Crucial role of sustainable liquid junction potential for solar-to-carbon monoxide conversion by photovoltaic photoelectrochemical system

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Electronic Supplementary Information (ESI†)

Detailed explanation of the theoretical estimation of solar-to-CO conversion efficiency

Theoretical estimation of electrode properties: Obtaining closer estimated results of solar-to-CO conversion efficiency requires accurate understanding of the overpotentials. Based on the Arrhenius equation, the reaction current density includes the mass transfer process and the charge transfer process according to the following equation:

\[ J = J_0 \cdot \left( \frac{C^*_R}{C^*_{eq}} \right) \cdot \exp\left( \frac{\alpha_a nF \Delta V_a}{RT} \right) - \left( \frac{C^*_O}{C^*_{eq}} \right) \cdot \exp\left( -\frac{\alpha_c nF \Delta V_c}{RT} \right) \]

where \( J \), \( J_0 \), \( C^*_R \), \( C^*_{eq} \), \( \alpha \), \( n \), \( F \), \( \Delta V \), \( R \), and \( T \) are respectively current density, exchange current density, electrode surface concentration, equilibrium concentration, transfer coefficient, chemical amount, Faraday constant, overpotential, gas constant, and temperature. Subscripts of \( O \), \( R \), \( a \), and \( c \) respectively indicate oxidant, reductant, anode, and cathode. The reaction overpotential \( \Delta V_{\text{react}} \) is related to the charge transfer process. If the mass transfer process is fast enough and the charge transfer process is a rate-determining process, the electrode surface concentration and equilibrium concentration of each reactant are regarded as being approximately equal (\( C^*_R \approx C^*_{eq} \), \( C^*_O \approx C^*_{eq} \)).

The current density of the reaction is therefore shown by the Butler–Volmer equation:

\[ J = J_0 \cdot \left[ \exp\left( \frac{\alpha_a nF \Delta V_{a_{\text{react}}}}{RT} \right) - \exp\left( -\frac{\alpha_c nF \Delta V_{c_{\text{react}}}}{RT} \right) \right] \]

Moreover, if the overpotential of each half reaction is high enough, the first or second term of Eqn (1) can be ignored and the remaining term simplifies to the Tafel equations:
\[ \Delta V_{a,\text{react}} = -\left(\frac{RT}{\alpha_a nF}\right) \cdot \ln J_{a,0} + \left(\frac{RT}{\alpha_a nF}\right) \cdot \ln J_a \]

\[ = -a_a + b_a \cdot \log J_a \quad (2) \]

or

\[ \Delta V_{c,\text{react}} = \left(\frac{RT}{\alpha_c nF}\right) \cdot \ln J_{c,0} - \left(\frac{RT}{\alpha_c nF}\right) \cdot \ln |J_c| \]

\[ = a_c - b_c \cdot \log |J_c| \quad (3) \]

\( a \) and \( b \) are respectively the intercept of Tafel equation and the Tafel slope. Each \( \Delta V_{\text{react}} \) is calculated from the Tafel equations for anode and cathode reactions. Fig. S4 shows Tafel plots of the current density of H\(_2\)O oxidation or CO production at various potentials, and \( J_0 \) and the transfer coefficient \( \alpha \) are calculated. Each \( \Delta V_{\text{react}} \) is also estimated by the following equations:

\[ \Delta V_{a,\text{react}} = 0.541 + 0.094 \cdot \log J_a \quad \text{(Ar bubbling)} \]
\[ \Delta V_{a,\text{react}} = 0.543 + 0.078 \cdot \log J_a \quad \text{(CO\(_2\) bubbling)} \]
\[ \Delta V_{c,\text{react}} = 0.236 + 0.072 \cdot \log J_c \]

In contrast, the concentration overpotential \( \Delta V_{\text{conc}} \) is concerned with the mass transfer process. According to Fick’s first law of diffusion, in the steady state the current density is expressed by the following equation:

\[ J = nFS = nFD \cdot \frac{C^b - C^s}{\delta} \]

\( S, D, C^b, \) and \( \delta \) are respectively the diffusion rate, diffusion coefficient, bulk concentration, and thickness of diffusion layer. If the overpotential of the half reaction is high enough and the mass transfer is a rate-determining step, the electrode surface concentration of reactant is regarded as zero (\( C^s \approx 0 \)). Therefore, the maximum current density (limiting current density, \( J_{\text{lim}} \)) is given by the following equations:

\[ J_a_{\lim} = nFD_R \cdot \frac{C_R^{\text{eq}}}{\delta} \quad \text{or} \quad |J_c_{\lim}| = nFD_0 \cdot \frac{C_0^{\text{eq}}}{\delta} \]

Moreover, if the bulk concentration and the equilibrium concentration are regarded as the same (\( C^s \approx C^{\text{eq}} \)), Eqn (1) can be written as the following equations:

\[ \Delta V_a = -\left(\frac{RT}{\alpha_a nF}\right) \cdot \ln J_0 + \left(\frac{RT}{\alpha_a nF}\right) \cdot \ln \left(\frac{C^s}{C_R}\right) \]

or

\[ \Delta V_c = \left(\frac{RT}{\alpha_c nF}\right) \cdot \ln J_0 - \left(\frac{RT}{\alpha_c nF}\right) \cdot \ln |J_c| + \left(\frac{RT}{\alpha_c nF}\right) \cdot \ln \left(\frac{C_0^{\text{eq}}}{C_0}\right) \]
The first and second terms in the above equations exhibit $\Delta V_{\text{react}}$ (Eqn (2) and (3)), and the third term exhibits $\Delta V_{\text{conc}}$.

$$
\Delta V_{a\_conc} = \left( \frac{RT}{\alpha_a nF} \right) \cdot \ln \left( \frac{C_R^a}{C_R^b} \right)
$$

or

$$
\Delta V_{c\_conc} = \left( \frac{RT}{\alpha_c nF} \right) \cdot \ln \left( \frac{C_O^c}{C_O^b} \right)
$$

This equation is exhibited by $J_{\text{lim}}$ as the following equations:

$$
\Delta V_{a\_conc} = \left( \frac{RT}{\alpha_a nF} \right) \cdot \ln \left( 1 - \frac{J_a}{J_{a\_lim}} \right)
$$

or

$$
\Delta V_{c\_conc} = \left( \frac{RT}{\alpha_c nF} \right) \cdot \ln \left( 1 - \frac{|J_c|}{|J_{c\_lim}|} \right)
$$

Therefore, in Tafel plots (Fig. S4), the log($J_{\text{lim}}$) is exhibited by a convergence value at a potential far from the equilibrium potential.$^1$

In addition, the resistance overpotential $\Delta V_{\text{resist}}$ is mainly generated from the resistance of the anion membrane, electrolytes, and electrodes. In this case the electrode resistance has little effect because the anode CoO<sub>x</sub> layer is very thin and the cathode is composed of Au metal. $\Delta V_{\text{resist}}$ is therefore regarded as membrane and solution resistances, which is calculated by electrochemical impedance analysis.$^2$ Fig. S5 shows the Nyquist impedance spectra of the reaction cell at different electrolyte conditions. In the high frequency region, the reactance part is ignored and only the resistance part is observed. Therefore, the resistance at $-Z''_{\text{lim}} = 0$ is regarded as the membrane and solution resistances (ohmic resistance, $R_{\text{ohm}}$) and $\Delta V_{\text{resist}}$ is given by the following equation:

$$
\Delta V_{\text{resist}} = R_{\text{ohm}} \cdot J \cdot A
$$

$J$ and $A$ are the operating current density and the electrode (acceptance) surface area, respectively. Therefore, the reaction activity of the electrodes is estimated by the following equation:

$$
V = 1.33 + \Delta V_{\text{react}} + \Delta V_{\text{conc}} + \Delta V_{\text{resist}}
$$

$$
= 1.33 + \left( \frac{RT}{\alpha_a nF} \right) \cdot \ln \left( \frac{J}{J_0} \right) - \left( \frac{RT}{\alpha_c nF} \right) \cdot \ln \left( \frac{J}{J_0} \right)
$$

$$
- \left( \frac{RT}{\alpha_n F} \right) \cdot \ln \left( 1 - \frac{J}{J_{a\_lim}} \right) + \left( \frac{RT}{\alpha_i nF} \right) \cdot \ln \left( 1 - \frac{|J|}{|J_{c\_lim}|} \right) + R_{\text{ohm}} \cdot J \cdot A
$$

Moreover, when the pH is different between an anolyte and a catholyte, the liquid junction potential ($\Delta V_{\text{pH}}$) is generated and acts as chemical bias. Therefore, the value of $\Delta V_{\text{pH}}$ must be deducted from $V$ in the calculated equation. However, an accurate calculation of $\Delta V_{\text{pH}}$ is difficult, so we estimated $\Delta V_{\text{pH}}$ as the pH difference between anolyte and catholyte assuming that the major ion moving in the electrodes is hydroxide (OH<sup>-</sup>). Therefore, the reaction activity is exhibited by the following equation:
\[ V = 1.33 + \Delta V_{\text{react}} + \Delta V_{\text{conc}} + \Delta V_{\text{resist}} - \Delta V_{\text{ph}} \]

\[ = 1.33 + \left( \frac{RT}{\alpha_nF} \right) \ln \left( \frac{J}{J_0} \right) - \left( \frac{RT}{\alpha_cF} \right) \ln \left( \frac{J}{J_0} \right) \]

\[ - \left( \frac{RT}{\alpha_nF} \right) \ln \left( 1 - \frac{J}{J_{a_{-\text{lim}}}} \right) + \left( \frac{RT}{\alpha_cF} \right) \ln \left( 1 - \frac{J}{J_{c_{-\text{lim}}}} \right) \]

\[ + R_{\text{sh}} \cdot J \cdot A - 0.0591 \cdot \Delta pH \]

Theoretical estimation of PV cell properties: In contrast, the PV cell property can be estimated from the current-voltage curve of the PV. In this simulation, the complicated 3jn-a-Si PV cell is regarded as a single-junction PV cell model for simplicity. The current-voltage curve of the PV cell is therefore exhibited by the following equation:\(^2\)

\[ J = J_{\text{ph}} - J_{\text{d}} \]

\[ = J_{\text{ph}} - J_s \left\{ \exp \left( \frac{q(V + J \cdot A \cdot R_s)}{n_kT} \right) - 1 \right\} - \frac{V + J \cdot A \cdot R_s}{R_{\text{sh}} \cdot A} \]

\( J_{\text{ph}}, J_{\text{d}}, J_s, q, n_k, k, R_s, \text{ and } R_{\text{sh}} \) are respectively the photocurrent density, dark current density, saturated current density, magnitude of the electrical charge on the electron, ideal factor of diode, Boltzmann constant, series sheet resistance, and shunt sheet resistance. However, the PV cell surface is coated with the CoO\(_x\) anode catalyst. The current-voltage curve therefore decreases due to its transmittance \( T_{\text{sum}} \), which is estimated by integration as the follows equation:

\[ T_{\text{sum}} = \int_{300}^{850} T(\lambda)I(\lambda)d\lambda \]

\( T(\lambda) \) and \( I(\lambda) \) are respectively the transmittance of each wavelength and light intensity of each wavelength. The actual specific curve of the PV cell is thus given by the following equation.

\[ J = T_{\text{sum}}J_{\text{ph}} - J_s \left\{ \exp \left( \frac{q(V + J \cdot A \cdot R_s)}{n_kT} \right) - 1 \right\} - \frac{V + J \cdot A \cdot R_s}{R_{\text{sh}} \cdot A} \]

The operating current density \( J \) is therefore the point of intersection between Eqn (4) and (5). Moreover, the partial current density of CO generation decreases the ratio of \( FE_{\text{CO}} \). Therefore, the partial current density of CO generation \( J_{\text{CO}} \) is obtained by the following equation:

\[ J_{\text{CO}} = J \cdot FE_{\text{CO}} \]

Theoretical estimation of faraday efficiency of CO \( FE_{\text{CO}} \): The \( FE_{\text{CO}} \) in the reaction is estimated from the same results as the Tafel plots measurement. Fig. S6 shows the actual applied potentials of the Au nanoparticle cathode in the PV PEC system for CO production in the type A and B conditions (Fig. 3). The initial potentials for types A and B are \(-0.36\) and \(-0.34\) V vs. RHE, so the \( FE_{\text{CO}} \) is respectively estimated as 97% and 96% for types A and B.
$J_{\alpha \text{lim}}$ at type B may be enough high than that at type A, and is regarded as the same value for type A.

### Table S1. Parameter values used to calculate the estimated solar-to-CO conversion efficiency.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Type A</th>
<th>Type B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas constant $R$ [m$^2$ kg s$^{-2}$ K$^{-1}$ mol$^{-1}$]</td>
<td>8.315</td>
<td></td>
</tr>
<tr>
<td>Temperature $T$ [K]</td>
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<tr>
<td>Chemical amount $n$ [mol]</td>
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<td></td>
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<tr>
<td>Faraday constant $F$ [C mol$^{-1}$]</td>
<td>96500</td>
<td></td>
</tr>
<tr>
<td>Elementary charge $q$ [C]</td>
<td>1.60×10$^{-19}$</td>
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</tr>
<tr>
<td>Ideal factor of diode $n_i$ [-]</td>
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</tr>
<tr>
<td>Boltzmann constant $k$ [m$^2$ kg s$^{-2}$ K$^{-1}$]</td>
<td>1.38×10$^{-23}$</td>
<td></td>
</tr>
<tr>
<td>Electrode (acceptance) surface area $A$ [m$^2$]</td>
<td>1.0</td>
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<tr>
<td>PV cell</td>
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<td></td>
</tr>
<tr>
<td>Photocurrent density $J_{ph}$ [mA cm$^{-2}$]</td>
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<td>Saturated current density $J_0$ [mA cm$^{-2}$]</td>
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<td>Series sheet resistance $R_s$ [Ω]</td>
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<td>Shunt sheet resistance $R_{sh}$ [Ω]</td>
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<tr>
<td>Anode</td>
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<td>Tafel slope $b_a$ [V dec$^{-1}$]</td>
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<td>0.078</td>
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<tr>
<td>Intercept of Tafel equation $a_a$</td>
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<td>-0.543</td>
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<tr>
<td>Transfer coefficient $a'_a$</td>
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<td>0.380</td>
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<tr>
<td>Exchange current density $J_{a,0}$ [mA cm$^{-2}$]</td>
<td>1.75×10$^{-6}$</td>
<td>1.06×10$^{-7}$</td>
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<tr>
<td>Limiting current density $J_{a,lim}$ [mA cm$^{-2}$]</td>
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<td>15.1</td>
</tr>
<tr>
<td>Transmittance $T_{sum}$ [%]</td>
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<td></td>
</tr>
<tr>
<td>pH</td>
<td>9.2</td>
<td>7.3</td>
</tr>
<tr>
<td>Cathode</td>
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<td>Tafel slope $b_c$ [V dec$^{-1}$]</td>
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</tr>
<tr>
<td>Intercept of Tafel equation $a_c$</td>
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<td>Transfer coefficient $a'_c$</td>
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<td>Exchange current density $J_{c,0}$ [mA cm$^{-2}$]</td>
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<tr>
<td>Limiting current density $J_{c,lim}$ [mA cm$^{-2}$]</td>
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<tr>
<td>Faraday efficiency of CO $FE_{CO}$ [%]</td>
<td>97</td>
<td>96</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.3</td>
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<tr>
<td>Ohmic resistance $R_{ohm}$ [Ω]</td>
<td>25.9</td>
<td>27.2</td>
</tr>
<tr>
<td>Estimated total current density $J_c$ [mA cm$^{-2}$] (experimental result at 10 min)</td>
<td>1.4 (1.6)</td>
<td>0.64 (0.92)</td>
</tr>
<tr>
<td>Estimated solar-to-CO conversion efficiency $\eta_{CO-e}$ [%] (experimental result at 10 min)</td>
<td>1.8 (2.3)</td>
<td>0.82 (1.28)</td>
</tr>
</tbody>
</table>
Fig. S1 XRD pattern of (a) CoO\textsubscript{x} anode and (b) Au nanoparticle cathode.
Fig. S2 XPS results for (a) CoO₄ anode and (b) Au nanoparticle cathode.

Fig. S3 Transmittance spectra of CoO₄ anode on ITO/Si substrate.
Fig. S4 Tafel plots of (a) anode electrode (●: type A and □: type B) and (b) cathode electrode.
Fig. S5 Nyquist impedance spectra of the reaction cell at (●) the type A and (□) the type B.

Fig. S6 Time-dependent changes in the applied potentials of Au nanoparticles cathode during the artificial photosynthesis of CO production at (●) type A and (□) type B. Reaction conditions are identical to those in Figure 2.