Supporting Information

Macroporous Silicon as a Model for Silicon Wire Array Solar Cells

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Fitting of Cyclic Voltammetry Data

The lithographic-galvanic (LIGA) electrodes analyzed by Neudeck and Dunsch in terms of their cyclic voltammetry behavior are similar to the porous electrodes used in this study (ref 44). The LIGA electrodes are hexagonal arrays of pores with regular pore dimensions and pore-pore spacing. The porous electrodes used in this study, although not regular in pore dimension and spacing, are structurally similar, and therefore their normalized peak current behavior with respect to scan rate can be modeled using the same approach.

Derivation of the expression for the peak potential requires several equations that relate the dimensionless radius, p, to the dimensionless potential, ξ, and the dimensionless current ψ, under various conditions. These quantities can be defined as:

$$p = r\sqrt{\frac{nFv}{RTD}} \qquad (1)$$

$$\xi = -\frac{nF}{RT}\left(E - E^0\right) \qquad (2)$$

$$\psi = \frac{I}{nFAc\sqrt{nFvD/RT}} \qquad (3)$$

where *r* is the radius of the electrode, *n* is the number of moles of electrons involved in the reaction ($n = 1$ for Me_2Fc), *F* is Faraday's constant, *v* is the scan rate, *R* is the gas constant, *T* is the absolute temperature, *D* is the diffusion coefficient (measured to be

1.02 x 10^{-5} cm^2 s^{-1} for Me_2Fc in methanol), E is the electrode potential, E^0 is the standard potential, A is the electrode area, and I is the current.

For a tubular electrode, at the peak potential, one obtains:

$$\xi_{tube,p} = 1.11\frac{\tanh\left[2.589\left(\log[p] - 0.4318\right)\right] + 1}{2} \tag{4}$$

$$\psi_{tube,p} = 0.446\frac{\tanh\left[1.755\left(\log[p] - 0.2706\right)\right] + 1}{2} \tag{5}$$

The dimensionless tubular current at the peak current for a planar electrode is given by:

$$\psi_{tube,1.11} = 0.446\frac{\tanh\left[1.999\left(\log[p] - 0.3285\right)\right] + 1}{2} \tag{6}$$

Finally, calculating the dimensionless charge at a tubular electrode at the peak potential for tubular and planar electrodes yields:

$$q_{tube,p} = 0.529 - 0.493\frac{\tanh\left[2.271\left(\log[p] - 0.2706\right)\right] + 1}{2} \tag{7}$$

$$q_{tube,1.11} = 0.781 - 0.747\frac{\tanh\left[2.063\left(\log[p] - 0.6965\right)\right] + 1}{2} \tag{8}$$

These quantities enable calculation of the peak current at a LIGA-produced macroporous metallic electrode, which will be used to approximate the mass-transport-limited current at a macroporous silicon electrode under high levels of illumination. Defining s_w as the pore width, s_b as the pore-pore spacing, and s_h as the pore length, along with $R_h = s_h/s_w$ and $R_b = s_b/s_w$, produces an expression for the peak potential at a LIGA electrode as:

$$\xi_{LIGA,p}\left[R_b, R_h, p\right] = \xi_{tube,p}[p] + \frac{0.446\left(1.11 - \xi_{tube,p}[p]\right)}{0.446 + \psi_{part}\left[R_b, R_h, p\right]} \tag{9}$$

where

$$\psi_{part}\left[R_b,R_h,p\right]=\frac{2R_h\psi_{tube,p}[p]}{\left(1+R_b\right)^2} \tag{10}$$

The dimensionless partial current and charge in the pores can then be approximated as follows:

$$\psi_{tube}^{LIGA,p}\left[R_b,R_h,p\right]=f_{\text{int}}\left[1.11,\psi_{tube,1.11}[p],\xi_{tube,p}[p],\psi_{tube,p}[p],\xi_{LIGA,p}\left[R_b,R_h,p\right]\right] \tag{11}$$

$$q_{tube}^{LIGA,p}\left[R_b,R_h,p\right]=f_{\text{int}}\left[1.11,q_{tube,1.11}[p],\xi_{tube,p}[p],q_{tube,p}[p],\xi_{LIGA,p}\left[R_b,R_h,p\right]\right] \tag{12}$$

where

$$f_{\text{int}}\left[x_1,y_1,x_2,y_2,x\right]=y_1+\frac{\left(y_2-y_1\right)\left(x-x_1\right)}{\left(x_2-x\right)} \tag{13}$$

The dimensionless current at a planar electrode can be approximated by:

$$\psi_{disc}=0.3801-0.1251\xi-0.0642\xi^2+0.00439\xi^3 \tag{14}$$

Given these values, the dimensionless peak current at the LIGA electrode can be calculated using:

$$\begin{aligned}&\psi_{LIGA,p}\left[R_b,R_h,p\right]=\psi_{disc}\left[\xi_{LIGA,p}\left[R_b,R_h,p\right]\right]\\&+\left(2R_h\psi_{tube}^{LIGA,p}\left[R_b,R_h,p\right]+\psi_{disc}\left[\xi_{LIGA,p}\left[R_b,R_h,p\right]\right]\times\left(q_{ttube}^{LIGA,p}\left[R_b,R_h,p\right]-1\right)\right)\\&\times\left(\left(1+R_b\right)^2\right)^{-1}\end{aligned} \tag{15}$$

The peak current is then given by:

$$I_{LIGA,p}=nFA_{disc}c\sqrt{\frac{nFvD}{RT}}\times\psi_{LIGA,p}\left[R_b,R_h,\frac{s_w}{2}\sqrt{\frac{nFv}{RTD}}\right] \tag{16}$$

where A_{disc} is the projected area of the electrode. Equation (16) can be rearranged to obtain the desired result in terms of the normalized peak current:

$$J_{p,proj}=\frac{I_{LIGA,p}}{A_{disc}}=nFc\sqrt{\frac{nFvD}{RT}}\times\psi_{LIGA,p}\left[R_b,R_h,\frac{s_w}{2}\sqrt{\frac{nFv}{RTD}}\right] \tag{17}$$

These calculations were performed to fit the peak currents for the porous electrodes normalized by their projected area, $J_{p,proj}$. At each scan rate, the expected peak currents were calculated based on the equations above, and the sum of the squares of the deviations from the measured data was calculated. The value of s_b (which approximates the pore-pore spacing) was then systematically varied to obtain the minimum sum of squares value, while all other parameters were held constant. Each fit always produced a clear minimum in the sum of squares with respect to s_b, typically at $s_b \sim 2$ μm, which is consistent with the pore-to-pore spacing observed in the SEM images.