Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information for:

A Practical Organic-Mediated Hybrid Electrolyser that Decouples Hydrogen Production at High Current Densities

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SI-1. General Experimental Remarks

9,10-anthraquinone-2,7-disulfonic acid disodium salt was purchased from Santa Cruz Biotechnology or Tokyo Chemical Industry and used without further purification. Solutions were prepared in 1 M H_2SO_4, which itself was prepared from concentrated sulfuric acid (>95 %, Sigma Aldrich) using reagent grade deionised water (18 MΩ · cm resistivity).

Nafion N-117 membrane, platinum mesh, and carbon felt used in initial electrochemical measurements were purchased from Alfa Aesar. Working and reference electrodes and other electrochemical materials were purchased from IJ Cambria Scientific Ltd. Specialist air-tight two-chamber H-Cell glassware was purchased from Adams & Chittenden.

Materials for the PEME cells are listed in section SI-4.

pH determinations were made with a Hanna HI 9124 waterproof pH meter. Experiments performed at “room temperature” were carried out at 22 °C.

SI-2. Electrochemical Characterisation

CH Instruments 600 or 760d, or Biologic SP-150 potentiostats were used with the accompanying CHI or EC-Lab software for all electrochemical measurements.

Cyclic voltammetry experiments were carried out using a 3-electrode setup. 3-electrode electrochemical experiments were performed using either a 3 mm diameter glassy carbon disc working electrode or a 2 mm diameter Pt disc working electrode with a large surface area Pt-mesh counter electrode and an Ag/AgCl (saturated KCl) reference electrode (BASi) at room temperature and pressure. All measurements were performed with 25 mM solutions of AQDS in 1 M H_2SO_4, degassed with argon before use. Working electrodes were polished using 6 µm and 1 µm diamond polish and rinsed thoroughly with methanol and DI water. Background measurements in 1 M H_2SO_4 were performed prior to sample measurements to ensure the cleanliness of the electrodes. All measurements were performed at a scan rate of 25 mV s^{-1} unless otherwise stated. Cyclic voltammetry experiments were performed over 100 cycles (Figure S1).

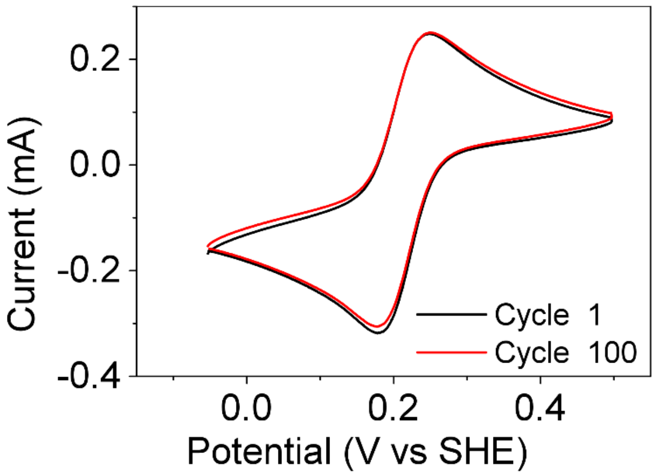

Figure S1. Cyclic voltammogram of anthraquinone-2,7-disulfonic acid in 1 M H_2SO_4, recorded on a glassy carbon working electrode at a scan rate of 25 mV s^{-1}. Only cycles 1 and 100 are shown for clarity purposes.

Bulk electrolysis experiments were performed in an air-tight, two-chamber H-cell as shown in Figure S2. The working compartment contained 25 mL of 25 mM AQDS in 1 M H_2SO_4, with a carbon felt working electrode and Ag/AgCl reference electrode. The counter compartment contained 25 mL of 1 M H_2SO_4 and a platinum mesh counter electrode. 1 M H_2SO_4 was chosen as the electrolyte in the gas-evolving side of the H-cells in order to maintain a pH and ionic concentration similar to that on the ECPB side of the cell. The two chambers of the H-cell were separated by a Nafion 117 membrane, so that protons could travel freely between compartments, but the movement of anions was attenuated. Both solutions were thoroughly degassed with argon prior to measurements. Both compartments were stirred using magnetic stirrer bars during measurements. Potentiostatic measurements were used to fully reduce/ oxidise the ECPB at potentials of -0.2 V/ +0.2 V (*vs.* Ag/AgCl) until the resulting current dropped to background levels. For capacity retention plots, the charge for each cycle was normalised by dividing by the charge passed during the first reduction.

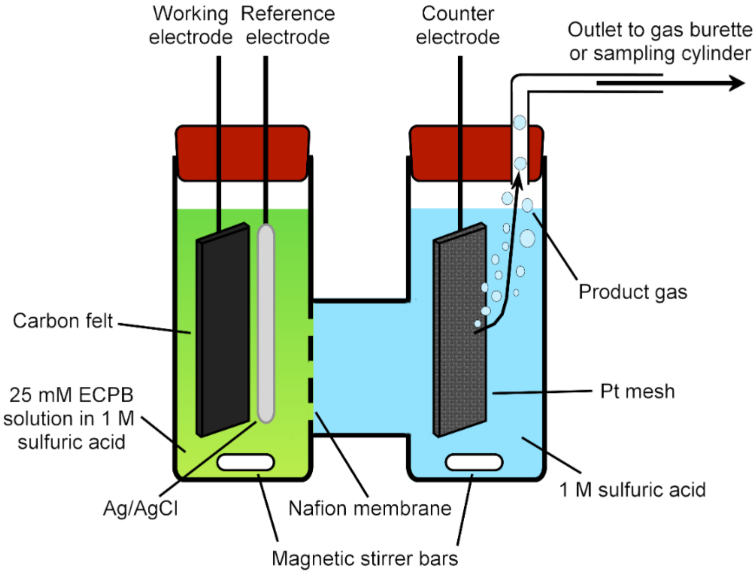

Figure S2. General H-cell configuration for bulk electrolysis experiments.

SI-3. Gas Headspace Measurements

Gas measurements were performed by both measuring the volumes of evolved gas, and by analysing the headspace using gas chromatography headspace analysis (GCHA).

Volumetric measurements were conducted by measuring the volume of gas evolved at the counter electrode during reduction/oxidation of the ECPB at ± 0.2 V *vs.* Ag/AgCl. An airtight two-chamber cell was used (as in Figure S2) with a gas burette connected to the counter compartment. The measured charge was recorded for every millilitre of gas evolved. These experiments were repeated three times and averaged. The averages of the three repeats for the reduction and oxidation of AQDS (O_2 and H_2 measurements, respectively) are shown in Figure S3.

Charges passed were converted into expected volume of hydrogen or oxygen by calculating the theoretical number of moles of gas (by dividing by 2F for H_2 and 4F for O_2, where F is the Faraday constant, 96485.33 C mol^{-1}), and then multiplying by the molar volume of an ideal gas at room temperature and pressure, taken to be 24.22 L mol^{-1} at 22 ˚C.

The headspace was then sampled by gas-tight syringe (volume taken per sampling event = 50 µL) and introduced onto the GC column by direct injection to confirm the presence of O_2/ H_2. The GC oven temperature was set to 27 °C and the carrier gas was Ar. The front inlet was set to 100 °C. The same procedure was repeated for the ECPB-containing working compartment, where no gas was observed.

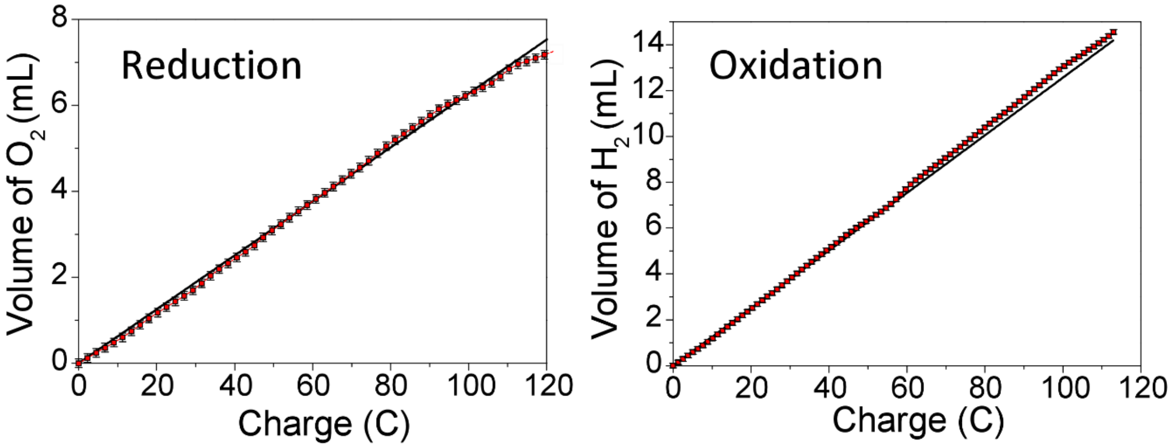

Figure S3. Volumetric gas measurements for the reduction (left) and oxidation (right) of AQDS. The results shown are the averages of three repeats. Red lines are the experimental volumetric data with error bars, and black lines are the theoretical volumes of gas evolved based on the charge passed during electrolysis.

SI-4. Hybrid PEME Construction and Operation

The hybrid PEM electrolyser cells were constructed as shown in the schematic in Figure 3a of the main text. The active area of each cell was 12.96 cm^2 (3.60 cm x 3.60 cm).

Cells consisted of components sourced from several companies. Titanium flow plates with serpentine flow channels were purchased from Glenhead Engineering. Catalyst-coated *Nafion* 115 membranes were purchased from Ion Power and were each coated with a catalyst on only one side: an iridium catalyst (1 mg cm^{-2}) for the anodic side of the OER cell (oxygen evolution) and a platinum catalyst (0.3 mg cm^{-2}) on the cathodic side of HER cell (hydrogen evolution). The catalyst was coated onto an area of 3.6 cm by 3.6 cm. A single layer of hydrophilic carbon cloth was used as the gas diffusion layer (GDLs) at each of the four electrodes and was purchased from FuelCellsEtc. PTFE insulating plates and aluminium end plates purchased from Euroscot Engineering were used to electrically insulate the cells and provide mechanical strength, respectively. PTFE gaskets were used in between the flow plates, GDLs, and membranes. Viton gaskets were used between the flow plates and the insulating plates. Cells were held together using 8 x M6 bolts tightened to 5 N m using a torque wrench.

Cells were constructed as shown in Figure 3a and S4. Electrolytes were transported to and from the cell using 6 mm OD PTFE tubing (purchased from Labtex). Thermocouples (purchased from TC Direct) were inserted into the tubing directly before the input to the cells, so that the temperature could be accurately controlled.

The electrolytes used at the OER and HER sides of the device were both 1 M H_2SO_4 (the “anolyte” and “catholyte”, respectively). The electrolyte used in the ECPB section of the device was 0.5 M AQDS in 1 M H_2SO_4 (the “mediator”). The electrolyte solutions were pumped through the cells using three separate Masterflex peristaltic pumps (Cole-Parmer), with all electrolytes circulating at a flow rate of 250 ml min^{-1}. The solutions were heated to 50 ˚C in oil baths and stirred using magnetic stirrer bars. All solutions were sparged with argon prior to operation.

The titanium flow plates were cleaned prior to use by sonicating in 1 M H_2SO_4 for 15 minutes, isopropanol for 15 minutes, detergent and deionised water for 5 minutes, then deionised water for 15 minutes (DI water rinsing between each step). New carbon cloth GDLs would be used for each construction and were not pre-treated. The *Nafion* membranes would be regenerated by heating in 1 M H_2SO_4 for one hour at 80˚C. They would then be rinsed and stored in ultrapure water.

All electrochemical measurements were taken with the ECPB solution in a 50 % state of charge, unless otherwise stated. This was done by reducing the oxidised ECPB solution in the OER cell with a cut-off when the charge reached 50 % of the full capacity of the ECPB (calculated from Faraday’s law).

Electrochemical analyses were performed using a Biologic SP-150 potentiostat with accompanying Biologic VMP-3B 20 A current booster. For high current measurements (> 1.6 A cm^{-2}), a VMP3B 80 A booster was used. These were controlled using the EC-Lab software. For operations where both cells were to be run simultaneously, each cell would be controlled by separate potentiostats. Where the current did not need to be recorded, an EA-PS-5040-20A power supply unit was used.

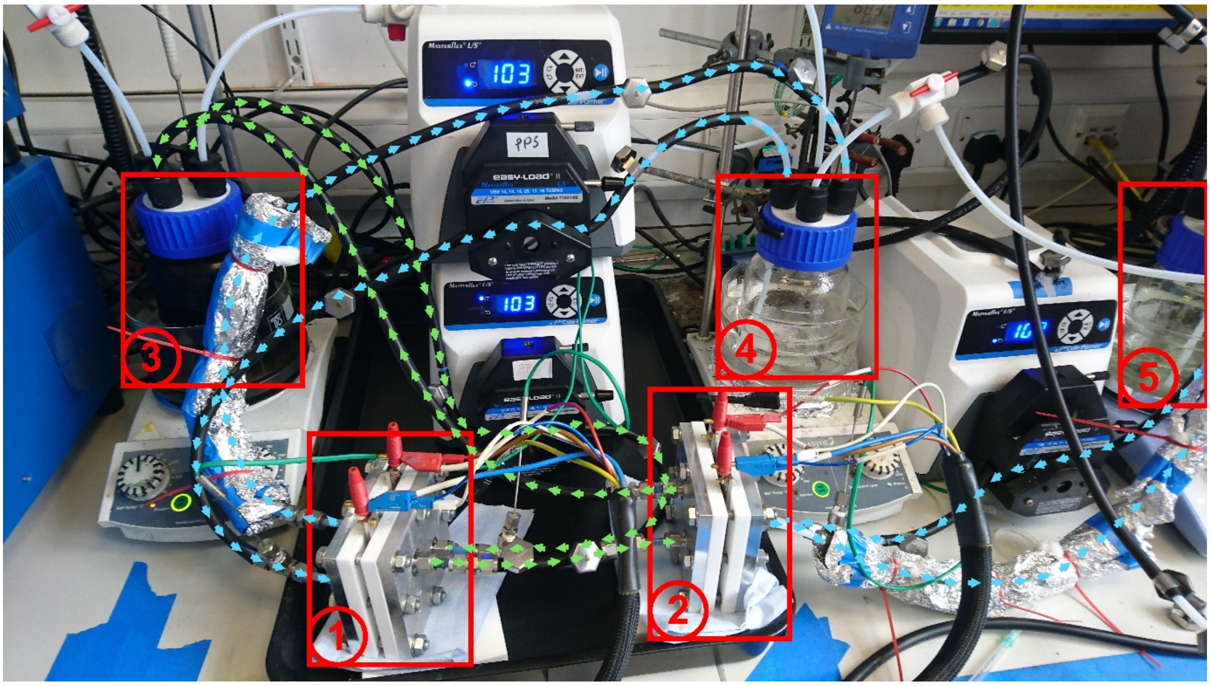

Figure S4. Electrolyser configuration composing of: 1) The OER cell, 2) The HER cell, 3) The ECPB reservoir, 4) The anolyte reservoir, and 5) The catholyte reservoir. The flow of ECPB is highlighted with green arrows, and the anolyte and catholyte pathways are shown in blue. Peristaltic pumps were used to transport the electrolytes to the cells.

SI-5. PEME Characterisation Methods

The current response of each cell was measured as a function of increasing potential using the I-V Characterisation function of the EC-Lab software. This entailed sweeping the cell potential from 0 V up to 2.5 V (or below if the current limit of the potentiostat was reached), at a scan rate of 100 mV/s. Current was plotted against cell potential to give iV polarisation curves. Currents were limited to just over 20 A due to the limitations of the current booster (Biologic VMP-3B 20 A).

High current measurements (> 20 A or 1.6 A cm^{-2}) were recorded using a VMP3B 80 A booster, using the same parameters as above. To minimise mass transport effects, the ECPB solution flow rate was increased to 400 mL min^{-1}. All other conditions remained the same.

Potentiostatic electrochemical impedance spectroscopy (PEIS) was used to quantify the resistances present in the internal cell processes. These measurements were taken on both cells operating at a steady state. Both the OER and HER cells were run simultaneously with a current density of 100 mA cm^{-2} for 30 minutes, before a sinusoidal potential was applied, sweeping from 100 kHz to 1 Hz with an amplitude of 5 mV. The resulting Nyquist impedance plots were fitted against the equivalent electric circuit L1+R1+R2/CPE2+R3/CPE3, where L1 represents an inductance caused by the potentiostat wiring, R1 is the ohmic resistance of the cell, and [R2 and CPE2] and [R3 and CPE3] are the resistances and pseudo-capacitances caused by the anode and cathode reactions. These impedances represent each cell individually, with separate measurements for the OER and HER cells.

Table S1. PEIS data after fitting to the equivalent electric circuit L1+R1+R2/CPE2+R3/CPE3. Active area of cells is 12.96 cm^2.

Circuit Element	OER Cell	HER Cell
L1 (H)	9.63×10^{-8}	7.43×10^{-8}
R1 (Ω)	0.0315	0.0380
CPE2 (F·s $^{(a-1)}$)	5.111 (a=0.6164)	41.02 (a=0.4822)
R2 (Ω)	0.03557	0.0218
CPE3 (F·s $^{(a-1)}$)	0.03807 (a=0.9267)	0.1771 (a=0.6885)
R3 (F)	0.0097	0.0193

Gas measurements were completed as described in section SI-3, with the product gas streams feeding directly into the gas burette from the electrolyte reservoirs. Measurements were repeated three times and averaged. Samples were taken from a sampling cylinder using a gas-tight syringe and analysed using gas chromatography by direct injection (with the same parameters as above). Figure S5 shows the GC spectra for the product gas streams from the OER and HER cells. No H_2 signal was seen in the oxygen stream, with a large O_2 peak and a small N_2 peak visible. The presence of N_2 is due to a small air-leak in the sampling equipment. The hydrogen stream showed a large H_2 peak with small O_2 and N_2 peaks, which has also been attributed to the presence of air. The relative N_2/ O_2 peaks areas are equivalent to those seen in a blank air sample, indicating an air leak in the sampling equipment is the cause of the contamination.

Stability tests were performed galvanostatically by applying a current of 0.25 A cm^{-2} to each cell simultaneously and measuring potential required to maintain this current. Electrolyte solutions were heated to 50 ˚C and circulated at 250 ml min^{-1}. The ECPB solution was at a 50 % state of charge. The 24 hours of operation were completed in four 6 hour segments. Due to the effects of electro-osmotic drag, the OER anolyte and HER catholyte solutions (both 1 M H_2SO_4) were replaced at the start of every 6 hour segment.

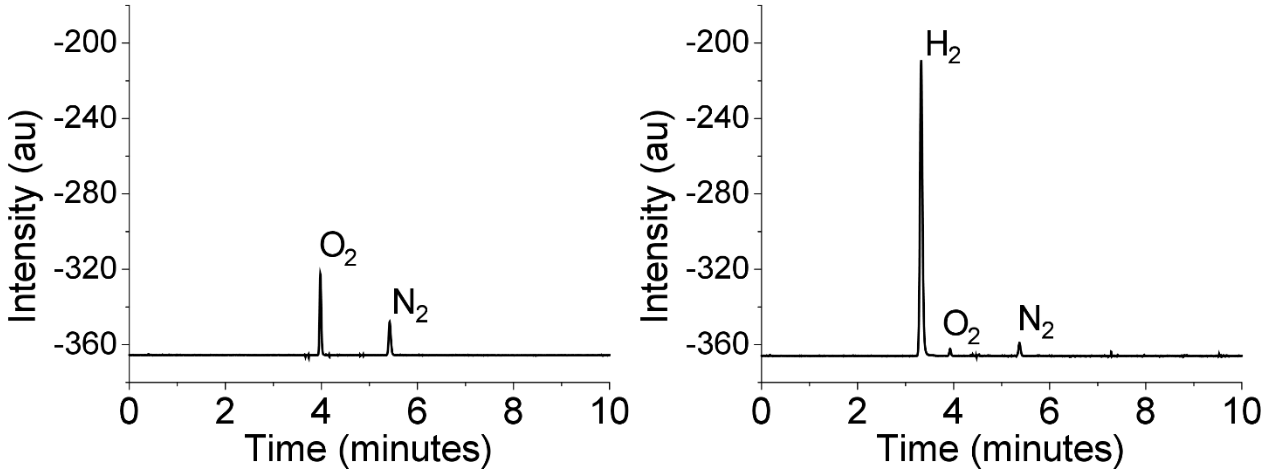

Figure S5. GC spectra of the product gas streams from the hybrid electrolyser. On the left is the product oxygen stream from the OER cell, and on the right is the product H_2 from the HER cell.

SI-6. PEME Efficiency Calculations

Faradaic efficiencies were calculated from the volumetric gas measurements as described in Section SI-3. Relative error on volumetric measurements is approximately ± 1 mL (not shown in calculations).

Tables S2 and S3. Volumetric gas measurements and Faradaic efficiencies of the two PEM cells.

O_2 (water ox/ AQDS red)

Run	Δ t (s)	I (A)	Q (C)	$V_{theoretical}$ (ml)	$V_{Experimental}$ (ml)	Faradaic Efficiency (%)
1	600	0.65	390.11	24.494	24.2	98.80
2	600	0.65	390.11	24.494	25.2	102.88
3	600	0.65	390.10	24.493	23.4	95.54
						99.07

H_2 (AQDS ox/ H^+ reduction)

Run	Δ t (s)	I (A)	Q (C)	$V_{theoretical}$ (ml)	$V_{Experimental}$ (ml)	Faradaic Efficiency (%)
1	300	0.65	195.1	24.499	24.3	99.19
2	300	0.65	195	24.487	24.1	98.42
3	600	0.65	390.1	48.986	48.9	99.82
						99.14

Energy efficiency calculations for the PEME were conducted in a similar manner, by comparing the energy contained in the evolved H_2 that can be released through conversion back to water, and the energy required to produce it in the PEME. It is important to note that only the energy consumed in the electrical processes of the electrolyser was considered, and not that of the entire setup (including pumps and heating, etc.). This was considered appropriate to compare the electrochemical cell with other electrolyser systems.

The energy of the product hydrogen was calculated through multiplying the number of moles produced by the higher and lower heating values (HHV and LHV) of hydrogen (HHV = 285.60 kJ · mol^{-1}, LHV = 237.35 kJ mol^{-1}).

$$E_{H2} = n \cdot \text{HHV (or LHV)}$$

The energy consumed in the production of the gas can be calculated by multiplying the voltage and charge for each cell separately, before summing together.

$$E_{consumed} = (V_{OER} \cdot I_{OER} \cdot t) + (V_{HER} \cdot I_{HER} \cdot t)$$

Where V_{OER} and I_{OER} are the voltage and current from the OER cell, and t is the time for which it was running to produce the gas. V_{HER} and I_{HER} are similarly from the HER cell. The efficiency can then be calculated by dividing the energy of the H_2 by the energy consumed in its production.

$$E_{efficiency} = E_{H2} / E_{consumed}$$

Table S4. Energy efficiency of the combined cell processes operating at 0.5 A cm^{-2}.

$E_{OER\ Cell}$ (V)	$E_{HER\ Cell}$ (V)	E_{Total} (V)	Energy Consumed (kJ mol^{-1})	Energy of H_2 (kJ mol^{-1})	Efficiency (%)
1.778	0.585	2.363	455.989	285.60	**62.63**

SI-7. Cost Calculations

Molar cost of AQDS versus Silicotungstic Acid

As mentioned in a study by Huskinson *et al.* (*Nature*, 2014, **505**, 195–198.), the price of AQDS could be as low as \$4.74 per kg if obtained from the sulfonation of anthraquinone at scale (shown to be viable in the mentioned study).[1] Anthraquinone has a molecular weight of 208.22 g mol^{-1}, making the cost \$0.99 per mole (equivalent to £0.76 per mole as of 02/08/17).

The price of silicotungstic acid (STA) is fundamentally limited by the price of tungsten ore, and so a base price for $H_4[W_{12}SiO_{40}]$ can be calculated based on the price of tungsten trioxide (WO_3). The price of tungsten trioxide was \$34.8 per kg, and with a molecular weight of 231.84 g mol^{-1}, this makes WO_3 \$8.07 per mole.[2] 1 mole of STA requires 12 moles of WO_3, making the base cost \$96.84 per mole (£73.86 per mole).

AQDS is therefore 1.02 % of the cost of STA on a mole-for-mole basis.

Cost of spent AQDS in production of 1 kg H_2

1 kg of H_2 equates to 495.05 moles. 1 mole of AQDS stores 1 mole of H_2, implying 1 mole of AQDS would need to be fully reduced/oxidised 495.05 times to produce 1 kg H_2.

With a loss of 0.06 % per full oxidation/reduction cycle (from the 100-cycle bulk electrolysis experiments), this gives a total loss of 29.70 % for 1 mole AQDS (a loss of 0.297 moles of AQDS).

As detailed above, the cost of AQDS is £0.76 per mole. The loss of 0.297 moles of AQDS in producing 1 kg of H_2 therefore costs £0.23.

References

1 B. Huskinson, M. P. Marshak, C. Suh, S. Er, M. R. Gerhardt, C. J. Galvin, X. Chen, A. Aspuru-Guzik, R. G. Gordon and M. J. Aziz, *Nature*, 2014, **505**, 195–198.

2 US Geological Survey, *Mineral Commodity Summaries, Tungsten*, 2014.