Permselectivity and thickness-dependent ion transport properties of overoxidized polyaniline: a mechanistic investigation†

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We report here the permselectivity of overoxidized polyaniline obtained using anodic polarization of polyaniline on glassy carbon electrodes. The contrasting redox behavior of overoxidized polyaniline coated electrodes towards [Fe(CN)₆]³⁻ and [Ru(NH₃)₆]³⁺ has been analyzed using cyclic voltammetry, hydrodynamic voltammetry and electrochemical impedance spectroscopy. This permselectivity vis a vis anion exclusivity arises from the incorporation of counter anions rather than by the formation of new functional groups in the polymer upon overoxidation – as inferred from FT Raman and UV-Visible spectral data. The surface charges of the polymeric films are also deduced from the zeta potential analysis. The thickness-dependent anion exclusion behavior of overoxidized polyaniline is quantitatively interpreted using diffusion coefficient measurements with rotating disc electrodes. The mechanism pertaining to the non-trivial role of film thickness in influencing anion exclusion is confirmed by additional impedance spectroscopy carried out during the overoxidation of polyaniline.

1. Introduction

Among various conducting polymers, polyaniline has been extensively investigated on account of its high conductivity, thermal stability and facile synthetic protocols.¹-³ Owing to its metal-like conductivity and polymeric properties, diverse applications of polyaniline (PANI) can be envisaged such as in sensors,⁴ supercapacitors,⁵ electrocatalysts,⁶ batteries,⁷ electrochromic devices,⁸ corrosion inhibitors,⁹ etc. The synthesis of PANI can be accomplished using chemical or electrochemical routes; electrochemical polymerization results in the formation of films on the electrodes and hence is especially convenient for analytical and catalytic applications. The most interesting feature of PANI is its existence in three different forms (emeraldine, leucoemeraldine and pernigraniline), depending upon the reaction conditions. In general, both chemical and electrochemical polymerization lead to the formation of materials in the oxidized (doped) state. However, the oxidized conducting polymers possess an enhanced sensing ability towards anionic species while the doped conducting materials in the presence of anionic substrates are more sensitive towards cationic species.¹⁰,¹¹ Hence the electrochemical properties and applications of conducting polymers crucially depend upon the swelling/shrinking process wherein the diffusion of counter ions plays an important role.¹²,¹³ In this context, overoxidation offers an additional advantage regarding the properties and applications of conducting polymers. Overoxidation leads to electrochemical degradation resulting in irreversible changes upon anodic polarization and is associated with variations in either conductivity or redox properties.¹⁴ Among various polymers investigated from this perspective, polypyrrole (PPy) and its derivatives, polyindole (PIn) and polythiophene (PTh) deserve mention, wherein large anodic potentials lead to overoxidation. Furthermore, the influence of electrolytes has also been investigated during the overoxidation process and it is inferred that the presence of strong nucleophilic groups such as OH⁻, Br⁻, etc. can alter the conjugated system by introducing new functional groups into the aromatic moiety.¹⁵ Consequently, overoxidation can lead to either electronic or structural changes. The physico-chemical changes occurring upon overoxidation have also been analyzed using various techniques, viz. electrochemical quartz crystal microbalance (EQCM), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS), Raman spectroscopy, etc.¹⁶-¹⁹

Although the precise mechanism of the overoxidation process has still not been elucidated, overoxidized PPy, PIn and PT have immense utility in electrocatalysis,²⁰ sensing,²¹ ion exclusion, permselectivity,²²,²³ etc. It is of interest to mention here the
detailed study by Burgmayer and Murray\textsuperscript{24} on the polymerization of pyrrole on Au electrodes in different solvents and electrolytes with consequent quantitative measurements of the ionic fluxes by a judicious experimental design. By employing impedance analysis and dc resistivity measurements in conjunction with scanning electron microscopy, the permeation characteristics were shown to depend on the oxidation state of polypyrrole \textit{vis a vis} nature of the electrolytes. The extent of ionic permeability can be appropriately tuned – a behavior termed as ion gate. These studies imply the crucial role of polymer-coated electrodes in controlling the ion transport phenomena at the interface. However, the overoxidization of PANI has been rarely studied\textsuperscript{25-27} in contrast to the extensive literature on diverse synthetic methods and applications of PANI.\textsuperscript{28} While the specific role of anions during the overoxidation of PANI has been investigated,\textsuperscript{25,27} the redox features of oxidized PANI have not been elucidated so far.

Here we report the synthesis of overoxidized polyaniline (oPANI) by potentiodynamic cycling of PANI using a large anodic potential range, and the extent of overoxidization is shown to depend upon the thickness of the PANI film. Furthermore, an impressive permselective behavior of the oPANI on glassy carbon (oPANI/GC) electrodes is demonstrated using cyclic voltammetric and electrochemical impedance spectroscopic (EIS) techniques for typical anionic and cationic redox probes. Interestingly, this behavior can be tuned by altering the thickness of the film, brought about by a systematic variation of the deposition time at a constant potential. The anion exclusion behavior of oPANI is also analyzed with the help of hydrodynamic voltammetry. The diffusion coefficients of the redox couples have been estimated in order to comprehend the thickness-dependent anion exclusion behavior. Further, EIS studies are carried out during the overoxidation of PANI in order to understand the mechanism behind the thickness-dependent permselectivity.

2. Experimental section

2.1 Chemicals

Aniline (Merck) was distilled under reduced pressure and stored in a refrigerator. Sodium dodecylsulphate (SDS) from Sigma-Aldrich was used as received. Hexamine ruthenium trichloride and potassium ferrocyanide from Alfa Aesar, and potassium chloride from SRL Chemicals India were used as received. All the chemicals employed here were of analytical grade. Triple distilled water was employed for all the studies.

2.2 Electrochemical measurements

All electrochemical measurements were performed using the CH 660A electrochemical work station (CH Instruments, USA) in a standard three-electrode cell. The glassy carbon (GC) disk electrode of 3 mm diameter (CH Instruments, USA) is the working electrode for polymerization of aniline, while the overoxidized PANI coated GC electrode functions as the working electrode for permselectivity studies. The saturated calomel electrode (SCE) (Bioanalytical Systems, USA) and a Pt wire (Bioanalytical Systems, USA) serve as reference and counter electrodes respectively. All the potentials have been reported here with respect to SCE. Prior to use, glassy carbon (GC) electrodes were cleaned by polishing the electrodes using alumina powder of various grades (viz. 0.30, 0.05 microns) followed by sonication for five minutes in water. For polymerization of aniline, chronocoulometry was employed while overoxidation was carried out using cyclic voltammetry. The potentiostatic polymerization of aniline (0.025 M) on the GC electrode was accomplished in the presence of 0.1 M SDS, which functions both as a supporting electrolyte and a surfactant. After polymerization, the electrode was washed repeatedly with water and dried at room temperature. This PANI coated GC electrode (PANI/GC) was dipped in 0.1 M KCl solution and subjected to potentiodynamic cycling in order to obtain oxidized polyaniline (oPANI). The electrochemical response of the oPANI coated GC (oPANI/GC) electrode was investigated using the redox probes [Fe(CN)\textsubscript{6}\textsuperscript{3-}/\textsuperscript{4-}] and [Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+}/\textsuperscript{4+}] with the aid of cyclic voltammetric (CV) and electrochemical impedance spectroscopy (EIS) techniques. The EIS study for overoxidation was carried out in the frequency range of 10\textsuperscript{5} to 10\textsuperscript{-1} Hz, with an amplitude of 5 mV at a constant potential of 0.8 V. The linear sweep voltammetry (LSV) for both PANI/GC and oPANI/GC electrodes was carried out using rotating disc electrodes. The FT-Raman, FTIR and UV-Vis spectra of both PANI and oPANI were recorded on transparent glass substrates, \textit{viz.} indium tin oxide (ITO) electrodes. ITO electrodes with a resistivity of 25 \(\Omega\) were obtained from CH Instruments, USA. These electrodes were cleaned prior to use by sonication in acetone and distilled water consecutively for five minutes each. All the electrochemical measurements were carried out at a constant temperature of 26 \(\pm 1\) °C.

3. Results and discussion

3.1 Electrochemical synthesis of PANI

Fig. 1 depicts the chronocoulamperograms pertaining to the formation of PANI on the GC electrode at a constant potential of 0.8 V for deposition times of 100 s. While the initial decrease
in current is ascribed to the passivation of the electrode, the subsequent small increase is associated with the nucleation process, leading to the formation of PANI film on the GC electrode. The temporal dependence of current is consistent with the Cottrell equation. We estimate the thickness of the film using the equation:

\[ d = \frac{Q M_w}{z F A \rho} \]  

where \( Q \) denotes the number of coulombs involved in the deposition and is calculated by integrating the area under the chronoamperogram. In eqn (1), \( M_w \) is the molecular weight of aniline (\( M_w = 93.1 \text{ g mol}^{-1} \)), \( \rho \) is its density (\( \rho = 1.02 \text{ g ml}^{-1} \)), \( A \) denotes the geometrical area of the electrode (0.0706 cm\(^2\)) and \( z \) represents the number of electrons per aniline unit (\( z = 0.5 \)). The deposition of PANI on GC electrodes at a constant potential with different deposition times enables a systematic variation of the thickness of the polymer film. From the estimated coulombs passed during the deposition, the thickness follows from eqn (1).

However, it must be emphasized that the estimation of film thickness using the above equation assumes that the faradaic reaction is 100% efficient and no competing reactions are involved during electrodeposition.

### 3.2 Overoxidation studies of PANI

Our essential objective in this study is to demonstrate the impressive features of the over-oxidized PANI and in order to prepare the latter, we have subjected PANI/GC electrodes (of different thickness prepared using different deposition times) to cyclic voltammetric studies in 0.1 M KCl solution using a potential window of 0 V to 1.0 V at a scan rate of 50 mV s\(^{-1}\) for ten cycles. As an illustration, for the PANI/GC electrode obtained using a deposition time of 100 s, a prominent oxidation peak at \( \sim 0.6 \text{ V} \) is noticed (along with a small hump at \( \sim 0.9 \text{ V} \)) during the first cycle in the voltammogram as shown in Fig. 2(A). However, with the increase in the number of cycles, a drastic change occurred wherein no peaks were observed from the 2nd cycle to the 10th cycle of the voltammogram. This implies an irreversible transformation of the polymer film and this feature is consistent with the overoxidation phenomena of PPy and PIn. This behavior may be indicative of either the loss of conjugation (due to the removal of electrons) or the doping of the counter ions (Cl\(^-\)) into the polymer matrix. The appearance of two anodic peaks during the overoxidation process can be interpreted as follows: initially the peak at lower potentials is due to the oxidation of emeraldine salt (of PANI) to pernigraniline which then gets converted to the completely oxidized pernigraniline salt at higher potentials. The formation of emeraldine salt due to the electro-polymerization of aniline was also confirmed from the color of the deposited PANI as well as from the UV-Vis studies (vide infra).

By varying the deposition times, the loading \textit{vis a vis} thickness of PANI film can be controlled. As shown in Fig. 2(B), a positive shift in the peak potential as well as an enhancement in the peak current (for the first cycle) is noticed with the increase in the thickness of the film. With the increase in the film thickness, the peak potential gets shifted to more positive values which indicates that more energy is required for overoxidation of PANI film at higher film thickness. This behavior can be interpreted as follows: (i) at higher film thickness, the extent of incorporation of counter anions is larger (during deposition of PANI) resulting in stable ion-pair formation which requires more energy for overoxidation; (ii) due to the bulky nature of the polymer moiety, the redox center of PANI gets shifted with the increase in polymer thickness necessitating higher energy for further overoxidation. However, the absence of any significant features from the second to the tenth cycle of the cyclic voltammograms is maintained for all thicknesses during overoxidation. Since the magnitude of the peak current depends upon the extent of overoxidation, a higher degree of doping of the counter anions occurs with the increase in the thickness of the film, thereby imparting an electrogative character to the polymer film. The mechanism underlying the overoxidation process may be visualized as follows: the application of higher anodic potentials leads to the facile transformation of PANI to its stable overoxidized form. Also, at lower deposition times, the incorporation of counter-anions occurs to a smaller extent during the deposition of PANI, partly due to their larger sizes [here CH\(_3\)(CH\(_2\))\(_{11}\)OSO\(_3^-\)]. Furthermore, the porous nature of the polymer film as noticed from the SEM images (vide infra) indicates facile entrapment of the counter ions thus causing overoxidation of PANI.

In this context, it is worth mentioning that the peak at \( \sim 0.6 \text{ V} \) (Fig. 2) indicates an irreversible behavior while in other reported studies PANI has been shown to exhibit quasi-reversible response during the overoxidation. In contrast to the earlier works, the present investigation has the following variations in the experimental protocol as regards the overoxidation: (i) potential window and (ii) supporting electrolytes. In our study, we have chosen a larger potential window (0.0 to 1.0 V) to carry out the overoxidation of PANI. At more positive potentials, the irreversible transformation of PANI occurs which yields an anodic peak. Initially the peak at \( \sim 0.6 \text{ V} \) is due to the conversion of emeraldine to the pernigraniline state which...
subsequently transforms to its overoxidized form. On the other hand, the lower potential window employed in earlier studies may inhibit the complete oxidation of the polymer thus causing the quasi-reversible response. Besides, the nature of the supporting electrolytes also plays an important role. In our investigation, we have employed neutral electrolytes for overoxidation while several other reported studies have employed strongly acidic solutions. In general, the irreversible or quasi-reversible behavior during the overoxidation may also be influenced by the oxidation state of PANI.

The influence of various experimental parameters during the overoxidation of PANI was investigated. A change in deposition potential can result in different states of PANI, i.e. emeraldine or pernigraniline, which may alter the extent of overoxidation. As the thickness or mass loading of PANI changes with the increase in the applied potential, the extent of overoxidation also varies. The PANI deposited at higher potential exhibits a larger extent of overoxidation compared that deposited at lower potential. However, PANI deposited at higher potential exhibits a quasi-reversible response during the overoxidation indicating that dopants were excluded to some extent during the reversible cycling. Indeed, PANI deposited at a relatively low applied potential shows irreversible response during the overoxidation. The cyclic voltammograms pertaining to the overoxidation process of PANI deposited at different potentials are provided in Fig. 3(A) and (B).

Further, the effect of electrolyte during the overoxidation process was also analyzed using three different types of electrolyte, i.e. neutral (KCl, KNO₃, etc.), acidic (HCl) and basic (NaOH) medium. The electrochemical response of PANI/GC electrodes in KNO₃ was similar to that in KCl solution. On the other hand, the overoxidation response of PANI was not effective in acidic medium. Although the current response was higher in acidic medium, a quasi-reversible response was observed indicating that overoxidation was not significant. Since in the present context our aim was to prepare overoxidized PANI as inferred from the irreversible appearance of the anodic peak, acidic solution was not preferable. In the case of alkaline solutions such as NaOH, the adherence of the polymer film on the electrode was not satisfactory and hence alkaline media were not considered. The overoxidation of PANI in different electrolyte solutions is provided in Fig. 3(C) and (D). Although the extent of overoxidation of PANI is comparable in KNO₃ and KCl, in the present studies we have deliberately chosen KCl solution for the following reason: the incorporation of counter anions (here Cl⁻) during overoxidation can be easily identified from EDAX studies (see Fig. 3). However, in the case of KNO₃, the inference of counter anions (incorporation) is quite difficult since the elements of NO₃⁻ (i.e. N and O) are also present in the polymer (PANI) and the surfactant (i.e. CH₃(CH₂)₇SO₃⁻). Another reason for choosing KCl may be the oxidation of the NO₃⁻ ion. As a large anodic potential window (0 to +1.0 V) was applied for overoxidation, there might be a chance of oxidation of the nitrate ion at the PANI modified electrode surface.

3.3 Characterization of PANI and oPANI

The characterization of PANI and overoxidized PANI (oPANI) was carried out using FT Raman, FTIR, SEM and UV-Visible spectral studies.

(A) SEM characterization. Fig. 4(A) depicts the SEM images of PANI indicating the sub-micro particle network along with a porous nature. The presence of the surfactant (SDS) yields an aggregated structure of the PANI. On the other hand, Fig. 4(B) represents the SEM images of the oPANI film wherein no significant differences are noticed between PANI and oPANI images. The surface becomes more compact and the porosity of PANI film decreases upon overoxidation. Due to overoxidation, the doping of counter ions into the polymer matrix increases, thereby effectively changing the volume of the polymer.

It is customary to employ strong acids in electro-polymerization since they lead to effective incorporation of counter anions. However, surfactants such as SDS play a dual role (surfactant and electrolyte) during the polymerization of aniline.35,36 The counter anions of the surfactant (SDS) act as dopants during
the polymerization process and due to their larger sizes, the polymerization is slower here in comparison with other strong acids. However, the use of SDS leads to effective overoxidation. In order to verify this, we further carried out the polymerization in LiClO₄ wherein overoxidation occurred to a lower extent. Thus, the use of surfactants during the polymerization leads to the following desirable features: (i) formation of polymers in an ordered manner, (ii) porous nature and (iii) larger extent of overoxidation.
The band at approximately 1595 cm\(^{-1}\) for both PANI/ITO and oPANI/ITO electrodes is associated with the C–C stretching vibration of the quinoid ring along with the C=C stretching vibration of the benzenoid ring of polymers. The band at \(~1505\) cm\(^{-1}\) is attributed to the C=N stretching vibration of the quinoid structure. The band at \(~1360\) cm\(^{-1}\) represents the C–N\(^{\prime}\) stretching vibration of the semiquinoid ring present in PANI indicating the doping phenomena as well as the conducting state of PANI which upon overoxidation leads to an increase in band intensity. This enhances the incorporation of counter anions in oPANI. Further, the band noticed at \(ca.\) 1175 cm\(^{-1}\) is due to the in-plane bending vibration of C–H for both quinoid and benzenoid rings of the polymer. The peaks at \(~730\) cm\(^{-1}\) and \(~520\) cm\(^{-1}\) are due to the imine deformation of the quinoid ring and out-of-plane C–N–C torsion respectively while the band at 415 cm\(^{-1}\) is attributed to the ring deformation or out-of-plane C–H wagging. These Raman spectral data are consistent with the earlier reported values regarding the position of the bands.\(^{37,38}\) However, the differences in the intensities of PANI and oPANI may be attributed to the formation of more quinoid rings as well as enhancement in the degree of protonation or doping of counter ions upon overoxidation.

The FTIR analysis of PANI and oPANI has also been carried out for further confirmation regarding the structural changes occurring upon overoxidation. The inference is consistent with that based on the FT-Raman spectra. The FTIR spectra of PANI and oPANI are provided in Fig. S1 of the ESL\(^{\dagger}\)

(C) UV-Vis spectral study. Since the GC surface is unsuitable for optical studies, we have employed ITO as the substrate for depositing PANI under identical deposition conditions (0.8 V for 200 s). Typically, for PANI/ITO obtained using a deposition time of 200 s, the UV-Vis spectrum shown in Fig. 5(B) exhibits two absorption bands at 418 and 770 nm due to the formation of polarons and localization of charge carriers by \(\pi\)-polarons respectively.\(^{39-41}\) These typical absorption bands are characteristic of the conducting form of PANI (emeraldine).\(^{42,43}\) The deposited PANI is green in color as observed from ITO electrodes after modification. The UV-Vis spectrum of the overoxidized PANI/ITO electrode is also shown in Fig. 5(B). For both PANI and oPANI, the location of the peaks is almost constant although the intensities are not identical. The absorption band intensity at 418 nm is lower for oPANI compared to that for PANI; in contrast, the band intensity at 770 nm for oPANI is larger compared to that for PANI. Furthermore, the color of the polymer changes from green (PANI) to pale brown (oPANI) upon overoxidation. The variation in the peak intensities reflects the change in the doping level, i.e., due to overoxidation, the incorporation of counter anions into the polymer matrix increases altering the behavior of the polaron transition.

From the FT Raman and UV-Vis studies, we infer that although the overoxidation process does not introduce any new functional group, structural or electronic changes occur. Interestingly, overoxidation may lead to the introduction of new functional groups into the aromatic ring of PPy and PT\(^{4,45}\) due to the nucleophilic attack by OH\(^{-}\) ions or H\(_2\)O molecules. However, the introduction of new functional groups can be prevented from the interaction of anions present in the polymer matrix with bipolarons. It has been shown that the presence of strong interactions between the anions present (such as ClO\(_4^{-}\), SO\(_4^{2-}\)) in the polymer matrix and bipolarons (of PANI) shields the nucleophilic attack.\(^{27}\) In this context, the counter anions of the surfactant, viz. CH\(_3\)(CH\(_2\))\(_{11}\)OSO\(_3^{-}\), incorporated into the polymer matrix interact strongly with bipolarons (of PANI) through hydrogen bonding as well as dipole–dipole interactions. This results in the shielding of bipolarons from nucleophilic attack by H\(_2\)O molecules, thereby preventing the installation of new functional groups. The plausible structure of oPANI is shown in Scheme 1.
(D) Thickness measurements. The thickness of polymer film was measured using the PANI coated ITO electrode prepared with different deposition times. Table 1 provides the thickness value evaluated from two different methods, i.e. (i) from eqn (1) and (ii) using an ellipsometry instrument.

In what follows, we have employed the thickness values estimated using eqn (1).

### 3.4 Electrochemical characterization of the modified electrodes and their permselective behavior

While the PANI modified electrodes have been extensively employed in diverse applications such as in sensor devices, supercapacitors, etc., the overoxidized form has not received much attention. As a preliminary step, we have investigated the redox behavior of the [Fe(CN)₆]³⁻/C₀ complex on PANI/GC and oPANI/GC electrodes. Fig. 6(A) depicts the corresponding cyclic voltammetric response of bare GC, PANI/GC and oPANI/GC electrodes wherein the PANI/GC electrode exhibits well defined anodic and cathodic peaks towards [Fe(CN)₆]³⁻. The anodic ($E^{a}_p$) and cathodic peak potentials ($E^{c}_p$) are shifted towards more positive and more negative values respectively in comparison with the bare GC electrode, thus altering the differences in the peak potentials ($\Delta E_p = |E^{c}_p - E^{a}_p|$). The current response is however lower than that for the bare GC electrode which may be due to the sluggish electron transfer caused by the hindrance of polymeric materials. Hence it follows that upon deposition of PANI on the electrode surface, the redox properties have been altered. While this redox behavior of the PANI/GC electrode is not unusual, an unexpected behavior arises in the case of the oPANI/GC electrode. A complete shutdown of the redox signal is observed when the oPANI/GC electrode is employed towards [Fe(CN)₆]³⁻. This observation implies that the oPANI film is negatively charged which repels the anionic species; indeed, this anionic character is imparted upon overoxidation of the PANI film. During overoxidation, the doping of counter anions into the polymer matrix occurs on account of electrostatic neutrality which provides the anionic nature. Energy dispersive X-ray analysis (EDAX) shows the presence of dopant in both PANI and its overoxidized form. EDAX studies of PANI and oPANI were carried out on the ITO electrode. From the EDAX spectrum the presence of dopant can be inferred; e.g. S and O represent the counter anions of SDS inserted during the deposition of PANI while Cl represents the incorporation of ions during the overoxidation. The EDAX spectrum of PANI and oPANI is provided in Fig. S2 of the ESI.

Nevertheless, it is worth mentioning here that the formation of new functional groups in the polymer chain can also impart anionic charges as has been demonstrated for overoxidized polythiophene and polypyrrole. Interestingly, we have accomplished here the synthesis of oPANI wherein only electronic changes occur without the formation of any new functional groups. In order to confirm this interesting redox property as well as the selectivity of oPANI, we have chosen [Ru(NH₃)₆]³⁺ as a typical cationic redox probe. At lower oPANI film thickness, the ruthenium complex has a voltammetric response analogous to that of the bare GC electrode as shown in Fig. 6(B), albeit with a small shift in the peak potentials.

### Table 1: Comparison of the thickness of PANI estimated using two different methods

<table>
<thead>
<tr>
<th>Deposition time (s)</th>
<th>Calculated thickness using eqn (1) (µm)</th>
<th>Estimated thickness from ellipsometry (µm)</th>
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<tbody>
<tr>
<td>100</td>
<td>1.33</td>
<td>1.01</td>
</tr>
<tr>
<td>150</td>
<td>1.59</td>
<td>1.16</td>
</tr>
<tr>
<td>200</td>
<td>2.03</td>
<td>1.94</td>
</tr>
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</table>

Both the calculated and estimated thickness values have an error of ±3%.
This implies the permselective behavior of the oPANI film. However, with the increase in the film thickness, the voltammetric response becomes distorted. Further, it is necessary to investigate whether the anion exclusion behavior of oPANI/GC varies with the concentration of the redox probe. In this study, when the concentration of the anionic redox species \([\text{Fe(CN)}_6]^{3-}\) was varied from 5 mM to 40 mM, the featureless voltammograms arise even at higher concentration albeit with minor changes in current (Fig. S3 of ESI†). This implies that the anion exclusion behavior of the oPANI/GC electrode is retained at higher concentrations too.

The oPANI/GC electrodes as prepared from different electrolyte solutions such as KNO\(_3\), KCl, HCl, etc. were employed for permselective analysis. Among these, the oPANI/GC electrode obtained from neutral electrolyte solution exhibited superior permselective behavior compared to that obtained from acidic medium. It can be recollected from the voltammetric behavior of PANI/GC in HCl that it shows a quasi-reversible response indicating a lower extent of dopant incorporation. This leads the less anionic nature of the PANI film. On the other hand, the irreversible voltammetric response of PANI/GC in KCl or KNO\(_3\) results in facile entrapment of the counter anions into the polymer matrix due to which the electrode exhibits superior permselectivity. The voltammetric response of the oPANI/GC electrode as obtained from different electrolytes is provided in Fig. S4 of the ESI. Further, the effect of deposition potential on the permselective behavior of oPANI/GC was also studied, and it was found that deposition at a relatively low potential is more preferable; the corresponding voltammetric response is shown in Fig. S5 of the ESI.

### 3.5 Effect of film thickness on permselectivity and anion exclusion behavior

The permselective behavior of oPANI/GC electrodes can also be further tuned by varying the thickness of the film. At a lower thickness of the PANI film \((d = 0.75 \mu m)\), the voltammetric response of the oPANI/GC electrode towards \([\text{Fe(CN)}_6]^{3-}\) corresponds to an irreversible electron transfer process. On the other

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**Fig. 6** Cyclic voltammogram for the electrochemical response of PANI and oPANI/GC electrodes towards (A) \([\text{Fe(CN)}_6]^{3-}\) and (B) \([\text{Ru(NH}_3)_6]^{3+}\). The inset in (A) depicts the featureless voltammogram of oPANI/GC towards \([\text{Fe(CN)}_6]^{3-}\). (C and D) The effect of oPANI film thickness for \([\text{Fe(CN)}_6]^{3-}\) and \([\text{Ru(NH}_3)_6]^{3+}\) respectively. Scan rate = 50 mV s\(^{-1}\).
hand, a complete suppression of the redox peaks is observed at higher thicknesses [Fig. 6(C)]. This voltammetric response at different thicknesses of polymer films can be explained in the following manner: at a lower thickness of the PANI film, the doping of counter anions (here Cl⁻) occurs to a lower extent which decreases the anionic character of oPANI. Hence, the diffusion of the anionic redox species towards the modified electrode surface is more facile. This is confirmed by the estimated diffusion coefficients at the oPANI/GC electrode (vide infra). However, the oPANI/GC electrode at lower thickness exhibits only the cathodic peak towards the anionic redox species within the applied potential window. Since oPANI possesses an anionic nature, it can function as a facile electron donor rather than as an electron acceptor. Hence [Fe(CN)₆]³⁻ can be reduced to [Fe(CN)₆]⁴⁻ at the oPANI/GC electrode (at lower film thickness) while [Fe(CN)₆]⁴⁻ cannot be oxidized to [Fe(CN)₆]³⁻. Consequently, the anodic peak of [Fe(CN)₆]³⁻ did not appear. On the other hand, due to the larger extent of the anionic nature of oPANI at higher polymer film thickness, the significantly lower diffusion coefficient of [Fe(CN)₆]³⁻ leads to a featureless voltammogram. Analogously, this crucial role of the film thickness is exhibited by [Ru(NH₃)₆]³⁺ too on oPANI/GC and a reversible electron transfer process is inferred for a thickness of 0.75 μm. With the increase in thickness, both the peak potentials get shifted towards more negative values in conjunction with a larger magnitude of ΔEₚ [Fig. 6(D)], finally culminating in a weak voltammetric response. This unexpected behavior may be attributed to adsorption of the complex at the modified electrode; at higher polymer film thickness, the adsorption of [Ru(NH₃)₆]³⁺ occurs in both PANI and oPANI/GC electrodes. This tends to decrease the electron transfer rate constant between the electrode and the analyte. Furthermore, the diffusion coefficients of [Ru(NH₃)₆]³⁺ too decrease with the increase in film thickness (Table 3). These two factors may be responsible for the flat voltammometric signal. This peculiar redox response of the oPANI/GC electrode at higher film thickness towards cationic and anionic redox probes can be misleading regarding the permselective behavior. However, analogous observations have also been made earlier for the ruthenium complex wherein the distorted voltammetric response occurs at higher polymer (PIn) thickness.¹⁴

For further confirmation of the permselective properties of oPANI, we carried out additional cyclic voltammetric and EIS experiments using the same polymer thickness for both the species. Fig. 7(A) depicts the cyclic voltammetric response of the oPANI/GC electrode towards [Ru(NH₃)₆]³⁺ and [Fe(CN)₆]³⁻ using the same thickness of the PANI film (0.92 μm). A quasi-reversible behavior is observed for the cationic redox probe while a featureless voltammogram arises for the anionic redox probe at the oPANI/GC electrode. This behavior is attributed to the anionic nature of the oPANI film caused by overoxidation. In order to comprehend the origin of this permselective behavior, we have employed EIS studies of the oPANI/GC electrode with a constant film thickness (0.92 μm) at an applied potential of −0.25 V. Although [Ru(NH₃)₆]³⁺ and [Fe(CN)₆]³⁻ have different standard reduction potentials (E⁰ = 0.10 V and 0.36 V respectively vs. standard hydrogen electrode⁴⁸), we have deliberately chosen a more negative potential in view of the satisfactory voltammetric response exhibited by both the species at this value. Fig. 7(B) depicts the Nyquist plots of the oPANI/GC electrode for [Ru(NH₃)₆]³⁺ and [Fe(CN)₆]³⁻ wherein the customary semi-circles are noticed in the high frequency region along with vertical lines at low frequencies. The diameter of the semi-circle yields the charge transfer resistance (Rₜ) which is significantly higher for [Fe(CN)₆]³⁻ compared to that for [Ru(NH₃)₆]³⁺. Indeed Rₜ is related to the exchange current density i⁰ as⁴⁹

\[
Rₜ = \frac{RT}{nFi⁰}
\]

Fig. 7 Comparative performance of oPANI/GC electrodes (thickness = 0.92 μm) towards [Fe(CN)₆]³⁻ and [Ru(NH₃)₆]³⁺ using (A) cyclic voltammetry and (B) Nyquist plots. The parameters employed in impedance studies are as follows: frequency = 10⁵ to 10⁻¹ Hz; amplitude = 5 mV. The inset in (B) depicts the equivalent circuit employed for fitting the Nyquist plots. The points denote the experimental data while the line indicates the fitting using the equivalent circuit.
with $n$ being the number of electrons transferred ($=1$). Furthermore, the exchange current density is directly proportional to the standard heterogeneous electron transfer rate constant ($k_0$) and bulk concentration of the reactant ($c_n$), i.e.

$$i_0 = nFACK_0$$

and hence

$$R_{CT} = \frac{RT}{nF^2ACK_0}$$

(4)

Since the charge transfer resistance is inversely proportional to the heterogeneous electron transfer rate constant, a sluggish reaction kinetics is inferred on account of the repulsive behavior of the negatively charged oPANI film towards $[\text{Fe(CN)}_6]^{3-}$. On the other hand, the considerable decrease of $R_{CT}$ for $[\text{Ru(NH}_3)_6]^{3+}$ is attributed to the facile electron transfer on account of the electrostatic attraction of the cationic species towards the negatively charged oPANI film. This contrasting behavior of the anionic and cationic redox couples in the case of oPANI/GC electrodes using the EIS data is consistent with the cyclic voltammetric behavior as regards the permselectivity. The equivalent circuit employed for fitting the Nyquist plots is shown in Fig. 7(B) and it consists of two constant phase elements (CPE$_1$ and CPE$_2$) with exponents $n_1$ and $n_2$, in addition to the solution resistance ($R_s$) and charge transfer resistance ($R_{CT}$). The system parameters are listed in Table 2.

It is of interest to enquire whether the redox response arises from PANI and oPANI themselves rather than from the redox probes. In order to verify this, we have studied the voltammetric response of PANI and oPANI/GC electrodes containing only the electrolyte (0.1 M KCl solution) without the redox probe. Since the cyclic voltammetric response was observed only in the presence of the redox probe (Fig. S6 of the ESI†), we attribute this behavior to the reactions involving the redox couple. The EIS data also confirm this inference (Fig. S6 of ESI†). Further insights regarding the origin of permselectivity may be obtained using zeta potential measurements.

### 3.6 Zeta potential analysis

In order to comprehend the above behavior regarding the permselectivity of the modified electrodes, the surface charges of the polymeric films were estimated using zeta potential analysis. The zeta potential measurements were carried out by dispersing the solid PANI or oPANI film in an aqueous solution. For brevity, we have chosen PANI of thickness 1.17 μm. Fig. 8 depicts the zeta potential values of PANI and oPANI. The zeta potential of PANI is approximately (1.12 ± 0.50) mV indicating the slight positive surface charge of the PANI film. This implies that due to the bulky nature of SDS counter anions, doping occurs to a lower extent. This value is in agreement with that of the emeraldine form in an earlier study. The zeta potential of oPANI has also been measured as $-(31.95 ± 0.07)$ mV indicating that the polymeric film here acquires a negative charge. Upon overoxidation, the entrapment of counter anions occurs into the polymer matrix in an efficient manner leading to the anionic nature of the PANI film. The zeta potential value of oPANI also suggests that the polymeric film is quite stable.

#### 3.7 Transport phenomena using rotating disk electrode voltammetry at different film thickness

Hydrodynamic voltammetry using rotating disk electrodes (RDE) provides quantitative information on both electrode kinetic and mass transfer parameters. It is of interest to analyze the thickness-dependent permselectivity from the diffusion coefficient data using RDE studies. The limiting current $i_L$ given by the Levich equation is employed to estimate the diffusion coefficient of the species:

$$i_L = 0.620nFAD^{2/3}L^{1/2}C_0^{1/6}$$

(5)

where $A$ is the area of the electrode surface (cm$^2$), $D$ and $c$ denote respectively the diffusion coefficient (cm$^2$ s$^{-1}$) and the concentration of the analyte (0.005 mol l$^{-1}$), $\omega$ is the rotation speed (rad s$^{-1}$), $n$ is the number of electrons transferred ($n = 1$) and $\nu$ is the kinematic viscosity of the solution $51^{1,2}$ $(\nu_{[\text{Fe(CN)}_6]^{3-}} = 8.59 \times 10^{-1} \text{ cm}^2 \text{s}^{-1}$ and $\nu_{[\text{Ru(NH}_3)_6]^{3+}} = 8.86 \times 10^{-3} \text{ cm}^2 \text{s}^{-1}$). The diffusion coefficients estimated from the slope of the $i_L$ vs. $\omega^{1/2}$ plot for $[\text{Fe(CN)}_6]^{3-}$ ($D = 7.80 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$) and $[\text{Ru(NH}_3)_6]^{3+}$ ($D = 7.64 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$) at the bare GC electrode are in agreement with the reported values. $51^{2,3-56}$ The corresponding LSV for the anionic and cationic redox couples at the bare GC electrodes is shown in Fig. S7 of the ESI.$^\dagger$ The LSV response of $[\text{Fe(CN)}_6]^{3-}$ and $[\text{Ru(NH}_3)_6]^{3+}$ on PANI/GC and oPANI/GC at different thickness is shown in Fig. 9 wherein an increase in the onset potentials as well as a decrease in the limiting current in comparison with the bare GC electrode is observed.

### Table 2

<table>
<thead>
<tr>
<th>Redox probe (Ω)</th>
<th>CPE$_1$</th>
<th>CPE$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe(CN)}_6]^{3-}$</td>
<td>185 22.14 1.1</td>
<td>0.62 0.65 0.35</td>
</tr>
<tr>
<td>$[\text{Ru(NH}_3)_6]^{3+}$</td>
<td>200 3.12 2.1</td>
<td>0.82 3.20 0.48</td>
</tr>
</tbody>
</table>
As the thickness of the PANI film increases, this shift in the onset potentials as well as the decrease in the limiting current deduced from the RDE studies for both the redox probes (Fig. 9A and B) is consistent with the cyclic voltammetric response. The LSV behavior of $[\text{Fe(CN)}_6]^{3-}/[\text{Fe(CN)}_6]^{4+}$ and $[\text{Ru(NH}_3)_6]^{3+}/[\text{Ru(NH}_3)_6]^{2+}$ for different rotational speeds at PANI/GC and oPANI/GC of different thickness is provided in the ESI† (Fig. S8 and S9).

The Koutecky–Levich plot has been made (Fig. 9C and D) from the limiting current response of the various modified electrodes towards $[\text{Fe(CN)}_6]^{3-}/[\text{Fe(CN)}_6]^{4+}$ and $[\text{Ru(NH}_3)_6]^{3+}/[\text{Ru(NH}_3)_6]^{2+}$ at different rotational speeds at PANI/GC and oPANI/GC of different thickness is provided in the ESI‡ (Fig. S8 and S9).

‡ The plots given in Fig. 9C and D are not passing through the origin since there is a kinetic component associated with the redox process in the case of both PANI/GC and oPANI/GC electrodes. On the other hand, for bare GC electrodes, the limiting current is essentially due to the mass transfer process. However eqn (5) is approximately applicable since the linear regime is concerned with the mass transfer controlled current and square root of the rotation rate.

Subsequently, we have estimated the diffusion coefficients of $[\text{Fe(CN)}_6]^{3-}$ and $[\text{Ru(NH}_3)_6]^{3+}$ at different thickness of PANI/GC and oPANI/GC electrodes (Table 3). At lower thickness of the PANI film ($d = 0.75 \, \mu m$), the diffusion coefficient of $[\text{Fe(CN)}_6]^{3-}$ at the PANI/GC electrode is nearly identical to that at the bare GC electrode; a slight decrease in the diffusion coefficient ($D$) is attributed to the presence of bulky polymeric species. However, the extent of decrease in $D$ is higher for the oPANI/GC electrode indicating the repulsive nature of oPANI. At a film thickness of 1.17 μm, $D$ pertaining to oPANI/GC is significantly smaller than that for PANI/GC, confirming the electrostatic repulsion of the negatively charged species due to the anionic nature of the film. With a further increase in the film thickness ($d = 1.35 \, \mu m$), a dramatic decrease in $D$ is observed for the oPANI/GC electrode in comparison with the PANI/GC electrode 

$$D_{[\text{Fe(CN)}_6]^{3-}}^{\text{PANI/GC}} = 18.6$$

A comparison based on the diffusion coefficients of $[\text{Fe(CN)}_6]^{3-}$ as estimated from RDE data at different thickness of both PANI/GC and oPANI/GC is shown in Fig. 10A. We infer that the extent
of overoxidation increases with the thickness of the polymer film inducing a higher anionic nature of the film which in turn retards the movement of anionic species at the interface of the oPANI/GC electrode.

The diffusion coefficient of \([\text{Ru(NH}_3\text{)}_6]^{3+}\) has also been estimated analogously at PANI/GC and oPANI/GC electrodes. While the general trend of the decrease in \(D\) with the increase in film thickness is valid here too, there are a few subtle aspects in the case of \([\text{Ru(NH}_3\text{)}_6]^{3+}\). Since the diffusion coefficient of \([\text{Ru(NH}_3\text{)}_6]^{3+}\) at lower film thickness \((d = 0.75 \, \mu\text{m})\) of both PANI/GC and oPANI/GC is almost equal to that for the bare GC electrode, we infer that the negative charge of oPANI does not play a role in altering the diffusion coefficient. However, as the thickness increases to 1.17 \(\mu\text{m}\), a substantial decrease in the diffusion coefficient is noted at oPANI/GC which is almost equal to that for PANI/GC. Upon further increase in PANI film thickness (from 1.17 to 1.35 \(\mu\text{m}\)), the diffusion coefficient of \([\text{Ru(NH}_3\text{)}_6]^{3+}\) decreases for both PANI/GC and oPANI/GC electrodes (whereas the \(D\) value is nearly the same for \([\text{Ru(NH}_3\text{)}_6]^{3+}\) at PANI/GC and oPANI/GC; \(D_{\text{PANI/GC}}^{[\text{Ru(NH}_3\text{)}_6]^{3+}} / D_{\text{oPANI/GC}}^{[\text{Ru(NH}_3\text{)}_6]^{3+}} \approx 1\)). Thus at higher thickness, the electron transfer process becomes sluggish either due to the hindrance of the polymeric species or due to the adsorption of the ruthenium complex. Fig. 10B compares the diffusion coefficients of \([\text{Ru(NH}_3\text{)}_6]^{3+}\) at different thickness of PANI/GC and oPANI/GC electrodes wherein almost similar diffusion coefficient values are obtained unlike for \([\text{Fe(CN)}_6]^{3-}\) indicating that overoxidation does not alter the response of the cationic species. On the other hand, the diffusion coefficient of \([\text{Fe(CN)}_6]^{3-}\) at the oPANI/GC electrode shows a significant and sequential decrease with the increase in thickness in contrast to PANI/GC (Fig. 10A).

3.8 Mechanistic investigation on the thickness dependent anion exclusion behavior of oPANI/GC electrodes

Further insights into the thickness-dependent permselective \(\text{vis a vis}\) anion exclusion behavior can be obtained by carrying out the impedance study during the overoxidation of PANI of different film thickness. Fig. 11(A) depicts the Nyquist plots pertaining to the overoxidation of the PANI/GC electrode at a constant potential of 0.8 V in the frequency range of \(10^5\) to \(10^{-1}\) Hz.\(^\text{§}\) We note that as the thickness of the polymer film increases, the charge transfer resistance decreases, indicating facile overoxidation at higher thickness. This behavior is consistent with the inference from the cyclic voltammetric analysis, \(\text{viz.}\) a larger extent of overoxidation at higher film thickness.

An alternate interpretation can be obtained by comparing the real and imaginary parts of the total impedance, \(\text{viz.}\),

\[
Z' = R_Q + R_{CT} + \sigma \omega^{-1/2}
\]

\[
Z'' = \sigma \omega^{-1/2} + 2 \sigma^2 C_d
\]

where \(R_Q\) denotes the solution resistance, \(\omega\) denotes the angular frequency \((= 2\pi f)\) and \(\sigma\) denotes the Warburg coefficient given by\(^{49}\)

\[
\sigma = \frac{RT}{n^2 F^2 A \sqrt{2} \left( \frac{1}{D_{\text{ox}}^{1/2}[\text{ox}]} + \frac{1}{D_{\text{red}}^{1/2}[\text{red}]} \right)}
\]

Although the above equation is in general valid for the reversible/ quasi-reversible reactions, the same may be rewritten for the anion doping/de-doping process represented as

\[
\text{PANI} + \text{Cl}^- \rightarrow (\text{PANI})\text{Cl}^- + e^-\]

The diffusion of the counter-ions from the bulk solution to the polymer matrix occurs during the overoxidation process and consequently eqn (8) is modified as

\[
\sigma = \frac{RT}{n^2 F^2 D_{\text{cl}}^{1/2} \sqrt{2} \left( \frac{1}{[\text{Cl}^-]_{\text{bo}}} + \frac{1}{[\text{Cl}^-]_{\text{pm}}} \right)}
\]

where \([\text{Cl}^-]_{\text{bo}}\) and \([\text{Cl}^-]_{\text{pm}}\) denote the concentration of \(\text{Cl}^-\) ions in the bulk and the polymer matrix respectively while \(D_{\text{cl}}\) represents the diffusion coefficient of \(\text{Cl}^-\) ions. The Warburg coefficient \(\sigma\) estimated from the slope of the \(Z'\) vs. \(\omega^{-1/2}\) plot (Fig. 11B) is inversely proportional to the thickness of the PANI film. This variation in the Warburg coefficient with the thickness of the film can be interpreted in the following manner: as the thickness of the PANI film increases, greater incorporation of counter ions (higher concentration of \([\text{Cl}^-]_{\text{pm}}\)) occurs into the polymer matrix during the overoxidation which effectively decreases the \(\sigma\) value (since \(\sigma\) is inversely proportional to \([\text{Cl}^-]_{\text{pm}}\)). This leads to the variation in the degree of the anionic character of oPANI with the change in the film thickness thus resulting in dissimilar voltammetric response towards the anionic redox probe [Fig. 6(C)]. Further confirmation regarding the incorporation of the counter ions during the overoxidation with the change in the thickness of the PANI film can be obtained from the UV-Vis spectral analysis. The UV-Vis spectra of PANI and oPANI at different thickness are shown in Fig. 12. The absorption band corresponding to the \(\pi\)-polaron transition at higher wavelength becomes more intense upon overoxidation. However, the extent of increase in the absorption band

---

\(^{\text{§}}\) This frequency range was chosen \((10^5\) to \(10^{-1}\) Hz) taking into account the time required for ten cycles in the potential window of 0 to 1.0 V at a scan rate of 50 mV s\(^{-1}\) for cyclic voltammetric study during the overoxidation.
(higher wavelength region) due to overoxidation at higher polymer film thickness is larger, thereby enhancing the doping of counter anions into the PANI matrix. This leads to the greater anionic nature of the oPANI film at higher film thicknesses. The overoxidized PANI of different thickness prepared using EIS was further employed for permselectivity studies wherein an analogous redox behavior was noticed, consistent with the potentiodynamic overoxidation. A schematic representation for the permselective behavior of oPANI is shown in Scheme 2.

The mechanism of charge transport through chemically modified electrodes has been a fascinating area of research on account of its implications in electrocatalysis and electroanalysis. In the case of redox polymer electrodes, several competing processes (electron hopping, counterion diffusion,
ion pair formation, etc.) play a crucial role in the mechanism of charge transport. On the other hand, electrodes coated with conducting polymers have an impressive range of applications in various fields. Hence it is imperative to investigate overoxidized conducting polymers as regards the formation mechanism and behavior towards redox probes. The permselectivity of polypyrrole coated on Au electrodes has been investigated earlier by Burgmayer and Murray using a combination of cyclic voltammetry, ac impedance, dc resistance, permeation measurements and microscopic studies. The tuneable nature solely arising from the charged state of PPy has been termed as ‘ion gate’ and rationalised in terms of ionic mobility vis a vis conductivity. On the other hand, we have elucidated here the mechanism of the permselective nature of overoxidized PANI using hydrodynamic voltammetry with two typical redox probes. The roughness of the polymeric film decreases upon overoxidation of PANI which leads to less porosity. Hence the origin of permselectivity or anion exclusivity may also arise due to the size effects. In this regard, the quantitative estimation of porosity is useful. However, in the present study we have proposed that anion exclusivity is imparted due to the anionic nature of the overoxidized polymer. In order to confirm this, we have measured the zeta potential of the oPANI films \((\zeta = -31.9 \text{ mV})\). This value indicates that oPANI possesses negative charge in contrast to the PANI film \((\zeta = 1.18 \text{ mV})\). This value suggests that the anion exclusivity arises on account of the negative charge of the oPANI film. It is also essential to extend this analysis to other anionic and cationic redox probes such as \([\text{IrCl}_6]^{2–}\) and \([\text{Pt(NH}_3)_2]^{4+}\) respectively for deciphering whether ionic sizes or charges are crucial in dictating permselectivity. Analogously, ionic conductivity and double layer capacitance of the chemically modified electrodes need to be estimated in order to obtain further insights.

4. Conclusions

The overoxidized PANI on glassy carbon electrodes has been demonstrated to possess an impressive anion-exclusion nature, as inferred from various electrochemical techniques using \([\text{Fe(CN)}_6]^{3–}\) and \([\text{Ru(NH}_3)_6]^{3+}\) as typical redox probes. Using FT Raman and UV-Visible spectral data, the permselectivity is shown to arise without the formation of any new functional groups within the polymeric moiety. The zeta potential values provide a quantitative measure of surface charges, confirming the origin of permselectivity. The diffusion coefficients of these redox couples estimated using the rotating disc electrodes provide a quantitative interpretation of ion transport at the film/solution interface. The crucial role of the film thickness in influencing the behavior of the redox couples has been pointed out.

![Fig. 12](image-url) UV-Vis spectra of PANI/ITO and oPANI/ITO electrodes at different film thicknesses.

![Scheme 2](image-url) Schematic representation of permselectivity of oPANI.
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