## - SUPPLEMENTARY INFORMATION -

### 6 pages

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

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#### General notes on the text

- NH4<sup>+</sup> FcSO3<sup>-</sup> was prepared as described in V. Weinmayr, *J. Am. Chem. Soc.*, 1955, 77, 3009. Selected characterisation details of PPy-FcSO3: elemental analysis, calcd. for (pyrrole)4.2 (FcSO3) ·2.42 H2O; C, 55.3%; H, 5.5%; N, 10.1%; Fe, 9.6%; found C, 55.1%; H, 5.5%; N, 10.2%; Fe, 9.7%. Conductivity (four-point probe technique): PPy-FcSO3 15.23 S cm<sup>-1</sup> (PPy-pTS 16.90 S cm<sup>-1</sup>).
- 2. Current function = peak current /  $(\text{scan rate})^{\frac{1}{2}}$ . See: R. S. Nicholson and I. Shane, *Anal. Chem.*, 1964, **36**, 706.
- 3. For equation (1): i<sub>p</sub> = peak current (amps), n = electrons per molecule oxidised or reduced, F = Faraday's constant (C), A = area (cm<sup>2</sup>), C<sub>o</sub>\* = bulk concentration (mol cm<sup>-3</sup>), R = gas constant (J mol<sup>-1</sup> K<sup>-1</sup>), T = temperature (K), v = scan rate (V s<sup>-1</sup>), and D<sub>o</sub> = diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>). See: A. J. Bard and L. R. Faulkner, Ch. 6 in *Electrochemical Methods*, John Wiley and Sons Inc., U.S.A., 1980.

#### **Enlarged View of Fig. 1(i)**



#### Note on Fig. 1(i)(e)

This figure depicts the poorest of the catalytic performances reported in ref. 9 for **1d** in 1 M strong acids (that is, when irradiated with a Xe-lamp)

#### **Enlarged View of Fig. 1(ii)**



## Notes on Fig. 1(ii)(a):

- 1. Range of data after 12 h at -0.44 V: 0.11 0.26 mA (over 8 runs).
- 2. Procedures used: Immediately prior to testing, the platinum disk electrode was

polished with Gamma Alumina powder (0.05 micron) (Leco Corporation, St. Joseph, Michigan) and 800 grit pads (Bioanalytical Systems, West Lafayette, Indiana), after which it was washed with Milli-Q water and shaken to dry. The electrode was tested in a vertical or a horizontal alignment without stirring of the solution; identical results were obtained. In the early stages of some experiments, the hydrogen bubbles formed were not readily released from the electrode surface, thereby blocking access by the bulk solution. In these cases, nitrogen bubbles were allowed to periodically sweep the platinum surface to remove the hindering gas. There was no noticeable effect on the data obtained after 12 h.

#### Notes on Fig. 1(ii)(c):

- Range of data after 12 h at -0.44 V: 0.79 1.33 mA (over 16 runs), excluding two anomalous results (0.32 mA and 1.95 mA).
- 2. Procedures used: The platinum disk electrode was cleaned and polished as described above. It was then coated with pyrrole (Merck) containing ferrocene sulfonate dopant as described in the text and allowed to dry for 30 min 1 h. After placing in the test cell, it was left to stand for 30 min to allow the coating to become thoroughly acidified (this could be achieved more rapidly by cycling the electrode, however this may result in de-doping of the ferrocene sulfonate, with an accompanying decline in the catalytic properties).
- 3. Comparative tests were also run using larger platinum electrodes. Similar results were obtained. Representative data after 12 h at -0.44 V:

Bare Pt mesh ( $2.3 \text{ cm}^2$ ):34 mA ( $14.8 \text{ mA cm}^{-2}$ )PPy-FcSO<sub>3</sub>-coated Pt mesh ( $3.27 \text{ cm}^2$ ):125 mA ( $38.1 \text{ mA cm}^{-2}$ )



Fig. 2Cyclic voltammogram (vs. Ag/AgCl (3 M NaCl)) of a platinum disk<br/>electrode modified by coating with PPy-FcSO3 in aqueous 1.0 M<br/>NaNO3. Scan rate: 100 mV s<sup>-1</sup>.



Fig. 3Polarization curves for water electrolysis in 1 M  $H_2SO_4$  (two-electrode<br/>system) after 1 h of operation at 20 °C or 80 °C by a platinum disk<br/>cathode before coating (dotted lines) and after coating with PPy-FcSO3<br/>(solid lines). The inset graph details the data at the bottom left of the<br/>main graph. The coating was deposited galvanostatically (1 mA cm<sup>-2</sup><br/>for 30 min). Electrochemical area of uncoated electrode: 0.0170 cm<sup>2</sup>;<br/>coated electrode: 0.0580 cm<sup>2</sup>.

#### Notes on Fig. 3

- 1. When poised at -0.44 V, the comparable three-electrode system generates the same current as the two-electrode system depicted in Fig. 3 at -2.0 V.
- 2. When poised at -3.0 V, the two electrode system depicted in Fig. 3 generates the same current as the comparable three-electrode system at -0.90 V.
- The data in Fig. 3 is comparative only and cannot be compared to data from optimally engineered commercial water electrolysers (see: A. P. Fickett and F. R. Kalthammer, Ch 1 in *Hydrogen: Its Technology and Implications, Volume I*

*Hydrogen Production Technology* (Eds K. E. Cox, K. D. Williamson), CRC Press Inc, Cleveland 1977).