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Electrical behavior of graphite epoxy composite electrodes in humid environment

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The present study demonstrates the development of graphite (GR)-enriched epoxy composites for possible application as electrode materials for supercapacitors operating in humid environment. The study was conducted through development of a series of adhesive compositions involving epoxy resin supplemented with various proportions of GR (50 to 85 %w/w) and 4,4'-diaminodiphenyl sulfone (1%, w/w), followed by curing over stainless-steel current collectors at 110 ºC. This has afforded a series of working electrodes (WEs) with improved electrical conductivity. The effect of temperature and voltage on the electrical behavior of WEs at varying composition was investigated in humid environment (40%, RH). The study demonstrates that WEs involving 50 wt% of GR exhibit a 10% increase in σDC at 1 V under 40% RH, 40ºC. Arrhenius plots revealed that the activation energies (Ea, J/mole) of WEs were dependent on GR concentration (50 to 75% w/w) and were found in the range of 2.10 to 4.76. In comparison to the humidity at room temperature (36% RH), the humidity exposure (40% RH) of WEs derived at 50 wt% GR has shown an increase in σDC by 7.69%.

Keywords: Humidity, Epoxy, Graphite, Electrical conductivity, Working electrodes

INTRODUCTION

The current century has witnessed a growing need of inexpensive electronic materials for microelectronics [1], energy conservation and storage [2-4]. Working electrodes (WEs) constitute a crucial component in portable electronic devices, including batteries and supercapacitors pertaining to power generation and charge storage. The exploration of renewable and energy-efficient WEs for batteries and supercapacitors relies on the utilization of electrically conducting and electroactive materials possessing commendable temperature, voltage regulated conducting behavior [1], sustainability in humid environment [5] and ease of fabrication [6]. The adequate performance of WEs necessitates their high heat resistance and stability in humid conditions. In this regard, electrically conducting WEs with stability up to 200°C were developed from polyindole in presence of tungsten carbide [7]. Another study demonstrated an enhancement in the semiconducting behaviour of polypyrrole by incorporating haemoglobin [4]. A study reported that supercritical CO_2 assisted the green method for the synthesis of composite with improved DC conductivity and thermal stability [3]. In a recent study, thermally stable WEs (1000ºC) were derived from carboxylate functional multi walled carbon nano tubes (MWCNTs) in presence of hexagonal boron nitride and polyvinyl butyral. The study reveals an increase in σDC ranging from 0.96 to 1.14 under humidity exposure (40%) up to 3 h. However, further humidity exposure up to 9 h has marginally declined the σDC from 1.11 to 1.10 under identical conditions [8].

Graphite is widely known as an electrically conducting filler for polymer materials, especially epoxy resin to afford the polymer composites for electronic and electrochemical applications Over decades, considerable progress has been noticed in development of polymer nanocomposites through reinforcing various allotropic variants of graphite with epoxy resins. The key allotropic variants used in the development of electrically conducting polymer nanocomposites involving epoxies are expanded graphite, graphite [10, 11], graphite nanoparticles [12, 13] and carbon black [14]. A study involving expanded graphite (8 wt %) reveals an 11-fold increase in σDC of epoxy [9]. However, graphite as a filler poorly contributes to σDC of epoxy composite, as reported [10, 11].

Reinforcing graphite by 5 to 25 % contributes to the σDC ($\times 10^{-6}$) S/cm ranging from 2.5 to 3.39 [10]. In another study the increase in graphite loading up to 55 wt% imparts the σDC of epoxy composite in the order of 10^{-4} S/cm [11]. Reinforcing graphite nano particles (0.3 to 30 wt %) into epoxy imparts σDC of polymer composite by the order of 10^{-3} S/cm [12].

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Although a wide range of allotropic variants of graphite has been investigated to develop the electrically conducting epoxy composites and their nano composite analogues, no efforts are yet reported on the investigation of their electrical behaviour in humid environment.

Epoxy is widely used as an insulating material, and its response to elevated humidity levels has been extensively studied [15-22]. Epoxy/epoxy compounds in humid environment can undergo dimensional changes [13-15], reduction in mechanical properties [16, 17], increased susceptibility to environmental stress cracking [19, 20] and altered thermal properties [23, 24]. Epoxy resins have shown different mechanisms of water absorption *via* hydrogen bonding under different RH exposure based on their structure and activation energies [25, 26]. In a study it was found that addition of MWCNTs (1 wt%) to epoxy resulted in moisture uptake similar to cured epoxy, however, reduction in diffusivity was observed [16]. The dependence of σDC of GR/epoxy composites on RH has not been extensively studied. The present study investigates the humidity and temperature dependence of electrical conductivity of epoxy GR composites at varying voltage.

EXPERIMENTAL

Materials and methods

Working electrodes (WEs) were fabricated using commercially available GR powder (purity 98%, surface area 250 μm) sourced from Loba Chemie Fine Chemicals Pvt. Ltd, India. Epoxy (CY-230, density 1.08 g/cc) and hardener (4,4'-diaminodiphenyl sulfone, HT-972) were obtained from Huntsman India Pvt Limited. Other chemicals and solvents (>99 %) were locally arranged and used without further purification.

Fabrication of working electrodes

A series of WEs was fabricated through curing of an adhesive composition involving epoxy resin supplemented with various proportions of GR in acetone medium over stainless steel current collectors (CC). The CC employed for development of WEs were of 1 cm^2 area and a thickness of 1.48 ± 0.01 mm. A representative procedure involving the adhesive composition of epoxy resin (CY-230) with GR (50 to 85 w/w%) was thoroughly mixed at 800 rpm, followed by thermal activation at 90°C±1°C for 1 h and curing over CC with 4,4'-diaminodiphenyl sulfone (1%, w/w) at 50°C ± 1°C. Prior to curing, the surface of CC was polished with emery paper and subsequently cleaned with acetone. WEs were post-cured at 110°C. WEs with GR (% w/w) 0, 50, 65, 75 and 85 were fabricated and abbreviated as WE-0, WE-I, WE-II, WE-III and WE-IV, respectively. WEs with coating thickness of 0.23 ± 0.01 mm were isolated and stored at 50 ± 1°C/400 mm Hg [27]. The morphology of the electrode surface was examined through gold sputtering on its surface followed by scanning electron microscopy (SEM) imaging on JEOL JSM-6610 LV at 15 kV.

DC conductivity measurement

DC conductivity (σDC) measurements were conducted at 25 ± 1°C using a four-probe setup equipped with Keithley nanovoltmeter 2182A and a 6221 DC current source. The activation energy (Ea, J/mol) of the WEs was calculated within the temperature (K) range of 313.15 to 373.15 according to the Arrhenius equation $\sigma DC = \sigma_o DC \exp(-Ea/K_B T)$, where σDC is electrical conductivity (μS/cm) of WEs, Ea is activation energy (eV) which indicates the energy needed for an electron to skip and move to adjacent vacancy, $\sigma_o DC$ is pre-exponential factor which corresponds to maximum electrical conductivity (that it would have at infinite temperature), T is absolute temperature, and K_B is Boltzmann's constant [28-30]. Oven-dried electrodes were aged in humid environment. Relative increase in σDC of WEs under humidity exposure at 36% and 40% were investigated at selected voltages over the interval of 1 h till 8 h at 40±1 °C.

RESULTS AND DISCUSSION

Microstructure

Dispersion of GR into epoxy matrix of WEs was revealed through SEM (Figure 2). Dispersion of GR into epoxy has been associated with occasional phase separation in the epoxy matrix. The bright and dark phases associated demonstrate the epoxy- and GR-rich phases of WEs. Early studies revealed saturation of the epoxy matrix with 55 wt% of GR cured with aliphatic amine hardener without significant phase separation [11]. In the present investigation, WEs derived through dispersion of 50 to 85 wt% of GR revealed phase separation at 1KX, 10 μm, due to the insoluble nature of the solid phase hardener (HT-972) into epoxy resin (Figure 2b). The concerned phase separation was well distinct at 3KX, 5μm indicating the dispersion of graphene layers derived from GR into epoxy matrix.

In a study on GR/epoxy it was reported that at the elevated temperature employed during the curing process of epoxy, the viscosity of epoxy resin diminished, thereby enhancing the mobilization of the filler phase within the polymer phase. This increased the affinity of the filler to engage with the

matrix and establish conductive filler networks [31]. On further increase in GR concentration in epoxy (85%), the WE-IV resulted in dense clusters of graphene layers into the epoxy matrix (Figure 2d). WE-IV at 1KX, 10 µm revealed a saturation of the graphene layers within the epoxy matrix, displaying a significant presence of clusters formed by epoxy-bonded GR (Figure 2b). Another study revealed that reinforcement of GR (80 wt.%) results in decreased processability due to high viscosity. In the current investigation, the loading of 85 wt% of GR was found to adequately bind with epoxy matrix while preserving a phase-separated morphology over WEs (Figure 2d) [32].

Electrical behavior

Figure 2 reveals the trend of σDC of WEs (36% RH) with concentration of GR (wt%) at selected voltages at 25 ± 1°C . In general, σDC of WEs increased with GR concentration (wt%) and voltage. The increase in σDC of WEs with GR concentration attributes to long-range conductive interconnections between the filler and the epoxy matrix. This observation is supported by the early reports of σDC on the close agreement with σDC epoxy nanocomposites involving MWCNT and GR [11, 33]. However, the relative difference in σDC for individual WEs was marginal at 1V and 10V. These observations revealed the electrically insulating behaviour of WEs up to 10V. This observation was in close agreement with epoxy nanocomposites prepared out of expanded graphite [9]. Present observations indicated that WE-IV with 85 wt% reinforcement of GR imparts enhanced σDC (859.80 µS/cm) at 100V over the epoxy composite (100 µS/cm) involving expanded graphite (8 wt%) at 1000 V. Moreover, an increase in voltage from 1 V to 100 V has raised the σDC of WE-IV 11 times over WE-0 [34]. Dispersion of carbonaceous fillers plays constructive role towards enhancing the electrical behavior of epoxy composites [35].

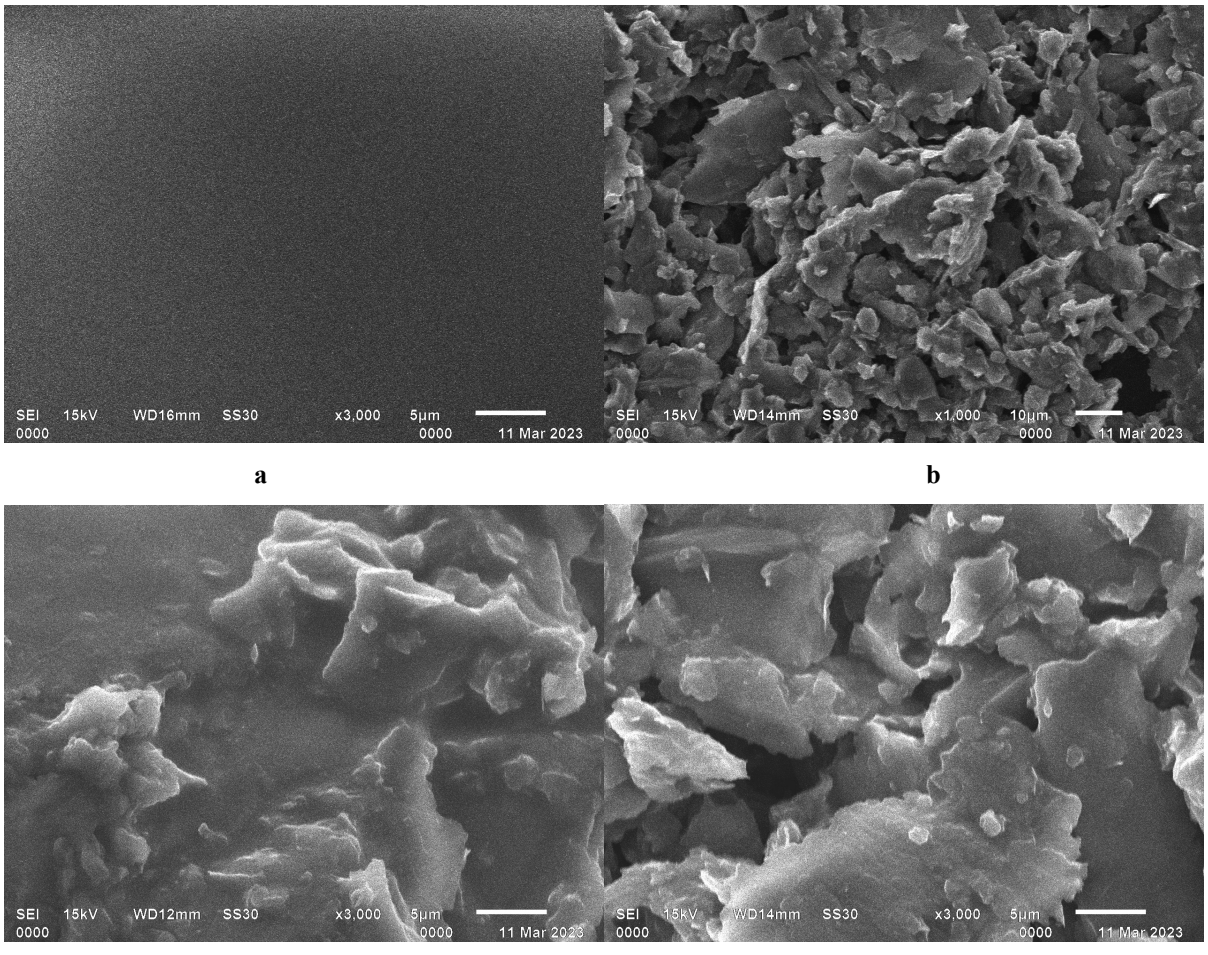

Fig. 1. SEM of WE-0 (a) and WE-IV (b) at 1KX, 10 µm, WE-I(c) and WE-IV(d) at 3KX, 5µm

In the present investigation the exceptionally enhanced σDC (859.80 µS/cm) of WE-IV at 100 V was supported by SEM which indicates the prominent dispersion of graphene layers (bright phase) into epoxy matrix (dark phase) (Figure 1c).

Figure 3. demonstrates the linear I-V characteristics of WEs at 25 ± 1°C. The ohmic behavior of WEs appeared in the range of 0.10 to 2.08 µA with corresponding voltage ranging from 20 to 55 V [36]. Table 1 shows the increase in σDC of WEs with varying voltage (1V–100V) and temperature ranging from 293 to 393 K. Figure 4 illustrates a decline in σDC of WE-IV with temperature (K) ranging from 333 to 393 at 100 V. This consistent trend attributes to the enhancement in the collaborative motion of the macromolecular segments of epoxy, triggered with temperature elevation. This movement leads to a greater dissipation of energy, thereby contributing to the observed decrease in σDC [37]. Using the theoretical Arrhenius model, the calculated activation energies from plots of log (σDC) against 1000/T at 100 V revealed Ea (J/mol) for WEs in the sequence of WE-0 (4.19), WE-I (2.10), WE-II (3.97), WE-III (4.76) (Figure 5).

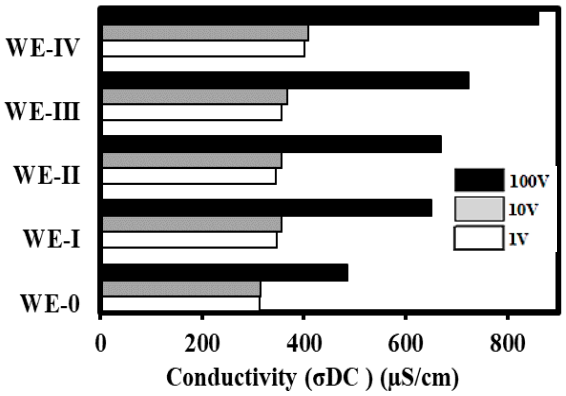

Fig. 2. Effect of voltage on σDC (µS/cm) of WEs

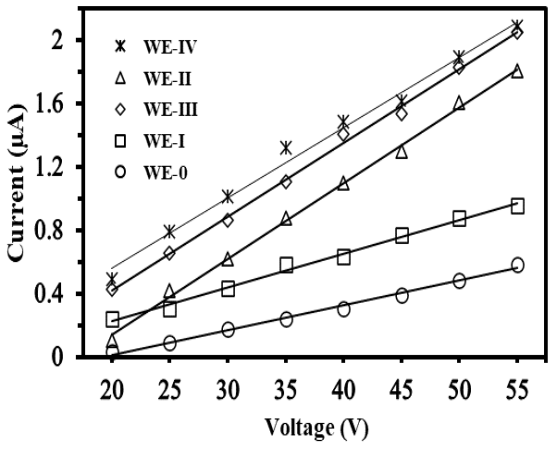

Fig. 3. Ohmic behavior of WEs

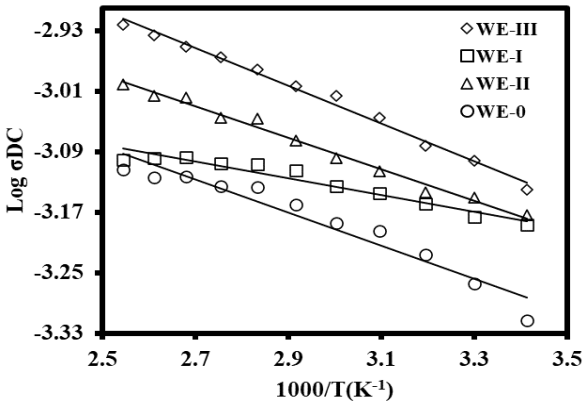

Fig. 4. Arrhenius plots of the DC conductivity for WEs

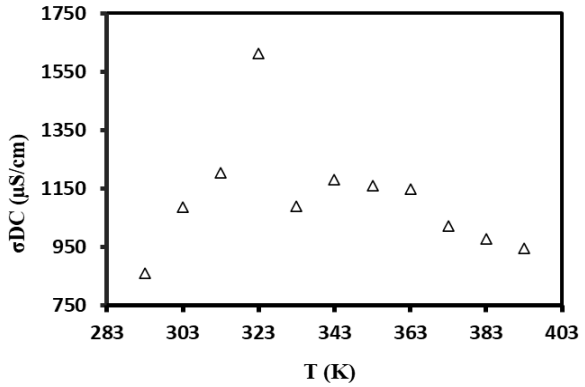

Fig. 5. Effect of temperature on σDC of WE-IV at 100 V

Effect of humidity

WEs were developed at selected wt% of GR and investigated for the electrical behavior after 8 h of exposure at 40% RH%. In general, the σDC (µS/cm) of WEs was dependent on their composition. Figure 6 demonstrates the effect of wt% of GR and voltage (V) on σDC of WEs. The σDC of WE-I was increased by 10.30% at 1 V and by 7.55% at 100 V. WE-II has shown an increase in σDC by 5.23 % at 1 V. However, at 100 V, WE-II has shown an increase of σDC by 1.44 % .The rest of the WEs has shown a significant decrease in their σDC (µS/cm) ranging from 859.39 to 822.2. Duration of humidity on WEs based on GR oxide/epoxy revealed an increase in their σDC from 10^{-6} to 10^{-2} S/cm when RH was increased from 30% to 100% [5]. Epoxy resins cured with amines are associated with inherrent hygroscopic nature due to the formation of hydroxyl group in their macromolecular segment [8, 15]. A study on carbon/epoxy composites has reported that the presence of carbonaceous fillers reduced the moisture-absorbing capacity of the composite by 3% [38]. For such reasons, WE-I, WE-II developed at higher proportion of epoxy absorbed the moisture to a great extent over those prepared at low proportion of epoxy (WE-III, WE-IV).

A detailed insight into the effect of humidity on σDC of Wes and their electrical behavior was obtained at competitive RH% selected at 36 and 40 (Figure 7). The increase in RH from 36 to 40, has raised the σDC of WE-I from 650 to 700 at 100 V. The calculations revealed that the increase in RH by 4% imparts 7.69% increase in σDC of WE-I at 100 V. However, subsequent Wes were found resistant towards humidity and have not contributed to further increase in their σDC under the differential exposure of RH by 4% at 100 V. The present investigation is in agreement with the literary report that reveals insulating properties of graphene oxide thin films at low RH. Presence of epoxy contributes to the ion conducting mechanism within the polymer matrix that causes an increase in σDC of WEs [39]. However, with increase in % GR, the relative proportion of epoxy decreased, that delivers the WEs, wherein the σDC is insignificantly increased, thus leaving WEs with intact electrical behavior.

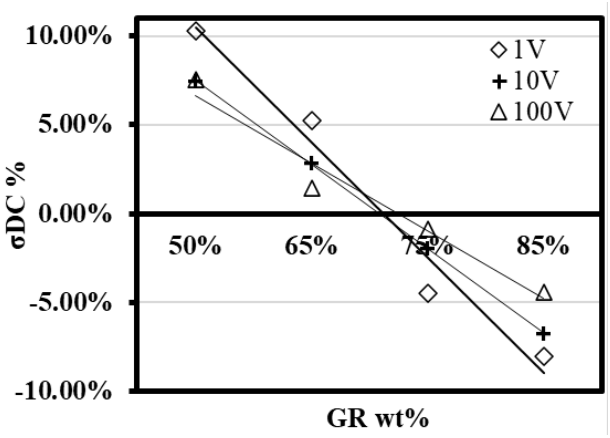

Fig. 6. Effect of composition and voltage on σDC of WEs at RH (40%)

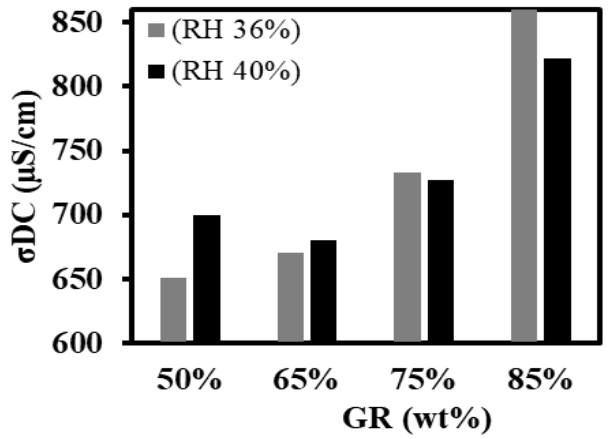

Fig. 7. Effect of composition and RH % on σDC of WEs.

Table 1. Effect of temperature on the conductivity of WEs at 100V

T(K)	WE-0	WE-I	WE-II	WE-III	WE-1V
393	486.35	650.95	670.24	743.54	946.71
383	543.97	667.41	707.84	791.04	977.17
373	594.69	694.72	717.84	826.94	1023.29
363	639.38	716.35	765.46	901.34	1024.20
353	654.49	733.11	797.00	963.84	1082.01
343	691.67	768.37	842.29	992.35	1092.13
333	729.38	783.39	899.00	1043.77	1389.70
323	732.77	784.14	902.77	1084.25	1612.37
313	754.89	800.25	958.71	1119.85	1319.50
303	751.18	796.64	963.08	1160.35	1096.13
293	771.11	792.29	998.98	1197.09	859.88

CONCLUSIONS

Working electrodes (WEs) based on epoxy supplemented with graphite (GR) (wt% 50 to 85) were developed *via* curing process on a stainless-steel current collector. The developed WEs revealed saturation at 85 wt% GR which showed clear phase separation and dense clusters of graphene layers within the epoxy matrix. With GR wt% the σDC (µS/cm) of WEs was found to increase by 859.80 for WE-IV at 100V, 36% RH and 25 ± 1°C. The study demonstrated an 11-fold increase in σDC of WE-IV over WE-0 at variable voltage ranging from 1 V to 100 V. The present investigation suggests that dispersion of carbonaceous fillers plays a constructive role towards enhancing the electrical behaviour of epoxy composites. The study also demonstrated that with the rise in temperature from 293 to 393 K and varying voltage (1 V–100 V) the WEs exhibited an increase in σDC with temperature. A detailed investigation on the effect of humidity on σDC of WEs revealed that σDC is greatly influenced by changes in relative humidity. WEs under differential exposure of RH by 4% at 100V showed an increase of 7.69 % in σDC of WE-I, however, other electrodes were insignificantly affected. The WE-I at 40% RH showed an increase in σDC by 10.30 % at 1 V and 7.55 % at 100 V. The present study demonstrates that the presence of relatively higher wt% of epoxy in WE-I, II, has significantly contributed to increased σDC owing to its hygroscopic nature and hydroxyl groups.

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