

Vogel-Tammann-Fulcher model for charging dynamics in an organic electrochemical transistor: electronic supplementary information

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Mathematical model

The results shown in fig. 2 demonstrate that two processes are primarily responsible for charging dynamics in organic electrochemical transistors. The two processes are ion currents in the dielectric and mixed ion-carrier diffusion in the organic semiconductor. These processes are coupled, ion-carrier pairs cannot diffuse into the organic semiconductor prior to the polarization of ions in the dielectric. We begin by specifying the problem in terms of two limiting cases. In the first case, the rate of ion-carrier diffusion is orders of magnitude faster than the movement of ions in the dielectric. In this case, the system can be modeled by considering only the behavior of the dielectric. It is common to use a stretched exponential function to model currents in a polymer electrolyte,^{1,2} we therefore model the RC charging behavior using the following function:

$$f(t) = A_0(1 - \exp[-(k_{RC}t)^\gamma]) \quad (1)$$

In eq. 1, A_0 represents the charge carrier concentration at steady state, $k_{RC} = (RC)^{-1}$ is the time constant of device charging from a simple RC circuit model and γ is a constant between 0 and 1 which is indicative of static and dynamic disorder in the ion conducting material.

In the second limiting case, the rate of ion polarization in the dielectric is orders of magnitude faster than the diffusion of ion-carrier pairs in the semiconductor. In this case, we model the problem as a simple case of 1-D diffusion with a single diffusivity, D , that is constant both in time and in position. To solve the differential equation, we assume a constant boundary condition at the semiconductor-dielectric interface and a no-flux boundary condition at the opposing side of the film. In our experiments, the opposing side of the film is in contact with a silicon substrate that is not being electrically addressed. We assume that it is impermeable to the ions. The solution to this problem is well known and is given in terms of a Fourier series.³

$$g(x, t) = A_1 \left(1 - \frac{4}{\pi} \sum_n^{\infty} c_n \sin \left[\frac{\lambda_n x}{L} \right] \exp \left[-\lambda_n^2 \frac{D}{L^2} t \right] \right) \quad (2)$$

In eq. 2, A_1 represents the steady state solution, a spatially uniform distribution of that value. Terms in the Fourier series are distinguished by $\lambda_n = (2n - 1)\pi/2$ which is used in the calculation of the coefficients, c_n along with the semiconductor film thickness, L .

$$c_n = \frac{2}{L} \int_0^L (h(x, 0) - A_1) \sin \left[\frac{\lambda_n x}{L} \right] dx \quad (3)$$

In equation 3, $h(x, 0)$ is the initial condition, the ion-carrier pair concentration at $t = 0$.

Combining these two limiting cases into a single solution requires that the boundary condition at the dielectric-semiconductor interface changes with time as described by eq. 1. This stipulation makes the boundary conditions for the diffusion equation inhomogeneous. We chose to develop a solution numerically. The calculation begins by assuming that there are no ion-carrier pairs throughout the semiconductor at $t = 0$. It is likely that trapped charges linger from a previous charge/discharge cycle, but in our data analysis, we subtract out any signal from trapped charge, causing $h(x, 0) = 0$ for the experiment as well as the simulation.

In the first time step, which we will call t_1 , we set $A_1 = f(t_1)$ and solve for $g(x, \Delta t_1)$ where $\Delta t_i = t_i - t_{i-1}$ is the time variable that is input into equation 3 during each step of the numerical solution. During the calculation for the next time step, we set $A_1 = f(t_2)$ and calculate the Fourier coefficients using the previous solution as our initial condition. In symbols, we set $h(x, t_2) = g(x, \Delta t_1)$ during our calculation of c_n for the second step of the time series. This process is repeated, always using the previous solution as the initial conditions for the next time step. Because of the iterative nature of the solution, convergence is not guaranteed. However, choosing sufficiently fine time samples at short timescales aids in obtaining convergence for rapidly varying components and choosing sufficiently fine spatial sampling aids in obtaining convergence for slowly varying components.

References

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