

Fast photo-chrono-amperometry of photosynthetic complexes for biosensors and electron transport studies

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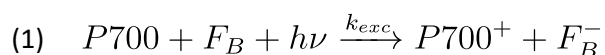
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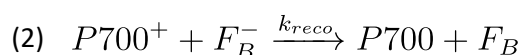
1. Kinetic Model

The model describes the concentration of the reaction kinetics of the involved species, namely PSI redox cofactors: chlorophyll special pair P700-P700⁺, iron sulfur cluster F_B-F_B⁻ and the paraquat analyte/redox mediator PQ⁺-PQ²⁺. The reactions, with rate k_x, are described below:

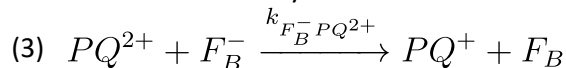
k_{exc}, photo-excitation rate of P700-F_B couple:



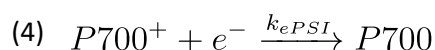
k_{reco}, recombination rate of P700⁺-F_B⁻ couple:



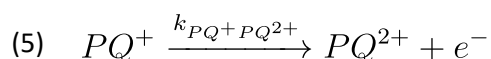
k_{FB-PQ2+}, reduction rate of PQ²⁺ by F_B⁻:



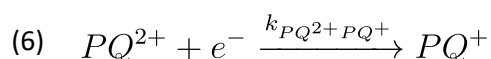
k_{ePSI}, electron transfer rate between electrode and P700⁺:



k_{PQ2+PQ+}, PQ reduction rate at the electrode:



k_{PQ+PQ2+}, PQ oxidation rate at the electrode:



For the last two rates (PQ electron transfer rate with the electrode) the dependence with the applied potential has been modeled empirically using sigmoidal functions (equations 7-8), where k_{PQ} is an effective rate; V is the applied voltage w.r.t. Ag electrode; V_{PQ} is the measured redox mid-point $V_{PQ} \sim -650$ mV/Ag; and α, β , are two fitting parameters with 1/V units.

$$(7) \quad k_{PQ+PQ^{2+}} = \frac{k_{PQ}}{1 + e^{\alpha(V-V_{PQ})}}$$

$$(8) \quad k_{PQ+PQ^{2+}} = \frac{k_{PQ}}{1 + e^{-\beta(V-V_{PQ})}}$$

The kinetic equations describe the rate of change in the concentrations of the species due to reactions (1-6):

$$(9) \quad \frac{d([P700])}{dt} = -k_{exc}[P700][F_B] + k_{reco}[P700^+][F_B^-] + k_{ePSI}[P700^+]$$

$$(10) \quad \frac{d([Fb])}{dt} = -k_{exc}[P700][F_B] + k_{reco}[P700^+][F_B^-] + k_{F_B^-PQ^{2+}}[F_B^-][MV^+]$$

$$(11) \quad \frac{d([P700^+])}{dt} = +k_{exc}[P700][F_B] - k_{reco}[P700^+][F_B^-] - k_{ePSI}[P700^+]$$

$$(12) \quad \frac{d([F_B^-])}{dt} = -\frac{d([F_B])}{dt}$$

$$(13) \quad \frac{d([PQ^{2+}])}{dt} = -k_{PQ^{2+}PQ^+}[PQ^{2+}] + k_{PQ+PQ^{2+}}[PQ^+] - k_{F_B^-PQ^{2+}}[F_B^-][PQ^{2+}]$$

$$(14) \quad \frac{d([PQ^+])}{dt} = -\frac{d([PQ^{2+}])}{dt}$$

In the absence of diffusion, the current flowing through the electrode is due to the charge exchange of the electrode with the redox species described by reactions (equations 4-6). To compute current density j the rates of charges flowing from (positive sign, equation 4 and 6) and to (negative sign, equation 5) are summed (equation 15) where e denotes electron charge, V cell volume, and S the electrode surface.

$$(15) \quad j = \frac{eV}{S} ([k_{PQ^{2+}PQ^+}[PQ^{2+}] + k_{ePSI}[P700^+] - k_{PQ+PQ^{2+}}[PQ^+])$$

The differential equation system (7-14) is solved numerically using MATLAB® ode23tb solver, an implicit Runge-Kutta algorithm suitable for stiff problems. All the reaction rates and α, β parameters are fit to minimize the square error between modeled and experimental current density with a non-linear least square algorithm (trust region reflective).