Electrochemically-stabilized carbon materials for supercapacitor prototypes

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Abstract. A study is presented on supercapacitor prototypes using chimney soot as the active electrode material. Despite its highly developed surface and the existence of capacitive properties, some compounds present in chimney soot make it unstable during the charge process. The irreversible electrochemical process leads to anodic oxidation and cathodic reduction of the soot. In this work, chimney soot was treated electrochemically with different electrochemical potentials, thus altering the initial organic compounds in the material; different parts of organic compounds were affected, so that more stable compounds remained, without all functional groups being removed. The altered material was investigated by IR and TEM spectroscopy. Supercapacitor prototypes were subjected to charge-discharge cycles and their capacitances were determined and compared.

Keywords: Supercapacitors, soot, electrochemistry, carbon materials, PAHs

1. Introduction

Supercapacitors (SCs) are well known devices, patented back in 1957 [1] and now being mass produced [2]. Many different electrode materials have been investigated for SCs production, such as carbon based [3, 4], polymers [5], composites [6], biochar [7, 8] etc. [9]. Soot is a particulate carbonaceous product formed during high-temperature pyrolysis or incomplete combustion of hydrocarbons; except for candle soot [10, 11], it has rarely been investigated for the application considered here. It consists mainly of carbon and small amounts of other elements, such as hydrogen and oxygen [12]. Soot, formed in a high-temperature gas-to-particle transition, comprises predominantly agglomerated primary particles with nanometer sizes [13, 14]. It has an internal graphite core and nascent polycyclic aromatic hydrocarbons (PAHs) with different functional groups [15]. In addition, depending on the conditions of burning, oxygenated PAHs (OPAHs) are present in the mixture. PAHs, OPAHs and black carbon (BC) make up 0.1 – 1% of the total particulate matter (PM) released during logwood combustion [16]. Furthermore, it has been found that OPAH emissions from birch burning correspond to 27% of PAH emissions for normal burning (NB) and 26% for high burning (HB). In normal spruce burning, the OPAH emissions corresponded to 60% of PAH emissions, while it decreased to 16% in HB [17].

The degradation of PAHs is highly dependent on whether they exist in a gaseous or in a condensed phase. Gas phase PAHs are efficiently oxidized in homogeneous reactions with •OH, •O₃ and •NO₃
radicals [18]. Heterogeneous reactions of particles-bound PAHs with the same reactants are substantially slower and are affected by the particle’s chemical composition and microstructure [19]. It is well known that the presence of alkaline metals (and to a lesser extent of alkaline-earth metals) improves the soot oxidation, either alone or as promoters [20]. An experiment described in [21] shows that PAHs degradation order in mixtures is as follows: benzo[a]pyrene (BzA) > fluoranthene (FLU) > pyrene (PYR). In [22], electrochemical treatment for 180 min increased the PAHs degradation from 72% to 82%.

In the work presented, chimney soot was alteration electrochemically to derive a material suitable for use in SCs.

2. Experimental

Before the electrochemical treatment, and with the purpose of removing contaminants from fly ash (Ca, Mg, K carbonates), the initial material (chimney soot) was subjected to cleaning procedures. The material collected from a household chimney was washed in a glass vessel with 1 M HCl and then with distilled H$_2$O over a 2-3 µm paper filter. The washed material was collected and placed in a Daniel type electrochemical cell with graphite electrodes shown in figure 1.

![Figure 1. Schematic of the electrochemical set up: 1 - wires, 2 - electrolyte bridge, 3, 4 - electrodes, 5 - surface of the content, 6 - vessel.](image)

In a Daniel electrochemical cell, the cathode and anode volumes are divided to prevent mixing of the oxidized and reduced particles. In the case described here, the distance between the electrodes was 33 mm and the diameter of the internal connecting bridge, 4 mm. These dimensions ensure a high resistances (1510 Ω), but diminish the polarization and prevent over-potentials and gas evolution on the electrodes. As a supporting electrolyte, we used 3 M KOH and applied different potentials – 3, 6 and 9 VDC. The duration of the electrochemical treatment was 24 hours. The derived materials were investigated by FTIR spectroscopy in the range 4000 – 550 cm$^{-1}$ (Tenzor 27-Bruker). TEM (HR STEM JEOL JEM 2100) was used to examine the morphology of the samples. The capacitors prepared were subjected to charge-discharge cycles, with the capacitance estimated at every cycle directly in farads (F) using an Arduino microcontroller and free Paul Badger software to measure the charging time constant $\tau_c = RC$, with $R = 240 \, \Omega$.

After the electrochemical processing, the materials produced were dried. Hereinafter they are denoted as: 3, 6 and 9 depending on the voltage applied, with added “C” for cathode material, “A” for anode material, and “AC” is for the capacitor. The next step in the process was preparing ink from the produced material using ethylene glycol and methanol. The ethylene glycol increases the viscosity of the ink, while the methanol dissolves the organic compounds which form a layer after drying. The ink proportions were: 1 g of carbon material was mixed with 500 µl ethylene glycol and 1600 µl methanol, the same receipt was applied to all six types of materials.
The ink was deposited on Cu foils serving as current collectors by a simple technique using small painting brush. The electrodes were placed on a hot plate to dry in air at 90 °C until the methanol and, more importantly, the ethylene glycol evaporated and the ink became a thick paste. The mass of each electrode was measured before and after ink deposition. The difference, i.e., the deposited ink mass is shown in table 1. The SC assembly consists of an electrode with material A and an electrode with material C joined by filter paper soaked in 0.2 ml 6M KOH; thus making up a sample AC, for example, 3A and 3C form capacitor 3AC.

### Table 1. Mass of ink deposited on the current collector electrodes.

|            | 3AC  | 6AC  | 9AC  |
|------------|------|------|------|
| m ink anode (g) | 0.1344 | 0.0475 | 0.0837 |
| m ink cathode (g) | 0.123  | 0.0747 | 0.1014 |

3. Result and discussion

#### 3.1. Infrared spectroscopy

Figure 2 shows IR spectra of the electrochemically treated soot and of the initial material. It can be easily seen that the treatment has affected the material. The hydroxide group band (3500 – 3000 cm\(^{-1}\)) is reduced; for capacitor 6AC, it completely vanishes from the cathode and anode material; the other peaks are also strongly changed. The vertical lines (1-4) shown in figure 2 correspond to main the bonds in soot. Thus, 1575 cm\(^{-1}\) corresponds to a C=C vibration in aromatic rings; the very sharp peak at 1367 cm\(^{-1}\) could be related to C-O and N-O; the C-H vibration and bending give rise to the peak at 1000 cm\(^{-1}\); while the peaks around 659 cm\(^{-1}\) are due to C-Cl bonds and also characterize the whole molecular deformation. The band about 3500 – 3000 cm\(^{-1}\) of the other two capacitors materials (3AC and 9AC) is also affected, but not so strongly. However, the peaks marked with vertical lines undergo strong changes, namely, the 3AC material exhibits the highest intensity in the area of peak 2, but an intensity lower than that of 9A at all other marked peaks. This can be explained by the extreme oxidizing conditions for 9A, whereas for 3C reduction conditions were applied with the lowest potential used in the experiment conducted.
3.2. Transmission electron microscopy

Figures 3, 4 and 5 present TEM images of anode and cathode particles treated at potentials of 3 V, 6 V and 9 V showing the shapes and structures of the particles. At a macroscopic level, the particles are very fine and possess a highly developed surface. Also, graphene sheets could be seen around some of the particles (figure 5, first column 9C).

The SAED images are characteristic for multilayer graphene sheets. The two concentric circles located at 1.23 Å and 2.13 Å are characteristic for graphene [23]. Particles can be distinguished with sharp edges, together with particles with soft curvy forms, the latter due to melting of the organic medium, which forms clusters of stacked particles. As mentioned, soot consists of polyaromatic hydrocarbons (PAHs), complex compounds that melt, sublimate and evaporate at temperature higher than 300 °C. This variety of hydrocarbons constitute the “organic medium” mentioned above.

![Figure 3](image1.png)

**Figure 3.** TEM images with corresponding diffraction pattern of the species from A and C type material treated at 3 V potential.

![Figure 4](image2.png)

**Figure 4.** TEM images with corresponding diffraction pattern of the species from A and C type material treated at 6 V potential.

![Figure 5](image3.png)

**Figure 5.** TEM images with corresponding diffraction pattern of the A and C type material treated at 9 V potential.

The sharpest particles are mainly composed of graphitized carbon, as seen in the SAED images – the particles consist of polycrystalline, but also of monocristalline species. In both type of materials (C and A) crystalline and polycrystalline structures exist.

3.3. Charge-discharge data

Figure 6 presents plots of the supercapacitors charge-discharge cycles. The capacitance was measured directly in farads (F) by an Arduino platform and free Paul Badger software making use of the time constant $\tau_C = RC$ for charging the SC, with $R = 240 \, \Omega$ in our case. To obtain the value of the capacitance in F/g, the measured capacitance value was divided by the “m ink” value in table 1.
Figure 6. Capacitance of the different capacitors 3AC, 6AC, 9AC depending on the mass of the material on the cathode and anode.

As seen, initially the capacitance decreases rapidly; after several cycles the slope becomes flatter. The capacitance depends also on the active adsorbing mass of the electrodes, so that the anode materials exhibit a higher capacity compared to the cathode one. The capacitance of the anode material does not depend linearly on the potential; the capacitance of 3A is lower than that of 6A, while one would expect the opposite. The capacitor 3AC exhibits a cathode-material capacitance higher than those of 6AC and 9AC, a behavior that should be expected. This is due to the electrochemical treatment whereby different functional groups are removed. For all materials, the anode-material capacitance is higher than that of the corresponding cathode one.

We assume that the decrease in the capacitance during the charge-discharge cycles is caused by the precipitation of metal carbonate crystals such as K$_2$CO$_3$. This reaction decreases the number of hydroxyl ions available for reaction at the anode. Furthermore, it modifies the composition of the electrolyte and thus reduces its ionic conductivity. It is shown in [24, 25] that the CO$_2$ does not cause any degradation of the electrodes; however, if the electrolyte is highly concentrated, carbonate precipitation may block the pores of the gas diffusion layer [26].

Another disadvantage is related to the amount of liquid electrolyte – too much or too little liquid in results in the electrodes being flooded or dried, respectively [27]. Another cause of the decrease in the capacitance is the rise in the resistance due to the formation of p-type Cu$_2$O over the anode surface [28].

4. Conclusion
With the purpose of preparing anode and cathode type of materials, chimney soot was treated electrochemically, which led to significant changes in its structure. The materials were investigated by TEM and IR spectroscopy. The infrared spectroscopy pointed to a removal of many functional groups. The TEM images demonstrated that the materials studied were very fine powders with layered structures and a highly developed surface. The altered materials were used to prepare several SCs. The capacitances value of the SCs were lower than expected. We assume that one reason for this is the high amount present of K$_+$. It was also found that the anode materials prepared possessed higher capacitance than those of the cathode materials in the SCs structures.

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