Electronic Supplementary Material (ESI) for Energy & Environmental Science

Extra Supplementary Information

Hydrogen production through oxygenic photosynthesis using the cyanobacterium *Synechocystis* sp. PCC 6803 in a bio-photoelectrolysis cell (BPE) system

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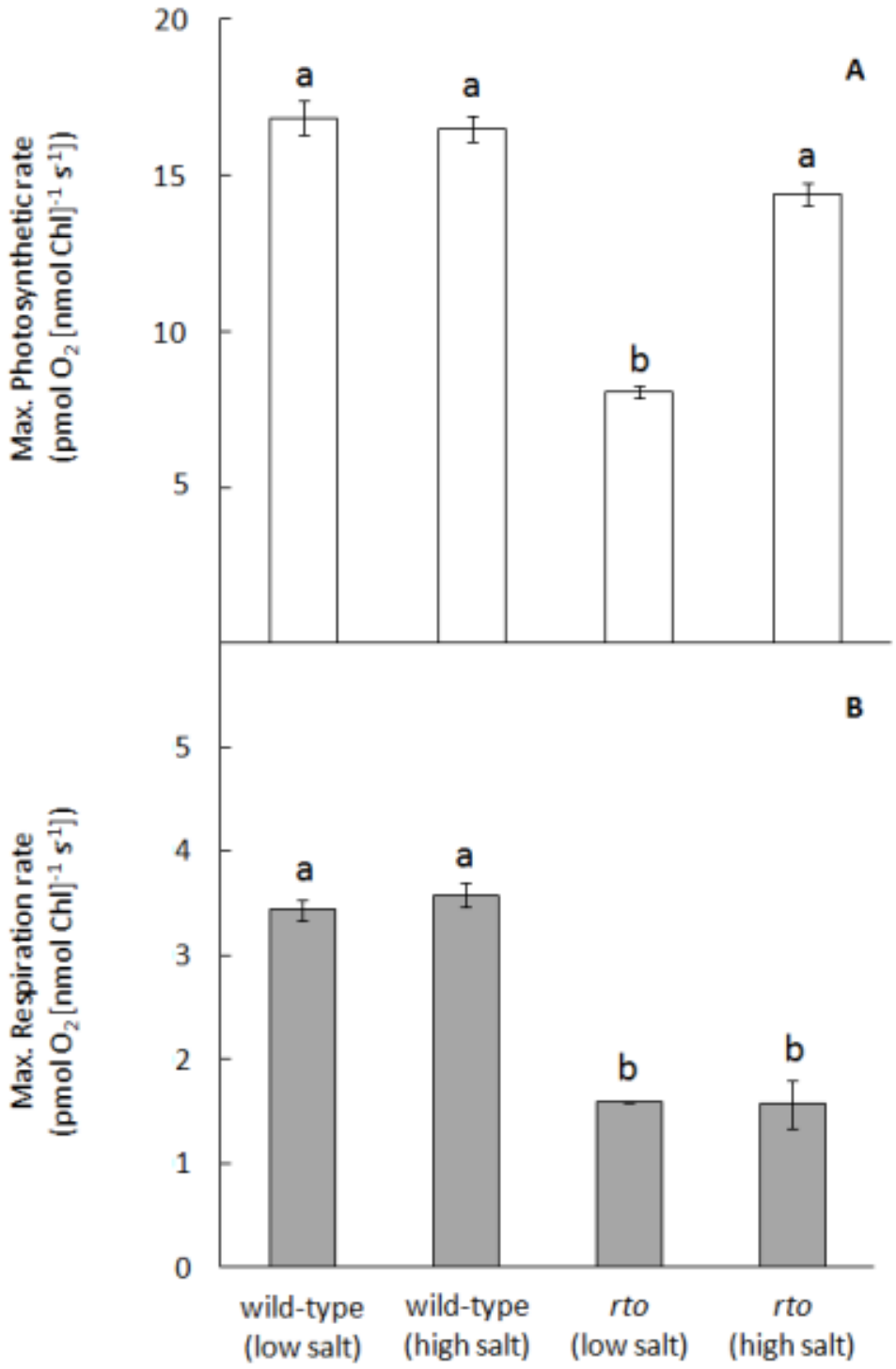
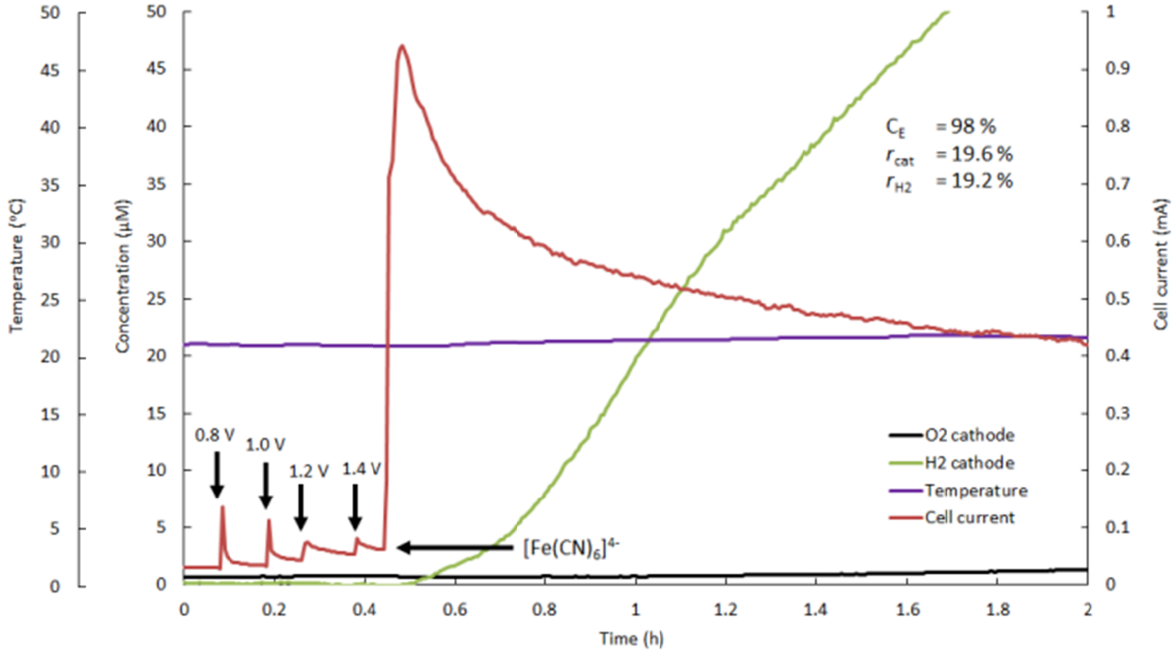
Supp. Table 1. Media conductivity

Solutions (approximately 5 ml) were measured at a reference temperature of 25°C. The conductivity of filter-sterilized sea water and deionised water are included as reference points.

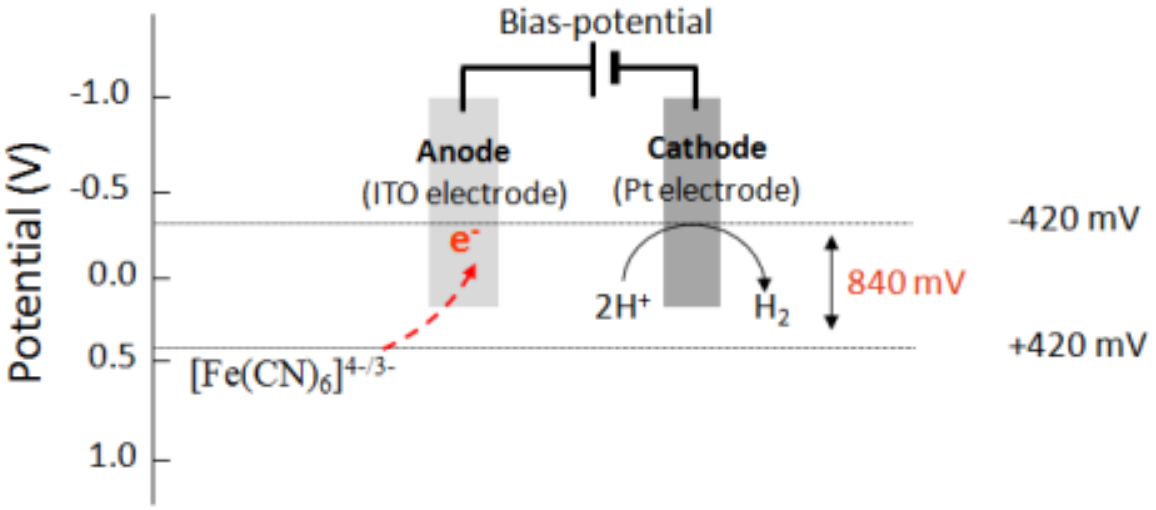
Media	**Conductivity (mS)**
BG-11	2.5
BG-11 + NaCl (0.25 M)	23.1
Sea water	40.7
Deionised water	0.002



Supp. Figure 1. Measured maximum photosynthetic (A) and respiration rates (B) of *Synechocystis* sp. PCC 6803 wild-type and *rto* mutant. Letters above mean ± SE bars (N=5) indicate whether cultures were significantly different ($P < 0.05$).



Supp. Figure 2. Production of H_2 requires $[Fe(CN)_6]^{4-}$. Application of a bias-potential (0.8-1.4 V) in a BPE device containing only media (no cells) did not produce H_2, regardless of the bias-potentials applied. Addition of $[Fe(CN)_6]^{4-}$ resulted in an increase in overall cell current and the initiation of H_2 production. The efficiencies of H_2 production are indicated and defined as in Table 2. Cathodic O_2 concentrations and temperature were also measured continuously during experiments as indicated.



Supp. Figure 3. Summary of reaction potentials of anodic and cathodic half-reactions in the BPE system**.** In the absence of an applied bias-potential the reaction is thermodynamically unfavourable. The $Fe(CN)_6^{4-/3-}$ couple (+420 mV) is more positive than the H_2 / $2H^+$ couple (-420 mV), so an extra energy input in the form of a bias potential (a minimum of 840 mV) is required to drive the reaction forward.