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POLYMER NANOCOMPOSITE ELECTRETS AS ELECTROCHEMICAL SENSORS FOR SOME P2Y12 PLATELET INHIBITOR CLASS OF DRUGS

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ABSTRACT

Pure and nano-ZnO doped PVDF-PMMA polymer blend-nanocomposites have been investigated for charge transfer effects in electrochemical sensors. Fourier transform infrared spectroscopy (FTIR) was used to characterize and elucidate the structure of the blended and doped polymers. Polymer microstructure and morphology were studied to establish the structure activity relations. Cyclic voltammetry (CV) furnishing information as a function of energy scan was the method of choice to test electronic properties of the modified polymers. Efficacy of CV results from its approach of rapidly observing the redox behavior of the analyte over a wide potential range. Electrode reactions of the intermediates and the products formed during the forward scan have been studied for Some P2Y12 Platelet Inhibitor Class of Drugs. Comparative electro activity of the PVDF-PMMA polymer blend-nanocomposite electrets electrode with the glassy carbon electrode was performed.

Keywords:
PVDF, PMMA, CV

INTRODUCTION

Sensitive and novel electrochemical sensor has been developed with pure and nanoZnO doped PVDF-PMMA polymer blend nanocomposite electrets.Decrease in charge transfer resistance in the sensor was studied through thermally stimulated discharge current studies [1,2]. The electrochemical behaviour of some P2Y12 Platelet inhibitor class of drugs was studied at pure and nanoZnO doped PVDF-PMMA polymer blend nanocomposite electret electrodes using cyclic voltammetry (CV). A well defined reduction peak was observed in Britton-Robinson (BR) buffer. Scan rate variations revealed the diffusion controlled nature of the electrode process.

Electrochemical sensor define their performance by chemical characteristics and physical construction of the material.[3–5] Carbon-based materials including, carbon paste, porous carbon, glassy carbon and carbon nanotubes are the matrices of choice for electrochemical sensors.[6–9] However, the time-honoured carbon-based electrodes[10–11] experience the snag of electrode fouling, limiting their long-term stability and requiring frequent polishing/disposal of the electrode. Smart materials for providing wider potential window, low background current, chemical inertness and desired mechanical stability have been reported.[12–19] Opportunistic efficacy of blends needs proper explanation of the charge injection and carrier migration process.

In this paper, charge transfer properties of the modified polymer are judged for electrochemical sensitivity of P2Y12 Platelet Inhibitor Class of Drugs using cyclic voltammetry. Investigations on charge transfer resistance were made.

The stout amorphous configuration of PVDF- PMMA composites, pure as well as doped with nano ZnO was modified by poling the composite polymer at elevated temperatures and steady functional voltage. The sample upon cooling to room temperature under constant applied voltage, gets its heterojunctions preset to furnish the desired electrets. In the nano blends, the mechanically robust polymer lattice substituted with ZnO nanoparticles improves electrical conductivity. Their biocompatibility provides resources suitable electrode material for various applications.

EXPERIMENTAL

Apparatus

Electrochemical measurements were carried out at Autolab potentiostat-galvanostat 302N (Netherlands) with software NOVA 1.8 (Fig.2). Electrodes were PVDF- PMMA blend electrets, bare as well as doped with nanoZnO as working electrodes, graphite rod as the auxiliary electrode and Ag/AgCl (1M KCl) as reference electrode. All pH measurements were made on a Decible DB-1011 digital pH meter fitted with a glass electrode and a saturated calomel electrode as reference. Pure nitrogen gas was purged into all solutions to eliminate dissolved oxygen, after which a blanket of pure nitrogen gas was maintained over the solutions throughout the CV experiments. Glassy carbon electrode was polished with fine grade emery paper followed by polishing

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alumina (0.5µm) and subsequently activated by triangular voltage sweeps from +1.0 to −1.0 V at the scan rate of 5 to 200 mV/sec. for 5 minutes. The activity of the electrode was checked for ferricyanide-ferrocyanide system in 0.1 M KCl. Coulometric measurements were performed in the potentiostatic mode with platinum foil of large surface area as the working electrode, Ag/AgCl as the reference electrode and platinum wire as the auxiliary electrode. From the decrease in current or increase in coulombs with time, the number of electrons transferred was calculated. Progress of electrolysis was monitored by recording cyclic voltammograms at different time intervals until the reduction peak completely disappeared. UV-Visible double beam spectrophotometer Systronic 2101 was used for spectral studies during electrolysis.

Reagents and chemicals

ZnO nanopowder (90−250 nm, 99.89% purity) was procured from Fischer Scientific (USA). All other chemicals were of analytical grade and used without further purification. Ticagrelor Tablets (Brillinta 90 mg) were procured from Astra Zeneca.

Analytical procedure

Standard solution of the Ticagrelor drug (1.3mg/mL) was prepared by dissolving the analyte sample in dimethylformamide and further dilutions were made with BR buffer to get final concentration in the working range (20–200 μg/mL). A series of Britton-Robinson (BR) buffer (2.2–11.8 pH) was prepared in ultra-pure water. For electrochemical measurements, a known volume of the analyte sample was added in voltammetric cell and total volume made up to 10 mL with 1 M KCl as supporting electrolyte. The solution was deoxygenated with pure nitrogen gas for 120 s. The voltammograms were recorded at room temperature by applying potential scan from -1600 to −1000 mV, frequency 50 Hz, pulse amplitude 50 mV/s and scan increment 10 mV/s.

Fabrication of ZnO - PVDF- PMMA blend electrodes

Glassy carbon electrode was polished with 0.3 μm alumina slurry and washed with deionised water. The cleaned electrode was gently blown under a nitrogen stream on the surface and dried at room temperature. Solution cast technique was employed to fabricate the blends of polymer with nanoZnO. Modified composites were caste on the glassy carbon electrode surface and the coated surface was cleaned after physical measurements followed by polishing with 0.3 μm alumina slurry and ultrasonic cleaning for 2 min. The electron transfer behaviour of the modified electrodes was investigated using thermally stimulated depolarization current studies. The poling field and temperature dependent TSDC thermograms for pure PVDF, PVK, blended PVDF-PVK and the blends doped with nano ZnO have been studied.

The lower charge transfer resistance of various PVDF-PMMA/nanoZnO electrets indicated that nanoZnO blends furnish higher electroactivity facilitating the electro-reduction of the analyte.

RESULTS AND DISCUSSION

Cyclic voltammetric study of Tikagrelor at PVDF-PMMA/nanoZnO electrets electrode and comparison with PVDF-PMMA blend electrode:

The electrochemical behaviour of Tikagrelor at PVDF-PMMA blend and PVDF-PMMA/nanoZnO electrets electrode exhibited a well defined reduction peak at the glassy carbon electrode (Fig. 3). The electroanalytical performance of PVDF-PMMA/nanoZnO electrets electrode was rewarding over that experimental at the bare PVDF-PMMA pure blend. The cyclic voltammograms of the analyte showed 63.8% enhancement in the reduction peak current at PVDF-PMMA/nanoZnO electrets electrode.(Fig. 2,curve c) as compared to a bare PVDF-PMMA blend electrode . (Fig. 2, curve b). At modified electrode, peak potential shifted towards negative side as the electron transfer kinetics facilitated at the PVDF-PMMA/nanoZnO electrets electrode, enhancing the sensitivity of voltammetric measurements.
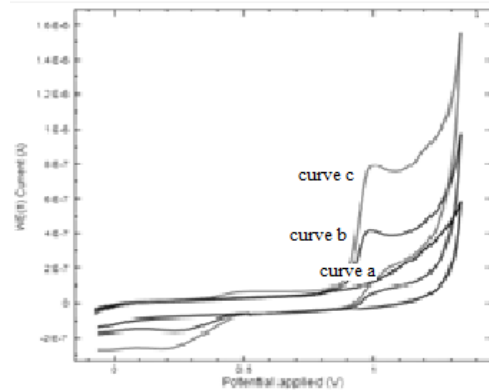
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Fig 1: Cyclic voltammograms of Ticagrelor analyte at pH 4.61, various scan rates 80 to160 ʋ/s at glassy carbon electrode

Effect of supporting electrolyte and pH

The most suitable supporting electrolyte and pH for best response of the analyte were carried out through preliminary investigations. Supporting electrolytes like KCl, phosphate buffer, acetate buffer, citrate buffer, and BR buffers were tested, BR buffer excelled with respect to signal enhancement and the symmetric peak shape. Effect of varying pH (2.2−11.8) of BR buffer was studied for the peak current of the analyte at various concentrations. Rise in pH decreasing the peak current indicates the involvement of protons in the electrode process. The current. potential curve is finally dislocated in highly alkaline medium due to lower number of available protons. With the rise in pH, the peak potential was also shifted towards negative side. This reveals that the pH of the supporting electrolyte exerted a significant influence on the electro reduction of the analyte.

Effect of scan rate

Voltammograms of Tikagrelor (100 µg/mL) were recorded at various scan rates in the range 10–240 mV/s. Ticagrelor at the *PVDF-PMMA/nanoZnO electrets electrode* exhibited a single, well defined reduction peak at 5.02 V (vs. Ag/AgCl). Since no peak was observed in reverse scan corresponding to the anodic reaction, it depicts the irreversible nature of the electrode process. The peak potential shifts towards right-hand with increase in the scan rate, again confirming the irreversible nature of the reduction process, which can be expressed by the equation,

$$EP = E^0 + RT(1-\alpha) \ nF\{\ln(ks/D^{1/2})-0.5\ln[(1-\alpha)nFv/RT] - 0.78\} \qquad (1)$$

Where, E^o is the standard electrode potential, D is the diffusion coefficient, v is the scan rate, F is faraday constant, R is gas constant and T is room temperature.

A linear plot of current (i_p) vs. square root of scan rate ($v^{1/2}$) is obtained when the process is diffusion controlled, whereas the adsorption controlled process results in a linear plot of i_p vs. v. In the present experiment a linear relationship between i_p and $v^{1/2}$ is obtained suggesting the diffusion of the analyte at the surface of PVDF-PMMA/nanoZnO electrets electrode, which can be expressed by the following equation,

$$i_p \ /\mu A = 0.5035 \ v^{1/2} \ (mV/s) - 1.3768, \ r^2 = 0.9935 \qquad (2)$$

Again a linear relationship was observed between $\log i_p$ and $\log v$ (Fig. 7C), corresponding to the equation,

$$\log i_p = 0.5067 \log v - 0.3730, \ r^2 = 0.9988 \qquad (3)$$

The slope of 0.5057 is close to the expected value of 0.5 for a purely diffusion controlled irreversible reaction.

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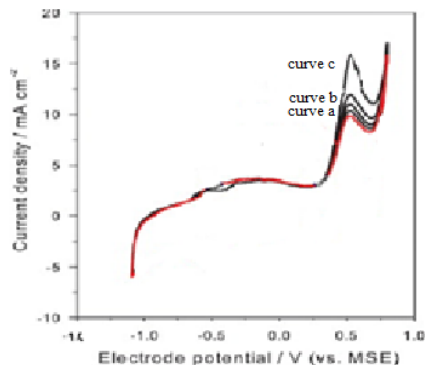

Fig2: Cyclic voltammograms of Ticagrelor analyte at pH 4.61, scan rate 160 υ/s at PVDF-PMMA/nanoZnO electret electrode (curve c), at bare PVDF-PMMA blend electret electrode (curve b) and blank (curve a).

CONCLUSION

An innovative and simple strategy for determination of Ticagrelor, a P2Y12 platelet inhibitor class of durgs at PVDF-PMMA/nanoZnO electret electrode is presented. Modification of the PVDF-PMMA blend with nanoZnO and subsequent poling significantly enhanced the activity of the quasielectrets electrode. Reduction of charge transfer resistance provided higher electrocatalytic behaviour to the sensor. Enhancement assessment was performed using CV technique. PVDF-PMMA/nanoZnO electrets electrode showed 73.64% current enhancements when compared with the simple PVDF-PMMA blend quasielectrets electrode. Calibration plot reveals linearity within the range of 20−200 μg/mL with correlation coefficient of 0.9732. Lower limit of detection (10.26 μg/mL) proved the sensitivity of the proposed method. Voltammetric study of the analyte at different scan rates revealed the irreversible and diffusion controlled reaction process.

ACKNOWLEDGMENT

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