

## Electrical characterization of polyindole/haemoglobin composites

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The present research investigates the electrochemical characteristics of Polyindole (PIN) and Hemoglobin (Hb) composites, namely PIN/Hb, as conductive polymers comprising benzene and pyrrole rings as structural units. Working Electrodes (WEs) coated with PIN/Hb were fabricated, varying Hb concentrations and denoted as C-I, C-II, and C-III, respectively. All WEs exhibited a linear I-V relationship. Electrical conductivities of the WEs were measured at room temperature (RT) by varying voltages at 1 V, 10 V, and 100 V. The results showed that the direct current conductivity ( $\sigma_{DC}$ ) of the composites was higher than that of pure PIN, with C-III exhibiting the highest conductivity of  $0.1 \times 10^{-2} \text{ S cm}^{-1}$  at 100 V. Furthermore, the conductivities of the developed WEs were analyzed at variable temperatures ranging from 25°C to 125°C. It was observed that for all WEs, the conductivity initially increased with temperature, reaching a peak value at 75°C, after which it gradually decreased. C-III coated WE achieved the highest conductivity value of  $0.16 \times 10^{-2} \text{ S cm}^{-1}$  at 100 V. Initially, the conductivity of the baked WEs increased with baking time and temperature up to 3 hours at 50°C, followed by a gradual decrease in conductivity until 6 hours, after which it stabilized. For C-III coated WEs, the maximum conductivity of  $0.51 \times 10^{-2} \text{ S cm}^{-1}$  was achieved at 50°C after 3 hours of baking, showing similar trends at 100°C baking temperature.

**Keywords:** Working electrodes, Polyindole, Haemoglobin, DC Conductivity

### INTRODUCTION

Massive amount of fossil fuels was used to power the economy at the start of industrial revolution, which contributed to the overall development of society and therefore the energy crisis and environmental pollution are two major concerns in today's world, not only because the main source of energy i.e., fossil fuels are running out, but also because fossil fuels contaminate the environment by releasing CO<sub>2</sub> and other toxic gases. As a result, there is a high expectation that renewable energy would eventually replace traditional fuels as the dominant source of energy in our daily life. However, some renewable energies, such as solar and wind energy, are inherently unstable and intermittent, leading to necessitating the use of energy storage in systems with long-term energy output. Various batteries with high energy density such as Pb/PbO<sub>2</sub> and lithium ion batteries, are commonly used in electric energy storage systems. Most batteries, on the other hand, have a slow power delivery or uptake that can't keep up with faster and higher-power energy demands [1]. Researchers have been challenged to develop green and sustainable energy storage technologies due to rise in energy consumption, fossil fuel depletion, and global

warming. Because of its highpower density, extended cycle life, fast charge-discharge process and environmental friendliness, the supercapacitor is thought to be one of the most promising candidates among other energy storage devices [2]. Since the discovery of highly conducting polyacetylene (PAC) in 1977, CPs have been the dominant materials in Polymer Science. Hideki Shirakawa, Alan J. Heeger, and Alan G. MacDiarmid were the first to discover oxidation of acetylene by iodine, which produced PAC with increase in conductivity [3]. Conductivity of iodine-doped PAC can match that of silver, which is one of the easily accessible electrical conductors. They were awarded with the Nobel Prize in Chemistry in 2000 for their groundbreaking discovery, which opened up new avenues for the study of electric organic polymers.

Conducting polymers (CPs) are polymers having conjugated chain structures. They have unique bonding patterns along the polymer backbones, consisting of alternating double and single bonds, which gives them semiconducting characteristics [4]. A number of factors influence polymer conductivity, including conjugation length, total chain length, and charge transfer to adjacent molecules [5]. These neutral conjugated polymers can be transformed into semi-conductive or

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conductive states *via* chemical or electrochemical redox processes. CPs are routinely doped with other functional materials to generate composites in order to extend the functionalities or increase the performances of these polymers [6]. CP composites with high stabilities and conductivities can be used as a key component in transistors [7, 8], light emitting diodes [9, 10], electrochromic devices [11, 12], electrochemical capacitors [13, 14], actuators [15, 16], sensors [17, 18], and photovoltaic cells [19, 20].

PIN is a well-known conductive polymer comprising benzene and pyrrole rings as structural units. It is an electroactive polymer produced via electrochemical oxidation of indole or chemical oxidation with  $\text{FeCl}_3$  or  $\text{CuCl}_2$ . Due to its simple polymerization, high redox activity, thermal stability, tuneable conductivity and environmental stability, PIN has been widely considered as an extrapolative material among many CPs [21]. Recently, PIN have been doped with NiO [22], ZnO [23], CuO [24],  $\text{Co}_3\text{O}_4$  [25] and  $\text{Fe}_2\text{O}_3$  [26]. Hb is a redox respiratory protein found in red blood cells. It is made up of four polypeptide chains, each with one iron haem group. Because of its commercial accessibility, high stability, affordability and high capability rate, Hb can be considered to as an ideal model for good electrochemical performance in supercapacitor applications [27]. Present investigation provides a pioneer attempt towards the development of working electrodes (WEs) of PIN/Hb composites and the effect of temperature on their conductivities.

## MATERIALS AND METHODS

### Materials

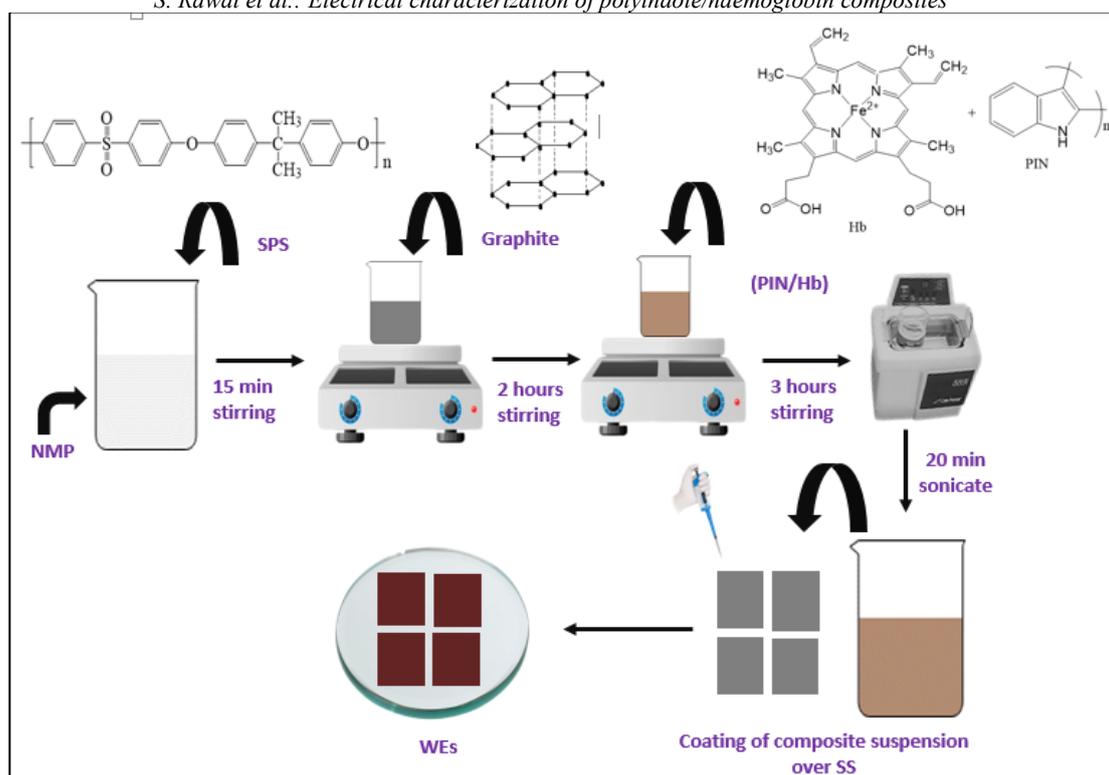
Pre-synthesized PIN and its composites with Hb were obtained from Department of Chemistry of College of Basic Sciences and Humanities, G.B.P.U.A.&T, Pantnagar, India [28]. PIN and its composites with 100 mg, 200 mg and 300 mg concentration of Hb were represented as C-I, C-II and C-III respectively. Polyvinyl butyral (PVB, Himedia, Delhi, India) and Tetrahydrofuran (THF,  $\geq 99\%$ , Merck, Mumbai, India) were purchased from respective firms. Graphite (Gr, 98.0%, 500  $\mu\text{m}$ ) was purchased from Loba-Chemi, Mumbai, India while N-methyl-2-pyrrolidone (NMP,  $\geq 99\%$ ) was purchased from Sigma Aldrich, Bangalore, India. Acetone ( $>98\%$ ) was procured from Sd. Fine, Chandigarh, India. Sulphonated polysulphone (SPS) used was pre-synthesized in lab [28]. Hb was purchased from (Otto Kemi, India). Distilled water was obtained from Merck Millipore water purification system. All other chemicals and solvents were of AR grade and were used without further purification. SS plates of 1  $\text{cm}^2$  area were fabricated by cutting and used as current collector for the development of WEs.

### Optimization of coating materials and fabrication of WEs

For the development of stable working electrodes of uniform surface morphology several binders, fillers were optimized with composites in different solvents.

**Table 1.** Surface morphologies of the developed WEs

S. No	Composite	Binder	Filler	Solvent	Surface Morphology on SS
1.	PIN (35mg)	SPS (15mg)	Gr (10mg)	NMP (1.5mL)	Uniform and even surface
2.	C-I (35mg)	PVB (15mg)	Gr (15mg)	THF (1.5mL)	Flaky and unable to adhere
3.	C-I (35mg)	SPS (15mg)	Gr (10mg)	NMP (1.5mL)	Uniform and even surface
4.	C-II (35mg)	SPS (15mg)	Gr (10mg)	NMP (1.5mL)	Uniform and even surface
5.	C-III (35mg)	SPS (15mg)	Gr (10mg)	NMP (1.5mL)	Uniform and even surface
6.	C-III (35mg)	PVB (7.5mg)	Gr (5mg)	THF (1.5mL)	Uneven surface Coating material delaminates and unable to adhere
7.	C-III (65mg)	SPS (70mg)	Gr (10mg)	NMP (1.5mL)	



**Fig. 1.** Schematic representation for fabrication of WEs

#### *Fabrication of WEs using PVB as binder and THF as solvent*

SS (1 cm<sup>2</sup>) was finished with emery paper and then pre-treated with different solvents (distilled water and acetone, respectively) in order to get smooth and shiny surface. PVB was weighed and dissolved in 1.5 mL of THF and then stirred for 15 min at Room temperature (RT). To this mixture, Gr was added and continued to stir for 2 h until the Gr get dispersed to obtained homogenous suspension. 35 mg of electroactive material (PIN/Hb) was added to the above suspension and stirred for 3 h at RT. Obtained suspension was then ultrasonicated for 20 min in ultrasonicator, then 50  $\mu$ L of prepared composite suspension was applied over SS using a micropipette and left to dry at RT for 24 h. Similar procedure was used for the development of WEs of C-III (Fig. 1).

#### *Fabrication of WEs*

Surface of SS was cleaned similarly as discussed as above. SPS was added to 1.5 mL NMP and stirred on magnetic stirrer for 15 min. To this 15 mg Gr was added and again stirred for 2 hr, till the Gr dispersed in the solution. PIN was added to the solution and stirred for another 3 hr and then ultrasonicated for 20 min. The developed suspension (50  $\mu$ L) was applied over SS and left to dry at RT for 1 week. Similar procedure was used for the development of WEs for all composites C-I, C-II and C-III. WEs were

fabricated at different concentrations and their conductivity was measured by varying conditions.

#### *Instrumentation and electrical characterization of WEs*

DC conductivity ( $\sigma_{DC}$ , S cm<sup>-1</sup>) data and I-V graphs were recorded over Keithley four-probe DC conductivity meter having current source (6221A) and voltage source (2182 V). The conductivities of PIN and its composites C-I, C-II and C-III were measured at variable temperature ranging from 25-125°C (298-398 K). For this purpose, a temperature regulated oven ( $\pm 1^\circ$ C) probe is enclosed in DC conductivity meter of Keithley four-probe nanovoltmeter. The effect of baking temperature on  $\sigma_{DC}$  of WEs was investigated with variation in time. Developed electrodes of PIN and its respective composites were baked at temperature ranging from 50-100°C in oven from 3-9 hr and their conductivity was measured on Keithley four-probe DC conductivity meter.

## RESULTS AND DISCUSSION

### *Fabrication and optimization of WEs*

The WEs of PIN and its Hb composites C-I, C-II and C-III were prepared using different combination and amounts of filler, binder and solvent. It was observed that the WEs that were obtained using PVB as binder and Gr as filler in THF solvent were unstable and showed delamination of coating material after sometime over SS. This may be due to

formation of non-homogeneous mixture of composites in THF and its poor binding over SS. WEs of PIN, C-I, C-II and C-III that were prepared using SPS as binder, Gr as filler and NMP as solvent were found to stable due to formation of homogeneous mixture, strong binding and even coating of suspension over SS [28]. Based on surface morphology and stability of coating over SS, SPS binder electrodes were used for further studies.

*Electrical characterization of WEs*

I-V data of fabricated WEs were recorded over Keithley four-probe DC conductivity meter having current source (6221 A) and voltage source (2182 V) in the voltage range of 5–25 V at RT. Electrical characteristics examinations reflect that

conductivity of developed composites (C-I, C-II, C-III) was higher over PIN and found to be maximum for C-III [29]. Fig. 2 reflects I-V graphs of PIN, C-I, C-II and C-III that show a linear variation of I-V at RT and implies ohmic conductive behavior of Hb in PIN [30].

The electrical conductivities of WEs were measured over temperature range of 25-125°C (298-398 K). It was found that all composites showed best conductivities at 100 V, therefore it was selected for further studies to check conductivities at variable temperatures (Fig. 3). At 100 V,  $\sigma_{DC}$  was measured at temperature of 25, 50, 75, 100 and 125°C in a temperature regulated oven ( $\pm 1^\circ\text{C}$ ) probe enclosed in DC conductivity meter (Fig. 4).

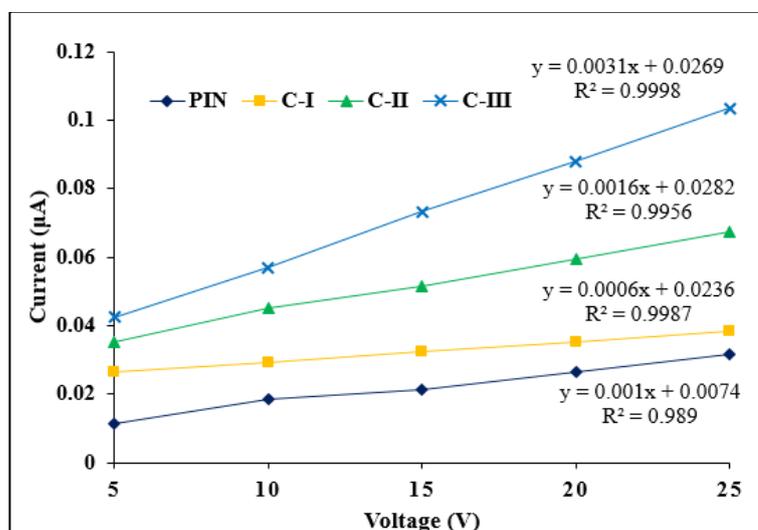


Fig. 2. I-V Characteristics of WEs at RT

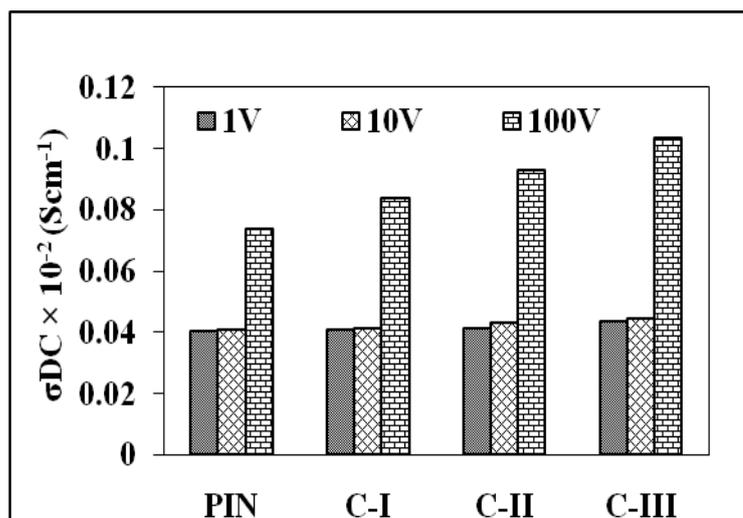
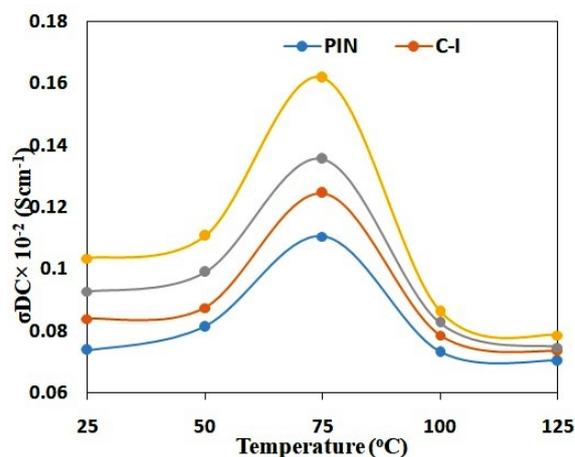


Fig. 3. Electrical conductivity of WEs at variable temperature

It was observed that the maximum conductivity was obtained at 75°C for all WEs. The conductivity of WEs were found to gradually increase till 75°C and then starts decreasing till 100°C, after this it become almost constant. The conductivity of composites was found to higher than that of PIN and maximum conductivity ( $0.16 \times 10^{-2} \text{ S cm}^{-1}$ ) was obtained for C-III at 75°C. Increase in the value of  $\sigma_{DC}$  with temperature indicate the semiconducting behaviour of PIN/Hb composites. The increased up to 75°C may be due to increase in conductivity with temperature as a result of polymer chain hopping, inter-chain ion exchange, and segmental movement of polymerized units. Raising temperature to a certain points aids electron mobility and also helps in overcoming the energy potential barrier. Increasing temperature generates alternate conducting paths for charge conduction, revealing PIN to be a better CP at elevated temperatures. However, above this temperature, the conductivity is inversely affected due to dopant loss and other factors [25]. After 75°C the conductivity starts decreasing due to morphological changes of coating material over the surface of SS. As the coating cannot withstand high temperature and it starts delaminating and the surface becomes uneven.

#### *Electrical conductivity of baked WEs with time*

To check the durability of developed WEs at higher temperature over time their baking characteristics were examined in a temperature regulated Oven. WEs of PIN and its composites were baked at temperature range of 50-100°C in oven and their conductivities were measured over the time duration of 3-9 h (3, 6 and 9 h). The conductivity of baked WEs were measured over voltage range of 1-100V and it was observed that there was slight change in conductivity at 1 V and 10 V with maximum values at 100 V (Figs. 5 & 7).



**Fig. 4.** Electrical conductivity of WEs at variable temperature over 100 V

At 50°C, it was observed that the baked electrodes showed a high increase in their conductivities till 3 h and then decreased up to 6 h and on further baking, conductivity remained constant (Fig. 6). This may be due to interchain hopping within the composites. When the temperature rises, the total charge migration is cut-off, causing a mechanical blockage in the flow of charge across the hole in PNCs [31]. Similar results were observed at 100°C but the conductivities of at this temperature was lower than that of 50°C (Fig. 8).

From the data it can be observed that composites have higher conductivity than PIN and maximum conductivity of  $0.51 \times 10^{-2} \text{ S cm}^{-1}$  was observed for C-III at 50°C for 3 h. At 100°C the conductivity of C-III was found to be  $0.25 \times 10^{-2} \text{ S cm}^{-1}$ . Highly doped composite C-III, exhibit higher conductivity over PIN, C-I, and C-II at baked conditions. Baking studies suggested that initially baking promote conductivity but after 3 h of baking the surface morphology of WEs changed and the coating layer starts to delaminate over SS.

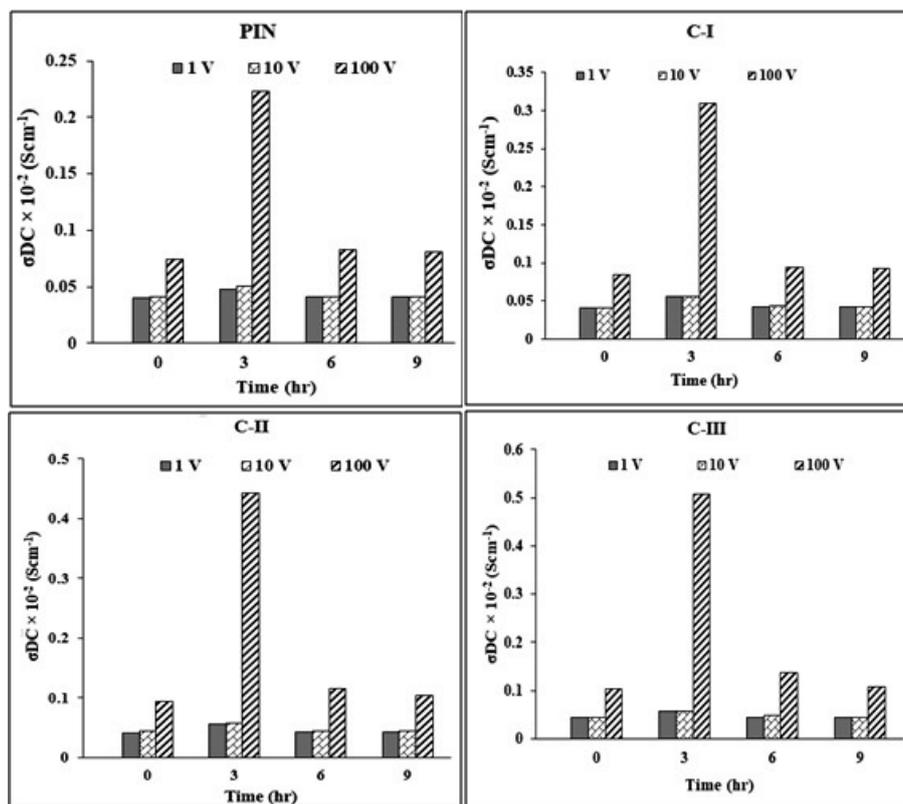


Fig. 5. Conductivity of different baked composites based WEs at 50°C at all voltages of 1, 10 and 100 V with time.

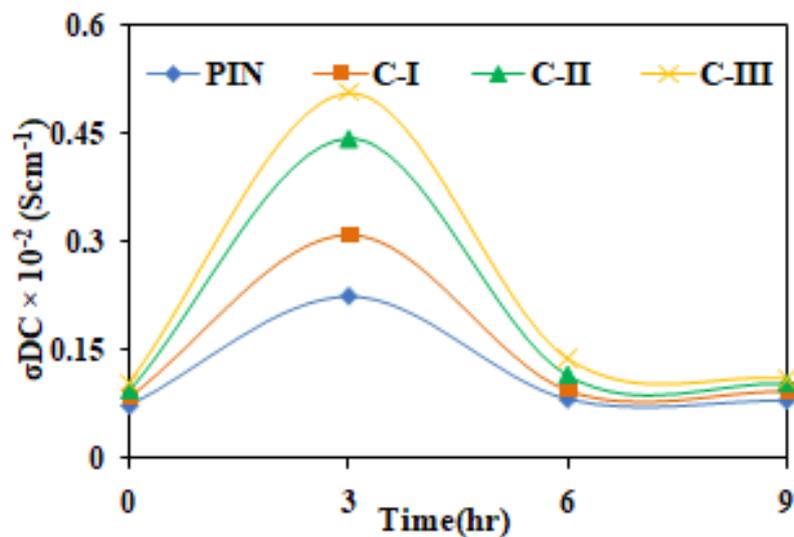


Fig. 6. Conductivity of baked WEs at 50°C over 100V with time

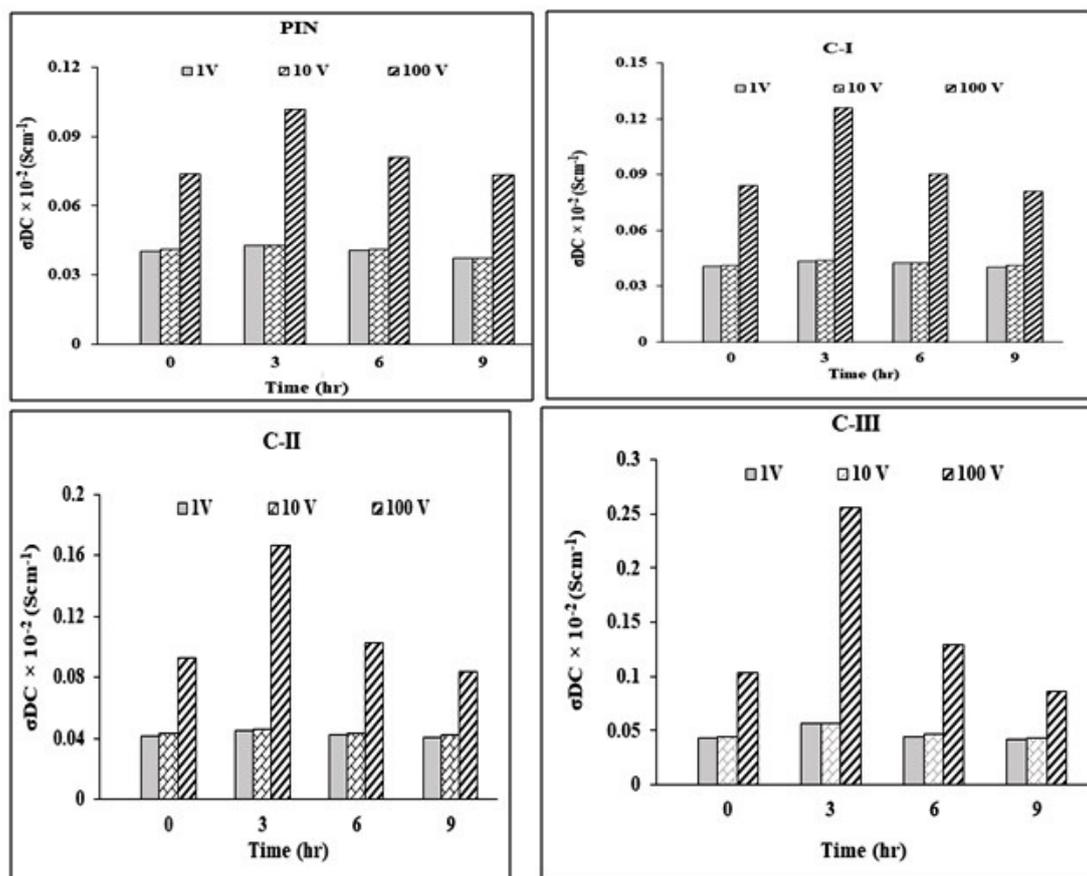


Fig. 7. Conductivity of different baked composites based WEs at 100°C at all voltages of 1, 10 and 100 V with time

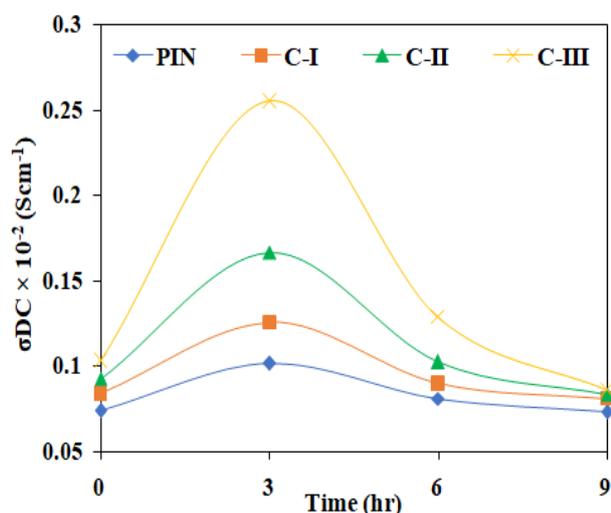


Fig. 8. Conductivity of baked WEs at 100°C over 100V with time

### CONCLUSIONS

In this investigation, working electrodes (WEs) based on Polyindole (PIN) and its Hemoglobin (Hb) composites were successfully fabricated and their electrical conductivities were thoroughly examined under different thermal conditions. The fabrication process involved coating PIN and its composites (C-I, C-II, and C-III) with an optimized combination of filler Gr, binder PVB or SPS, and solvents THF or

NMP. Through experimentation, it was found that filler Gr, binder SPS, and solvent NMP yielded a compatible and uniform coating over stainless steel (SS), resulting in stable and durable WEs. Electrical characterization of the WEs, including PIN, C-I, C-II, and C-III, demonstrated a linear I-V relationship, indicating Ohmic behavior in the developed WEs. Moreover, the electrical conductivities of the WEs were measured at room temperature (RT) under various voltages (1 V, 10 V, and 100 V). The results revealed that the composites exhibited higher direct current conductivity ( $\sigma_{DC}$ ) than pure PIN, with C-III displaying the maximum conductivity of  $0.1 \times 10^{-2} \text{ S cm}^{-1}$  at 100 V. The conductivity increased with the concentration of Hb and was most significant at 100 V, while remaining constant at 1 V and 10 V. Subsequently, the conductivities of the WEs were assessed at variable temperatures (25°C to 125°C) while maintaining a constant voltage of 100 V. It was observed that all WEs initially showed an increase in conductivity with rising temperature, peaking at 75°C, followed by gradual decreases. The highest conductivity value ( $0.16 \times 10^{-2} \text{ S cm}^{-1}$ ) was achieved for C-III at 100 V. Furthermore, the WEs were subjected to baking at temperatures ranging from 50°C to 100°C for up to 9 hours, and their conductivities were evaluated at 3, 6, and 9 hours.

The maximum conductivity of  $0.51 \times 10^{-2} \text{ S cm}^{-1}$  was attained for C-III coated WEs at  $50^\circ\text{C}$  after 3 hours of baking, with similar trends observed at  $100^\circ\text{C}$  baking temperature. However, at  $100^\circ\text{C}$  and a baking time of 3 hours, the conductivity ( $0.25 \times 10^{-2} \text{ S cm}^{-1}$ ) of C-III WEs was lower than that at  $50^\circ\text{C}$ . This investigation presents a simplified and optimized approach for fabricating stable WEs with enhanced electrical conductivities across variable temperature ranges, baking conditions, and time durations.

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