Materials Letters 273 (2020) 127978

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Supercapacitor studies of activated carbon functionalized with poly (ethylene dioxythiophene): Effects of surfactants, electrolyte concentration on electrochemical properties

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ARTICLE INFO

Article history:
Received 17 April 2020
Received in revised form 8 May 2020
Accepted 11 May 2020
Available online 13 May 2020

Keywords:
Surfactants
Activated carbon
PEDOT
Electrolyte
Supercapacitor

ABSTRACT

Electropolymerization of poly(ethylene dioxythiophene) (PEDOT) on activated carbon (AC) was performed using different surfactants such as anionic surfactant (sodium dodecyl sulfate), protonic surfactant (camphor sulphonic acid) and non-ionic surfactant (Triton) in 0.1 M H_2SO_4. The effects of concentration of different surfactants for electrodeposition of PEDOT on AC were analyzed using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and SEM techniques. Supercapacitors (SC) were fabricated using AC/PEDOT composite electrodes and 0.1 M H_2SO_4 as an electrolyte. The specific capacitance (C_s) values were calculated using CV at different concentrations of surfactants, electrolytes and variation of potential. The electrolyte containing 0.1 M H_2SO_4 and 0.02 M camphor sulphonic acid showed to have the highest specific capacitance value of 240 Fg^{-1} than other surfactant based SCs. Galvanostatic charge/discharge at varying current density were performed on SCs containing different surfactant based electrodes to study their cyclic stability.

1. Introduction

The supercapacitor (SC) is the device having power and energy densities in between batteries and capacitors. The market of SC is forecasted to attain $3.5 billion by the year 2025 with an increase in demand from sectors such as portable electronics and electrical automobiles. [1]. Hybrid SCs provides higher energy density over double-layer capacitors. These hybrid SCs consist of electrode materials such as metal oxides and conducting polymers which generate pseudocapacitance along with double-layer capacitance. Among many conducting polymers, poly(ethylene dioxythiophene) (PEDOT) was found to have high stability in both aqueous and non-aqueous electrolytes [2]. PEDOT was used to functionalize material such as carbon [3], carbon nanotube [4], graphene oxide [5], metal oxides [6], and all of these hybrid materials have shown high energy density, long cycle life, and excellent rate capability in SC application. The property of the electrodeposition of PEDOT depends on organic solvents, dopants, surfactants and potential of deposition. However, the surfactant plays a major role in dispersing and forming undistorted small particles of monomers during the chemical synthesis of conducting polymers [4]. Varying the concentration of non-ionic surfactant during chemical oxidative polymerization of PEDOT:polystyrene sulfonate blends resulted in high stretchable, conductive and flexible films [7]. Nonetheless, tailoring of PEDOT properties was done using numerous additives, but on addition of surfactants improved the mechanical and electronic properties [8]. The film roughness was also found to decrease in the presence of surfactant [9]. The role of surfactants on electrodeposition on conducting polymer is rare because as discussed above the other reports mainly focused on chemical in-situ synthesis. In the present work, three different types of surfactants namely, sodium dodecyl sulfate (SDS), camphor sulphonic acid (CSA) and Triton-X100 was used along with sulfuric acid as supporting electrolyte. The effectiveness of electrochemical properties was investigated by varying the concentration of surfactants during cyclic voltammetric deposition of PEDOT on activated carbon (AC). Moreover, the SCs fabricated with AC/PEDOT electrodes prepared using different surfactants were subjected to electrochemical studies for the first time under varying electrolyte

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https://doi.org/10.1016/j.matlet.2020.127978
0167-577X/

concentrations, varying concentration of surfactants and varying potential.

2. Materials and methods

The working electrode was developed using AC (60 μm, and the surface area 800 m^2/g Merck) paste made using polyvinylidene fluoride in N-methyl pyrrolidone (analytical grade, Merck) and brush coated on stainless steel (SS) (304 grade, 0.2 mm thickness). Reagent grade SDS (98%), CSA (98%), and Triton from Merck were used as surfactants. The electrodeposition of PEDOT was performed by potentiostatic polymerization of ethylene dioxythiophene (EDOT) (97%, Merck) in the presence of Pt foil as the auxiliary electrode, saturated calomel electrode as reference electrode on AUTOLAB (The Netherlands). PEDOT was electrochemically deposited by varying the potential (0.6 V to 1.6 V) in H_2SO_4 (Analytical grade, Loba chemie). The surface morphology was examined using SEM images (JEOL). The AC/PEDOT electrodes prepared using three different surfactants were used to fabricate SCs. Fabrication was done by soaking separator in H_2SO_4 and sandwiching between two symmetrical AC/PEDOT electrodes. The specific capacitances (C_s) were calculated from cyclic voltammetry (CV) under the varying concentration of electrolytes and surfactants. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range 1 mHz–10 MHz for all the SCs. The galvanostatic charge/discharge (GCD) method was applied for SCs at varying current densities to determine cyclic stability.

3. Results and discussion

3.1. SEM and electrochemical characteristics

SEM images of PEDOT electrodeposited on AC using different surfactants are shown in Fig. 1(a–c). In all the images uniform aggregates of PEDOT are deposited on the irregular surface of AC. In Fig. 1a (CSA based AC/PEDOT) the particle size is small and has high porosity which is ideal for SC application to yield better C_s. In Fig. 1b and c (Triton and SDS based AC/PEDOT, respectively) the particle size is comparatively greater than CSA based PEDOT. In Triton based AC/PEDOT, the deposition was less indicating that the monomers trapped in non-ionic surfactant molecules were not efficiently attracted by the charged electrodes. In SDS based AC/PEDOT, larger aggregates of PEDOT are observed implying that a mass flow of monomer towards electrode led to the piling of PEDOT on the surface of AC. Fig. 1d shows the EIS plot of the AC/PEDOT hybrid electrode deposited using different surfactants. Triton and SDS based electrodes showed almost similar charge transfer resistance (R_{ct}) at low-frequency region. Whilst, CSA based electrode showed semicircle with a smaller radius at the high-frequency region and a straight line leaning more towards the imaginary axis. The combination of resistance and capacitance led to the formation of the semicircle at the high-frequency region. At low-frequency region, due to Warburg impedance a straight line is found leaning towards an imaginary axis [2] indicating good capacitive behavior. Fig. 1e, f, and g show CVs of CSA, SDS and Triton based AC/PEDOT electrodes, respectively at different scan rates. The C_s of CSA, SDS and Triton based single electrodes were 465, 426 and 388 Fg^{-1}, respectively. The CVs of CSA and SDS were a combination of redox and double-layer mechanism pattern, while Triton showed more of a rectangular pattern due to double-layer mechanism. This indicates that in both CSA and SDS based electrodes the PEDOT is well deposited on the AC but in Triton based electrode the deposition is comparatively less. This result matches with the SEM analysis. Moreover, the current window in CV was largest in CSA based AC/PEDOT compared to other electrodes. The scan rate of (a) 60, (b) 40, (c) 30, (d) 20, (e) 10 and (f) 5 mV s^{-1} had no significant change on the CVs implying that the electrode material is stable at higher potentials.

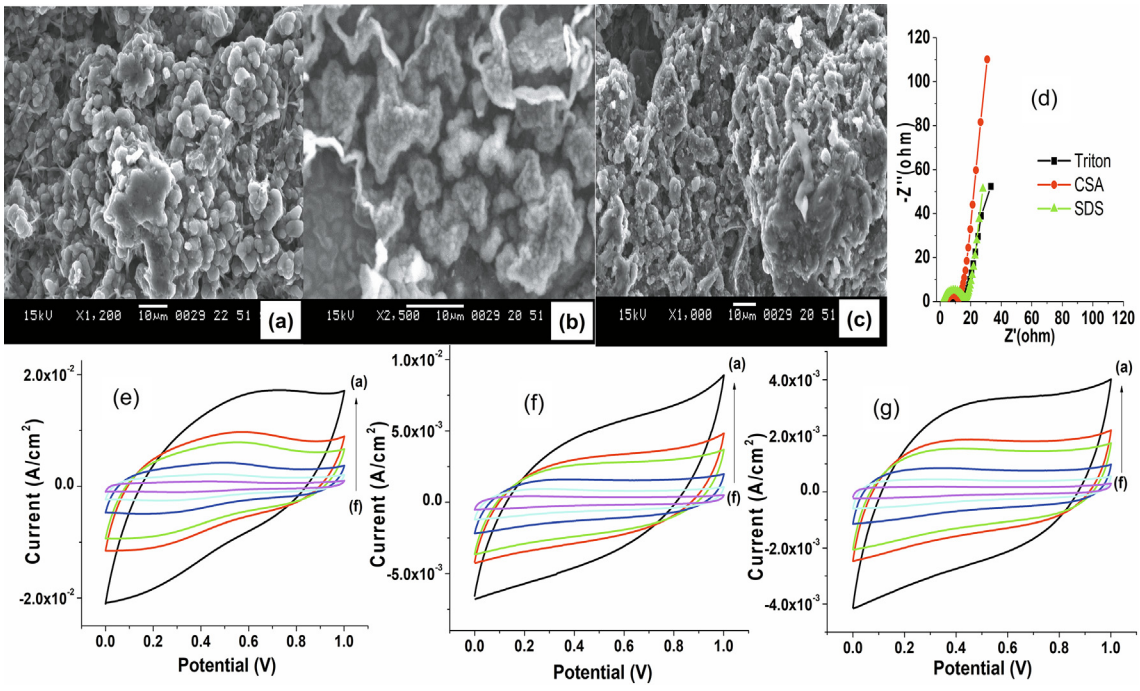

Fig. 1. SEM image of AC/PEDOT prepared using (a) CSA, (b) Triton, (c) SDS; (d) EIS of AC/PEDOT single electrodes based on different surfactants; CVs of AC/PEDOT electrodes prepared using (e) CSA, (f), SDS, and (g) Triton at different scan rates.

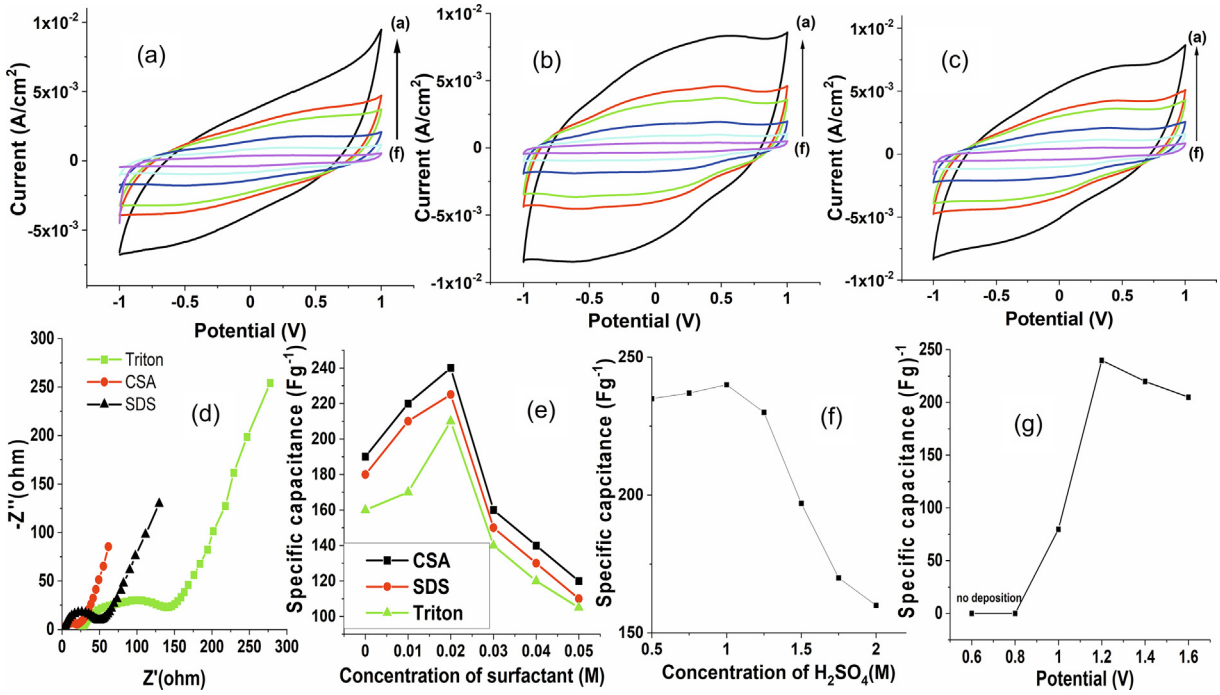

Fig. 2. CVs of SCs made using (a) Triton, (b) CSA and (c) SDS based AC/PEDOT electrodes; (d) EIS of these SCs; (e) C_s values of SCs with varying concentration of surfactants; (f) C_s values of SCs with varying concentration of H_2SO_4; and (g) C_s values of SCs containing CSA based AC/PEDOT prepared with varying potential.

3.2. Supercapacitor studies

CVs of symmetrically fabricated SCs using AC/PEDOT electrodes prepared with Triton, CSA and SDS are shown in Fig. 2a, b, and c, respectively. The C_s of Triton, CSA and SDS based electrodes were 154, 240 and 221 Fg^{-1}, respectively at 10 mV s^{-1}. As noticed that the single electrode capacitances were almost twice that of the double electrode setup. The enhanced C_s in CSA based AC/PEDOT SC indicates that the charge carriers are easily accessible on the porous electrode/electrolyte interface region. The decrease in scan rate from (a) 60, (b) 40, (c) 30, (d) 20, (e) 10 and (f) 5 mV s^{-1} decreases the current window because at lower scan rates there is lack of time for the movement of ions through the pores of the electrode material. Nonetheless, the pattern of CV had no significant deviation in increasing scan rate except Triton based electrode. This implies that non-ionic surfactant is not constructive for the electrodeposition of PEDOT. In the EIS plot (Fig. 2d), the CSA based AC/PEDOT SC showed the least R_{ct} value while highest for Triton. This low value of R_{ct} may be due to the hopping transport mechanism of H^+ ion on the water molecules towards the electrode/electrolyte interface region and forming double layer. Fig. 2e shows dependence of C_s on the concentration of surfactants in the AC/PEDOT electrode. The C_s value increased up to 0.02 M concentration and decreased with further increase in concentration. This might be because of a considerable change in morphology at this concentration. At 0.02 M CSA concentration, the dependence of C_s on the concentration of H_2SO_4 (0.5 to 2.0 M) was shown in Fig. 2f. There is a decrease in C_s either by decreasing or increasing the concentration of H_2SO_4 from 0.1 M. The dependence of C_s on varying potential during electrodeposition of PEDOT using 0.02 M CSA and 0.1 M H_2SO_4 solution is shown in Fig. 2g. At a potential of 1.2 V, the activation energy is sufficient for uniform deposition of PEDOT. Table 1 shows a comparison of C_s obtained from similar electrodes.

The GCD cycles at different current densities of SCs fabricated using Triton, CSA and SDS based AC/PEDOT electrodes are shown in Fig. 3a, b, and c respectively. CSA containing large molecules stabilizes the segmental motions of PEDOT during charge/discharge, hence showed a broad and linear pattern of charge–discharge curves. The C_s (Fig. 3d) measured using GCD varied only by 90% from initial C_s value indicating cyclic stability up to 5000 cycles.

Table 1
Comparison of C_s.

Materials	C_s (Fg^{-1})	Ref.
AC/PEDOT, β-napthalenesulphonate	158	[3]
PEDOT/SS, SDS	250	[2]
PEDOT:PSS/graphene	82.4	[10]
SiO_2/PEDOT nanospheres, hydrofluoric.	121	[11]
Present, AC/PEDOT, Triton, CSA and SDS	154, 240, 221	

4. Conclusion

PEDOT deposition on AC material showed significant changes in electrochemical properties by utilizing different surfactants and varying their concentration. The surface morphology of the AC/PEDOT showed that the presence of porosity, uniform particle size led to increase the capacitance. The single electrode prepared using CSA showed to have the highest C_s and more uniform growth of PEDOT particles than other prepared electrodes. SC fabricated using this CSA based electrode showed to have the comparatively highest C_s and cyclic stability.

CRediT authorship contribution statement

Y.N. Sudhakar: Synthesis, Characterization, Writing - original draft. **M. Selvakumar**: Investigation, Project administration, Writing - review & editing. **D. Krishna Bhat**: Formal analysis, Investigation, Methodology. **Smagul Karazhanov**: Resources, Software, Supervision. **Raghu Subash Chandrabose**: Validation, Visualization.

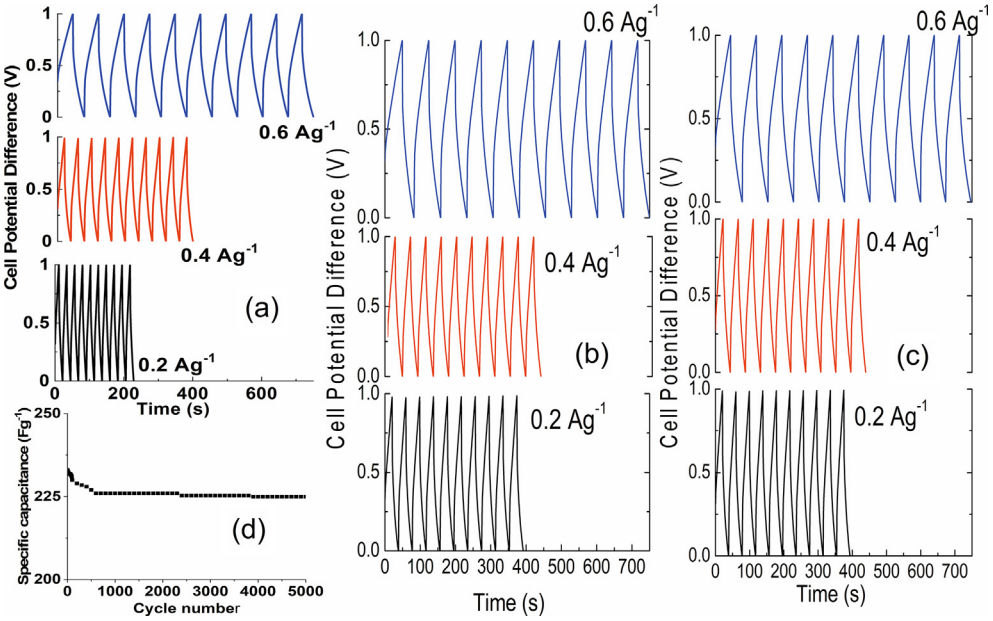

Fig. 3. GCD cycles of SCs made using (a) Triton, (b) CSA and (c) SDS based AC/PEDOT electrodes; (d) Cyclic stability of C_s up to 5000 cycles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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