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 miniaturized, 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

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

Figure 2. Schematic of layer-by-layer deposition controlled by a custom-made robot.

3) Electrochemical characterisation of pH electrodes

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

<table>
<thead>
<tr>
<th>N° of bilayers</th>
<th>Slope (mV/pH)</th>
<th>R²</th>
<th>E° (mV)</th>
<th>R (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-48.53</td>
<td>0.9999</td>
<td>680.84</td>
<td>31.42</td>
</tr>
<tr>
<td>4</td>
<td>-48.53</td>
<td>0.9999</td>
<td>680.84</td>
<td>31.42</td>
</tr>
<tr>
<td>6</td>
<td>-48.53</td>
<td>0.9999</td>
<td>680.84</td>
<td>31.42</td>
</tr>
<tr>
<td>8</td>
<td>-48.53</td>
<td>0.9999</td>
<td>680.84</td>
<td>31.42</td>
</tr>
<tr>
<td>14</td>
<td>-48.53</td>
<td>0.9999</td>
<td>680.84</td>
<td>31.42</td>
</tr>
</tbody>
</table>

Figure. Cyclic voltammogram of layer-by-layer prepared IrOx electrodes with 2, 8 and 14 bilayers. Scan rate 10 mV s⁻¹, pH electrode size 1 cm², phosphate buffer, pH 7.

4) pH measurement

Figure. Calibration curve for 14-bilayer pH electrode.

5) Calibration curve for 14-bilayer pH electrode

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

Table. pH properties of 14-bilayer IrOx electrode as a function of preconditioning potential (E0).

<table>
<thead>
<tr>
<th>E0 (mV)</th>
<th>pH properties of 14-bilayer IrOx electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>648.76</td>
<td>Standard potential at pH 0</td>
</tr>
<tr>
<td>648.76</td>
<td>y = 648.76 - 70.49 x</td>
</tr>
<tr>
<td>R²</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

Resolution = Unit/Sensitivity

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 = 0.9999) and sensitivity of 74 mV/pH (14-bilayer). The implementation into the Environrobot 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.

References