ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

A COMPARISON BETWEEN SEVERAL TEXTILE-BASED ELECTRODES FOR FLEXIBLE SUPERCAPACITOR APPLICATIONS

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Abstract: *Combining the features of supercapacitors and textiles solves many of the downsides that conventional electronics have, such as heavy weight, lack of recyclable parts and toxicity. Generally, the electrodes that are used in the manufacturing of energy-storage devices are obtained using toxic solvents and corrosive acids, bases and salts. Herein, in order to address these issues, we report the preparation of seven flexible textile-based electrodes, in which the textile substrates consisted in a woven fabric with cotton and silver threads. One of the substrates was coated using a mixture of glycerol (GlOH), gum arabic (GA) and activated carbon (AC) and, for the rest of them, six different salts were added to this mixture – sodium chloride (NaCl), ammonium chloride (NH_4Cl), 1-butyl-1-methylpyrrolidinium hexafluorophosphate ($BuMePyPF_6$), sodium acetate (NaAc), ammonium hexafluorophosphate (NH_4PF_6) and carboxymethylcellulose sodium salt with low viscosity (NaCMC). Their electrical resistance was measured and the electrical conductivity was then computed. The GlOH-GA-AC-NH_4Cl electrode was found to be the most conductive one ($244 \cdot 10^{-4}$S/m), while GlOH-GA-AC-$BuMePyPF_6$ was the least conductive electrode ($73 \cdot 10^{-4}$S/m). The surface characterization of the materials was performed using SEM and EDX, through which the morphology electrodes was observed; the size and the shape of the aggregates formed determined the performance of the electrodes.*

Key words: *supercapacitors, textiles, energy storage, activated carbon, gum arabic*

1. INTRODUCTION

E-textiles are emerging hybrid materials that bring together the features of textile materials and electronics. They are promising candidates for the replacement of traditional devices because they can respond to stimuli in the environment [1], having many advantages, such as flexibility [2]. One way to turn textiles into versatile electronic devices is to integrate them with supercapacitors (SCs), which are hybrid devices that exhibit properties close to both capacitors and batteries. These devices are characterized by high power capacity, longevity, low weight, large heat range, ease of packaging and affordable maintenance [3]. Such devices consist of two electrodes, an electrolyte, and a separator [4]. The electrodes play a key role in the construction of a SC because, according to their energy storage mechanism, there are three types of SCs – electric double-layer capacitors (EDLCs), which owe their good capacitance to the electrostatic charge accumulation at the electrode–electrolyte interface; pseudocapacitors (PCs), based on fast and reversible redox processes at the electroactive material surface; hybrid capacitors (HCs), their capacitance being attributed to the capacitance of EDLCs and the pseudocapacitance [5]. In order to deliver the best results, these SC components need to be electrically conductive, thermally stable, resistant to corrosion, relatively cheap, non-toxic and they have to have a large specific surface area as well [6]. This is why carbonaceous materials represent a good option for the production of next-generation SC electrodes. Among them, activated carbons (ACs) are conductive, stable and cheap compounds. Another advantage of ACs is the variety of synthesis options, with a lot of precursor materials to choose from – wood materials, waste from agricultural and food industries (coconut shell, walnut shell, banana peel, coal-based materials (anthracite, bitumen), petroleum materials (petroleum coke, pitch) and plastic materials [7]. In this paper, seven textile-based SC electrodes were synthesized using glycerol, activated carbon, gum arabic and six salts, in order to determine the best formulation in terms of electrical conductivity and surface coating parameters.

2. MATERIALS AND METHODS

2.1. Materials

Glycerol and ammonium chloride were supplied by Consors SRL. Activated carbon was bought from Supelco Analytical. Sodium chloride and sodium acetate were supplied by Fluka. Gum Arabic, carboxymethylcellulose sodium salt with low viscosity, 1-butyl-1-methylpyrrolidinium hexafluorophosphate and ammonium hexafluorophosphate were purchased from Sigma-Aldrich. The woven fabric containing cotton and silver threads, acting as a textile substrate, was manufactured.

2.2. Synthesis of textile-based electrodes

All electrodes were synthesized using the same procedure and labeled as follows: GlOH-GA-AC, GlOH-GA-AC-NaCl, GlOH-GA-AC-NH_4Cl, GlOH-GA-AC-$BuMePyPF_6$, GlOH-GA-AC-NaAc, GlOH-GA-AC-NH_4PF_6 and GlOH-GA-AC-NaCMC. Gum arabic and glycerol (0.16:1 mass ratio) were mixed in a beaker, at room temperature, until GA dissolved. Then, the corresponding salt (0.11:1 mass ratio to GlOH) and AC (2:1 mass ratio to GA) were added to the polymer solution. In the case of GlOH-GA-AC-$BuMePyPF_6$ and GlOH-GA-AC- NH_4PF_6, the salts were melted in order to increase the homogeneity of the mixture. After thoroughly stirring it, the mixture was spread on a square-shaped fabric (3.25 cm on average, in length, and 0.5 cm in thickness) using a laboratory spatula. Finally, the coated fabric was placed on a Petri dish and kept inside an oven for one hour, at 100°C. The obtained materials are presented in **Fig. 1**.

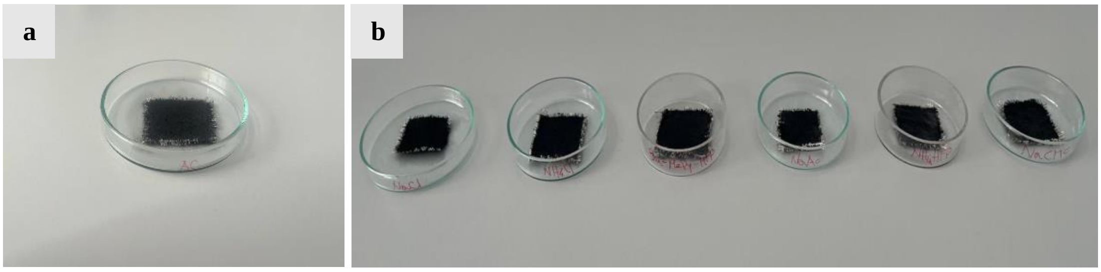

Fig. 1*: a. The GlOH-GA-AC electrode; b. The six electrodes containing salts*

2.3. Electrical conductivity measurements

The electrical resistance of each electrode was measured using a Fluke digital multimeter. Five measurements were performed for each coated substrate and the average values were then computed and tabulated.

Table 1: *The linear electrical resistance of each electrode*

Electrode	Linear electrical resistance, Ω/cm
GlOH-GA-AC	$1.39 \cdot 10^4$
GlOH-GA-AC-NH_4Cl	$8.19 \cdot 10^3$
GlOH-GA-AC-NH_4PF_6	$8.61 \cdot 10^3$
GlOH-GA-AC-NaCMC	$1.45 \cdot 10^4$
GlOH-GA-AC-NaCl	$1.73 \cdot 10^4$
GlOH-GA-AC-NaAc	$2.02 \cdot 10^4$
GlOH-GA-AC-$BuMePyPF_6$	$2.73 \cdot 10^4$

Then, these values were used to determine the electrical conductivity for each material, by inverting the product of the linear electrical resistance (R_l) and the thickness (d) of each electrode.

$$\sigma = \frac{1}{R_l \cdot d} \; [S/m] \quad \textbf{(1)}$$

The obtained values are presented in **Fig. 2**.

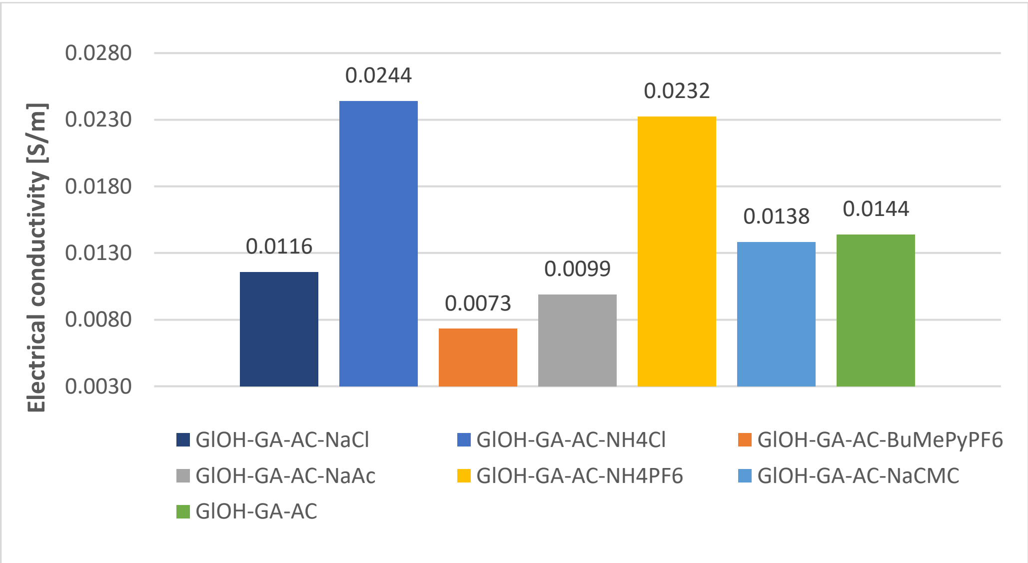

***Fig. 2**: The electrical conductivity of each electrode*

2.4. SEM and EDX characterization

The surface morphology and the elemental composition of the electrodes were studied using SEM and EDX. The SEM images are presented in **Fig. 3**. It can be seen that AC formed aggregates with the GA solution and most of the salts, leading to porous irregular structures that favour the flow of electrons. In the case of GlOH-GA-AC-NH_4Cl, which exhibited the highest electrical conductivity, the porosity is lower and its shape is rather regular. The GlOH-GA-AC-$BuMePyPF_6$ electrode was found to be the least conductive and this could be attributed to the formation of the biggest aggregates, which hindered the charge storage.

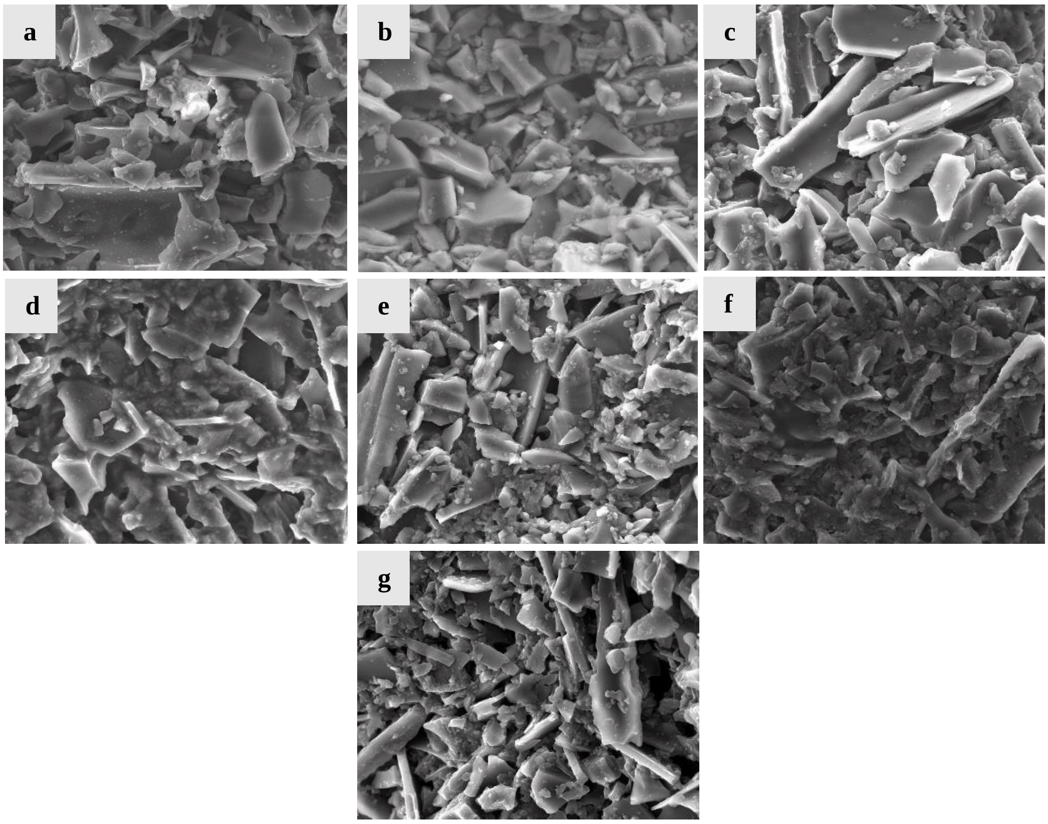

***Fig. 3**: SEM images of the electrodes at a magnification of 4,000 times – a. GlOH-GA-AC-NaCl; b. GlOH-GA-AC-NH_4Cl; c. GlOH-GA-AC-$BuMePyPF_6$; d. GlOH-GA-AC-NaAc; e. GlOH-GA-AC-NH_4PF_6; f. GlOH-GA-AC-NaCMC; g. GlOH-GA-AC*

The EDX graph in **Fig. 4** shows the elemental composition of the GlOH-GA-AC electrode, against which the compositions of GlOH-GA-AC-NaCl and GlOH-GA-AC-NaAc were compared (**Fig. 5** and **Fig. 6**). The graphs prove that both mixtures containing salts have a good homogeneity, with all the expected elements appearing on them (C, O, Na and Cl). Nevertheless, the presence of other elements, such as Al and Si, indicate certain impurities.

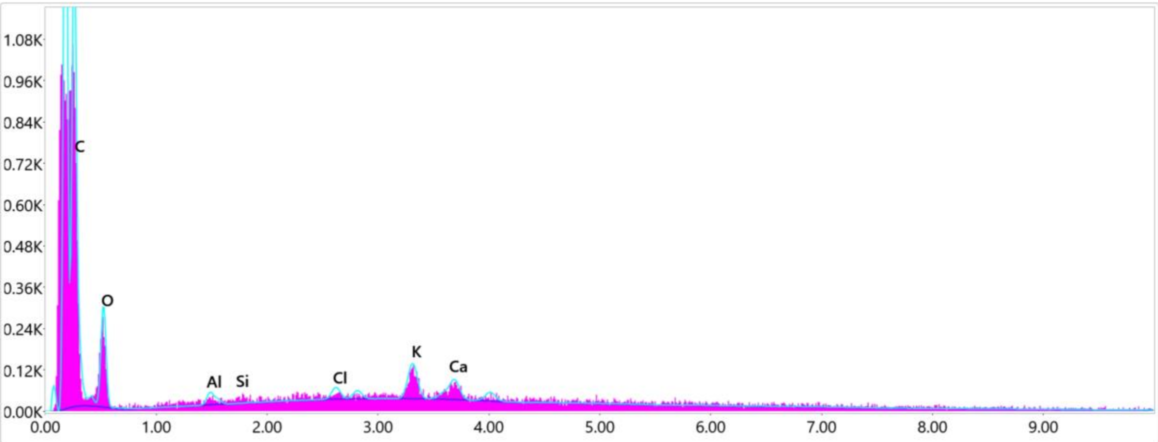

Fig. 4*: The EDX analysis of the GlOH-GA-AC electrode*

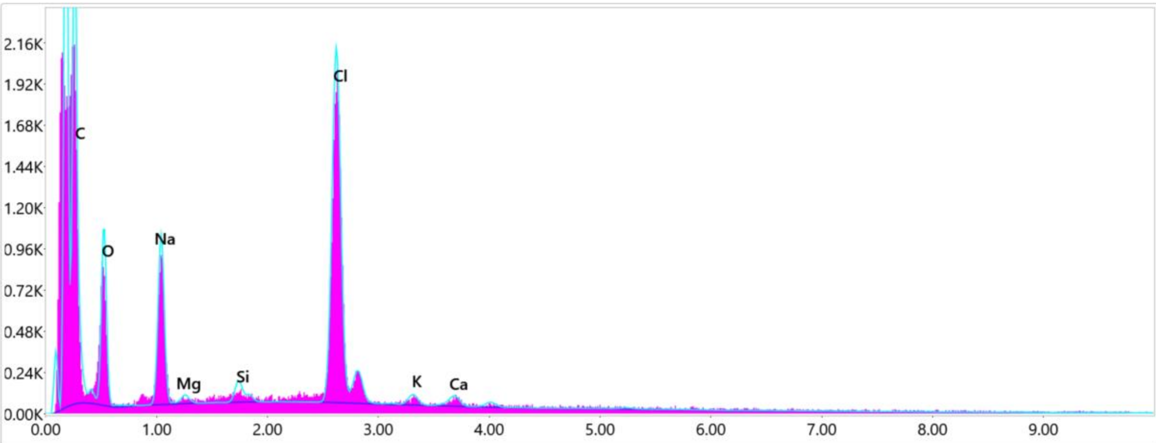

Fig. 5*: The EDX analysis of the GlOH-GA-AC-NaCl electrode*

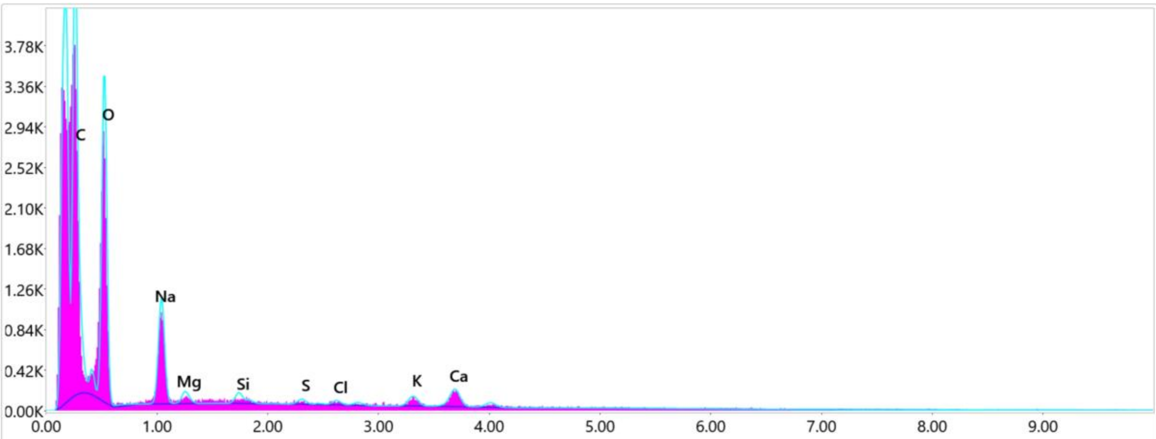

Fig. 6*: The EDX analysis of the GlOH-GA-AC-NaAc electrode*

5. CONCLUSIONS

In this study, we presented seven textile-based electrodes that were obtained by spreading a polymeric AC-based coating on a woven substrate. The electrochemical analysis showed that the electrical conductivities exhibited by the electrodes are situated between $73 \cdot 10^{-4}$ S/m and $244 \cdot 10^{-4}$ S/m and greener salts like ammonium chloride and sodium chloride are good replacements for the toxic 1-butyl-1-methylpyrrolidinium hexafluorophosphate and ammonium hexafluorophosphate because they conduct electricity better than their counterparts in this kind of mixture. The surface characterization of the materials revealed the porous structures of the electrodes, which are due to the adsorption properties of AC. This characteristic is crucial for a material to be used as an electrode, since charge is stored through its pores. Also, the analysis showed that regular shapes lead to an enhanced electrical conductivity if they are combined with porosity. Thus, our findings indicate the potential use of such materials as electrodes for the manufacturing of flexible supercapacitors.

ACKNOWLEDGEMENTS

This work was carried out through the Core Programme within the National R&D&I Plan 2022-2027, carried out with the support of MCID, project no. 6N/2023, PN 23 26 01 03, project 3D-WearIoT. The publication of the scientific paper is funded by Ministry of Research, Innovation and Digitization within Program 1 – Development of the national R&D system, Subprogram 1.2 – Institutional Performance - RDI excellence funding projects, contract no. 4PFE/2021.

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