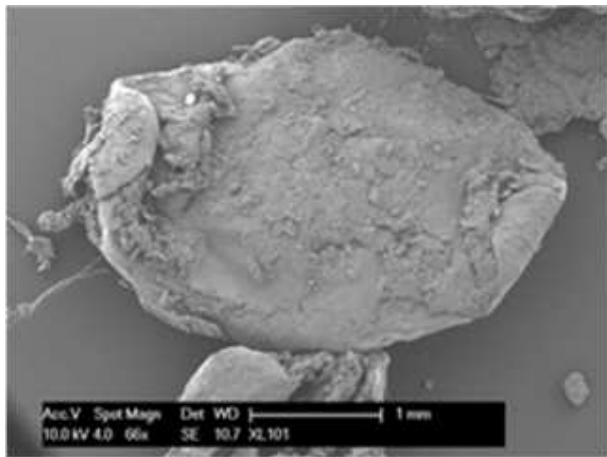
Figure 4

10
11
12
13
14

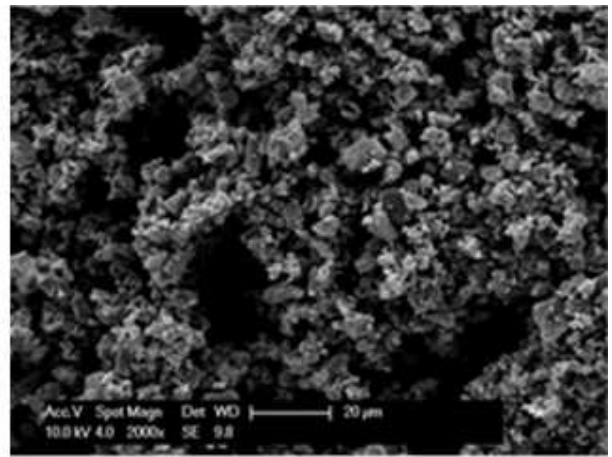


1
2
3
4
5
6
7
8

Figure 5



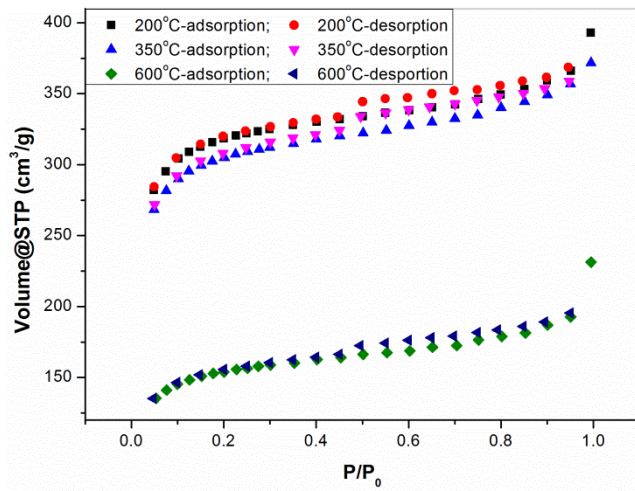
a



b

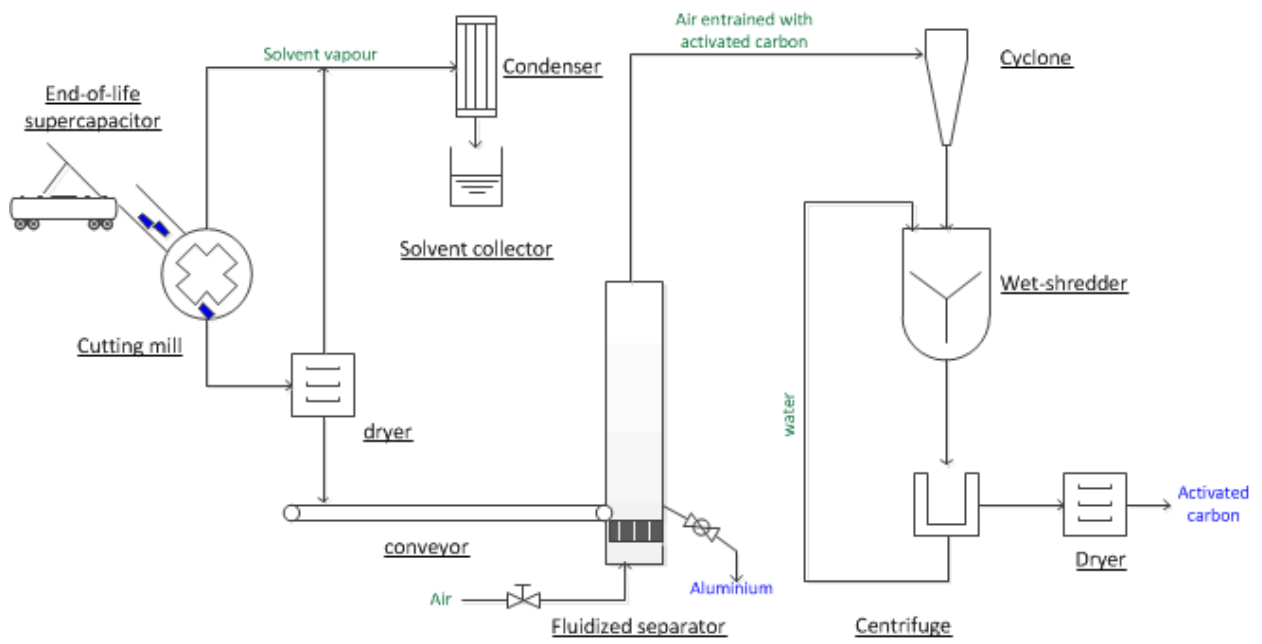
9
10
11
12
13
14
15
16

Figure 6



1
2
3
4
5
6
7
8

Figure 7



9
10
11
12
13
14
15
16
17
18
19
20
21
22

Figure 8

1
2
3
4

Table 1. Evaporation and decomposition temperatures of acetonitrile, binder and electrolyte determined using thermogravimetric analysis.

Heating rate (°C/min)	2 nd Acetonitrile evaporation (°C)	Binder decomposition (°C)	Electrolyte decomposition (°C)
20	71	374	562
50	95	387	579
100	104	398	584
<i>Kinetic constants</i>			
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

5
6
7
8
9
10
11
12

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

Recycling Temperature (°C)	BET m ² /g	Langmuir m ² /g	DA micropore		BJH mesopore	
			Vol. (cm ³)	diameter (nm)	Vol. (cm ³)	diameter (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

13
14
15
16