New generation, metal-free electrocatalysts for fuel cells, solar cells and water splitting

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PERSPECTIVE

New generation, metal-free electrocatalysts for fuel cells, solar cells and water splitting

Bjorn Winther-Jensen*[a] and Douglas R. MacFarlane[b]

New electrocatalysts have become of increasing significance due to the need for inexpensive and effective catalysis in energy generating, converting and storage devices. Intrinsically conducting polymers such as PEDOT have recently been shown to provide an important new family of electrocatalytic materials. Studies thus far have demonstrated effective electrocatalysis in a range of contexts including for example in the iodine/iodide reaction and other similar reactions important in the dye sensitised solar cell, the oxygen reduction reaction fundamental to the fuel cell and metal–air batteries, and proton reduction in water to produce hydrogen. A general catalytic behaviour seems to be emerging in these studies. This article surveys recent progress in this field from our laboratories and others and foreshadows important new areas requiring study.

1. Introduction

The prospect of global warming, in combination with limited fossil fuel reserves, is calling for radical changes in our global energy production and consumption patterns. The practice of relying on energy sources that have been built up and stored underground over millions of years must ultimately be transformed into a situation where the global energy requirement is produced more or less "*in situ*" from renewable sources. For the transport and distribution sector this means that the traditional petroleum-based fuels have to be replaced either with renewable

sources of the fuels or with other energy carriers. This change in the energy landscape has already gathered pace: installed wind turbine capacity is accelerating, various solar-energy collecting systems are commercial and ethanol from crops, bio-diesel, hydrogen *etc.* are already on the market as alternatives in the transport sector.

In this scenario, the ability to effectively interconvert energy between a chemical form and an electric form is becoming crucial, for example, in fuel-cells, photo-electrochemical solar cells, batteries and water-splitting devices for hydrogen generation. All of these technologies have at their heart electrochemical processes that require catalysis; in many cases the lack of adequate catalysts is either a performance or economic limiting factor in these technologies and has been the focus of extensive research over many years.[1–4] For example, low temperature fuel-cells (running on hydrogen or methanol/ethanol) are seen as a part of the longer term solution to automotive energy needs.[2,3,5]

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Broader context

The challenge of developing efficient, low-cost and stable electrocatalysts from abundant elements for emerging energy storage and conversion technologies has stimulated investigation of materials different from the traditional metal and metal-oxide based catalysts. For example, the broader use of fuel-cells in vehicles is ultimately dependent on finding suitable alternatives to the current platinum electrocatalysts, which are both too expensive and too rare to be a feasible solution. This perspective article highlights the recent work which uses conjugated polymers as electrocatalysts for a range of important electro-reactions, including the oxygen reduction reaction, which is key to the fuel cell, and water reduction to form hydrogen, which is key to the "water splitting" process. We thereby emphasize the general nature of this catalytic behavior for both reduction and oxidation reactions. The unique redox properties of the conjugated polymers are the key to understanding the mechanism of the catalytic activity on these materials, which is significantly different to that occurring on metals. For example, whereas Pt based air-electrodes are well-known to be easily poisoned by CO, conducting polymer electrodes are immune to this effect. We also discuss the need for deeper understanding of the transport properties and binding events during operation in these materials.

Unfortunately, one of the limitations of existing fuel cell technologies is the cost and stability of the platinum-based electrocatalyst that is standard in these devices, as well as its sensitivity to CO poisoning.[6–11] Most electro-catalysts are currently based on rare metals such as platinum and palladium and their alloys[1–3,12,13] making them too costly for implementation in fuel-cell powered cars.[4] A number of technical issues also arise with the use of Pt based catalysts, for example in fuel-cells catalyst particles (normally Pt and Pt alloys) are not fixed by chemical bonds or entrapments and can diffuse during operation. This can lead to the well-known drift phenomenom,[5] whereby eventually agglomerates are formed, compromising the performance of the catalyst.

Thus a major focus of our research program in recent years has been an investigation of alternative electrocatalysts for a number of significant electrochemical device technologies. In particular, we have focused our attention on the possibility of non-metallic materials based on conducting polymers for this purpose. In this perspective we survey progress in this field, discuss some of the mechanistic insights that are developing and foreshadow likely future areas of productive research in the hope that others may take up the challenge in this important area.

2. Inherently conducting polymers (ICPs) as electrocatalysts

In the year 2000 the Nobel Prize was awarded to Heeger, MacDiarmid and Shirakawa for changing the general view of polymers as dielectrics only, by their discovery that a polymer, polyacetylene, can be made conductive almost like a metal. Polyacetylene was only known as a black powder until in 1974 it was prepared as a silvery film by Shirakawa and co-workers from acetylene, using a Ziegler–Natta catalyst. But despite its metallic appearance it was not a conductor. In 1977, however, it was discovered that oxidation with chlorine, bromine or iodine vapour made polyacetylene films 10^9 times more conductive than they were originally.[14] Treatment with halogen was called "doping" by analogy with the doping of semiconductors. Unfortunately doped polyacetylene is not suitable for practical use because it is easily (and vigorously) oxidized by the oxygen in air and is also sensitive to humidity. This stimulated studies of other conjugated polymer systems including polypyrrole, polythiophene (and various polythiophene derivatives), polyphenylenevinylene polyaniline, *etc.* Many of these may be synthesized directly in the doped form and are much more stable in air.

ICPs were investigated for catalytic purposes early in the history of conducting polymers, but success was limited by low conductivity and instability of the ICPs available at the time.[15–17] Over the last two decades, the development of chemical polymerization (in particular the process known as vapor phase polymerization (VPP)), as well as "designed" ICP derivatives has produced materials with higher conductivity and stability, and is also allowing the control of porosity at the nanolevel.[18–21] Such properties significantly improve the potential use of these materials for electrocatalytic applications, as demonstrated by the recent work on the catalytic mechanisms of various reactions on conjugated polymers,[22–24] as discussed in more detail below. With this said, it is indeed still the case that most ICPs can be irreversibly over-oxidized when higher oxidative potentials are applied. For this reason pure PEDOT, polyaniline and polypyrrole, for example, cannot be used for water oxidation as they are immediately destroyed in the process, however ICPs may be developed that are sufficiently stable for this reaction. For reduction processes the picture is quite different; here the conducting polymer is forced by the applied potential to be in a more reduced state than under ambient conditions, effectively avoiding any over-oxidation processes.

Oxygen reduction on ICP electrocatalysts

The reduction of dissolved oxygen

$$O_2 + 4e^- + 4H_2O \rightarrow 4OH^-$$

on conducting polymers has been known from the early days of ICP research. In fact, generations of researchers and students have faced the task of having to remove oxygen from various electrolytes in order to obtain electrochemical measurements reflecting the REDOX nature of the conducting polymer itself. Fig. 1 illustrates these phenomena, where pseudo-steady state measurements of the reduction of poly(3,4-ethylenedioxy-thiophene) (PEDOT) are shown with and without the presence of dissolved oxygen. Clearly therefore the PEDOT electrode is active towards this process.

The oxygen reduction reaction is a vital part of both metal–air batteries and fuel-cells, and efficient, low-cost oxygen reduction electrodes (also known as "air-electrodes") are essential to make these technologies viable on a larger scale.

An important step towards using ICP electrocatalysts for these applications was made recently by constructing a membrane based electrode with an efficient 3-phase interface between oxygen/air, the electrolyte and an ICP[22] as illustrated in Fig. 2. In this case, a 80 μm thick Goretex membrane (a hydrophobic, porous structure which is gas permeable but prevents penetration of the aqueous electrolyte into the membrane) was coated with a ~500 nm thick layer of PEDOT to achieve high surface area as well as access of both the electrolyte and oxygen to the ICP.

The efficiency of the PEDOT based electrode was comparable to platinum catalysed electrodes prepared on Goretex
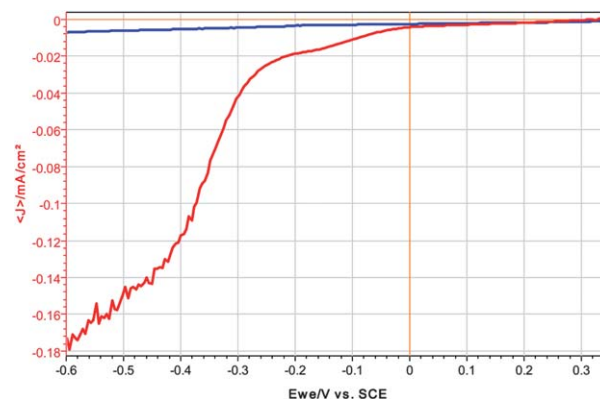

Fig. 1 Vapour phase polymerised PEDOT on a Au coated Mylar substrate. Pseudo-steady state (*i.e.* very low scan rate, 0.167 mV s^{-1}) measurement in 0.1 M sodium paratoluenesulfonate (NaPTS) with (a) nitrogen bubbling (blue curve) and (b) oxygen bubbling (red curve).
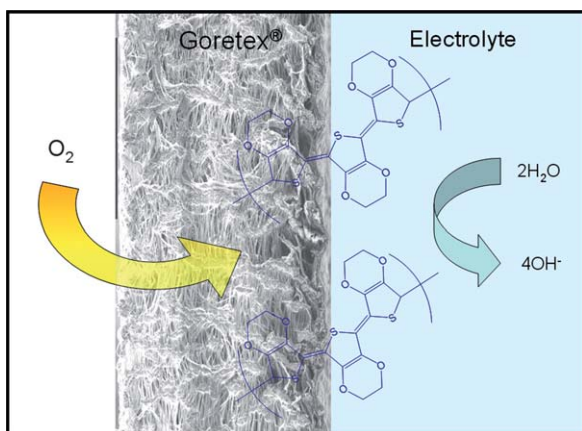
Fig. 2 Schematic of PEDOT-based air electrode.

membranes in a similar manner. Under acidic conditions platinum based electrodes show superior performance, but in neutral and basic environments the PEDOT and platinum electrodes performed very similarly.[22]

Also very encouraging was the durability of the PEDOT based electrode to CO poising. Fig. 3a shows the operation of the PEDOT based air-electrode compared with a Pt based electrode in a 10% CO atmosphere.[22] The Pt catalysed electrode shows the expected rapid decrease in O_2 conversion when exposed to CO (Fig. 3a at time "0 hours"), whereas the PEDOT electrode shows no sign of degradation of performance even after several hours of exposure to CO. This strongly indicates that the electro-catalytic mechanisms involving ICPs are of a different nature than those
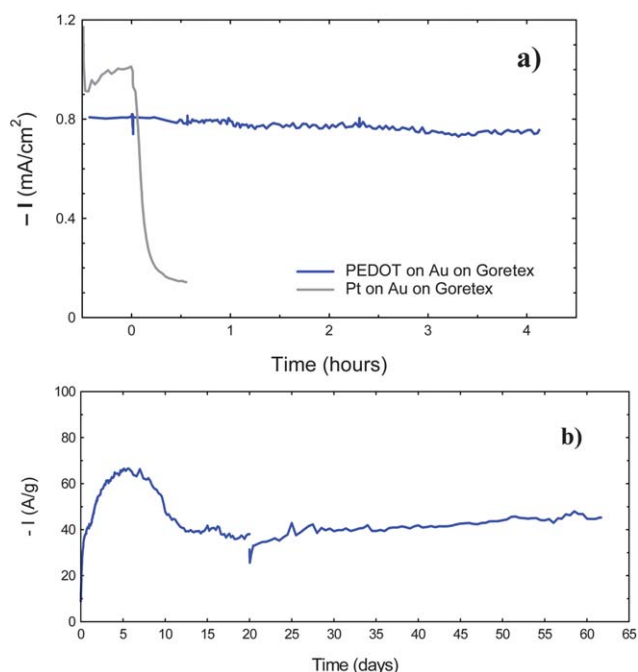

Fig. 3 (a) Response of the PEDOT air-electrode to CO (-0.3 V *vs.* SCE, 0.1 M phosphate buffer pH 7), current *vs.* time in air contaminated by 10% CO compared to a similar Pt catalyzed electrode. (b) Long-term stability of the PEDOT air-electrode (-0.3 V *vs.* SCE, 1 M H_2SO_4). Reproduced with permission from ref. 22.

known from metallic catalysts. Also the long-term stability of the PEDOT air-electrode was confirmed (Fig. 3b, ref. 22) over more than 1500 hours with a total conversion current of over 3 A h cm^{-2}. This corresponds to a Turnover Number in excess of 1.2×10^6, when this is calculated on the basis of a maximum oxidation level of 0.25, *i.e.* 1 charged EDOT unit per 4 units in the backbone, and that all of these are accessible and active as catalytic sites.[25] This indicates that the homogeneous and continuous nature of the PEDOT catalyst is not sensitive to the drift phenomena well-known in the platinum based systems.

These findings show the potential of using ICPs for air-electrodes. However, the nature of the catalytic layer on the Goretex membrane electrode is still more or less two dimensional, which is the reason for low current densities obtained (<10 mA cm^{-2}). A substantial effort is needed in order to extend the system into a true 3-D structure and thereby reach the current densities in the order of 1 A cm^{-2} required for large scale air-electrode applications (*e.g.* fuel-cells in cars). Similarly, for dissolved oxygen applications such as many biofuel cell designs, development and optimisation of the electrode structure would no doubt produce further improvements.

3.   The general nature of ICPs as electrocatalytic materials

Recent work by several groups, and in very different areas, has also indicated the broader application of ICPs as electro-catalysts for molecules in solution.[26–36] These redox reactions (described in more detail below) on ICPs indeed all show a similar trend: the I/V steady state measurements show a straight line through zero current, indicating that these ICPs (in this case PEDOT) indeed are able to work as electro-catalysts in both redox directions. Thus PEDOT can act as an electron donor (for reduction reactions) as well as an electron receiver (for oxidation reactions) and do so when forced away from the open circuit potential (OCP) as a consequence of the cell reaction. We discuss some examples of this general behaviour below.

Iodine–iodide redox reaction

One very successful application of ICPs is their use as replacements for platinum electrocatalysts in dye sensitised solar-cells (DSSCs), catalyzing the cathode reaction: $3I^- + 2e^- \Rightarrow I_3^-$ as reported by several groups.[26–34] Unfortunately most of the publications only report the decrease in the performance of the DSSCs (where efficiencies comparable to platinum are reported), but do not investigate the nature of the catalytic behavior of the ICP. The number of different ICPs reported to catalyze the iodine–iodide reaction in DSSCs, including polyaniline (PANI),[31] PEDOT[26–30] and other thiophene derivatives,[32,34] underlines the general character of the phenomenon. Very importantly in deconvoluting the role of the counterion in this electrocatalysis, some of these reports using PEDOT involved the polystyrenesulfonate countrion[30] which is specifically chosen to avoid its loss into the electrolyte solution during electrochemical cycling. This immobilisation of the counterion produced no effect on the effectiveness of these catalysts in the DSSC, suggesting that the counterion does not play a significant direct role in the catalytic mechanism.

Fig. 4 shows steady state measurements using a conventional electrolyte, optimised for the DSSCs (with stirring). The conversion current of I_3^-/I^- on PEDOT (on a Ti foil substrate) and Pt on FTO (deposited by thermal decomposition as widely used and optimised for DSSCs) are compared at various potentials. PEDOT and Pt-on-FTO both show almost straight line behaviour through the reversible potential, indicating almost no over-potential for both the reduction and oxidation reactions; in other words the reaction is electrochemically reversible on these catalyst materials. However, the slope of the PEDOT curve is significantly steeper than the platinum electrode—much steeper than can be explained by the difference in resistance of the underlying current collectors.[23] The slope of the curves around zero current is a measure for 1/resistance of the entire cell tested, giving cell resistances of 20 Ω and 168 Ω of PEDOT on Ti and Pt on FTO, respectively with identical cell configuration and electrolyte. The FTO itself contributes at most ∼35 ohms to the Pt/FTO measurement. Assuming that all other resistance components are equal in these two experiments then it appears that the charge transfer resistance (R_{CT}) is about half an order of magnitude lower in the PEDOT case. The fundamental exchange current density, i_o, is given by:

$$i_o = RT/nFR_{CT}$$

where R, T, F and n have their usual meanings. Therefore i_o for the PEDOT electrode is about half an order of magnitude higher than Pt. Since $i_o = nFAk^0C$ where A is the electro-catalytically active surface area, C is the concentration of the redox species and k^0 is the standard homogeneous rate constant, this may be a result of improvement in either the active area, or k^0 and further investigation is needed to discriminate between these two. At more negative potentials the diffusion limit is rapidly reached with the PEDOT electrode.

The high efficiency of PEDOT for the I_3^-/I^- reaction means that PEDOT may lead to better (and cheaper) DSSCs; however, it requires that the c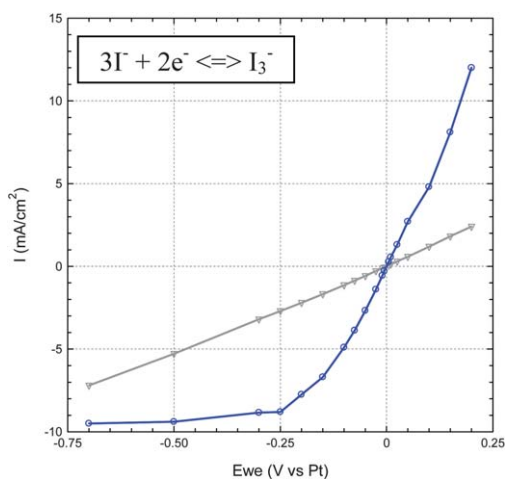onductivity and structure are fitted to the other details of the DSSC design; for example roughness and swelling of the ICP layers may need to be optimised to avoid issues arising from short circuits.[34]

Ferrocene/ferrocenium

The ferrocenium/ferrocene redox couple is one (among many) candidates that might be used to replace the I_3^-/I^- in DSSCs and it is therefore interesting to notice that PEDOT also in this case can be used as the cathode electrocatalyst for the reduction reaction. The steady state measurements (Fig. 5) show a similar trend as the I_3^-/I^- case.

The cell layout for the iodine and ferrocene measurements was identical and it is worth noting that also the slopes of the curves through zero current are identical in both cases (comparing Fig. 4 and 5), suggesting that in both cases the total resistance of 20 Ω is limited by material resistance in the polymer (and the electrolyte) rather than by the charge transfer resistance. Hence it is possible that the actual charge transfer resistance is even lower and that corresponds to an electrocatalytic effect (i_o) even greater than apparent in the $i–V$ slope around zero current.

Hydroquinone

Another important investigation of electro-catalytic activity on ICPs has been reported by Buttner and Holze,[35] where hydroquinone is successfully *oxidized* on a PANI electrode (coated on Pt) in 1 M H_2SO_4 (0.02 M hydroquinone). In this study it was found that the PANI/Pt electrode caused a very significant decrease in overpotential for a given current compared to pure Pt (measured on rotating disk electrodes, at 2000 min⁻¹). An important outcome of the study was that the PANI was in an *intermediate* redox state (measured by UV-vis) during operation as an electro-catalyst. We have reproduced the experiment with PEDOT on Ti in the same electrolyte. Compared to PANI/Pt, PEDOT shows an even lower overpotential (∼25 mV) at the same current density and slope of the scan. It should be noted that this was realised *without* rotating disk conditions, only by bubbling N_2 through the electrolyte.
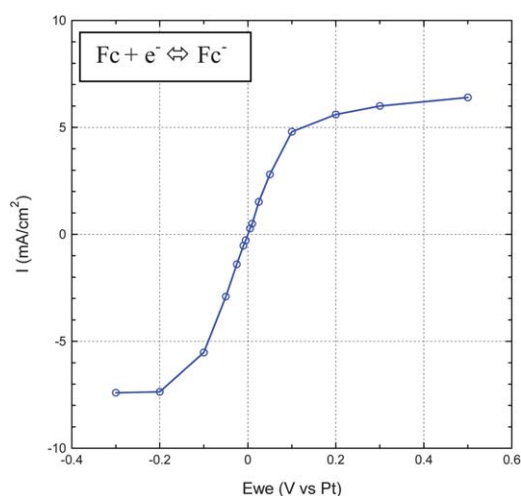
Fig. 4 Redox reactions of I_3^-/I^- (standard acetonitrille-based DSSC electrolyte, 0.03 M I_2 and 0.6 M I^-) on (1) PEDOT on Ti foil (blue curve) and (2) Pt on FTO standard DSSC cathode (grey curve). The solutions were stirred at 500 rpm.

Fig. 5 PEDOT on Ti foil in 0.1 M ferrocene/ferrocenium in water/H_2SO_4/acetonitrille 2 : 1 : 2 solution with stirring at 500 rpm.

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The choice of an acidic environment in the study by Buttner and Holze was dictated by the low conductivity of PANI in neutral or basic conditions (PANI becomes too reduced under these conditions). PEDOT has a wider operational window with regard to pH and therefore steady state measurements of the hydroquinone/*p*-benzoquinoline redox reaction were possible at pH 7 (in 0.1 M phosphate buffer, 0.02 M hydroquinone, Fig. 6).

The measurement was started at higher potentials, producing *p*-benzoquinoline in the process. This *p*-benzoquinoline, now present in the solution, was reduced at potentials below 0.063 V (*vs.* SCE). The response indicates that both the reduction and oxidation reactions are catalysed strongly on the PEDOT electrode. Compared to the experiment in 1 M H_2SO_4, the OCP is shifted by ~0.35 V, which fits with the expected Nernstian change (0.354 V) due to the 6 units of shift in pH.

Hydrogen peroxide (H_2O_2)

The redox reaction of H_2O_2 occurs readily on PEDOT at neutral pH as seen in Fig. 7. The reduction and oxidation of hydrogen peroxide at pH 7 presumably involve the two distinct reactions:

$$H_2O_2 + 2H_2O \rightarrow O_2 + 2H_3O^+ + 2e^- \text{ (oxidation)}$$

$$2H_3O^+ + H_2O_2 + 2e^- \rightarrow 4H_2O \text{ (reduction)}$$
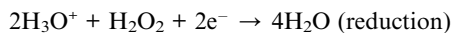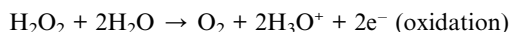
and a linear *I–V* relation through zero current—as shown in Fig. 7—is therefore not expected and presumably a coincidence. PEDOT is stable over 24 hours as catalyst for the oxidation reaction (producing O_2 at 0.4 V *vs.* SCE), but degrades visibly over 24 hours as catalyst for the reduction reaction (at 0 V *vs.* SCE). This degradation of PEDOT under reduction conditions is somewhat surprising as the conditions are in the range where PEDOT normally is expected to be stable. The reason for this is still under investigation.

The four redox reactions mentioned above indeed all show the same trend: the *I/V* steady state measurements show a straight
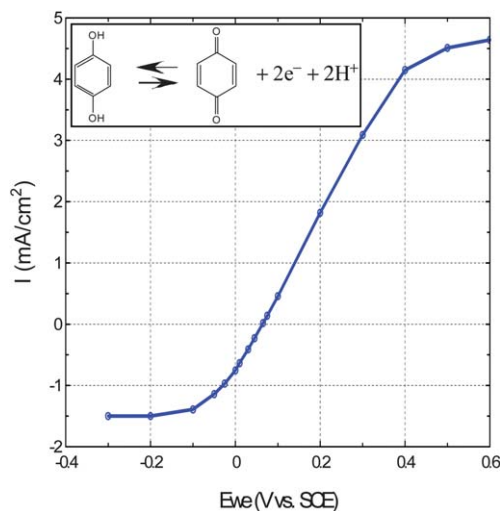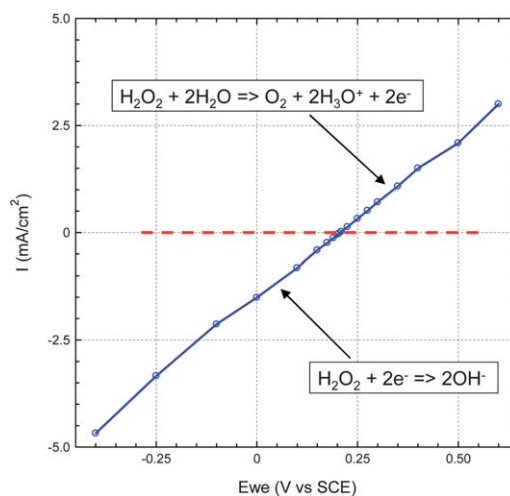
Fig. 7 Redox reaction on PEDOT in 2% H_2O_2 (0.1 M PB buffer pH 7 with N_2 bubbling).

line through zero current of high slope, indicating a low charge transfer resistance for these redox reactions in solution (Fig. 4–7). It should be noted that the gaseous oxygen reduction reaction catalysed on PEDOT described above is showing a very significant over-potential, especially under acidic conditions. The fact that the oxygen reduction reaction involves a reactant in a gaseous phase may play an important role, but the nature of the reaction mechanism in this structure is not sufficiently understood to justify a conclusion at this point.

4. Water and proton reduction—discovering further limitations

Among the most challenging, yet vitally important, electro-catalytic processes are those related to applications in water splitting ($2H_2O \Rightarrow 2H_2 + O_2$) and its conceptual reverse process the hydrogen fuel-cell reaction. In common to these reactions is that there is—for all practical purposes—a liquid as well as a gaseous phase involved as well as the normally solid electrode material. For these applications, not only do good electro-catalysts have to be developed, but also the electrode/electrocatalyst interfaces have to be engineered to interact in an optimal way with both the gaseous and electrolyte phases.

The structure of the air-electrode based on PEDOT (described above) is in line with conventional air-electrodes, in that the porous structure allows diffusion of air (or oxygen) into the electro-catalytically active centers. This concept is widely used in both "air" and hydrogen electrodes based on carbon/Pt for use in fuel-cells and has been a significant part of their development over the last 40 years. For water splitting applications the concept of porous electrodes, containing a three phase interphase between gas, solid and electrolyte to allow direct egress of the gaseous product, has not been widely used. This is surprising as this kind of electrode offers obvious advantages for gas separation. Fig. 8 shows a schematic of a PEDOT based hydrogen electrode used for evaluating the possibility of using such electrodes for proton reduction[24] and reduction of water at neutral pH.
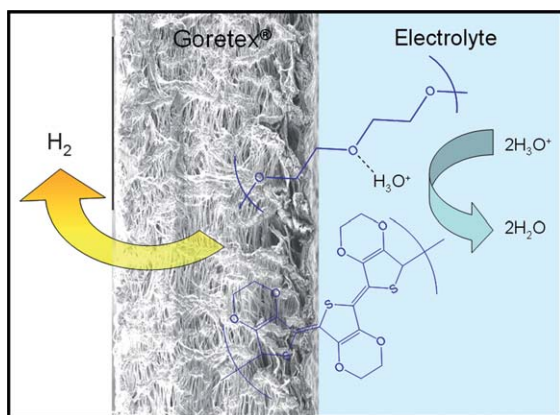
Fig. 6 Hydroquinone/*p*-benzoquinoline reaction on PEDOT on Ti foil at pH 7 with N_2 bubbling (0.1 M PB buffer pH 7 with N_2 bubbling, 0.02 M hydroquinone).

Fig. 8 Schematic of PEDOT-based hydrogen generating electrode.

Production of hydrogen on ICP-composite electrodes has previously been reported.[36] Here ferrocene redox centres were incorporated into polypyrrole (PPy) by co-polymerisation with a custom-made pyrrole derivative. The copolymer was coated onto Pt electrodes, improving the current density and lowering the overpotential for the reaction. However, when the composite was coated onto stainless steel the efficiency dropped away over 20 hours, strongly indicating that Pt still plays an important role in the system reported. More recently highly efficient proton reduction on blends of PEDOT with a second, but non-conducting, polymer, polyethylene glycol (PEG) has been reported.[24] Here conversion currents comparable to Pt and over-potential of only ~50 mV were reported for proton reduction from strong acidic solutions (1 M H_2SO_4). These results were only obtained for the PEDOT/PEG blend, not for "pure" PEDOT electrodes. The role of the PEG in the system was proposed to be to increase the proton diffusion in the blend (not the swelling of the materials) and surprisingly also increased conductivity of the material.

During our work on proton reduction, other electrolytes were investigated. This led to an extended understanding of the possibilities and limitations of using ICPs for electro-catalysis. Fig. 9 shows the steady state reduction currents on a PEDOT/
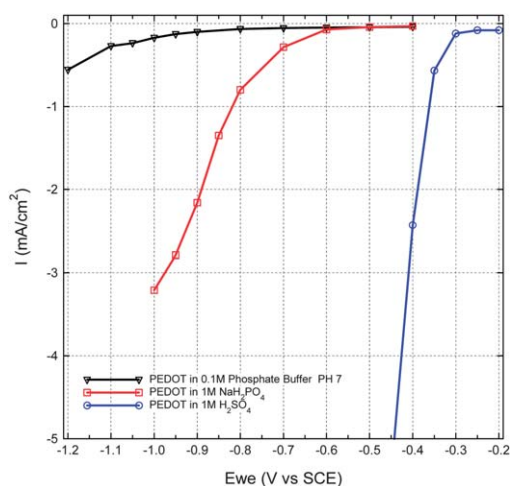
PEG blend (under a N_2 atmosphere) as a function of pH. It is obvious that reduction of water at neutral pH (0.5 M NaPTS) is only very poorly catalysed on the PEDOT cathode, even at over-potentials $\gg$100 mV. In 1 M NaH_2PO_4, with a pH of 4, the over-potential for measurable proton reduction is of the order of 100 mV and at pH 1 (1 M H_2SO_4) the over-potential is reduced even further. It is well known that PEDOT is almost totally reduced at -0.9 V vs. SCE (see also Fig. 10) and is therefore also almost non-conducting at this potential. This may well limit or obstruct the catalytic reaction due to very high ohmic losses in the material.

5. Understanding of the mechanism of electro-catalysis by ICPs

The mechanistic details of the different redox reactions on PEDOT have not yet been thoroughly investigated, i.e. how ions and molecules approach and bind to the catalytic sites, what is the nature of these sites if the material is not uniformly catalytic, and how charge is exchanged? However, there seem to be some general trends in the overall mechanism as described below. Among the common conducting polymers, PEDOT has the least pronounced oxidation and reduction peaks in cyclic voltammetry, Fig. 10, in simple aqueous electrolytes. Instead the change in reduction and oxidation of PEDOT is almost evenly distributed over a wide potential range starting from around -0.8 V up to >0.5 V (vs. SCE). This property gives PEDOT a wide potential window before it becomes totally reduced and thereby non-conducting. This gradual oxidation and reduction provide a close to linear dependence of state of charge on potential that is unique to PEDOT. We have shown above that PEDOT can act as an electron donor (for reduction reaction) as well as an electron receiver (for oxidation reaction) because of this partial and variable state of charge. In acting as a source or sink of electrons
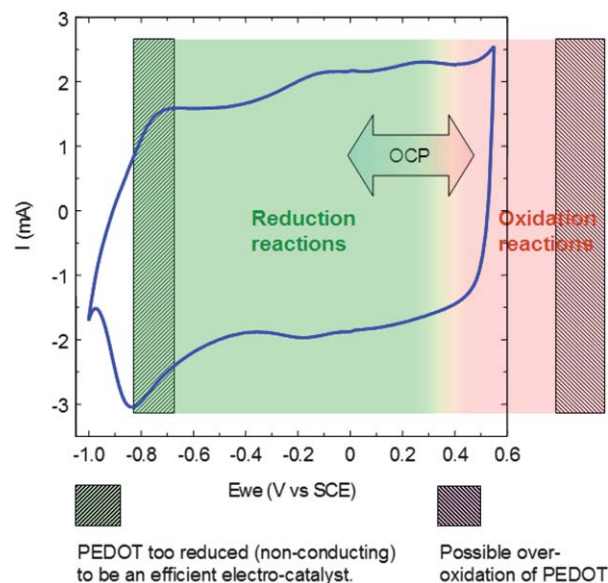

Fig. 9 Conversion currents vs. potential on spin-coated PEDOT-PEG on Au/Goretex electrodes under nitrogen at different pH.

Fig. 10 CV of PEODT in 1 M NaCl, scan rate 5 mV s^{-1}. "$\langle$OCP$\rangle$" indicates the open circuit potential and the double headed arrow the variation with pH. The green and red potential areas indicate where possible reduction and oxidation reaction may be catalyzed.

it is forced away from its Open Circuit Potential, OCP (and state of charge), as a consequence of the cell reaction. The OCP of conducting polymer electrodes in an electrolyte is well-known to depend on a number of parameters (apart from the ICP itself) including solvent, electrolyte concentration and pH. As OCP indicates the borderline between possible oxidation and reduction reactions on the ICP, the position of the OCP—and ways to change it—in a given solution becomes of great importance. The OCP for PEDOT will change with pH as indicated by the "OCP" double headed arrow in Fig. 10 and the onset of possible reduction and oxidation reactions (indicated by green and red regions in Fig. 10) will follow the OCP. If the reduction potential of a give reaction is lower than ~-0.7 V (vs. SCE), the PEDOT will be too reduced and thereby non-conducting before the catalytic reaction can occur. On the other hand; if the oxidation potential is too high for a given reaction, PEDOT will reach the potential range where destructive over-oxidation becomes possible ($>\sim0.8$ V vs. SCE, depending on pH).

In Fig. 11 the catalyzed reactions on PEDOT that have been reported above are sketched on a common potential scale. During operation in the electro-catalytic reaction the PEDOT is kept in an equilibrium state maintained by the reduction or oxidation of the particular reactant present, e.g. oxygen or iodide, avoiding further reduction or oxidation of the PEDOT being driven by the applied potential.

For reduction reactions, this leads to a higher conductivity of the PEDOT during operation at increasingly negative potentials compared to the conductivity of PEDOT, at that potential, where no other reduction is possible i.e. in N_2. For example, the conductivity of PEDOT in Fig. 12 is reaching a plateau at lower potentials when a "reducible" reactant is present, establishing an equilibrium between reduction of these reactants and re-oxidation of PEDOT, which maintain PEDOT in an intermediate state of reduction. This is similar to what has been reported for PANI in the case of hydroquinone oxidation.[35] In the case of oxygen–reduction on PEDOT (Fig. 12, red curve) the decrease in conductivity only represents a change in degree of doping from 0.25 to 0.2. The higher overall conductivity in the iodine–iodide example in Fig. 12 is caused by the low pH of the electrolyte.[37]

A schematic of the proposed mechanism is shown in Fig. 13, illustrated by the reduction of H^+ to H_2. In this schematic it is anticipated that the PTS counter-ions in PEDOT are not moving during the intermediate (reduced) state. This would require
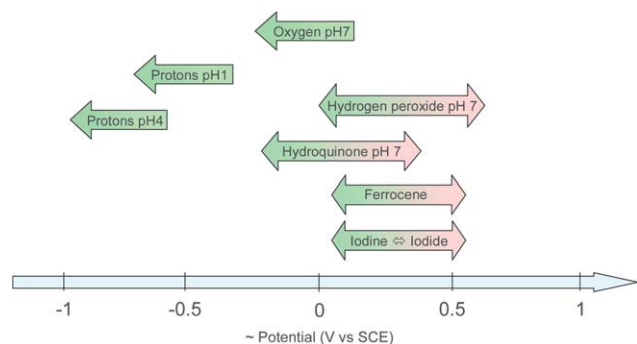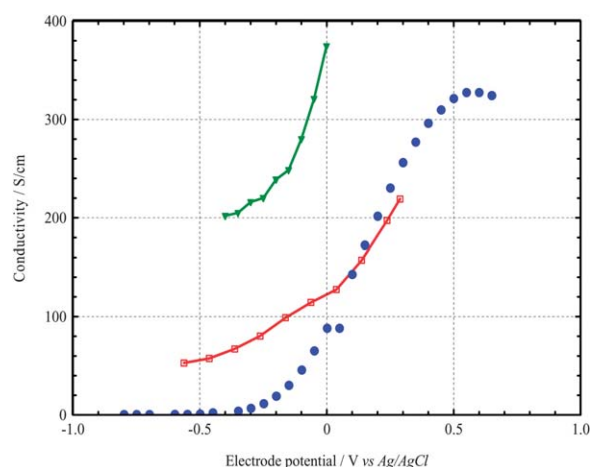

Fig. 12 Conductivity of PEDOT under N_2 (0.1 M NaCl, blue circles) and in contact with oxygen (0.1 M phosphate buffer, red curve) or iodide (0.03 M I_2 in DSSC electrolyte, green curve).

diffusion, which would be significantly slower than the re-oxidation of PEDOT. Similar schemes can be sketched for the other reduction and oxidation reactions on PEDOT.

The above discussion as much highlights what we do not yet fully know and understand about the overall mechanistic phenomena on these materials. Clearly, much more in-depth investigation is required, using a variety of techniques in order to provide further insights. Just as the last 3 or 4 decades of research in the field of electrocatalysis by metal surfaces has produced an increasingly thorough understanding of the molecular level events, the application of these materials will benefit from similar advances. Increasingly significant application of conducting polymers as electrocatalysts will certainly justify this effort. Techniques such as STM, in situ electrochemical Raman and perhaps ESR and NMR spectroscopies should shed light on some of the transient species present. In situ synchroton based
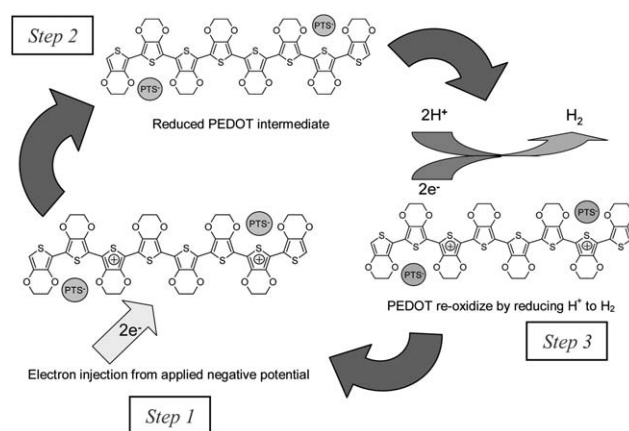

Fig. 11 The electrocatalytic working range for PEDOT illustrated by various redox reactions.

Fig. 13 The mechanism of the electro-catalytic reduction of H^+ on PEDOT:PTS is proposed as follows: the applied negative potential injects (step 1) electrons into the normally oxidized PEDOT:PTS creating an intermediate state of reduced PEDOT:PTS (step 2). The reduced PEDOT:PTS is not stable in the presence of H^+ and therefore readily re-oxidizes by reducing $2H^+$ to H_2 (step 3). (Previously published for the iodine/iodide reaction in ref. 23.)
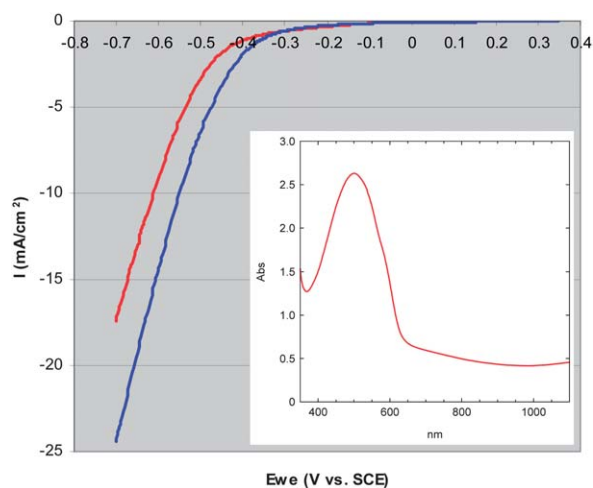
Fig. 14 Proton reduction on a PBTh composite in 1 M H$_2$SO$_4$ under N$_2$ (red curve) and enhanced by light (blue curve). Inset: UV-vis absorption of vapour phase polymerised PBTh.

FTIR measurements also may contribute here. The role of morphology of the material and its method of polymerisation are certainly important issues, especially given recent observations of enhanced order in polymers produced by VPP.[21] The role (or lack of) of the counterion could be further confirmed by experiments involving other types of counterions coupled with EQCM studies.

6. Towards photo-enhanced electrocatalysis based on conjugated polymers

We have in this article addressed the possibility of using conducting polymers as electro-catalysts as substitutes for metallic catalysts like platinum in a range of reactions and so providing a viable and inexpensive alternative. However, the nature of conjugated polymers as semiconducting band-gap materials opens a further possibility of enhancing the electro-catalytic performance by engineering materials or composites that can undertake the dual function of photo-excitation and electro-catalysis. Such materials would offer a number of attractive features, since the rate of an active redox process could be altered by action of light on the electrode. This could be of use in sensing technologies, switches, and even in solar energy technology. As an example of the latter, Fig. 14 shows proton reduction on such a composite material based on polybithiophene (PBTh) as the photoactive conjugated polymer electrocatalyst, recorded with and without exposure to visible light. It is clearly seen that the reduction wave is shifted *positive* by about 70 mV by the action of light. PBTh is chosen in this case because it has a band-gap around 2.4 eV and is quite absorbing in the visible region of the spectrum (see UV-vis spectrum, Fig. 14, inset). Thus band gap photoexcitation of the polymer presumably generates a population of high energy electrons which are available for the reduction reaction, thereby requiring a lower applied potential to drive the reaction. The results shown in Fig. 14 are quite preliminary and much research and optimisation lies ahead to further investigate this effect. However, the results clearly show the future possibilities of using light enhanced or light driven electro-catalysis for various REDOX reactions.

7. Conclusions

More than 30 years after the discovery of inherently conducting polymers the development of conducting polymers with enhanced stability and conductivity has led to an emerging field of using these materials as electro-catalysts for a wide range of reactions. The possibility of using polymeric organic materials to substitute precious metals like *e.g.* platinum in fuel-cells and dye sensitized solar-cells is indeed thrilling and should be a driving force for many further developments in the field. This research will without doubt lead to a significant increase in efficiencies, but also to applications in new areas like hydrogen (and *e.g.* methanol) oxidation. However, for this development to occur it is crucial that the mechanistic understanding of the phenomena is rapidly developed. At present—although quite a number of electro-catalytic reactions have been reported—the in-depth understanding of the mechanism(s) involved in the catalysis is only slowly emerging and calls for a collaborative effort from scientists and researches from several disciplines. The possibility of combining the electro-catalytic properties of conducting polymers with their photo-chemical properties opens a range of further, new and largely unexplored applications—as well as an urgent need for understanding the interplay between these properties.

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