

Electrochemically co-deposited MnO₂–polypyrrole hybrid cathode for efficient hydrogen peroxide reduction in alkaline media: Experimental and interfacial insights

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ABSTRACT

Hydrogen peroxide fuel cells are promising energy-conversion systems owing to their high theoretical cell voltage and simple architecture. However, efficient and low-cost cathodes for the hydrogen peroxide reduction reaction (HPRR) remain challenging. Here, a MnO₂-polypyrrole (PPy) hybrid cathode was electrochemically co-deposited onto fluorine-doped tin oxide (FTO) and evaluated in alkaline media. Structural and morphological analyses confirmed a homogeneous, predominantly poorly crystalline hybrid film with MnO₂ particles incorporated into the PPy matrix. Compared with pristine MnO₂, the hybrid showed enhanced HPRR activity, lower charge-transfer resistance, and higher electrical conductivity (0.368 vs. 0.254 S cm⁻¹). The cathodic current increased linearly with H₂O₂ concentration ($R^2 = 0.9677$), while impedance and chronoamperometric measurements indicated improved charge transfer and sustained activity. DFT and atoms-in-molecules analyses provided further insight into interactions among MnO₂, PPy, and ClO₄⁻. These results highlight MnO₂-PPy as a promising cathode for alkaline HPRR.

1. Introduction

Fuel cells are promising electrochemical energy-conversion technologies for meeting the growing demand for efficient and low-emission power-generation systems. Their applications extend from portable electronic devices and electric vehicles to aerospace systems, stationary power generation, and off-grid energy technologies [1–6]. Despite these advantages, the broader implementation of conventional hydrogen fuel cells remains associated with challenges, including catalyst cost, durability, and susceptibility to poisoning under certain operating conditions, particularly in alkaline environments [7–9]. These limitations

have stimulated the development of alternative fuel-cell configurations based on earth-abundant materials and simplified reaction pathways.

Hydrogen peroxide-based fuel cells have emerged as an attractive alternative because of their high theoretical cell voltage, liquid-phase oxidant, and compatibility with alkaline electrolytes. Nevertheless, the hydrogen peroxide reduction reaction (HPRR) at the cathode is kinetically demanding and therefore requires electrocatalysts combining high activity, adequate stability, and low cost. Among non-noble metal oxides, manganese dioxide (MnO₂) is particularly attractive because of its low cost, natural abundance, relatively low environmental impact, and versatile redox chemistry involving manganese oxidation states

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[10–15]. These characteristics make MnO_2 a promising material for peroxide-related electrochemical reactions. However, its intrinsically low electrical conductivity and limited interfacial charge-transfer capability can hinder its electrochemical performance [16,17].

Combining MnO_2 with electrically conducting polymers is an established strategy for addressing these limitations. Such hybrid materials can integrate the redox activity of the metal oxide with the electronic conductivity and structural flexibility of the polymer phase [18,19]. Conducting polymers also provide interconnected pathways for charge transport and can facilitate electrolyte penetration and ion transport within the electrode architecture [1,20–22]. Among these materials, polypyrrole (PPy) is particularly attractive because of its electrical conductivity, environmental stability, facile electrochemical polymerization, and compatibility with a variety of electrode architectures [23,24]. Consequently, MnO_2 -PPy composites have been investigated for applications in electrocatalysis, energy storage, and electrochemical energy-conversion systems [25–29].

Previous studies have demonstrated that MnO_2 -PPy composites prepared by chemical oxidation, in situ polymerization, and related synthesis routes can exhibit improved electrochemical properties compared with pristine MnO_2 [30–32]. However, most reported studies have primarily focused on supercapacitive applications or general electrochemical performance. In contrast, systematic investigations of MnO_2 -PPy hybrid electrodes specifically for hydrogen peroxide reduction under alkaline conditions remain comparatively limited. In addition, although macroscopic electrochemical behavior has been extensively characterized, the molecular-level origin of charge transfer at the polymer-oxide interface remains insufficiently understood. In particular, the influence of polymer doping and interfacial electronic redistribution on the interaction between PPy and MnO_2 requires further investigation. MnO_2 -based electrodes have previously demonstrated potential for peroxide-related electrochemical reactions [33], providing a basis for exploring hybrid polymer-oxide architectures for HPRR.

Electrochemical co-deposition offers an effective route for preparing hybrid polymer-oxide electrodes because it can promote intimate contact between the different components while allowing the deposition process to be controlled electrochemically [34–36]. During PPy electropolymerization, anions such as perchlorate (ClO_4^-) originating from the supporting electrolyte can be incorporated into the oxidized polymer to maintain charge neutrality. Such doping can influence the electronic structure of PPy and may consequently affect charge redistribution and interfacial interactions within the MnO_2 -PPy hybrid.

In the present study, a MnO_2 -PPy hybrid electrode was prepared by electrochemical co-deposition onto fluorine-doped tin oxide (FTO) and evaluated as a cathode for hydrogen peroxide reduction in alkaline media. Structural, spectroscopic, morphological, and electrochemical characterization techniques were combined to establish the relationship between the hybrid electrode structure and its electrochemical performance. In parallel, density functional theory (DFT) calculations and atoms-in-molecules (AIM) analysis were employed to investigate the interfacial interactions among PPy, MnO_2 , and the ClO_4^- dopant. The objective was to obtain complementary experimental and computational evidence for the role of the polymer-oxide interface in charge transfer and HPRR performance. The resulting insights are expected to contribute to the rational design of conductive polymer-metal oxide hybrid cathodes for alkaline hydrogen peroxide electrochemical systems.

2. Material and methods

2.1. Materials and reagents

All chemicals used in this study were of analytical grade and employed without further purification unless otherwise stated. Pyrrole monomer (Py, 98%, Aldrich) was stored at 4 °C in the dark to prevent oxidative degradation prior to use. γ -Manganese dioxide (γ - MnO_2 , 99%,

Aldrich) particles were used as received. The supporting electrolyte was prepared by dissolving anhydrous lithium perchlorate (LiClO_4 , Fluka) at a concentration of 0.1 M in distilled acetonitrile (CH_3CN , Aldrich). Acetonitrile was selected due to its wide electrochemical stability window and good solvation capability for both the monomer and dopant ions, ensuring controlled electropolymerization and homogeneous hybrid film formation. All aqueous solutions were prepared using distilled water.

2.2. Instruments

Electrochemical experiments were carried out using a Voltalab 301 potentiostat/galvanostat operating in a conventional three-electrode configuration. The MnO_2 -PPy hybrid film deposited on fluorine-doped tin oxide (FTO) substrates served as the working electrode. A platinum wire was used as the counter electrode, while a saturated calomel electrode (SCE) acted as the reference electrode. All potentials reported in this work are referenced to the SCE. The surface morphology and elemental composition of the deposited hybrid films were examined by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX), using a JEOL JSM-7001 F field-emission microscope.

Phase composition and crystallographic structure were analyzed by X-ray diffraction (XRD) using a Rigaku SmartLab diffractometer equipped with monochromated $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). The diffractometer was operated at an accelerating voltage of 20 kV and a current of 10 mA, with diffraction patterns recorded over a 2θ range of 20–80°. The electrical conductivity of the prepared electrodes was determined using a standard four-probe method to minimize contact resistance effects. Measurements were performed on compacted pellets with an effective thickness of approximately 100 nm, using a Keithley 2400 source meter in conjunction with a Lucas Labs Pro 4 probe station. The reported conductivity values represent averaged measurements to ensure reproducibility. The electrocatalytic activity of the MnO_2 -PPy hybrid electrodes toward hydrogen peroxide reduction was evaluated at room temperature in alkaline media using an aqueous 1 M NaOH solution. Electrochemical measurements, including cyclic voltammetry and impedance spectroscopy, were conducted after stabilization of the open-circuit potential to ensure steady-state conditions.

2.3. Preparation of MnO_2 -co-PPy hybrid electrodes and electrochemical deposition mechanism

The MnO_2 -co-PPy hybrid electrodes were synthesized by electrochemical co-deposition using cyclic voltammetry, a well-established approach for producing conducting polymer-metal oxide composites with intimate interfacial contact [34–36]. Electrodeposition was performed in a 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte containing 0.1 M pyrrole monomer and γ - MnO_2 particles. Fluorine-doped tin oxide (FTO) substrates were used as conductive supports. Prior to deposition, the FTO substrates were cleaned with ethanol and distilled water and dried under ambient conditions to ensure reproducible film adhesion. The co-deposition was carried out by cycling the potential between -0.4 and $+1.1 \text{ V}$ vs SCE at a scan rate of 50 mV s^{-1} for 20 successive cycles. This potential window was selected to simultaneously activate MnO_2 redox processes and initiate pyrrole electropolymerization, while avoiding solvent degradation [35,36]. The growth mechanism of the hybrid films can be elucidated from the evolution of the cyclic voltammograms shown in Fig. 1.

2.3.1. Electrochemical behavior of MnO_2

Fig. 1a shows the cyclic voltammogram of the MnO_2 /FTO electrode recorded in $\text{LiClO}_4/\text{CH}_3\text{CN}$, followed by operation in alkaline conditions. In alkaline media, the redox activity of MnO_2 is governed by surface-confined proton-coupled electron-transfer processes involving hydroxide ions rather than protons [34]. The cathodic features observed

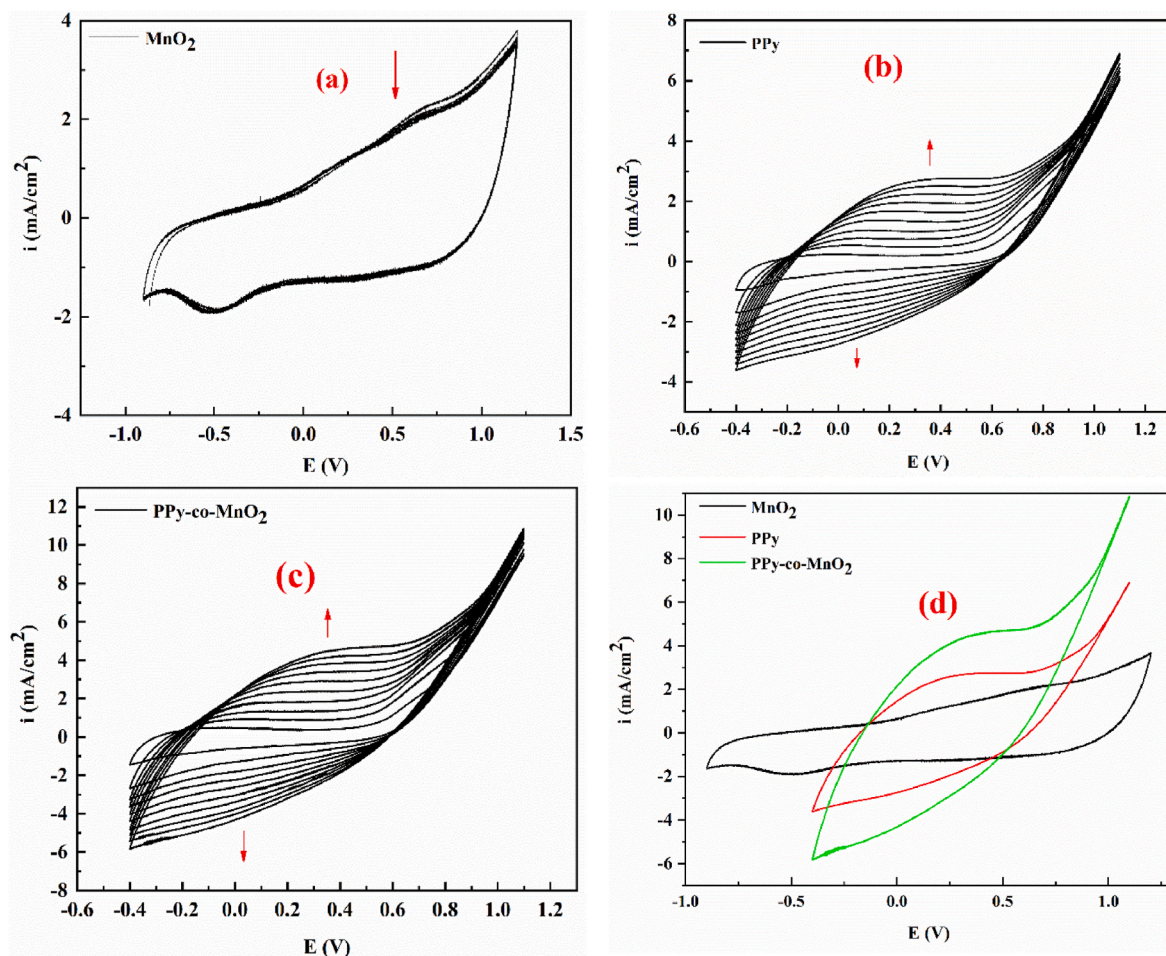
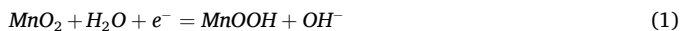


Fig. 1. Cyclic voltammograms relating to: MnO_2/FTO , PPy/FTO , and $\text{MnO}_2\text{-co-PPy}/\text{FTO}$ in a $\text{CH}_3\text{CN}/\text{LiClO}_4$ 0.1 M solution, at a scan rate of 50 mV s^{-1} .

around -0.50 V and 0.40 V vs SCE are attributed to the stepwise reduction of MnO_2 according to the following reactions in alkaline medium:



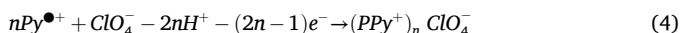
During the anodic sweep, the oxidation peak observed near 0.65 V vs SCE corresponds to the partial reoxidation of $\text{Mn(II)}/\text{Mn(III)}$ species back to MnO_2 through the reverse of reactions (1) and (2) [34]. The broad nature of these peaks reflects diffusion limitations and the poor intrinsic conductivity of MnO_2 .

2.3.2. Electropolymerization of pyrrole in alkaline-compatible non-aqueous media

The electropolymerization of pyrrole, shown in Fig. 1b, proceeds via anodic oxidation of pyrrole monomers. This process is independent of solution pH due to the non-aqueous CH_3CN -based medium used during deposition [35]. The fundamental electrochemical step is given by:



The radical cations subsequently undergo coupling reactions, forming oligomeric species that propagate into polypyrrole chains. Charge neutrality is maintained through the incorporation of perchlorate anions from the supporting electrolyte, yielding a doped conducting polymer:



MnO_2 and PPy were coelectrodeposited onto an FTO electrode in a solution of 10^{-1} M acetonitrile (CH_3CN) in lithium perchlorate (LiClO_4)

containing 0.2 mg of MnO_2 and 0.1 M pyrrole. The twenty cycles were carried out in the potential range -0.4 to 1.1 V vs. SCE, at a scan rate of 50 mV/s , as can be seen, similar voltamperograms of polypyrrole.

2.3.2.1. Co-deposition mechanism of MnO_2 -PPy hybrid electrodes. When MnO_2 particles are present in the pyrrole-containing electrolyte (Fig. 1c), the electrochemical processes described by reactions (1)–(4) occur simultaneously. MnO_2 particles undergo surface redox transitions governed by hydroxide-mediated reactions, while pyrrole monomers polymerize electrochemically to form a conductive PPy matrix. The MnO_2 particles become physically embedded and electrostatically stabilized within the growing PPy network, forming an intimate polymer-oxide interface [36].

The presence of MnO_2 introduces additional faradaic reactions associated with $\text{Mn}^{4+}/\text{Mn}^{3+}/\text{Mn}^{2+}$ transitions in alkaline conditions, whereas PPy provides continuous electron-transport pathways. This synergistic interaction results in enhanced charge-transfer kinetics and higher electrochemical currents compared with individual MnO_2 or PPy electrodes.

2.4. Computational methodology

All calculations were performed within the framework of density functional theory (DFT) using a two-stage strategy that combines DMol³ (Materials Studio 2024) and Turbomole 7.7 [37].

2.4.1. Geometry optimization

Initial geometries of pristine MnO_2 , PPy, $\text{PPy}\cdot\text{ClO}_4^-$, PPy@MnO_2 , and

PPy-ClO₄@MnO₂ were optimized using the DMol³ module. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was employed together with Grimme's D3(BJ) dispersion correction to account for van der Waals interactions between the polymer chains and the MnO₂ surface. A double numerical basis set with polarization functions (DNP) was used for all atoms, and spin polarization was considered for Mn 3d states [38]. The SCF energy convergence threshold was 1×10^{-6} Ha, and the maximum force criterion for geometry relaxation was 1×10^{-3} Ha Å⁻¹.

2.4.2. Electronic-structure refinement and wavefunction analysis

Single-point energy and orbital calculations were subsequently performed with Turbomole 7.7 using the M06-2X meta-hybrid functional, which includes a built-in empirical treatment of medium-range dispersion and accurately describes non-covalent interactions (NCI) and electron delocalization. A def2-TZVP basis set was employed for all atoms, and integration grids were of m5 quality [39]. The M06-2X functional was chosen because it provides a more realistic description of π -d hybridization and hydrogen bonding at the PPy/MnO₂ interface than GGA-PBE alone. Wavefunctions were exported in.molden format for further analysis with Multiwfn 3.8, including frontier molecular orbitals (HOMO/LUMO), density-of-states (DOS/PDOS), electrostatic potential (ESP), non-covalent interaction (NCI) index, and atoms-in-molecules (AIM) topological properties (electron density ρ , Laplacian $\nabla^2\rho$, and bond critical points). Visualization of $\Delta\rho$ and NCI isosurfaces was performed with VMD, and energy-level and DOS plots were generated with GnuPlot. Adsorption energies were calculated as:

$$E_{\text{ads}} = E_{\text{complex}} - (E_{\text{MnO}_2} + E_{\text{adsorbate}}) \quad (5)$$

Where negative E_{ads} values denote exothermic adsorption and a stronger interaction between the polymer and the oxide surface.

3. Results and discussion

3.1. XRD analysis

Fig. 2 presents the X-ray diffraction (XRD) patterns of the MnO₂/FTO and MnO₂-co-PPy/FTO electrodes. The diffraction pattern of the MnO₂/FTO electrode exhibits well-defined reflections characteristic of crystalline manganese dioxide, in good agreement with the standard reference data (JCPDS No. 01-082-2169). The reflections observed at $2\theta = 38.83^\circ$, 53.39° , 60.72° , 66.42° , and 87.49° can be indexed to the (111), (510), (321), (421), and (040) planes, respectively. The relatively

sharp diffraction peaks indicate a comparatively high degree of crystallinity for the MnO₂ electrode deposited on the FTO substrate. The crystalline structure of MnO₂ is associated with its redox activity and can influence its electrochemical behavior. However, the relatively low intrinsic electrical conductivity of MnO₂ can limit electron transport and interfacial charge-transfer kinetics. This limitation provides a rationale for combining MnO₂ with the conductive PPy matrix.

In contrast, the MnO₂-co-PPy/FTO electrode exhibits a substantially different diffraction profile. The characteristic reflections are observed at $2\theta = 55.90^\circ$, 63.07° , 66.65° , and 88.03° , which are assigned to the (221), (511), (421), and (122) planes, respectively. The attenuation and modification of the MnO₂ diffraction features after incorporation of PPy indicate changes in the structural organization and crystallinity of the MnO₂ phase within the hybrid electrode. This behavior is consistent with the incorporation of MnO₂ crystallites into the polymer matrix during electrochemical co-deposition. The average crystallite size, D , was estimated from the XRD peak broadening using the Scherrer equation according to the approach reported by Arjun et al. [40]. The calculated crystallite sizes were 5.11 nm for MnO₂ and 7.55 nm for the MnO₂-co-PPy composite. These values indicate that the MnO₂ phase remains nanocrystalline after incorporation into the PPy matrix. The difference between the crystallite size determined by XRD and the larger particle size observed by SEM suggests that the microscale particles are composed of smaller coherent crystallite domains. The incorporation of PPy, therefore, appears to modify the aggregation and structural organization of the MnO₂ phase within the hybrid electrode. The characteristic MnO₂ reflections are substantially attenuated after incorporation into PPy, while the broad diffuse background indicates a predominantly poorly crystalline or partially disordered hybrid structure. The calculated Scherrer crystallite size nevertheless indicates that nanoscale crystalline MnO₂ domains are retained within the polymer matrix. This behavior confirms the successful incorporation of MnO₂ particles within the polypyrrole matrix during the electrochemical co-deposition process and is consistent with previous reports on conducting polymer–oxide hybrid systems [41,42].

The amorphization observed for the MnO₂-co-PPy electrode can be attributed to the confinement of MnO₂ particles within the growing polymer network and the strong interfacial interactions between MnO₂ and PPy chains. The presence of the amorphous PPy phase disrupts the long-range ordering of MnO₂ crystallites, leading to reduced crystallinity. While amorphous materials are often considered structurally disordered, this structural feature is advantageous for electrochemical applications, as it generally promotes higher defect density, increased active surface area, and improved ion accessibility. The reduced crystallinity and nanoscale organization of MnO₂ within the PPy matrix may improve electrolyte accessibility and increase the fraction of structurally accessible interfacial sites. These structural features, together with the conductive PPy network, may contribute to the enhanced electrochemical response observed for the hybrid electrode. This structural evolution, evidenced by XRD analysis, plays a key role in explaining the improved conductivity and electrocatalytic activity of the MnO₂-co-PPy electrode observed in subsequent electrochemical measurements.

3.2. FTIR analysis

Fourier-transform infrared (FTIR) spectroscopy was used to identify the characteristic functional groups and chemical features of PPy, MnO₂, and the MnO₂-co-PPy hybrid electrodes. The corresponding FTIR spectra are presented in Fig. 3. For PPy, the absorption band observed at 1548 cm^{-1} is assigned to the stretching vibration of the C=C bonds in the pyrrole ring [43]. The band around 1630 cm^{-1} can be attributed to C–N stretching vibrations [44]. A weak band at approximately 2365 cm^{-1} is associated with atmospheric CO₂.

The absorption band observed at around 1079 cm^{-1} is assigned to C–H vibrations of the pyrrole ring [45]. For MnO₂, the bands observed around 1660 and 1515 cm^{-1} can be associated with O–H bending

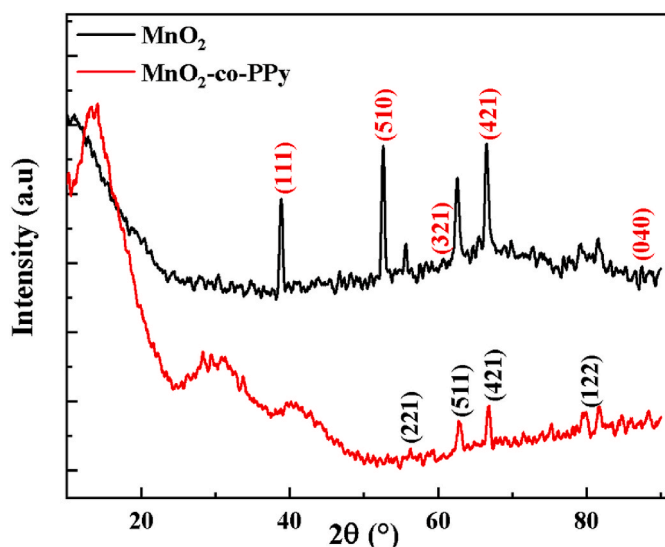


Fig. 2. XRD patterns of MnO₂/FTO and MnO₂-co-PPy/FTO electrodes.

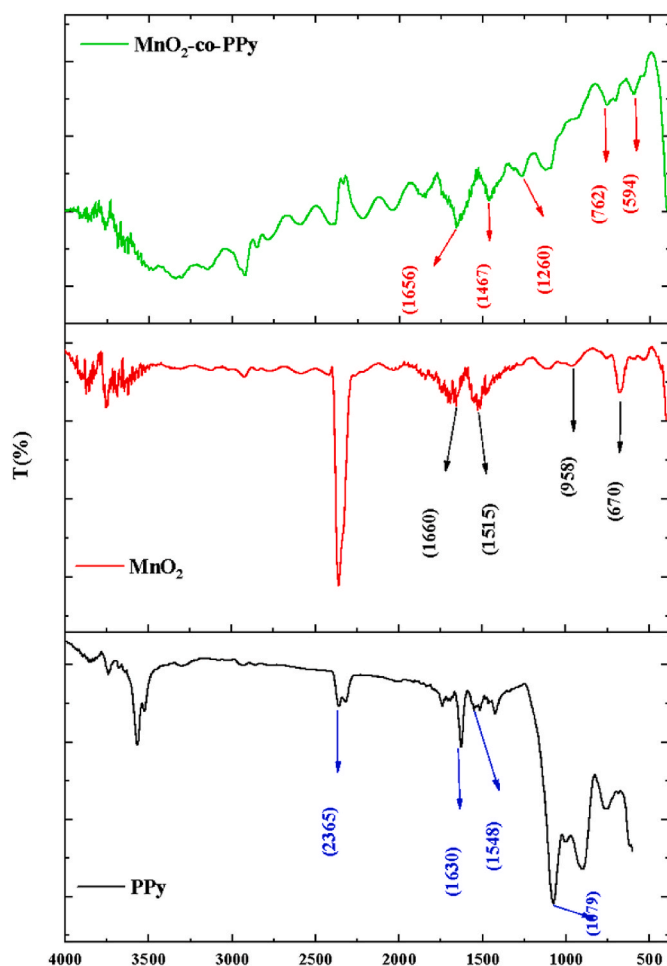


Fig. 3. FTIR spectra of PPy, MnO_2 , and MnO_2 -co-PPy electrodes deposited on FTO.

vibrations involving surface hydroxyl groups, while the bands located in the $670\text{--}958\text{ cm}^{-1}$ region are characteristic of Mn–O stretching vibrations [28]. The FTIR spectrum of the MnO_2 -co-PPy hybrid electrode exhibits characteristic bands associated with both PPy and MnO_2 , particularly at approximately 3156 , 1260 , 762 , and 594 cm^{-1} . No additional absorption bands attributable to the formation of new chemical functionalities are observed. However, several characteristic PPy bands undergo slight shifts after incorporation of MnO_2 . These spectral changes suggest that the interaction between PPy and MnO_2 is primarily associated with interfacial physical interactions and/or changes in the local chemical environment, rather than the formation of entirely new chemical bonds [46,47]. Overall, the FTIR results confirm the coexistence of PPy and MnO_2 within the hybrid electrode and support the successful formation of the MnO_2 -co-PPy composite.

3.3. Morphology characterization by SEM and EDX

The surface morphology and elemental composition of PPy, MnO_2 , and MnO_2 -co-PPy hybrid materials electrodeposited on FTO substrates were investigated by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). Representative SEM micrographs and the corresponding EDX spectra are presented in Fig. 4. The SEM image of the PPy film (Fig. 4a) reveals a micro-spherical granular morphology composed of densely packed nodules separated by large voids, forming a characteristic cauliflower-like structure. This morphology is typical of electropolymerized polypyrrole and has been widely reported in the literature [48]. The porous architecture

originates from the nucleation-and-growth mechanism during electropolymerization and is known to favor electrolyte penetration and ion transport. The average grain size of PPy was estimated to be approximately $0.5\text{ }\mu\text{m}$, indicating the formation of a relatively uniform polymer layer with a high specific surface area.

In contrast, the $\gamma\text{-MnO}_2$ electrode (Fig. 4b) exhibits a markedly different morphology characterized by an urchin-like structure composed of radially oriented nanoneedles. These hierarchical aggregates display overall dimensions in the range of $0.5\text{--}1\text{ }\mu\text{m}$, with individual nanoneedles extending outward from the particle core. Such a morphology is commonly associated with $\gamma\text{-MnO}_2$ synthesized or deposited under electrochemical conditions. It is known to provide a large number of exposed active sites, although electrical connectivity between particles remains limited due to the intrinsic low conductivity of MnO_2 . The SEM micrograph of the MnO_2 -co-PPy hybrid material (Fig. 4c) demonstrates a homogeneous and well-integrated morphology, distinct from those of the individual components. The surface is composed of uniformly distributed spherical to quasi-spherical MnO_2 microparticles embedded within the PPy matrix. Morphological and structural analyses reveal the hierarchical nature of the pristine MnO_2 and MnO_2 -PPy composite electrodes. For pristine MnO_2 , the SEM-derived particle-size distribution gives an average particle diameter of approximately 235 nm .

In contrast, the crystallite size estimated from the XRD data using the Scherrer equation is only 5.11 nm .

This substantial difference indicates that the observed sub-micrometer particles are composed of smaller coherently scattering crystallites. It also highlights the distinction between the **physical particle size determined by SEM** and the **coherent crystallite size estimated from XRD**. After incorporation of PPy, the SEM images show the formation of larger, highly contrasted microscale aggregates. At the same time, the XRD analysis gives a crystallite size of approximately 7.55 nm for the MnO_2 phase within the MnO_2 -PPy composite. The increase in apparent crystallite size compared with pristine MnO_2 may indicate changes in the aggregation and structural organization of MnO_2 during co-deposition. The PPy matrix may provide a structural framework that promotes the incorporation and aggregation of MnO_2 nanocrystallites within the polymer network, resulting in the formation of larger composite aggregates while retaining nanoscale MnO_2 domains. Such a hierarchical organization may be beneficial for electrochemical applications by providing accessible interfacial sites and facilitating contact between the MnO_2 phase and the conductive PPy matrix [49]. The homogeneous dispersion of MnO_2 within the PPy matrix provides extensive interfacial contact between the redox-active oxide and the conductive polymer, which may facilitate charge transport within the hybrid electrode. Moreover, the hierarchical porous structure of the hybrid electrode is expected to enhance electrolyte accessibility and facilitate ion diffusion, thereby contributing to improved charge-transfer kinetics and electrocatalytic performance. The average particle size of the MnO_2 -co-PPy composite was estimated by considering the maximum and minimum dimensions observed in the SEM images. While this approach provides an approximate value, it is sufficient to confirm the nanoscale nature of the embedded MnO_2 particles and their uniform distribution within the polymer matrix. The elemental composition of PPy, MnO_2 , and MnO_2 -co-PPy materials was further analyzed by EDX, as shown in Fig. 4. The EDX spectra of the hybrid electrode confirm the presence of manganese (Mn), oxygen (O), carbon (C), and nitrogen (N), verifying the successful incorporation of MnO_2 into the PPy matrix [50]. Intense Mn characteristic peaks were observed at approximately 6.03 and 6.10 keV , confirming the presence of manganese oxide. The detection of carbon (C) and nitrogen (N) signals at around 0.31 keV and 0.40 keV , respectively, is characteristic of the polypyrrole backbone.

In addition, chlorine (Cl) signals detected at approximately 2.68 and 2.81 keV , together with oxygen peaks around 0.57 keV , indicate that the PPy film is doped with perchlorate (ClO_4^-) ions originating from the

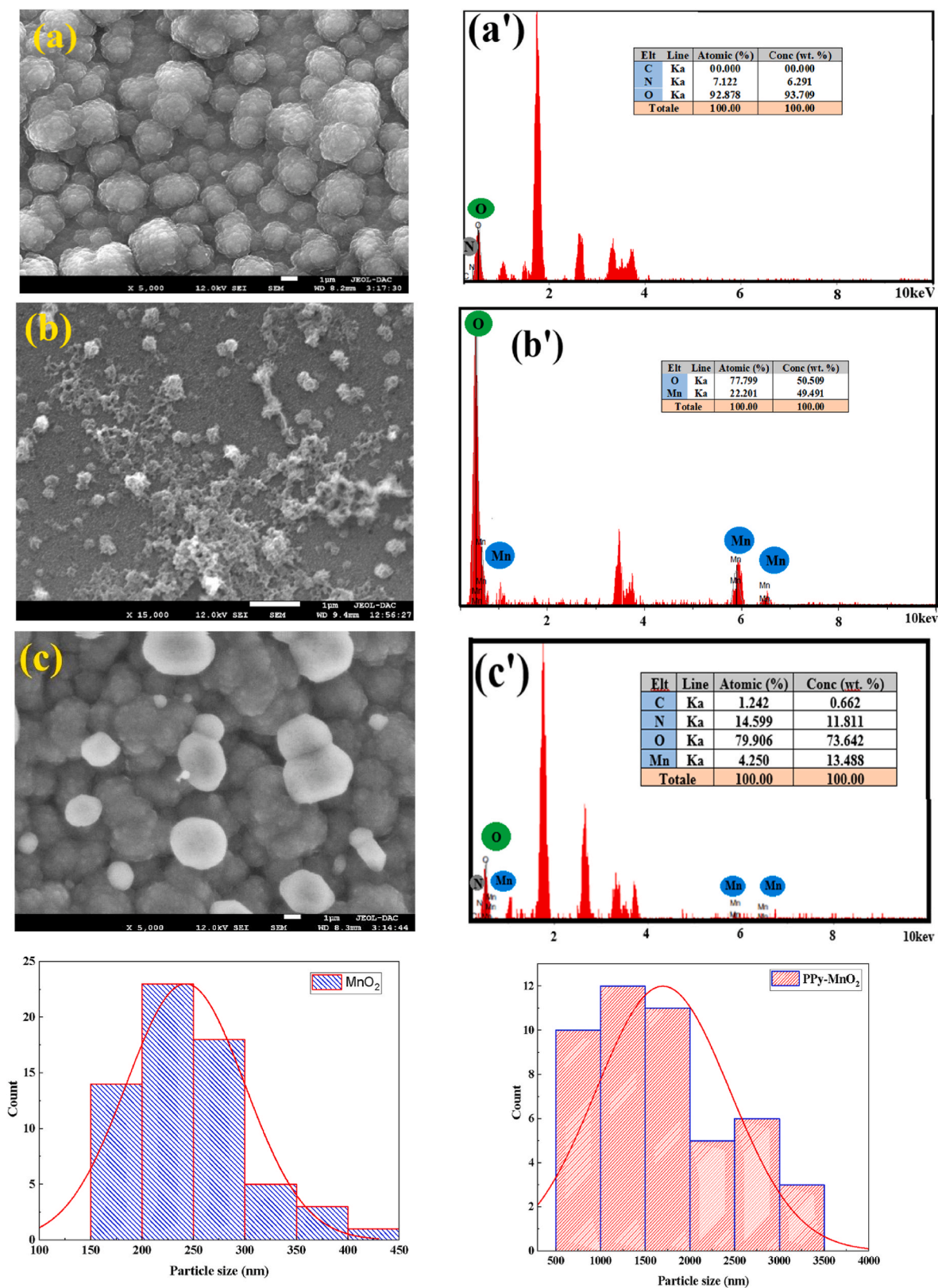


Fig. 4. SEM images and EDX patterns of (a,a') PPy, (b,b') MnO₂, (c,c') MnO₂-co-PPy/FTO and the distribution of pore versus particle size for MnO₂ and MnO₂-co-PPy/FTO hybrid materials.

LiClO₄ supporting electrolyte. This observation is consistent with previous reports and confirms the formation of a doped, electrically conductive PPy phase within the hybrid electrode [51]. The presence of ClO₄⁻ dopant ions plays a crucial role in stabilizing the oxidized state of PPy and enhancing interfacial charge transport within the MnO₂-co-PPy system.

Overall, SEM and EDX analyses demonstrate that electrochemical co-deposition yields a structurally homogeneous MnO₂-PPy hybrid electrode with hierarchical porosity, uniform dispersion of MnO₂ particles,

and effective polymer doping. These morphological and compositional features are expected to significantly contribute to the enhanced electrical conductivity, improved charge-transfer behavior, and superior electrocatalytic performance observed in subsequent electrochemical studies.

3.4. Electrocatalysis of (MnO₂-co-PPy) hybrid material towards HPRR

The electrocatalytic activity of the MnO₂-co-PPy hybrid electrode

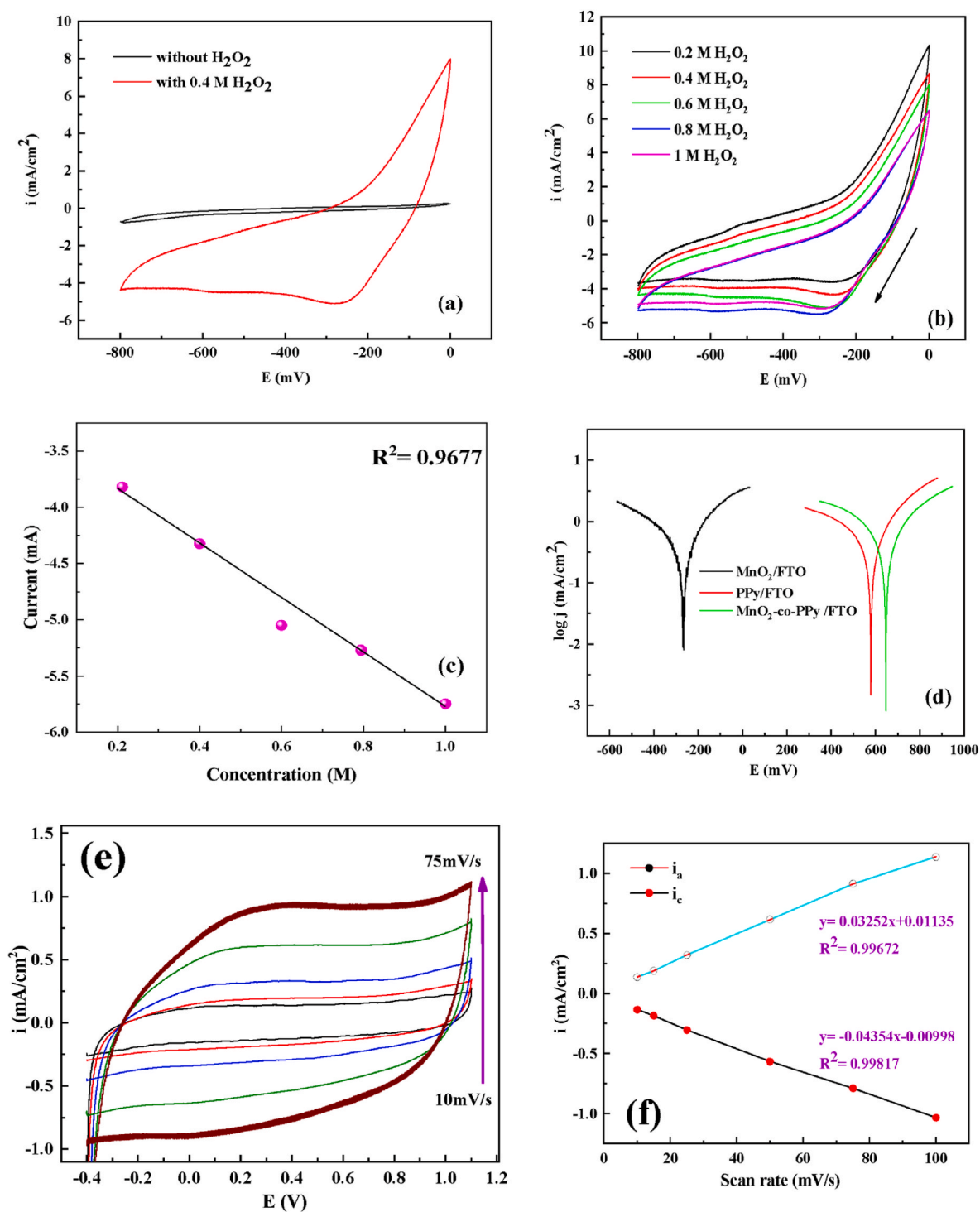


Fig. 5. (a) Cyclic voltammograms of the MnO₂-co-PPy/FTO electrode in 1 M NaOH in the absence and presence of H₂O₂; (b) cyclic voltammograms recorded at different H₂O₂ concentrations; (c) calibration plot of cathodic current density as a function of H₂O₂ concentration; (d) Tafel plots of MnO₂/FTO, PPy/FTO, and MnO₂-co-PPy/FTO electrodes; (e) cyclic voltammograms of MnO₂-co-PPy/FTO at different scan rates; and (f) variation of peak current with scan rate.

toward the hydrogen peroxide reduction reaction (HPRR) was investigated by cyclic voltammetry (CV). Measurements were carried out in 1 M NaOH solution in the absence and presence of hydrogen peroxide, at a scan rate of 25 mV s⁻¹, within the potential window from -800 to 0 mV vs SCE. The corresponding voltammetric responses are shown in Fig. 5.

Fig. 5a illustrates the electrochemical behavior of the MnO₂-co-PPy electrode in alkaline medium without H₂O₂. In the absence of hydrogen peroxide, no distinct cathodic peaks or faradaic responses are observed within the investigated potential range, indicating that the hybrid electrode remains electrochemically inactive toward background reactions under these conditions. This behavior confirms that the observed currents in the presence of H₂O₂ arise predominantly from peroxide reduction rather than from capacitive or parasitic processes. Upon the addition of 0.4 M H₂O₂ and 1 M NaOH, the alkaline electrolyte, a pronounced cathodic response appears, characterized by a well-defined reduction peak centered at approximately -300 mV vs SCE. This cathodic feature corresponds to the electrochemical reduction of hydrogen peroxide in an alkaline medium:



The emergence of this peak clearly demonstrates the electrocatalytic activity of the MnO₂-co-PPy electrode toward HPRR. The relatively low overpotential and the pronounced cathodic response indicate a favorable electrochemical response under the investigated conditions.

Fig. 5b presents the cyclic voltammetric responses of the MnO₂-co-PPy electrode at various hydrogen peroxide concentrations ranging from 0.2 to 1 M in 1 M NaOH solution. As the H₂O₂ concentration increases, the cathodic peak current density increases progressively, while the peak potential exhibits only a minor shift. This behavior indicates that the cathodic response is strongly dependent on H₂O₂ concentration and reflects the combined influence of interfacial electron transfer and reactant availability at the electrode surface. The approximately linear increase in cathodic current with increasing H₂O₂ concentration demonstrates a concentration-dependent electrochemical response of the hybrid electrode under the investigated conditions.

The enhanced electrocatalytic performance of the MnO₂-co-PPy electrode can be rationalized by considering the complementary roles of its two components. MnO₂ provides active redox centers associated with Mn⁴⁺/Mn³⁺ transitions, which facilitate the adsorption and activation of hydrogen peroxide molecules. Meanwhile, the PPy network ensures efficient electron transport and reduces charge-transfer resistance, enabling rapid electron delivery to the MnO₂ active sites. In alkaline medium, surface MnOOH species are believed to act as key intermediates, promoting the catalytic reduction of H₂O₂ through a surface-mediated electron-transfer mechanism [29,52–54].

Among the tested conditions, the MnO₂-co-PPy electrode exhibits the highest catalytic activity in 1 M NaOH containing 1 M H₂O₂, as evidenced by the maximum cathodic current density observed under these conditions. This condition produced the highest cathodic current density among the investigated H₂O₂ concentrations. The increase in cathodic current with H₂O₂ concentration indicates that reactant concentration strongly influences the measured HPRR response under the investigated conditions.

Overall, the cyclic voltammetry results demonstrate that the MnO₂-co-PPy hybrid electrode exhibits strong and concentration-dependent electrocatalytic activity toward hydrogen peroxide reduction in alkaline media. The absence of a faradaic response without H₂O₂, combined with the pronounced and tunable cathodic currents upon peroxide addition, supports the assignment of the observed cathodic response predominantly to H₂O₂ reduction under the investigated conditions. These findings are consistent with previous reports on MnO₂-based and polymer-modified electrodes and further highlight the advantages of polymer-oxide hybridization for peroxide electrocatalysis [29,52–54]. The cathodic current response increased progressively with increasing H₂O₂ concentration over the range of 0.2 to 1.0 M, exhibiting

a linear correlation with a coefficient of determination of R² = 0.9677. This concentration-dependent response confirms the sensitivity of the MnO₂-co-PPy/FTO electrode toward H₂O₂ under the investigated alkaline conditions. Fig. 5d presents the Tafel plots obtained for the MnO₂/FTO, PPy/FTO, and MnO₂-co-PPy/FTO electrodes. The calculated Tafel slopes were -266.37 mV dec⁻¹ for MnO₂, 578.4 mV dec⁻¹ for PPy, and 637.36 mV dec⁻¹ for MnO₂-co-PPy, respectively. The polarization curves of the hybrid electrode also exhibit a shift toward higher current densities, indicating an enhanced electrochemical response compared with the individual components. The Tafel slopes should be interpreted cautiously in terms of intrinsic reaction kinetics.

The MnO₂-co-PPy electrode exhibits a higher Tafel slope (637.36 mV dec⁻¹) than pristine MnO₂ (-266.37 mV dec⁻¹). Therefore, the present Tafel analysis does not support a conclusion of improved intrinsic kinetic parameters for the hybrid electrode. Rather, the higher cathodic current density observed for MnO₂-co-PPy/FTO indicates an enhanced overall electrochemical response under the investigated conditions. This behavior is more appropriately attributed to the combined effects of the redox-active MnO₂ phase and the conductive PPy matrix, which can improve electrical transport and interfacial charge-transfer characteristics. These interpretations are further supported by the EIS and conductivity measurements discussed below. Fig. 5e shows the cyclic voltammograms of the MnO₂-co-PPy/FTO electrode recorded at different scan rates. As the scan rate increases, the anodic peak current increases and the anodic peak potential shifts toward more positive values.

In contrast, the cathodic peak current varies with the scan rate, indicating the influence of mass transport and interfacial electron-transfer processes on the electrochemical response. The observed scan-rate dependence alone should not be described as definitive evidence of diffusion-controlled behavior unless the corresponding quantitative relationship and regression analysis are provided. The electrochemical surface area (ECSA) of the MnO₂-co-PPy/FTO electrode was estimated from the electrochemical double-layer capacitance according to Equation (7):

$$\text{ECSA} = \frac{C_{dl}}{C_s} \quad (7)$$

where C_{dl} is the electrochemical double-layer capacitance obtained from the slope of the linear relationship between the capacitive current density and scan rate in the non-faradaic potential region, and C_s is the specific capacitance of an ideally smooth reference surface. Following the value adopted in the literature for manganese oxide-based electrodes, C_s = 0.040 mF cm⁻² was used, within the commonly reported range of 0.035–0.040 mF cm⁻². Based on the experimentally determined C_{dl}, the ECSA of the MnO₂-co-PPy/FTO electrode was estimated to be 266.75 cm². Table 1 compares the electrochemical characteristics of the MnO₂-co-PPy/FTO electrode with selected electrodes reported in the literature [55–58]. The comparison indicates that the present hybrid electrode exhibits a competitive electrochemical response toward H₂O₂ reduction under the investigated conditions.

Because the reported studies differ in reaction type, electrode

Table 1

Comparison of selected electrochemical characteristics of MnO₂-PPy and related electrodes reported in the literature.

Electrodes	Onset potential (V)	Peak potential (V)	Current density (mA cm ⁻²)	Ref
PPy MnO ₂ -NWs@Ni-NPs/C	-0.08	-0.09	0.365	[55]
M-PPy240/G	0.9	0.714	/	[56]
PPy/MnO ₂ /ITO	1.4	-0.369	-0.9	[57]
MnO ₂ /GO	-0.68	0.75	-4.3	[58]
PPy-co-MnO ₂ /FTO	-0.27	-0.3	-5.3	Present study

configuration, electrolyte composition, potential reference, and experimental conditions, the values are provided for contextual comparison rather than as a strict one-to-one ranking of HPRR activity.

3.4.1. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy was employed to gain deeper insight into the charge-transfer and mass-transport properties of MnO_2/FTO and $\text{MnO}_2\text{-co-PPy}/\text{FTO}$ electrodes under hydrogen peroxide reduction conditions. The impedance measurements were performed in an electrolyte containing 1 M NaOH and 0.4 M H_2O_2 , over a frequency range from 100 kHz to 10 mHz, using a sinusoidal perturbation amplitude of 10 mV. The resulting Nyquist plots are shown in Fig. 6a. Both impedance spectra exhibit a characteristic semicircle in the high-frequency region, followed by a linear tail in the low-frequency region. The high-frequency semicircle is associated with the charge-transfer resistance (R_{ct}) at the electrode-electrolyte interface in parallel with the double-layer capacitance.

In contrast, the low-frequency linear segment corresponds to diffusion-controlled processes related to ion and reactant transport within the porous electrode structure and the electrolyte [28,36]. A clear distinction between the two electrodes is observed in the diameter of the semicircle. The $\text{MnO}_2\text{-co-PPy}/\text{FTO}$ electrode displays a significantly smaller semicircle compared with the pristine MnO_2/FTO electrode, indicating a substantial reduction in charge-transfer resistance upon incorporation of the conducting polymer. This decrease in R_{ct} indicates improved interfacial charge-transfer characteristics, which can be attributed to the formation of an efficient electronic percolation network provided by the PPy matrix and is consistent with improved electrical connectivity within the hybrid electrode.

The lower apparent charge-transfer resistance of the hybrid electrode is consistent with improved interfacial charge transport following incorporation of PPy. In addition, the more vertical low-frequency line observed for the $\text{MnO}_2\text{-co-PPy}$ electrode suggests improved ion diffusion and a more capacitive behavior, which is consistent with the hierarchical porous morphology observed in SEM analysis and the increased electroactive surface area of the hybrid system. To further corroborate the enhancement in electrical conductivity induced by polymer incorporation, direct conductivity measurements were performed using a four-point probe method, as shown in Fig. 6b. The electrical conductivity of the MnO_2/FTO electrode was determined to be 0.254 S cm^{-1} , whereas the $\text{MnO}_2\text{-co-PPy}/\text{FTO}$ hybrid electrode exhibited a significantly higher conductivity of 0.368 S cm^{-1} . This increase in conductivity is consistent with a beneficial contribution of the PPy phase to electron transport within the hybrid electrode.

Notably, the conductivity value obtained for the $\text{MnO}_2\text{-co-PPy}$ hybrid electrode exceeds that reported for pure polypyrrole in similar systems, highlighting the synergistic effect arising from the intimate interaction between MnO_2 and PPy [59]. The combined EIS and four-point probe results demonstrate that the incorporation of PPy not

only lowers the charge-transfer resistance but also improves the overall electrical conductivity of the electrode, thereby directly contributing to the enhanced electrocatalytic performance observed for hydrogen peroxide reduction.

Overall, the EIS analysis provides strong evidence that the $\text{MnO}_2\text{-co-PPy}$ hybrid electrode possesses superior interfacial charge-transfer characteristics and improved electron-transport properties compared with pristine MnO_2 . These features are essential for efficient hydrogen peroxide reduction and further validate the effectiveness of the polymer-oxide hybridization strategy for developing high-performance cathode materials.

3.5. Cathodic charging test

The cathodic charging behavior of the $\text{MnO}_2\text{-co-PPy}$ hybrid electrode was investigated in an alkaline electrolyte, as shown in Fig. 7. This test was performed to evaluate the dynamic electrochemical response, polarization behavior, and reversibility of the electrode under cathodic operating conditions relevant to hydrogen peroxide reduction [60].

At the beginning of the experiment, the electrode exhibits a stable open-circuit potential of approximately 0.4 V vs SCE, which remains constant for about 25 s, indicating good thermodynamic stability of the $\text{MnO}_2\text{-co-PPy}$ interface in the alkaline peroxide medium. Upon application of the cathodic polarization (ON state), a sharp drop in potential is observed, reflecting the rapid activation of cathodic processes and the

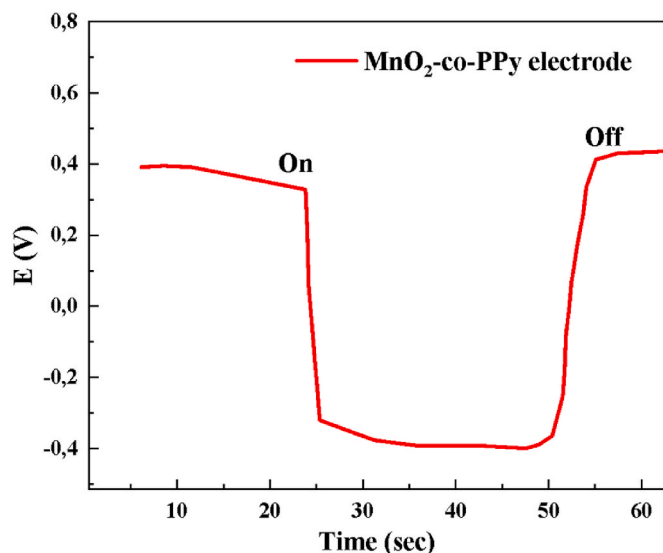


Fig. 7. Cathodic charging curves in 1 M NaOH+0.4 M H_2O_2 solution.

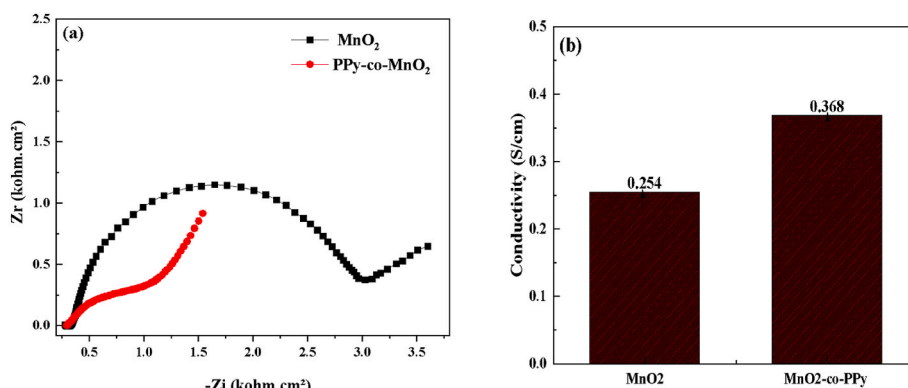


Fig. 6. (a): Nyquist diagrams corresponding to MnO_2 and $\text{MnO}_2\text{-co-PPy}$ composite in 1 M NaOH+0.4 M H_2O_2 (b) Conductivity of MnO_2 and $\text{MnO}_2\text{-co-PPy}$ electrodes.

onset of hydrogen peroxide reduction at the electrode surface. This sudden potential decrease is characteristic of efficient charge transfer and fast electron injection into redox-active MnO_2 sites facilitated by the conductive PPy matrix. Following the initial polarization, the potential gradually decreases and reaches a quasi-steady value around -0.4 V vs SCE. This stabilization indicates the establishment of a steady-state regime in which the rate of electron transfer is balanced by mass transport of H_2O_2 and hydroxide ions within the porous hybrid electrode. The absence of pronounced potential oscillations or drift during this stage suggests good electrochemical stability and effective buffering of charge within the MnO_2 -co-PPy architecture. When the cathodic polarization is switched off (OFF state), the electrode potential rapidly returns toward its initial value, stabilizing again near 0.4 V vs SCE within approximately 50 s. This rapid and nearly complete recovery of the open-circuit potential demonstrates the reversible electrochemical behavior of the hybrid electrode and indicates minimal irreversible degradation during the cathodic charging process. The observed cathodic charging–discharging profile reflects the synergistic contribution of MnO_2 and PPy. MnO_2 provides redox-active centers capable of reversible $\text{Mn}^{4+}/\text{Mn}^{3+}$ transitions, while the PPy network ensures efficient electron transport and charge accommodation. This combination results in rapid polarization, stable operation under load, and fast recovery upon release, all of which are essential characteristics for cathode materials in hydrogen peroxide-based fuel cell systems. Overall, the cathodic charging test confirms that the MnO_2 -co-PPy hybrid electrode exhibits stable, reversible, and efficient electrochemical behavior under alkaline peroxide conditions, further supporting its suitability as a robust cathode material for HPRR applications [60].

3.6. Test of stability of the MnO_2 -co-PPy

The electrochemical stability of the MnO_2 -co-PPy hybrid electrode toward the hydrogen peroxide reduction reaction (HPRR) was evaluated by chronoamperometry under constant cathodic polarization. The experiment was conducted in an alkaline electrolyte containing H_2O_2 , and the applied cathodic potential was selected within the electrochemically active region based on the open-circuit potential (OCP) and the cathodic peak potential identified from cyclic voltammetry. The chronoamperometric measurement was extended to 5 h, as shown in Fig. 8. A pronounced initial decrease in current was observed during the first few seconds following the application of the cathodic potential. This initial transient can be associated with electrochemical double-layer charging and the establishment of a quasi-steady interfacial state

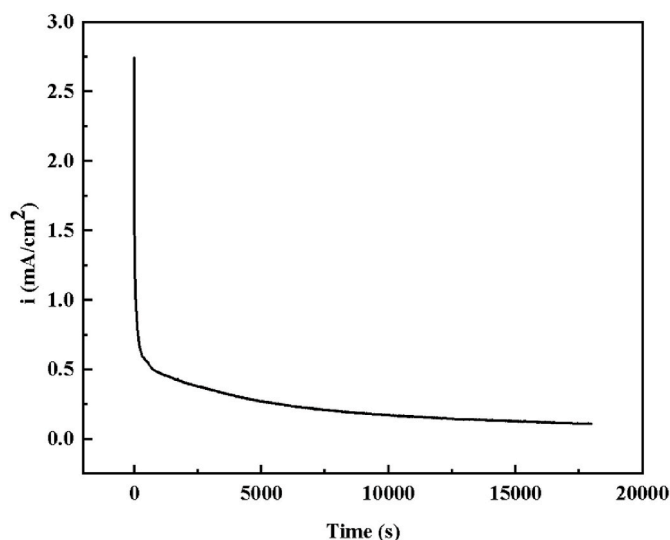


Fig. 8. Current-time transient for the reduction of H_2O_2 on the MnO_2 -co-PPy.

involving reactant adsorption and surface redox processes. Following this initial decrease, the current exhibited a more gradual decay and approached a quasi-steady-state response during the subsequent polarization period. This behavior indicates that the MnO_2 -co-PPy electrode maintained its electrochemical response over the 5 h measurement under the investigated conditions. The sustained response can be attributed, at least in part, to the complementary functions of the two components: MnO_2 provides redox-active sites associated with $\text{Mn}^{4+}/\text{Mn}^{3+}$ transitions, while the conductive PPy matrix provides an interconnected pathway for electronic transport and promotes intimate contact between the oxide phase and the electrode surface.

Importantly, no abrupt loss of current or pronounced oscillatory behavior was observed during the chronoamperometric measurement, including at the most negative applied potential. This behavior indicates that the MnO_2 -co-PPy hybrid electrode maintained a relatively stable electrochemical response during the 5 h polarization period under the investigated conditions. However, chronoamperometry alone cannot establish the absence of passivation, dissolution, or mechanical degradation. Nevertheless, the sustained current response without pronounced deactivation suggests satisfactory electrochemical durability of the hybrid electrode under the tested alkaline peroxide conditions.

Overall, the chronoamperometric results demonstrate that the MnO_2 -co-PPy/FTO electrode maintains a stable electrochemical response during prolonged cathodic polarization toward HPRR. The relatively gradual current decay following the initial transient and the absence of abrupt deactivation over 5 h support the operational stability of the electrode under the investigated conditions. These results highlight the potential of the MnO_2 -co-PPy hybrid architecture as a candidate cathode material for hydrogen peroxide-based electrochemical energy-conversion systems. However, longer-term testing and post-electrochemical structural characterization would be required to establish its durability under practical operating conditions [36].

3.7. Computational results

The calculated adsorption energies presented in Table 2 indicate that both polypyrrole (PPy) and its perchlorate-doped derivative, $\text{PPy}\cdot\text{ClO}_4^-$, interact favorably with the MnO_2 surface. The $\text{PPy}@ \text{MnO}_2$ system exhibits an adsorption energy of -0.2140 Ha (-5.824 eV), whereas the $\text{PPy}\cdot\text{ClO}_4^-@ \text{MnO}_2$ complex shows a less negative adsorption energy of -0.1042 Ha (-2.838 eV). Thus, within the adopted computational model and reference states, $\text{PPy}@ \text{MnO}_2$ is approximately 0.1098 Ha (2.99 eV) more strongly stabilized upon adsorption than $\text{PPy}\cdot\text{ClO}_4^-@ \text{MnO}_2$. This difference suggests that incorporation of the ClO_4^- counterion modifies the interfacial interaction and reduces the net adsorption stabilization relative to the undoped PPy system. The weaker adsorption of the doped derivative may arise from changes in charge distribution, electrostatic interactions, and the availability of the PPy π -electron system for interaction with the MnO_2 surface.

Upon adsorption, the MnO_2 surface and PPy framework undergo modest structural rearrangements, including slight elongation of Mn–O bonds in the interfacial region ($\Delta r \approx 0.03$ Å) and minor distortion of the PPy backbone. These changes are consistent with the formation of interfacial interactions involving the nitrogen atoms of PPy and surface oxygen sites of MnO_2 , together with possible π -d interactions between

Table 2
Energetic stability and adsorption behavior.

System	Total energy (Ha)	Adsorption energy (Ha (eV))
MnO_2	−4086.9568	—
PPy	−2507.6080	—
PPy^+	−2506.812718	—
$\text{PPy}\cdot\text{ClO}_4^-$	−3268.4014	—
$\text{PPy}@ \text{MnO}_2$	−6594.7913	−0.2140 (−5.824)
$\text{PPy}\cdot\text{ClO}_4^-@ \text{MnO}_2$	−7355.4626	−0.1042 (−2.838)

the conjugated PPy backbone and the MnO₂ surface [61,62]. However, assignment of these interactions specifically as hydrogen bonding or strong orbital coupling should ideally be supported by additional analyses, such as charge-density-difference, charge-transfer, or PDOS calculations. The progressive decrease of the frontier-orbital gap (Table 3), from 1.875 eV for isolated PPy to 0.018 eV for PPy@MnO₂ and approximately 0.014 eV for PPy·ClO₄[−]@MnO₂, indicates increased frontier-orbital accessibility and enhanced electronic coupling upon formation of the polymer–oxide interface. The MnO₂ cluster exhibits a very small calculated frontier-orbital gap (0.033 eV), indicating closely spaced frontier states within the adopted cluster model. Orbital interactions between the π -conjugated PPy states and the Mn-3d/O-2p states of MnO₂ further modify the interfacial electronic structure. [63]. The doped complex exhibits the smallest calculated frontier-orbital gap, which can be associated with the modified charge distribution and electronic structure of oxidized PPy upon incorporation of the ClO₄[−] counterion.

This charge compensation can promote polaronic or bipolaronic electronic states and modify the electronic coupling between PPy and MnO₂. The electron-density difference maps ($\Delta\rho$) reveal electron accumulation around the Mn and O atoms (red regions in Fig. 9) at the interface and depletion on the polymer backbone, confirming a net charge flow from PPy toward MnO₂ [63].

The magnitude of transfer increases from 0.16 e[−] in PPy@MnO₂ to 0.22 e[−] in the doped complex (Table 4), clearly evidencing stronger interfacial polarization. The ClO₄[−] group exerts a strong electron-withdrawing field, which further enhances the alignment of the PPy Fermi level with that of MnO₂, producing a more strongly polarized electronic interface.

Projected DOS analysis (Fig. 10) shows that for both hybrid systems, the valence-band maximum and conduction-band minimum are primarily composed of Mn-3d and O-2p orbitals with notable contributions from PPy's N-2p states. In PPy⁺·ClO₄[−]@MnO₂, additional occupied states appear near the Fermi energy (−4.2 eV), bridging the polymer and the oxide bands and confirming enhanced electronic coupling. Spin-density plots indicate partial localization of unpaired electrons on Mn atoms adjacent to the adsorption sites, while the doped complex displays more delocalized spin density across the polymer chain—characteristic of polaronic conduction [63].

This redistribution of spin density suggests the development of a mixed-valence electronic environment involving Mn⁴⁺/Mn³⁺ centers, which may facilitate redox transitions at the PPy/MnO₂ interface. The PPy·ClO₄[−]@MnO₂ complex exhibits a very small frontier-orbital gap (approximately 0.014 eV) and a larger calculated charge transfer (0.22 e[−]) than PPy@MnO₂ (0.16 e[−]), indicating enhanced interfacial polarization and electronic coupling in the presence of the ClO₄[−] dopant. However, the adsorption-energy results show that PPy@MnO₂ is more strongly stabilized overall, with an adsorption energy of −0.2140 Ha (−5.824 eV), compared with −0.1042 Ha (−2.838 eV) for PPy·ClO₄[−]@MnO₂. Thus, ClO₄[−] doping should not be interpreted as strengthening the overall adsorption energetics. Rather, the dopant modifies the electronic structure and local interfacial interactions, promoting charge redistribution and additional hydrogen-bonding and electrostatic contacts at the polymer–oxide interface. The reduced frontier-orbital gap and enhanced charge transfer obtained for the doped

complex are consistent with stronger electronic polarization and orbital interaction. However, they should not be regarded alone as direct evidence of increased bulk electrical conductivity or faster electron-transfer kinetics. The ClO₄[−] counterion can also stabilize the oxidized, charge-compensated form of PPy and modify its electronic interaction with MnO₂. Taken together, the DFT, charge-density, PDOS, and AIM results provide a molecular-level interpretation of the electronic coupling and interfacial charge redistribution within the PPy/MnO₂ hybrid. These computational findings complement the experimental evidence of enhanced conductivity and reduced charge-transfer resistance and support the role of PPy in improving the electrochemical response of the MnO₂-based electrode [63].

3.7.1. Atoms-in-molecules (AIM) topological analysis

The topological analysis of the electron density was performed according to Bader's Atoms-in-Molecules (AIM) theory to elucidate the nature of the interfacial interactions in PPy@MnO₂ and PPy·ClO₄[−]@MnO₂ (see Fig. 11). The main AIM descriptors—including electron density at the bond critical point (ρ_{BCP}), Laplacian of the electron density ($\nabla^2\rho$), kinetic and potential energy densities (G and V), total energy density ($H = G + V$), and the ratio $|V|/G$ —are summarized in Table 5.

These parameters allow the identification of the bonding type: $|V|/G < 1$ corresponds to *closed-shell (electrostatic or hydrogen-bond)* interactions, whereas $|V|/G > 1$ suggests *partial covalent character* with appreciable electron sharing.

a. PPy@MnO₂ complex

In the undoped PPy@MnO₂ interface, seven relevant BCPs were identified, corresponding mainly to O···H, O···C, N···O, Mn···N, and O···C contacts.

- The strongest interaction appears for O(134)···H(53) with $\rho_{\text{BCP}} = 0.044 \text{ e } \text{\AA}^{-3}$, $H = -0.021 \text{ Ha } \text{\AA}^{-3}$, and $|V|/G = 1.14$, typical of a moderate hydrogen bond possessing partial covalent character.
- The O(130)···H(49) contact ($\rho = 0.009 \text{ e } \text{\AA}^{-3}$, $|V|/G = 0.74$) represents a weaker closed-shell hydrogen bond, dominated by electrostatic attraction.
- The O(128)···C(42) and O(104)···C(40) bonds show ρ values around 0.009–0.012 e $\text{\AA}^{-3}$ with $|V|/G \approx 0.76$ –0.83, indicating weak O···C van der Waals-type interactions between the polymer backbone and surface oxygen atoms.
- The N(52)···O(129) and Mn(124)···N(44) interfacial interactions ($\rho \approx 0.008 \text{ e } \text{\AA}^{-3}$, $|V|/G \approx 0.76$ –0.87) display small negative $H(r)$, characteristic of closed-shell donor–acceptor (coordination) interactions that electrostatically tether the polymer to the MnO₂ surface.
- Finally, the O(108)···C(34) BCP ($\rho = 0.002 \text{ e } \text{\AA}^{-3}$, $|V|/G = 0.62$) corresponds to a very weak dispersive contact.

Overall, the bonding in PPy@MnO₂ is dominated by weak electrostatic and hydrogen-bonding interactions, with limited charge delocalization. The absence of strong covalent components ($|V|/G > 1.2$) indicates that the interface is predominantly stabilized by closed-shell interactions, including electrostatic and hydrogen-bonding contributions, with limited regions exhibiting partial covalent character.

b. PPy·ClO₄[−]@MnO₂ complex

The introduction of the ClO₄[−] dopant modifies the interfacial topology, yielding new BCPs and an overall increase in the variety and strength of non-covalent interactions.

- The O(120)···O(102) contact ($\rho = 3.99 \times 10^{-4} \text{ e } \text{\AA}^{-3}$, $|V|/G = 0.53$) represents a weak O···O electrostatic interaction between the oxide

Table 3
Frontier molecular orbitals and electronic gaps.

System	HOMO (eV)	LUMO (eV)	$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ (eV)
PPy	−3.318	−1.443	1.875
PPy ⁺	−3.798	−3.705	0.093
PPy ⁺ ·ClO ₄ [−]	−3.845	−3.698	0.147
MnO ₂	−5.169	−5.136	0.033
PPy@MnO ₂	−3.998	−3.980	0.018
PPy ⁺ ·ClO ₄ [−] @MnO ₂	−4.228/ −4.244	−4.214/ −4.206	≈ 0.014

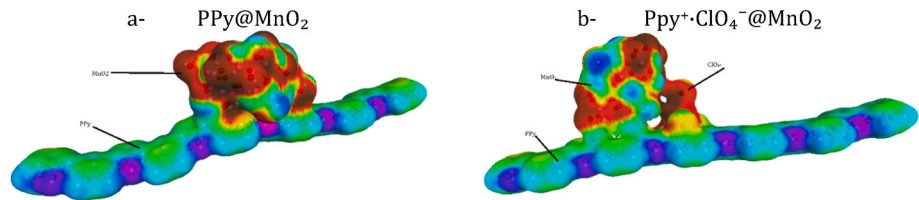


Fig. 9. Electron density distribution.

Table 4
Charge-transfer and interfacial electronic coupling.

System	Δq (Polymer $\rightarrow$ MnO_2) (e^-)	Dominant interacting orbitals	Nature of interaction
PPy@ MnO_2	+0.16	N(2p), C(2p) $\rightarrow$ Mn(3d)	Covalent + π -d coupling
PPy $^+\cdot\text{ClO}_4^-$ @ MnO_2	+0.22	N(2p), O(2p) $\rightarrow$ Mn(3d)	Covalent + electrostatic + π -d hybridization

lattice oxygen (O120) and the anionic oxygen of ClO_4^- (O102). Despite its low electron density, this contact is crucial because it provides an electrostatic bridge linking the dopant anion to the MnO_2 surface.

- The H(45)···O(101) contact exhibits the highest electron density among the identified BCPs and a $|V|/G$ ratio above unity, indicating a relatively strong interaction with appreciable shared-electron character.

- Two additional hydrogen bonds, O(100)···H(51) ($\rho = 0.017 \text{ e } \text{\AA}^{-3}$, $|V|/G = 0.81$) and H(41)···O(101) ($\rho = 0.024 \text{ e } \text{\AA}^{-3}$, $|V|/G = 0.92$), display moderately negative H values, confirming their closed-shell but stabilizing nature.
- The O(103)···C(42) interaction ($\rho = 0.018 \text{ e } \text{\AA}^{-3}$, $|V|/G = 0.88$) corresponds to a weak polar contact between the dopant oxygen and the polymer chain, while N(28)···O(125) ($\rho = 0.004 \text{ e } \text{\AA}^{-3}$, $|V|/G = 0.67$) represents a minor donor-acceptor coupling.
- The remaining O(103)···H(156) contact has extremely low $\rho = 7.0 \times 10^{-5} \text{ e } \text{\AA}^{-3}$, confirming an insignificant dispersive interaction.

The increase in both the number and the strength of hydrogen-bond interactions (ρ up to $0.059 \text{ e } \text{\AA}^{-3}$, $|V|/G \approx 1.3$) demonstrates that ClO_4^- doping significantly enhances the interfacial cohesion through multiple complementary weak interactions. These contacts create a more polarized environment that facilitates charge redistribution across the polymer-oxide boundary.

c. Comparative interpretation

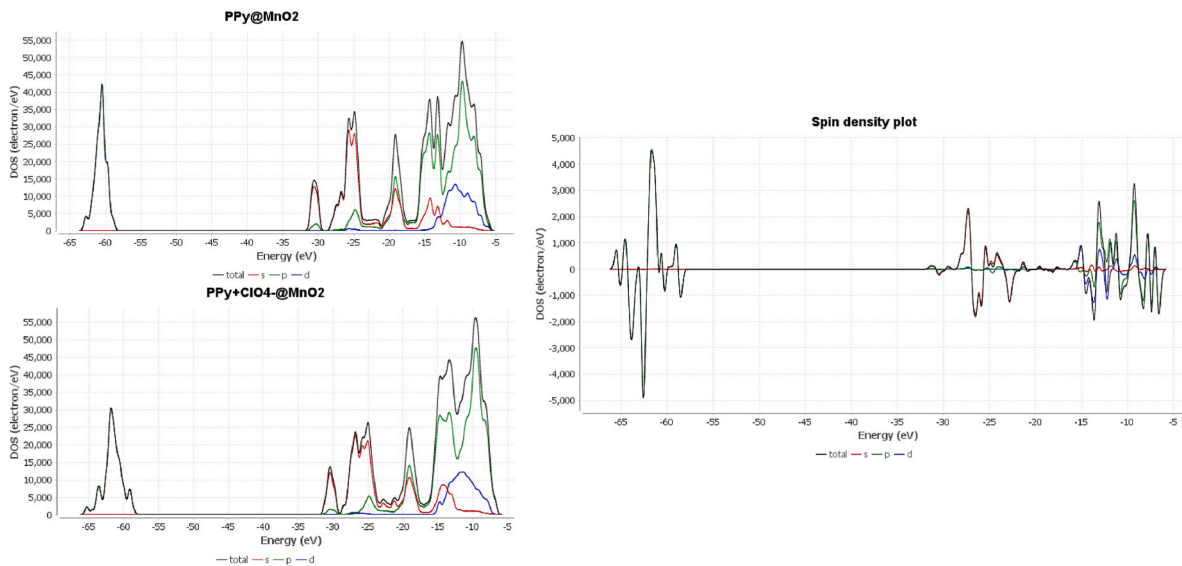


Fig. 10. Density of states.

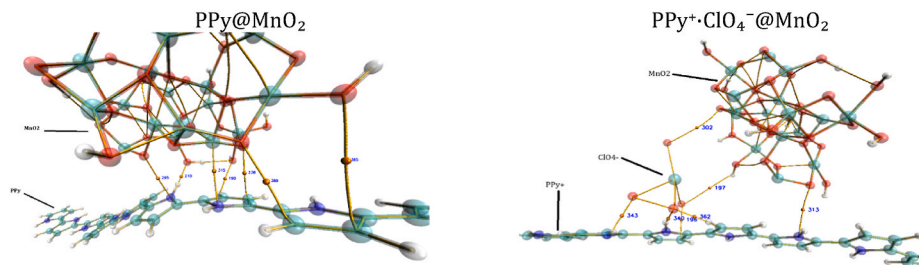


Fig. 11. AIM analysis of the PPy@ MnO_2 and PPy· ClO_4^- @ MnO_2 complexes.

Table 5AIM parameters at selected BCPs for PPy@MnO₂ and PPy-ClO₄@MnO₂(Energies in Ha).

PPy@MnO ₂								
BCP N°	CONNECTED ATOMS	$\rho(r)$	laplacian	G	V	E _{HB}	H = G + V	V /G
190	130(O) – 49(H)	9.35E-03	3.80E-02	7.52E-03	–5.55E-03	–2.77E-03	1.98E-03	0.74
210	134(O) – 53(H)	4.44E-02	1.31E-01	3.78E-02	–4.29E-02	–2.14E-02	–5.13E-03	1.14
238	128(O) – 42(C)	1.19E-02	3.77E-02	8.08E-03	–6.73E-03	–3.37E-03	1.35E-03	0.83
295	52(N) – 129(O)	7.98E-03	2.68E-02	5.39E-03	–4.07E-03	–2.03E-03	1.32E-03	0.76
315	124(Mn) – 44(N)	7.93E-03	1.68E-02	3.71E-03	–3.21E-03	–1.61E-03	4.98E-04	0.87
385	108(O) – 34(C)	2.43E-03	8.59E-03	1.56E-03	–9.68E-04	–4.84E-04	5.90E-04	0.62
389	104(O) – 40(C)	8.81E-03	3.05E-02	6.16E-03	–4.70E-03	–2.35E-03	1.46E-03	0.76
PPy + ClO ₄ @MnO ₂								
196	103(O) – 42(C)	1.85E-02	6.57E-02	1.47E-02	–1.29E-02	–6.44E-03	1.77E-03	0.879
197	103(O) – 156(H)	7.05E-05	5.28E-04	8.83E-05	–4.47E-05	–2.23E-05	4.36E-05	0.506
302	120(O) – 102(O)	3.99E-04	1.72E-03	2.93E-04	–1.56E-04	–7.78E-05	1.37E-04	0.532
313	28(N) – 125(O)	4.42E-03	1.63E-02	3.06E-03	–2.04E-03	–1.02E-03	1.02E-03	0.668
340	45(H) – 101(O)	5.91E-02	1.38E-01	4.87E-02	–6.29E-02	–3.15E-02	–1.42E-02	1.293
343	100(O) – 51(H)	1.72E-02	7.46E-02	1.57E-02	–1.28E-02	–6.39E-03	2.94E-03	0.813
362	41(H) – 101(O)	2.41E-02	8.80E-02	2.04E-02	–1.89E-02	–9.43E-03	1.57E-03	0.923

The AIM descriptors indicate that ClO₄[−] doping modifies the nature and distribution of the interfacial interactions in the PPy/MnO₂ system. In the undoped PPy@MnO₂ complex, the highest electron density at a bond critical point (ρ_{BCP}) is 0.044 e Å^{−3}, whereas the doped PPy-ClO₄@MnO₂ complex exhibits a higher maximum value of 0.059 e Å^{−3}. Several BCPs in the doped system also exhibit |V|/G values below unity, consistent with predominantly closed-shell interactions involving electrostatic and hydrogen-bonding contributions. The O(120)⋯O(102) contact represents an additional weak closed-shell interaction between the oxide surface and the perchlorate oxygen. Although its electron density is low, its presence indicates a local electrostatic association between the dopant and the oxide interface. Together with the H⋯O contacts identified in the doped complex, these interactions indicate enhanced local polarization and charge redistribution at the polymer–oxide interface [63]. These AIM features should, however, be distinguished from the overall adsorption energetics. The calculated adsorption energy is −5.824 eV for PPy@MnO₂, compared with −2.838 eV for PPy-ClO₄@MnO₂, indicating that the undoped PPy system is more strongly stabilized in terms of the overall adsorption energy.

In contrast, the doped complex exhibits a smaller frontier-orbital gap (~0.014 eV) and greater calculated charge transfer (0.22 e[−] versus 0.16 e[−]), suggesting enhanced electronic polarization and interfacial electronic coupling induced by the presence of ClO₄[−]. Therefore, the AIM results support the conclusion that ClO₄[−] doping modifies and locally strengthens specific interfacial interactions, rather than increasing the overall adsorption strength. This distinction provides a more consistent molecular-level interpretation of the electronic interactions within the PPy-ClO₄@MnO₂ hybrid.

d. Linking AIM with $\Delta\rho$ and PDOS.

The AIM descriptors delineate a transition from predominantly weak, closed-shell contacts in PPy@MnO₂ to a denser network of hydrogen bonds and an electrostatic O(120)⋯O(102) bridge in PPy-ClO₄@MnO₂. This topological shift matches the $\Delta\rho$ maps, which show systematic electron depletion on the PPy π -backbone and accumulation on the Mn–O lattice, particularly in the vicinity of O(102) and adjacent oxide oxygens. In the doped interface, BCPs with higher ρ and more negative H (e.g., H(45)⋯O(101), $\rho \approx 0.059$ e Å^{−3}, |V|/G ≈ 1.29) coincide with stronger positive $\Delta\rho$ isosurfaces on the oxide side, evidencing tighter electrostatic anchoring and limited electron sharing consistent with |V|/G $\lesssim 1$ –1.3. The O(120)⋯O(102) contact, although weak in ρ , provides a directional electrostatic conduit that stabilizes the ClO₄[−] orientation and funnels charge redistribution across the boundary. Correspondingly, the PDOS reveals enhanced mixing between Mn-3d/O-2p states and PPy N-2p/C-2p states near the frontier-energy region for the doped system, together with an increased density of occupied states

near the Fermi level. These features are consistent with enhanced electronic polarization and orbital mixing at the PPy/MnO₂ interface. Importantly, however, the overall adsorption energy remains more negative for PPy@MnO₂, indicating stronger net adsorption stabilization in the undoped system. The AIM, $\Delta\rho$, and PDOS results therefore suggest that ClO₄[−] doping primarily modifies the local electronic structure and specific interfacial interactions rather than increasing the overall adsorption strength.

4. Conclusion

In this study, a MnO₂–polypyrrole (PPy) hybrid electrode was successfully prepared by electrochemical co-deposition onto fluorine-doped tin oxide (FTO) and evaluated as a cathode for the hydrogen peroxide reduction reaction (HPRR) in alkaline medium. XRD, FTIR, and SEM-EDX characterization confirmed the incorporation of MnO₂ within the PPy matrix and revealed a modified structural and morphological organization of the oxide phase following co-deposition. Electrochemical measurements demonstrated that the MnO₂–co-PPy/FTO electrode exhibits an enhanced cathodic response toward H₂O₂ reduction compared with pristine MnO₂. The cathodic current increased with increasing H₂O₂ concentration over the investigated range, with a correlation coefficient of $R^2 = 0.9677$. The hybrid electrode also showed a lower charge-transfer resistance and a higher measured electrical conductivity (0.368 S cm^{−1}) than MnO₂ (0.254 S cm^{−1}), highlighting the beneficial contribution of the conductive PPy network to interfacial electron transport. Using the adopted specific capacitance of 0.040 mF cm^{−2}, an apparent ECSA of 266.75 cm² was estimated. Because the calculated value depends on the assumed specific capacitance and the selected non-faradaic potential region, it is used primarily for comparative assessment of electrochemical accessibility. Cathodic charging and chronoamperometric measurements demonstrated a rapid electrochemical response and sustained current under the investigated alkaline peroxide conditions, indicating good operational stability during the tested periods. However, these results should be interpreted as evidence of electrochemical stability under the investigated conditions, rather than definitive proof of the absence of structural or chemical degradation.

The DFT and AIM analyses provided complementary insight into the polymer–oxide interface. The calculations indicate favorable interactions between PPy and MnO₂, while incorporation of the ClO₄[−] dopant modifies the interfacial electronic structure and increases the calculated charge transfer from the polymer toward the MnO₂ phase. The AIM results further indicate that the interface is stabilized by a combination of hydrogen-bonding, electrostatic, and other predominantly closed-shell interactions, with ClO₄[−] doping modifying the local interaction topology and electronic polarization rather than increasing the overall adsorption energy. These calculations help explain the

experimentally observed decrease in charge-transfer resistance and increase in electrical conductivity.

Overall, the results demonstrate that electrochemical co-deposition of MnO₂ and PPy is an effective strategy for constructing conductive polymer-oxide hybrid electrodes with improved electrochemical performance toward alkaline H₂O₂ reduction. The combination of the redox-active MnO₂ phase and the conductive PPy matrix provides a promising platform for the development of low-cost cathode materials for hydrogen peroxide-based electrochemical energy-conversion systems.

CRedit authorship contribution statement

Djamel Eddine Hamza: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Leila Lamiri:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ouafia Belgherbi:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Boussaha Bouchoul:** Formal analysis, Investigation, Validation, Visualization. **Samia Latreche:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Assia Tounsi:** Writing – original draft, Visualization, Validation, Methodology, Investigation. **Mabrouk Khemliche:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Conceptualization. **Mohammed Alamro:** Formal analysis, Validation, Visualization, Writing – review & editing. **Byong-Hun Jeon:** Writing – review & editing, Visualization, Validation, Methodology, Investigation. **Hyun-Jo Ahn:** Visualization, Validation, Investigation. **Yacine Benguerba:** Writing – review & editing, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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