Influence of real-life conditions on response of miniature, solid-state ion-selective sensors

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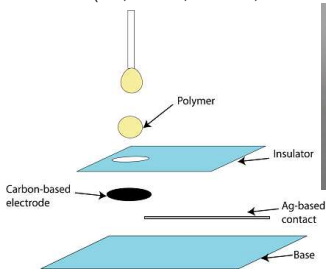
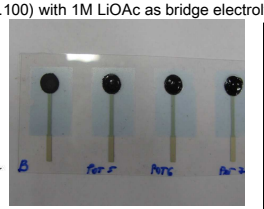
OVERVIEW: Electrochemical impedance spectroscopy (EIS) is a powerful tool for the analysis of various electrochemical systems because it allows the separation and characterization of individual kinetic processes. In this paper we describe our work on monitoring the condition of solid-state ISE membranes to determine whether they are ideally functioning, physically damaged, biofouled, have lost components (ionic sites, ionophore, plastisizer) through leaching, or whether there is an internal interfacial water layer present; all using EIS as a diagnostic tool. More investigations will answer to what extent we can evaluate the functionality (damaged, fouled, components leached out – "good" or "bad") of these sensors using a simple electric signal. This will be a vital tool for probing the condition of remotely deployed ISEs in widely distributed chemo-sensor networks (e.g. for environmental monitoring) and for enhancing the reliability of these devices, and thereby simplifying the way in which they are used. Our ultimate goal is to implement such tools so that ISEs can be deployed for weeks or months with minimal calibration or maintenance (ideally none or only at intervals detected by the sensor condition monitoring tools).

Development of "solid contact" ISEs

Potentiometric measurements were performed at room temperature (21^{0}C) using a custom-made 4-channel electrode monitor. EMF measurements were conducted in stirring solutions using a Metrohm 728 stir plate and taken against a double junction Ag/AgCl reference electrode (IFS, 3M KCl, Metrohm, 6.0729.100) with 1M LiOAc as bridge electrolyte.



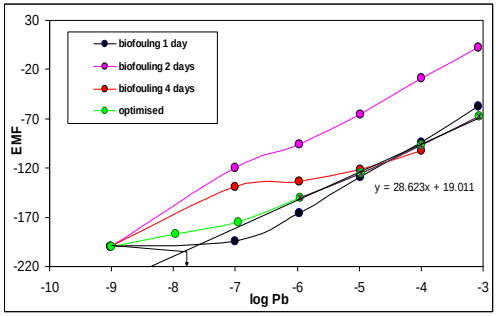


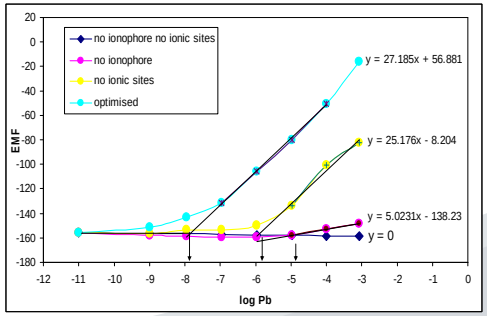
Drop-cast ISE membrane on top of a POT layer (~0.60 mm) thick

Experimental data

I. Potentiometrical measurements

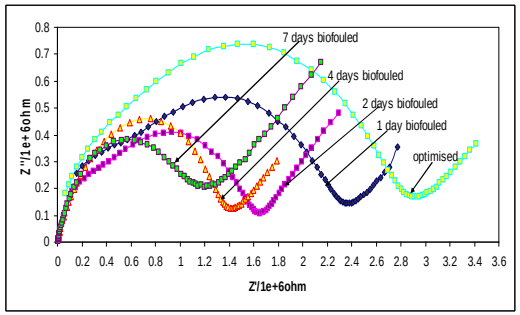
Biofouled ISEs - exposed 1,2,4,7 days to samples from the River Tolka showed a gradual decrease in resistance (diameter of semicircle was reducing) while potentiometrically we observed a gradual loss of signal until in the case of 4 days of exposure, we saw big drifts and loss of Nerstian slope.



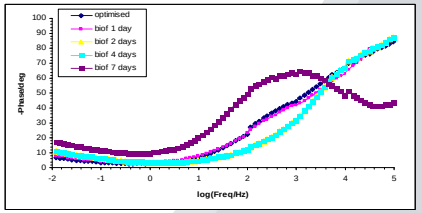


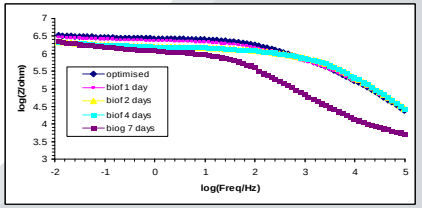
II. EIS measurements

BIOFOULED SAMPLES



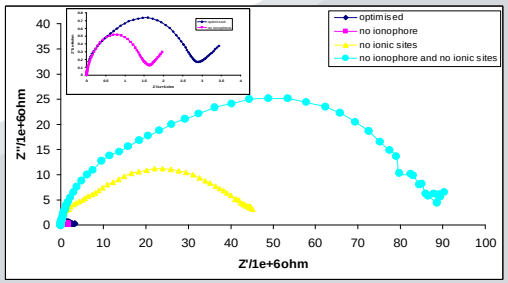
BIOFOULED SAMPLES





	membrane resistance Rb, MΩ	geometric capacitance Cg, nF
no ionophore	1.6	1.6
no ionic sites	60-70	0.7-0.8
no ionic sites no ionophore	88-93	1.1-1.4
no ionophore	1.6	1.6
optimised	2.9	0.5
biofouled	1d - 2.4; 2d - 1.7; 4d - 1.4; 7d - 1.2	0.4

SAMPLES WITHOUT SOME OF THE COMPONENTS



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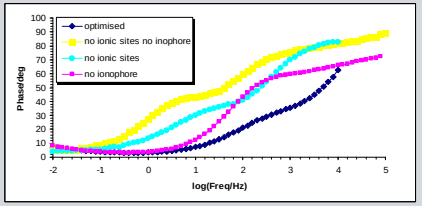

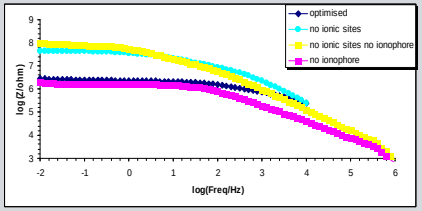

Conclusions: The effect of biofouling, physical damage and leaching of components on the characteristics of ISEs was investigated. This particular set of conditions was chosen due to the likelihood of their occurrence in real-life conditions. ISEs were tested both potentiometrically and using EIS and results were compared. Preliminary data indicate excellent potential of using electrical signals for probing the state of ISEs therefore reducing the need for their calibration. A simple construction, good detection limit, simple experimental setup coupled with miniaturization opportunities arising from the solid-state format make ISEs an excellent prospect for integration in autonomous devices and ultimately their integration in large wireless sensing networks.

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