Supplementary Information for:

Design principles for efficient photoelectrodes in solar rechargeable redox flow battery applications

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S1. LSV from Pt and carbon on Si

The LSV experiments for 0%, 50%, and 100% of SOC were carried out using the samples with Pt and carbon layer deposited on a degenerately doped n⁺-Si substrate. For making the 0% and 100% SOC electrolytes, 0.4M K₃[Fe(CN)₆] and K₄[Fe(CN)₆]·3H₂O were mixed with 1M NH₄Cl supporting electrolyte. The 50% SOC electrolyte is a mixed electrolyte with 0.2M K₃[Fe(CN)₆] and 0.2M K₄[Fe(CN)₆]·3H₂O. The measured LSV curves can be found in Fig. S1.

S2. Band alignment calculation

In the case of the interface between the n⁺-Si and metallic conductor and carbon, we assume that the interface forms a Schottky barrier with no metal-induced gap states. If this is the case, the barrier height $\Phi_B$ at the interface is the difference between the metal work function and the n⁺-Si work function (i.e., ionization energy for degenerately doped Si case, $\phi_{n⁺} = 4.15$ V) plus the deviation between the flat band potential and the conduction band using the following equation:

$$\Phi_B = \phi_{\text{metal}} - \phi_{n⁺\text{-Si}} - \frac{kT}{e} \ln \frac{N_{C\text{-Si}}}{N_{D\text{, n⁺Si}}},$$

where $\phi_{\text{metal}}$ is the work function of conducting layer (5.12 and 5.0 for Pt and carbon, respectively), $\phi_{n⁺\text{-Si}}$ is the work function of n⁺-Si, $k$ is Boltzmann’s constant, $T$ is temperature (298 K), $e$ is the elementary charge, $N_{C\text{-Si}}$ and $N_{D\text{, n⁺Si}}$ are density of states of Si at conduction band (2.8·10¹⁹ cm⁻³) and donor density of degenerately doped n⁺-Si (5·10²⁰ cm⁻³), respectively. The depletion width can be determined via the following equation:

$$W_d = \sqrt{\frac{2\varepsilon_0 \varepsilon_{Si} \Phi_B}{e N_{D\text{, n⁺Si}}}},$$

where $\varepsilon_0$ (8.8·10⁻¹² F m⁻¹) is the permittivity in a vacuum, and $\varepsilon_{Si}$ is the relative permittivity of the Si (11.7). Using these equations, $\Phi_B$ within the Si substrate was found to be 0.7~0.8 V resulting in a depletion width of...

**Supplementary Fig. 1.** LSVs recorded on Pt/Si (black, inset) and C/Si (blue) samples in 0.4 M ferro/ferricyanide solutions (in 1M NH₄Cl supporting electrolyte at pH 7) in ratios matching that expected for different SOCs (0%, 50% and 100%). The scan rate is 10 mV sec⁻¹. Note that both Pt and carbon sputtered films have average thickness of 1-2 nm.
approximately 1.4 nm (~1.5 nm for the carbon case), which allows electron tunneling across the upward band bending.

In the case of n'-Si/SiO\textsubscript{X} interface the depletion width can be determined using the following equations:

\[ W_{n'^{+}nc-Si} = \sqrt{\frac{2\varepsilon_Si V_{n'^{+}Si}}{eN_{n'^{+}Si}}} = \frac{E_{ox}E_{ox}}{eN_{n'^{+}Si}} \]

where \( E_{ox} \) is the electric field in the oxide layer, and it can be determined as follows:

\[ E_{ox} = \frac{V_{ox}}{\delta} \]

where \( V_{ox} \) is the voltage drop across the oxide and satisfies \( V_{g} = V_{FB} + \psi_S + V_{ox} \). \( V_{FB} \) is the flat band voltage. \( \delta \) is the thickness of the SiO\textsubscript{X} layer (we assume that the native oxide has a thickness of 3 nm at most due to self-limiting oxygen migration). \( V_{g} \) is the gate voltage and it satisfies \( V_{g} = V_{FB} \) at equilibrium condition and \( \psi_S \) is the potential drop at the n-Si/SiO\textsubscript{X} interface can be determined via the following equation:

\[ \psi_S = \frac{eN_{D,n'^{+}Si}\varepsilon_Si\varepsilon_0}{2C_{ox}^2} \left[ \frac{2C_{ox}^2(V_{g} - V_{FB})}{eN_{D,n'^{+}Si}\varepsilon_Si\varepsilon_0} \right] - 1 \]

The \( V_{FB} \) is the potential gap between the redox couple (\( V_{Ferro/Ferricyanide} \) in this case) and n'-Si which is ~0.77 V. \( C_{ox} \) is the capacitance of SiO\textsubscript{X} layer, and it can be determined using the equation:

\[ C_{ox} = \frac{\varepsilon_{SiO_2}}{\delta} \]

Assuming that the permittivity of SiO\textsubscript{2} (i.e., \( \varepsilon_{SiO_2} = 3.45 \times 10^{-13} \) F m\textsuperscript{-1}), \( C_{ox} \) is approximately 1.73 \times 10^{-6} F cm\textsuperscript{-2}, and \( \psi_S \) of n'-Si starts from 0.67 V at zero bias voltage leading to a depletion width of 1.3 nm.

In the case of n'+Si/(Ti)TiO\textsubscript{2} interface the barrier height at the n'+Si/Ti interface has a difference between the Ti work function (\( \varphi_{Ti} = 4.33 \) V) and the n'+Si work function (\( \varphi_{n'^{+}} = 4.15 \) V). Using the equation above, \( \Phi_B \) was found to be 0.11 V. Since Ti is a metallic layer, and has a high carrier density compared to the Si, thus the bias will be distributed entirely over the n' Si region. The barrier width was found to be approximately 0.5 nm, and electron
transfer from the Si to the Ti would most probably have to occur through tunneling. From the measured Mott-Schottky plot in Fig. S2, the TiO$_2$ conduction band was determined to be -0.32 V NHE, the donor density was 2.5 · 10$^{21}$ cm$^{-3}$. The depletion region width of TiO$_2$ at the interface ($W_{TiO_2/liquid} = 4.2$ nm) is given according to the calculation demonstrated above and also in previous studies.$^{1,5}$ Unlike the TiO$_2$/liquid junction, the TiO$_2$/Pt interface behaves differently. Using the equation described above for $\Phi_B$, the barrier height at the interface is around 0.8 V leading to a depletion width of 1.6 nm.

A comparison study on electron or hole tunneling transfer from the c-Si surface to the Pt has been conducted by using the Wentzel–Kramers–Brillouin (WKB) approximation shown below:

$$J_t = eN_Av_\text{th}\exp\left(-\frac{4}{3}W_t\sqrt{\frac{2m_{eff}\Phi_B e}{\hbar^2}}\right)$$

$$W_t = \frac{W_B \Phi_B}{2V_B}$$

where $v_\text{th}$ is the thermal velocity ($10^7$ cm s$^{-1}$), $\hbar$ is the reduced Planck constant ($\hbar/2\pi$), and $m_{eff}$ is the effective mass of holes (electron in the case of n-type) in Si (0.16 $m_0$; $m_0$ is the electron mass which is 9.11·10$^{-31}$ kg). $W_t$ is the width of the triangular tunnel barrier. Using the depletion width calculated using the equation described earlier, we find that the p-Si/Pt and the n-Si/Ti have $W_t$ of 0.2 nm and 2.9 nm, respectively. This discrepancy results in tunneling current limit across the p-Si/Pt is one order of magnitude higher than the one through the n-Si/Ti interface.

Supplementary Fig. 3. Schematic energy diagrams for both p-type (a) and n-type surface samples (b) with Pt NP and carbon, respectively.

Supplementary Fig. 4. Current-voltage curves measured in a three-electrode experiment with carbon-felt anodes in 0.4M of TEMPO (red) and Br$^-$ (blue). Note that the y-axes on the right side were calculated based on projected area ($J_{project}$) and documented electrochemically active surface area ($J_{ECSA}$) for the SGL carbon-felt.
S3. Long-term photo-charging records

The long-term photo-charging results of this study are shown in Figure S2. It shows the long-term performance under light illumination (AM 1.5G). During illumination, the device operates without bias potential. However, it is important to note that this zero-bias (i.e., unbiased condition) is not the actual potential at the semiconductor surface, due to the photovoltage developed by the photoelectrode.

S4. Sample preparation method

The silicon-based photoelectrodes used in this study were prepared using an n- and p-type CZ c-Si wafer (350 μm thick, 1-20 Ohm cm). Both pn+- and np+-junctions were formed using processes described in our previous...
publications. Thin films of 2-nm-thick Pt and carbon were prepared at room temperature with reactive sputter deposition on the back-side of the photoelectrodes. The deposition rate was calibrated with an in-chamber QCM (quartz crystal microbalance). A ring-shaped Au layer was deposited on the light-illuminated surface using a reactive sputtering with a home-made metallic mask at room temperature. The surface was cleaned with Ar-sputtering in a vacuum to remove the native oxide layer.

For the electrochemical experiments under the dark, various conducting layers, including the Pt, C, and TiO₂, were deposited onto degenerately-doped n⁺-Si substrates. The carbon was sputtered at room temperature or 400°C. In the case of the TiO₂, a thin layer of titanium was sputtered on first to prevent silicon oxidation in the subsequent TiO₂ reactive sputtering step at 400°C as described elsewhere.

S5. Chemicals for electrolyte

The synthesis of TEMPO-4-sulfate was prepared from 4-Hydroxy-TEMPO (Henan Tianfu Chemical Co. LTD, >99%) at the Aarhus University, and detail preparation procedure can be found in our previous publication. K₃[Fe(CN)₆] and K₄[Fe(CN)₆]·3H₂O (Sigma-Aldrich, ≥99%) and NH₄Br (Sigma-Aldrich, ≥99.99%) were used as received after mixing with 1M NH₄Cl to make Fe(CN)₃⁻ catholyte, Fe(CN)₆⁴⁻ and Br⁻ anolytes, respectively. CuSO₄ (Sigma-Aldrich, ≥99%) were mixed with H₂SO₄ to make a Cu²⁺ catholyte at pH 2 to prevent oxidation of the copper ions.

S6. Theoretical calculations

The simulated curves in Fig. 5 (in the main manuscript) are obtained using the model, as described in our previous work, with the exception of the approach in calculating kinetic overpotential. In the previous work, the overpotential is assumed to be a constant value, while present work utilizes the Butler-Volmer equation for a single-electron reaction to account for the theoretical dependence of the kinetic overpotential on current-density:

\[
j = j_{0,br} \left[ \exp \left( \frac{-e\alpha \eta k_B T}{k_B T} \right) - \exp \left( \frac{e(1 - \alpha) \eta k_B T}{k_B T} \right) \right]
\]

Supplementary Fig. 7. The STC% is plotted as a function of the cell voltage for different state-of-the-charge (SOC%). The dashed line represents the case in which the overpotential (\( \eta \)) of the system is 50 mV (for obtaining a 10 mA cm⁻²).
where \( j_{0,br} \) is the exchange current density, \( \alpha \) is the charge transfer coefficient (assumed to be 0.5), \( \eta_k \) is the kinetic overpotential, \( k_B \) is the Boltzmann constant, \( T \) is temperature and \( e \) is the elementary charge. To obtain the curves at varying overpotential, the exchange current density is varied, such that the overpotential (\( \eta_k \)) is 0, 50, 100, and 200 mV respectively at a current density of 10 mA cm\(^{-2}\).

For these specific curves, ideal absorption is assumed (i.e., all photons with an energy larger than the silicon bandgap energy of 1.12 eV are absorbed), the series resistance is assumed 5 \( \Omega \) cm\(^2\) and the open-circuit photovoltage is 0.51 V, in accordance with experimentally obtained photo-voltages for the silicon photo-electrodes.

To quantitatively evaluate the photo-charging efficiency of the system, the following solar-to-chemical efficiency (STC%) is calculated based on the equation:

\[
\text{STC\%} = \frac{j_{op} \cdot E_{\text{redox}}}{P_{\text{input}}} \times 100
\]

in which \( P_{\text{input}} \) is the input power of the incoming solar radiation (AM 1.5G; 100 mW cm\(^{-2}\)). The operating current \( j_{op} \) can be obtained from the current-voltage characteristic of 2-electrode measurement. \( E_{\text{redox}} \) is the thermodynamic

**Supplementary Fig. 8.** Charge/discharge curves in a 25 cm\(^2\) RFB cell with a constant current density of 3.3 mA cm\(^{-2}\) and electrolyte concentration 0.4M ferrocyanide and 1M NH\(_4\)Br in 1M NH\(_4\)Cl. The inset shows a charge/discharge curves of the same catholyte using a pair of carbon-rods, but with a different anolyte (TEMPO-sulfate) at charging/discharging rate of 5 mA and 2 mA, respectively.

**Supplementary Fig. 9.** The solar conversion efficiency as a function of SOC\% under continuous flow (~70 mL min\(^{-1}\)) is shown for various operating environments. The membrane is Nafion-117 and the electrolyte volume is 25 mL for black, blue and red circles, and 15 mL for grey and green circles on each side.
potential which is equivalent to the difference between the redox potentials of redox couples. In general, $E_{\text{redox}}$ is a function of the state of charge (SOC) of the system, governed by the Nernst equation, rewritten in terms of the SOC:

$$E_{\text{redox}} = E_{\text{redox}}^0 + \frac{RT}{nF} \ln \left( \frac{SOC}{1 - SOC} \right)^2$$

where $E_{\text{redox}}^0$, is the experimentally observed redox potential (at 50% SOC), $R$ is the gas constant, $n$ is the number of electrons participating in the reaction, and $F$ is Faraday’s constant.

**S7. Two-electrode charging/discharging experiments**

Charge/discharge curves at constant current density were measured using a two-electrode configuration (Fig. S5) under the dark condition with 70 mL min$^{-1}$ pumping rate. Note that the curve for the cell with Fe(CN)$_6$ and NH$_4$Br obtained partly from our previous work, and reproduced with permission from ref. [7], Copyright 2019 by Royal Society of Chemistry.

**S8. Electrochemically active surface area (ECSA) of the carbon-felt**

To estimate electrochemically active surface area (ECSA) of the porous carbon electrodes, the electrochemical double-layer capacitance (EDLC; $F$) was measured according to the well-documented protocol$^9$ prior to the ECSA calculation. We have used the same redox flow cell setup as described in the manuscript but with a blank electrolyte composed of 1M NH$_4$Cl. Cyclic voltammetry (CV) was performed between −0.3 V and 0.3 V at 5 different scan rates (10, 20, 50, 100 mV s$^{-1}$) and the current was recorded. The electrochemical double-layer capacitance (EDLC) extracted from the extrapolated straight line of capacitive current as a function of scan rate, and it was served for ECSA calculation using the following equations:

$$i_{\text{EDLC}} = \frac{i_{\text{positive}} + |i_{\text{negative}}|}{2}$$

$$\text{EDLC} = \frac{i_{\text{EDLC}}}{\text{Scan rate}}$$

$$\text{ECSA} = \frac{\text{EDLC}}{C_{\text{spec}} m_e}$$

Where $i_{\text{positive}}$ and $i_{\text{negative}}$ are positive and negative non-Faradaic currents extracted at 0V, $C_{\text{spec}}$ is the specific capacitance (F cm$^{-2}$), and $m_e$ is the mass of the carbon-felt used in this work (g). $C_{\text{spec}}$ was obtained by performing CV experiments on a polished glassy carbon electrode (3 mm) with a known geometric surface area. The ECSA
of the Sigracet SGL 39AA felt electrode (~0.56 m² g⁻¹) is given according to the calculation demonstrated above. This value well agrees with the previous result using the same carbon felt electrode.⁹

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