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Supplementary information

Working Area Effects on the Energetic Distribution of Trap States and Charge Dynamics of Dye-Sensitized Solar Cells

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S1.Theoretical derivation of chemical capacitance

When the quasi-Fermi level (E_{Fn}) of a dye-sensitized solar cell is much lower than the band edge energy of conduction band (E_{cb}) of its TiO_2 photoanode, the chemical capacitance (C_{μ}) is dominated by the trap state distribution. C_{μ} can be written as[S1]:

$$C_{\mu} = e^2 \frac{\partial n_T}{\partial E_{Fn}} \quad \text{(s1)}$$

where e is the unit charge, n_T is the density of trapped electrons. At this time, the chemical capacitance reflects the capability of a system to accept or release additional trapped electrons with density n_T due to a change of quasi-Fermi level.

n_T can be written as[S2]

$$n_T = \int_{E_{vb}}^{E_{cb}} g_T(E) f(E, E_{Fn}) \mathrm{d}E = N_T \exp\left[\left(E_{Fn} - E_{cb}\right) / k_B T_T\right] \quad \text{(s2)}$$

Where E_{vb} is the band edge energy of the valence band, $g_T(E)$ is the density of trap states as a function of energy E, $f(E, E_{Fn})$ is the Fermi-Dirac function, N_T and T_T are the total density and the characteristic temperature of the trap states.

For trapped electrons in Boltzmann distribution, C_{μ} can be expressed as[S3]

$$C_{\mu} = e^2 \frac{N_T}{k_B T_T} \exp \frac{E_{Fn} - E_{cb}}{k_B T_T} \quad \text{(s3)}$$

Because of $V_{ph} = (E_{Fn}\text{-}E_{redox})/e$, E_{redox} is the redox energy of electrolyte. Eq. (s3) can be expressed as

$$C_{\mu} = e^2 \left[B \exp\left(\frac{e}{k_B T_T} V_{ph} \right) \right] \quad \text{(s4)}$$

So C_{μ} is exponentially dependent on V_{ph}. The pre-exponential factors B is

$$B = \frac{N_T}{k_B T_T} \exp\left(\frac{E_{redox} - E_{cb}}{k_B T_T} \right) \quad \text{(s5)}$$

References

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