Soot as electrode coating for supercapacitor prototypes

M Petrov¹,³, K Lovchinov², S Valkov¹ and N Tyutyundzhiev¹

¹Acad. E. Djakov Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
²Acad. J. Malinowski Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 109, 1113 Sofia, Bulgaria

E-mail: petrov80@abv.bg

Abstract. Black powders were prepared from chimney soot by means of treatment with different solvents and drying. The powders were used to prepare inks, which were deposited on copper foils. The as prepared electrodes were assembled as supercapacitor structures with KOH as electrolyte. The charge-discharge characteristics were measured to evaluate the electrical capacitance and to compare the technology for soot treatment. The soot was studied as a source before and after treatment using IR spectroscopy, XRD and SEM EDX.

1. Introduction

Soot is a particulate carbonaceous matter with a characteristic lattice structure. It is formed during incomplete high-temperature pyrolysis or combustion of hydrocarbons [1] and is a fine black or brown powder that can be slightly sticky. A major component of soot is “black carbon”. Soot is the common term for a type of particle pollution known as PM₂.₅, which is particulate matter with a diameter of 2.5 μm or less. Soot is composed of a variety of chemicals [2], mainly poly-aromatic hydrocarbons (PAHs), which are among the most widespread organic pollutants. In addition to their presence in fossil fuels, they are also formed by incomplete combustion of carbon-containing fuels, such as wood, coal, diesel fuel, fat, tobacco, and incense. [3] The different types of combustion yield different distributions of PAHs in both relative amounts of individual PAHs and of isomers produced. Thus, coal burning produces a different mixture than motor-fuel combustion or a forest fire, making the compounds potentially useful as indicators of the burning history. Hydrocarbon emissions from fossil-fuel-burning engines are regulated in developed countries [4]. Assuming that soot is formed as described in [5], it consists of an internal graphite core and nascent PAHs with different functional groups [6], which increase the absorbing ability of the material. [7] The PAHs motif is extended to large 2D sheets in graphene, which can be regarded as graphene or graphite segments and is one of the most intensively investigated classes of compounds in synthetic chemistry and materials science [8].

2. Experimental

In this work, four types of powders were derived from soot collected from a household chimney and were used to prepare electrode coatings. The powder samples were numbered from 0 to 3 depending on the treatment. Number 0 is soot sieved through a 63-μm mesh with no further treatment. Number 1 is derived from 0 by extraction benzine treatment so that the PAHs are dissolved. Number 2 is the

² To whom any correspondence should be addressed.
same as 1, but the solvent is ethanol; and 3 is produced after treatment with methanol. Table 1 summarizes the results.

**Table 1.** Solvents used for sample preparation.

| sample | 0     | 1     | 2     | 3     |
|--------|-------|-------|-------|-------|
| solvent| -     | extraction benzine | ethanol | methanol |
| sieve hole | 63 µm | 63 µm | 63 µm | 63 µm |

Figure 1 presents the FTIR spectra of the samples in the range 4000 – 550 cm\(^{-1}\) (Tenzor 27-Bruker). The analysis reveals O-H at 3190 cm\(^{-1}\), C-O at 1150 cm\(^{-1}\) and 1040 cm\(^{-1}\), C-H valence vibrations in the range 2960 – 2850 cm\(^{-1}\), and the characteristic CH\(_3\)CH\(_3\) vibrations in the range 1420 – 1370 cm\(^{-1}\). Carbonyl and carboxyl absorption lines are also seen, respectively, at 1720 – 1700 cm\(^{-1}\) and 1150 – 1040 cm\(^{-1}\). The absorption lines in the range 3100 – 3030 cm\(^{-1}\) are typical for aromatic compounds; those at 1600 – 1450 cm\(^{-1}\) arise from C=C bonds in the benzene ring. In general, the absorbance curves are very close to each other and could be divided in two groups (sample 0, sample 1) and (sample 2, sample 3). The differences between the spectra of these groups are in the range 1710 – 595 cm\(^{-1}\) and in the area of O-H groups (~3190 cm\(^{-1}\)) [9].

The differences are due to the extraction of low molecular weight compounds dissolved in ethanol and methanol, while the lower absorbance and the increase of the signal in the area of O-H groups are probably due to absorbed solvents, which are alcohols.

3. Results and discussion

3.1. Ink preparation

Figure 2 shows SEM micrographs of the particles in the samples; as seen, the size of the particles is from 0 to 63 µm. Sample-0 and sample-1 are similar and have a highly developed surface. The particles in sample-2 and sample-3 are agglomerated; their surface is rougher because of missing bituminous compound.

In a next step, to prepare inks, powder from the samples was added to a solution of polyvinyl alcohol (PVA) 5 wt %; DI H\(_2\)O. In all ink samples thus formed, the amount of binder (PVA) and water was about 69%.
3.2. Supercapacitor assembly and cycling

To form the electrodes of the supercapacitor (SC) devices, the ink prepared was deposited on copper foils; these were measured before and after the deposition to ensure that comparable amounts of ink were added. As a separator we used borosilicate filter paper soaked with 0.5 ml saturated KOH (34 M KOH). The cross-section of an assembled device is shown schematically in figure 3. The electrodes and the separator are joined together by hot lamination.

![Figure 3. Schematic of as prepared supercapacitors.](image)

The estimated ink mass shown in table 2 allowed us to estimate the electrical capacitance with respect to the mass. Because the mass of the electrodes differ, for every electrode pair the lowest mass was taken into account when the SC capacitance was estimated, which was carried out by conducting several charging and discharging cycles.

The capacity was measured directly in farads by an Arduino platform and free software from Paul Badger 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 capacity in F/g, the value calculated was divided by the value of “m ink 2” in bold in table 2. The results shown in table 3 are the estimated value of capacity per gram for every SC after each of the five charge-discharge cycles performed.

![Figure 2. SEM micrographs of the particles in sample-0 (a); sample-1 (b); sample-2 (c); sample-3 (d).](image)

| Table 2. Mass of the electrodes and deposited ink. |
|-----------------------------------------------|
| sample | 0   | 1   | 2   | 3   |
| m electrode 1 [g] | 1.145 | 1.200 | 1.158 | 1.185 |
| m electrode 2 [g] | 1.145 | 1.135 | 1.189 | 1.180 |
| m electrode 1 + ink [g] | 1.260 | 1.372 | 1.252 | 1.292 |
| m electrode 2 + ink [g] | 1.236 | 1.304 | 1.268 | 1.259 |
| m ink 1 [g] | 0.115 | 0.172 | 0.094 | 0.107 |
| m ink 2 [g] | **0.091** | **0.169** | **0.079** | **0.079** |

As seen in table 3, the capacitance of the sample made with untreated soot powder (sample 0) exhibits relatively constant capacitance after each charge-discharge cycles. The same holds true for sample 1. The devices made of inks 2 and 3 show a capacitance diminishing as the number of charge-discharge cycles is raised, although their initial capacitance is higher. This behavior may be caused by the lack of low-molecular weight compounds that cover the active zones of the large-molecule highly carbonized compounds. The decreasing capacitance could also be explained by irreversible redox reactions taking place between KOH and organic acids that may be present. In the case of the SC made with ink 1, the somewhat lower capacitance may be due to the higher in-series resistance of the thicker ink layer.
Table 3. Estimated capacitance as a function of the deposited ink mass.

| sample | 0     | 1     | 2     | 3     |
|--------|-------|-------|-------|-------|
| capacitance [F/g] |       |       |       |       |
| 0      | 1.10  | 0.75  | 1.77  | 1.28  |
| 1      | 1.10  | 0.69  | 1.33  | 1.21  |
| 2      | 1.11  | 0.67  | 1.16  | 1.19  |
| 3      | 1.12  | 0.64  | 1.04  | 1.02  |
|        | 1.13  | 0.63  | 0.96  | 1.02  |

4. Conclusions
Prototypes of supercapacitor devices were fabricated by means of a simple technology using inks derived from soot and subjected to different treatments. It is demonstrated that the type of treatment affects the initial capacitance and the SCs performance after several charge-discharge cycles. The difference in the SCs performance may be alleviated by applying procedures of ink stabilization or aging.

Acknowledgement
This work was supported in part by the Bulgarian National Science Fund under Contract No. KP-06-M27/7.

References
[1] Xi J and Zhong B J 2006 Chem. Eng. Technol. 29 65–73
[2] Donev J M K C et al. 2019 Energy Education - Soot Online available: https://energyeducation.ca/encyclopedia/Soot
[3] Incense link to cancer 2001 http://news.bbc.co.uk/2/hi/health/1467409.stm BBC News 2001-08-02
[4] EPA regulations for small engines 40 CFR §90.103; see emission standard for more information
[5] Kholghy M R, Veshkini A and Thomson M J 2016 Carbon 100 508-36
[6] Raj A, Robert da Silva G and Chung S H 2012 Combustion and Flame 159 3423–36
[7] Ternero-Hidalgo J J, Rosas J M, Palomo J, Valero-Romero M J, Rodriguez-Mirasol J and Cordero T 2016 Carbon 101 409-19
[8] Xinliang F, Wojciech P and Klaus M 2009 Pure Appl. Chem. 81/12 2203–4
[9] https://www.sigmaaldrich.com/technical-documents/articles/biology/ir-spectrum-table.html