

Supporting Information

pH-Tuning a Solar Redox Flow Battery for Integrated Energy Conversion and Storage

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Experimental Details

Flow Battery Measurements All flow battery electrochemical measurements were performed using a commercial Scribner redox flow cell with an active area of 5 cm². The I₃⁻/I⁻ based catholyte was circulated using a PTFE diaphragm pump (Cole-Parmer) and PTFE tubing. The anthraquinone-2,7-disulfonic acid (AQDS, TCI) anolyte was circulated using a peristaltic pump (Cole-Parmer) and PTFE tubing (except at the pump head where flexible silicone tubing is required for pump operation). Both the anolyte and catholyte were circulated at a flow rate of 40 mL/min. A nitrogen atmosphere was maintained above the electrolytes to prevent oxidation of the AQDS. Nafion 212 membranes (DuPont) were used as the cation exchange membrane to separate the positive and negative electrolytes. The Nafion membranes were pretreated prior to use according to the following procedure: (1) stirred in a deionized (DI) water bath at ~ 80°C for 30 mins. (2) stirred in a 3% H₂O₂ aqueous solution at ~ 80°C for 45 mins. (3) washed with DI water (4) stirred in a 0.5 M H₂SO₄ solution at ~ 80°C for 1 hour. (5) washed and stored in DI water until use. Carbon felt GFD 4.6 mm (SGL Carbon) was used for both electrodes. Flow battery cycling was conducted using a maccor model 4304 battery tester with a current density of 50 mA (10 mA/cm²) unless otherwise stated. The pH of the flow battery electrolyte was controlled using a 0.3 M buffer. The following pH buffers were used: sulfuric acid (pH 0, 1 M), Hydrochloric acid (pH = 1.0, 0.1 M) citrate (pH 2.0-6.0, 0.3 M), phosphate (pH 6.0-8.0, 0.3 M), Trizma (pH 8.0-9.0, 0.3 M). All pH measurements were collected using an oakion acorn 6 pH probe. Buffers were purchased from Sigma-Aldrich.

Electrochemical Measurements Cyclic voltammetry was used to measure the redox potential of the anthraquinone-2,7-disulfonic acid (AQDS) at different pH values. A glassy carbon working

electrode, graphite rod counter electrode and Ag/AgCl reference electrode (BASi) were used in conjunction with a Reference 600 potentiostat/galvanostat (Gamry Instruments). The solution consisted of a 0.3 M pH buffer with 10 mM anthraquinone-2,7-disulfonic acid. Electrochemical measurements of the solar redox flow battery were collected using a Maccor model 4304 4-channel battery tester (used for discharging the SRFB and to monitor the voltage difference between the anolyte and catholyte during photocharging). The photocurrent of the SRFB was measured using a reference 600 potentiostat. The working electrode was a dye sensitized TiO₂ photoelectrode (area = 1.27 cm²) in contact with I₃⁻/I⁻ and the counter/reference electrode was carbon felt (in contact with AQDS). These 2 electrodes were used to photocharge the battery with 0 V of applied bias. Electrolytes were circulated through the photocharging module and discharging module simultaneously as pictured in **Figure S4**.

Photoelectrochemical Measurements The photoelectrode for the SRFB was fabricated in the following manner. Transparent fluorine doped tin oxide (FTO) glass substrates (2.2 mm Thickness, Hartford Glass Co.) were cleaned in a detergent solution using an ultrasonic bath for 15 mins, then this process was repeated with DI H₂O and finally ethanol. TiO₂ paste (Sigma Aldrich, 18NR-T) was used to coat a TiO₂ film on the FTO substrate using the doctor blade technique. The resulting films were sintered at 450°C for 30 min using a 2°C/min ramp rate. After the films were allowed to cool to room temperature they were immersed in a 40 mM TiCl₄-THF complex (Sigma Aldrich) aqueous solution and heated to 70°C for 30 min. The dried films were sintered again using the prior procedure and then immersed in the dye solution for 24 hours prior to use. The dye solution consisted of 0.3 mM Z907 dye (Solaronix) and 30 mM chenodeoxycholic acid (CDCA, Sigma Aldrich) in ethanol solvent.

The photoelectrode was used as the working electrode (area = 0.424 cm²) and the performance was analyzed using a 3 electrode cell to allow for insertion of a Ag/AgCl (Sat. KCl, 0.198 V v.s NHE) reference electrode. Platinum coated FTO glass was used as the counter electrode and was fabricated by dropping 65 μ L of a 10 mM aqueous solution of H₂PtCl₆ (Sigma Aldrich) onto the FTO substrate followed by thermal decomposition at 400°C for 15 mins. The electrolyte for this measurement consisted of 2.0 M NaI (Sigma Aldrich), 20 mM I₂ (Sigma Aldrich) and 0.5 M guanidinium thiocyanate (Sigma Aldrich) with saturated CDCA in water as the solvent. All photoelectrochemical cells were illuminated using a 300 W xenon lamp with an AM 1.5 filter (Newport). The light source was calibrated to a power density of 100 mW/cm² using a calibrated silicon reference cell with a KG5 window to compensate for the difference in absorption between silicon and the DSSC photoelectrode. The Si reference cell certification is accredited by NIST to the ISO-17025 standard.

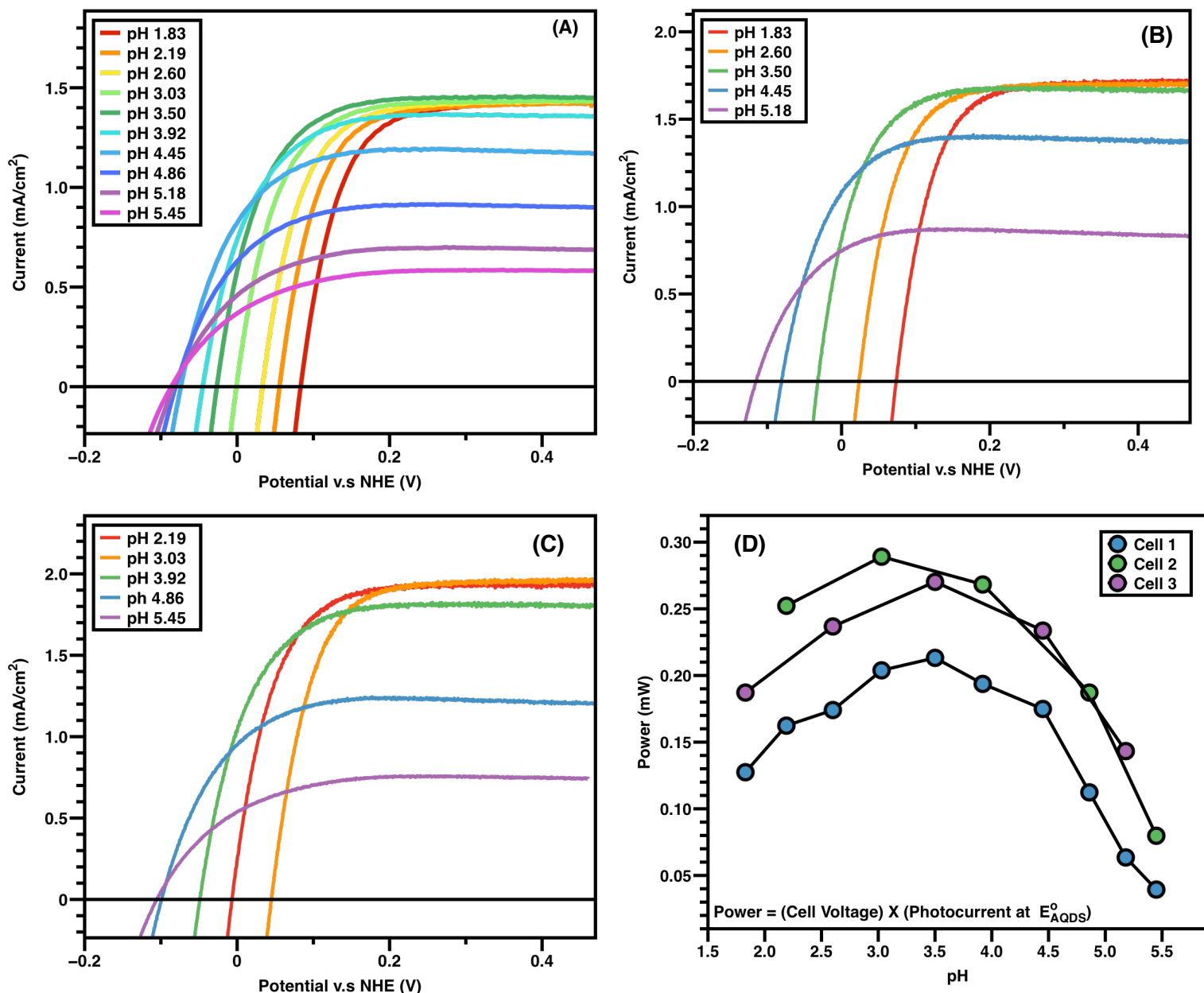


Figure S1. Results from 3 different cells in different pH (a-c). Summarized photo charging power d)

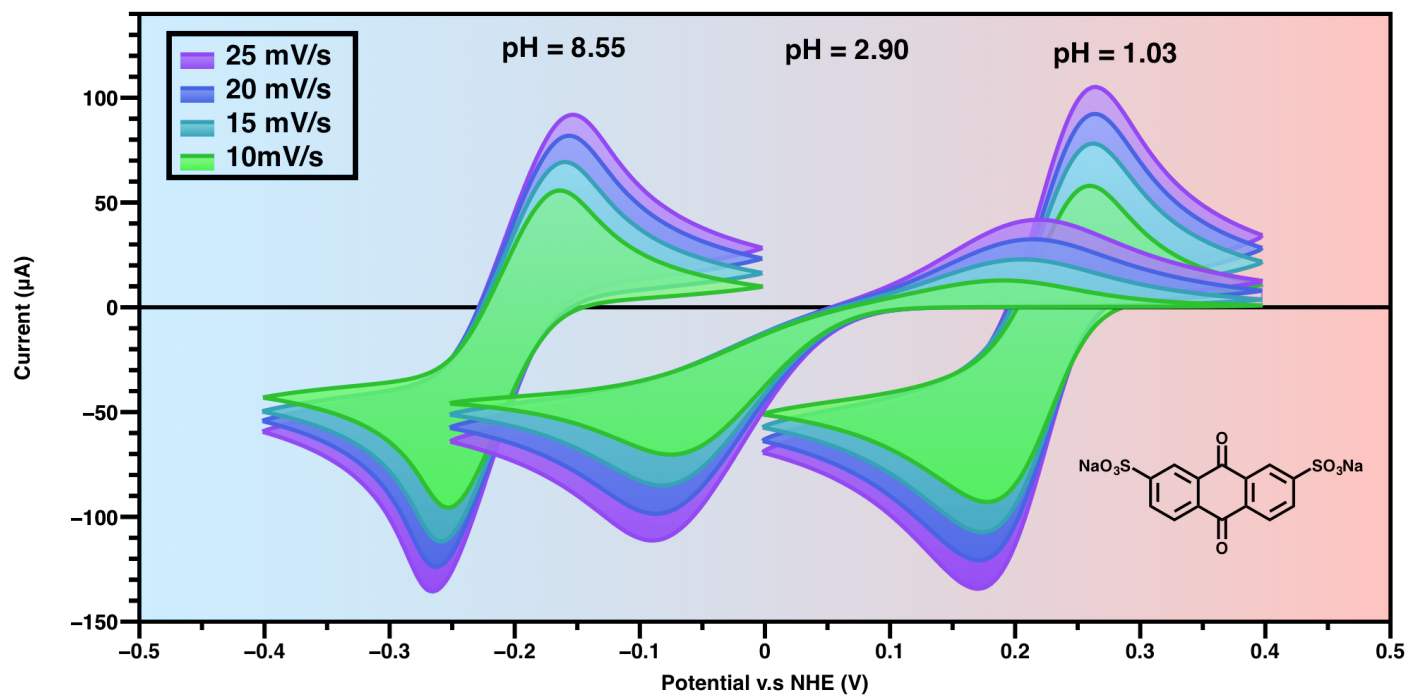


Figure S2. Cyclic voltammograms of AQDS at different pH values 8.55, 2.90 ,1.03

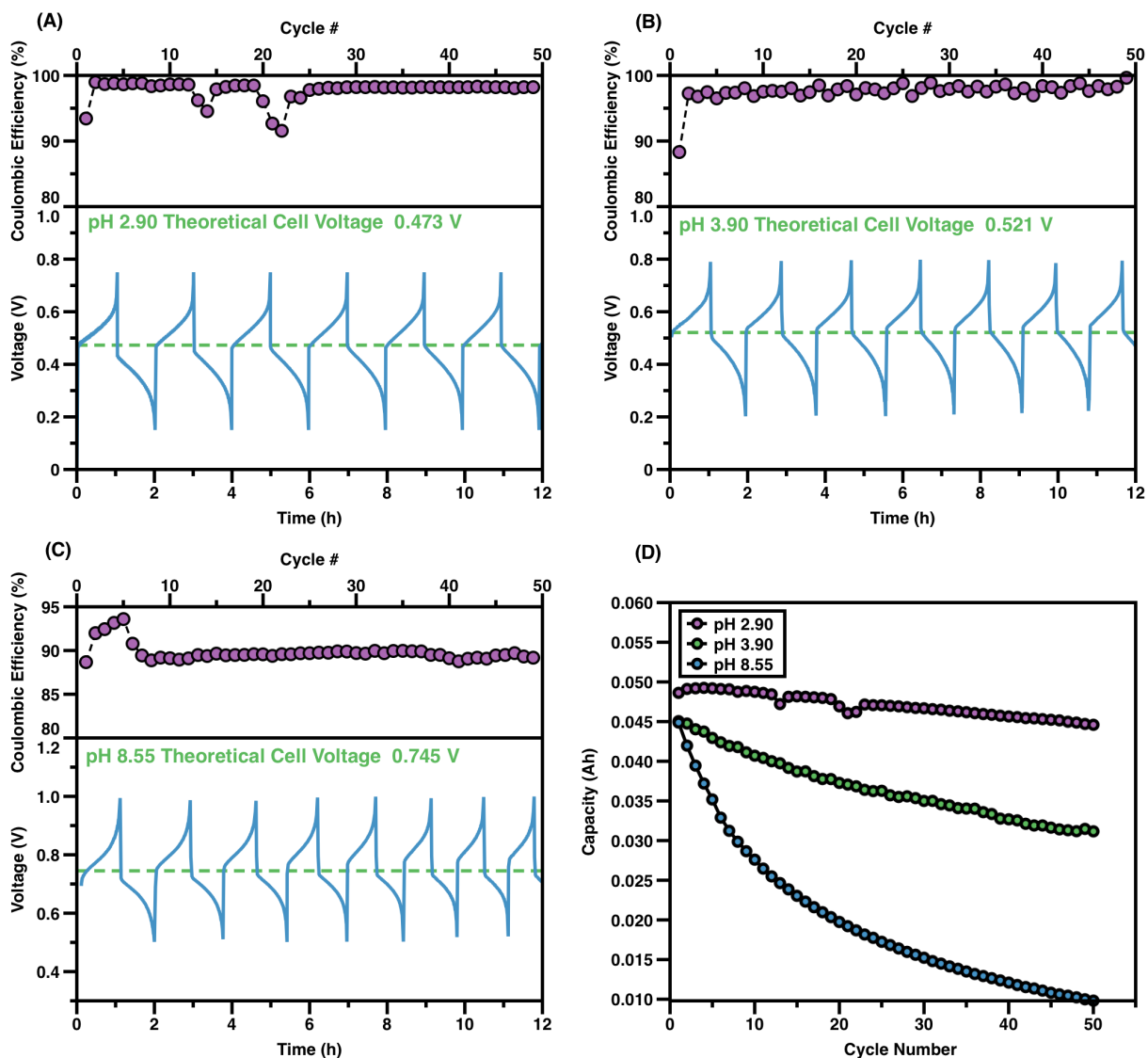


Figure S3 a) Discharge/Charge Cycling of AQDS-iodine RFB buffered to pH 2.90 (citrate buffer) b) pH 3.90, c) pH 8.55 d) capacity of AQDs-iodine RFB's buffered to different pH values

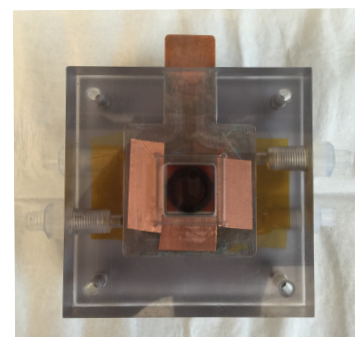
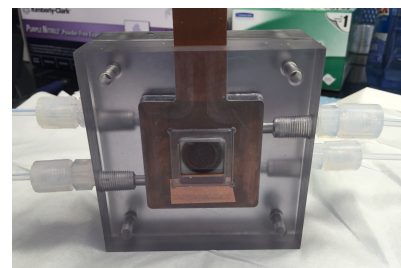
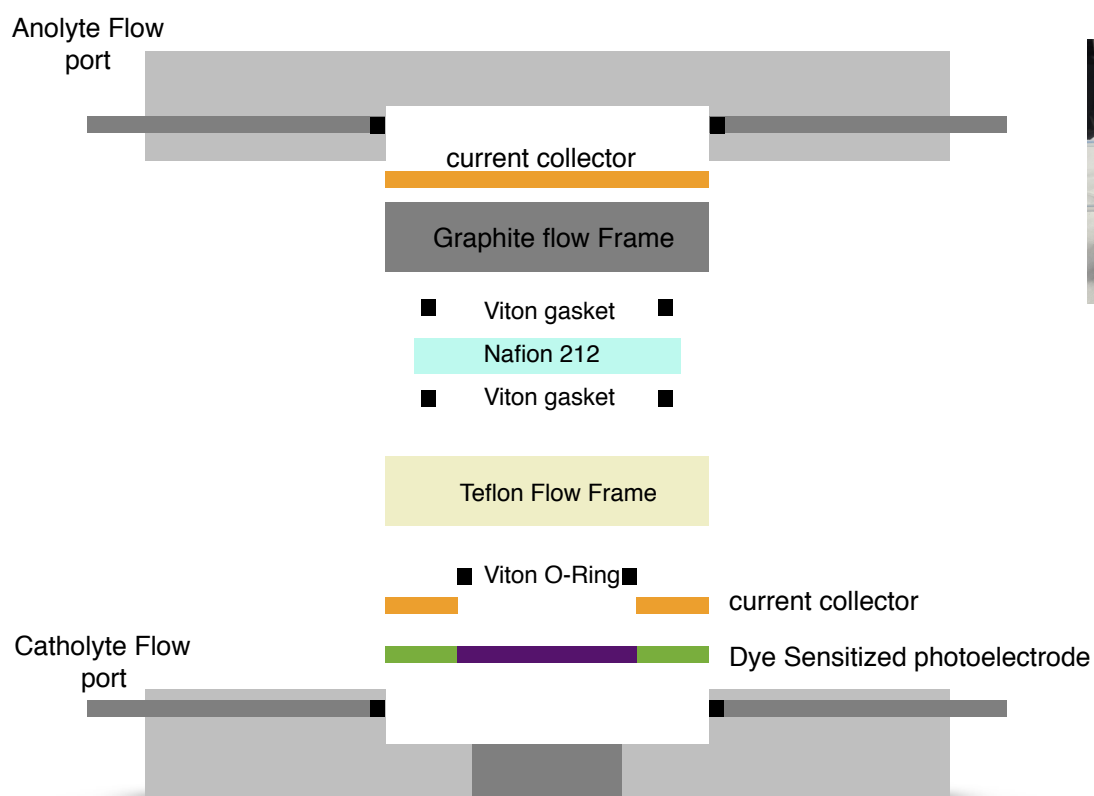
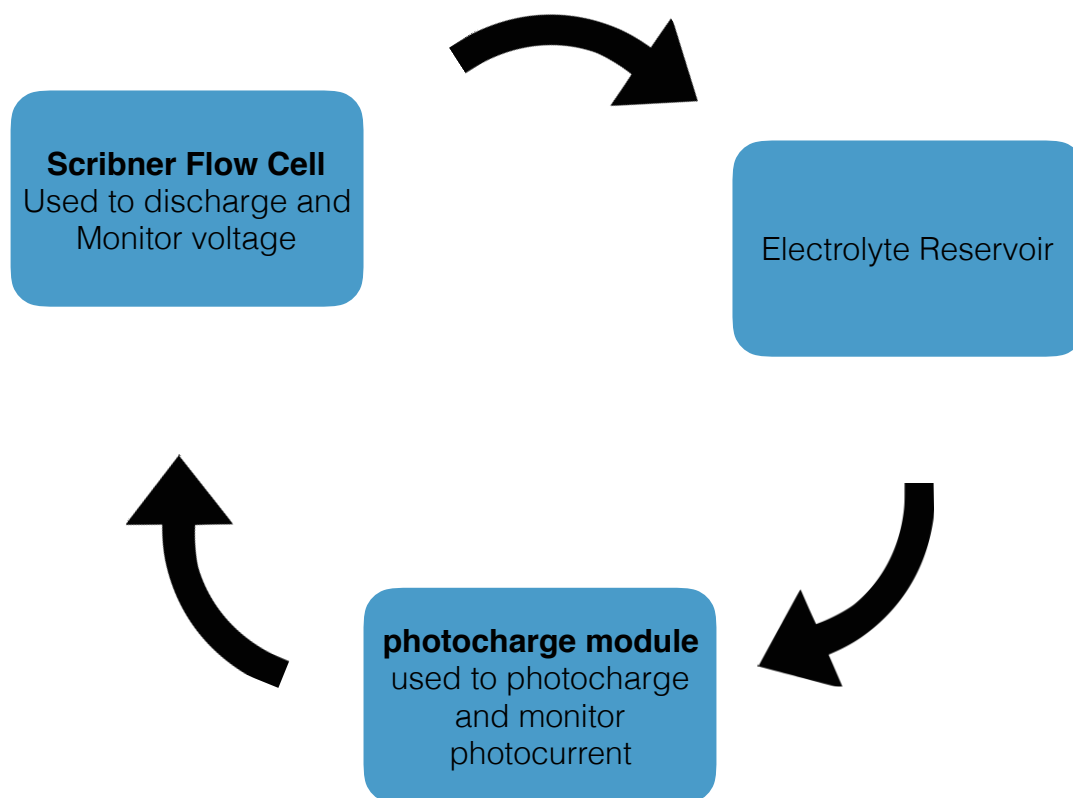


Figure S4. Depiction of the in house Solar flow battery and photo charging setup

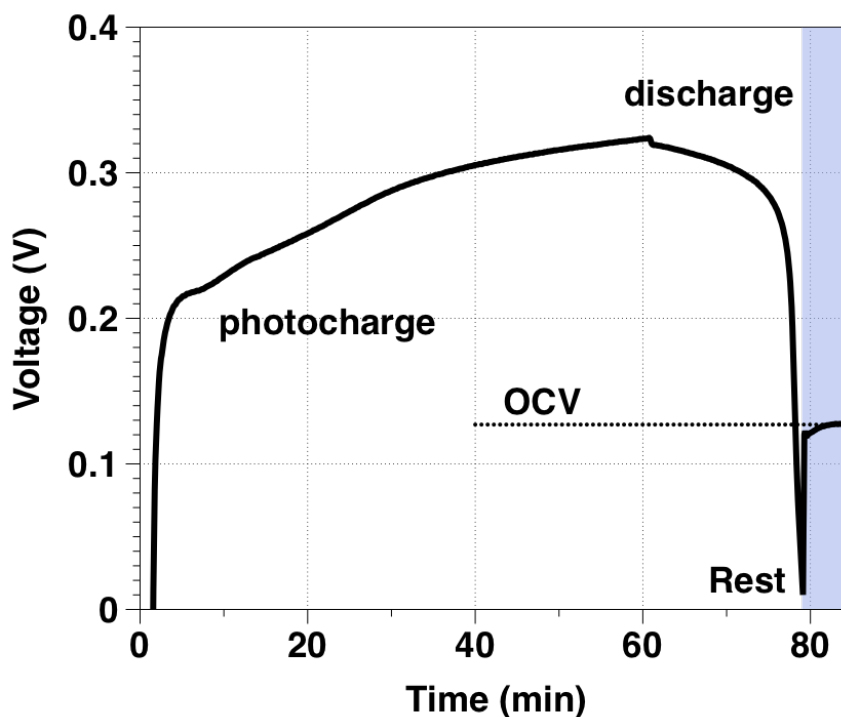


Figure S5. Open circuit voltage after initial photo charge curve

During the operation of the SRFB in **Figure 4**, a low coulombic efficiency is noted on the first cycle. A low first cycle efficiency is also observed for a quinone-iodine RFB regardless of pH as seen in **Figure S3a-c**. This indicates that the low first cycle efficiency is not entirely due to the photo charging process. One possible contribution is that after the first cycle there are undischarged species still within the electrolyte due to mass transport issues. The state of charge can be monitored by the open circuit voltage (OCV). As seen in **Figure S5** the OCV is higher after the 1st discharge than that of the initial state indicating there is the presence of some undischarged species within the electrolyte remaining, but due to mass transport issues the discharge is terminated as seen by the abrupt change in the discharge curve. Another possibility is that atmospheric oxygen may leak into the system and oxidize the anolyte resulting in a loss of reduced species and lower coulombic efficiency.