Statistical tools for the improvement and optimization of electrochemical sensors

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Introduction

The response of electrochemical sensors for substance detection critically depends on the sensing potential, the value of which is often selected by the visual inspection of the sensor's response, as given by, for example, electrochemical methods like cyclic voltammetry (CV) [2]. Using experimental data from CV, we show how the selection of the sensing potential can affect the sensitivity and linear range of the measurements. Whenever the magnitude of the sensor's response is crucial, it can be better to optimize the sensor for its sensitivity; however, if the testing conditions involve a variable range of concentrations, with putative very small or high concentrations, a reliable response can be obtained if the sensor is optimized for the linear range.

Method

We electrodeposited Ni on restrictive nanoporous membranes (Fig. 1**A**). The nanowire length was achieved by monitoring the electrodeposition time in PCTE restrictive nanoporous membranes with a pore size of 0.1 μm and 0.6 μ thickness. Lengths were measured using a scanning electron microscope. Sensor response were masured using Cyclic voltammetry (CV) with scan rate of 100 mVps, with a range of -0.6, 0.6 V (Fig. 1**B**), with concentrations of 0, 0.5, 1, 1.5, 2.54 and 6.5 H_2O_2 mM.

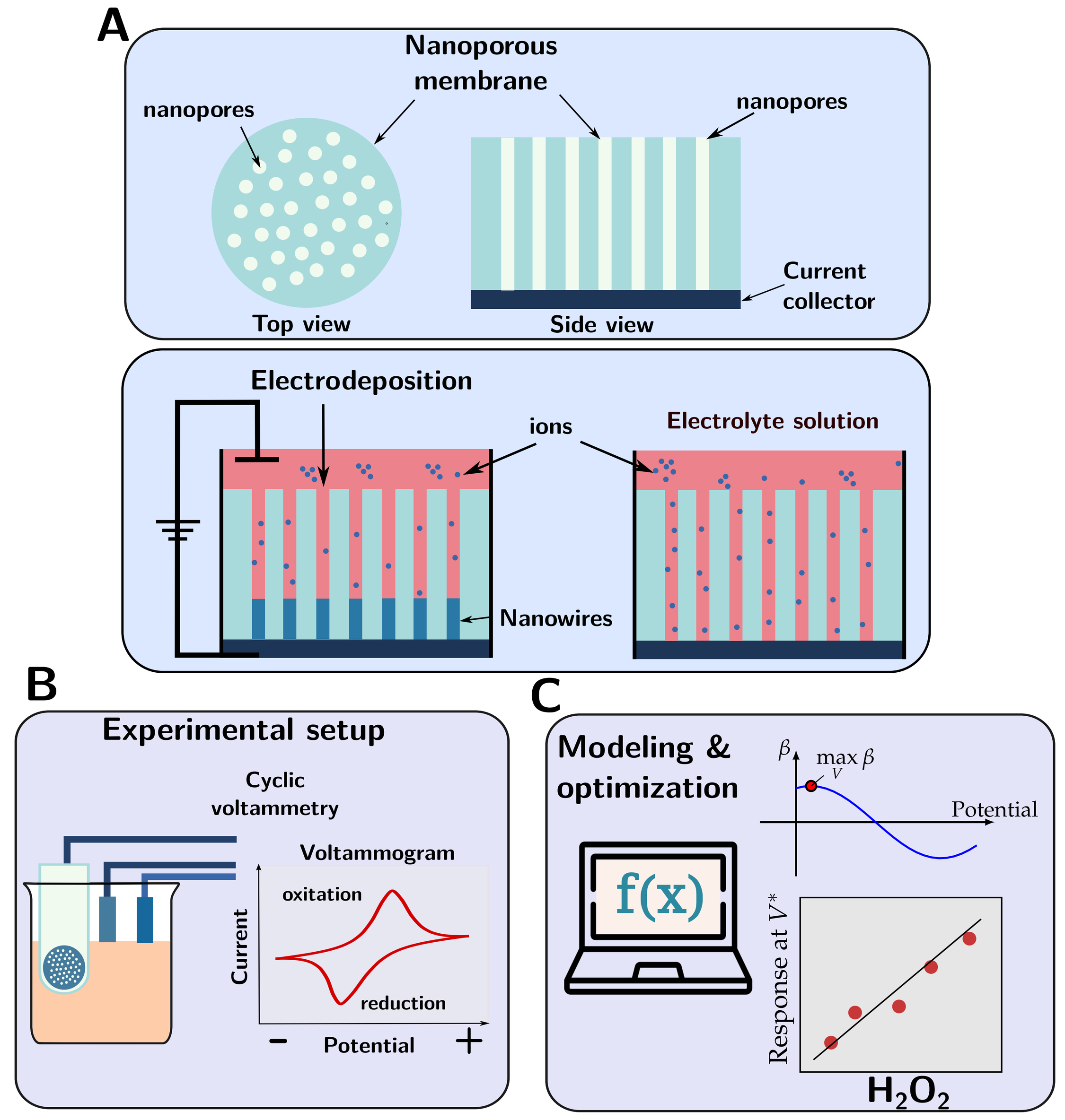

Fig. 1: Experimental setup and data recollection

With the CV data, linear regression relating the sensor response with H_2O_2 concentrations was applied at different potentials, and estimated the slope β_1 in Response $= \beta_0 + \beta_1 H_2O_2$, which we interpret as the sensor sensitivity in mA/mM·cm^2 (see Fig. 1**C**). We used the R-squared of the linear regression as a proxy of the linearity of the calibration curve, and compared the results obtained by maximizing the slope vs maximizing the R-squared.

For our analysis, we used bootstrapping to compute the 95% CI for all estimates. The bootstrap is a statistical technique used for the interval estimation. We simulated the sampling distribution variation by taking samples with replacement. For each resample, the slope of a linear regression model was computed and stored. After $B = 1000$ resamples, the resulting variation was summarized with the lower and upper 95% percentile [1, 3].

Results

Tab. 1 shows the slope-maximizing and R^2-maximizing potentials. Fig.2**A** shows the sensitivity estimated with OLS over the range -0.25 to 0.25 V. Panel **B** shows the CV data for the concentrations used, indicating the potential at which was maximized R^2 and β. Panels **C** and **D** shows how the response as a function of the H_2O_2 concentration, for the potential selected at max R^2 and max β.

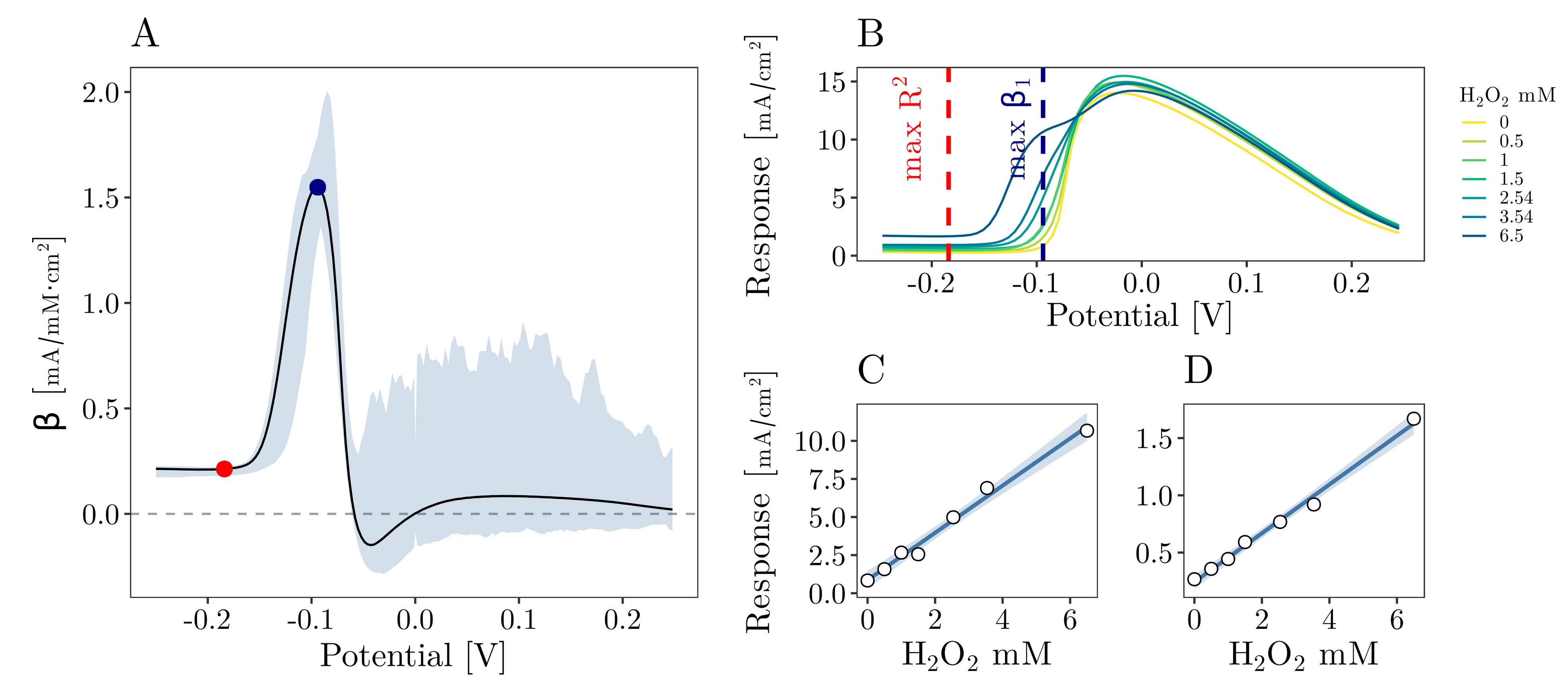

Fig. 2: A: slope β as a function of potential; dots are located at slope-maximizing potential (blue), or R^2-maximizing potential (red). B: CV data for all concentrations; dashed lines show the potential which maximizes R^2 (red) or β (blue).

At both maximizing potentials, we fitted a linear regression model relating Response with H_2O_2 concentration and estimated the 95% CI with the statistical technique of bootstrapping [3]. Tab. 1 shows the estimates [95% CI] of the sensitivity, limits of detection (LOD) and quantification (LOQ).

	Potential	Sensitivity	LOD	LOQ
max β	−0.094	1.55 [1.3, 1.8]	0.81 [0.12, 0.98]	2.71 [0.39, 3.28]
max R^2	−0.184	0.21 [0.181, 0.22]	0.61 [0.008, 0.79]	2.05 [0.027, 2.65]

Tab. 1: Estimates of sensitivity, LOD, and LOQ at the R^2-maximizing potential and slope-maximizing potential.

Conclusions

If we optimize the sensor's measuring potential for the sensitivity, the calibration curve has greater uncertainty, especially for larger concentrations. At Tab. 1 shows, the LOD and LOQ at the slope-maximizing potential (-0.094 V) are greater than those at the R^2-maximizing potential. This means that more reliable measures can be obtained at R^2-maximizing potential but at the cost of reducing the sensitivity.

References

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