Lampblack of soybean oil as a low-cost electrode material in supercapacitor application

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Abstract: Lampblack of soybean oil was investigated as a potential low-cost material to make electrodes of supercapacitors. The lampblack carbon was characterized using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). The electrochemical performance of the lampblack carbon electrode was tested using a three-electrode system, where a platinum wire was used as a counter electrode, a carbon electrode as a working electrode, and Ag/AgCl electrode as a reference electrode. The experiments, Galvanostatic Charge-Discharge (GCD) and Cyclic Voltammetry (CV) were performed in 3M aq. KOH. The specific capacitance of the lampblack carbon electrode from GCD was found to be 49.27 F g⁻¹ at 1 A g⁻¹. The lampblack carbon electrode showed good capacitive behavior at both low and high scan rates. The results indicated that lampblack carbon of soybean oil can be a new efficient alternative material for low-cost high-performance supercapacitors.

Keywords: Supercapacitors; Lampblack; Low cost; Scanning Electron Microscopy.

Introduction

Supercapacitors are the enhanced form of standard dielectric capacitors, capable of storing a larger amount of charge within the same dimensional constraints. They possess an energy density surpassing that of traditional capacitors and a power density exceeding that of batteries. The power density of the supercapacitor is in the order of 10 KW/Kg¹. For comparison, lead-acid batteries and lithium-ion batteries have power densities of about 1 KW/Kg and 2 KW/Kg respectively¹. So, supercapacitors are primarily used for harvesting energy and delivering high pulse power for short periods such as in regenerative braking². The use of supercapacitors is also in hybrid energy storage systems, medicine, electronics, aerospace, and defense³.

Based on the energy storage mechanisms, supercapacitors can be divided mainly into two categories: Electric Double-Layer Capacitors (EDLCs) and pseudocapacitors. The EDLCs are the basic type of supercapacitors, constructed from two carbon-based electrodes, an electrolyte, and a separator, in which the energy is stored as an electrostatic field generated by charges gathering at the interface between the electrode surface and the electrolyte. So, there is no transfer of charge between the electrode and electrolyte⁴. On the other hand, pseudocapacitors are distinctly different from EDLCs. In this, charge is stored faradaically through the transfer of charge between electrode and electrolyte. This is accomplished through electrosorption, reduction-oxidation reactions, and intercalation processes⁵.

Despite the high power densities, supercapacitors have yet to match the energy densities of mid to high-end batteries and fuel cells. Therefore, the most important issue for supercapacitor research is to enhance energy density⁴, which can be improved by either increasing the specific capacitance of the electrode or widening the operating voltage⁶. The specific capacitance of EDLCs depends upon the surface texture such as surface area and porosity of the electrode material⁷. So, different types of carbonaceous

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Received: 20 Jun 2023; Received in revised form: 29 June 2023; Accepted: 03 July 2023.

Doi: https://doi.org/10.3126/sw.v16i16.56828

electrode materials are used such as activated carbon^{7–13}, graphene¹⁴, carbon nanotubes¹⁵, and mesoporous carbon microspheres¹⁶. Each have its own unique properties and advantages, nevertheless, all these materials are synthesized using complicated processes and are expensive in comparison with the preparation technique and cost of lampblack: soot produced by burning oil or other combustible organic materials. So, in this paper, we investigate the capacitive performance of low-cost lampblack of soybean oil and compared it with the performance of commercially available activated carbon.

Experimental Methods

Preparation of lampblack from soybean oil

The lampblack of soybean oil was prepared using a similar process as described by Lawaju et al.,¹⁷. For this, the soot of the flame was deposited onto the concave surface of a mortar by blocking the flame with the mortar from the top. The process of deposition of lampblack was carried out for a few hours. Then the flame was extinguished, and the lampblack was collected.

Fabrication of electrodes

A mixture of 9 mg of soybean oil lampblack powder and 1 mg of Polyvinylidene Fluoride (PVDF) (Purchased from Apollo Scientific) were grinded in the mortar. Then 250 μ L of 1-Methyl-2-pyrrolidinone (Purchased from Glentham Life Sciences) was added to disperse PVDF. The obtained mixed slurry was then coated on a nickel foam of size 1 cm². Then, it was dried at ~70 °C overnight. Here PVDF was used as binder only.

For the comparison of the capacitive performance of the lampblack carbon, electrode of commercial activated carbon (Charcoal activated - 250 from Fisher Scientific) was also fabricated using similar procedure as described above.

The dried carbon electrodes were then pressed using metal paper clips for about 10 minutes. Then, they were soaked overnight in 3 M aqueous KOH solution prior to the electrochemical measurement.

Electrochemical measurement

The electrochemical characterization was performed by three electrode system where carbon electrodes were used as working electrode, platinum wire as counter electrode, Ag/AgCl electrode as reference electrode and 3 M aqueous KOH solution as electrolyte. Cyclic Voltammetry (CV) and Galvanostatic Charge-Discharge (GCD) tests were conducted via Interface 1010E (Gamry Instrument, USA).

The specific capacitance of the electrode material was calculated from the GCD test as well as from CV curves. The following equation was used for the calculation from the GCD curves¹².

$$C_{sp} = \frac{I\Delta t}{m\Delta V}$$
(1)

Where I is the discharge current (A), Δt is the discharge time (s), ΔV is the potential window (V) and m is the active mass (g) of the material in the electrode.

For the calculation using CV curve, following equation was used¹⁸.

$$C_{sp} = \frac{A}{2 \text{km} \Delta V} \dots \dots \dots (2)$$

Where A is area under curve, k is scan rate (mV/s), ΔV is potential window (V) and m is active mass (g) of material in the electrode.

Material Characterization

The Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) of soybean oil lampblack film was carried out at Texas State University, USA. For the preparation of film, paste of lampblack powder and aqueous solution of Carboxymethyl Cellulose (CMC) sodium salt (2% concentration) was doctor bladed (a coating technique) on a cleaned glass plate.

Result and Discussion

Figure 1 is the SEM image of the lampblack film coated on the glass plate with carboxymethyl cellulose as a binder. In figure 1(a), the particles of the lampblack are seen to form clusters. On further magnification, in figure 1(b), individual particle of the lampblack can be seen with an average size of $\sim 100-200$ nm.



Figure 1: SEM image of lampblack film with (a) 1500 times magnification and (b) ~10,000 times magnification.

Figure 2 is the energy dispersive X-ray spectrum of the carbon film. The spectrum shows that the carbon and oxygen contained in the scanned area is 95.12% and 4.88% by weight, respectively.



Figure 2: Energy dispersive X-ray spectrum of the lampblack carbon film.

The elements present in the lampblack film is shown in the table 1.

Table	1:	Elements	on	the	lam	pbl	ack	film.
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Element	Weight %	Atomic %
C K	95.12	96.29
O K	4.88	3.71

The EDS mapping of the carbon and oxygen are shown in figure 3. This shows that the carbon and oxygen are homogeneously distributed in the film. The presence of oxygen could be attributed to the utilization of CMC during preparation of the film and also to the absorption of moisture by the carbon from the surrounding air.



Figure 3: Energy dispersive X-rays spectrum (EDS) mapping of (a) carbon and (b) oxygen.

Figure 4 shows the cyclic voltammogram of lampblack carbon and commercial activated carbon at different scan rates. The CV curves of the lampblack carbon exhibit quasi-rectangular shape which is the characteristics of the electric double layer capacitor. Also, even at high scan rate of 100 mVs⁻¹, the CV curve maintains the characteristics rectangular shape indicating good charge transfer ability¹¹ and excellent capacitive behavior in quick charge discharge operations.

The CV curves of the activated carbon also exhibit quasirectangular shape as shown in figure 4(b). But, at high scan rate 100 mVs⁻¹, the CV curve become tilted and distorted dramatically. So, it not suitable for quick charge discharge operation¹⁹.





Figure 4: CV of the (a) soybean oil lampblack electrode and (b) commercial activated carbon electrode at different scan rates.

In figure 5(a), it is seen that at 2 mVs⁻¹ activated carbon electrode possesses higher inner integrated area than lampblack carbon electrode, indicating the specific capacitance of the activated carbon electrode is higher than that of lampblack carbon electrode. But, as seen in figure 5(b), at 100 mVs⁻¹ the inner integrated area of the activated carbon is much lower than that of the lampblack carbon. As a result, the specific capacitance of the activated carbon is much less than that of lampblack carbon.



Figure 5: CV of the soybean lampblack electrode and commercial activated carbon at (a) low scan rate (2 mVs⁻¹) and (b) high scan rate (100 mVs⁻¹).

Figure 6 shows the values of specific capacitances of the lampblack compared with the activated carbon at different scan rates of CV. The value of specific capacitanc decreases with the increase in scan rate for both carbon. This shows that at high scan rate, less electrochemically active surface area of the pores are utilized¹⁹.

The specific capacitances of the commerical activated carbon at 2 mVs⁻¹ and 100 mVs⁻¹ are 70.27 F g⁻¹ and 9.89 F g⁻¹, respectively, whereas the specific capacitance of lampblack carbon at 2 mVs⁻¹ and 100 mVs⁻¹ are 55.74 F g⁻¹ and 26.95 F g⁻¹, respectively. This shows that the capacitive performance of the activated carbon at high scan rate is very poor. This type of behaviour is the characteristics of microporous carbon particle²⁰. So, the majority of the activated carbon can be regarded as microporous. At slow scan rate, ions have enough time to diffuse into the micoporoes surface of the activated carbon. But at high scan rate, ions can only enter into the surface of electrode with larger pore size¹⁹.

As the CV of the lampblack carbon retains the rectangular shape at high scan rate, and have relatively high specific capacitance at high scan rate, it is resonable to assume that lampblack carbon particles contain high number of mesoporous particles. So, ions can have easy access to the surface of the electrode. Another factor which may affect the performance is the particle size. As, the particle size of lampblack carbon is only 100-200 nm, the path-length in lampblack carbon is smaller than activated carbon. This helps the lamplack carbon based system to react faster and perform better at high scan rates¹⁴.



Figure 6: Specific capacitances of lampblack carbon and activated carbon electrode at different scan rates.

Figure 7(a) and 7(b) are the GCD curves of the lampblack carbon and activated carbon at various current densities, respectively. The specific capacitance of the lampblack carbon electrode at 1 A g^{-1} is 49.27 F g^{-1} and that of activated carbon at 1 A g^{-1} is 75.55 F g^{-1} .

In both types of carbon, all the curves maintain ideal linear shapes keeping a symmetrical relation in charge and discharge parts, which confirm the double layer formation on the elctrodes-electrolytes interface¹³. Also, the IR drop is very small, indicating excellent stability and reversibility of both carbon²¹.



Figure 7: GCD curves of (a) lampblack carbon and (b) commercial activated carbon at different current densities.

Conclusion

In this study, lampblack carbon of the soybean oil was successfully prepared using traditional method at very low cost and effort. The prepared lampblack carbon showed good electric double layer capacitor behavior. When compared to the commercial activated carbon, the capacitive performance of the lampblack carbon was excellent at high scan rate and comparable at low scan rate. Although, the specific capacitance of the lampblack carbon electrode (49.27 F g⁻¹ at 1 A g⁻¹) was less than that of commercial activated carbon (75.55 F g⁻¹ at 1 A g⁻¹), the overall performance of the lampblack carbon can be considered to make low-cost supercapacitor electrode.

Acknowledgments

The authors are thankful to Associate Professor Sudarshana Shakya, Bhaktapur Multiple Campus (BMC), Dr. Tanka Mukhiya, chemistry department, BMC, Dr. Dibyashree Shrestha, chemistry department, Patan Multiple Campus (PMC), T.U., Prof. Dr. Shankar Prasad Shrestha, physics department, PMC, and Shared Research Operation (SRO) facility for providing opportunity to use the SEM at Texas State University, San Marcos, Texas.

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