Supporting Information for:

Optical Sensing with a Potentiometric Sensing Array by Prussian Blue Film Integrated Closed Bipolar Electrodes

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Theory of ion-selective bipolar electrode

The redox indicator film, Prussian blue (PB)/Prussian white (PW) deposited onto a transparent ITO electrode is connected in series to the ion-selective electrode (ISE) in the sample compartment in a closed bipolar configuration, as shown below. Each element is labeled by a number in red color.

1  Working electrode connection, Ag/AgCl element in contact with detection compartment:

\[ E_{AgCl/Cl} = E_{AgCl/Ag}^0 - s \log a_{Cl}^{det} \]  \hspace{1cm} (S1)

2  Potential at PB film on the ITO electrode:

\[ E_{\text{det}} = E_{PW/PB}^0 - s \log \frac{c_{PW}}{c_{PB}} + s \log a_{K}^{det} \]  \hspace{1cm} (S2)

or, after inserting the apparent mass balance equation for Prussian Blue:

\[ E_{\text{det}} = E_{PW/PB}^0 - s \log \frac{c_T - c_{PB}}{c_{PB}} + s \log a_{K}^{det} ; c_{PW} = c_T - c_{PB} \]  \hspace{1cm} (S3)

where \( c_T \) is the total film concentration. To approximately express the concentration in terms of absorbance based on Beer’s law:

\[ A_{\text{max}} = \varepsilon_{PB} \cdot c_T \cdot l \]  \hspace{1cm} (S4)

\[ A_{PB} = \varepsilon_{PB} \cdot c_{PB} \cdot l \]  \hspace{1cm} (S5)

Equations S4 and S5 are inserted into eq S3 to obtain:

\[ E_{\text{det}} = E_{PW/PB}^0 - s \log \frac{A_{\text{max}} - A_{PB}}{A_{PB}} + s \log a_{K}^{det} \]  \hspace{1cm} (S6)
3 Potential at Ag/AgCl element in the inner solution of the ISE:

$$E'_{AgCl/Cl} = E'^0_{AgCl/Ag} - s \log a^{ifs}_{Cl}$$

(S7)

4 Membrane potential at the ISE:

$$E_M = s \log \frac{a^{sample}_i}{a^{ifs}_i}$$

(S8)

5 Ag/AgCl element of the reference electrode, in contact with the reference solution (ref):

$$E'_{AgCl/Cl} = E'^0_{AgCl/Ag} - s \log a^{ref}_{Cl} + E_J$$

(S9)

where $E_J$ is the liquid junction potential.

When a constant applied potential is imposed in the bipolar electrode cell, the elements described above are combined together as follows:

$$E_{cell} = (1) - (2) + (3) + (4) - (5)$$

Specifically,

$$E_{cell} = E'^0_{AgCl/Ag} - E'^0_{PW/PB} - s \log \left( a^{det}_{Cl} a^{det}_{K} a^{ifs}_{Cl} \right) + s \log \frac{A_{max} - A_{PB}}{A_{PB}} + s \log \frac{a^{sample}_i}{a^{ifs}_i} - E_J$$

(S10)

or, simplified:

$$E_{cell} = E_{const} + s \log \frac{A_{max} - A_{PB}}{A_{PB}} + s \log a^{sample}_i$$

(S11)

This equation is rewritten as follows to express the absorbance change as a function of sample activity:

$$\frac{A_{max} - A_{PB}}{A_{PB}} = (a^{sample}_i)^{-1/z_i} \cdot \psi \quad \text{with} \quad \psi = 10^{\frac{E_{cell} - E_{const}}{s}}$$

(S12)

The Prussian Blue film absorbance is given by solving eq S12 as follows:
\[ A_{PB} = A_{\text{max}} \left( \frac{\psi}{a_i^{1/z_i}} + 1 \right)^{-1} \]  

(S13)

**Photograph of experimental setup**

The closed bipolar electrode sensor array contains two separate compartments. One is the detection compartment and the other is the sample compartment. Ion-selective electrodes (ISEs) are in contact with the sample compartment and connected to the PB electrodes in the detection compartment, as shown in the photograph below. The detection compartment contains 3 M KCl into which the PB electrodes are immersed. In the bipolar configuration, a constant potential is imposed in the bipolar cell between the working electrode (Ag/AgCl wire) in detection compartment and Ag electrode (CE) in sample compartment, where the double junction reference electrode (RE) is in a bulk solution in sample compartment. The camera is placed in front of the detection compartment to record consecutive images.

![Photograph of experimental setup](image)

**Schematic illustration**

This scheme shows the connection between each individual ISE and the PB electrode in a closed bipolar sensor array configuration.
Flow cell in the sample compartment for inserting numerous ISEs

The flow cell contains openings for inserting three ion-selective electrodes as labeled with ISE 1, ISE 2 and ISE 3 (Ostec electrode bodies). Visible are the inlet and outlet holes, by which the sample is guided into and out to the bulk solution by peristaltic pumping. An Ag electrode is inserted into the flow cell at CE to serve as a counter electrode. The reference electrode is placed just outside the outlet in a beaker filled with electrolyte solution.

Fabrication of patterned PB array

The conductive ITO film coated glass slide (25×25×1.1mm) is etched into 3 channels as an example. The entire ITO glass surface was first covered by insulating tape. To remove the ITO film, the tape was cut by a cutter. The exposed ITO film was removed by immersing in concentrated HCl for 10-20 minutes. Complete removal was confirmed by measuring with an Ohmmeter, confirming insulation. In this design there are three ITO electrodes on the same glass slide.
**Figure S1.** Cyclic voltammogram of the PB electrode in 3 M KCl (pH 2). The scan rate is 5 mV s\(^{-1}\). An Ag/AgCl element is used as the reference/counter electrode.

**Figure S2.** (Left) Cyclic voltammogram of PB electrode in a solution of 3 M KCl (pH 2) at different scan rates. (Right) Linear relationship between peak height and scan rate for the PB film.
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