

Supplementary Information

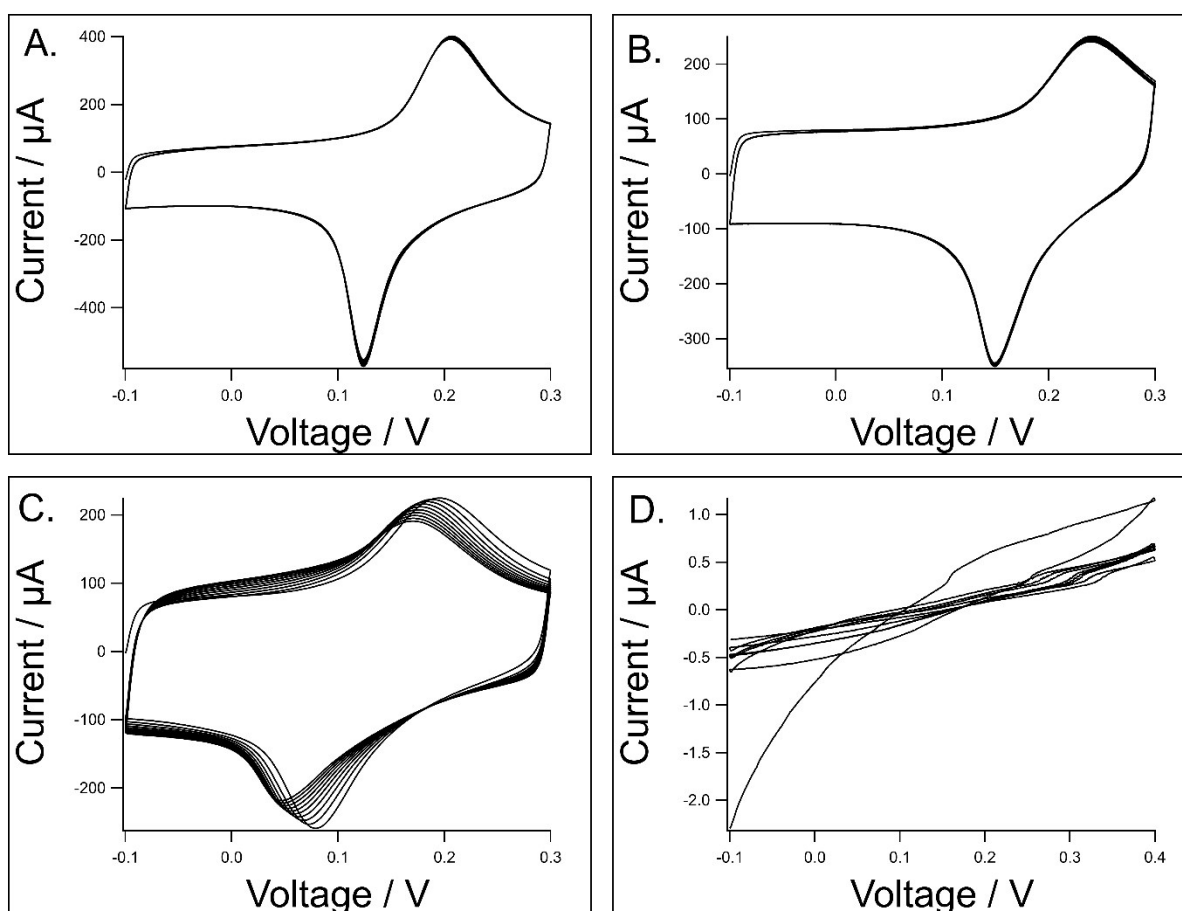


Figure 1 [A-C; Cyclic voltammetry of PEDOT:PSS-PB-EG-DVS in different buffer A. 0.01M HCl + 0.1M KCl, B. pH7.4 0.1M potassium phosphate buffer + 0.1M KCl C. pH7.4 10mM phosphate buffer silane (PBS).] [D. Cyclic voltammetry of drop casted PB in PBS]

Figure 1A and B demonstrated good electrochemical stability of PEDOT:PSS-PB-EG-DVS in acidic and neutral environment without the presence of sodium. Figure 1C and D showed degeneration of PB due to sodium ions in PBS, nonetheless because of the conducting polymer layer PB is protected from dissolution and the process is significantly retarded.

Kinetics studies of electrochemistry on a film modified electrode surface with rotating disc electrode is a well-established method and has been evaluated theoretically by Saveant's group in late 1970s and 1980s [1, 2]. The limiting factors in an electroactive layer includes:

- 1) i_l - Diffusion of analyte in solution
- 2) i_s - Diffusion of analyte in electroactive layer (case S)
- 3) i_e - Electron diffusion in electroactive layer (case E)
- 4) i_k - Catalytic reaction (case R)

Or any combination of the limiting factors where they have comparable rates.

The overall current can be re-written as[1, 2]:

$$\frac{1}{i} = \frac{1}{i_l} + \frac{1}{i_s} + \frac{1}{i_e} + \frac{1}{i_k}$$

To diagnose the limiting factor the following procedure is followed:

- 1) Koutecky-Levich plot (K-L plot)
- 2) 1/slope of K-L plot against concentration
- 3) 1/intercept of K-L plot against concentration

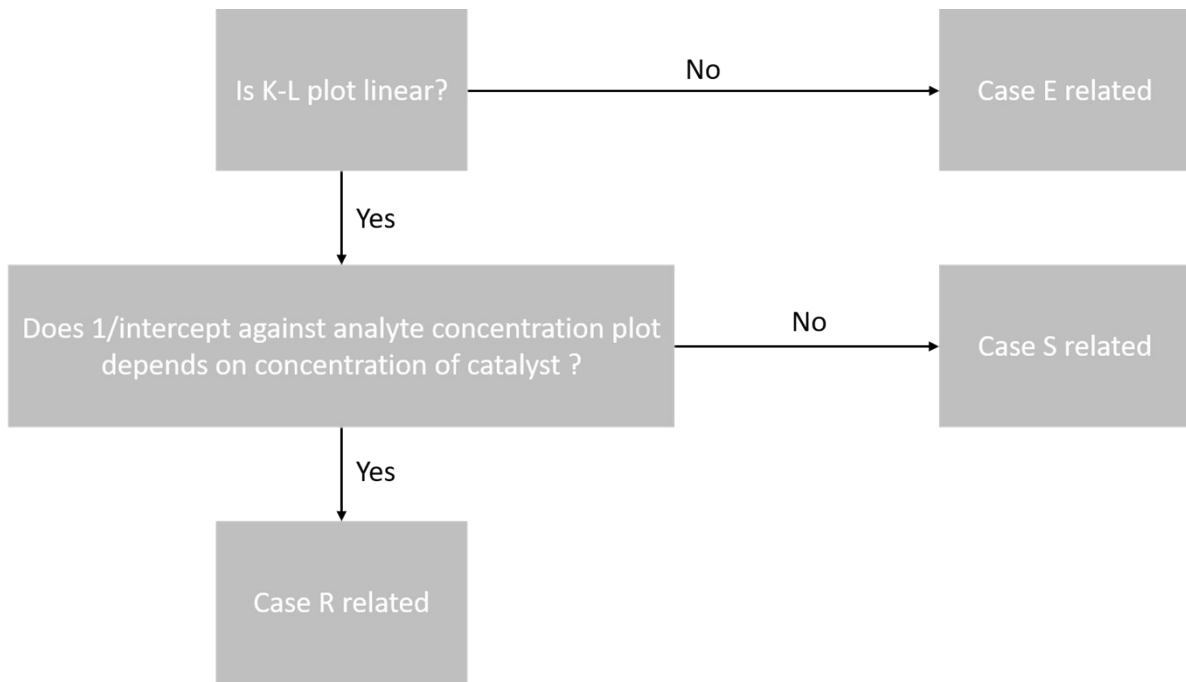


Figure 2 First stage logic table for limiting factor diagnostics

However, since the limiting factor could be a combination of any single limiting extreme, to distinguish the specific limiting combination would require further assessments. Here we state the summary of all possible cases summarised from Andrieux *et al.* [1].

Case	Condition	Overall current
R+S	$\frac{\text{Electron diffusion}}{\text{Analyte diffusion in solution}} \rightarrow \infty$	$\frac{1}{i} = \frac{1}{i_l} + \frac{1}{FAC_A^\infty C_p D_s^{0.5} k_l \kappa \times \tanh(C_p^{0.5} D_s^{-0.5} k_l^{0.5} \phi)}$
R	$\frac{\text{Electron diffusion}}{\text{Analyte diffusion in solution}} \rightarrow \infty,$ $\frac{\text{Catalytic reaction}}{\text{Analyte diffusion in film}} \rightarrow 0$	$\frac{1}{i} = \frac{1}{i_l} + \frac{1}{FAC_A^\infty k_l \Gamma_0}$
SR	$\frac{\text{Electron diffusion}}{\text{Analyte diffusion in solution}} \rightarrow \infty,$ $\frac{\text{Catalytic reaction}}{\text{Analyte diffusion in film}} \rightarrow \infty$	$\frac{1}{i} = \frac{1}{i_l} + \frac{1}{FAC_A^\infty \kappa \sqrt{C_p D_s k_l}}$
SR+E	$\frac{\text{Catalytic reaction}}{\text{Analyte diffusion in film}} \rightarrow \infty$	$\frac{1}{i} = \frac{1}{i_l} + \frac{1}{FAC_A^\infty C_p^{0.5} \kappa D_s^{0.5} k_l^{0.5} \sqrt{1 - \frac{i\phi}{FAC_p D_E}}}$
R+E	$\frac{\text{Analyte diffusion in film}}{\text{Analyte diffusion in solution}} \rightarrow \infty$	$\frac{i_l^{0.5}}{\sqrt{i_l - i}} = C_p \sqrt{C_A^\infty \kappa D_E k_l} \tanh(\sqrt{C_A^\infty \kappa k_l} \phi \sqrt{1 - \frac{1}{ii_l}})$
ER	$\frac{\text{Analyte diffusion in film}}{\text{Analyte diffusion in solution}} \rightarrow \infty,$ $\frac{\text{Catalytic reaction}}{\text{Electron diffusion}} \rightarrow \infty$	$\frac{i_l^{0.5}}{\sqrt{i_l - i}} = FAC_p \sqrt{C_A^\infty \kappa D_E k_l}$
ER+S	$\frac{\text{Catalytic reaction}}{\text{Electron diffusion}} \rightarrow \infty$	$\frac{i_l^{0.5}}{\sqrt{i_l - i \left(\frac{D_A \phi}{D_s \delta \kappa} \right)}} = FAC_p \sqrt{C_A^\infty \kappa D_E k_l}$
S	$\frac{\text{Catalytic reaction}}{\text{Electron diffusion}} \rightarrow \infty,$ $\frac{\text{Analyte diffusion in film}}{\text{Analyte diffusion in solution}} \rightarrow 0$	$\frac{1}{i} = \frac{1}{i_l} + \frac{\phi}{FSD_s C_A^\infty \kappa}$
S+E	$\frac{\text{Catalytic reaction}}{\text{Analyte diffusion in film}} \rightarrow \infty$	$\frac{i}{i_l} = \frac{\delta(C_A^\infty \kappa D_s + C_p D_E)}{C_A^\infty (\delta \kappa D_s + D_A \phi)}$
E	$\frac{\text{Electron diffusion}}{\text{Analyte diffusion in solution}} \rightarrow 0$	$\frac{1}{i} = \frac{\phi^2}{F\Gamma_0 D_E}$

Table 1 Summarised RDE limiting factor diagnostics table [1]

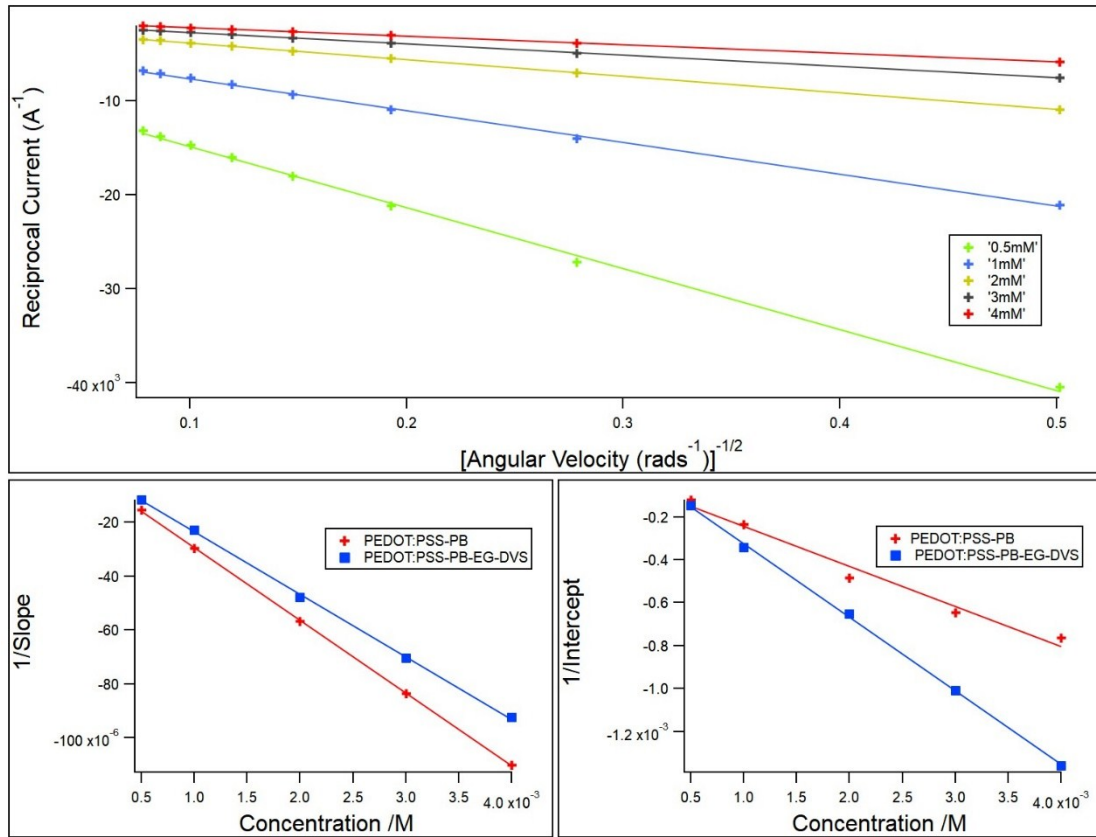


Figure 3 Upper plot demonstrated the Koutecky-Levich (KL) plot with various concentration of hydrogen peroxide with PEDOT:PSS-PB modified GC electrode. Bottom left showed 1/slope of PEDOT:PSS-PB and PEDOT:PSS-PB-EG-DVS KL plot against hydrogen peroxide concentration. Bottom right showed 1/intercept of PEDOT:PSS-PB v.s. PEDOT:PSS-PB-EG-DVS against hydrogen peroxide concentration

The upper plot in Figure 3 demonstrated linearly correlated Koutecky-Levich plot with respect to different hydrogen peroxide concentration, thus we could limit the performance-limiting factor to either case SR, SR+E, S+E, and S according to Andrieux et al. [1]. Additionally, we can extract gradient and intercept data as a function of hydrogen peroxide concentration and obtain the lower plots in Figure 3.

Both the 1/slope and 1/intercept vs. concentration plots are linearly correlated and showing no evidence of deviation from zero at 95% confidence level. Hence, with both plots passing through origin, the plausible limiting cases are further reduced to case S and SR. [1]

From 1/slope against hydrogen peroxide concentration we can calculate the hydrogen peroxide diffusion coefficient (D) from the gradient of the plot with equation

$$\text{gradient} = 1.61FAD^{\frac{2}{3}}\nu^{\frac{-1}{6}}$$

Where F is Faraday's constant, A is the electrode area, D is the diffusion coefficient of analyte in solution phase, ν is the kinematic viscosity.

The diffusion coefficient was calculated to be $\sim 1.23 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$

From 1/intercept against hydrogen peroxide concentration we can calculate the diffusion block coefficient (d_s) that includes diffusion coefficient of analyte in film. Since limiting case is now narrowed to 2 possibilities, we could first assume the limiting case to be S i.e. film diffusion rate much significantly slower than PB-hydrogen peroxide catalysis rate.

The diffusion block coefficient is defined as:

$$d_s = \frac{D_s \kappa}{\phi}$$

where D_s is the hydrogen peroxide diffusion coefficient in PEDOT:PSS-PB film and k is the partition coefficient and ϕ is the film thickness.

The diffusion block coefficient is related to the slope of 1/intercept against hydrogen peroxide concentration given by:

$$\text{gradient} = FAd_s$$

Hence the diffusion block coefficient is calculated as 9.88×10^{-3} for PEDOT:PSS-PB and 1.81×10^{-2} cm^2s^{-1} for PEDOT:PSS-PB-EG-DVS respectively. With the measured average film thickness of 923 nm and 864 nm for PEDOT:PSS-PB and PEDOT:PSS-PB-EG-DVS respectively and assumed near unity partition coefficient we could estimate hydrogen peroxide diffusion coefficient in the film as 9.12×10^{-7} and 1.56×10^{-6} cm^2s^{-1} for PEDOT:PSS-PB and PEDOT:PSS-PB-EG-DVS respectively.

To correctly diagnosed the limiting factor, we need to compare the determined hydrogen peroxide diffusion coefficient in the film to catalysis rate of PB. Kinetics of PB was measured as $3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ by Karayakin et al.[3], we can then further compute non-dimensional to compare catalytic reaction rate to diffusion in film (λ/σ^2) to conclude the limiting factor. [1] Where λ/σ^2 was calculated as 5.07 and 2.77 for PEDOT:PSS-PB and PEDOT:PSS-PB-EG-DVS respectively, thus the catalytic reaction rate is significantly larger than diffusion in film hence the performance-limiting factor is established as hydrogen peroxide diffusion rate in film. As the results suggested, adding the crosslinker ethylene glycol and divinyl sulfone we can improve the diffusion of hydrogen peroxide in the film thus increasing sensor sensitivity whilst retaining mass transport in the film as the rate-determining factor.

1. Andrieux, C.P., J.M. Dumasbouchiat, and J.M. Saveant, *CATALYSIS OF ELECTROCHEMICAL REACTIONS AT REDOX POLYMER ELECTRODES - KINETIC-MODEL FOR STATIONARY VOLTAMMETRIC TECHNIQUES*. Journal of Electroanalytical Chemistry, 1982. **131**(JAN): p. 1-35.
2. Leddy, J.A., et al., *KINETICS OF FILM-COATED ELECTRODES - EFFECT OF A FINITE MASS-TRANSFER RATE OF SUBSTRATE ACROSS THE FILM SOLUTION INTERFACE AT STEADY-STATE*. Journal of Electroanalytical Chemistry, 1985. **187**(2): p. 205-227.
3. Karyakin, A.A., E.E. Karyakina, and L. Gorton, *The electrocatalytic activity of Prussian blue in hydrogen peroxide reduction studied using a wall-jet electrode with continuous flow*. Journal of Electroanalytical Chemistry, 1998. **456**(1-2): p. 97-104.