Hydrogen storage capacity of polypyrrole in alkaline medium: effect of oxidants and counter anions

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Abstract
Polypyrrole(Ppy) synthesized by wet chemical method using FeCl3 and (NH4)2S2O8 as oxidants were subjected to analysis by Scanning Electron Microscopy, X-ray diffraction, UV-visible spectroscopy, Differential scanning calorimetry, Raman and 1H NMR techniques. Electrochemical analysis such as cyclic voltammetry, linear sweep voltammetry and impedance spectroscopy of Ppy were performed. Charge/Discharge studies in 0.01 M NaOH showed hydrogen storage capacity of PpyFeCl3 and PpyAPS as 27.24 and 24.4 mA h/g respectively, implying stable hydrogen storage by PpyFeCl3. This variation in the ability of storing hydrogen by Ppy with change in oxidants is attributed to the formation of anion induced H-bonded structures in the backbone of Ppy as supported by Raman and 1H NMR analysis.

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1. Introduction
Improving the energy-storage capacity of supercapacitors with high power density has become inevitable to cater the needs of electronic applications. It has been established that the energy density of supercapacitors can be enhanced by either increasing the device capacitance with novel electrode materials or widening the working potential windows employing suitable electrolytes [1-3]. As electrode materials for pseudocapacitors, conducting polymers such as polypyrrole(Ppy) exhibit good electrocatalytic activity. Due to the conjugation with anion during polymerization the band gap of Ppy is reduced effectively [4,5]. When it comes to the synthesis of Ppy, chemical oxidative polymerization is simple, cost effective, fast and easy to scale up. Electrochemically synthesized Ppy normally displays very poor solubility in common organic solvents as well as water, thereby limiting its processability.

To overcome these disadvantages, counter ions are introduced into the polymer backbone. Protonation with an organic acid increases the solubility, electronic structure and crystallinity of Ppy [6].

Elemental analysis of Ppy films indicate that the polymers are composed of about 66–75% by weight of pyrrole(py) units and about 25–33% by weight of the counter anion from the electrolyte [7]. Many different anions, both inorganic and organic, may be incorporated in Ppy films. These include ClO4−, NO3−, BF4−, Cl−, PF6−, SO42− and toluene sulphonate...
The electrical conductivity and electrochemical behaviour of Ppy films vary with the incorporated anions, conditions of preparation and the solvent used [7]. Raman Spectroscopy is a significant technique to obtain structural evidence on conducting polymers like Ppy. The Raman vibrational modes of Ppy at different stages of reduction are assigned to the bands of neutral, radical cation and dicaticonic species [8]. Voltammetric method is used to estimate equilibrium charge storage features of conducting polymers [9]. Many efforts have been done for hydrogen storage possibilities through electrochemical studies of Ppy in acidic medium [10] but very limited investigations on alkaline medium based hydrogen storage is noticed in the literature [11–13]. Thus the major objectives of the present investigation are (i) determination of maximum charge stored from i–V profile of Ppy in 0.01 M NaOH, (ii) analysis of the transitions of both polaron-bipolaron states of Ppy by Raman spectroscopy, (iii) determination of the electrical and ionic conductivity of Ppy before and after hydrogen evolution through Electrochemical Impedance Spectroscopy (EIS), (iii) identification of better catalyst for Ppy synthesis (iv) prediction of plausible mechanism for hydrogen storage and the stability of Ppy synthesized.

2. Experimental details

2.1. Preparation of Ppy using different oxidants

Ppy is prepared by chemical oxidative polymerization using pyrrole (py) monomer. Freshly distilled py (60 drops) and FeCl₃ (24.3 g) were dissolved in 1M HCl in separate vials. Both the solutions were simultaneously mixed with vigorous shaking for 30 s. The mixture is allowed to settle for 2 h and the obtained product is washed with deionized water and dried under vacuum for 24 h at 50 °C. Analogously, the same procedure is carried out with APS as oxidant (Schemes 1–3) [14]. The oxidants create chemically active cation-radicals of py, which reacts with py molecules to form the polymer chain. The Ppy chain is concurrently doped during polymerization. The counter anions in the reaction medium are incorporated into the growing Ppy chain to maintain electrical neutrality [15].

2.2. Material characterization

Surface morphology of Ppy is studied using FESEM FEI Quanta, Model–FEG 200 in the magnification range of 500 nm to 3 µm under high vacuum. The XRD analysis of Ppy is carried out employing Xpert pro with copper target (Cu Kα), λ = 1.54 Å. UV–vis spectroscopy is done using Evolution 220 PC spectrophotometer in the wavelength range of 250–1200 nm. Micro Raman is employed to obtain Raman Spectroscopy of the Ppy. Raman spectra are acquired with a 632.8 nm excitation laser source in the range of 600–2000 cm⁻¹. X-Ray photoelectron spectroscopy (XPS) is carried out by ESCALAB 250XI base system with UPS and XPS image mapping. ¹H–NMR (Bruker: 500 MHz) is used to characterize the molecular structure of the polymer samples. The polymers were dissolved in DMSO–d₆ to record the NMR spectra.

2.3. Electrochemical studies

Cyclic Voltammetry (CV), LSV and EIS experiments were done employing three electrode setup using Zahner Zennium (Germany) electrochemical workstation. The electrodes utilized are Ag/AgCl (reference electrode), Platinum (counter) and Ppy coated copper (working). All experiments were carried out in 0.01 M NaOH at different scan rates in the potential range of −1 to 1 V.
EIS is measured in the frequency range from 100 mHz to 100 kHz at an amplitude of 10 mV. Galvanostatic charge/discharge studies of Ppy coated copper is done using IVIUM Potentiostat. Scheme 4 represents the coating methodology.

3. Results and discussion

The synthesized Ppy is characterized employing SEM, XRD, UV–vis, Raman spectroscopy, 1HNMR techniques and analysis of the same is discussed in the following sections.

3.1. Morphological and structural analysis

The morphological features of PpyFeCl₃ and PpyAPS are shown in Fig. 1(a and b). SEM images exhibit chain like polymer and also confirms the presence of agglomerated Ppy chain. The average particle size calculated from SEM for PpyFeCl₃ and PpyAPS were 329 and 352 nm respectively.

The average particle size for PpyFeCl₃ is small compared to PpyAPS.

XRD shows broad peaks at 26.1° and 24.5° for PpyFeCl₃ and PpyAPS respectively (Fig. 2a and b).

It is observed from Fig. 2 that the polymer is semi crystalline in nature with broad peak [16]. The crystallite size is estimated using Scherer formula as follows:

\[ D = \frac{K\lambda}{\beta\cos\theta} \]  

where \( D \) is crystallite size, \( K \) denote shape factor, \( \beta \) represents the diffraction angle at maximum peak intensity and \( \theta \) depicts the full width at half maximum of diffraction angle in radians. The crystallite size calculated for PpyFeCl₃ and PpyAPS are 0.9 and 0.54 nm. In general, if the transition metal ion is used as oxidants in the polymerization, it leads to shift in the peaks towards higher angle.

In the present case for PpyFeCl₃, Fe³⁺ leads to higher shift compared to PpyAPS. This indicates that the interplanar spacing decreases with the addition of transition metal ion oxidants. Doping leads to shift of the peaks towards the higher angle by about 1° [17]. This would make the chains come closer with stronger interaction of dopants leading to higher overlap of bonds. This can cause increase in the conduction as supported by UV–vis spectroscopy analysis in Section 3.3. Thus PpyFeCl₃ show low intensity peaks than PpyAPS and the peak shift towards higher 2θ also occurs.

3.2. Thermal stability test

Differential Scanning Calorimetry (DSC) analysis of PpyFeCl₃ and PpyAPS are shown in Fig. 3. PpyFeCl₃ exhibits exothermal peak at 104.4 °C whereas PpyAPS possessed melting point at 96.3 °C. PpyFeCl₃ showed slightly higher glass transition temperature. This reveals that PpyFeCl₃ has achieved a better and higher thermal stability during synthesis compared to PpyAPS. This could be attributed to the variance in the nature of chem-
Fig. 1 – SEM images of Ppy using (a) FeCl₃ (b) APS as oxidant.

Fig. 2 – XRD for (a) PpyFeCl₃ and (b) PpyAPS synthesized using two different oxidants.

Fig. 3 – DSC of PpyFeCl₃ and PpyAPS.

Fig. 4 – Optical absorption spectrum of (a) PpyFeCl₃ and (b) PpyAPS.

3.3. Electronic spectroscopic analysis

The optical band gap of synthesized Ppy is determined employing UV–vis spectroscopy. The samples for UV–vis analysis were prepared by dissolving Ppy in DMSO and ultrasonicated for 10 min. PpyFeCl₃ shows peak at 273 nm corresponding to the \( \pi-\pi^* \) transition. The peak at 407 nm is caused by bipolaron transition state. PpyAPS exhibited the absorption band in the range of 274 nm corresponding to the \( \pi-\pi^* \) transition and small hump at 322, 394 nm indicating bipolaron transition (c.f Fig. 4(a)). The band gap of Ppy is found from Tauc’s plot (Fig. 4(b and c)) to be 1.29 and 1.4 eV for PpyFeCl₃ and PpyAPS respectively. The obtained bandgap is in the lower end of the literature reported range of 1.3–2.32 eV [19] for Ppy. Thus PpyFeCl₃ have achieved slightly higher conductivity compared to PpyAPS in Fig. 4(d). In general, conductivity of Cl⁻ doped Ppy is higher compared to SO₄²⁻ doped Ppy [20].

Ppy synthesis methodology demonstrated in the present scenario indicates that even with APS as oxidant, the polymer-
ization is carried out in the presence of HCl. Thus the anionic contribution comes from Cl\(^-\) as well as SO\(_4\)\(^{2-}\) (cf. Scheme 3). Therefore, the band gap of PPy\(_{FeCl_3}\) and PPy\(_{APS}\) show very less variation amongst themselves as well as lie in the lower end of the reported band gap for Ppy. Similar observation of increased conductivity by using FeCl\(_3\) was reported by Chitte et al. [17].

This phenomenon could be attributed to the structural difference between the two oxidizing agents and their interaction with py during the synthesis [16].

The rationale behind the higher conductivity of PPy\(_{FeCl_3}\) than PPy\(_{APS}\) are listed below:

### 3.3.1. Oxidation potential effect

As the oxidation potential of Ppy matches with that of FeCl\(_3\) (ca.0.77 V), overoxidation of pyrrole does not occur. Due to this similar oxidation potential, the conductivity of PPy\(_{FeCl_3}\) increases [21]. In addition, the octahedral Fe\(^{3+}\) complexes possess higher occupied orbital as 4s and incomplete d-orbitals, with unpaired electrons. Thus the high energy valence band electron from incomplete d-orbitals, jump to conduction band leading to higher conductivity of PPy\(_{FeCl_3}\) whereas in the case of PPy\(_{APS}\) absence of transition metal ions leads to higher band gap and hence less conductivity in comparison with PPy\(_{APS}\).

### 3.3.2. Common ion effect

In general, the conductivity of Cl\(^-\) doped Ppy is greater compared to SO\(_4\)\(^{2-}\) doped Ppy but band gap of Cl\(^-\) and SO\(_4\)\(^{2-}\) doped Ppy is nearly the same due to proton doping. In this present scenario, PPy\(_{FeCl_3}\) & PPy\(_{APS}\) were synthesized in the presence of
HCl and the existence of common ion Cl⁻ in PpyFeCl₃ increases its conductivity via HCl [22].

### 3.4. Raman analysis

Raman spectra of PpyFeCl₃ and PpyAPS are shown in Fig. 5. The polymeric chain has to accommodate the charges created by the oxidation process. The accommodation of these extra charges (cation and dication) involves conformational and structural changes that can be identified by Raman Spectroscopy.

PpyFeCl₃ displays high intensity band at 738, 854, 1039, 1337, 1594, 1754 cm⁻¹ (Fig. 5a).

PpyAPS exhibited peaks at 850, 948.9, 985, 1101, 1311, 1377, 1515, 1616 and 1711 cm⁻¹ (Fig. 5b).

The positions of these bands were observed in the 600–2000 cm⁻¹ region of the spectrum.

In Fig. 5a, band at 1594 cm⁻¹ is assigned to the C=C backbone stretching of Ppy and 1337 cm⁻¹ is attributed to the ring stretching mode for Ppy. The band at 1754 cm⁻¹ represent the symmetrical C–H in-plane deformation. In Fig. 5b, two doublet peaks at 948.9 and 985 cm⁻¹, 1311 and 1377 cm⁻¹ arises due to the hydrogen bonding of SO₄²⁻ with Ppy as shown in Scheme 4. The band at 1515 cm⁻¹ is assigned to the C=C backbone stretching of Ppy, and 1311 cm⁻¹ is attributed to the ring stretching mode for Ppy. 1101 cm⁻¹ band represent symmetrical C–H in-plane deformation and the peaks at 948.9 and 985 cm⁻¹ are associated with the polaron structure. The peak at 850 cm⁻¹ in Ppy is attributed to the ring deformation induced by dication (bipolaron) [7,8].

The relatively large intensity of 948.9 and 985 cm⁻¹ band in the spectrum of PpyAPS may be attributed to the fact that vibration of SO₄²⁻ is contributing to the intensity of the band. A weak shoulder at 850 and 1101 cm⁻¹ (Fig. 5b) indicate doping by Cl⁻ anion in PpyAPS [7]. The eminent peak at 1616 cm⁻¹ represents C=C symmetry stretching [8]. The two peaks located at 1311 and 1377 cm⁻¹ were assigned to the inter-ring (C–C) stretching [8]. The vibration at 1101 cm⁻¹ is attributed to a ring deformation mode [8] and the two bands at 948.9 and 985 cm⁻¹ are assigned to ring deformation associated with dication (dipolaron) and radical cation (polaron) respectively [7,8] (cf. Fig. 5e and f). Fig. 5c and d shows Raman spectra of Ppy after CV analysis. The bimodal peak observed at 1380 and 1515 cm⁻¹ (Fig. 5c) and 1340 and 1551 cm⁻¹ in (Fig. 5d) are due to the hydroxyl group from the electrolyte attaching the positive charges on the Ppy backbone, leading to overoxidation of the polymer and hence reduction in the peak intensity of C=C and C–H modes. In Fig. 5(d), the peak at 1380 cm⁻¹ is assigned to the ring stretching of oxidized Ppy [23]. After CV analysis the hydrogen gets evolved from the system, while Ppy gets oxidized and hence the protonated peak intensity is reduced. Before CV, due to the negative charge of Cl⁻ and SO₄²⁻ a local deformation to the quinoid structure occurs. The combination of positive backbone with the quinoid structure, is referred to as a polaron. As oxidation continues further, another electron is removed from a Ppy chain that already contains a polaron (radical cation) and leads to the formation of bipolaron (dication) [15].

### 3.5. ¹H-NMR analysis

The ¹H-NMR spectra for PpyFeCl₃ and PpyAPS are provided in Fig. 6. ¹H residual solvent chemical shift at 2.50 ppm is for DMSO-δ₆, ¹H HOD chemical shift at 3.3 ppm accounts for DMSO-δ₆.

¹H-NMR Spectra for PpyFeCl₃: Triplet peak occurs between 7.0 and 8.3 ppm due to aromatic protons on py ring [20] (Fig. 6a).

¹H-NMR Spectra for PpyAPS: The peaks between 7.0 and 8.5 ppm in the spectra is assigned to the aromatic protons on
Fig. 6 – $^1$H–NMR Spectra for (a) $\text{Ppy}_\text{FeCl}_3$, (b) $\text{Ppy}_{\text{APS}}$ and (c) $\text{Ppy}_{\text{APS}}$ dissolved in $\text{H}_2\text{SO}_4$.

Scheme 5 – The hydrogen bonding between oxygen of $\text{SO}_4^{2-}$ anion and the H–N protons of Ppy.
Fig. 7 – CV of (a) PPyFeCl₃ and (b) PPyAPS (Inset figure: Bare copper in 0.01 M NaOH).

py ring identical to the former case with high peak intensity (Fig. 6(b)). The broad peak occurs at 4.0 ppm due to the presence of hydroxyl protons. The presence of hydroxyl protons can be justified via the hydrogen bonding between oxygen of SO₄²⁻ anion and the H–N protons of Ppy. Since the peak is not sharp, hydrogen bonding rationalizes the broadening of the peak between 3.6 and 4.6 ppm (cf. Scheme 5). To confirm that the 3.6–4.6 ppm peak is due to SO₄²⁻ in Ppy, ¹H–NMR spectra of the PPyAPS dissolved in two drops of H₂SO₄ is recorded. Sharp peak around 4.6 ppm is noticed indicating the removal of SO₄²⁻ due to common ion effect. The common ion effect is expected to change broad peak to sharp peak at 4.6 ppm [24].

3.6. Electrochemical analysis

3.6.1. Cyclic voltammetry

Fig. 7(a) and (b) represents CV of PPyFeCl₃ and PPyAPS in 0.01 M NaOH. The scan rate varies from 25 to 100 mV/s in the potential window of −1 to +1 V. The peak at 0.035 V indicates adsorption of hydroxyl ion on the Ppy backbone. At higher scan rates positive peak shift towards 0.26 V occurs. The peak at 0.9 V is observed due to charge transfer degradation of Ppy. From Raman studies, we infer that −OH group from NaOH (electrolyte) attack the positive centers on the Ppy backbone. Instantaneously, Ppy undergoes overoxidation and degradation [23,25]. Three reverse peaks were noticed at −0.57, −0.2 and 0.1 V representing the reduction of Ppy. The positive centers created on the polymer backbone (polarons) are the charge carriers for the electrical conduction. Charge transport occurs via mobility along segments of conjugated polymer chain and hopping of charges from chain to chain. Bipolarons (radical di-ions) also play a major role in the electronic and transport properties of conducting polymers [26].

CV of PPyAPS (Fig. 7(b)), possess peak 1 at 0.01 V exhibiting the adsorption of hydroxyl ion to the surface of PPyAPS and the peak potential shifted to 0.12 V with increase in the scan rate. Peak 2 at 0.19 V gets shifted to 0.27 V at 50 mV/s and disappears at higher scanrates. In the reverse scan, Peak 2 at −0.45 V shows the polaron formation which with further oxidation becomes bipolaron in peak 3 at −0.8 V. This oxidation/reduction process creates charge carriers in the form of polarons (radical ions) and bipolarons (dication and dianions) in the polymer. Inset figure indicates the CV of bare copper in 0.01 M NaOH. It exhibits the hydroxyl ion attack on the copper (Cu) leading to the formation of CuO [27–29].

Mechanism of Ppy in alkaline medium: Based on the CV peaks of PPyFeCl₃ and PPyAPS in 0.01 M NaOH, following mechanism is proposed for the hydrogen evolution reaction on Ppy and further oxidation (cf. Schemes 6) of Ppy on copper substrate.

3.6.2. Linear sweep voltammetry

LSV for PPyFeCl₃ and PPyAPS is studied at different scan rates (25 mV/s–100 mV/s) in the potential range of −1 to +1 V (Fig. 8). Equilibrium charge stored in F/cm² can be calculated using charge density (C/cm²): Fig. 8 shows proton stored in PPyFeCl₃ and PPyAPS at different scan rates (Scheme 6).

Charge density in C/cm² and specific capacitance in F/g are calculated as follows.

\[
\text{Chargedensity} = \frac{\text{I} \times \text{t}}{\text{A}}
\]

where I, t and A represents current in Amps, time in secs and area of the electrode in cm² respectively. Fig. 8(a and b) exhibits five bands at same potential range but different current density. This variation is due to counter ion (SO₄²⁻) of PPyAPS bonded to the hydrogen in the pyrrole ring. Region I explains the metal hydrogen bond formation, Region II shows the adsorption of hydroxyl anion into the Ppy surface, Region III indicates oxidation of Ppy, Region IV is formation of quinoid structure of Ppy and Region V is Hydrogen Evolution (Figs. 9 and 10).

Capacitance can be calculated as follows.

\[
\text{Capacitance} = \frac{\text{Charge}}{\text{massofactivematerial} \times \text{g}}
\]

The PPyFeCl₃ and PPyAPS possess maximum charge stored as 4727 m F/g and 3927 m F/g respectively. With increase in the scanrate, the charge stored decreased.

3.6.3. Charge/discharge studies

The charge–discharge behavior of the Ppy was examined at constant current density of 1 mA/cm². The alkaline electrolyte is expected to give best electrochemical performance in conjunction with the mesoporous structure (cf. Figs. 9 and 10) of the Ppy electrode. Mesoporous Ppy can easily accommodate Na⁺
Fig. 8 – LSV of (a) \( \text{Ppy}_{\text{FeCl}_3} \) and (b) \( \text{Ppy}_{\text{APS}} \) in 0.01 M \( \text{NaOH} \).

Step 1:

\[ \text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \]

Electrolyte

Step 2: M-H bond formation

\[ \text{M} \cdot \text{H} \rightarrow \text{H} \cdot \text{Ppy} \rightarrow \text{M} \cdot \text{H} \cdot \text{Ppy} \rightarrow \text{M} \cdot \text{H} \cdot \text{Ppy} \cdot \text{Na}^+ \cdot \text{OH}^- \]

Step 3:

Hydrogen evolution and PPy oxidation

\[ + \text{H}_2 \uparrow + \text{O}_2 \]

Oxidised Ppy (dication)

Scheme 6 – Mechanism of Ppy in 0.01 NaOH medium.
and electrosorption of the OH− anions [30]. This property increases the conductivity and ionic mobility of Ppy [30].

In general, specific capacity is calculated as follows

\[ C = \frac{I \cdot \Delta t}{m} \]  

(4)

where I in mA is discharge current density (1 mA), \( \Delta t \) in seconds denote discharging time, and m represents the weight of Ppy coated on Cu substrate (10 mg). PpyFeCl₃ exhibits higher capacity compared to PPYAPS. Initial capacity of PpyFeCl₃ is 27.24 mAh/g and remains stable up to 100 cycles demonstrating the stability of PpyFeCl₃ in 0.1 M NaOH. PpyAPS shows initial hydrogen storage capacity of 24.4 mAh/g and falls to 16.72 mAh/g after 60 cycles.

Specific capacitance of Ppy is calculated by using the formula

\[ C = \frac{I \cdot \Delta t}{m \cdot \Delta V} \]  

(6)

From charge/discharge profile of PpyFeCl₃ and PpyAPS in 0.1 M NaOH, the initial capacitance is obtained as 98 and 88 F/g respectively. After 99 cycles, PpyFeCl₃ and PpyAPS shows 108.4 F/g and 60.2 F/g respectively. Thus PpyFeCl₃ and PpyAPS exhibits excellent capacitance compared to the literature value of 36.01 F/g at a scan rate 0.05 V/s in 1 M KOH [31]. Capacitance of Ppy derived porous carbon exhibited 108 F/g for 0.5A/g in 1 M KOH [31]. This proves the stability of PpyFeCl₃ is higher than PpyAPS in alkaline solution. PpyFeCl₃ stores hydrogen better than PpyAPS and upon further optimizing the process enhancement in the hydrogen storage capacity can be achieved.

3.7. Electrode kinetics from EIS analysis

Typical Nyquist plot for the PpyFeCl₃ and PpyAPS coated Cu in 0.1 M NaOH solution before and after HER is given in Fig. 11 and its equivalent circuit fitting presented in Fig. 11(c–f) where the parameters Rₛ and Rₜ denote charge transfer resistance and solution resistance, Rₜ is Diffusion resistance, Q₁, Q₂, Q₃ are constant phase elements. In general, the empirical exponent (a) associated with constant phase elements (CPE) varied between 0 and 1. The empirical component was introduced to account for surface inhomogeneities, roughness factors and adsorption characteristics [32,33]. An ideal capacitor corresponded to a = 1, while a = 0.5 represented Warburg component [34–39], caused by diffusion process in the system.

For PpyFeCl₃ before HER, the linear portion noticed in the lower frequency region, represents the diffusion resistance (Rₜ). The constant phase elements (CPE) in the present case were Q₁ = 0.001Ω⁻¹ S₀.6, Q₂ = 0.03Ω⁻¹ S₀.01 with its exponent parameter Q₁, Q₂ = 0.6 and 0.01. Therefore the CPE accounts for diffusion resistance in the system.

After HER, the Nyquist plot of PpyFeCl₃ exhibits semi-circle corresponding to the charge-transfer resistance (Rₛ/Rₜ) developed at Cu-PpyFeCl₃ electrode/electrolyte interface. Solution resistance in Rₛ. The constant phase elements (CPE) in the present case were Q₁ = 0.0008Ω⁻¹ S₀.06, Q₂ = 0.0007Ω⁻¹ S₀.86 with its exponent parameter Q₁, Q₂ = 0.06 and 0.86.

PpyAPS before HER, possess a straight line at high frequency, indicating Warburg impedance (W) caused by distorted resistance in the system. The high-frequency cut off of the semi-circle on the real axis offers the solution (electrolyte) resistance (Rₛol). The constant phase elements (CPE) in this case were Q₁ = 0.0004Ω⁻¹ S₀.5 indicating diffusion resistance developed in the system.

After HER, there is only semicircle present in the higher frequency of the system which denotes the charge transfer resistance (Rₛ/Rₜ) developed at PpyAPS electrode/electrolyte interface. The constant phase elements (CPE) were Q₁ = 0.0027Ω⁻¹ S₀.005, Q₂ = 0.0005Ω⁻¹ S₀.86
Table 1 – Equivalent circuit fitting parameters and its value for PpyFeCl₃.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rₛ (Ω)</th>
<th>Qₚ₁</th>
<th>Qₚ₂</th>
<th>R₁ (Ω)</th>
<th>Qₚ₂</th>
<th>Qₚ₂</th>
<th>R₂ (Ω)</th>
<th>R₃ (Ω)</th>
<th>C₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before HER</td>
<td>40.2</td>
<td>0.001</td>
<td>0.6029</td>
<td>1623.72</td>
<td>0.0037</td>
<td>0.0136</td>
<td>1723.79</td>
<td>1723.82</td>
<td>–</td>
</tr>
<tr>
<td>After HER</td>
<td>2.22×10⁻¹⁶</td>
<td>0.00083</td>
<td>0.0674</td>
<td>229.681</td>
<td>0.000729</td>
<td>0.8685</td>
<td>393.525</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 2 – Equivalent circuit fitting parameters and its value for PpyAPS.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rₛ (Ω)</th>
<th>Qₚ₁</th>
<th>Qₚ₂</th>
<th>Rₛ/R₁ (Ω)</th>
<th>Qₚ₂</th>
<th>Qₚ₂</th>
<th>R₂ (Ω)</th>
<th>R₃ (Ω)</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before HER</td>
<td>96.415</td>
<td>0.000952</td>
<td>0.5490</td>
<td>2367.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>12608.84</td>
</tr>
<tr>
<td>After HER</td>
<td>2.22×10⁻¹⁶</td>
<td>0.0027</td>
<td>0.0285</td>
<td>397.71</td>
<td>0.000590</td>
<td>0.866</td>
<td>377.03</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

According to the Arrhenius equation [14]

\[ k_{net} = k_B T \exp \left( \frac{-\Delta G^f}{RT} \right) \]  

(8)

where \( k_B \), \( T \), \( \Delta G^f \), \( R \), \( k_{net} \) represents Boltzmann constant in J/K, Temperature in (K), Planck’s constant in Js, activation energy in kJ/mol, Gas constant in K/mol, heterogeneous rate constant (cm/s) respectively. Using Eqs. (7) and (8), the calculated free energy of activation \( \Delta G^f \) for charge transfer process on Ppy before and after HER is shown in Table 3. The electrical and ionic conductivity of PpyFeCl₃ and PpyAPS before and after HER in 0.01 M NaOH were calculated using Arrhenius model [29] as follows:

\[ \sigma = \sigma_0 \exp \left( \frac{-\Delta G^f}{RT} \right) \]  

(9)

where \( \sigma_0 \) – conductivity of Ppy before HER, \( \sigma \) – conductivity of Ppy after HER.

The electrical conductivity’ before and after HER for PpyFeCl₃ is calculated to be 0.616×10⁻⁸ S/cm and 4.3×10⁻³ S/cm using Eq. (9) respectively; for PpyAPS is 0.422×10⁻³ S/cm and 2.51×10⁻³ S/cm. The electrical conductivity of the Ppy are strongly influenced by the preparation conditions such as the nature/concentration of electrolyte or counterion, doping level, current density, synthesis temperature, and solvent [30,31].

The ionic conductivity of Ppy before and after HER is calculated as 0.58×10⁻⁸ S/cm and 2.54×10⁻³ S/cm for PpyFeCl₃ and 0.422×10⁻³ S/cm and 2.65×10⁻³ S/cm using Eq. (9) for PpyAPS respectively.

Foot note*: For PpyFeCl₃ before HER: \( \rho = 1.623.72\Omega \); Resistivity \( \sigma = 616 \times 10^{-8} \) S/cm. After HER, \( R = 229.681 \Omega \); Resistivity \( \sigma = 616 \times 10^{-8} \) S/cm. For PpyAPS before HER, \( \rho = 2367.612 \Omega \); Resistivity \( \sigma = 616 \times 10^{-8} \) S/cm. After HER, \( \rho = 397.711 \Omega \); Resistivity \( \sigma = 616 \times 10^{-8} \) S/cm.

Foot note**: For PpyFeCl₃ before HER: \( \rho = 1723.79\Omega \); Resistivity \( \sigma = 616 \times 10^{-8} \) S/cm. After HER, \( \rho = 393.525 \Omega \); Resistivity \( \sigma = 616 \times 10^{-8} \) S/cm. For PpyAPS before HER, \( \rho = 2367.612 \Omega \); Resistivity \( \sigma = 616 \times 10^{-8} \) S/cm. After HER, \( \rho = 397.711 \Omega \); Resistivity \( \sigma = 616 \times 10^{-8} \) S/cm.

The electrical and ionic conductivity of before and after HER of PpyFeCl₃ is higher than PpyAPS. After HER both PpyFeCl₃ and PpyAPS show a higher conductivity.

The equivalent circuit fitting values for the Nyquist plots are provided in Tables 1 and 2 for PpyFeCl₃ and PpyAPS respectively.

Exchange current density(\( i_0 \)) for HER on Ppy can be calculated from EIS studies by equivalent circuit fitted values using the following expression [14]

\[ R_{ct} = \frac{RT}{nF_i} \]  

(7)

![Fig. 11 – Nyquist plot for (a) PpyFeCl₃ and (b) PpyAPS and its equivalent circuit fitting for before and after HER in 0.01 M NaOH.](image)
and $Ppy_{APS}$ conductivity increases due to the hydroxyl group attached to the Ppy ring. In general, oxidized derivatives of Ppy are good electrical conductors. Thus from EIS analysis, we can conclude that $Ppy_{FeCl_3}$ is better electrolyst in alkaline medium for proton storage and it shows good electrical and ionic conductivity than $Ppy_{APS}$. Hydrogen storage performance of $Ppy_{APS}$ is less in comparison to $Ppy_{FeCl_3}$.

4. Conclusion

Ppy is synthesized via wet chemical method using $Ppy_{FeCl_3}$ and $Ppy_{APS}$ as oxidants. $^1$HNMR analysis confirms the hydrogen bonding between oxygen of SO$_4^{2−}$ anion and the H–N protons of Ppy in $Ppy_{APS}$. In Raman analysis, the transition of benzene to quinonoid form of Ppy before and after HER confirms the hydrogen bonding between oxygen of SO$_4^{2−}$ anion and the H–N protons of Ppy in $Ppy_{APS}$. Electrochemical studies of $Ppy_{FeCl_3}$ possess excellent hydrogen storage ability with lower hydrogen evolution rate whereas $Ppy_{APS}$ showed hydrogen storage with faster HER kinetics in 0.1 M NaOH. In impedance spectroscopy $Ppy_{FeCl_3}$ exhibits higher conductivity than $Ppy_{APS}$. Charge/Discharge studies showed hydrogen storage capacity of $Ppy_{FeCl_3}$ and $Ppy_{APS}$ as 27.24 and 24.4 mAh/g respectively. From the spectroscopic, electrochemical and Raman studies it can be inferred that $Ppy_{FeCl_3}$ is a better electrocatalyst for hydrogen storage, whereas $Ppy_{APS}$ can be a better electrocatalyst for both storage and evolution of hydrogen.

Conflicts of interest

The authors declare no conflicts of interest.

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