Electroactive polymer materials.

- Electroactive polymers are macromolecular materials which exhibit a capacity to:
  - Pass electric current.
  - Store charge.
  - Display redox activity.
    - Sites in polymer may undergo oxidation/reduction when a potential is applied to the material.
- Applications:
  - Battery materials
  - Electrochromic displays
  - Microelectronic devices
  - Molecular electronics
  - Electrocatalysis
  - Chemical/biological sensor technology
  - Energy conversion
  - Corrosion protection
  - Actuators.
Nobel Prize in Chemistry 2000
Electrically Conductive Plastic

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Some ECP materials.

Scheme 1. Examples of a few conjugated polymers, note the bond-alternated structures.
Polymer modified electrodes.

- Have potential induced redox transformations within polymer matrix which enables electronic communication to be made between underlying support electrode surface and sites located within the bulk of the polymer film.
- Real situation: Bound spaghetti model. Complex intermixing between polymer strands and solvent medium.

Classification of electroactive polymer materials (I).

- Redox Polymers
  - Localized state conductors
  - Contain redox active groups covalently bound to an electrochemically inert polymer backbone.
  - Electron transfer occurs over macroscopic distances via process of sequential electron self exchange between neighbouring redox groups. (Tarzan swing mechanism). This is termed redox conduction or electron hopping.
  - Magnitude of electronic conductivity depends on mole fraction of oxidized sites in polymer film.
  - E.g. poly(vinylferrocene).

- Electronically Conducting Polymers
  - Polymer backbone extensively conjugated resulting in considerable charge delocalization.
  - Polymer chains are electronically conducting.
  - Charge transport occurs via defects on polymer chain (polarons, bipolarons, solitons) which are generated via chain oxidation or reduction.
  - Material is hydrophobic and insulating in reduced state and hydrophilic and conducting in oxidized state.
  - Conductivity is due to transport both of electrons and counterions.
  - Charge transport along polymer chain rapid, interchain charge transfer is usually rate limiting.
  - High conductivity values obtained (ca $10^5$ S cm$^{-1}$). Conductivity value obtained depends on quality of polymer chains formed.
  - E.g. poly(pyrrole), poly(aniline).
Classification of electroactive polymer materials (II).

- **Loaded Ionomers.**
  - Ionomer: electroinactive polymer material containing fixed charged sites attached to polymer chain. Formed via drop or spin coating of dissolved polymer onto a support surface.
  - Counterions are associated with fixed charged sites. These can undergo ion exchange with counterions of the same charge sign present in solution.
  - Can load ionomer matrix with charged redox active inorganic complex ions via ion exchange and partition. Hence a loaded ionomer is a composite system containing a three dimensional dispersion of redox active species within an inert polymer matrix.
  - Incorporated redox species bound to fixed sites on ionomer via electrostatic binding. Resultant material exhibits redox conductivity.
  - Observed conductivity facilitated by:
    - Local electron hopping between electrostatically bound redox sites as in redox polymer
    - Local physical diffusion of redox groups in ionomer matrix.
  - E.g. ferricyanide in protonated poly(vinyl pyridine, ruthenium hexammine in Nafion.

Fabrication of PME thin films.

- **Solution casting.**
  - Spin coating, drop coating of pre-formed (via standard synthetic methods) polymers dissolved in suitable solvent onto support electrode surfaces. Once solvent evaporates adherent polymer film with good mechanical properties remains.
  - Layers formed may be inhomogeneous wrt thickness.
  - Polymer material readily characterised via standard spectroscopic methods prior to solution coating.
  - Typically used for redox polymers and loaded ionomer materials.

- **Electropolymerization.**
  - In situ oxidative electropolymerization of redox active monomer to form insoluble polymeric multilayer on support electrode surface.
  - Deposition can be accomplished via constant potential, constant current or cyclic potential methods.
  - Layers formed are homogeneous with well defined thickness.
  - Layer thickness directly related to deposition charge via Faraday law of electrolysis.
  - Method good for reproducible fabrication of thin films.
  - Layers formed are difficult to characterise fully via standard spectroscopic methods although some progress has been made using methods such as probe beam deflection, ellipsometry and FTIR.
  - Mainly used for electronically conducting polymer materials.
Film characterization methods.

- **Electrochemical.**
  - Cyclic voltammetry (electrochemical spectroscopy).
  - Complex impedance spectroscopy.
  - Potential step chronoamperometry/chronocoulometry.
  - Hydrodynamic voltammetry.
  - Electrochemical quartz crystal microbalance.
- **Spectroscopic.**
  - FTIR spectroscopy.
  - ESR spectroscopy.
  - UV/Vis spectroscopy.
  - Probe beam deflection methods.
  - ESCA analysis.
  - AFM/STM methods.
  - Ellipsometry (single wavelength and spectroscopic modes).
Monolayer vs multilayer modified electrodes.

2D microstructure.
Redox active monolayer.
Surface coverage ca. 10^{-10} mol cm^{-2}.

Monolayer derivitized electrodes developed first.
New interest in these systems:
Redox active self assembled monolayers, e.g., ferrocene containing alkane thiols.
CMO systems based on 3D microstructures are preferable for chemical sensor and electrocatalytic systems, since there is a 3D dispersion of active sites throughout the material and a high concentration of active sites is achieved even though the quantity of active material is small.

3D microstructure.
Redox active multilayer.
Surface coverage ca. 10^{-8} mol cm^{-2}

Electronically conducting polymers.

- Polyacrylonitrile
- Polypropylene
- Polyethylene
- Polymethylene
- Polyfuran
Conductivity variation with temperature for a range of technologically useful materials.

Electropolymerization mechanism of ECP materials.
Organic chemistry of Poly(pyrrole) formation.

RR coupling most probable
RM coupling also possible.

Driving force: re-establishment of aromatic rings

Poly(pyrrole) deposition:
potential sweep and potential step experiments.

Salient features of conducting polymer electrogeneration from solution.

Initiation.
Anodic oxidation of monomer and generation of oligomers via RR or RM coupling mechanism.

Propagation.
Accumulation of oligomers in solution. At a certain chain length, solubility of oligomer chain is exceeded and get precipitation of oligomer onto support electrode surface.

Growth.
Growth of polymer occurs via oxidative attachment of monomers. Rate of expansion of polymer phase controlled by ohmic resistance of polymer layer during growth.

Nucleation/growth of electronically conducting polymers.

- Nucleation processes.
  - Instantaneous: all nuclei formed at same time.
  - Progressive: nuclei formed gradually.
  - These are limiting behaviours.

- Layer growth.
  - 1D needle type (normal direction only)
  - 2D layer by layer (lateral direction only)
  - 3D (lateral and normal directions).

- NG mechanism established via analysis of the current/time response curves recorded at different applied potentials. Emphasis placed on short time response profile before nuclei begin to overlap.
Nucleation/growth kinetics: analysis of chronoamperometric transients.

Simplified expressions for the transient current describing nucleation and growth at short times before overlap of the growth centres

<table>
<thead>
<tr>
<th>Nucleation Type</th>
<th>Growth Type</th>
<th>1-D (needles)</th>
<th>2-D (discs)</th>
<th>3-D charge transfer control</th>
<th>3-D diffusion control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instantaneous</td>
<td>nFNkSk</td>
<td>2naF[M_f/p]hN,k ( \alpha ) ( t )^2</td>
<td>2naF[( M_f/p ) ( \alpha ) ( t )^2]</td>
<td>nF[( 2(2Dc)^{3/2}M^{3/2}\rho^{1/2}\rho )^2]</td>
<td></td>
</tr>
<tr>
<td>Progressive</td>
<td>nFkNSk( \alpha )</td>
<td>2naF( M_f/p )hN,k ( \alpha ) ( t )^2</td>
<td>2naF( M_f/p )hN,k ( \alpha ) ( t )^2</td>
<td>4( \alpha F \rho )( c ) ( 2 \rho^{1/2} )</td>
<td></td>
</tr>
</tbody>
</table>

(a) Growth geometry assumed to be hemispherical. Single rate model. (b) Spherical diffusion pertains.

Symbols used: \( n \) = number of electrons transferred; \( F \) = Faraday constant; \( M \) = molar mass (g mol\(^{-1}\)); \( \rho \) = density (g cm\(^{-3}\));

\( c^* \) = bulk concentration of monomer (mol cm\(^{-3}\)); \( D \) = diffusion coefficient (cm\(^2\) s\(^{-1}\));

\( k_n \) = nucleation rate constant (s\(^{-1}\)); \( N_0 \) = number density of nucleation sites (cm\(^{-2}\));

\( k_g \) = growth rate parameter (mol cm\(^{-2}\) s\(^{-1}\)); \( h \) = height of growth centre.

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Some experimental results.

- **PPy/Cl\(^+\) layers.**
  - IN 3-DG mechanism.

- **PPy/DBS\(^-\) layers.**
  - PN 1-DG mechanism (short times)
  - IN 1-DG mechanism (long times)

- **PAn/Cl\(^+\) layers.**
  - IN 3-DG mechanism

- **PAn/DBS\(^-\) layers**
  - Currently being examined

- Need to examine current transient response at short times before onset of appreciable overlap between growing centres.
- IN 3-DG mechanism most commonly observed.
- NG mechanism can depend on nature of dopant counterion.
- Always correlate NG mechanism with layer morphology determined via SEM/TEM.
Fig. 2. Chronoamperometric curve of PPy deposited on a base-treated Au/HOPG substrate at different anodic potentials.

Fig. 3. Dimensionless plot of current maximum shown in Fig. 2 compared with theoretical curves for 3D instantaneous and progressive nucleation.
Polymer properties depend on deposition conditions.

- PPy/Cl\textsuperscript{−} oxidised conducting state
- PPy/DBS\textsuperscript{−} oxidised conducting state
- Surface morphology counterion dependent
- CV response counterion dependent

C.H. Lyons
Ph.D Thesis
TCD, 1993

0.1M KCl

0.1 M NaDBS

Fig. 4. Diminishing plot of current maximum shown in Fig. 2 compared with theoretical curves for 3-D instantaneous and progressive oxidation.
Redox chemistry of poly(pyrrole) thin films: redox switching.

Redox switching refers to a potential driven change in oxidation state of the sites within the polymer layer, usually accompanied by a change in layer conductivity.

Redox Switching in ECP materials.

- Redox switching refers to a potential driven change in oxidation state of the sites within the polymer film.
- Usually accompanied by a change in layer conductivity.
- Oxidative (reductive) redox switching causes an increase (decrease) in oxidation state of redox sites on polymer chain.
- Electroneutrality requires a corresponding ingress (egress) of anions X\(^-\) from the solution into the polymer film or an egress (ingress) of cations C\(^+\) from the polymer layer into the solution in order to ensure charge compensation.
- The observed redox switching rate depends on how quickly charge can be transferred through the polymer matrix.
- Volume, nature and morphology of electroactive polymer film can change during redox switching.
- Redox switching is a complex mechanism involving electron, ion, salt, and solvent transport. Polymer conformational changes may also occur (polymer chain relaxation). Any of these processes can be rate determining.
- Electrochemical techniques provide information only on the transport of charged species. Exclusive reliance on electrochemical techniques implies that the specific role of electroinactive species such as counterions, ion pairs and solvent molecules, cannot be directly deduced.
- Non electrochemical techniques such as FTIR, ellipsometry, Probe Beam deflection and electrochemical quartz crystal microbalance can be used to obtain fuller information on the specifics of redox switching.
- Time scales for electron transfer, counterion transport (which is coupled to electron transfer via the electroneutrality condition), are in general quite different from the timescale involved in transferring such heavy species as a solvent, neutral molecule or a salt.
- Hence the question of whether an electroactive polymer film is at complete thermodynamic equilibrium when the activities of all mobile species must equal those of their counterparts in solution can be difficult to ascertain.
Non electrochemical methods for interrogating the redox switching mechanism.

- **FTIR spectroscopy.**
  - Can be useful yielding information on polaron and bipolaron levels as a function of polymer oxidation state, but, when considering ions and solvent molecules, it is difficult to distinguish between species present in the polymer film and the large excess of the same species present in the adjacent solution phase.

- **Ellipsometry.**
  - Ellipsometric measurements (polarization state of light is determined) can be used to determine the film thickness, in situ, as a function of polymer oxidation state. It can also be used to obtain information on the optical properties (refractive index) of the polymer film.

- **EQCM.**
  - Electrochemical quartz crystal microbalance can be used to directly measure changes in film mass during redox switching to a very high level of sensitivity.

- **PBD method.**
  - Probe beam deflection can be used to examine the ingress or egress of charge compensating counterions during redox switching.
Fundamental transmission line parameters.

- Total TL resistance $R_L = R_E + R_I$
- Total distributed layer pseudocapacitance $C_x$
- These parameters extracted via analysis of complex impedance
  response at low frequencies.
- Can also define a coupled diffusion coefficient via $R_E C_x = L^2/3D_{CT}$.

$$R_E = \frac{RT}{F^2} \frac{c}{ab} \frac{L}{AD_x}$$

$$R_I = \frac{RT}{F^2} \frac{L}{AbD_y}$$

$$\frac{1}{C_x} = \frac{1}{C_D} + \frac{1}{C_N} + \frac{1}{C} = \frac{RT}{F^2} \frac{c}{ab} + \frac{RT}{F^2} \frac{1}{ab}$$

$C = \text{Feldberg capacitance}.$

$C_N = \text{Nernst capacitance}.$

$C_D = \text{Donnan capacitance}.$

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Equivalent circuit representation of electroactive polymers.

- Equivalent circuits not taken from shelf but derived via analysis of
  Nernst-Planck transport equations and TL theory.
$R_{CT}$ measures facility of charge injection/ejection at metal/polymer interface.
$R_L$ = low frequency resistance measures facility of ionic diffusion/migration through pores in polymer matrix.

Transport information for PPy/Cl\textsuperscript{-} obtained via analysis of complex impedance spectrum.

Species distribution in PPy as a function of potential (degree of oxidation).

Neutral PPy
PPy\textsuperscript{-} (polarons)
PPy\textsuperscript{2-} bipolarons

Polaron/bipolaron formation can be examined using ESR in conjunction with CV.
Band theory of solids: a brief summary.

Conductivity:

\[ \sigma = nq\mu \]

- Solid consists of N atoms.
- Each energy state splits into N levels closely spaced, N \( \approx 10^{22} \text{ cm}^{-3} \).
- Continuous energy bands formed.
- Energy gaps generated because of periodic nature of lattice.

Conduction processes in electronically conducting polymer films.

- Electronically conducting polymers are conjugated organic materials.
- Conductivity imparted chemically via addition of donor or acceptor dopants in large quantities (ca. 10 mol%) into polymer matrix, or electrochemically via oxidation/reduction of the polymer backbone.
- In the case of chemical doping have charge transfer between dopant species and polymer chain causing oxidation or reduction of sites on the chain. Partial oxidation of the polymer chain termed p doping, partial reduction of polymer chain termed n doping.
- The precise nature of the charge carriers generated via doping depends on the polymer type.
- Charge carriers (solitons, polarons, bipolarons) are defects delocalised over a number of repeat units on polymer chain.
- The physics of microscopic charge transport in complex. Various microscopic models have been postulated and it is difficult from measurements of electrical conductivity as a function of temperature to fully differentiate between the different transport mechanisms, since all theoretical expressions may fit the experimental data.
- Macroscopic charge transport represents a superposition of local transport mechanisms.
- We differentiate between intrinsic conductivity (conduction processes within polymer strand) and non intrinsic conductivity (interstrand and macroscopic inter fibre hopping).
- Various hopping and tunneling models have been developed to describe non-intrinsic transport processes.

Intrachain hopping

Interchain hopping

Fig. 16. Schematic view of chemically doping in polymers to illustrate the superposition of various conduction mechanisms.
**Electronic conductivity measurements.**

- Much fundamental work done on poly(acetylene).
- Little dependence of $\sigma$ on $T$ when the PA samples are highly doped with $I_2$ (p doping).
- Large $T$ dependence for low doping levels.
- Typical metallic behaviour not observed (negative temperature coefficient of conductivity $\sigma$) at any doping level.
- Most highly doped samples behave as dirty metals or disordered alloys.
- Phenomenologically the $\sigma$ vs $T$ data may be fit via the Mott equation for variable range hopping of charge carriers, which was originally developed for amorphous materials.

Curve fitting parameters = $\sigma_0$, $T_0$

$$\sigma = \sigma_0 \exp \left[ -\left( \frac{T}{T_0} \right)^\gamma \right]$$

1 < $\gamma$ < 1/4

**Temperature variation of electronic conductivity.**

Large temp range must be examined for data fitting to model.

**Structure of electrodeposited poly(pyrrole) films.**

- Poly(pyrrole) films are insoluble and poorly crystalline. Hence studies limited to solid state spectroscopy.
- Information concerning average length of polymer chains, chain conformation, distance between rings, crosslinking etc not available from direct measurement, but through interpretation of spectroscopic data through models and theoretical calculations.
- NMR and IR studies suggest that PPy is constituted by chains joined mainly via $\alpha$-carbon linkage.
- XPS analysis indicates presence of both $\alpha$-$\alpha'$ and $\alpha$-$\beta'$ bonds. This implies presence of certain degree of crosslinking.
- XRD studies suggest polymer essentially macroscopically amorphous. Some indication of order along plane of electrode surface (coplanar orientation of pyrrole rings along electrode).
- Disorder associated with (i) random loss of ring orientation (ii) crosslinking and ring opening producing non aromatic segments.
- Distribution of chain lengths not assigned yet with certainty. Polymer matrix assumed to consist of a conglomerate of oligomers of low molar mass. UV/VIS, FTIR and ellipsometry indicate chain length between 4 - 35 monomer units.
Charge carriers in electronically conducting polymer materials.

- When an electron is removed from the top of the VB of a conjugated neutral polymer such as poly(pyrrole) a hole or radical cation (called a polaron) is created. The polaron exhibits only partial delocalisation over several monomer units. This results in a structural deformation of these units.
- If another electron is removed from the oxidised polymer containing the polaron either:
  - Another independent polaron can be generated in a different segment of the polymer chain.
  - The electron can be removed from the same chain segment as before and a dication or bipolaron is formed. Again the bipolaron causes structural deformation since the two positive charges are not independent but act as a pair.
- The oxidative doping of poly(pyrrole) may be described via the following sequence of reactions.
  
  \[
  PPy \rightarrow PPy^{*+} + e^- \\
  PPy^{*+} \rightarrow PPy^{2+} + e^- \\
  2PPy^{*+} \rightarrow PPy^{2+} + PPy
  \]

- The effect of doping (oxidation) can be expressed in terms of band structure diagrams.
- Neutral unoxidised polymer has well defined valence and conduction bands separated by a band gap. Hence it is a semiconductor.
- Oxidation of the polymer chain results in the generation of both polaron and bipolaron energy levels in the band gap region.
- Polaron which are paramagnetic (spin = \(\frac{1}{2}\)) arise from light doping whereas bipolarons which are spinless and diamagnetic arise from heavy doping.
- Bipolaron bands can form at very high doping levels.

Neutral polymer

Polymer oxidation, Generation of polaron energy levels, bipolaron levels, and bipolaron bands in band gap region.

Optical transitions in conducting polymer films.
Experimental evidence for polaron and bipolaron formation in PPy.

- Evidence of polaron and bipolaron formation obtained from:
  - Optical absorption spectroscopy.
  - ESR spectroscopy.
- Optical absorption spectroscopy of PPy at low doping level exhibits 3 absorption bands at 0.7 eV, 1.4 eV and 2.1 eV. These are attributed to polaron levels located within the energy gap region.
- At intermediate doping levels, the 1.4 eV absorption associated with the transition between polaron levels disappears. This implies that polaron concentrations decrease with increasing level of oxidation (see ESR data).
- At very high doping levels, two wide bands appear giving rise to transitions at 1.0 eV and 2.7 eV which are assigned to transitions involving bipolaron bands in the gap region.
- Also the direct transition (VB to CB or π, π* transition) shifts from ca. 3.2 eV to ca. 3.6 eV on going from a lightly doped to a heavily doped polymer.
- The ESR signal initially increases with increasing potential or degree of oxidation since polarons are paramagnetic with a spin ½. The ESR signal reaches a maximum and subsequently decreases reflecting the recombination of polarons to form bipolarons. Both can co-exist. Both can contribute to conductivity.
- At high doping levels (highly oxidised polymer), there is no ESR signal but the conductivity of the polymer material remains high, indicating that the charge carriers are spinless bipolarons at this point.
- In situ ellipsometry indicates a polaron conjugation length of 12 monomer units and a bipolaron conjugation length of 3 monomer units.
- The oxidation peak observed in the cyclic voltamogram is assigned to a changeover in dominant carrier type (polaron/bipolaron) accompanied by a dramatic contraction of the layer due to electrostriction caused by bipolaron formation.
Electropolymerization of poly(aniline).

- Polyaniline (PANI) is best made in thin film form via electropolymerization at either a Pt or GC electrode via a potential cycling method. Typical conditions are 0.5M aniline monomer in 1M HCl at 50 mVs⁻¹.
- The potential is cycled between -300 mV to ca. 900 mV for a fixed number of cycles to form a uniform layer of polymer.
- The polymerization occurs most efficiently in solutions of low pH (especially in strongly acidic media).
- The electropolymerization mechanism is similar to that proposed for polypyrrole.

Poly(aniline) PAN.

0 < y < 1

3 main oxidation states

Have various degrees of protonation depending on solution pH.

<table>
<thead>
<tr>
<th>y</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
</tr>
</thead>
</table>
| Name | Leuco-| emeraldine | per
|      | cocrystalline| 5:1 | nigrosine
|      | all B units | E/BQ ratio | 1:3 E/BQ
|      | Description | Completely | Intermediate | Completely
|      |             | reduced     | Oxidized     |
|      | Conductivity | Insulator   | Conductor    | Insulator   |

Redox switching in PANi.

A → R" + e⁻

R⁺ → Q + 2H⁺ + e⁻

Acid doping

Details of stoichiometry of redox transitions depend on solution pH.

Redox switching

PANi can be made electronically conductive by treating emeraldine base with HCl.
pH effect on redox switching stoichiometry.

**Redox Process I**
\[ \text{dE/d pH} = \text{-59 mV/pH unit} \]
Strong acid
\[ \text{dE/d pH} = \text{-59 mV/pH unit} \]
Equal numbers of electrons and protons transferred.

**Redox Process II**
\[ \text{dE/d pH} = \text{120 mV/pH unit} \]
\[ 2\text{H}^+, 1\text{e}^- \text{ process.} \]

**Poly(aniline) redox chemistry.**

- Poly(aniline) base (insulator)
- Poly(aniline) salt (insulator)
- Protonation:
  - \( \text{H}^+ \text{C}^- \) (pH 4 to 6)
  - \( \text{H}^+ \text{C}^- \) (pH 0 to 4)
- Oxidation:
  - \( \text{H}^+ \text{A}^- \) (pH 0 to 4)
  - \( \text{H}^+ \text{A}^- \) (pH 4 to 6)
- Reduction:
  - \( \text{H}^+ \text{C}^- \) (pH 0 to 4)
  - \( \text{H}^+ \text{C}^- \) (pH 4 to 6)
Redox chemistry of PANi: 1st redox peak.

Anion incorporation important during redox switching.

PANi redox chemistry: 2nd redox peak.

Anion and proton loss important.
PANi redox switching: EQCM experiments.

- Complete description of redox switching requires a consideration of concomitant changes in ion and solvent populations.
- This can be achieved using the EQCM method.
- The quartz crystal microbalance is a piezoelectric device capable of monolayer mass sensitivity. The method involves sandwiching a quartz crystal between two electrodes, one of which is used as the working electrode of an electrochemical cell. These electrodes are used to impose a radio frequency RF electric field across the crystal at a resonant frequency determined by the crystal’s dimensions and mass loading.
- A change in the mass of the working electrode causes a change in the resonant frequency of the device which can then be used to determine the quantity of added mass.
- This effect is quantified via the Sauerbrey equation which relates the change in resonant frequency \( \Delta f \) from its start of the experiment, and the mass change \( \Delta M \) per unit area of the electrode.
- The Sauerbrey equation is valid if polymer is a rigid layer, if \( \Delta f << f \), and if the layer is thin.

\[
\Delta f = -\frac{2 f^2}{\rho_U}
\]

Density of crystal
Velocity of acoustic shear wave in polymer film

Probe Beam Deflection.

- The PBD method detects ion transport across the polymer/solution interface. The technique probes concentration gradients near the electrode surface.
- The sign of the laser beam deflection indicates whether an interfacial redox reaction is accompanied by a net ion flux away from the electrode surface or towards the electrode surface.
- Cation expulsion from the film during redox switching gives rise to an increase in concentration at the polymer/solution interface. The concentration gradient is negative so the laser beam path is deflected in a negative manner toward the electrode. The voltammetric current is positive (oxidation). Negative beam deflection accompanied by positive (oxidation) current indicates cation expulsion.
- A positive beam deflection away from the electrode (reflecting a positive interfacial concentration gradient) combined with a positive voltammetric current indicates cation insertion into the film.
- Furthermore, a negative beam deflection combined with a negative (reduction) current indicates anion expulsion from the layer, a positive deflection combined with a negative current indicates anion insertion.
PANi redox switching: PBD experiments.

PBD experiments on PANi in HCl solution show that the PBD signal exhibits both negative and positive deflections during the oxidative potential sweep. Hence both proton expulsion and anion insertion occur during polymer oxidation. Proton release proceeds anion ingress during the oxidative sweep. Subsequently there is consecutive anion ejection and proton insertion during the reverse reductive sweep. Cyclic deflectograms recorded during layer oxidation, as a function of acid concentration, indicate a more enhanced negative deflection as the acid concentration increases. Positive deflections also noted at higher oxidation potentials. Proton expulsion is the dominant mode for electroneutrality preservation in concentrated acid media, but anion insertion also occurs at more positive potentials.

Redox chemistry of PANi

Scheme of squares. Proton transfer vertical and ET horizontal. Position in scheme depends on pH of solution.

Polymer degradation products generated if upper potential limit is too positive.
Conductivity behaviour of PANi

3 state conductivity behaviour.

Figure 1. Electrochemical doping of polyaniline in pH 5.0 electrolyte solutions. Correlation between the change in electrical conductivity and the absorption spectra. (A) Frequency of polyaniline oxidation at the electrochemical potential vs. SCE, where $n_b$ = 0.2 kcmole. (B) Absorption of the polyaniline film at 520 nm as a function of the doping potential and switching on and off of the conductive form. The inset is the 300-nm band correlation with the oxidation from the insulator to the conductive state.

Figure 2. Characteristic changes during oxidation of optical absorption spectra at pH 5.0 electrolyte solutions. Curves with a 450, 530, and 630 nm vs. SCE are spectra of the unoxidized insulating, the conductive, and the oxidized-insulating forms.