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One-step electrochemical synthesis of PEDOT based composites for supercapacitor applications

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Abstract

The aim of this work was to determine the optimal synthesis conditions for the preparation of a poly(3,4-ethylenedioxythiophene) (PEDOT) layer by the electrochemical method from an electrolyte containing graphene oxide (GO) and a sodium dodecylsulfate (SDS) micellar solution. Besides an SDS anion, GO is also incorporated within the PEDOT layer as a negative counter ion. Therefore, this is a one-step electrochemical method for a PEDOT/GO composite layer preparation. The results displayed that PEDOT composites were successfully synthesised by applying a potential in the value range from 0.94 to 1.00 V, and with a synthesis duration of up to 600 s. It was concluded that the optimal concentration of EDOT monomer is 0.02 mol dm^{-3}, and SDS 0.01 mol dm^{-3}. The incorporation of GO into the PEDOT layer improved the polymer response in KCl solution influencing the pseudocapacitive properties, which is significant for its supercapacitor applications. The morphological and structural properties of the obtained layers were characterized by means of scanning electron microscopy and ultraviolet-visible spectrophotometry. The pseudocapacitive properties were determined in a 0.1 mol dm^{-3} KCl solution by using cyclic voltammetry and electrochemical impedance spectroscopy methods.

Keywords:
electropolymerisation; graphene oxide; poly(3,4-ethylenedioxythiophene); sodium dodecylsulfate

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most attractive conducting polymers in terms of practical applications, especially in energy conversion and storage devices, such as solar cells, supercapacitors and fuel cells (**Adekoya et al., 2020; Ljubek, 2019; Xia and Dai, 2020**). PEDOT has excellent properties, including low-cost, flexibility and good electrical conductivity which results in a fast electrochemical redox reaction (**Gueye et al., 2020**). PEDOT layers can easily be generated by chemical or electrochemical methods. The choice of method significantly affects the morphology and capacitive properties of the obtained material (**Liu et al., 2013**). Chemical synthesis is carried out in a reactor at temperatures ranging from 0°C to 80°C with the addition of oxidants such as FeCl$_3$, (NH$_4$)$_2$S$_2$O$_8$, KMnO$_4$ or H$_2$O$_2$ (**Rahimzadeh et al., 2020**). In this way it is possible to obtain large quantities of powder material. The electrochemical method is more suitable for direct preparation of PEDOT layers at the electrode surface and it provides a good control of the layer thickness by controlling the electrochemical conditions during layer preparation. Furthermore, there is no need for any chemicals as oxidants and the obtained conductive polymers can be directly used as active electrode materials (**Zuo et al., 2016**). Generally, electropolymerisation of PEDOT requires organic media, but in terms of environmental and economic requests, aqueous solutions are preferable. Moreover, by adding the surfactants to the aqueous solutions it is possible to increase the low solubility of 3,4-ethylenedioxythiophene (EDOT) in water, reduce the EDOT oxidation potential, accelerate EDOT polymerisation and improve PEDOT mechanical and hole-transport properties (**Gribkova et al., 2016; Romyen et al., 2017**).

The main disadvantages of PEDOT are low cycling stability due to poor mechanical strength and limited capacitance due to the material's low utilization (**Peng et al., 2008; Wilamowska et al., 2016**). Also, the activity of PEDOT is decreased by limited ion transport in the bulk of the material. To solve these problems, composites of PEDOT and graphene or its derivatives have gained a lot of scientific ground during recent years, especially in the field of energy storage systems (**Karakoti et al., 2022; Selvam et al., 2022; Teng et al., 2022; Huang et al., 2022**). The incorporation of graphene into the polymer structure can improve the electrical conduc-

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Table 1: Synthesis conditions for the PEDOT layer with the CP method

PEDOT layer	EDOT concentration / mol dm⁻³	SDS concentration / mol dm⁻³	Current / mA	Time /s
PEDOT-CP1	0.01	0.1	0.03-0.08	250
PEDOT-CP2	0.02	0.1	0.03-0.08	250

Table 2: Synthesis conditions for the PEDOT layer with the CA method

| PEDOT layer	EDOT concentration /mol dm⁻³	SDS concentration / mol dm⁻³	Potential / V	Time /s
PEDOT-CA1	0.02	0.1	0.88	300
PEDOT-CA2	0.02	0.1	0.90	300
PEDOT-CA3	0.02	0.1	1.00	300
PEDOT-CA4	0.02	0.01	0.88	300
PEDOT-CA5	0.02	0.01	0.94	300-1200
PEDOT-CA6	0.02	0.01	0.97	300

Table 3: Synthesis conditions for the PEDOT/GO and PEDOT/GO/SDS layers with the CA method

PEDOT layer	EDOT concentration / mol dm⁻³	SDS concentration / mol dm⁻³	Potential / V	Time / s
PEDOT/GO1	0.02	-	0.88	300
PEDOT/GO2	0.02	-	1.00	300
PEDOT/GO3	0.02	-	1.04	300
PEDOT/GO4	0.02	-	1.10	300
PEDOT/GO/SDS1	0.02	0.01	0.88	300 - 2000
PEDOT/GO/SDS2	0.02	0.01	0.94	300
PEDOT/GO/SDS3	0.02	0.01	1.04	300
PEDOT/GO/SDS4	0.02	0.1	0.88	300
PEDOT/GO/SDS5	0.02	0.1	0.90	300
PEDOT/GO/SDS6	0.02	0.1	0.95	300
PEDOT/GO/SDS7	0.02	0.1	1.04	300

tivity as well as the porosity of the material which facilitates the overall redox reaction process. However, graphene is a 2D material with 3D strain (**Sun et al., 2019**) that exhibits hydrophobicity, which makes dispersion of graphene in an aqueous medium unstable. To overcome this challenge, it is possible to incorporate graphene oxide (GO) into the polymer structure. GO contains hydrophilic oxygen functional groups that enable its solubility in an aqueous medium (**Sačer et al., 2016**). Since GO is less conductive than graphene, it will not increase the material conductivity, however it provides good porosity of the material. PEDOT composites with graphene or GO can be synthesised via both oxidative chemical polymerisation and electrochemical polymerisation. Even though there are many publications where the dependence of properties of the electrodeposited PEDOT layers on the polymerisation conditions have been studied (**Sakmeche et al., 2000; Du and Wang, 2003; Han et al., 2007; Jiang et al., 2012; Romyen et al., 2017; Eickenscheidt and Stieglitz, 2019**), the results can hardly be correlated because of the different process parameters. Thus, it is interesting to investigate the influence of the different electrochemical methods, sur-

factants, different monomer or surfactant concentrations, polymerisation potential and time on the electrochemical synthesis of the PEDOT layer.

In this paper, we report the one-step electrochemical deposition of PEDOT and PEDOT/GO composite layers from micellar surfactant solutions. PEDOT is synthesised by polymerisation of the EDOT monomer. Considering that EDOT monomer is an organic substance partially immiscible in water (2.1 g l⁻¹ at 25°C) (**Elschner et al., 2010**), a micellar solution of surfactant sodium dodecylsulfate (SDS) was used. As a result, the solubility of the EDOT monomer was increased and its oxidation potential E_{ox} was lowered (**Sakmeche et al., 1996; Sakmeche et al., 1997; Sakmeche et al., 1999; Nasybulin et al., 2012**). A micellar structure of the surfactant is necessary to disperse and stabilise the EDOT monomer in water (**Duić et al., 1995; Starbird et al., 2012**). Further, GO should be intercalated into the conductive polymer layer as a negative counter ion and the improvement of pseudocapacitive properties suitable for supercapacitor applications were expected for composite materials. Two different electrochemical methods, chronopotentiometry (CP) and chronoamperometry (CA), were used
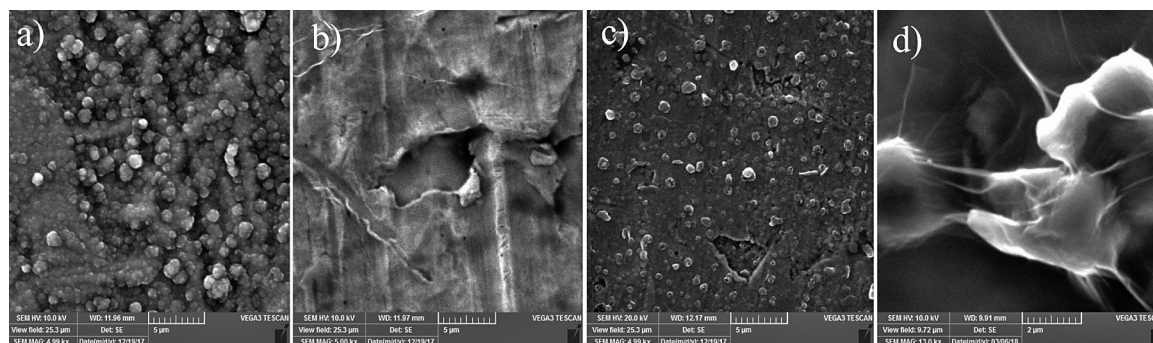
Figure 1: SEM images of a) PEDOT/SDS, b) PEDOT/GO and c) PEDOT/GO/SDS layers synthesised from 0.1 mol dm^{-3} SDS solution and d) PEDOT/GO/SDS layer synthesised from 0.01 mol dm^{-3} SDS solution

and process parameters were optimised to prepare PEDOT layers with good pseudocapacitive properties. The PEDOT layers were characterised using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron spectroscopy (SEM). Ultraviolet-visible (UV/Vis) spectrophotometry was used to confirm that GO was intercalated in the composite layer during the electropolymerisation.

2. Experimental

2.1. Chemicals

The following analytical grade chemicals were purchased: 3,4-ethylenedioxythiophene (EDOT) (Acros Organics), sodium dodecyl sulfate (SDS) (Sigma – Aldrich), graphene oxide (GO) (Graphanea), potassium chloride (KCl) (Lachner). All solutions were prepared by using double distilled water. EDOT monomer was used as received without further purification.

2.2. Poly (3,4-ethylenedioxythiophene) synthesis

The polymerisation process for the PEDOT layer was carried out using chronopotentiometry (CP) (see **Table 1**) and chronoamperometry (CA) methods (see **Table 2**). PEDOT/GO layer was synthesised from a solution containing 1 g l^{-1} GO and 0.02 mol dm^{-3} EDOT monomer, while the PEDOT/GO/SDS layer was prepared from the same solution with the addition of 0.1 or 0.01 mol dm^{-3} SDS (see **Table 3**). All the experiments were carried out in a one compartment three-electrode electrochemical cell using a potentiostat/galvanostat PAR model 263A. The Pt-foil (area, A = 1 cm^2) served as a counter-electrode and a saturated calomel electrode (SCE) was used as a reference electrode. The glassy carbon electrode (area, A = 0.07 cm^2) served as a working electrode. The working electrode was mechanically polished with an Al$_2$O$_3$ slurry (particle size 0.3 μm), washed with double distilled water and degreased with ethanol prior to use. All potentials are referred to as SCE reference electrode and all the experiments were carried out at room temperature (T = 24 ± 1°C).

The obtained layers were tested using cyclic voltammetry (CV) in the potential range from -0.5 to 0.5 V in 0.1 mol dm^{-3} KCl solution at a scan rate of 50 mV s^{-1}.

2.3. SEM measurements

The SEM morphology analysis of all samples was performed by VEGA 3 SEM TESCAN at an acceleration voltage of 10-20 kV, with a detector of secondary electrons. No metal coating was needed prior to SEM imaging.

2.4. UV/Vis measurements

The UV/Vis absorption spectra of solutions was collected with an Ocean Optics 200 UV/Vis spectrophotometer (Model D 1000 CE, Analytical Instrument Systems Inc.) by using 1 cm quartz cuvettes. The PEDOT layers were prepared on the ITO glass substrate. The duration of the synthesis was estimated based on the colour and transparency of the layer. After synthesis, the layers were polarized to 200 mV for 80 s in 0.1 mol dm^{-3} KCl solution. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Morphology of the PEDOT layer

SEM method provided insight into the morphological properties of different PEDOT layers (see **Figure 1**). Layers obtained in the presence of surfactants are characterised by pebble-like structures homogeneously distributed over the electrode surface. These structures are the result of the perpendicularly oriented and/or columnar structures of PEDOT due to the presence of SDS molecules and micelles between the polymer layers (**Naoi et al., 1995; Sakmeche et al., 1999**). The surface morphology of the PEDOT/GO layer (see **Figure 1b**) is compact and different from the pebble-like structure of the pristine PEDOT layer (see **Figure 1a**). It is well known that electropolymerisation of PEDOT in the presence of large dopant ions i.e. GO will result in a compact surface morphology (**Shi et al., 2018**). Furthermore, the
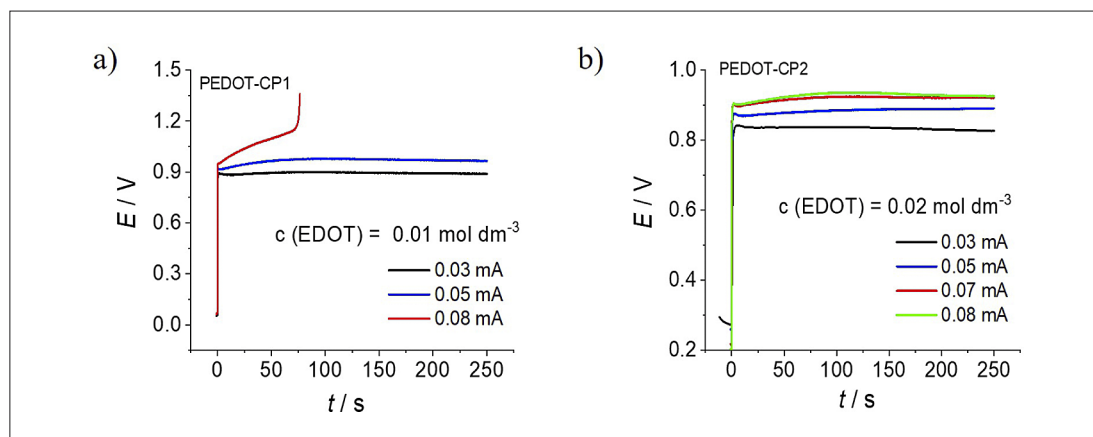
Figure 2: Chronopotentimetric responses obtained during the synthesis of
a) PEDOT-CP1 and b) PEDOT-CP2 layers at different current values;
the SDS concentration was 0.1 mol dm^{-3} and the deposition time was 250 s
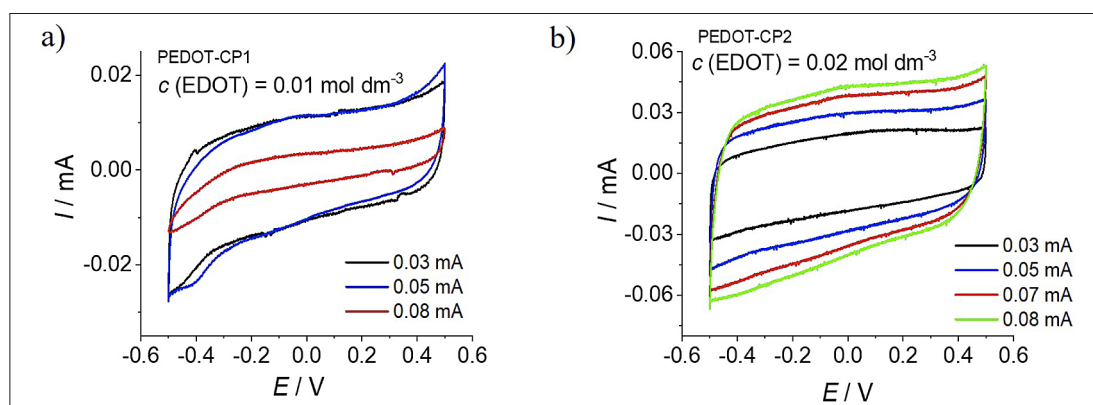
Figure 3: Cyclic voltammograms of a) PEDOT-CP1 and b) PEDOT-CP2 layers obtained
at different current values

SEM micrograph show the wrinkled morphology typical for graphene structures (**Österholm et al., 2012; Lerf et al., 1997**). As expected, the morphology of PEDOT/GO/SDS layer (see **Figure 1c**) is between pebble-like and compact, with wrinkled structures which prove the intercalation of GO into the polymer layer. Interestingly, surface morphology of PEDOT/GO/SDS layer obtained from 0.1 mol dm^{-3} SDS solution (see **Figure 1c**) appears to be different than the surface morphology of the layer obtained from 0.01 mol dm^{-3} SDS solution (see **Figure 1d**). It is clear that the morphological properties of the conductive polymer can be controlled by varying the surfactant concentration (**Hazarika et al., 2013**).

3.2. Optimisation of the PEDOT layer synthesis

The electropolymerisation of PEDOT was generated under galvanostatic and potentiostatic conditions as a function of various experimental parameters as presented in **Tables 1** and **2**. **Figure 2** shows the potential (*E*) vs time (*t*) curves registered during the electrodeposition of the PEDOT layers using the galvanostatic process. The figure compares layers obtained at different current values (0.03, 0.05 and 0.08 mA) and different concentra-

tions of EDOT monomers (0.01 and 0.02 mol dm^{-3}). The concentration of SDS in all cases was 0.1 mol dm^{-3}. The selected current values were chosen based on the information in the literature (**Sonmez et al., 2005**). As the current pulse was applied, a sharp increase in the potential value between 0.84 and 0.92 V was observed. Then, a constant potential related to monomer oxidation and polymerisation process is obtained, which leads to the conductive polymer being deposited on the electrode surface. The value of the potential depends on the value of the applied current and the concentration of the monomer. Higher potentials were obtained with higher current values and lower concentration of EDOT monomer. It is reasonable since, under these conditions, the reaction takes place at higher overvoltages. For the PEDOT-CP1 layer obtained at 0.08 mA, at the 70th second the working electrode potential has abruptly changed. It can be concluded that all of the monomer at the electrode surface is exhausted, and its concentration drops to zero. Prepared layers were tested with the CV method and capacitive behaviour was obtained. From **Figures 2** and **3** it is clear that as the synthesis current and monomer concentration increase, the current response of the obtained layer also increases. This was not observed for the layer synthe-
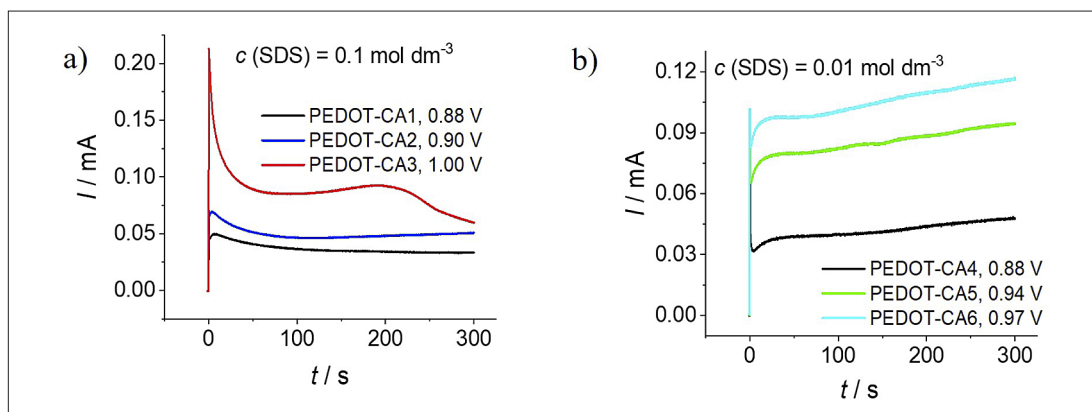
Figure 4: Chronopotentimetric responses obtained during the synthesis of PEDOT layers in a) 0.1 mol dm^{-3} and b) 0.01 mol dm^{-3} SDS solution at different potential values; c(EDOT) = 0.02 mol dm^{-3}
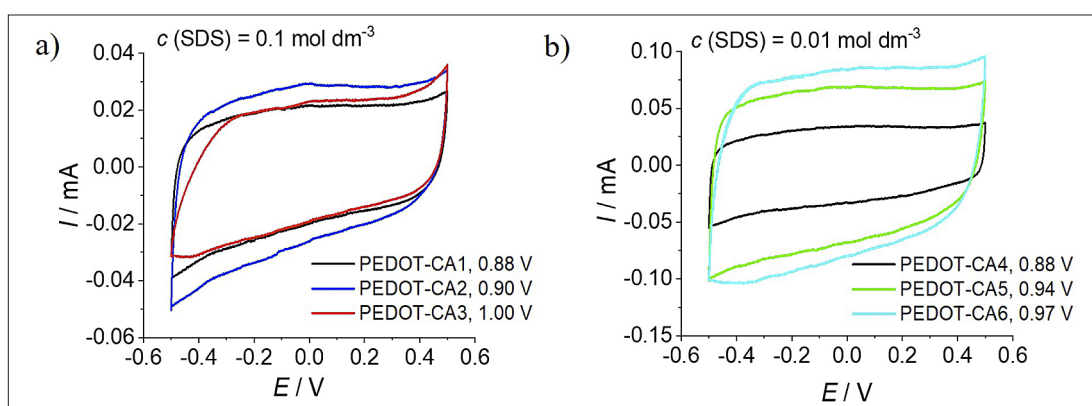

Figure 5: Cyclic voltammograms of PEDOT layers obtained in a) 0.1 mol dm^{-3} and b) 0.01 mol dm^{-3} SDS solution at different potential values

sised at 0.08 mA (see **Figure 2a**), where the response of the prepared film showed the lowest current value (see **Figure 3a**).

Figure 4 illustrates current (I) vs time (t) transients obtained at different potentials (0.88 – 1.00 V) and different SDS concentrations (0.1 and 0.01 mol dm^{-3}). The selected potential values were chosen based on the potential recorded with the CP method (see **Figure 2**). The concentration of EDOT monomer was 0.02 mol dm^{-3}. Immediately after applying the potential step, there was an initial sharp current increase corresponding to the charging of the double layer. This increase was followed by a significant current decrease due to the diffusion-controlled process occurring at the electrode. Then, the current was either slowly decreasing or increasing again. All the transients exhibit a current maximum that represents a nucleation process at the electrode surface (**Du et al., 2003; Kraljić Roković et al., 2006**). The current increase related to maximum reveals the polymerisation process and the increase of active sites at the electrode surface, which govern the polymerization rate (**Mandić et al., 1997**). From the obtained results, it is evident that a larger amount of conductive polymer was obtained at higher potentials. The cyclic voltammograms of PEDOT

layers prepared at 0.88 - 0.97 V show a nearly rectangular shape indicating good pseudocapacitive behaviour (see **Figure 5**). When the PEDOT layer was prepared at 1.00 V, the cyclic voltammogram shows a current peak which is an indication for disturbed pseudocapacitive properties. Also, there is a constant current drop during the preparation of the layer at 1.00 V (see **Figure 4a**) indicating that degradation of the layer takes place (**Kamensky et al., 2019**). Therefore, only PEDOT layers prepared at a potential under 1.00 V will show good pseudocapacitive properties.

In this work, PEDOT was synthesised by polymerisation of the EDOT monomer, that is an organic substance poorly soluble in water and a surfactant is required to achieve a homogeneous aqueous dispersion. The surfactants are amphiphilic molecules that have a long hydrophobic carbon chain and a small hydrophilic head group. After reaching a certain value of concentration (critical micelle concentration, CMC) surfactants produce complex units called micelles. As the micelle forms in an aqueous solution, the hydrocarbon chains are oriented towards the interior of the micelle and the hydrophilic, charged parts of the molecule are oriented towards the water as illustrated in **Figure 6** (**Batina 1986**).
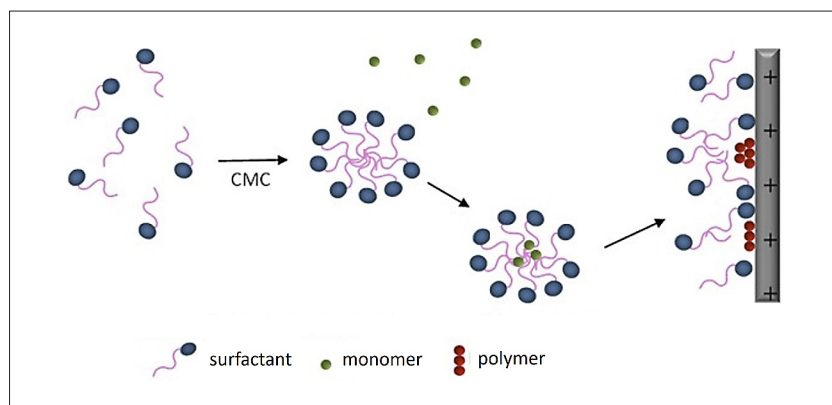
Figure 6: Illustration of the micelle formation process and incorporation of the EDOT monomer into the hydrophobic part of the micelle; when the micelle is destabilised, EDOT is released and polymerised on the electrode surface
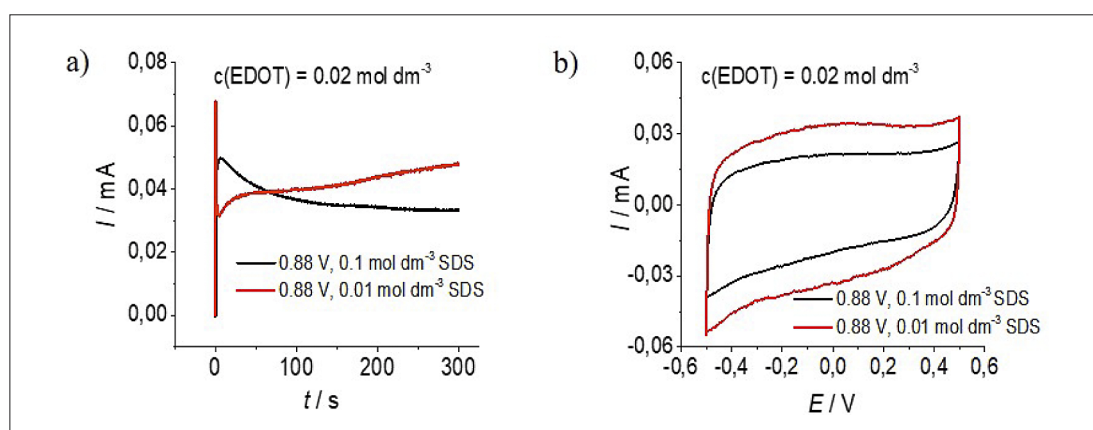
Figure 7: a) Chronoamperometric responses and b) cyclic voltammograms obtained during the synthesis of PEDOT layers in 0.1 mol dm⁻³ and 0.01 mol dm⁻³ SDS solution during 300 s at 0.88 V; c(EDOT) = 0.02 mol dm⁻³
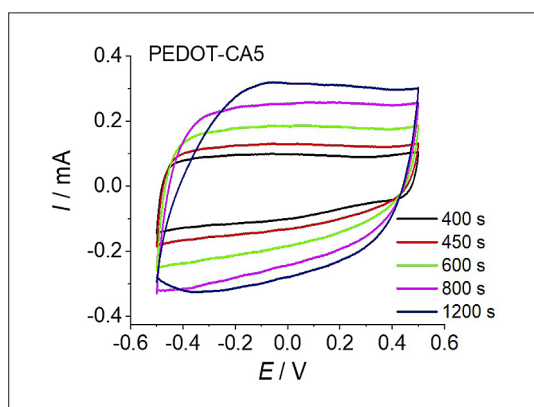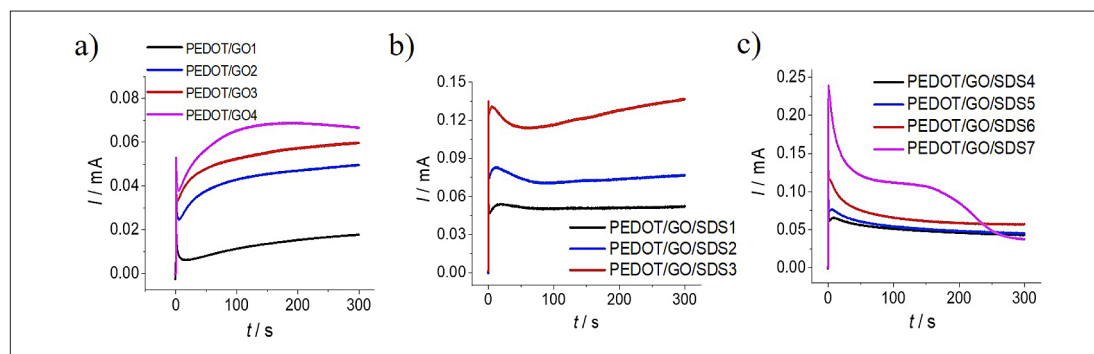

Figure 8: Cyclic voltammograms of PEDOT-CA5 layer synthesised at different deposition times in 0.1 mol dm⁻³ KCl solution; scan rate: 50 mV s⁻¹

ity of the EDOT monomer during the polymerisation process.

Figure 7 compares the current transients and cyclic voltammograms obtained during the synthesis of PEDOT layers from the solutions with different SDS concentrations (0.1 and 0.01 mol dm⁻³), both above CMC (CMC (SDS) = 0.0088 mol dm⁻³) (**Tyowua et al., 2012**). From the current maximum position (see **Figure 7a**), it is possible to estimate the nucleation rate. For 0.1 mol dm⁻³ SDS concentration current maximum was recorded at 5 s, while for 0.01 mol dm⁻³ SDS it is not clearly defined, but it is obvious that the nucleation process is slower. The higher micelle concentration is expected in 0.1 mol dm⁻³ SDS solution therefore fewer EDOT monomers will be incorporated within one micelle (**Jang et al., 2002; Hazarika et al., 2013**). These micelles will diffuse more easily to the electrode surface, which ensures a fast nucleation process. In 0.01 mol dm⁻³ SDS solution, the nucleation process is slow, resulting in a more porous layer (see **Figure 1d**) with many active sites for its growth. The nucleation will influence the further layer growth, therefore in a solution with a lower SDS concentration, the layer grows faster. This conclusion is supported with **Figure 7b**, where higher current response is obtained for 0.01 mol dm⁻³ SDS.

When the EDOT monomer is added in the surfactant solution, it will be predominately solubilised in the hydrophobic parts of the surfactants micelles (**Zhan et al., 2010**). Then, by the interaction of the hydrophilic part of the micelle with the electrode surface, the micelle is destabilised and the EDOT monomer is released and undergoes a polymerization process on the electrode surface. It is evident that CMC is an important factor in aqueous micellar media since it influences the availabil-

Figure 9: Chronoamperometric responses obtained during the synthesis of a) PEDOT/GO,
b) PEDOT/GO/SDS layers in 0.01 mol dm⁻³ SDS solution and c) PEDOT/GO/SDS layer
in 0.1 mol dm⁻³ SDS solution at different potential values
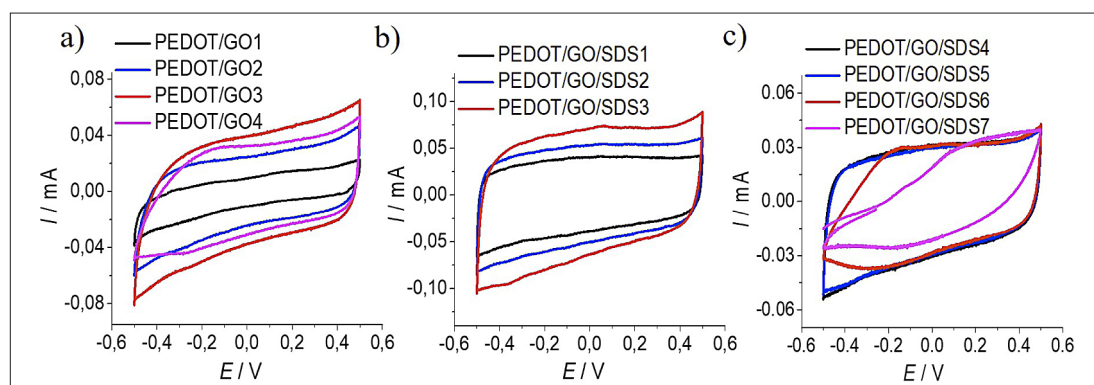
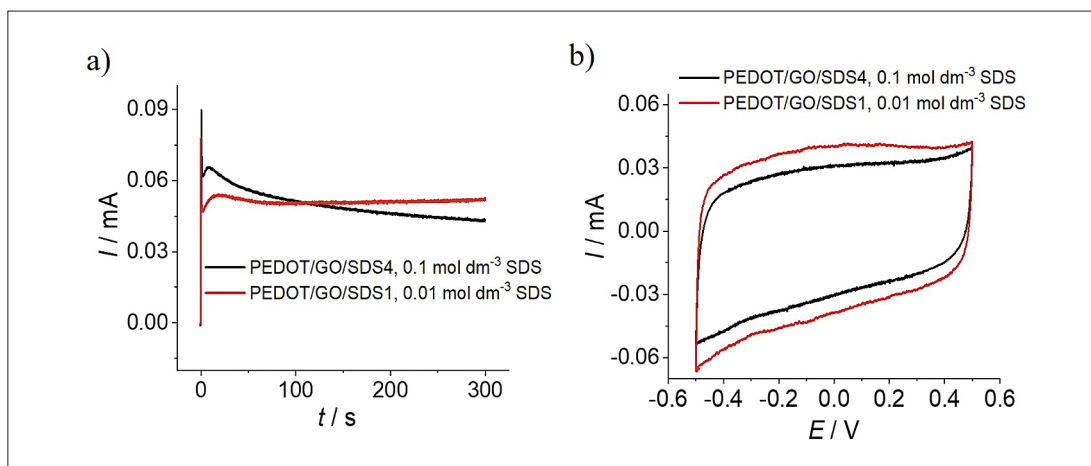**Figure 10:** Cyclic voltammograms of a) PEDOT/GO and b) PEDOT/GO/SDS layers synthesised
at 0.01 mol dm⁻³ SDS solution and c) PEDOT/GO/SDS layer synthesised
at 0.1 mol dm⁻³ SDS at different potential values

To determine the optimal synthesis time, the PEDOT layer was obtained during different times (400 - 1200 s) (see **Figure 8**). It is evident that more polymer is deposited onto the electrode surface as time increases, but it leads to a deterioration of the pseudocapacitive properties. Furthermore, the synthesis of layers in time over 1200 s was not possible. By visual inspection of the electrode surface, it was found that the layers were cracking and separating from the electrode surface. From **Figure 8** it is evident that good pseudocapacitive response was obtained for all layers expect for the one obtained at 1200 s, where significant deviation from rectangular response was obtained.

3.3. Optimisation of the PEDOT/GO and PEDOT/GO/SDS layer synthesis

Two different composites were prepared, PEDOT/GO and PEDOT/GO/SDS. The electrochemical synthesis was performed by the CA method from the GO solution, with or without SDS (see **Table 3**). When there is no surfactant in the solution, due to its anionic character, GO should be able to act as the main counterion during electrochemical polymerisation (**Sačer et al., 2016**). Thus, GO can be intercalated into the polymer to balance the positive charge on the polymer backbone, si-

multaneously realising the deposition of PEDOT/GO composite directly on the electrode. When SDS is present in the solution along with GO, the function of the main counterion will be taken over by SDS, due to its smaller dimensions and better mobility than GO. However, under these conditions, a certain amount of GO will surely act as a counterion and be intercalated into the conductive polymer layer. **Figure 9** illustrates current transients obtained during the synthesis of PEDOT/GO and PEDOT/GO/SDS composite layers. At the beginning of the polarisation there is a sharp current increase followed by a significant current decrease for all electrodes. Then, for the PEDOT/GO layers the current increases continuously and for the PEDOT/GO/SDS layers nucleation maximum is formed. It is obvious that the nucleation process is much slower for the GO solution compared to GO/SDS, and it is also evident that nucleation maximum appears within a shorter period of time for higher concentrations of SDS. After the nucleation process, it is evident that with a lower SDS concentration (0.01 mol dm⁻³), the current increases (see **Figure 9b**), and with a higher SDS concentration (0.1 mol dm⁻³), the current decreases (see **Figure 9c**), indicating faster polymer growth with lower SDS concentration. The obtained results are in accordance with the previous results and indicate that with a lower SDS concentration,

Figure 11: a) Chronoamperometric responses and b) cyclic voltammograms obtained during the synthesis of PEDOT/GO/SDS layers in 0.1 mol dm⁻³ and 0.01 mol dm⁻³ SDS solution during 300 s at 0.88 V
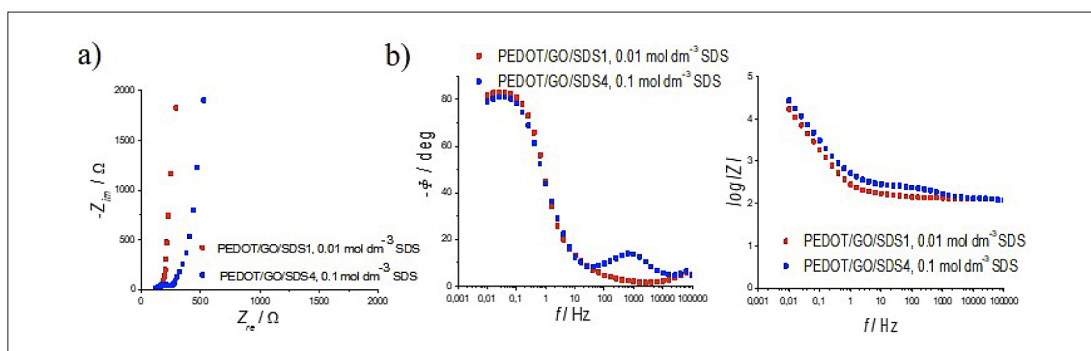
Figure 12: a) Nyquist plot and b) Bode plot for the SDS/GO/PEDOT layers obtained at different SDS concentrations
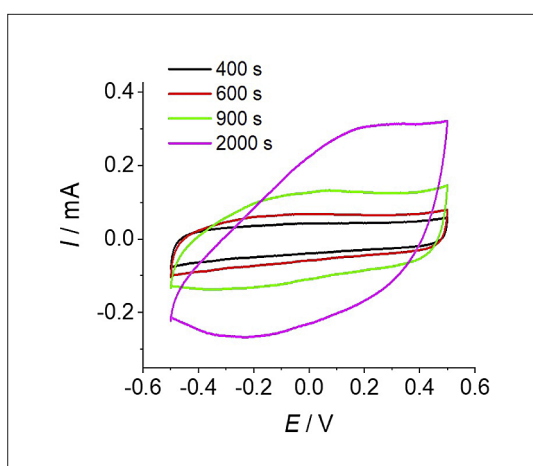
Figure 13: Cyclic voltammograms of PEDOT/GO/SDS1 layers synthesised at different deposition times in 0.1 mol dm⁻³ KCl solution; scan rate:50 mV s⁻¹

down the diffusion of monomers to the electrode surface, which affects the polymerisation rate (**Österholm et al., 2012; Tsagkalia et al., 2017; Tsagkalia et al., 2019**) and poor electrical conductivity of GO reduces the electrical conductivity of the polymer layer. As the synthesis potential increases, the current increases for all three composite layers.

From **Figure 10**, it is evident that with the increase of the synthesis potential, for all three composite layers, the value of the current increases. Cyclic voltammograms for the PEDOT/GO and PEDOT/GO/SDS layers obtained from 0.1 mol dm⁻³ SDS solution (see **Figures 10 a** and **c**) show that lower currents were obtained during the synthesis at a potential of 1.1 V than at 1.04 V. It is well known that at the sufficiently positive electrode potentials, irreversible degradation of the polymer layers occurs leading to drastic changes in the pseudocapacitive properties. When PEDOT/GO/SDS layer is synthesised from a 0.01 mol dm⁻³ SDS solution (see **Figure 10b**), no change of the capacitive properties was observed at higher potentials. The reason for this is the slower nucleation process leading to a more porous structure. In the case of the PEDOT/GO layer, it is difficult to compare the nucleation rate because the nuclea-

the number of active sites for polymer growth increases with time. In the presence of GO, it is expected that the number of active sites would reduce compared to the pristine PEDOT, leading to a more compact morphology (see **Figure 1**). In addition, GO in the solution slows

Figure 14: Chronoamperometric responses obtained for the PEDOT and PEDOT/GO/SDS layers in a) 0.1 mol dm⁻³ and b) 0.01 mol dm⁻³ SDS solution
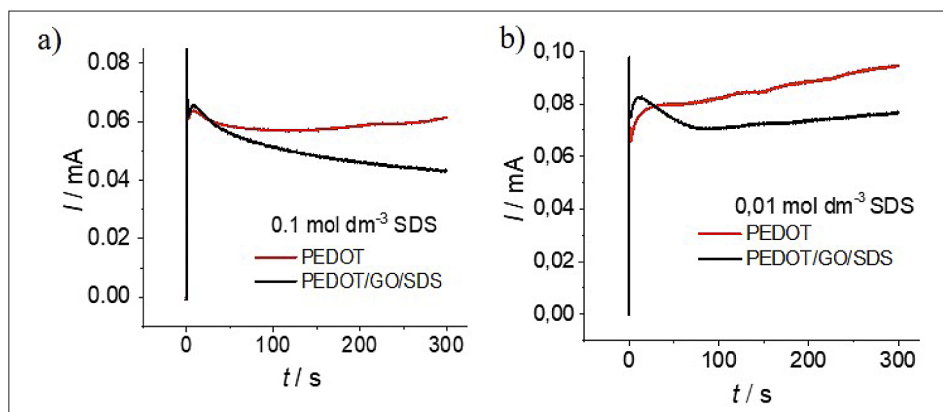
Figure 15: a) UV/Vis spectra of different PEDOT layers; $c(\text{SDS}) = 0.1$ mol dm⁻³ and b) photographs of samples obtained from different solutions
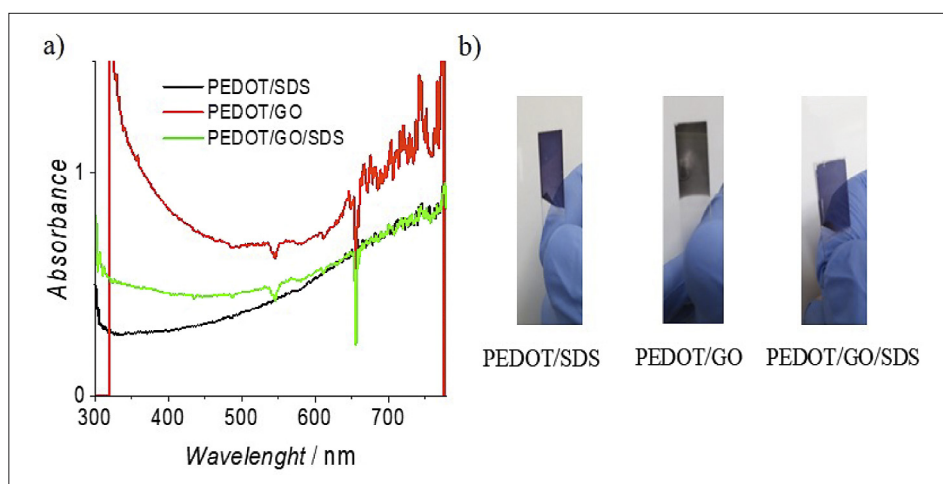
tion peaks are not observed. However, the properties of the layer obtained in the presence of GO without the addition of SDS will be different, which was confirmed by morphological analysis (see **Figure 1**).

Figure 11 compares the current transients and cyclic voltammograms obtained during the synthesis of PEDOT/GO/SDS layers from the solutions with different SDS concentrations. From cyclic voltammogram response, it is evident that higher current was obtained by 0.01 mol dm⁻³ SDS and therefore it is clear that the optimal SDS concentration is 0.01 mol dm⁻³ which was further confirmed by EIS results (see **Figure 12**). The influence of SDS concentration on the nucleation process is similar to the result obtained without the presence of GO (see **Figure 7**). From **Figure 12**, it is evident that the PEDOT layers obtained at different SDS concentration show capacitive behaviour, but the real impedance changes significantly only for the layer obtained at the higher SDS concentration (0.1 mol dm⁻³). Careful inspection of this layer revealed a small semicircle at high frequency, indicating additional resistances.

PEDOT/GO/SDS1 layer was obtained during different synthesis times (400 - 2000 s) and the results are shown in **Figure 13**. Similar to the results obtained for PEDOT layer without GO (see **Figure 8**), more polymer is deposited onto the electrode surface as time increases,

but the time increase leads to a deterioration of the pseudocapacitive properties.

3.4. The influence of GO on the PEDOT layer synthesis

To obtain additional insight into the process of polymer synthesis in the presence of GO, current transients for the PEDOT and PEDOT/GO/SDS were compared (see **Figure 14**). It is evident that the polymerisation rate is slower and nucleation currents are higher in the presence of GO. The morphology in the presence of pure GO is compact which is not suitable for good pseudocapacitive response of PEDOT, however careful optimisation of SDS and GO ratio will result in a modified layer of good pseudocapacitive properties.

3.5. UV/Vis analysis of the obtained PEDOT layers

Figure 15 shows the absorption spectra of PEDOT/SDS, PEDOT/GO and PEDOT/GO/SDS layers at a potential of 200 mV. The polymers prepared in the presence of GO (PEDOT/GO and PEDOT/GO/SDS) show increased absorbance intensity in the range from 300 to 400 nm, which corresponds to the $\pi \rightarrow \pi^*$ transitions in GO. The higher absorbance was observed in the case of PEDOT/GO layer due to a large amount of GO in the

polymer structure. As expected, the lowest absorbance was obtained for the PEDOT/SDS layer. From the results, it can be concluded that GO is incorporated into layers obtained from a solution containing GO. A significantly higher amount of GO was incorporated when the synthesis was performed from a pure GO solution than when it was conducted from a mixture of SDS/GO. The obtained UV/Vis spectra are characteristic of the PEDOT layer regardless of whether the polymerisation was carried out in the presence or absence of GO (**Nasybulin et al., 2012**). **Figure 15b** shows the different colour of the PEDOT layers. The layer prepared from the PEDOT/GO solution is black due to large amount of the GO, while other two layers are a characteristic blue colour (**Sydam and Deepa, 2012**).

4. Conclusions

From the obtained results, it is evident that PEDOT layers were successfully synthesised by the electrochemical methods from an electrolyte containing surfactants. The polymerization rate depends on the applied potential, surfactants and monomer concentrations. Special attention should be given to the selection of the potential value at which the polarisation will be carried out because of the irreversible oxidation of the polymer. The results showed that good pseudocapacitive properties of PEDOT layers are achieved by applying a potential in the value range from 0.94 to 1.00 V, and with a synthesis duration of up to 600 s. It was concluded that the optimal concentration of EDOT monomer is 0.02 mol dm^{-3} and SDS 0.01 mol dm^{-3}. The presence of GO in the synthesis solution reduces the rate of polymerisation and contributes to a more compact morphology of the layer. Given that higher nucleation currents were recorded in the presence of GO, it can be concluded that GO accelerates the nucleation process, thereby increasing the compactness of the layer and slowing down its growth. In addition, GO is not conductive, which reduces the conductivity of the layer and slows down the polymerisation.

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5. References

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SAŽETAK

Elektrokemijska sinteza PEDOT kompozita u jednome koraku za primjenu u superkondenzatorima

Cilj ovoga rada bio je odrediti optimalne uvjete sinteze za pripremu slojeva poli(3,4-etilendioksitiofena) (PEDOT) elektrokemijskom polimerizacijom iz elektrolita koji je sadržavao grafenov oksid (GO) i micelarnu otopinu natrijeva dodecilsulfata (SDS). Osim SDS aniona GO je također ugrađen u PEDOT sloj kao negativni protuion. Rezultati su pokazali da je sinteza PEDOT kompozita uspješna ako se primijene potencijali od 0,94 do 1,00 V u trajanju do 600 s. Zaključeno je kako je optimalna koncentracija EDOT monomera 0,02 mol dm^{-3}, a SDS 0,01 mol dm^{-3}. Ugradnja GO-a mogla bi poboljšati pseudokapacitivna svojstva sloja koja su bitna za primjenu u superkondenzatorima. Morfološka i strukturna svojstva dobivenih slojeva ispitana su pomoću pretražne elektronske mikroskopije (SEM) i ultraljubičaste i vidljive spektrofotometrije. Pseudokapacitivna svojstva određena su metodama cikličke voltametrije i elektrokemijske impedancijske spektroskopije u 0,1 mol dm^{-3} otopini KCl.

Ključne riječi:
elektropolimerizacija, grafenov oksid, poli(3,4-etilendioksitiofen), natrijev dodecilsulfat

Author's contribution

Gabrijela Ljubek (1) (PhD, postdoctoral researcher) performed experiments, characterisation and wrote the article.
Marijana Kraljić Roković (2) (PhD, Full Professor) proposed and planned the research, supervised the experiments, and scientifically edited the paper.