A readily-prepared electrocatalytic coating that is more active than platinum for hydrogen generation in 1 M strong acid†

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Coating of a platinum electrode with conducting polypyrrole containing ferrocene sulfonate as counter-ion induces a 0.27 V anodic shift for hydrogen gas evolution in 1 M strong acids and a 7-fold amplification in hydrogen production when poised at −0.44 V.

The two-electron reduction of inorganic acids (H^+) to hydrogen gas (H_2) is efficiently catalyzed by the hydrogenase enzymes in biology.[1] However, the best non-biological, heterogeneous catalyst is platinum metal, which serves as the standard for electrochemical potentials in the normal hydrogen electrode. A long-standing goal in redox catalysis involving small gaseous molecules like O_2, H_2, and N_2, has been to discover molecular catalysts whose activity exceeds that of the best available heterogeneous catalyst and approaches that of the relevant enzymes.[2] In this work, we describe a readily prepared electrocatalytic coating which generates hydrogen more rapidly than platinum in 1 M strong acids.

The formation of H_2 from H^+ involves several steps, including the uni-atomic reduction step ($H^+ + e^- \rightarrow H\cdot$) in which atomic hydrogen is formed. On metal surfaces, this step is highly unfavourable (E^o *ca.* −2.10 V for Pt);[2] two $H\cdot$ species must also find each other in order to form H_2. An overpotential is therefore required to drive the reaction.

Molecular species in which stabilised $H\cdot$ atoms are formed in close proximity to each other prospectively overcome these limitations. One class of such catalysts is the [1.1]*ferrocenophanes* **1a–d**, which catalyse the formation of H_2 from H^+ by a homolytic combination of two reduced protons which are formed on the ferrocene iron atoms during protonation (Scheme 1).[3,4,5] The bis(ferrocenium) ions **3**, can be regenerated *in-situ* using a sacrificial reductant to close the catalytic cycle, or by direct electron transfer from an electrode.[3] INDO-SCF calculations indicate that the key catalytic intermediate **2** involves two $^+Fe–H\cdot$ moieties in which the positive charge of the protons effectively reside on the Fe atoms, with the hydrogens in an activated atomic form ($H\cdot$).[6] These species undergo rapid Fe–H ↔ Cp C–H exchange, with lifetimes too short to be observed on the NMR timescale, even at −125 °C.[4,7] For this reason, catalysis only occurs if the participating ferrocenes are held in the correct proximity and disposition to each other.[8] Free ferrocene, diferrocenylmethane, diferrocenylethane, and [0.0]ferrocenophane therefore do not catalyse the reaction.[4,8] [1]⁴Ferrocenophane does catalyse the reaction, albeit poorly, because flexing causes opposing ferrocenes to be correctly disposed and proximate for a lesser, but still significant proportion of the time.[4]
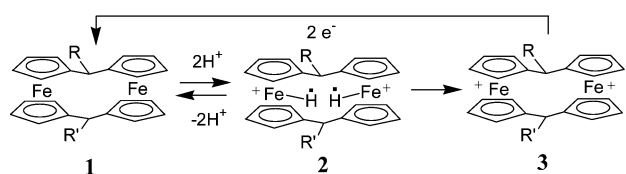
This combination of very short-lived activated intermediates, a transition state involving multiple stabilising groups, and catalysis which is dependent on correctly proximate and disposed catalytic groups is strongly reminiscent of the type of catalysis that is observed in enzymes.[5] While there is great interest in "synergistic" catalysis of this type, discovering and studying small-molecule catalysts which operate in this fashion is challenging because of the need to understand and engineer correct proximities and dispositions.[2,5]

Conducting electroactive polymers (CEP's) offer a useful means of immobilising and continuously regenerating redox catalysts if they are attached to the polymer or present within it as a counter-ion. Given the capacity of proximate ferrocene groups in **1a–d** to catalyze hydrogen formation from acids, we were interested in examining the effect of tethering [1.1]ferrocenophane to a conducting polymer. We were also interested to know whether a conducting polymer could be induced to incorporate unusually high local concentrations of a monomeric ferrocene species and, if so, whether it would be an efficient catalyst. A series of platinum electrodes were therefore coated with co-polymer **4**[10] or with polypyrrole containing ferrocene sulfonate counter-ions (PPy–FcSO₃) and tested for hydrogen generation (Scheme 2). Because the electrocatalytic properties of **1d** in 1 M strong acids have been described in detail,[9] testing was performed in 1 M HCl, H_2SO_4 and $HClO_4$. As a control, we also coated the platinum electrodes with polypyrrole containing *p*-toluene sulfonate (PPy–pTS), or nitrate (PPy–NO₃).

Polypyrrole–ferrocene sulfonate (PPy–FcSO₃)† was electrodeposited on platinum by potentiostatic growth at 0.60 V (*vs.* Ag/AgCl (3 M NaCl)) from an aqueous coating solution containing pyrrole (0.50 M) and ammonium ferrocene sulfonate (0.02 M). PPy–pTS, and PPy–NO₃ were similarly prepared. Polymer **4** was prepared by potentiostatic electrodeposition as described elsewhere.[10]

The average "concentration" of ferrocene sulfonate within PPy–FcSO₃ was calculated to be 2.02–2.30 M (over 5 samples) by determining the weight and dimensions of uniformly deposited coatings of PPy–FcSO₃, whose weight percentage of Fe was known from elemental analysis. This is substantially more than the saturation concentration of NH_4^+ FcSO₃⁻ in 1 M H_2SO_4 open solution, which is 0.41 M.

The electrocatalytic properties of PPy–FcSO₃ and **4** were then examined. In the representative results described below, all coatings were deposited to a charge of 100 mC on a platinum disk electrode of electrochemical area 0.0177 cm². This provided the greatest catalytic effect for PPy–FcSO₃, which formed a uniform layer, 5 μm thick, under these conditions. A custom-designed cell

a: R = R' = H; b: R = Me, R' = H; c: R = R' = Me; d: R = Me, R' = methyl-polystyrene

Scheme 1

PPy-FcSO₃
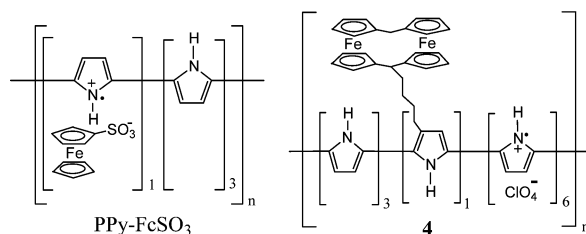
Scheme 2

was used in the experiments to ensure precise invariance in the positions of the electrodes and for collection and measurement of the gases produced. To ensure that the $2H^+\rightarrow H_2$ catalysis at the cathode was always rate limiting, a large platinum mesh was employed as the anode.

Initial studies examined the most positive potential at which hydrogen generation was observed. When the bare platinum electrode was swept from positive to negative potential, a current due to hydrogen formation commenced at −0.20 V (Fig. 1(i)(a)). The coated electrodes began generating hydrogen from −0.24 V (Pt/PPy–pTS; Fig. 1(i)(b)) and −0.25 V (Pt/PPy–NO$_3$). When coated with PPy–FcSO$_3$ or 4 however, ferrocene redox peaks were observed (points *f* in Fig. 1(i)(c)–(d)) followed by distinctly increasing currents from 0.07 V (PPy–FcSO$_3$) or 0.02 V (4). An unusual feature of these currents was the presence of maxima at −0.20 V (points *g* in Fig. 1(i)(c)–(d)). These currents and maxima are not due to the polypyrrole backbone, whose electrochemical response in this region is minuscule (*c.f.* PPy–pTS in Fig. 1(i)(b)).

To understand these results, we compared them with the voltammetric profile previously observed for catalytic hydrogen generation by polystyrene-bound [1.1]ferrocenophane 1d in 1 M strong acid (Fig. 1(i)(e)).[9] As can be seen, the current associated with hydrogen generation by 1d commences at the same potential as that observed for 4. This, along with the response of the bare platinum and the PPy–pTS-coated electrode, and the absence of other possible processes, indicates that the currents at potentials negative of the asterisks in Fig. 1(i)(c)–(d) are also due to hydrogen formation. Moreover, the mechanism of the catalysis by 4 is suggested to be the same as that in 1a–d. A substantial anodic shift therefore occurs in the most positive potential for hydrogen generation on platinum when it is coated with PPy–FcSO$_3$ or 4. This shift is greater for PPy–FcSO$_3$ than for 4 presumably because FcSO$_3^-$ is fully reduced at more positive potentials than 1a–d.

The maxima at points *g* in Fig. 1(i)(c)–(d) are not observed for 1d and must therefore be associated with the polypyrrole. The peak currents were linearly dependent upon scan rate. The current function† also increased with scan rate. The maxima are therefore due to adsorption of hydrogen by the polymer; this must block bulk transport of the reactants or the products, thereby starving the catalytic process.[11] The adsorption is substantial at potentials positive of −0.24 V, being > 100-fold larger than the corresponding hydrogen adsorption peaks on bare platinum.[11] The adsorption effects disappear at potentials negative of −0.24 V, when polypyrrole is progressively reduced.

Further tests examined the rate of hydrogen generation under potentiostatic conditions. To avoid complications due to the adsorption effects, these experiments were conducted at −0.44 V,
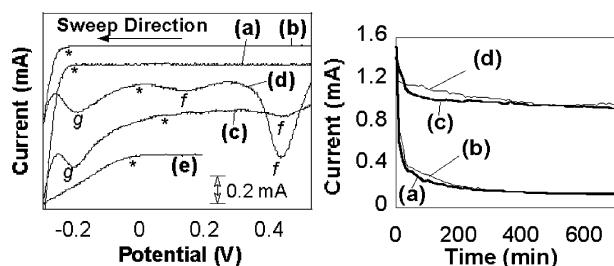
which is 0.20 V cathodic of −0.24 V. As polypyrrole is substantially in its neutral state at −0.44 V, the FcSO$_3^-$ anions are largely physically trapped rather than ion-paired within the PPy–FcSO$_3$ coating during these experiments. They therefore cannot be present in significant quantities at the polymer surface.

As can be seen in Fig. 1(ii)(a), the current at the uncoated platinum electrode declined sharply in the initial period of operation at −0.44 V; this is typical of freshly-cleaned platinum even in ultra-pure water (< 10 ppb organics).[12] After 12 h, a steady current of 0.130 mA was obtained. Under analogous conditions, the same electrode produced a 7-fold greater current after 12 h when coated with PPy–FcSO$_3$ (0.930 mA) or 4 (0.980 mA) (Fig. 1(ii)(c)–(d)). By contrast, coating with PPy–pTS resulted in a current of only 0.140 mA after 12 h (Fig. 1(ii)(b)). Similar results were obtained with PPy–NO$_3$. Separate experiments indicated these results to be general for PPy–FcSO$_3$ *vs.* bare Pt over a range of potentials (to −3 V at 20 °C/80 °C).†

This divergence is not due to different coating densities or quantities, since varying the PPy–pTS/NO$_3$ coating charge from 20–100 mC did not substantially change its rate of hydrogen generation after 12 h. The morphology of PPy–FcSO$_3$ and PPy–pTS/NO$_3$ also does not differ significantly. The volumes of hydrogen gas collected in these and other systems employing larger electrodes were typically within 10% of the quantity expected from the cumulative charge passing through the electrode. GC-MS of the gas indicated it to be pure hydrogen.

Studies also examined the effect of area on the rate of catalysis. Cyclic voltammetry (10 mV s^{-1} in 0.1 M K$_4$Fe(CN)$_6$/1.0 M NaNO$_3$) applied to eqn. (1),†

$$i_p = 0.4463nFAC_o*(nF/RT)^{1/2}v^{1/2}D_o^{1/2} \tag{1}$$

indicated the electrochemical areas of the electrodes to be 0.0177 cm^2 (bare Pt), 0.0355 cm^2 (Pt/PPy–FcSO$_3$), 0.0364 cm^2 (Pt/4), and 0.0209 cm^2 (Pt/PPy–pTS). The current densities after 12 h of operation were therefore 7.33 mA cm^{-2} (uncoated platinum), 26.20 mA cm^{-2} (Pt/PPy–FcSO$_3$), 26.93 mA cm^{-2} (Pt/4), and 6.76 mA cm^{-2} (Pt/PPy–pTS). The ferrocene-containing modified electrodes were consequently more active per unit electrochemical area. Moreover, increasing the electrochemical area of the platinum electrode by coating it with PPy–pTS had a negligible effect on its overall rate of catalysis.

PPy–FcSO$_3$ is therefore a vigorous catalyst of H$^+\rightarrow$H$_2$, which is considerably more easily prepared than the expected catalyst, 4. Future reports will examine its mechanism of action.

Notes and references

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Fig. 1 (i) Current–potential plot (first scan, 100 mV s^{-1}) (left) and (ii) current–time plot when poised at −0.44 V (right) in 1 M H$_2$SO$_4$ of a Pt electrode (*vs.* Ag/AgCl (3 M NaCl)), (a) before coating, and after coating with: (b) PPy–pTS, (c) PPy–FcSO$_3$, and (d) 4. Curve (e) indicates the comparative area-equivalent response of 1d during catalytic hydrogen generation in 1 M HClO$_4$ as displayed in ref. 9. The asterisks in Fig. 1 (i) mark the commencement of hydrogen generation in each system.