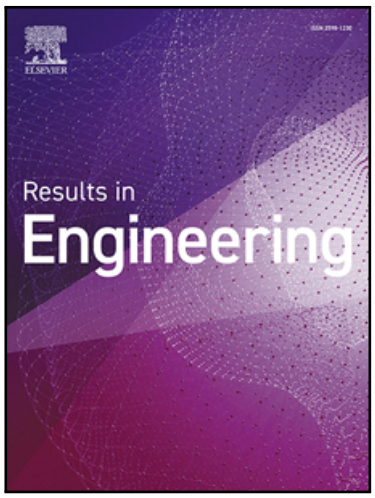

Flexible Electrochemical Capacitors based on ZnO-Carbon Black Composite

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Highlights

- Flexible electrochemical capacitors based on ZnO-Carbon black composite electrode.
- ZnO-carbon composite electrode exhibits a conductivity of 60.75 kS/m.
- Electrochemical capacitor has a specific capacitance of 99.21 $mF.cm^{-2}$ at 1 $mV.s^{-1}$
- The energy and power density of the devices are 54.1 $\mu W.h.cm^{-2}$ and 0.104 $mW.\ cm^{-2}$.

Flexible Electrochemical Capacitors based on ZnO-Carbon Black Composite

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Abstract

Flexible electrochemical capacitors (EC) or supercapacitors are found to be an efficient energy storage device for modern and future electronic gadgets that offer lightweight and compact energy solutions. In this work, we investigated the electrochemical and energy-storing performances of a flexible ZnO-carbon black (ZnO-CB) composite-based EC. The prepared ZnO-CB composite electrode exhibits a conductivity of 60.75 kS/m and it shows rough surface morphology which was observed through the scanning electron microscopic images. The cyclic voltammetry analysis reveals that the flexible ZnO-CB composite-based EC has a specific capacitance of 99.21 $mF.cm^{-2}$ and a charge contribution of 0.198 $C.cm^{-2}$ at a low scan rate of 1 $mV.s^{-1}$. The energy density of the EC gives 13.80 $\mu W.h.cm^{-2}$ at 1 $mV.s^{-1}$ and 0.53 $\mu Wh.cm^{-2}$ at 100 $mV.s^{-1}$. The energy storing performances are also observed through galvanostatic charging discharging analysis and provides a specific capacitance of 5.70 $mF.cm^{-2}$ with energy and power densities of 54.11 $\mu W.h.cm^{-2}$ and 0.104 $mW.\ cm^{-2}$ respectively at a current density of 0.25 $mA.cm^{-2}$. The bendability study of the device carried out in angles of 20°, 40° and 60° predicts its energy-storing performance under various bending angles. The observed energy-storing performances of the EC reveals its potential as a power source for operating flexible and wearable devices.

Keywords: Electrochemical capacitor, metal oxide, flexible energy storage, ZnO-carbon black composite, electrochemical properties.

1. Introduction

Flexible and bendable electronics found significant interest in wearable, portable devices and robotics [1-6]. For the proper and stable operation of these devices currently, flexible and bendable energy storage devices such as batteries and supercapacitors or electrochemical capacitors (EC) are utilised [7-10]. The emergence of flexible energy storage devices demanded that electrodes with a property of lightweight, high storage capacity, reliable, less environmental impact and a cost-effective approach of fabrication [11-14]. To enhance the performances including power density, energy density and life cycle recently, research has focused on developing pseudocapacitors (PCs) based ECs, which store energy through redox reactions between electrode and electrolyte, allowing chemical energy storage and higher specific capacitance compared to electric double-layer capacitors. In the recent work, it was found that the conducting polymers and metal oxides with the possession of their flexible and pseudocapacitance property can bring revolutionary enhancement in terms of structural end electrochemical performance in ECs [13, 15, 16]. On this aspect, there are various reports on composite-based materials for flexible energy storage devices fabrication which includes metal oxide-carbon [10], polymer-carbon [17], metal oxide-polymers [18, 19] and ceramic materials [20, 21].

Metal oxides are promising electrode materials due to their abundance, cost-effectiveness, high specific capacitance, and large surface areas, making them ideal for large-scale applications. Additionally, metal oxides' biocompatibility allows safe interaction with biological systems without harmful side effects, making them suitable for environmentally friendly applications. They promote sustainability through their minimal ecological impact and diverse compositions, optimizing supercapacitor performance and contributing to sustainable energy solutions [22]. Metal oxides offer higher energy density than carbon-based materials and better electrochemical stability than polymer materials. They facilitate faradaic reactions, enabling energy storage through electrostatic and chemical processes[23]. Their high specific power enables rapid energy transfer, which is crucial for applications requiring short bursts of power. Various metal oxides are implemented for EC fabrication, including RuO_2, Co_3O_4, NiO_x, V_2O_5, MoO_3, Fe_3O_4 and MnO_2 [24]. However, the toxicity, expensive nature, low energy density and cyclic stability, formation of agglomerates, fast degradation of material during electrochemical reactions, lack of

biocompatibility and the lack of conductivity of metal oxides limited their applications in flexible ECs, especially for wearable and portable devices[24-31]. For example, RuO_2 is an outstanding candidate for supercapacitor development. However, their toxicity and expensive nature limit their implementation. To overcome the issues of toxicity for wearable and sustainable applications biocompatible materials including iron oxide (Fe_2O_3), manganese dioxide (MnO_2), Zinc oxide (ZnO), Titanium Oxide (TiO_2), Tungsten oxide (WO_3), etc are found significant advantages. Their unique biocompatible materials and ability to exist in multiple oxidation states, allow them to participate in reversible redox reactions for high capacitive energy storage electrode materials[32-38]. In addition to this to overcome the low conductivity of the electrodes involved in electrochemical reactions, recently multiple works have reported the incorporation of carbon materials in metal oxides[39]. The supercapacitor fabricated with of Mn_3O_4/Carbon cloth shows that the incorporation of carbon cloth has enhanced the flexibility and conductivity of the Mn_3O_4 particles along with seizing the tendency of agglomeration of metal oxide[40]. In another work, the composite of reduced graphene oxide-wrapped MoO_3 exhibited a specific capacitance of 617 F g^{-1} at a current density of 1 A g^{-1} further compared with a bare MoO_3 the specific capacitance is observed to be much higher[41]. These studies reveals that the combination of carbon with biocompatible metal oxide will enhance the performances of ECs for flexible applications.

In this work, we developed a flexible EC by using a ZnO-carbon black (ZnO-CB) composite for a portable or wearable application. ZnO crystallizes in two primary forms: hexagonal wurtzite and cubic zinc blend. The hexagonal wurtzite structure is stable and preferred due to its superior electrochemical properties, making it ideal for supercapacitors and electronic devices. The cubic zinc blende form is less stable and less widely used in supercapacitor applications. Overall, hexagonal wurtzite is the preferred choice for ZnO applications[42]. ZnO is being explored as an electrode material for EC because of its low cost, environmental friendliness, and biocompatibility as compared to other metal oxides[43]. ZnO, a non-toxic, biocompatible metal oxide, widely used in biomedical applications due to its antibacterial properties, including wound healing, drug delivery systems, dental materials, and medical implant coatings[43, 44]. One of the main benefits of ZnO is its good electrochemical activity, which allows for effective charge storage through faradaic reactions[45-48]. This enables ZnO to

contribute significantly to the capacitance of the EC. However, its practical use is limited by certain drawbacks, notably low-rate capability and poor reusability during cycling. These limitations from slow faradic redox kinetics and high resistivity, which hinder effective electron transport at elevated rates. As a result, achieving cycle stability and high power density becomes challenging[49]. To overcome these issues, researchers are exploring the development of composite materials that combine ZnO with carbon-based materials[46, 49-51]. This approach takes advantage of the complementary properties of both components. The metal oxide contributes faradaic capacitance, which enhances charge storage through redox reactions, while the carbon materials provide double-layer capacitance, benefiting from their large specific surface areas. This synergy not only improves overall capacitance but also enhances energy and power capabilities. By leveraging the strengths of both ZnO and carbon materials, these composites offer a promising solution for developing more efficient ECs[52]. It was noticed that the aerogel carbon/ZnO composite of [52] and activated carbon ZnO composite of [53] as have similar properties due to their similarity in structure. To achieve a proper composite, we considered ZnO-CB as an electrode material of flexible EC where their studies are limited. Compared to those reported works on ZnO and carbon-based electrodes, here we prepared a printable paste of ZnO-CB and flexible EC was developed by manual printing. The proposed approach is low-cost and sustainable for the development of flexible wearable or other portable applications. For the prepared EC we carried out the interaction of the material with electrolyte through electrochemical studies such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) analysis and galvanostatic charging discharging method.

2. Experimental Section

2.1. Preparation of Paste and Electrodes

ZnO-CB composite paste (8:1) was prepared by mixing ZnO (99.9% Purity, Sigma Aldrich), carbon black (CB, Graphene Supermarket), ethyl cellulose (Sigma Aldrich) as a binder and N, N-dimethylformamide (DMF, 99.8%, Sigma Aldrich) as a solvent. The paste was prepared by using a pestle and mortar with hand grinding for around 30 min. For the electrode fabrication initially, the multi-layer graphene sheet (Graphene Supermarket, USA) was used current collector. The graphene sheet

was bonded on the top of a polyvinyl chloride (PVC) substrate with a binder paste (JE Solution). The substrate after binding with the graphene sheet was dried in an oven at 80°C for 30 minutes. On the top of this current collection ZnO-CB composite was printed and heated in an oven at 80°C for 1 hr. After printing the active electrode on the other end of the current collector, a silver conductive ink (RS components) is used to attach a copper wire to a substrate, for external electrical connection, and the assembly is dried in an oven at 80°C for 30 min. An insulating layer (TPU Protective Ink, JE Solution) is then applied on top of silver conductive ink and dried for 30 min in the oven to protect the conductive layer from electrolytes. The final active area of the electrode is 1 cm^2 and the schematic of the developed device is shown in Fig. 1a, and the electrode-electrolyte interaction is shown in Fig. 1b.

2.2. Characterisation of the electrodes

Surface morphology of the ZnO-CB electrodes was performed using scanning electron microscopic (SEM, Hitachi S-4800). The sheet resistance and conductivity of the electrode were measured through a four-probe system (Ossila). The hydrophobic and hydrophilic nature of the electrodes was determined through the contact angle measurement by using Ossila contact angle goniometer. The functional groups present in the composite electrode film were studied by using Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Frontier). FTIR spectroscopy was utilized to identify functional groups, evaluate chemical interactions, and investigate chemical vibration bonding in the material mixtures. The electrochemical properties and performances of the ECs were investigated using an electrochemical workstation (IVIUM Soft). The electrochemical measurements were carried out through cyclic voltammetry (CV, scan rate from 1 to 1000 $mV.s^{-1}$), and EIS analysis in the frequency range from 0.1Hz to 1MHz. The charging-discharging properties and energy storing of the ECs were studied using GCD under different current density ranges. The specific capacitance and energy-storing performances were measured by using equations reported in previous works[54-56]. The bendability study of the EC was carried out by static bending of the EC under various bending angles (20, 40 and 60°) and its charging and discharging performance were evaluated.

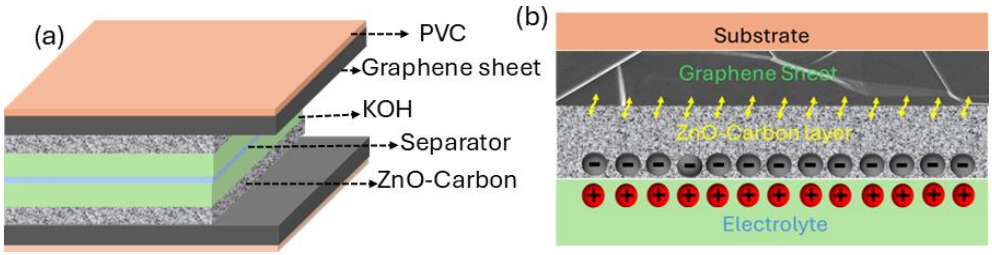

Fig. 1: (a) Schematic representation of (a) ZnO-CB composite-based EC and (b) the electrode-electrolyte interaction of ZnO-CB electrode

3. Results and Discussion

3.1.Material Characterisation

The SEM image shown in Fig. 2a represents the surface morphology of the ZnO-CB composite electrode. The image highlights the composite's texture, granularity, and microstructural features like particle distribution and surface roughness. The surface shows a rectangular particle of the composite with a uniform distribution of the particles. A zoomed version of this rectangular particle is shown in the Fig. 2a. These strictures provide a vast specific surface area for allocating the interaction of electrode and electrolyte. These rough morphologies also provide a platform for the ions from the electrolyte to exhibit a large adhesive property with the active layer. More the adhesion results in the enhanced electrochemical property of double-layer capacitance. The presence of pores will favour the intercalation that further enhances the property. This rough surface morphology enhancing electrical conductivity and active sites for electrochemical reactions [57]. The composite electrode shows a conductivity of 60.75 kS/m (sheet resistance 164.62 mΩ/square) as measured through four-probe measurements. The surface property was also investigated through the contact angle measurement. The hydrophobic and hydrophilic properties of composite material coated on a graphene substrate in a DI water and KOH electrolyte are shown in Fig. 2b and 2c. The contact angle measurements show an average angle of 35.33° for H_2O and 80.79° for KOH and the composite electrodes showed a nearly hydrophilic surface. Which indicates slightly good wettability and better interaction between the electrode and the electrolyte. The solvent used in the KOH solution was water, so the measure of contact angle for the both the liquids was to assess the wettability of the material when the pH is hiked. Fig. 2b and 2c imply that an alkaline medium tends to increase the hydrophobicity tremendously. This might

be referring to the inclination towards more of the formation of a double layer at the electrode-electrolyte interphase behaviour than intercalation.

Fig. 2d displays the FTIR spectra of ZnO-CB composite electrodes at wavelengths ranging from 400 to 4000 cm^{-1}. The ZnO-CB composition showed peaks at 3332, 2924, 2854, 1711, 1675, 1470, 1385, 1340, 1239, 1017, 872, 723, 504, 434 cm^{-1}. An absorption band at around 3332 cm^{-1} is observed, attributed to the –OH group vibration from water molecules adsorbed on the surface of ZnO nanoparticles[58]. The absorption peaks at 2924 cm^{-1}, 2854 cm^{-1}, can be attributed to the elongation vibrations of C–H groups originating from the Zn[59]. Absorption peaks in 1711, and 1675 cm^{-1} are due to carbonyl (C=O) stretching vibrations and H-O-H bonds respectively. The peak at 1505.44 cm^{-1} describes the ZnO stretching[60]. 1550.07 cm^{-1} might be pointing out the presence of NH bend, peak at 1094.69 cm^{-1} indicates the stretching of CO and the absorbance at 1408 cm^{-1} indicates OH bend[61]. Absorption peaks at 1470, 1239, and 1340 cm^{-1} is due to C-C stretching, C–O bonds and deformation vibrations of C–H bonds respectively. The absorbance at 1385 cm^{-1} *gem*-Dimethyl or "iso"- (doublet) or Trimethyl or "*tert*-butyl" (multiplet)[61]. Absorption peaks at 1017,872, and 722cm^{-1} confirm the presence of ZnO in the composite. Also, the C-H out of plane bend is represented by the peaks at 792.29 cm^{-1} and 969.37 cm^{-1}[61]. Absorption peaks at 504, and 434 cm^{-1} is attributed to the Zn–O bending and stretching vibration respectively[62].

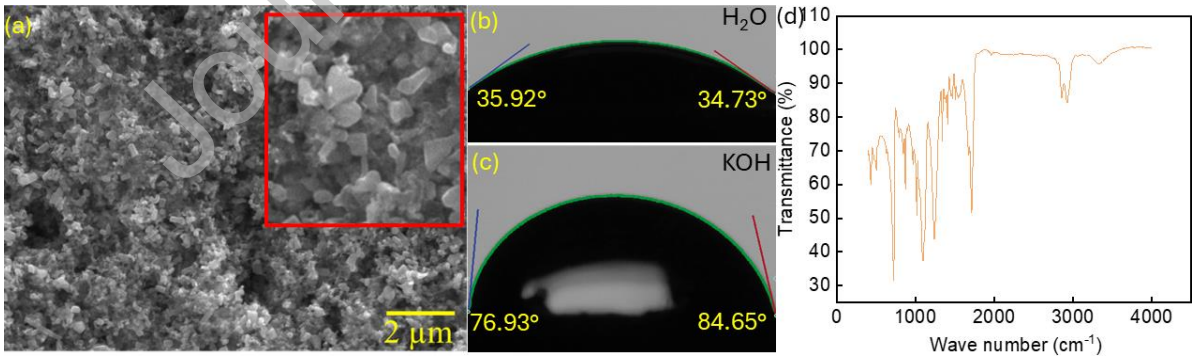

Fig. 2: (a) SEM image of the ZnO-CB composite electrode (b) and (c) contact angle measurement in H_2O and KOH respectively for the electrode. (d) FTIR spectra for ZnO-CB composite electrode.

3.2.Electrochemical Performance

The SEM image shows a rough surface morphology for the composite and its interaction with electrolytes was investigated using the EIS analysis. Fig. 3a displays the Nyquist plot for the EIS data in the frequency of 0.1 Hz to 1MHz. The equivalent series resistance (ESR) value was calculated from the intercept of the real part of the impedance at high frequency and is observed 5.05 $\Omega.cm^{-2}$, as seen from the zoomed plot. The lower ESR shows the device's high conductivity and less power loss. The absence of a clear semicircle at high frequency points shows a less charge transfer resistance, which is beneficial for energy storage applications. The inclined line at low frequency represents the Warburg impedance, indicating the ion diffusion into the electrode material pores and the formation of an electric double layer. Fig. 3b shows a Bode plot of ZnO-CB composite-based SC. In the Bode impedance magnitude plot, the impedance decreases rapidly as the frequency increases. This indicates that the ZnO-CB composite shows capacitive dominance at low frequencies and lower impedance at higher frequencies, which is ideal for fast charge-discharge processes. In phase angle plot shown in Fig. 3c sharply decreases with decreasing frequency, displaying a value of -62°, indicating high capacitive behaviour. The observed capacitance value with frequency variation is shown in Fig. 3d and the device exhibited almost 2 $mF.cm^{-2}$ at 0.1 Hz frequency.

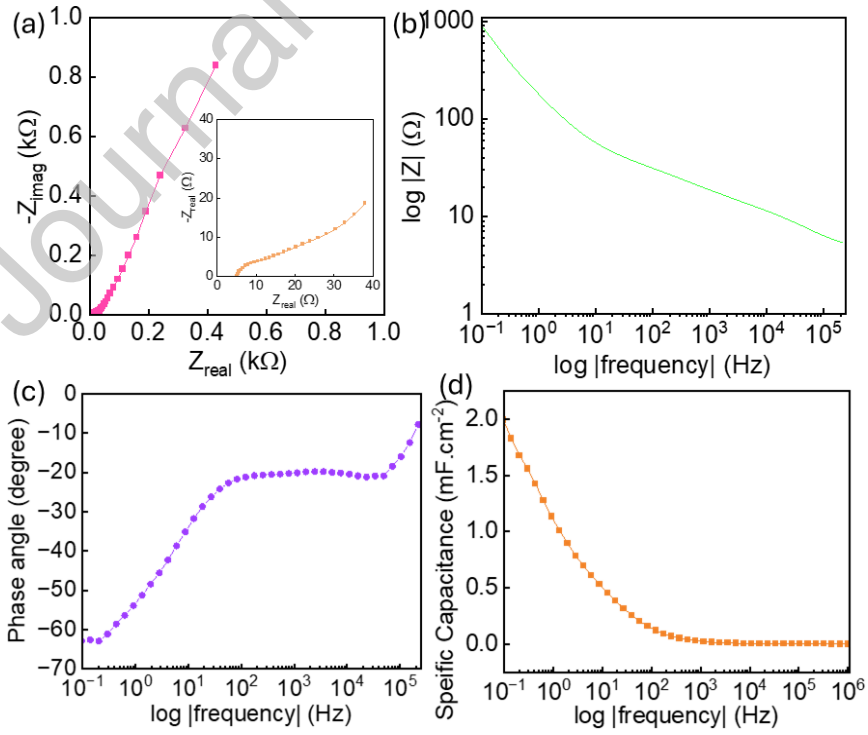

Fig. 3: Electrochemical impedance spectroscopic analysis of the ZnO-CB composite-based EC (a) Nyquist plot (inset shows in the high-frequency range of the Nyquist plot) (b) Bode impedance plot (c) Bode phase angle plot and (d) variation of specific capacitance with frequency.

Fig. 4a shows the CV curves for the ZnO-CB composite EC, at different scan rates (1-1000 $mV.s^{-1}$). CV curve predicts the pseudo rectangular shape and could be due to the diffusion-controlled pseudocapacitive processes associated with Faradaic reactions of ZnO and the electrochemical double layer formation due to the carbon composite. The CV curve shows that, with increasing the scan rate the peak current increases and it leads to changes in the capacitance and charge contributions (Q_t) of the device. At a low scan rate such as 1 $mV.s^{-1}$ the EC exhibit a specific capacitance of 99.21 $mF.cm^{-2}$ and a charge contribution of 0.198 $C.cm^{-2}$. The variation of specific capacitance and charge contribution of the EC is shown in Fig.4b. At low scan rates, electrolyte ions fully penetrate the electrode, enhancing capacitance through Faradaic reactions and double-layer formation. As scan rates increase, ion access to inner sites decreases, resulting in reduced capacitance, making charge storage primarily surface-based with limited deeper contributions. Further, we also measured the energy density of the EC, and it gives 13.80 $\mu Wh.cm^{-2}$ for 1 $mV.s^{-1}$ and 0.53 $\mu Wh.cm^{-2}$ at 100 $mV.s^{-1}$. Due to the rough surface morphology as shown in SEM image (Fig. 2a), the developed ZnO-CB composite electrode shows a high specific surface area for ion interaction which leads to the adhesin of more ions from electrolytes that in turn increase the capacity of the device. Due to the presence of carbon, the electrical and ionic conductivity is enhanced with the accumulation of K^+ and OH^- ions on some pores and surfaces leading to the formation of the double layer. Further, it is observed that at a lower scan rate, a symmetric redox reaction tends to decrease when the scan rate is increased, that is due to the diffusion of ions being suppressed at a higher scan rate, hindering its transportation[52]. Further, the composite reveals a -hydrophilic property towards KOH (Fig. 2c). This can lead to the intercalation of the electrolyte into the active layer despite the surface. Thus, the fabricated device has the potential to behave as a pseudocapacitor as well.

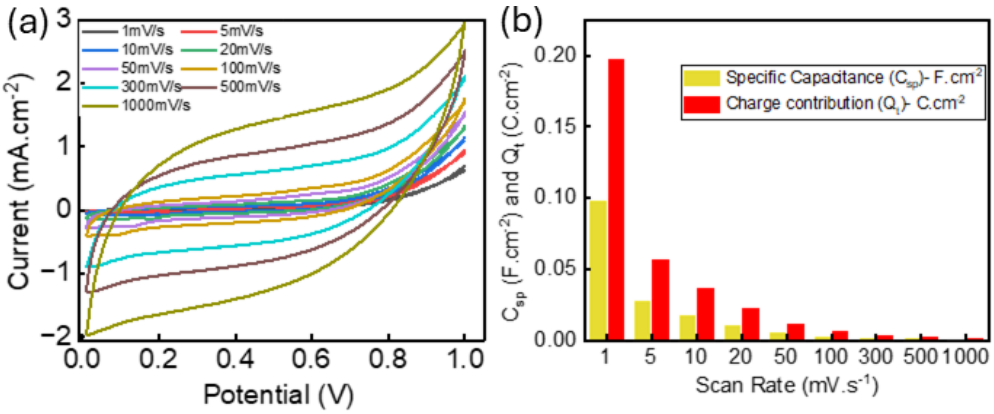

Fig. 4: Cyclic voltammetry analysis of the ZnO-CB composite EC (a) CV curve (b) variation of specific capacitance and charge contribution with scan rate.

Fig. 5 shows the GCD curve of ZnO-CB composite EC at current density in the range of 0.25 mA.cm^{-2} to 0.50 mA.cm^{-2}. The lower current density curve reveals a plateau-like shape during the charging phase, confirming pseudo-capacitance, where faradaic reactions contribute to charge storage. At higher currents, the triangular curves indicate faster charge/discharge processes dominated by electrostatic capacitance with minimal faradaic reactions. The specific capacitance, energy and power density of the ZnO-CB composite EC were measured from GCD using the previously reported equations[56]. For a low current density (0.25 mA. cm^{-2}) the EC gives a specific capacitance of 5.70 mF.cm^{-2} with energy and power densities of 54.11 µWh.cm^{-2} and 0.104 mW.cm^{-2} respectively. The variation of specific capacitance with current density is given in Fig. 5b. The Ragone plot (energy density vs power density) for the EC is shown in Fig. 5c and represents the high energy storing performances of the developed EC. In this EC, the device shows an IR drop seen in the inset of Fig. 5c revealing the resistance in the electrode material, electrolyte, and interfaces. A significant IR drop reduces the efficiency of energy storage devices by wasting energy as heat. We noticed low current density the EC shows an efficiency of 61.84%. As compared to other reported flexible supercapacitors based on ZnO and carbon compounds the observed energy and power densities are better and comparable. For example, the energy density of PVP-based ZnO$_P$/C composite is 49 µWh cm^{-2} at a power density of 2 mW.cm^{-2} [63], $ZnMn_2O_4$/rGO based EC shows 0.098 mWh.cm^{-2} at a power density of 1.6 mW.cm^{-2}[64] and nitrogen-doped graphene-like carbon nanosheets (H-NCNs) based SC from zinc-based biometal–organic frameworks (Zn-bioMOFs) shows 5.8 µWh.cm^{-2} at a power density of 20 µW.cm^{-2} [65]. These studies

show that the method of material preparation, electrode properties and electrolytes influence on the performances of the ECs. In addition, the electrochemical properties of our device is comparable with reported works [52, 53]. Evaluating our device with [52], the Nyquist plot reveals our device has better conductivity and higher diffusion rate because of the incorporation of carbon reinforcement. The solution resistance, charge transfer resistance and the Warburg resistance of our device is observed to be diminishing compared to [52]. It might be because of the fabrication of the composite with carbon black material.

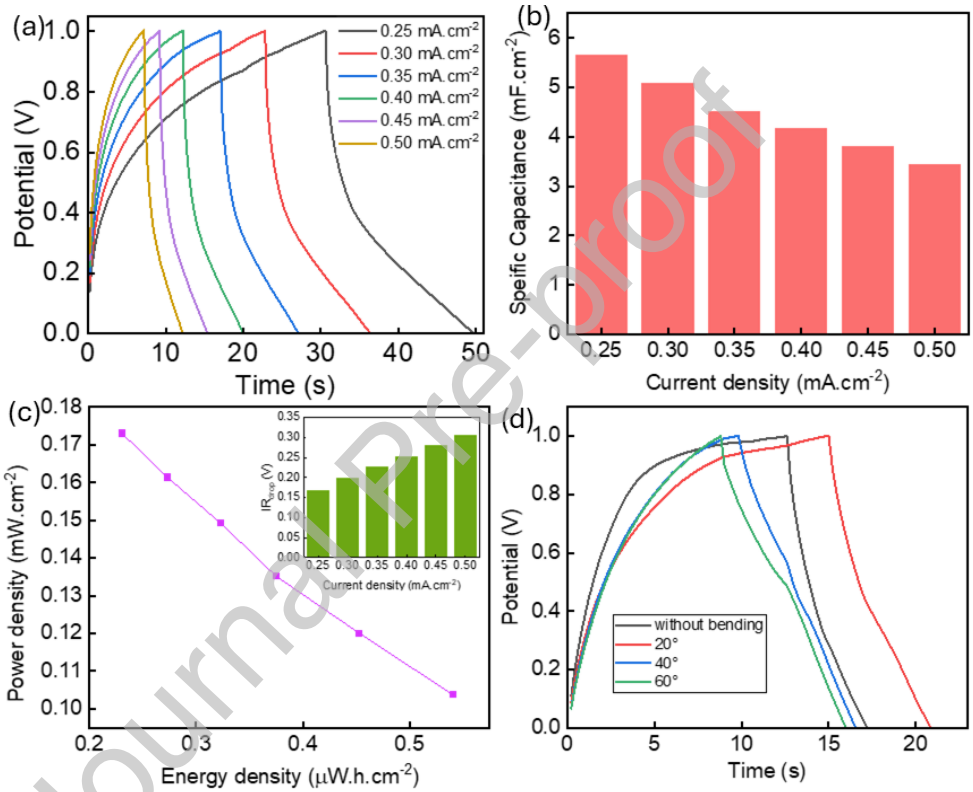

Fig. 5: (a) GCD curve for the ZnO-CB composite EC in different current densities (b) variation of the specific capacitance with current density (c) Ragone plot of the developed EC with IR drop of the device in different current densities (d) GCD curve under various bending angle.

The energy storing performances of the energy storage device under different bending angle is important for EC in wearable or portable devices. We measured the GCD performances of the devices without and with bending at different angles. The variations of the GCD curve in different bending angles are shown in Fig. 5d. We noticed that by increasing the bending angle voltage drop of the devices decreased. Without bending the EC shows a voltage drop of 0.142 V and under bending at 60°, the voltage drop is 0.098V. This voltage variation could be due to better electrode-electrolyte interaction while bending.

These changes in electrode-electrolyte interaction led to the enhancement of the specific capacitance of the EC by increasing the bending angle. Compared to without bending the EC bent at 60° exhibits 44.86% enhancement of specific capacitance. From Fig. 5d it can be analysed that, the bending is bringing changes in terms of internal resistance. The more it is bent, aids towards the eradication of the IR drop within the material. Also, the plot without bending and with minimum bending (20°) inclines more towards the electrochemical mechanism of the electric double layer, whereas the mechanism is more relevant towards the intercalation (pseudocapacitance) for the EC bend at 40° and 60°. An enhanced performance is shown for the bending at 20° compared to the bending without the EC. An increase in contact with the electrode and electrolyte can improve the specific capacitance. However, this can be only successful if the ions from the electrolyte manage to possess an adhesion on the surface of the electrode. So, the morphology of the electrode should be in a way for the attachment of the ions. The larger the contact area with bending larger the interaction of the ions and active layer. It corresponds to the flexibility of the device owing to the increment in the active sites of the device for the storage of the charge carriers at 20°. This shows the developed EC can potentially be used in flexible circuits to power low-power sensors and electronic components for wearables and portable devices.

For the evaluation of cyclic stability, the flexible ZnO-CB-based EC were carried out for 10000 charging-discharging cycles. Fig. 6a shows the electrode's GCD curve in different stages of the cycle during the long charging-discharging and it shows the variation in the performance of the device. After the 10000 cycles, the device exhibited a retention of 77.43%, as shown in Fig. 6b. This further promises the practical application and cyclic stability of this composite. This further might suggest the stable structural integrity of the reinforcement (CB) and matrix (ZnO)[66]. The EIS analysis given in Fig. 6c shows that during initial charging discharging there is no charge transfer resistance for the electrode and low ion diffusion resistance. However, after 10000 cycles of charging and discharging, the electrode shows a charge transfer resistance with high solution resistance and ion diffusion resistance. This could be due to the variation of electrode properties and the electrolyte degradation.

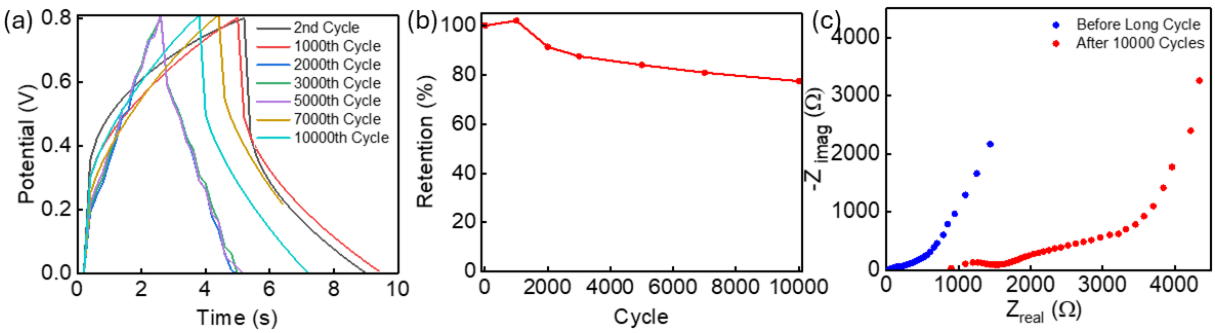

Fig. 6: (a) GCD curve for the ZnO-CB composite EC in long charging-discharging cycles (b) capacitive retention of the EC during 10000 charging-discharging cycles (c) Nyquist plot for the EC before and after 10000 charging-discharging cycles.

Conclusion

In this work, we developed a flexible electrochemical capacitor (EC) by using a ZnO-carbon black (ZnO-CB) composite. The ZnO-CB composite was prepared by solid-state reaction method. The prepared composite was printed on a multilayer graphene sheet which acts as a current collector. The electrode shows rough surface morphology and contact angle of 35.33° for H_2O and 80.79° for KOH composite electrodes. The electrode shows excellent conductivity of 60.75 kS/m and sheet resistance of 164.62 mΩ/square. We carried out the interaction of the material with electrolyte through electrochemical studies such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) analysis and galvanostatic charging discharging (GCD) method. The electrochemical impedance spectroscopy analysis reveals its excellent electrode-electrolyte interaction with negligible charge transfer resistance. The CV analysis provides that the flexible ZnO-CB composite-based EC has a specific capacitance of 99.21 $mF.cm^{-2}$ and an energy density of 13.80 $\mu Wh.cm^{-2}$ at 1 $mV.s^{-1}$. The energy storing performances are also observed through GCD analysis and give a specific capacitance of 5.70 $mF.cm^{-2}$ with energy and power densities of 54.11 $\mu W.h.cm^{-2}$ and 0.104 $mW.\ cm^{-2}$ respectively at a current density of 0.25 $mA.cm^{-2}$. This device exhibits excellent performance under different bending angles. Further analysis of different composites of ZnO-CB in different ratios and its integration with sensors or other low-powered electronics will lead the EC to become an excellent energy source.

The combination of carbon and metal oxide leads to a device performing both the electric double-layer principle and pseudocapacitance. However, for practical application it is highly important to enhance

the energy density of the device. The modification of electrode materials with conductive polymer is one of the options for increasing the conductivity and mechanical properties which leads to energy-storing performances as well. The optimization in the aspect of dimension, shape and porosity of carbon is also required. It is ideal to control the pore dimension, thickness and quantity for shorter ion diffusion onto the electrode surface. Further, the electronic conductivity validates for the rate capability of the electrode. Since metal oxide has low conductivity, it is important to ensure intimate contact of the carbon nanostructure and the current collector to minimize the interfacial resistance.

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Credit Author Statement

Wajeeha Habib: Data curation, Formal analysis, Methodology, Investigation, Roles/Writing - original draft, Writing – Review and Editing. **Anju Saji:** Data curation, Formal analysis, Methodology, Investigation, Roles/Writing - original draft. **Febin Paul:** Methodology, Investigation, Roles/Writing - original draft. **Prasutha Rani Markapudi**, Methodology, Investigation, Roles/Writing - original draft. **Callum Wilson**, Investigation Writing – Review and Editing. **Libu Manjakkal:** Conceptualization, Formal analysis, Methodology, Investigation, Supervision, Resources, Project administration, Roles/Writing - original draft, Writing – Review and Editing, Funding acquisition

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Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: