Supplementary Information for:

Hidden Figures of Photo-charging: *A Thermo-electrochemical approach for solar-rechargeable redox flow cell system*

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Method 1 | Theoretical method for heat transfer

A heat balance method is a tool which uses radiative as well as convective heat fluxes, depending on the temperature of the several components and is given in equation:

$$\phi_{in} = \sigma(T^4 - T_{el}^4) + \sigma(T^4 - T_{air}^4) + h_{air/abs}(T - T_{air}) + h_{el/abs}(T - T_{el})$$

in which T is the photo-absorber temperature, T_{air} and T_{el} are the ambient air and electrolyte temperature, respectively. $h_{air/abs}$ and $h_{el/abs}$ are the heat transfer coefficient for the air/photo-absorber and the electrolyte/photo-absorber interfaces. ϕ_{in} is the part of the incoming solar energy, which is dissipated into heat. Note that the heat balance in this study is assumed to have a rapid temperature equilibration owing to the sufficiently low thickness of a photo-absorber (in general, 200-300 μm). As assumed above, the unutilized photon energy (*i.e.*, $E_{ph} - eV_{oc}$) is dissipated and fed into the heat balance (*i.e.*, contribution to ϕ_{in}) as follows:

$$\phi_{in} = \int_0^{\lambda_g} H(E(\lambda) - eV_{oc}) \cdot (E(\lambda) - eV_{oc}) \cdot N(\lambda)d\lambda$$

where *H(x)* is the Heaviside step function, which is defined to be zero for x < 0 and one for x > 0, to eliminate the non-physical negative contributions. In the case of the electrolyte temperature, the steady-state heat balance cannot be used due to the slow equilibration process caused by high specific heat ($\sim$70 J mol^{-1} K^{-1}; see table S1 in Supplementary Information). Therefore, the following transient heat balance is applied to describe the heat balance of the electrolyte:

$$\sigma A(T_{el}^4 - T^4) + \sigma A_{el/air}(T_{el}^4 - T_{air}^4) + h_{el/abs}A(T_{el} - T) + h_{el/air}A_{el/air}(T_{el} - T_{air}) = -\rho V c_v \frac{dT_{el}}{dt}$$

in which A and $A_{el/air}$ are the contact area at the electrolyte/photo-absorber and electrolyte/air interfaces, and V, ρ and c_v are the volume, density and specific heat of the electrolyte. Discretizing the transient heat balance in the same way gives:

$$T_{el}(t + dt) = T_{el}(t) + \frac{Q_{in,el}(t)}{\rho V c_v} dt$$

in which $Q_{in,el}$ is the incoming heat flux for the electrolyte which corresponds to the left-hand side of the equation above (the one before last).

Method 2 | Theoretical method for *J-V* behavior

As in our previous study,[1] photo-absorbers in this work are generally assumed to meet the following conditions: (i) Photon absorptivity with an energy level lower than the band gap is not considered. (ii) Unless otherwise specified, the photo-device has ideal contact with both the counter electrode and the solid/liquid interface (i.e. no energy level mismatch at the interface is considered). (iii) The flux of the electrolyte is sufficient for the current output not to be limited by mass transport. (iv) Only the fraction of the photon energy which corresponds to eV_{oc} (open-circuit voltage) is used to effectively increase the electron energy, while the rest is dissipated into heat. Along with the assumptions mentioned above, the following diode equation derived by Shockley and Queisser[2] is used to calculate the temperature-dependent *J-V* behaviour:

Table S1. Temperature dependant isochoric specific heat of water

Temperature	Isochoric Specific Heat		
°C	J mol^{-1} K^{-1}	kJ kg^{-1} K^{-1}	kWh kg^{-1} K^{-1}
0	75.981	4.2174	0.001172
10	75.505	4.1910	0.001164
20	74.893	4.1570	0.001155
25	74.548	4.1379	0.001149
30	74.181	4.1175	0.001144
40	73.392	4.0737	0.001132
50	72.540	4.0264	0.001118
60	71.644	3.9767	0.001105
70	70.716	3.9252	0.001090
80	69.774	3.8729	0.001076
90	68.828	3.8204	0.001061
100	67.888	3.7682	0.001047

$$j = j_{max.\ ph} - j_0 \cdot \left[\exp\left(\frac{q(V + j\Omega_s)}{nkT} \right) - 1 \right] - \frac{(V + j\Omega_s)}{\Omega_{sh}}$$

$$j_0 = nqA_{ph} \left(\frac{2\pi kT}{h^3 c^2} \right) \cdot \left[E_g^2 + 2kTE_g + 2(kT)^2 \right] \cdot \exp\left(\frac{-E_g}{kT} \right)$$

where $j_{max,\ ph}$ is the theoretical maximum photocurrent density, q is the elementary charge, V is voltage, k is Boltzmann's constant, T is temperature and Ω_s and Ω_{sh} are the series and shunt resistances, respectively. Note that performance-loss by these resistant parameters is not considered in this work. j_0 is the saturation current density in the dark condition simplified by Green et al.[3] based on the temperature-dependency study conducted by Tiedje et al.[4] The A_{ph} is the emitting area of the photo-absorber relative to the absorbing area (*e.g.*, in general, this would be a factor of 2 as described previously[1]). h is Planck's constant, c is the speed of light, and E_g is the band-gap of photo-absorber (*e.g.*, for the c-Si – 1.12 eV).

The electrochemical behaviour with a kinetic barrier (*i.e.*, overpotential) is estimated using the Butler-Volmer equation, in which mass transfer limitations are neglected for now:

$$j = j_{0,bv} \left[\exp\left(\frac{-\alpha nq(E - E_0)}{kT} \right) - \exp\left(\frac{(1 - \alpha)nq(E - E_0)}{kT} \right) \right]$$

where $j_{0,bv}$ is the exchange current density, α is the transfer coefficient, which accounts for the symmetry of the kinetic overpotential losses, as the kinetics for the oxidation and reduction reactions of the same species are not identical in general. E_0 is the cell voltage (*i.e.*, thermodynamic redox potential gap between the redox couples), $E - E_0$ is the overpotential. Since $j_{0,bv}$ is a function of temperature, the probability of a reaction, *i.e.*, the kinetic overpotential barrier, decreases with increasing temperature[5]:

$$j_{0,bv} = j_{0,ref} \cdot \exp\left(-\frac{E_a}{kT} \right)$$

in which $j_{0,ref}$ is the exchange current density at a reference temperature, while E_a is the activation energy, which is typically determined experimentally. Note that the activation energy depends on the electrode and the reaction kinetics of the redox species involved, which makes it difficult to predict its value in a specific case. For Fig. 1e and 2c in the main manuscript, values for the water oxidation reaction ($j_{0,ref}$ = 4.62 A cm^{-2}; E_a = 48.6 kJ mol^{-1}), which are widely accepted in previous reports, are used for modeling the reaction with sluggish kinetics.[6,7]

In the case of redox reaction systems, the concentrations of the redox species change over time, as they are reduced/oxidized (*i.e.*, as the battery increases its state-of-charge). This state-of-charge (SOC) effect is described by the Nernst equation:

$$E_{redox} = E_{redox}^0 + \frac{RT}{nF} ln \frac{C_O}{C_R}$$

where E_{redox} is the concentration-dependent redox potential, E^0_{redox} is the standard redox potential defined at 50% of SOC, and C_O and C_R are the concentrations of the oxidative and reductive species, respectively. Rewriting this in terms of the SOC for single-electron reactions gives the following equation:
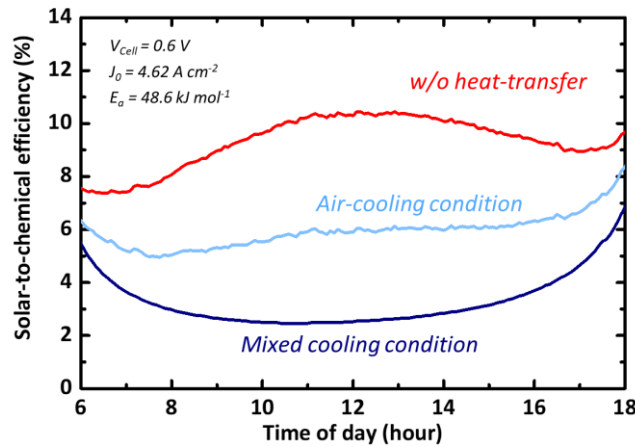
Fig. S1. Time-dependant STC% curves of the system with a V$_{cell}$ of 0.6 V with sluggish kinetics for various heat-transfer scenarios.

$$V_{cell} = \Delta E_{cell}^0 + \frac{RT}{F} ln\left(\frac{SOC^2}{(1-SOC)^2}\right)$$

in which ΔE^0_{redox} is the difference in voltage between the two standard redox potentials of the active species, and SOC is in a range between 0 and 1.

In addition, electrochemical losses (e.g. solution resistance) are not considered in this study. In general, the thermodynamic redox potential (E_{redox}) is a function of the SOC of the electrolyte, governed by the Nernst equation (see Method 2 in Supplementary Information). The STC% can be calculated using the following equation:

$$STC\% = \frac{j_{op} \cdot E_{redox}}{P_{input}} \cdot 100$$

where P_{input} is the input power, which is obtained from the experimentally measured data plotted in Fig. 1b. The operating current j_{op} is calculated as the maximum possible current density in the *J-V* characteristic of the equation described above.

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