Supplementary material

1. Cyclic voltammetry study for hydroquinone



**Figure 1**. Cyclic voltammograms for hydroquinone (5 mM in 0.1 M phosphate, pH 7.0, 23 °C)

**Table 1**. The impact of scan rate on the voltammograms of hydroquinone

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Scan Rate****(mV s-1)** | **Epa****(V)** | **ipa****(A)** | **Epc****(V)** | **ipc****(A)** | **ipa/ipc****(A)** | **E****(V)** |
| 20 | 0.181 | 22.499 | -0.239 | 20.592 | 1.09 | 0.420 |
| 50 | 0.207 | 30.076 | -0.259 | 31.684 | 0.95 | 0.466 |
| 100 | 0.225 | 36.859 | -0.282 | 43.259 | 0.85 | 0.507 |
| 200 | 0.245 | 53.975 | -0.302 | 55.109 | 0.98 | 0.547 |
| 500 | 0.286 | 78.258 | -0.330 | 77.501 | 1.01 | 0.616 |
| 1000 | 0.319 | 103.430 | -0.353 | 104.971 | 0.99 | 0.672 |

**Figure 2**. Cyclic voltammetry of H2Q at 1000 mV/s in 0.1 M phosphate, pH 7.0

**Figure 3.** Standard curve of peak current of H2Q with CV at 1000 mV/s scan rate

**Figure 4** Voltammogram of hydroquinone (2 mM in 0.1 M phosphate, pH 7.0)

**Table 2. Impact of crosslinking factors on the steady state current and inhibition by 1 mM As(III)** (The concentration of AchE was fixed at 5.3 g/electrode)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Electrode** | **pH** | **BSA (g)** | **GA (%)** | **Steady State****Current (A)** | **Inhibition (%)** |
| 1 | 7.5 | 30 | 0.015 | 82.2 | 59.1 |
| 2 | 7 | 20 | 0.015 | 87.5 | 65.7 |
| 3 | 6.5 | 30 | 0.005 | 77.4 | 69.6 |
| 4 | 7 | 20 | 0.01 | 79.2 | 61.7 |
| 5 | 7 | 10 | 0.01 | 88.6 | 63.0 |
| 6 | 6.5 | 20 | 0.01 | 90.9 | 68.0 |
| 7 | 7.5 | 20 | 0.01 | 81.2 | 63.4 |
| 8 | 6.5 | 30 | 0.015 | 86.2 | 65.1 |
| 9 | 7.5 | 10 | 0.015 | 65.9 | 67.1 |
| 10 | 6.5 | 10 | 0.005 | 93.3 | 71.7 |
| 11 | 7 | 30 | 0.01 | 105.3 | 65.8 |
| 12\* | 7.5 | 30 | 0.005 | 36.3 | 74.7 |
| 13 | 7.5 | 10 | 0.005 | 106.1 | 70.7 |
| 14 | 7 | 20 | 0.01 | 88.0 | 66.9 |
| 15 | 6.5 | 10 | 0.015 | 70.0 | 66.0 |
| 16 | 7 | 20 | 0.005 | 95.2 | 69.3 |

\*Electrode 12 was excluded as an outlier as the steady sate current was atypically low.

Figure 5. Change of steady state current of the AchE electrode in repeated uses

**Modeling AchE inactivation by As (III)**

1. **Reaction**

  **Eq 1**

Assumption: [As] >> [AchE], therefore this reaction can be reduced to a reversible pseudo-first order reaction.

 **Eq 2**

The unit for constant: k1: M-1 min-1, k-1: min-1.

1. **Rate law and kinetic model**

 **Eq 3**

Assumption: when reaching the equilibrium, the concentration of free enzyme is

Mass balance relationship: , **Eq 4**

At equilibrium:

Or: **Eq 5**

Substitute in **Eq 4** and rearrange the equation to relate [E] and [EAs]

 **Eq 6**

Substitute **Eq 6** into rate law **Eq 3**.

 **Eq 7**

Factor **Eq 7** for integration

 **Eq 8**

Integration of **Eq 8** gives kinetic model

 **Eq 9**

1. **The relationship between and**

Based on the two equations, solve for

, **Eq 4**

 **Eq 5**

 **Eq 10**

1. **Determination of *k*1 and *k*-1 through least-square fitting**

Independent variables: *t* (s-1), and [As]

Dependent variable: =

Parameters (coefficients): *k*1 and *k*-1.

The relationship between dependent variable and in the model (**Eq 9**)

Let , rearrange gives **Eq 11**

From **Eq 9**:

 **Eq 12**

Estimation of :

* Select starting value for *k*1 and *k*-1
* Determine with **Eq 12**
* Determine with **Eq 10**
* Estimate dependent variable with **Eq 11**

Determine Sum of Square Residues (SSR):

Fitting to estimate *k*1 and *k*-1 by minimizing SSR