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SILVER COATED TEXTILES AS ELECTROCHEMICAL PSEUDOCAPACITIVE MATERIALS

STEVAN STUPAR
Ministry of Defense, Military Technical Institute, Ratka Resanovića 1, 11030 Belgrade, Serbia
stevan.stupar13@gmail.com

MIHAEL BUČKO
University of Defense, Military Academy, Pavla Jurišića Šturma 33, 11000, Belgrade, Serbia
mihaelbucko@yahoo.com

DUŠAN MIJIN
University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia
kavur@tmf.bg.ac.rs

DENIS DINIĆ
University of Defense, Military Academy, Pavla Jurišića Šturma 33, 11000, Belgrade, Serbia
denis.dinic@yahoo.com

TANIĆ MILAN
University of Defense, Military Academy, Pavla Jurišića Šturma 33, 11000, Belgrade, Serbia
milantanic@yahoo.com

MARINA KNEŽEVIĆ
Ministry of Defense, Military Technical Institute, Ratka Resanovića 1, 11030 Belgrade, Serbia
katarinac2008@gmail.com

JELENA KARANOVIĆ
Ministry of Defense, Military Technical Institute, Ratka Resanovića 1, 11030 Belgrade, Serbia
jelenka74gmail.com

Abstract: *Among numerous active electrode materials, silver is a promising electrode in electrochemical capacitors. In this work we investigate the electrochemical capacitance of two textile materials: polyester and cotton fabrics, coated with silver particles. The electrodes were prepared in a manner that the fabrics were immersed into a silver complex solution and subsequently dried in the air and heated to induce silver deposition by annealing. This synthesis method does not require the use of expensive and toxic chemicals or electricity, which makes the process more economically acceptable for production of lightweight and flexible conductive materials. The capacitance and energy density were measured in various electrolytes (KCl and NaOH), and for electrodes prepared by one, three, or five cycles of fabrics immersion in the silver solution. Characterization of the modified tissues was performed by scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS). The capacitance was investigated by recording cyclic voltammograms, while the energy density was calculated from the recorded charge-discharge curves at the textile working electrodes. These findings promote the application of silver coated textiles as electrochemical pseudocapacitor materials.*

Keywords: *pseudocapacitor, textile electrode, silver deposition.*

1. INTRODUCTION

Electrochemical capacitors, known also as supercapacitors and pseudocapacitors, are energy storage devices that store and release electric energy by electrostatic mechanism and through the Faradaic processes [1]. The first capacitors were based on high surface area carbon materials, yet these materials come with drawbacks like a large pore volume, which reduces the conductivity and material density [2]. Later, transition metal oxides such as oxides of nickel, iron or ruthenium, had been introduced as pseudocapacitive materials to solve the problems observed with carbon-based electrodes, the RuO_2 oxide being the most successful [3]. However, the ruthenium materials come with issues such as high ecotoxicity and cost, and the quest for its replacement is ongoing.

Silver has been recognized as a transition metal that is very conductive, non-toxic to the environment, may

exhibit Faradaic redox reactions, with high surface area, reasonable wettability and low flammability, thus a desirable material for ruthenium replacement in supercapacitor applications. As a result, the electrochemical capacitors based on Ag wires, Ag dendrites, Ag thin films, Ag/graphene composites, etc., have already been reported [4].

This work aims to investigate the application of silver coating, applied with a special method on various fiber materials, as a novel supercapacitor material. Namely, textile capacitors are based on excellent textile characteristics demanded for a substrate: high toughness, strength and flexibility, low price and easy availability [5]. Most importantly for military application, due to their lightness, fiber-based supercapacitors are wearable and thus may be converted into wearable energy storage devices that may provide energy to a soldier when needed [6].

To prepare fiber-based capacitors in this work, a silver coating was applied to a textile substrate (cotton and polystyrene), by immersion and subsequent annealing. The electrochemical performance of the prepared capacitor materials was tested by cyclic voltammetry and chronoamperometry.

2. EXPERIMENTAL PART

2.1. Reagents and materials

Silver nitrate ($AgNO_3$, 99.0 %) and ammonium hydroxide solution (NH_4OH, 30%) were produced by Carlo Erba Reagents (France). Sodium acetate (CH_3COONa) was obtained from Fisher Scientific (UK). The methanol and formic acid were produced by Sigma-Aldrich (USA). The used chemicals were of analytical grade or higher. The Arium® Pro Ultrapure Water System (Sartorius, Germany) provided deionized water. The polyester and cotton fabrics were obtained by YUMCO Company (Serbia). Ethanol (C_2H_5OH, 95%) was obtained from Zorka Šabac (Serbia) and used for sample rinsing.

2.2. Silver conductive complex synthesis

Synthesis of Silver Conductive Complex begins by dissolving 30 g of silver nitrate and 60 g of sodium acetate in 75 ml of deionized water in two separate systems. After complete dissolution of the salt, the solutions were combined and stirred vigorously at room temperature. In two separated systems, 30 g of silver nitrate and 60 g of sodium acetate dissolved in 75 ml of deionized water. After the complete dissolution of the salts, the solutions were merged and intensively mixed at room temperature. The synthesized silver acetate was filtrated and rinsed with deionized water and methanol. The rinsed filtrate was dried at room conditions for 24 hours without exposure to light.

The synthesis of the silver conductive complex is further performed by modified Tollens process. The synthesized silver acetate (20 g) was dissolved in 45 ml of ammonium hydroxide solution by mixing thoroughly at room temperature. After 20 minutes, 1 ml of formic acid was added to the silver acetate and ammonium hydroxide solution. After adding the last drop of formic acid, the solution was mixed for 24 hours and filtrated through the 0.45 nm nylon syringe filter (Sartorius, Germany).

2.3. The textile surface modification by silver deposition

The metallization of fabrics was studied using the polyester and cotton fabrics. The synthesized conductive silver complex was applied by immersing onto one side of fabric in the dark at ~21°C. All samples were set to air dry to evaporate the ammonia from the complex, changing the silver and formic acid complex solution from colorless to a silver-colored solution. After the evaporation of ammonia, fabrics with the applied silver complexes were heated for 40 minutes at 90°C in a thermostatic chamber (G209A, SDL Atlas, UK). By heating the fabric under the stated conditions, formic acid evaporates from the complex, and a film of elemental silver is firmly formed on the surface. After the heat treatment, the samples were rinsed using ethanol.

2.4. Textile surface characterization

The morphology, microstructure, and semi-quantitative elemental analyses of raw and modified textiles were determined using the scanning electron microscopy Energy-Dispersive X-ray Spectroscopy (20 kV, JEOL 6610LV, Japan).

2.5. Electrochemical characterization

The electrochemical characterization of silver/fiber electrodes was carried out using cyclic voltammetry (CV) and chronoamperometry measurements to investigate a specific capacitance and the charge-discharge ability of the prepared electrodes. These analyses were performed using a CH Instruments potentiostat, model 400C, with a typical electrochemical cell setup of the saturated Ag/AgCl reference electrode, Pt counter electrode, and the working electrode. The working electrodes were exposed to the two different electrolytes: 1.0 mol dm^{-3} KCl and 0.5 mol dm^{-3} NaOH aqueous solutions.

The specific capacitance analysis was conducted using CV at potential range of ±400 mV (depending on the electrode material) versus the open circuit potential, at several scan rates ranging from 50 to 500 mV/s.

3. RESULTS

3.1. SEM-EDS characterization of silver/textile electrodes

SEM-EDS was applied for analysis of the fabrics' morphological, structural, and semi-quantitative characteristics after the silver deposition process. The SEM microphotographs of the polyester and cotton fabrics modified by one cycle of silver deposition, the distribution of diameter of the particles, and silver coverage of the textile, are presented in Figure 1. In addition, the corresponding EDS spectrum is given.

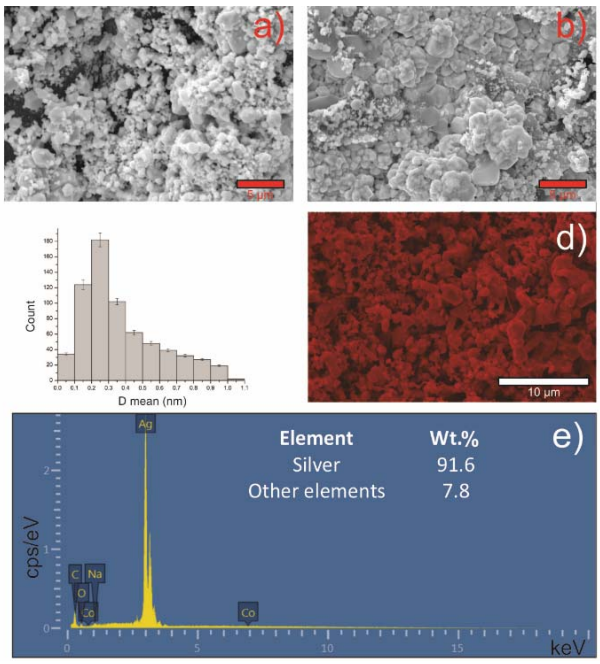


Figure 1. The SEM photographs of (a) polyester and (b) cotton fabrics modified by one cycle of silver deposition, (c) distribution of diameter of silver particles, (d) EDS mapping of the textile surface, and (e) EDS spectrum of the mapped area

The SEM microphotographs in Figure 1 show good coverage of the modified fabrics samples' surface after one silver deposition cycle. According to the determined distribution of the diameter of the particles, the average diameter of silver particles was between 0.2 and 0.3 µm. The distribution of silver particle sizes was obtained from the images where individual particles were distinguishable, and their diameters were measured using the image analysis software Image-pro. The SEM images also show the silver particles' agglomeration after the annealing treatment repetition. The porosity of multilayered silver particles is confirmed by SEM analysis and SEM micrographs of modified textiles shown. The complete mapping, obtained by energy-dispersive X-ray spectroscopy of the marked area of the SEM photograph, confirms the excellent coverage of the fabric by silver particles. The weight percentage (wt. %) of silver in polyester fabrics modified by one cycle of silver deposition, was 91.6%. The other elements exist as residuals from earlier textile industrial treatment.

3.2. Cyclic voltammetry

Among all the prepared and tested electrode materials, only some have shown a typical capacitive or pseudocapacitive behavior. Namely, independently on the electrolyte present in the cell (KCl whether NaOH), the electrode made of cotton with Ag deposit, shows only a purely Faradaic redox reaction, without any capacitive response, as demonstrated in Figure 2. The same stands for a polyester with Ag deposit, when only one immersion cycle is applied, as Figure 2 also shows. One may assume that the reason for the absence of a capacitive behavior in these samples, is such a silver deposit morphology that does not provide sufficient porosity and a sufficiently high surface area.

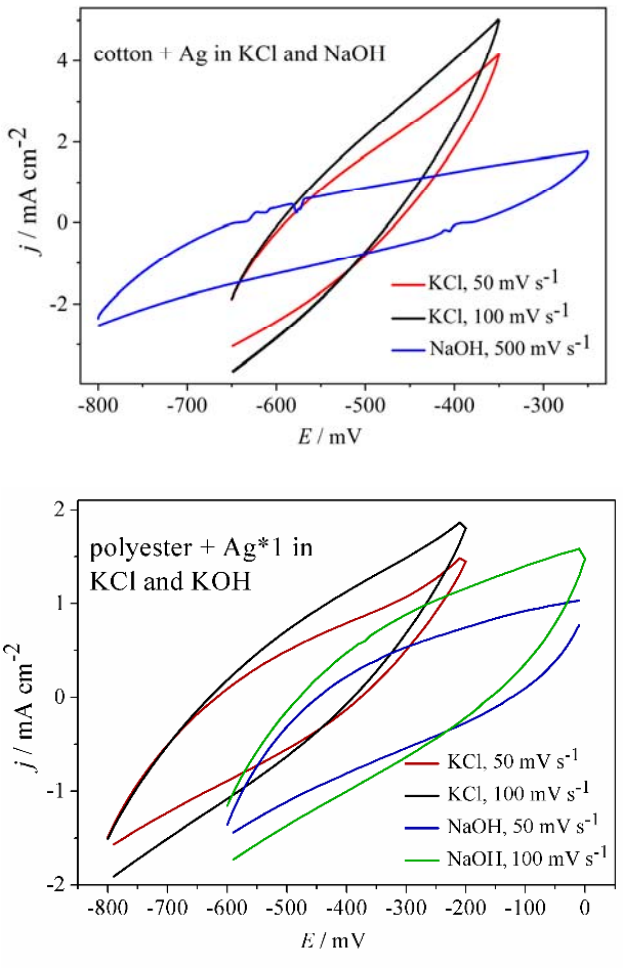


Figure 2. Cyclic voltammetry at various potential scan rates and in two different electrolytes, of cotton + Ag and polyester + Ag, after one immersion cycle

On the contrary, Figure 3 shows the cyclic voltammograms of the electrodes prepared by polyester modified by silver thin films, after three and five cycles of immersion. The diagrams recorded in NaOH show a purely capacitive response, with a square-like voltammogram and a significant gap between the positive and negative current, that increases with the scan rate. On the other hand, the voltammograms recorded in KCl contain one pair of peaks, placed in the potential range between -800 and -600 mV. The anodic and cathodic peaks are due to the oxidation and reduction of silver thin film by the chloride anion. These peaks are an indication of the pseudocapacitive behavior of polyester + Ag material in KCl solution.

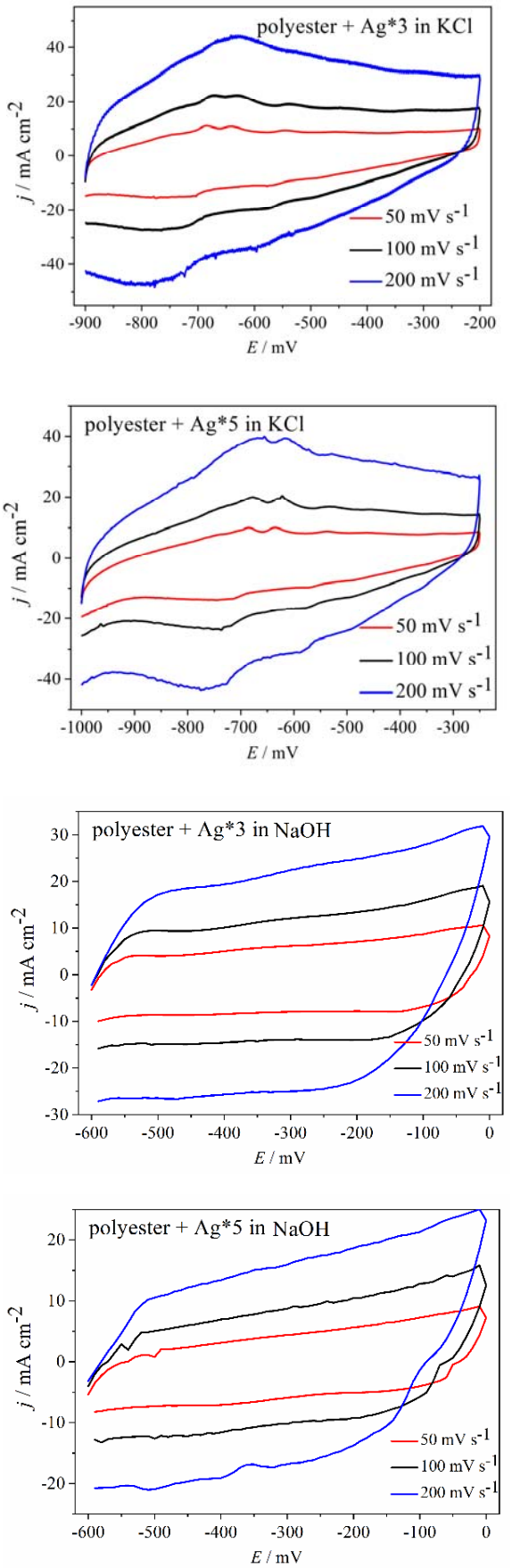


Figure 3. Cyclic voltammetry at various potential scan rates and in two different electrolytes, of polyester + Ag, after three and five immersion cycles

The specific capacitance of the electrode surface was calculated from the CV curves using the equation:

$$Cs = \frac{\int I(V)dV}{m * \upsilon * \Delta V} \quad (1)$$

where Cs is the specific capacitance ($F\ g^{-1}$), ΔV is the scanning potential range (V), υ is the scan rate ($V\ s^{-1}$), m is the working electrode mass (g), and the $\int I(V)dV$ deputes an area of the *CV* curves [7].

The capacitance values, measured in the two electrolytes, from voltammograms recorded at 100 mV s^{-1}, are presented in Table 1. Firstly, it is noticed that the fiber with three immersion cycles exhibits slightly higher capacitance in comparison to the samples obtained with five immersion cycles. It may be speculated that three immersion cycles are sufficient to form a silver layer of a sufficient thickness and compactness for capacitive behavior. And in case of five immersion cycles, the capacitive behavior is observed, but at the same time, the sample mass increases as well, which leads to the lower calculated capacitance. Secondly, the capacitance is higher in KCl solution, but this is probably the result of a Faradaic (pseudocapacitive) process involved, that increases the measured current.

The results obtained are quite lower than in earlier reports on similar, fiber-based electrodes, for example in [5, 8], yet still, the capacitive behavior is clearly present in our work.

Table 1. Specific capacitance of polyester + Ag samples, obtained after three and five immersion cycles in silver solution

	KCl, 3 cycles	KCl, 5 cycles	NaOH, 3 cycles	NaOH, 5 cycles
C, $F\ g^{-1}$	66	61	43	32

3.3. Chronoamperometry

To further investigate the application possibility of the synthesized materials as capacitors, the material performances were examined under potentiostatic conditions. As shown in Fig. 4, the current was quickly increased upon applying voltage of + 300 mV from the open circuit potential, denoting the charging of the capacitor. During the 10 s period of the applied positive potential, a slow current decay is observed, denoting the spontaneous capacitor discharging.

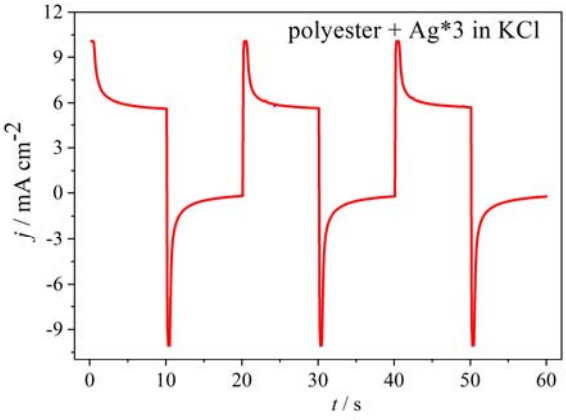
When the applied voltage was removed, the device current quickly decreased. Here, interestingly, the device current did not stop at 0 A after removing the applied voltage, but it did immediately overshoot to the negative direction. Furthermore, the negative current underwent a slow decay process after reaching the (negative) maximum values. This negative current part can be corresponded to the net charges stored by the previous potentiostatic charging operation [9].

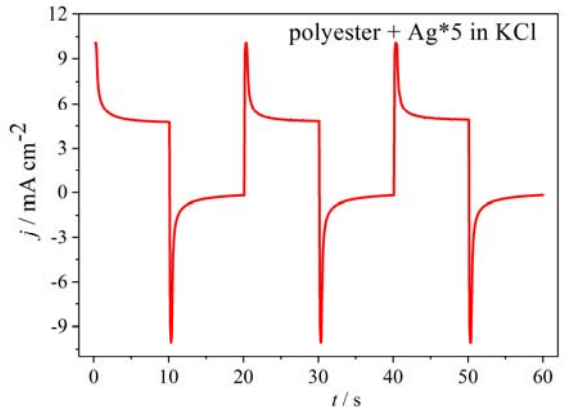
The amount of charge (Q) stored can be calculated by integration of the area in the negative current part, and the integration results are shown in Table 2. Contrary to the CV results, the chronoamperometry evidences that polyester samples immersed in NaOH possess a much higher capacitance, i.e. the ability to store charges. This discrepancy is easy to understand. As explained, the voltammograms record both capacitive and pseudocapacitive response, while chronoamperometry, in the narrow potential range (up to 300 mV in this work), records only the purely capacitive response.

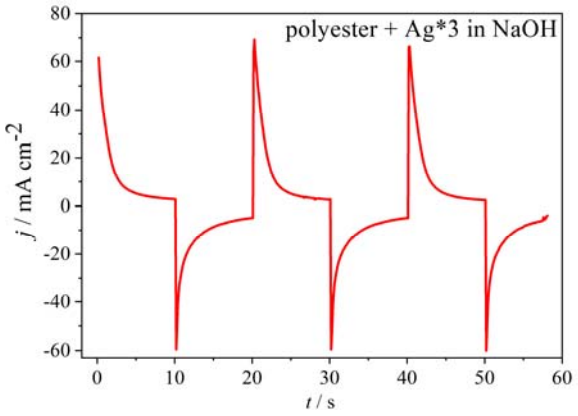
To conclude, the polyester modified with silver in three immersion cycles, when placed in NaOH electrolyte, is the best option for electric charge storage.

Table 2. The charge stored at the capacitor surface during the positive potentiostatic pulse in the two electrolytes, for polyester + Ag samples, obtained after three and five immersion cycles

	KCl, 3 cycles	KCl, 5 cycles	NaOH, 3 cycles	NaOH, 5 cycles
Q, mC cm^{-2}	10.9	8.4	119.8	37.0







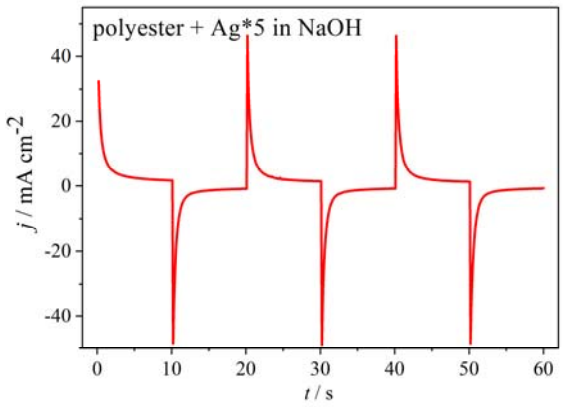


Figure 4. Repeated potentiostatic charge/discharge curves in two different electrolytes, for polyester + Ag electrode, after three and five immersion cycles in Ag solution

4. CONCLUSION

In this work, two different textile substrates were modified with a thin film of silver, by a novel immersion and annealing method. While the SEM shows excellent fiber coverage by silver particles even after the first immersion cycle, the electrochemical tests show significant differences between the samples. The cyclic voltammetry evidences that a cotton with silver deposit, and a polyester modified in only one immersion cycle in silver solution, do not exhibit any capacitive response. On the other hand, polyester modified with silver in three or five immersion cycles, shows a textbook-example of capacitive or pseudocapacitive behavior. This finding opens the door for production of wearable energy carriers, important in military applications.

As calculated from chronoamperometry measurements, the best charge carrying capacity shows polyester modified with silver in three immersion cycles, when placed in aqueous electrolyte containing 0.5 mol dm^{-3} NaOH.

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