2.1. Scope of the investigation

Nanocomposites constitute a class of hybrid materials composed of a polymer matrix and an inorganic component, which has at least one dimension in the nanometer (<100 nm). To improve and extend the functions of these inorganic nanomaterials, one or more components are often incorporated to form multifunctionalized nanocomposites for various applications in the fields of electronics, sensors, catalysis, energy, electromagnetic interference shielding, electrorheological fluids and biomedicine. Conducting polymer composites with nanostructures have attracted significant academic and technological attention because of their unique physical properties and potential applications in nanoelectronics, electromagnetic and biomedical devices. To obtain materials with synergetic advantage that is between PAni and inorganic nanoparticles, such as CeO$_2$, TiO$_2$ [204-207], BaTiO$_3$, MoO$_3$, SnO$_2$, Fe$_3$O$_4$ [208, 209] Co$_3$O$_4$, NiO, ZnO [210], PAni-CNT [211-213] are reported.

As well known, the oxygen reduction reaction (ORR) is the main current-producing cathodic process in fuel cells. The high cost of platinum, sensitivity towards admixtures of CO and sulfur-containing compounds, limited amount of resources determines the necessity of searching for alternative ORR electrocatalysts free of platinum or with its considerably decreased content [214]. A decrease in Pt content in the catalyst or catalytic layer was achieved by using Pt-based alloys Pt [215], particles of the core–shell type, where the base metal (core) is coated by a thin platinum layer [216] or nanostructured supports are used, particularly carbon nanotubes [217] in order to enhance the dispersion degree of platinum and provide effective transport in the catalytic layer. Despite the significant progress in
development of such electrocatalysts, the problem of their high cost remains very acute.

Several approaches are developed in the recent years for full substitution of platinum in ORR electrocatalysts [218]. In particular, one of these consists in using other noble metals and alloys on their basis instead of Pt (primarily, Pd [219] or Ru [220]); the other corresponds to application of alloys of transition metals, various chalcogenides, and also metal-N$_4$ macrocycles based on Fe, Co, Ni, or Cu (phthalocyanines, porphyrins, Schiff bases etc.) [214]. The main fault of electrocatalysts based on metal-N$_4$ macrocycles is their low stability in acidic media (or under the conditions of cathode components in an acidic medium under operation of fuel cells with polymer electrolyte) [221, 222].

Thermal treatment in the form of pyrolysis causes an increase in the stability of such electrocatalysts [223], however the catalytic activity in ORR of even the most effective pyrolyzed iron and cobalt metal porphyrins [223–225] is as yet considerably inferior to conventional platinum catalysts [214, 218]. Thus, search and development of new effective and readily available electrocatalysts of low production cost is due to the minimum content of noble metals or complete absence of it is related to wide commercialization of fuel cells.

New-generation functional materials undoubtedly include organic conducting polymers (CPs) and composite materials on their basis that are especially characterized by reversible redox activity and high conductivity, which causes particular interest towards electrochemical aspects of application of such materials for development of chemical power sources, energy transducing systems, supercapacitors, electrochemical sensors, electrocatalysts of different processes etc
Thus, CPs can be used for development of ORR electrocatalysts as a support matrix of catalytically active compounds, especially metal-phthalocyanine complexes [230-232] of cobalt [218, 233] or platinum [227, 228, 234, 235] and PANi-Molybdenum doped Ruthenium Selinide (MRS) composites shown to catalyse the ORR effectively from aqueous acidic solutions. In the presence of methanol the activity of PANi-MRS composites remains more stable than that of Pt, proving that MRS does not undergo severe poisoning [236].

In the latter case, such an approach allows decreasing the noble metal content in the catalyst; however, the issue of stability of such materials remains herewith unsolved [228, 234]. At the same time, it is known [228, 202] that such CPs as polyaniline (PAni) and polypyrrole (PPy) can directly feature electrocatalytic properties in ORR, which is attractive for development of ORR electrocatalysts on their basis. To enhance catalytic efficiency of CPs in ORR, it is suggested [237, 238] to use Keggin-type heteropoly acids (HPAs) forming molecular dispersion of catalytically active particles (the so called “Keggin units”) as specific polymer dopants in the CP matrix.

It was found earlier [239-241] that three-component nanocomposites consist of CPs (PAni or PPy), heteropolyacids (HPA) and V_2O_5-CP. HPA/V_2O_5 and also their bifunctional analogs additionally contain up to 5 wt % of nanosize platinum-CP-HPA/V_2O_5/Pt. Uniting properties in a single material the properties of both CP-HPA/V_2O_5 and CP/Pt composites are characterized by rather high electrocatalytic activity in ORR due to nanostructurering and interaction between the components. With account for this, it was of interest to elucidate the possibility of using other nanosize transition metal oxides for development of hybrid CP-based nanocomposites capable
of manifesting electrocatalytic properties in ORR. Titanium dioxide featuring catalytic activity in a number of chemical, electrochemical, and photochemical redox processes attracted our attention as the oxide component of CP-based nanocomposites. In particular, as shown in [242-244], various TiO$_2$ forms can demonstrate electrocatalytic properties in ORR in acidic electrolytes and the prevailing process herewith, according to [243], is the two-electron oxygen reduction with formation of hydrogen peroxide. The CP dopant was chosen to be 12-phosphomolybdic acid, H$_3$PMo$_{12}$O$_{40}$ (PMA) that features the highest electrocatalytic activity in ORR among the unsubstituted Keggin or Dawson-type HPAs [245].

Importantly, PANi-inorganic oxide nanocomposites are effective electrocatalysts in many reactions and find applications in sensors [246, 247]. PANi/WO$_3$ composites have been prepared and used as humidity sensor [248]. Phosphomolybidic acid doped PANi/V$_2$O$_5$ composite has been proved to be an effective electrocatalyst for oxygen reduction in weak acidic solution [249]. Metal oxides such as MoO$_3$ and VO$_2$ offered electrocatalytic properties when incorporated into PANi matrix [250-252]. Electroactivity of the NiO$_x$/PoT$_y$ (x = amount of NiO-NPs (mg), y = concentration of o-toluidine (oT) (mM)) films showed dependence on x and y. Efficient electrocatalysts could be obtained by tuning x and y reported by Komathi et al. [253]. Gang Wu et al., reported that the Nitrogen-doped TiO$_2$-supported PANi-Fe catalyst exhibits much improved catalytic activity for oxygen reduction when compared to traditional carbon-supported materials [254]. Kurys et al reported that nanocomposites CP (polyaniline, polypyrrol) PMA
phosphomolybdic acid/TiO₂ and CP PMA/TiO₂/Pt are capable of manifesting electrocatalytic properties in ORR [255].

Thus, the aim of this work was to study the regularities of electrochemical behavior and electrocatalytic properties in the oxygen reduction reaction of the hybrid nanocomposites based on different CPs, and nanosize ceramic and also their methanol reduction in different atmospheric condition.

2.2. Selection of monomer

Electrically conducting nanocomposites formed by the combination of inorganic materials and organic polymers, such as polyaniline (PAni), polypyrrole (PPY) and polythiophene (PTh), etc. have received greater attention over the last few years [256-259]. Electroconductive polymers are of great interest for a large number of applications [260-267] due to their easy processing and relatively low cost compared to other materials such as the inorganic one. Among all conducting polymers polyaniline and its derivatives such as Poly (o-toluidine) [when there is -CH₃ group blockage at the ortho position of the aniline’s aromatic ring, PAni derivative is obtained and it is called PoT] are the most promising polymeric material which can be frequently used because of its easy synthesis, flexibility, high electrical conductivity, environmental stability and effective material for sensing applications [268-270].

The conductivity of Poly(o-toluidine), which has lower crystallinity and large interchain distance than PAni has two orders of magnitude lower than that of polyaniline, though the electronic structure of the two polymers are nearly same [271, 272] yet it has been extensively investigated in diverse studies as the active CP material. Choudhury et. al., Ding et. al. and Bavastrello et. al. synthesized PoT
composites with multi-wall carbon nanotubes (MWCNT) to improve its electrical conductivity and other related properties [273-275]. Moreover, advantageous properties of PoT over PANi, e.g. faster switching times between its reduced/oxidized states [273, 275, 276], better solubility [277], long-term stability [276], and interesting electro-optical properties [271] facilitate its characterization and easier processing [277] for the common technological applications of field effect transistors, light-emitting diodes, solar cells, immunodiagnostic assay, smart windows and biosensors.

Selected monomer structures are

![Aniline](image)

![o-toluidine](image)

2.3. Selection of ceramic

The PANi/TiO$_2$ core-shell nanocomposite showed better photocatalytic activity for MeO photodegradation in aqueous solution compared to the pristine TiO$_2$ nanoparticles under both UV and visible light illuminations [46]. Srivastava et al., reported that the sensitivity of TiO$_2$/PAni nanocomposite thin film based sensors toward hydrogen gas increases with increasing the TiO$_2$ concentration in PAni matrix [278]. Huiling Tai et al., showed that the response, reproducibility and stability of the PANi/TiO$_2$ thin film to NH$_3$ were superior to CO gas [279]. A PANi/TiO$_2$ nanocomposite was obtained by in-situ enzymatic polymerisation of aniline in the presence of sulfonated polystyrene (SPS) and TiO$_2$ NPs which is a template and
nanoparticle respectively [280]. The addition of PAni improved the gas sensing properties of TiO$_2$ thin films at room temperature. The nanocomposite TiO$_2$ thin film exhibits a satisfactory response towards ethanol and methanol vapour [281]. The n-p contacts between TiO$_2$ nanoparticles and PAni matrix give rise to variety of shallow donors and acceptor levels increasing the physical adsorption sites for gas molecules thus enhancing the gas sensitivity [282].

Xu et al. reported that with increasing contents of TiO$_2$, the relative contents of the conducting polymer PAni decreased, which caused a decrease from $0.704 \times 10^3$ to $0.116 \times 10^3$ S.m$^{-1}$ in the conductivity of composites [283]. The increased conductivity is attributed to the formation of a better charge transport network in the relatively insulating polyaniline matrix [284]. Zhang et al. reveals that photocatalytic method can be effective for solid-phase PAni degradation and the PAni-TiO$_2$ composite has a potential viability to be used as a photodegradable product. The photocatalytic degradation in the solid polymer matrix proceeded much faster than the direct photolytic degradation under air [285].

Stejskal et al showed that PAni imparts new physical and chemical properties to the silica gel carrier that can be exploited in various applications [286]. Silica particles are successfully incorporated into PAni in the media of pH 10.0 through electrophoresis of the particles towards anode as aniline anodically electropolymerizes [287]. Luo et al. showed that the enhancement in the biosensor response was likely due to the special structure of the silica-PAni core-shell particles, as silica particles coated with a nanofilm of PAni should adsorb HRP more effectively and increase the active electrode surface area [288]. Yu et al., synthesized silica nanoparticle-armored polyaniline microspheres (SNAPMs) in a Pickering emulsion.
The silica nanoparticles were attached to the surfaces of the polyaniline microspheres by hydrogen bonds. The amount of the silica nanoparticles added in the emulsion had a distinct effect on the morphology and size of the SNAPMs [289].

Liu et al. reported that the redox pair related to the degradation of PANi on cyclic voltammogram of the hybrid film was well depressed, demonstrating the stabilization effect of the incorporation of N-substituted aniline. The cyclic stability of PANi/ND42-SiO₂ which was measured through charging-discharging experiments was also improved [290]. The enhancement in optical contrast is attributed to the higher doping level of the PANi/SiO₂ composite films. Besides, the presence of SiO₂ might have retarded the formation of the highly oxidized PANi and hence improved the stability reported Chen et al [291].

The rheological study supports that the PANi/nano-silica based Electrorheological (ER) fluid performs better, showing a higher yield stress than pure PANi reported by Liu et al [292]. Jia et al., reported that the ER behaviors of SiO₂ doped by polyaniline in silicone oil are investigated with different doping degrees under different shear rate, and the results show that properly doping polyaniline improves electrorheological behavior of SiO₂ [293]. Torres et al. studied both mass and specific capacitance of silica-PANi hybrid materials and found that they are higher than the equivalent electrodes modified with PANi [294]. When inorganic nanosilica particles were incorporated into the polymer hybrids, higher thermal stability, Tg, and extensibility were obtained due to the higher degree of phase separation was reported by Wang et al [295]. Hsieh et al., studied the saturation magnetization of SiO₂/γ-Fe₂O₃ nanoparticles and found that magnetization decreased with increasing the (tetraethyl orthosilicate) TEOS content due to the increase of silica shell thickness at
high TEOS contents [296]. Huang et al., synthesized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ composite microspheres and modified with about 2.7 wt.% PAni and show the highest photocatalytic activity in the photodegradation of methylene blue under the visible light illumination [297].

When the silica-PAni core-shell nanoparticles were incorporated into polyurethane (PU) matrix, the PU-PAni-silica nanocomposites showed superior electrical conductivity and mechanical properties compared with the PU-silica nanocomposites [41]. The photoluminescence of PAni/SiO$_2$ composites showed an increase in intensity compared to neat PAni. The composite films exhibited an increase in electrical conductivity over neat PAni. The increase in conductivity of PAni/SiO$_2$ composites may be partially due to the doping or impurity effect of SiO$_2$, where the SiO$_2$ particles compete with chloride ions [298]. The conductivities of PAni/silica nanosheet (SNS) composites are higher than that of pure PAni and are enhanced with the increase in the SNS/monomer mass ratio because of the moisture absorption [299]. The PAni/PoT/SiO$_2$ film is electroactive and can be used as an electrode modifier for performing Fe$^{2+}$/Fe$^{3+}$ and H$_2$Q/Q redox processes on its surface [300].

Teoh et al. synthesized PAni-Al$_2$O$_3$ nanocomposite fibers by seeding with Al$_2$O$_3$ nanofibers and oxidative polymerization of the monomers. The composite materials were formed from strong interaction between the polymer and Al$_2$O$_3$ [301]. Polyaniline and polyaniline composites, with aluminium oxide (PAni-Al$_2$O$_3$), were prepared using the in-situ polymerization technique and used as anticorrosive pigments in the acrylic paints system to be applied on the carbon steel samples [302].
Selected ceramics structures are

![TiO₂](image1.png)  ![Al₂O₃](image2.png)  ![SiO₂](image3.png)

Based on the above mentioned papers the aniline and o-toluidine were chosen as the monomers for the present research work. Chemical oxidative polymerisation of the monomers was carried out by incorporation of ceramic like silica, alumina and titania into the polymer matrix.

Now a days, coated electrode / modified electrode systems are very much employed to characterize organic-inorganic hybrid compounds. Hence conducting polymer modified glassy carbon electrodes such as polyaniline (PAni/GCE), poly (o-toluidine) (PoT/GCE) and conducting polymer-ceramic nanocomposites modified glassy carbon electrode such as polyaniline-SiO₂ (PAniSNCs/GCE), polyaniline-Al₂O₃ (PAniANCs/GCE), polyaniline-TiO₂ (PAniTNCs/GCE), poly (o-toluidine)-SiO₂ (PoTSNCs/GCE), poly (o-toluidine)-Al₂O₃ (PoTANCs/GCE), and poly (o-toluidine)-TiO₂ (PoTTNCs/GCE) deposited on glassy carbon electrode are utilised here to study redox behavior and electrocatalytic activity.

2.4. The main objectives of the present investigation are as follows

✓ To synthesis polymers of aniline and o-toluidine using potassium persulphate as the oxidant.
✓ To synthesis ceramic incorporated polymer nanocomposites of aniline and o-toluidine.

✓ To investigate the spectral behaviour (UV-Vis and FTIR) of polymers and polymer-ceramic nanocomposites.

✓ To determine the structural properties and particle size through XRD experiments.

✓ To study the surface morphological behaviour using SEM and TEM.

✓ To confirm the incorporation of the metal oxide in the polymer matrix with the help of EDAX.

✓ To study the thermal behaviour of polymer and polymer-ceramic nanocomposites using thermo analytical techniques (TGA/DTA).

✓ To find out the electrochemical behaviour in modified electrode systems of the polymer and polymer-ceramic nanocomposites.

✓ To study the effect of pH.

✓ To study different atmospheric condition.

✓ To find out the diffusion coefficient values through chronoamperometry.

✓ To find out the charge and number of electron through chronocoulometry.

✓ To find out the reduction behaviour in methanol.

✓ To find out the resistance using electrochemical impedance spectra.