

# Supporting Information

## Dye-Sensitized Photoelectrolysis Cells

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## Appendix:

### Coupling of Solar Cells and Electrolysis Cells

Consider a battery of series-connected solar cells (SCs), of number  $N_{SC}$ , each of which has an area of  $A_{SC}$  parallel connected to a battery of series-connected electrolyzers, of number  $N_{ELC}$ , each of which has anode and cathode of equal area of  $A_{EL}$ . The voltage of the solar cell  $U_{SC}$  is related to its current density  $j_{SC}$  according to the current-voltage characteristic.

$$U_{SC} = U_{SC}(j_{SC}) \quad (1)$$

The simpler form of such a relation is the well-known p-n photodiode equation [APP-1]

$$j_{SC} = j_{PH} - j^0 \left[ \exp \left\{ \frac{eU_{SC}}{mk_B T} \right\} - 1 \right] \quad (2)$$

where  $j_{PH}$ ,  $j^0$ ,  $m$ ,  $e$ ,  $k_B$ , and  $T$  are the short-circuit photocurrent, reverse saturation dark current, diode ideality factor, proton charge, Boltzmann constant, and absolute temperature, respectively.

The voltage of the electrolysis cell  $U_{ELC}$  is related to its current density  $j_{ELC}$  according to the current-voltage characteristic.

$$U_{ELC} = U_{ELC}(j_{SC}) \quad (3)$$

For simplicity's sake both cathode and anode are supposed to be of the same area.  $U_{SC}$  is defined from the equilibrium cell voltage  $U_{SC}$ , the anodic and cathodic overvoltages  $|\eta_{an}|$  and  $|\eta_{ca}|$  and the ohmic overpotential (drop)  $|\eta_{\Omega}|$ , all functions of  $j_{SC}$ :

$$U_{ELC} = U_{ELC(eq)} + |\eta_{an}| + |\eta_{ca}| + |\eta_{\Omega}| \quad (4)$$

If Tafel's law is considered for  $|\eta_{an}|$  and  $|\eta_{ca}|$  [APP-2] and Ohm's law for  $|\eta_{\Omega}|$ ,

$$\begin{aligned} |\eta_{an}| &= \mathcal{A}_{an} + \mathcal{B}_{an} j_{ELC} \\ |\eta_{ca}| &= \mathcal{A}_{ca} + \mathcal{B}_{ca} j_{ELC} \\ |\eta_{\Omega}| &= \mathcal{R}_{\Omega} j_{ELC} \end{aligned} \quad (5)$$

where a  $\mathcal{A}_{an}, \mathcal{A}_{ca}$  and  $\mathcal{B}_{an}, \mathcal{B}_{ca}$  are and are the Tafel intercepts and slopes, and  $\mathcal{R}_{\Omega}$  is the cell resistance per unit electrode area,  $U_{ELC}$  is expressed, within the current range of Tafel's law applicability [APP-2], as

$$U_{ELC} = [U_{ELC(eq)} + (\mathcal{A}_{an} + \mathcal{A}_{ca})] + (\mathcal{B}_{an} + \mathcal{B}_{ca}) j_{ELC} + \mathcal{R}_{\Omega} j_{ELC} \quad (6)$$

The total voltage of the SC battery is equal to the total voltage of the ELC battery:

$$N_{SC} U_{SC} = N_{ELC} U_{ELC} \quad (7)$$

The current across each SC is equal to that across each ELC:

$$I_{SC}^{MPP} = I_{ELC} \quad (8)$$

or equivalently, since  $I$  and  $j$  are linked as

$$\begin{aligned} I_{SC} &= j_{SC} A_{SC} \\ I_{ELC} &= j_{ELC} A_{ELC} \end{aligned} \quad (9)$$

it is

$$j_{SC}^{MPP} A_{SC} = j_{ELC} A_{ELC} \quad (10)$$

By specifying  $N_{SC}$ ,  $A_{SC}$ , and  $N_{ELC}$ , as well as, as previously mentioned, by stipulating that the SC operate at the maximum power point, the solution, in Eqs. (6), (7) and (9), gives  $A_{ELC}$ ,  $U_{ELC}$  and  $j_{ELC}$ .

Firstly, Eq. (7) gives  $U_{ELC}$ . Several values of  $N_{ELC}$  may be possible. In principle, should be chosen so that  $U_{ELC}$  has a value of the desired order of magnitude (e.g.  $10^2$ - $10^3$  Am<sup>-2</sup>). Subsequently,  $j_{ELC}$  is determined from the current density vs. voltage

electrochemical cell characteristic according to Eq. (6). Finally, Eq. (7) gives the necessary cell area  $A_{\text{ELC}}$ . There a compromise between selecting a lower and higher  $U_{\text{ELC}}$  for a specified number of series-connected SCs. In the former case, the overpotential and ohmic losses will be lower. In the latter case, the larger current will necessitate a lower  $A_{\text{ELC}}$  as well as lower  $N_{\text{ELC}}$ . Therefore the cell construction cost will be lower.

Assuming 100 % Faradaic efficiency, the energy storage efficiency is

$$\eta_{\text{ST}} = \frac{N_{\text{ELC}} j_{\text{ELC}} U_{\text{ELC}}}{N_{\text{SC}} A_{\text{SC}} P_{\text{light}}} \quad (11)$$

where  $P_{\text{light}}$  is the irradiance (incident power per unit surface and time). In addition to the conversion of solar energy to stored chemical energy, there is a possibility of simultaneous conversion of solar energy to electricity and stored chemical energy, e.g. by considering the coupling an ohmic resistor in series to the electrolysis cell. An example could be the case of combining two solar cells, each of them giving 1.3V at the maximum power point with a water electrolysis cell operating at around 1.7 V at 100-1000 A m<sup>-2</sup>. The combining voltage of 2.6 V will be too high for electrolysis, with very vigorous gas evolution and excessive heat generation. One possibility is to connect an additional load in series, so that only part of the two-cell voltage is converted to the chemical energy of water decomposition.

### **Space-Charge-Layer**

The space-charge layer  $L_{\text{SC}}$  should not be confused with the Debye length  $L_{\text{D}}$  [APP-3][APP-4], see the detailed analysis below.

### **Debye Length:**

$$L_D = \left( \frac{\varepsilon_{SC} \varepsilon_0 k_B T}{e^2 N_D} \right) \quad (12)$$

### Space-charge length

$$L_{SC} = L_D \left( \frac{2Q_0}{k_B T} |\varphi_{SC}| \right)^{1/2} \quad (13)$$

$$L_D = \left( \frac{\varepsilon_{SC} \varepsilon_0 k_B T}{Q_0^2 N_D} \right)^{1/2}$$

$$L_{SC} = \left( \frac{\varepsilon_{SC} \varepsilon_0 k_B T}{Q_0^2 N_D} \right)^{1/2} \left( \frac{2Q_0}{k_B T} \right)^{1/2} |\varphi_{SC}|^{1/2} \quad (14)$$

$$L_{SC} = \left( \frac{2\varepsilon_{SC} \varepsilon_0}{Q_0 N_D} \right)^{1/2} |\varphi_{SC}|^{1/2}$$

$$\varphi_{SC} = \frac{E_{CB(S)} - E_{CB(B)}}{Q_0} = \frac{E_{CB(S)} - E_F - \Delta E_{FC}}{Q_0}$$

$$E_{CB(B)} = E_F + \Delta E_{FC}$$

$$\Delta E_{FC} = k_B T \ln \frac{\tilde{N}_{e(B)}}{N_D}$$

$$L_{SC} = \left( \frac{2\varepsilon_{SC} \varepsilon_0}{Q_0 N_D} \right)^{1/2} \left| \frac{E_{CB(S)} - E_F - \Delta E_{FC}}{Q_0} \right|^{1/2}$$

$$L_{SC} = \left( \frac{2\varepsilon_{SC} \varepsilon_0}{Q_0^2 N_D} \right)^{1/2} |E_{CB(S)} - E_F - \Delta E_{FC}|^{1/2} \quad (15)$$

$Q_0$ : proton charge

(S): surface

(B): bulk

$\varphi_{SC}$ : voltage across the space-charge layer

## REFERENCES FOR THE APPENDIX

[APP-1] J. Bisquert, The physics of solar cells, perovskites, organics, and photovoltaic fundamentals, Taylor & Francis Group, LLC, Boca Raton, FL, 2018.

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[APP-3] M. A. Butler (1977) Journal of Applied Physics 77, 1914-1920.

[APP-4] Y.V. Pleskov and Y.Y. Gurevich, Semiconductor Photoelectrochemistry, Consultants Bureau, New York, 1986.