3.1. Reagents and chemicals used

Aniline, o-toluidine were obtained from M/S sigma Aldrich. Potassium perdisulphate, hydrochloric acid (Merck 98 %), TiO₂, Al₂O₃ (Sigma-Aldrich Co) and SiO₂ were received from M/S E.Merck, Germany and were used as received. Sodium hydrogen phosphate, citric acid, phosphorous acid and sodium hydroxide (Sigma-Aldrich Co) were used as such.

The supporting electrolyte solutions were also prepared by using ultrapure water. The buffer solutions prepared were used in the present study given in table 3.1.

<table>
<thead>
<tr>
<th>Table 3.1. Electrolytes and its pH</th>
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</thead>
<tbody>
<tr>
<td>Electrolyte</td>
</tr>
<tr>
<td>0.1 M H₂SO₄ (AR grade) solution</td>
</tr>
<tr>
<td>Buffer tablets (Merck)</td>
</tr>
<tr>
<td>0.1 M aqueous solution of KCl</td>
</tr>
<tr>
<td>0.1 M NaOH (AR grade) solution</td>
</tr>
</tbody>
</table>

The supporting electrolytes of other pHs (2.0, 3.0, 5.0, 6.0, 8.0, 10.0, 11.0 and 12.0) were prepared by Teorell and Stenhagen buffer mixture stock solution using sodium hydrogen phosphate, citric acid, phosphorous acid and sodium hydroxide. 20 mL of buffer mixture was taken and x mL of 0.1 M HCl was added and made up to 100 mL using carbon dioxide free water to get solutions of different pHs. The pH of the solutions was checked using Hanna pH meter.
3.2. Synthesis of polymers and polymer-ceramic nanocomposites

3.2.1. Synthesis of Polyaniline (PAni) and Poly (o-toluidine) (PoT)

About 9 mL of aniline (0.1 M), 13 g of potassium perdisuphate (0.25 M) and 1 M hydrochloric acid (6 mL) were made up to 200 mL using conductivity water. The solution was kept stirred for 3 hours with the help of a magnetic stirrer at room temperature then it was kept overnight in the refrigerator, after which the dark green powder was obtained and was filtered and dried. The solubility of PAni was tested and was found to be soluble in dimethyl sulfoxide and dimethyl formamide.

The synthesis of poly (o-toluidine) was carried out in the same way and o-toluidine was used as monomer instead of aniline.

3.2.2. Synthesis of PAni-Ceramic (SiO$_2$, Al$_2$O$_3$ and TiO$_2$) nanocomposites

The PAni-SiO$_2$ nanocomposite was synthesized by bulk polymerization of 0.1 M aniline monomer (9 mL) using 0.25 M potassium perdisulfate as an oxidant in the presence of SiO$_2$ and 6 mL of 1 M hydrochloric acid were made up to 200 mL. The solution was stirred for 3 hours to obtain a uniform suspension containing SiO$_2$ particles. The temperature of the nanocomposite was maintained at $\approx 0^\circ$C for 24 hours to complete the reaction. Then the obtained precipitate was filtered and washed successively by distilled water until the washed solution turned colourless. The synthesised PAniSNCs were dried at room temperature. Different concentrations of SiO$_2$ (0.25, 0.5, 0.75, 1.0, 1.25 and 1.5 g) were mixed with 0.1 M aniline monomer to obtain PAni-SiO$_2$ nanocomposites (PAniSNCs) of varied compositions of SiO$_2$ which are designated as PAniSNC1-PAniSNC6.
Similarly PANi-Al\textsubscript{2}O\textsubscript{3} and PANi-TiO\textsubscript{2} nanocomposite were synthesized and in the same way Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} ceramics were used instead of SiO\textsubscript{2}.

### 3.2.3. Synthesis of PoT-Ceramic (SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}) nanocomposites

The PoT-SiO\textsubscript{2} nanocomposite was synthesized by bulk polymerization of 0.1 M o-toluidine monomer (9 mL) using 0.25 M potassium perdisulfate as an oxidant in the presence of SiO\textsubscript{2} and 6 mL of 1 M hydrochloric acid were made up to 200 mL using conductivity water at room temperature. The solution was mechanically stirred for 3 hours to obtain a uniform suspension containing SiO\textsubscript{2} particles. The temperature of the nanocomposite was maintained at \(\approx 0^\circ\text{C}\) for 24 hours to complete the reaction. Then the obtained precipitate was filtered and washed successively by distilled water until the washed solution turned colourless. The synthesised PoTSNCs were dried at room temperature. Different concentrations of SiO\textsubscript{2} (0.25, 0.5, 0.75, 1.0, 1.25 and 1.5 g) were mixed with 0.1 M o-toluidine monomer to obtain PoT-SiO\textsubscript{2} nanocomposites (PoTSNCs) of varied compositions of SiO\textsubscript{2} which are designated as PoTSNC1-PoTSNC6.

Similarly PoT-Al\textsubscript{2}O\textsubscript{3} and PoT-TiO\textsubscript{2} nanocomposite were synthesized and in the same way Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} ceramics were used instead of SiO\textsubscript{2}.

### 3.3. Instrumentation

The polymer and polymer-ceramic nanocomposites are characterized by various instrumental techniques. For recording the UV-Vis absorption spectra, a computer controlled Jasco V-530 spectrophotometer was used. The FTIR spectra were recorded by SHIMADZU instrument in the frequency range of 400-4000 cm\(^{-1}\). The X-ray diffraction (XRD) patterns were recorded for the powdered materials using
a BRUKER AXS (D8 ADVANCE) X-ray diffractometer in the scanning range of 20-80° (2θ) using CuKα radiation having a wavelength of 1.5405 Å. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) experiments were performed using Perkin-Elmer instruments. The morphology of the polymer and polymer-ceramic nanocomposites has been studied by Scanning Electron Microscopy (SEM) method. Scanning electron micrographs were obtained using Model: JEOL JSM 6360. TEM images were taken using PHILIPS model CM 200 in operating voltages 20-200 kV and with a resolution of 2.4 Å.

3.4. Electrochemical workstation

Electrochemical workstation CHI 650C (CH Instruments, USA) was employed for the various electrochemical studies performed. This instrument uses the latest analog and microcomputer design to provide high performance, better precision and greater versatility in electrochemical measurements. This instrument was employed for performing voltammetric studies, chronoamperometry, chronocoulometry, linear sweep voltammetry and impedance studies.

3.4.1. Cell setup

The cell used for experiment is made of glass, having a capacity of 15 mL, with the teflon lid with four separate holes for the gas purging and three electrodes viz. working electrode, counter electrode and reference electrode. The cell setup is kept in a Faraday cage. The cell top also has the purging and blanketing facilities for nitrogen (N₂) and oxygen (O₂) gas with separate tubes to remove any other gas. Pt is used as counter electrode and silver-silver chloride electrode as reference electrode. N₂ and O₂ gases are used in these electrochemical studies. In these studies, the normal
condition (without saturated buffer with any other gases) is changed by passing $N_2$ or $O_2$ gas for three minutes continuously into the buffer solution through the top of the cell using a very small tube. During the process, the tube is removed from the solution and is maintained above the solution until the process is completed.

### 3.4.2. Glassy Carbon Electrode-Working electrode

In the case of Cyclic voltammetric studies the polymer and polymer-ceramic nanocomposites were coated on a glassy carbon electrode by pasting a pinch of the polymer and polymer-ceramic nanocomposites samples in dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO).

### 3.4.3. Reference and counter electrodes

Silver-Silver chloride was used as reference electrode in this investigation. A platinum wire was used as counter electrode. All electrochemical experiments were performed at $25.0 \pm 2^\circ$C.

### 3.5. Working electrode preparation

Polymer and Polymer-ceramic nanocomposites modified glassy carbon electrodes were employed in the present investigation. It was dissolved in dimethyl sulfoxide (DMSO) to form polymer and polymer-ceramic nanocomposite solutions. Polymer and polymer-ceramic nanocomposite films were produced by casting the solutions (1 drop) onto a clean and pre-treated $0.0314 \text{ cm}^2$ GCE and then allowing the solvent to evaporate. They were consequently rinsed with water and then transferred to an electrochemical cell for experimental purpose. A three electrode cell with a saturated calomel reference electrode (SCE), a platinum wire counter electrode, and polymer and polymer-ceramic nanocomposites modified glassy carbon working
electrode were employed. All electrochemical experiments were carried out at a thermostatic temperature of 25.0 ± 2°C.

Cyclic voltammetric studies of polymer and polymer-ceramic nanocomposites modified GCE were performed for different pH, different concentration and different atmospheric (N₂ and O₂ gases) conditions. The CVs were obtained in 1.0 M H₂SO₄ electrolyte by casting the nanocomposite on GC working electrode and scanned between -1.2 to 1.2 V at scan rates between 50 to 500 mV/s.

N₂ and O₂ gases were used in these electrochemical studies. In these studies, the normal condition (without saturated buffer) was changed by passing N₂ or O₂ gas three minutes continuously into the buffer solution through the top of the cell using a very small tube. During the process, the tube was removed from the solution and was maintained above the solution until the process got completed.

3.6. Experimental procedures

3.6.1. Cyclic Voltammetry

Cyclic voltammetry is the most widely used electrochemical technique acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, on kinetics of heterogeneous electron-transfer reaction, and on coupled chemical reaction or adsorption processes. In a typical cyclic voltammetry, a solution component is electrolysed (oxidized or reduced) by placing the solution in contact with an electrode surface, and then imposing sufficiently positive or negative potential on that surface using a triangle potential waveform to force electron transfer.
In simple cases, the electrode surface gets particular potential with respect to a reference electrode. The electrode potential is swept to a higher or lower value at a linear rate, and finally, the potential will sweep back to the original value at the same linear rate. The electrochemical reaction of interest takes place at the working electrode. Electrical current at the working electrode due to electron transfer is termed as faradaic current. An auxiliary or counter electrode is driven by a potentiostatic circuit to balance the faradaic process at the working electrode with an electron transfer of opposite direction. The process at auxiliary electrode is typically not of interest, and in most experiments the small currents observed mean that the electrolytic products at auxiliary electrode have no influence on the processes at the working electrode.

Depending on the information sought, single or multiple cycles can be applied. During potential sweep, the potentiostat measures the faradaic current at the working electrode resulting from the applied potential. The resulting plot of current versus potential is called cyclic voltammogram, which is complicated, time-dependent function of a large number of physical and chemical parameters.

Before performing each set of experiments, the electrochemical cell was scrupulously washed with double distilled water. The glassy carbon electrode was preconditioned and then coated with the synthesized polymer by dissolving it in dimethyl sulfoxide or dimethyl formamide and then dried for half an hour. The counter electrode platinum was cleaned with double distilled water. Reference electrode Ag/Ag$^+$ was also thoroughly washed with double distilled water. 10 mL of the study solution was placed in the electrochemical cell, it was then placed inside the Faraday cage and the three electrodes were inserted into the cell. Then cyclic
voltammogram were recorded at various sweep rates for different synthesized polymer and polymer-ceramic nanocomposites.

### 3.6.2. Chronoamperometry

Chronoamperometry was readily performed with CH Electrochemical Workstation Instruments model 650 electrochemical analyser. The electrochemical cell as well as the electrode system was the same as utilised in cyclic voltammetry studies. The chronoamperometric behaviour of the polymer and polymer-ceramic nanocomposites chosen were studied at pH 1.0 under different atmospheric conditions.

The potential of the working electrode is stepped and the resulting current from faradaic processes occurring at the electrode (caused by the potential step) is monitored as a function of time. Chronoamperometry generates high charging currents, which decay exponentially with time as any RC circuit. The Faradaic current—which is due to electron transfer and is most often the current component of interest—decays as described in the Cottrell equation. Using the slope values of I vs t⁻¹/₂, the diffusion coefficient values of PANi modified GCE was determined using the Cottrell equation: \( I = nFD^{1/2}AC_p t^{-1/2} \) and \( \text{Slope} = nFD^{1/2}AC_p t^{-1/2} \). By substituting the known parameters in the above equation, the D value was arrived at by known electrons transferred or vice versa.

### 3.6.3. Chronocoulometry

Chronocoulometric experiments were carried out in a similar type of cell used for voltammetric studies. The chronocoulometric behaviour of the polymer and
polymer-ceramic nanocomposites chosen were studied at pH 1.0 under different atmospheric conditions.

The potential was stepped up from an initial potential to a final potential. A pulse width of the range 2 to 10 seconds was maintained. The initial potential was chosen, where no redox reaction occurred and the final potential was chosen where the reaction of interest was over. The cyclic voltammetric data obtained were used as the criterion to fix these potentials. Instead of measuring the current directly, it was integrated and the charge was measured.

3.6.4. Linear Sweep Voltammetry

Linear sweep voltammetry were carried out in a similar type of cell used for voltammetric studies. The chronocoulometric behaviour of the polymer and polymer-ceramic nanocomposites chosen were studied at pH 1.0 under different atmospheric conditions. It can identify unknown species and determine the concentration of solutions. $E^{1/2}$ can be used to identify the unknown species while the height of the limiting current can determine the concentration. The sensitivity of current changes vs. voltage can be increased by increasing the scan rate. Higher potentials per second result in more oxidation/reduction of a species at the surface of the working electrode.

3.6.5. Electrochemical Impedance Spectroscopy

The first step involves the measurement of open circuit potential (OCP). Electrochemical Impedance measurements were then carried out in the frequency range from 1 KHz to 0.01 Hz at the open circuit potential.

The charge transfer resistance was obtained from the diameter of the semi circles of the Nyquist plots.