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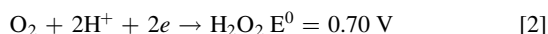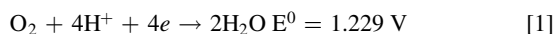[5]*Warsaw University of Technology, Faculty of Chemistry, Warsaw, Poland*

Efficient electrochemical generation of hydrogen peroxide via oxygen reduction is of great interest for industrial and clean energy applications. In this work, we report the application of conducting polymer—polyindole (PIN) films for electrogeneration of hydrogen peroxide. Polyindole films were electrochemically polymerized on gold substrates in non-aqueous electrolytes and then tested for electrocatalytic properties in acidic aqueous solutions. We find that PIN can serve as an electrocatalyst for oxygen reduction reaction via a two-electron pathway. Electrolysis performance indicates that PIN is an efficient, selective, and stable electrocatalyst for hydrogen peroxide generation at low pH, and suggests PIN as a conducting polymer with useful electrocatalytic properties in scientific experiments and applications.
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The oxygen reduction reaction (ORR) is one of the fundamental electrochemical processes playing a key role both in biology (e.g. plant respiration) and in electrochemistry.[1] ORR is extensively studied for its exploitation in energy conversion systems, batteries, and corrosion processes.[2–4] In acidic aqueous solutions, ORR can go through two pathways[1]: via four-electron reduction of O_2 to produce water (Reaction 1) or via two-electron O_2 reduction to hydrogen peroxide generation (Reaction 2):

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \; E^0 = 1.229 \text{ V} \qquad [1]$$

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 \; E^0 = 0.70 \text{ V} \qquad [2]$$

In fact, the mechanism of ORR is more complex, involves a large number of intermediate reactions and depends on various factors, e. g. pH of the electrolyte or the physical or chemical properties of the electrode material.[5,6] The 4-electron O_2 reduction to form water is often the most desirable, for instance in the case of hydrogen fuel cells.[1] Recently, the O_2 reduction via the two-electron pathway has attracted increasingly more attention because H_2O_2 is a highly demanded chemical on the market and it is regarded as a green, environmentally benign oxidant, widely used for applications in numerous fields including medicine, pulp and paper bleaching, chemical synthesis etc. For commercial large-scale production, hydrogen peroxide is obtained via the anthraquinone autooxidation process.[7] It requires high temperature and pressure, H_2 of fossil fuel origin, a large amount of organic solvents, and noble metals as catalysts. This motivates the search for more ecological and low-cost methods. For this reason, recent studies on H_2O_2 generation have focused on identifying novel catalysts for efficient two-electron ORR. The electroreduction of oxygen to hydrogen peroxide has been widely studied at several materials including noble metals[8] graphite,[9] carbon nanotubes[10] and gas diffusion electrode.[11] Among various materials conducting polymers (CPs) have emerged as promising candidates for ORR. During last decades CPs have attracted considerable interest due to their electrical properties, electrochemical stability and simplicity with respect to synthesis and processing. That makes them attractive for versatile applications including solar energy conversion, sensors, biomedical engineering

etc.[12,13] One of the CPs is polyindole (PIN), which exhibits high redox activity and thermal stability making it a successful electro-active material in solar cells, batteries, and biosensors or as corrosion inhibitors.[14–16]

The electrocatalytic activity of CPs towards oxygen reduction has been studied in the case of polyaniline, polypyrrole, polythiophene, and PEDOT.[17,18] PEDOT, in particular, exhibits excellent properties for peroxide evolution. With regard to ORR, PIN was utilized as a co-material (co-catalyst) in hybrid systems.[19,20] However, oxygen reduction reaction on PIN itself has not been explored yet. Here, we present that PIN in fact is a CP with good intrinsic catalytic capability. PIN acts as an efficient and durable electrocatalyst for oxygen reduction via a 2-electron pathway to hydrogen peroxide generation.

Materials and Methods

Polyindole (PIN) was electrochemically synthesized by cyclic voltammetry (CV) on gold thin film substrates (Si/SiO$_2$ wafer covered by Cr/Au (2 nm/50 nm)) from non-aqueous electrolyte in a three-electrode arrangement. The Ag/AgCl electrode was used as a reference electrode, and a Pt mesh served as a counter electrode. All electrochemical measurements were performed using a Keithley 2450 EC. PIN was synthesized from a solution containing 0.05 M concentration of the monomer (indole, Sigma-Aldrich) and 0.1 M LiClO$_4$ in acetonitrile (ACN) electrolyte. In cyclic voltammetry the potential range was set up from 0 V to 1.2 V, and back to 0 V at the sweep rate of 10 mV s^{-1}. Polymerization of PIN was carried out by applying 15 consecutive CV scans. The electrocatalytic properties of PIN were then tested in aqueous Na$_2$SO$_4$ solution with an ionic strength of 0.1 M at pH 2 (H$_2$SO$_4$ adjusted for proper pH). All electrolytes were prepared from reagent grade chemicals.

The concentration of hydrogen peroxide was determined by the spectrophotometric method with horseradish peroxidase and tetra-methybenzidine assay by Synergy H1 Microplate Reader (BioTek Instruments, Inc.). Before each analysis the calibration curve with solutions containing known concentration of H$_2$O$_2$ was done.

Electrolysis was conducted in O$_2$-saturated Na$_2$SO$_4$ solution (with 0.1 M ionic strength) at pH 2 with a cathodic current density of 0.25 mA cm^{-2}. Galvanostatic electrolysis was performed in an electrochemical cell comprising two chambers connected by an agarose salt bridge (H-cell configuration). The surface area of the
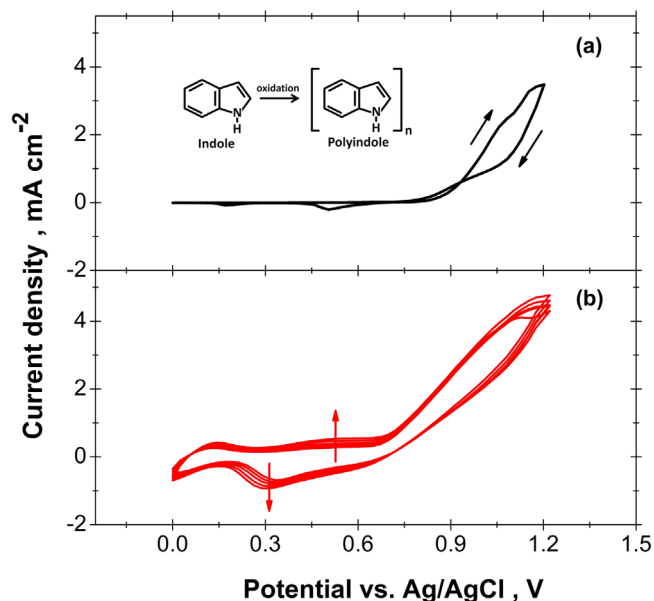
Figure 1. Electrochemical preparation of polyindole films on gold substrate via cyclic voltammetry method in 0.05 M indole + 0.1 M LiClO$_4$ in acetonitrile; scan rate 10 mV s^{-1}, 15 cycles-first scan (a), following scans (b).

Figure 3. XRD analysis of polyindole film.

working electrode (PIN) was 0.6 cm^2 and the volume of the electrolyte in each chamber was 10 ml.

Rotating Disc Electrode (RDE) measurements were performed on glassy carbon electrodes (0.07 cm^2) covered by PIN layer formed at the same electrochemical conditions as for Si/SiO$_2$/Au/Cr substrate mentioned above. Linear sweep voltammetry curves were recorded at various rotation speed in oxygenated Na$_2$SO$_4$ solution with ionic strength 0.1 M (pH 2).

The morphology of polyindole films was determined by Scanning Electron Microscopy (SEM) (ZeissSigma 500).

The thickness of the polyidole film was estimated by Atomic Force Microscopy (AFM) (Bruker).

The structural characterization of PIN film was performed by X-ray Diffraction (XRD) and Raman Spectroscopy. XRD experiments were carried out using Bruker D8 GADDS system with CuKα radation. 1D XRD patterns were obtained by integration of raw 2D data over azimuthal angle.

Raman Spectroscopy analysis was done using Thermo Scientific DXR Raman Microscope with excitation wave at 633 nm.

Results and Discussion

Experimental conditions during polymerization are key factor influencing the morphology of polyindole film. Within several experiments we proposed optimal number of polymerization cycles to obtain tight polymer film. After 2 CV scans of indole polymerization the film exhibits irregular structure (Supplementary, Fig. 1a is available online at stacks.iop.org/JES/167/086502/mmedia). It
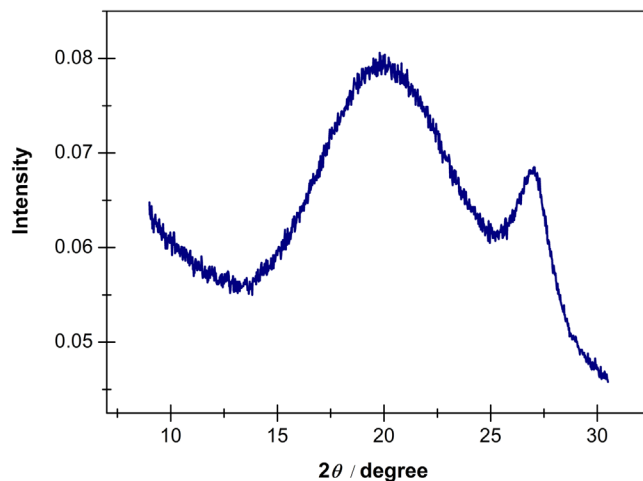
forms random polymer islands and does not cover the whole electrode surface. Applying 5 CV scans allows to obtain tighter structure and more regular homogeneous layer, although the polymer is full of cracks (Supplementary, Fig. 1b). Polyindole film formed during 8 CV scans (Supplementary, Fig. 1c) covers regularly the whole electrode surface, tighter than after 5 scans and forms cauliflower-like structure. Although it is thicker and tighter, still the material is too porous. It was found that in case of electrocatalysis optimal experimental conditions for deposition within CV technique with 20 mV s^{-1} are 15 cycles of polymerization.

Additionally, the tests of tightness of polyindole layers vs number of polymerization cycles were performed using acetonitrile-TCNQ probe in LiClO$_4$ supporting electrolyte (Supplementary, Fig. 2). And the conclusion is that applying of 15 CV scans ensures the complete of polymer layer. Reduction of scans number below 12 causes permeability, so in case of electroreduction, the electrocatalytic processes would take place on the substrate instead of polymer.

Thus, within optimization to ensure pinhole-free films, operational stability and good electrochemical properties of the PIN film, we found out that 15 consecutive applied CV scans was suitable production protocol.

PIN films were prepared by electrochemical oxidation of monomer (indole) in solution of LiClO$_4$ dissolved in acetonitrile using a cyclic voltammetry (CV) method. Typical CV curves of indole polymerization are shown in Fig. 1. During the first scan (Fig. 1a) the oxidation process at above 0.9 V is observed and the position of this anodic peak is attributed to the oxidation of the monomer.[21] The shape of the first scan, as it lacks a reduction peak, indicates that the electrochemical oxidation of indole is an irreversible process. The characteristic loop on the CV curve, related to nucleation of the polymer on the electrode surface and the formation a first thin layer of PIN,[22] is well visible. The nature of the subsequent scans differs (Fig. 1b). Apart from the peak of monomer oxidation, the redox couple characteristics for PIN appears on CV plots in the potential range from 0.15 V to 0.7 V. Current densities of
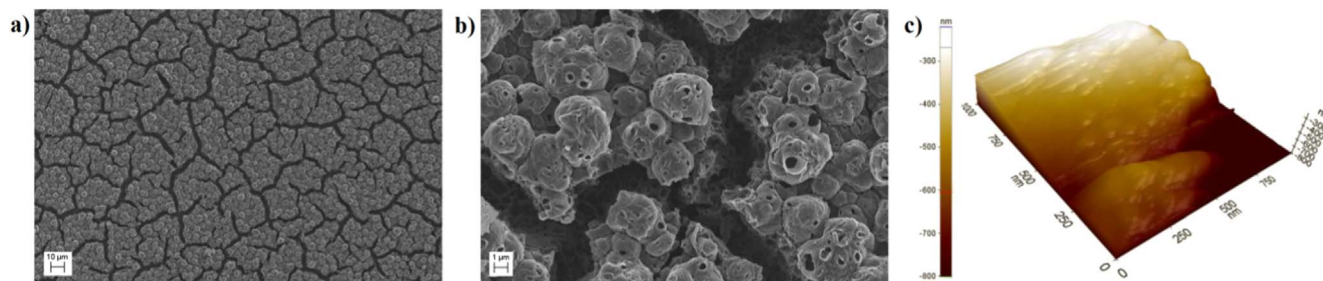

Figure 2. SEM (a), (b) and AFM (c) images of polyindole films deposited on gold substrate by cyclic voltammetry (15 cycles).
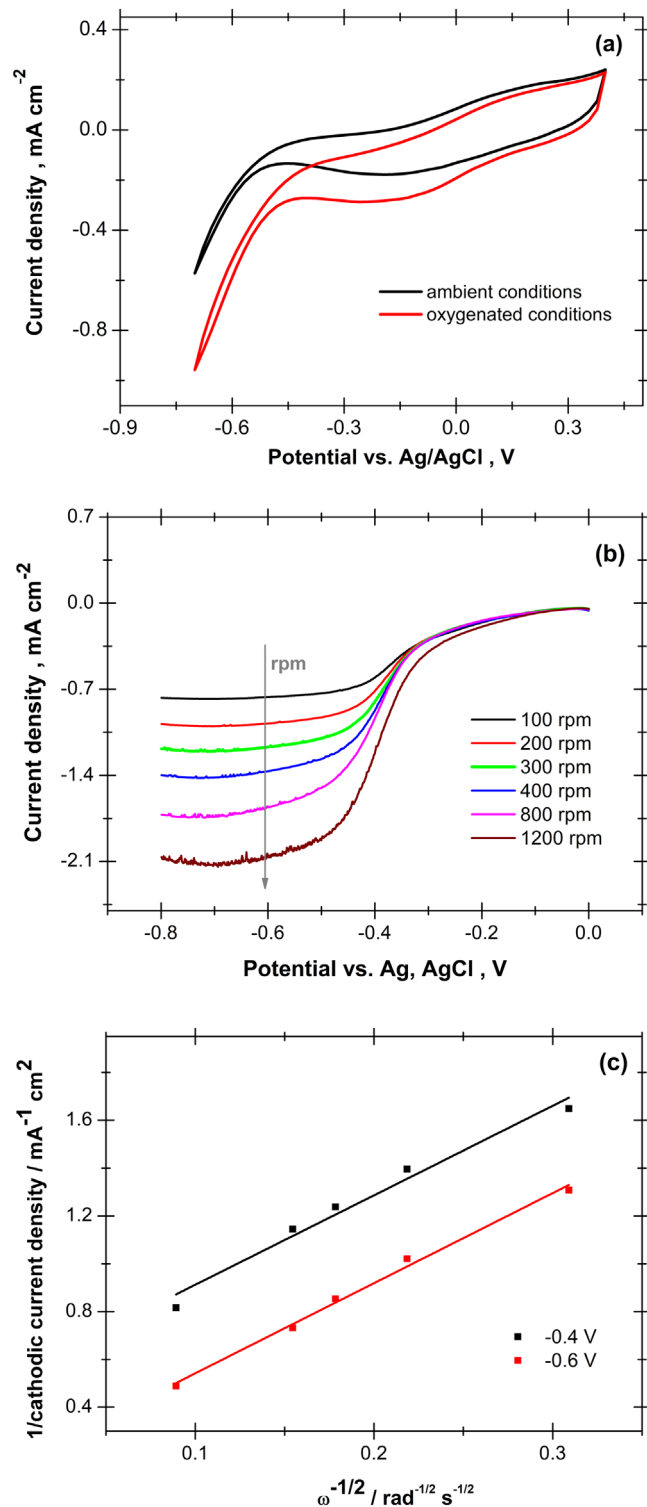
Figure 4. (a) Comparison of cyclic voltammograms recorded for PIN electrodes in Na_2SO_4 solution at pH 2 at ambient (black line) and oxygenated conditions (red line); scan rate 5 mV s^{-1}; (b) linear sweep voltammograms for PIN film on glassy carbon electrode recorded in O_2-saturated Na_2SO_4 solution at pH 2; scan rate 5 mV s^{-1}; (c) Koutecký–Levich plot.
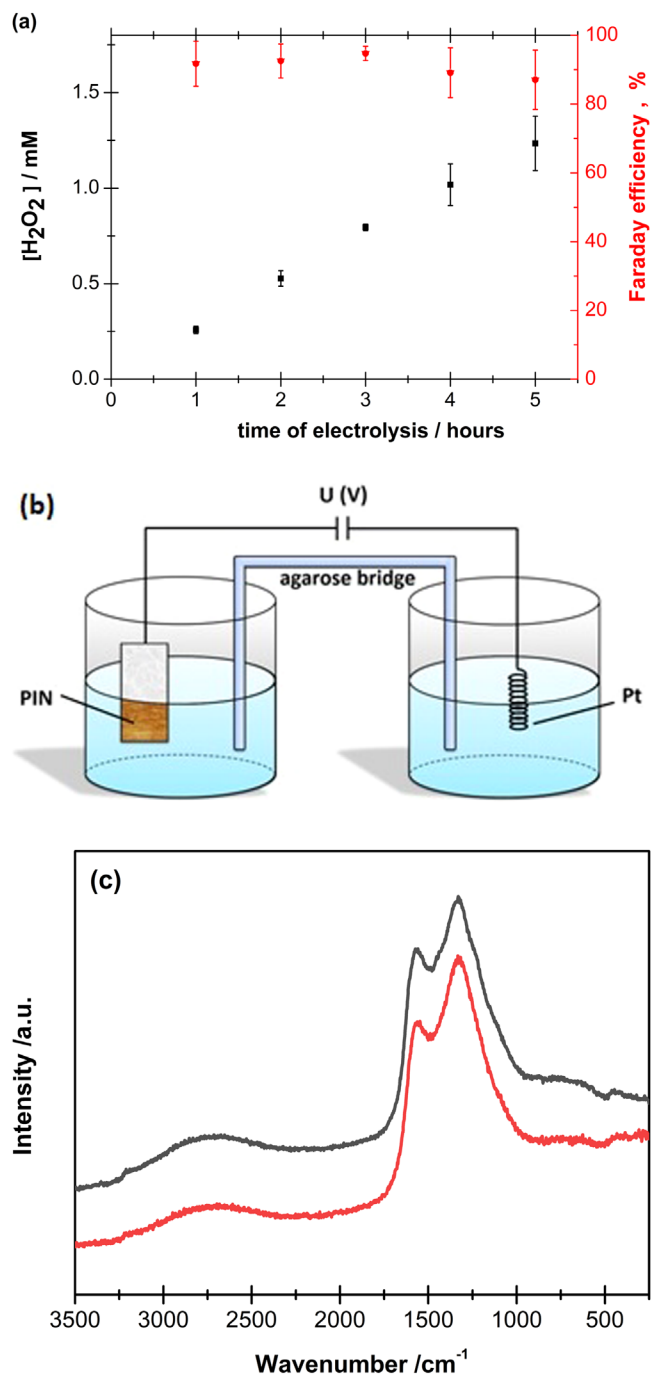

Figure 5. (a) Galvanostatic oxygen to hydrogen peroxide electrolysis—H_2O_2 performance and Faraday efficiency over time for cathodic current density of 0.25 mA cm^{-2} at pH 2; (b) scheme of the setup applying for electrolysis—two compartment electrochemical cell connected by agarose salt bridge; (c) Raman analysis of polyindole film performed before (black curve) and after 5-hour electrolysis (red curve).

these redox peaks increase with number of scans indicating the growth of a PIN film on the electrode surface.

The morphology of PIN films was studied by scanning electron microscopy (Figs. 2a, 2b). The PIN film grows in a dendritic fashion, initiated by several nucleation sites along the substrate which generates a morphology that is porous (1 μm) with a relatively high density of PIN content. The film grows in a 3D fashion with respect to the CV polymerization scans/charge/time. After 15 CV polymerization scans polymer uniformly covered the whole electrode surface and prevent to permeate/penetrate ions from the electrolyte through the film to the substrate. At the 10 μm scales cracks appear due to drying of the PIN electrode.

Atomic Force Microscopy (AFM) was used to study the thickness of the polyindole films. The gathered AFM images (Fig. 2c) show that PIN films after 15 polymerization cycles has at least 500 nm thickness.

XRD method was applied to confirm the structure of the electrochemically synthesized polyindole. The results are shown in Fig. 3. There are two reflection peaks: one broad at 19° which confirms the polymerization of indole and second sharp at 27° which denotes the partial crystalline structure of polyindole.[23]

To evaluate the electrochemical properties of PIN films, especially paying attention to ORR, electrochemical experiments were conducted in Na_2SO_4 solution at pH 2 in ambient and oxygenated conditions and the results are shown in Fig. 4a. In O_2-bubbled electrolyte (red line) the recorded cathodic current density was much higher, corresponding to ORR, with onset potential at ca. 0.1 V. This simple experiment, as oxygen is added, reveals that the cathodic process is indeed ORR.

To verify and establish the mechanism of ORR on PIN films, we conducted rotating disc electrode (RDE) measurements (Figs. 4b and 4c). The number of transferred electrons per oxygen molecule was calculated according to the Koutecký–Levich equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B}\omega^{-1/2}$$

$$B = 0.62nFAC_{ox}D^{2/3}\nu^{-1/6}$$

Where: i_k—the kinetic current [A], ω—rotating rate of electrode [rad s^{-1}], n—the number of transferred electron, F—Faraday constant [96 485 C mol^{-1}], A—the electrode area [cm^2], C_{ox}—the oxygen concentration [1.3×10^{-3} mol l^{-1} in 0.025 M Na_2SO_4 at 298 K[24]], D—the diffusion coefficient [3×10^{-5} cm^2 s^{-1} for oxygen in 0.025 M Na_2SO_4[25]], ν—kinematic viscosity [0.009 cm^2 s^{-1} for 0.025 M Na_2SO_4[25]].

The linear sweep voltammetry scans were recorded in the potential window from -0.7 V to 0.4 V at various rotating rate (Fig. 4b). The number of transferred electrons calculated from the Koutecký–Levich plot (Fig. 4c) was 1.98 at -0.6 V vs Ag/AgCl electrode and is similar for that estimated at -0.4 V vs reference electrode which means that oxygen reduction via a 2-electron pathway is dominant.

The electrocatalytic activity of conducting polymers toward oxygen reduction is related to possibility of interaction between the oxygen and conducting polymers being in the reducing state (close to fully undoped state).[17] Thus, the catalytic reduction of oxygen at polyindole results from the fact that PIN can be electrochemically reduced in the potential window where the oxygen reduction occurs, and the mechanism of oxygen reduction at PIN film is based on the oxidation of reduced PIN by oxygen resulting hydrogen peroxide generation.[17]

Having established the efficacy of 2-electron electrocatalytic oxygen reduction to hydrogen peroxide on PIN by horseradish peroxidase and tetramethybenzidine assay and RDE measurements, we conducted long-term galvanostatic electrolysis with cathodic current density of 0.25 mA cm^{-2} under O_2-bubbled Na_2SO_4 electrolyte at pH 2 (Fig. 5a). To prevent reoxidation of H_2O_2 at the anode (Pt mesh), experiments were performed in separated chambers connected by a salt bridge. The experimental scheme is depicted in Fig. 5b. After 5 h-electrolysis with a polyindole cathode, we were able to obtain 1.23 mM [H_2O_2]. The faradaic efficiency for ORR remained high during the whole electrolysis and is found to be between 85%–100%. These results highlight PIN as a suitable electrocatalyst for peroxide generation at low pH and in comparison with literature data e.g. with GDE cathode having current efficiency after 1-h electrolysis below 50%,[11] our results seem to be promising.

The comparison of the concentration of H_2O_2 electrogenerated through ORR reported in literature is difficult to evaluate because in most cases the higher current density is applied resulting in higher concentration of H_2O_2 e.g. for GDE ca.8 mM of H_2O_2 can be obtained with much higher current density (30 mA cm^{-2})[11] or utilizing polyacrylonitrile-based carbon fiber brush cathode for ORR allows to electrogenerate ca.30 mg l^{-1} but with significantly

higher current (50 mA)[26] than in our case for PIN electrode (0.25 mA cm^{-2}).

The stability of the PIN films were evaluated by electrochemical methods: (a) applying at least 100 CV scans in 0.1 M $LiClO_4$ in ACN in potential range of 0 and 0.6 V vs ref electrode—the films were stable and we did not observed any significant changes in CV curves recorded for 1. and the last scans; (b) performing the CV scans in the presence of TNCQ in the electrolyte to evaluate the tightness of the film and by (c) Raman analyses performed before and after 5-h electrolysis. As shown in Fig. 5c the shapes of Raman spectra recorded before and after electrolysis are similar and exhibit two well visible sharp peaks in the region of 1300–1600 cm^{-1}, characteristics for polyindole. According to literature, we can attribute to them the following vibrational mode: stretch of pyrrole ring (at 1319 cm^{-1}), C=N stretch (1388 cm^{-1}), NH + C2C3 + C6H (1419 cm^{-1}), C5H + C8N + C4C5 (1455 cm^{-1}), C9C4 + C6C7 + C7C8 (1580 cm^{-1}) and C7C8 + C5C6 + C8C9 (1614 cm^{-1}).[27] The positions of the peaks are the same for PIN film recorded before and after electrolysis, confirming the same structure, but the intensity of them is a little bit lower after electrolysis which is related to the different thickness of the film. The difference in film thickness is not due to its degradation, but rather to the fact that the measurement was not carried out exactly in the same place of the sample and, as SEM and AFM images show (Fig. 2), the thickness of the film varies slightly over the entire sample surface but based on series of electrochemical measurements it does not significantly affect the device performance as whole.

Conclusions

In this communication we demonstrate that a 0.6 cm^2 polyindole (PIN) electrode, synthesized via electrochemical polymerization, displays high activity and durability as an electrocatalyst for oxygen reduction to form hydrogen peroxide with a catalytic performance reaching 1.3 mM of H_2O_2 after 5 h of electrolysis. PIN electrodes can operate at low pH with high faradaic efficiency (80%–100%). These results make PIN attractive and alternative electrocatalyst for ORR and open up new possibilities for PIN exploitation in electrocatalysis field.

Acknowledgments

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