

## Electronic Supplementary Information

### Membrane-less organic-inorganic aqueous flow batteries with improved cell potential

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#### Experimental section:

##### Chemicals

Analytical grade zinc chloride, 1,4-benzoquinone (parabenzoquinone), 1,4-hydroquinone, 1,2-hydroquinone (catechol), 1,2-hydroquinone-3,5-disulfonic acid, sodium hydroxide and reagent grade aqueous hydrochloric acid were supplied from Sigma Aldrich (Germany) and Fisher Scientific (UK). Solutions were prepared with ultra-pure water (18 M $\Omega$  cm resistivity) from a Millipore water purification system (Milli-Q Integral 3). Metallic zinc sample of 1.6 mm thickness (foil, code: 10438, 99 % purity) was supplied from Alfa Aesar (UK).

##### Cyclic voltammetry

Cyclic voltammetry was conducted in a three-electrode glass cell with a glassy carbon working electrode (exposed area of 0.07 cm<sup>2</sup>). Counter and reference electrodes were platinum and silver-silver chloride (Ag|AgCl, 1 mol dm<sup>-3</sup> KCl, ABB, Series 1400, Switzerland). The cyclic voltammetry measurements were made using a Bio-logic VMP potentiostat (Bio-logic SAS, France) for both the negative zinc and positive quinone reactions in an electrolyte containing 10 mmol dm<sup>-3</sup> active materials in 1.0 mol dm<sup>-3</sup> sodium chloride solution. To evaluate the influence of pH on the electrochemical behaviour of the two reactions, electrolytes were adjusted between pH 1 and 12 using sodium hydroxide and hydrochloric acid solutions. For the zinc electrodeposition reaction, cyclic voltammetry was carried out between the potential ranges of -0.5 and -1.6 V vs. Ag|AgCl at a potential sweep rate of 100 mV s<sup>-1</sup>. A similar scan was carried out between -0.3 and +1.2 V vs. Ag|AgCl at the same potential sweep rate (100 mV s<sup>-1</sup>) for the positive electrode reaction.

##### Zinc dissolution tests

Measurements of the zinc dissolution rate was carried out in different electrolyte compositions using zinc samples from Alfa Aesar (1.6 mm thickness, *c.a.* 9.5 mm  $\times$  *c.a.* 9.0 mm  $\times$  *c.a.* 1.6 mm, 99 %, Ref. 10438, United Kingdom). The pretreatments of zinc samples were carried out by polishing with silicon carbide paper (grade P120), degreasing with detergent, and etching in concentrated acid (30 % HCl, 30 % H<sub>2</sub>SO<sub>4</sub>) for 30 s. Following these procedures, the samples were ultrasonic cleaned for 1 minute and rinsed with ultrapure water (Milli-Q Integral 3). The total exposed areas of the zinc sample surfaces were 2.3 – 2.5 cm<sup>2</sup>. The weight loss measurements were made every few hours over

a total period of 168 – 190 h with the use of an electronic balance ( $\pm 0.01$  g accuracy, Scout Pro SP202, Ohaus, United States).

### Flow battery experiments

Galvanostatic charge-discharge experiments were carried out in a commercial parallel-plate flow cell (Proingesa, Spain) based on a membrane-less configuration. The single cell consisted of two electrodes, two acrylic flow channels (2 mm thickness each) and four neoprene rubber gaskets (1 mm thickness each). There was one inlet at the lower side of the negative electrode and one outlet at the upper side of the positive electrode. The reference electrode was silver-silver chloride ( $0.1 \text{ mol dm}^{-3}$  KOH, ABB, Switzerland) placed at the entrance of the inlet in line with the electrolyte circuit. Within the cell, planar carbon polyvinylester ( $2.0 \text{ cm} \times 2.0 \text{ cm}$ , Electrocell, Denmark) was used as the substrate material for both the negative and positive electrodes. For the positive electrode, a piece of carbon felt ( $2.0 \text{ cm} \times 2.0 \text{ cm}$ , Sigratherm GFA-05, SGL Carbon, 5 mm thickness, Germany) was attached on the substrate material and compressed with the use of polyester tapes (Cole-Parmer Inc., United States). A single electrolyte of  $1.5 \text{ mol dm}^{-3}$  zinc chloride and  $50 \text{ mmol dm}^{-3}$  hydroquinone molecules ( $40 \text{ cm}^3$ ) was circulated through the battery at a volumetric flow rate of *c.a.*  $90 \text{ cm}^3 \text{ min}^{-1}$ .

Prior to the flow battery tests, the planar carbon electrodes used for the negative electrode reactions were charge-discharge cycled at  $30 \text{ mA cm}^{-2}$  in a pure  $1.5 \text{ mol dm}^{-3}$  zinc(II) chloride to obtain more than 90 % half-cell coulombic efficiencies over 20 cycles. In typical experiments, negative and positive currents ( $120 \text{ mA}$ ,  $30 \text{ mA cm}^{-2}$ ) were applied under a 15 min charge – 15 min discharge regime. The negative and positive electrode potentials and the overall cell voltages were continuously monitored using a Bio-logic VMP potentiostat (Bio-logic SAS, France)

The coulombic, voltage and energy efficiencies of the redox flow battery were calculated from the following formulae:

$$\text{Coulombic efficiency} = j_d \Delta t_d / j_c \Delta t_c \times 100 \%$$

$$\text{Voltage efficiency} = V_d / V_c \times 100 \%$$

$$\text{Energy efficiency} = j_d V_d \Delta t_d / j_c V_c \Delta t_c \times 100 \%$$

where  $V$  is the cell voltage,  $j$  is the applied current density,  $\Delta t_c$  is the charge duration and  $\Delta t_d$  is the discharge duration.

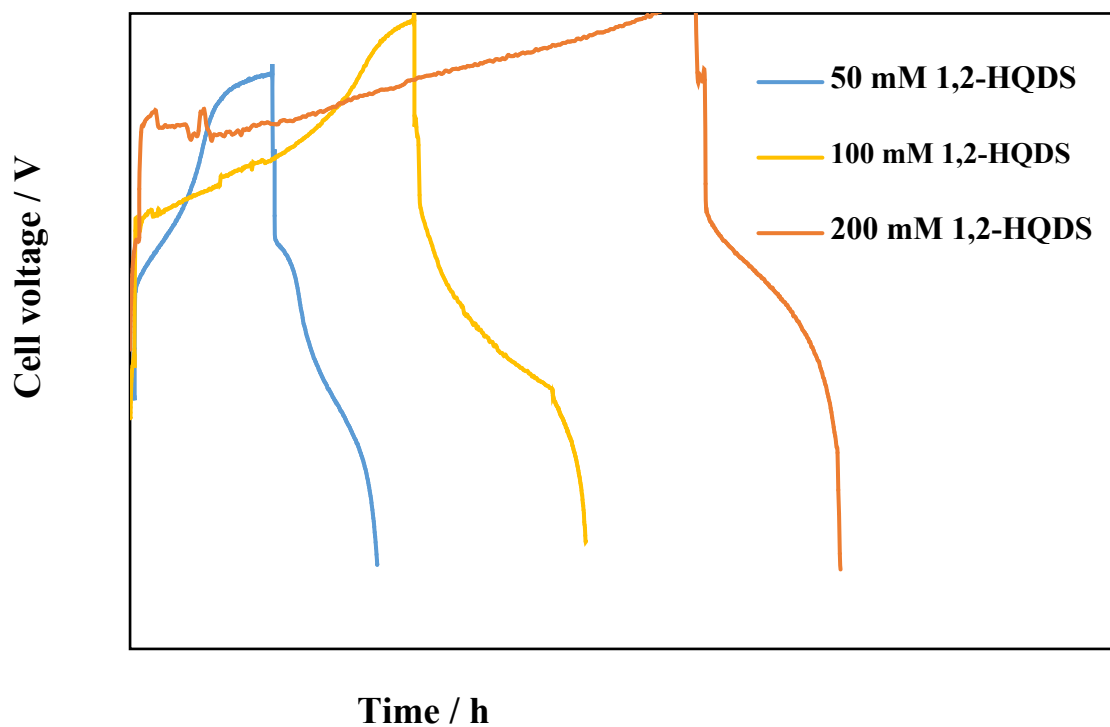


Figure S1. Charge-discharge performance of a zinc-1,2-BQDS hybrid flow battery at different hydroquinone concentrations (50 mM, 100 mM and 200 mM). Electrolytes: 1.5 M  $\text{ZnCl}_2$  and hydroquinone; negative electrode: planar carbon; positive electrode: carbon felt. Current density:  $30 \text{ mA cm}^{-2}$ ; Room temperature.

DOD / %	[1,2-BQDS] / mM	[1,2-HQDS] / mM	$j_{cor} / \text{mA cm}^{-2}$
0	50	0	6.4
20	40	10	5.7
40	30	20	4.9
60	20	30	4
80	10	40	2.9
100	0	50	0

Table S1. Calculated corrosion current densities at different depth-of-discharges for a 50 mM Zn/1,2-BQDS system. Experimental conditions are the same as those in Figure 2.