Modeling the Effects of Molecular Length Scale Electrode Heterogeneity in Organic Solar Cells

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Hypothesis to test

Scientific Method approach:

- Observation – electrode homogenization improves performance
- Hypothesis for phenomena
  - $\delta$ – characteristic diffusion length
  - $D$ - diffusion coefficient
  - $V$ - average front velocity due to charge generation at D-A interface
- Rooted in electrochemical studies

Thus we hypothesized:

- When $\delta > d$… heterogeneity should not matter.

Figure (B) provides estimates

- $\delta \sim 400$ nm for 4 mA-cm$^{-2}$
- $\delta \sim 200$ nm for 15 mA-cm$^{-2}$
- based on mobility corresponding to CuPc of $\sim 2.9 \times 10^{-4}$ cm$^2$-V$^{-1}$-s$^{-1}$
**Evolution of simulation**

- Polaron-pair placed across D-A interface
  - Braun’s ‘extension’ of Onsager theory applied to limit recombination
  - Periodically placed depending on theoretical maximum photocurrent

- Equation 1-2 applied to calculate rate for each possible nearest neighbor hop
  - Site $i$ to site $j$

- Equation 3 applied to calculate probability for each of the possible nearest neighbor hops

- Actual hop selected from the weighted probability and implemented at time determined by Equation 1

**Equations of transport**

\[ V_{ij} = A_{ij} \exp \left(\frac{-\Delta G^*_{ij}}{kT}\right) \]  
\[ \Delta G^*_{ij} = \frac{\lambda}{4} \left(1 + \frac{\Delta G_{ij}}{\lambda}\right)^2 \]  
\[ P_{i,+y} = \frac{V_{i,+y}}{V_{i,+y} + V_{i,-y} + V_{i,+x} + V_{i,-x} + V_{i,+z} + V_{i,-z}} \]
‘Flat-band’ simulation

• In contrast to a continuum model simulation approach, this nanometer scale approach is computationally voracious!
  • All simulations were performed at a single-operating point
  • The ‘flat-band’ condition – transport dominated by diffusion
    • Achieved by use of symmetric and ‘neutral’ contacts
    • The ‘flat-band’ condition is NOT \( V_{OC} \)

Some results

Recognize 100 watts-m\(^{-2}\) represents ~10% power conversion efficiency
Some trajectories

(1)

(2)
Conclusions

• We see the effects of heterogeneity for all the electrode constructs implemented

• Our hypothesis predicted we would not see much effect
  • $\delta \sim 400$ nm for 4 mA-cm$^{-2}$
  • $\delta \sim 200$ nm for 15 mA-cm$^{-2}$

• The PVs in our simulation were sensitive to ~2x orders of magnitude less heterogeneity than we predicted

• Our simple hypothesis ignored space-charge effects in vicinity of electrode and trapping by image forces in front of electrically inactive regions
  • Significantly reduces the effective diffusion coefficient (D)

• Interlayers are necessary in low mobility/conductivity active layers to achieve practical power conversion efficiencies
Does the low percentage of electrically active area of the electrode matter for PVs?

- Blocked showerhead

CuPc|C_{60} PHJ @ P_{MAX} => J ~ 3 mA-cm^{-2}

Does this magnitude of current density stress the electrode?

Cu wire => J ~ 10^6 mA-cm^{-2}

Single molecule junctions => 10^{-9} – 10^{-6} mA-molecule^{-1}

with an electrostatic potential of 0.2 V applied (1)

~10^{13} molecules-cm^{-2} => 10^{4} – 10^{7} mA-cm^{-2}

~10^{12} molecules-cm^{-2} => 10^{3} – 10^{6} mA-cm^{-2}