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Flexible pH sensor based on layer-by-layer assembled iridium oxide nanoparticles

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1. Introduction

The pH sensor is one of the most commonly used tools in the research and industry since many of chemical and biological reactions are pH dependent. In the recent years aim is focused on the development of miniaturised, cost-effective sensors for usage in the environmental, biomedical, clinical or food monitoring applications in which standard pH sensors can not be easily employed. The objective of the present work was to fabricate small, flexible, potentiometric pH sensor based on biocompatible iridium oxide nanoparticles (IrOx). The sensor was fabricated using the simple layer-by-layer (LbL) deposition technique, where alternate layers of the oppositely charged iridium oxide nanoparticles and the poly(diallyldimethylammonium chloride) (PDDA) polymer were deposited on the flexible indium tin oxide foil (ITO/PET).

2. Experimental part & Results

1) Synthesis of the iridium oxide nanoparticles

Figure 1. Synthesis of the citrate-stabilized IrOx nanoparticles, following the method by Mallouk and co-workers.[3]

pH sensitivity of IrOx nanoparticles

$$Ir_2O_3 + 6H^+ + 6e^- \leftrightarrow 2Ir + 3H_2O$$

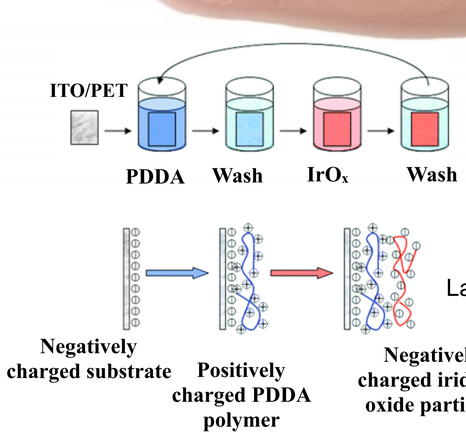
$$IrO_2 + 4H^+ + 4e^- \leftrightarrow Ir + 2H_2O$$

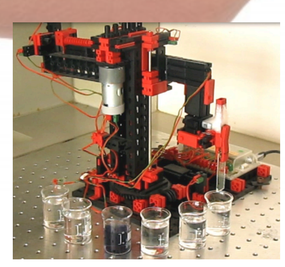
$$2IrO_2 + 2H^+ + 2e^- \leftrightarrow Ir_2O_3 + H_2O$$

and the redox potential is determined by

$$E = E^0 - 2.303\frac{RT}{F}pH = E^0 - 0.05916\ pH$$

2) Layer-by-layer deposition (electrostatic approach)





Layer-by-layer deposition controlled by a custom-made robot

3) Electrochemical characterisation of pH electrodes

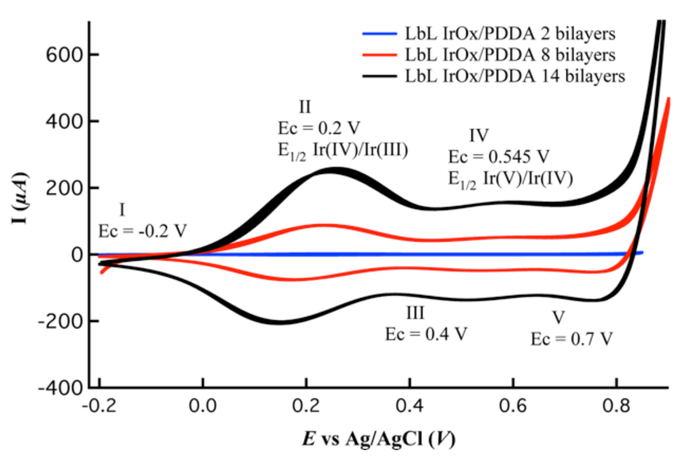
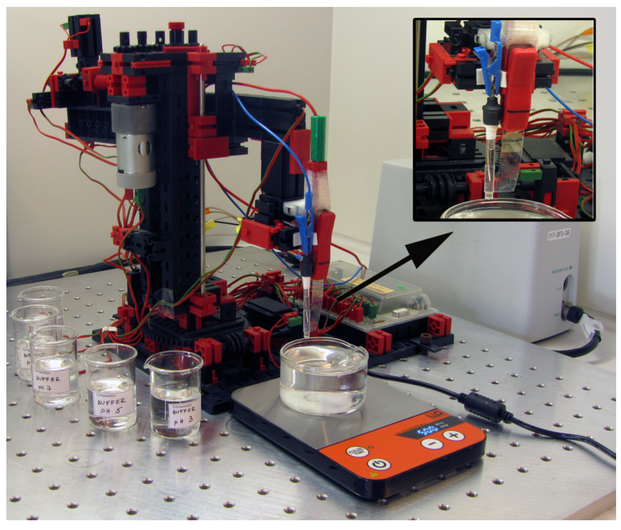


Figure. Cyclic voltammogram of layer-by-layer prepared IrO_x electrodes with 2, 8 and 14 bilayers. Scan rate 10 mV s^{-1}. pH electrode size 1 cm^2, phosphate buffer, pH 7.

4) pH measurement



Picture. Calibration of LbL prepared IrO_x electrode by measuring the open-circuit potential (OCP) as a function of the pH response of different buffer solutions against the conventional Ag/AgCl (3 M KCl) reference electrode. Inset plot: arm holder with positioned pH electrode and reference electrode.

5) Calibration curve for 14-bilayer pH electrode

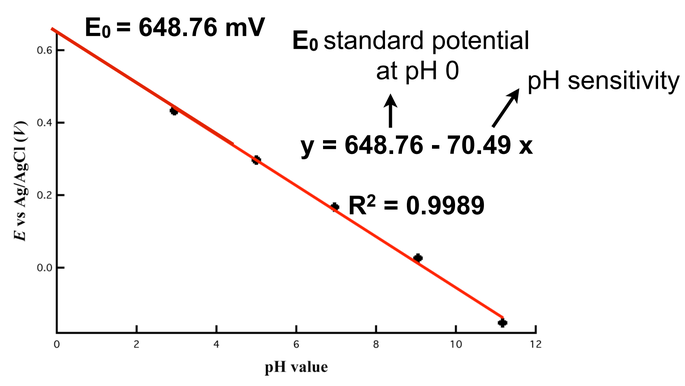


Figure. Potential - pH dependence of the 14-bilayer IrO_x electrode. Error bars represent the standard deviation for five measurements.

Table. Influence of the number of bilayers on the pH sensitivity

N⁰ of bilayers	Slope (mV/pH)	E⁰ (mV)*	R²	Drift (mV)
2 bilayers	72.63	779.93	0.9996	1.83 – 38.33
8 bilayers	67.89	621.19	0.9988	0.67 – 12.08
14 bilayers	70.49	648.74	0.9989	0.01 – 5.89

E^0 – Offset value of potential at pH 0

6) Electrode preconditioning

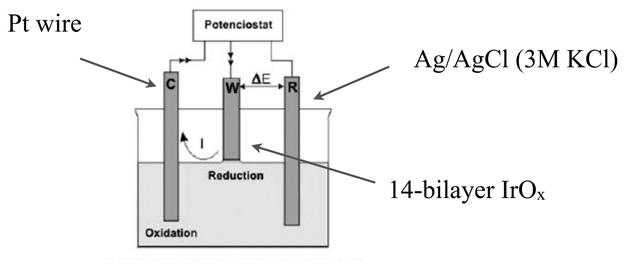


Table. pH properties of 14-bilayer IrO_x electrode as a function of preconditioning potential (E_c).

N⁰ of bilayers	E_c (V)	Slope (mV/pH)	E⁰ (mV)	R²	Drift (mV)
14 bilayers	- 0.2	47.37	282.09	0.9957	6.85 – 61.59
14 bilayers	0.2	74.20	711.78	0.9993	0.7 – 2.14
14 bilayers	0.45	78.74	928.75	0.9992	2.68 – 22.89
14 bilayers	0.545	80.24	1016.60	0.9993	3.94 – 33.26
14 bilayers	0.7	82.01	1130.40	0.9991	5.1 – 46.69

7) Reproducibility of the pH electrode

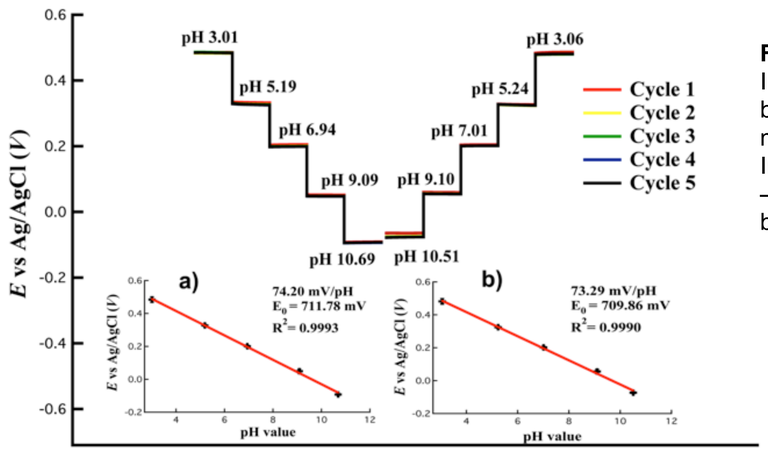
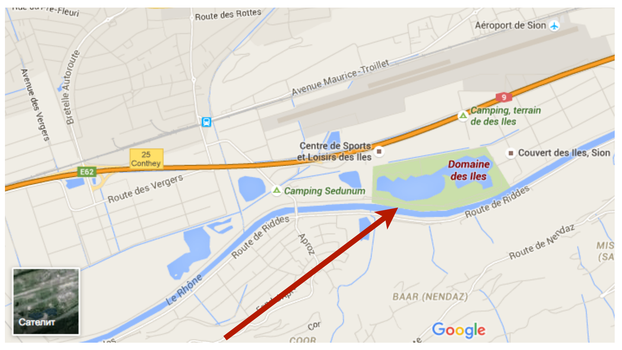


Figure. Reproducibility of the 14-bilayer IrO_x electrode for acid-to-base and base-to-acid direction of pH measurement in five cycles. Inset plots represent average potential – pH dependence plots for a) acid-to-base and b) base-to-acid direction.

Resolution = Unit/Sensitivity
R = 1/74 mV
± 0.01

8) Measurement of the environmental samples



Lake water sample taken from the surface of Des Iles Lake (Sion, Switzerland), on 21.09.2015.

Tap water sample taken from the municipal water supply of Sion on 21.09.2015.

Sample	Glass electrode	14-bilayer IrO_x coated with Nafion
Tap water	7.50 ± 0.01	7.67 ± 0.02
Lake water	6.85 ± 0.02	6.97 ± 0.07

3. Conclusions & Perspectives

We showed that layer-by-layer methodology represents a flexible, reproducible and scalable approach that could be successfully utilised for the fabrication of the iridium oxide-based pH sensors. After optimisation of the different parameters, such as number of layers and preconditioning potentials, the obtained sensor showed extraordinary stability in the tested pH range, excellent reproducibility (R2 = 0.999) and sensitivity of 74 mV/pH (14-bilayer). The implementation into the Envirobot platform where it will be used as portable pH sensor for on-field environmental monitoring is in the progress. Furthermore, the insights gained in this study will serve as the basis for development of methodology for preparing large-scale pH sensors using the ink-jet printing technology.

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References

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2. Prats-Alfonso, E; Abad, L.; Casan-Pastor, N.; Gonzalo-Ruiz, J.; Bardlich, E. Biosensor and Bioelectronics (2013) 39, 163-169.
3. Hara, M.; Mallouk, T. E.; Chem Comm. (2000) 1903-1904.

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