

Supporting information

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SI Text

Before fitting voltammetric currents to Eq. 10, as is shown in Fig. 5, the currents were first normalized to correct for small amounts of continuous film loss (see *Materials and Methods*). Current in the positive and negative sweep was then averaged

to eliminate the capacitive contribution. In cases where deactivation of the enzyme takes place at high potential, this region was eliminated before the fitting.

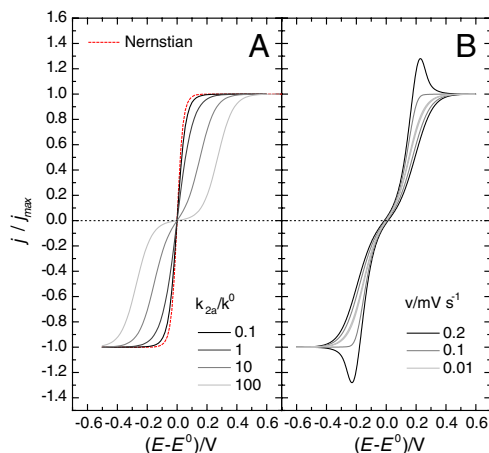


Fig. S1. Typical curves obtained from Eqs. 5 to 7 with the following parameters: (A) $e_2 = 1$ and k_{2a}/k^0 as indicated. The dashed line indicates the behaviour given by the Nernst law, which occurs when k^0 is sufficiently large (B) non steady-state solution of Eqs. 5 and 6 with $k^0 = 0.1 \text{ s}^{-1}$, $k_{2a} = 1 \text{ s}^{-1}$, $q_{ML} = 0.1 \text{ } \mu\text{C cm}^{-2}$ and sweep rate, v , as indicated.

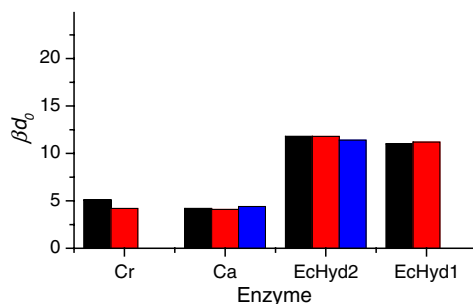


Fig. S2. The parameter βd_0 corresponding to the best fits shown in Fig. 5 for each enzyme, for the experiment at 22 °C, except CrHydA1 at 18 °C.

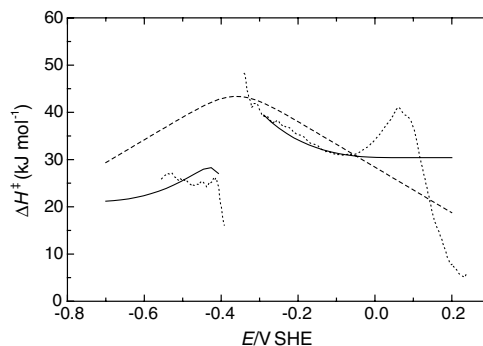


Fig. S3. A comparison of the “apparent” activation enthalpy obtained from the Eyring plot of the experimental data for CrHydA1 (dotted line) and the potential dependence predicted by the model (solid line) using the k^0 and j_{lim} values obtained from the best fit to the experimental data. The good agreement between the two curves means that the decrease in activation enthalpy between -0.3 and 0 V is not contrary to the model. The expected variation from the electron transfer step, with a slope of αF according to Butler–Volmer kinetics, is also shown (dashed line). The similarity between the gradient of this curve and that of the data is fully consistent with dominance of the electron-transfer step in determining the rate of catalysis. While the model predicts a leveling of the curve at higher potentials, the experimental data shows a complex behavior due to the oxidative deactivation of the enzyme.