

Diagnostic of functionality of polymer membrane – based ion selective electrodes by impedance spectroscopy

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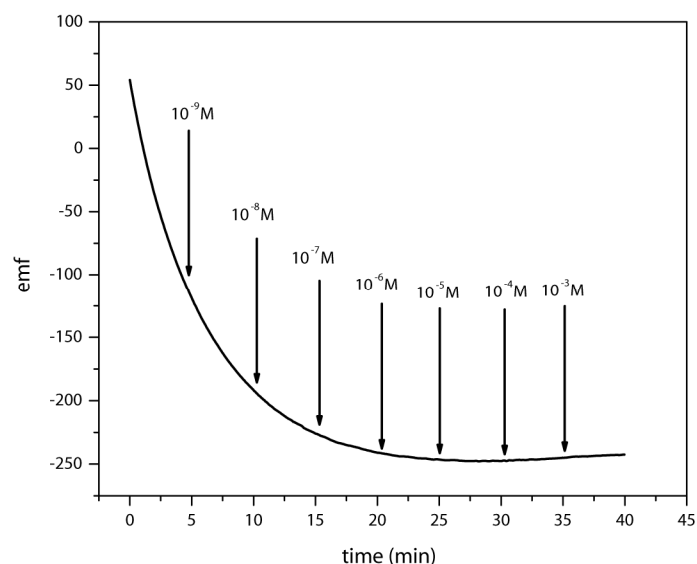


Figure S1. Response of LCISE upon inflicting a slight physical damage on the membrane. Arrows point at the addition of aliquots of standard solution to make the noted sample concentration.

Water layer test

The electrodes were first immersed in a solution of 10^{-3} M $\text{Pb}(\text{NO}_3)_2$ and the potential was followed to stabilize for four hours. The electrodes were then transferred in 10^{-3} M NaCl and the potential monitored overnight. The electrodes were then re-immersed in 10^{-3} M $\text{Pb}(\text{NO}_3)_2$ and the potential was monitored for a further four hours. It should be noted that pH of 10^{-3} M $\text{Pb}(\text{NO}_3)_2$ and 10^{-3} M NaCl solutions were 4.6 and 7.2. Considering selectivity coefficients of Pb IV ionophore to Na^+ and H^+ of $K_{\text{Pb.Na}}^{\text{Pot}} = -6.3$ and $K_{\text{Pb.H}}^{\text{Pot}} = -6.3$ respectively, effect of pH of the used solutions is negligible.

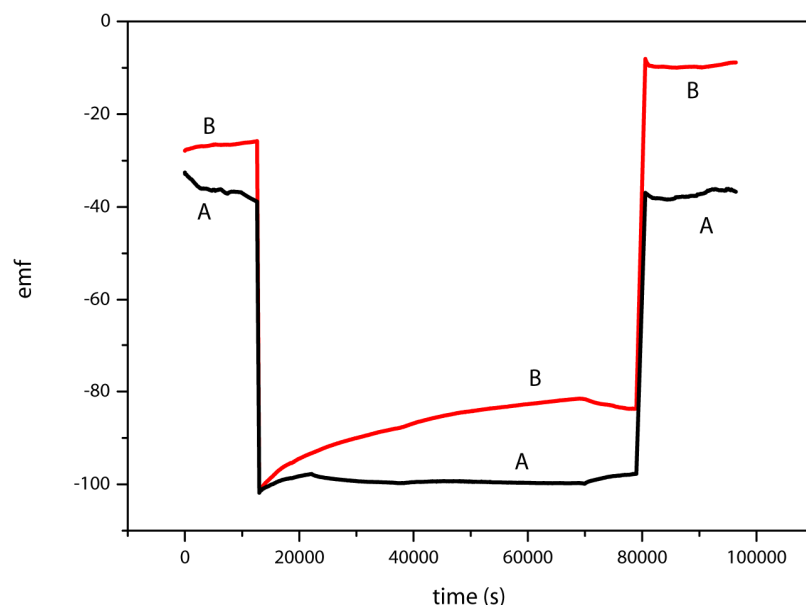


Figure S2. Responses of electrodes A (POT-based) and B (without conductive polymer) while testing for the presence of water layer between the ion-selective membrane and solid support. Strong drifts in the case of electrode B indicate the existence of the water layer.

Calculation of theoretically expected limit of detection

Equation used for predicting limit of detection (LOD) is developed elsewhere.¹

$$\log a_{\text{pb,EDL}} = \left(\frac{1}{3}\right) \log \left[K_{\text{pb,H}}^{\text{pot}} \left(\frac{a_{\text{H}} q R_{\text{T}}}{2} \right)^2 \right] \quad (\text{SEq1})$$

Under these experimental conditions and assuming that ion fluxes originate only from ion exchange at the sample/membrane phase boundary, a detection limit of $a_{\text{pb}} = 6.3 \times 10^{-9} \text{ M}$ was predicted, using the following values;

selectivity coefficient for protons $\log K_{\text{pb,H}}^{\text{pot}} = -3.5$ ¹, R_{T} (the total amount of ionic sites in the membrane) = 0.005 mol/kg, pH = 4.0 (proton activity of $a_{\text{H}} = 1 \times 10^{-4} \text{ M}$) and $q = 0.0001$,
 The parameter q is expressed as:

$$q = \frac{D_{\text{org}} \delta_{\text{aq}}}{D_{\text{aq}} \delta_{\text{org}}} \quad (\text{SEq2})$$

where D and d are the diffusion coefficients and diffusion layer thicknesses of the organic (org) and aqueous (aq) phases, respectively. The parameter q was estimated using the diffusion coefficient of lead in water ($1.35 \times 10^{-5} \text{ cm}^2/\text{s}$)², the diffusion coefficient of primary ion-ionophore complex in the membrane ($1 \times 10^{-8} \text{ cm}^2/\text{s}$)³ and a ten-fold smaller thicknesses of the aqueous compared to organic layer, which is a reasonable assumption based on a fast stirring rate⁴.

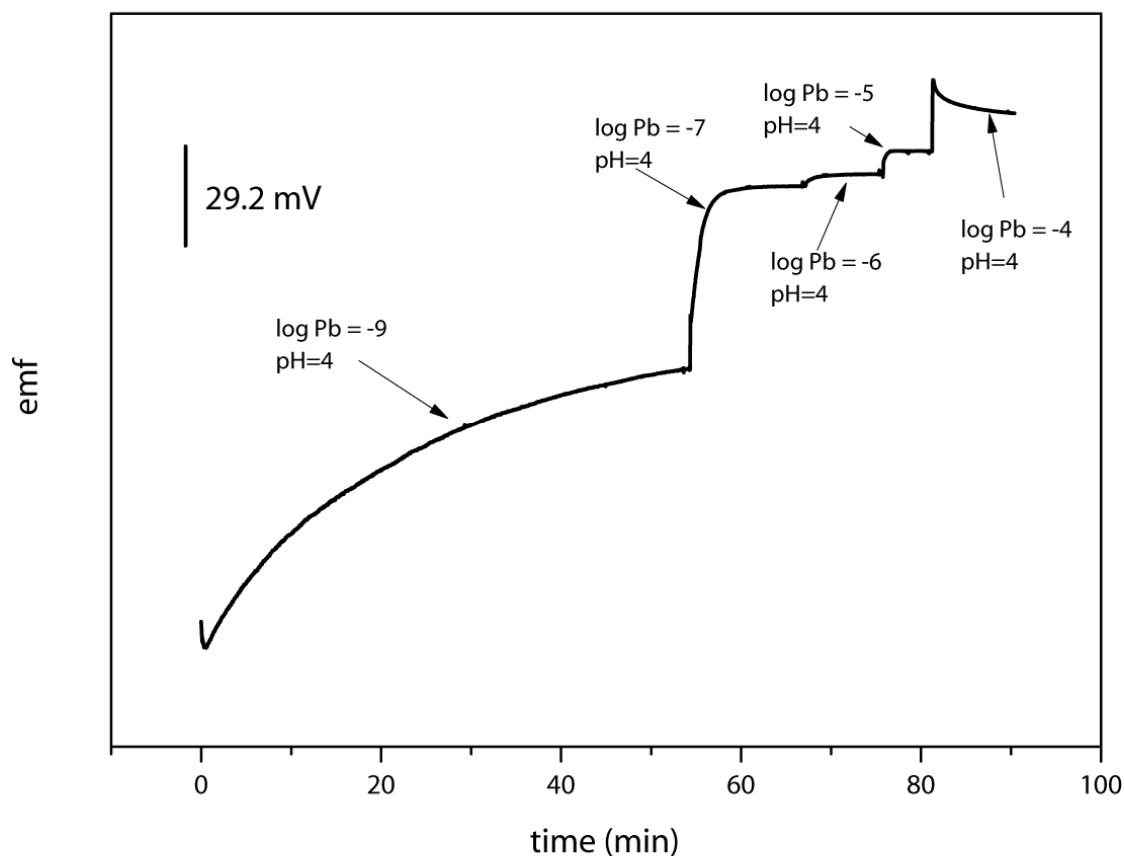


Figure S3. Time traces of Pb²⁺-selective electrode exposed to bacteria-rich water for four days (electrode #8 from Table 1 in main document).

LITERATURE

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- (2) Valente, A. J. M.; Ribeiro, A. C. F.; Lobo, V. M. M.; Jimenez, A. *Journal of Molecular Liquids* **2004**, *111*, 33-38.
- (3) Puntener, M.; Fibbioli, M.; Bakker, E.; Pretsch, E. *Electroanalysis* **2002**, *14*, 1329-1338.
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