Tunable nanopores: Resistive pulses and current rectification

This item was submitted to Loughborough University's Institutional Repository by the/an author.


Additional Information:

- This is a conference presentation.

Metadata Record: https://dspace.lboro.ac.uk/2134/22459

Version: Submitted for publication

Publisher: University of Leicester

Rights: This work is made available according to the conditions of the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) licence. Full details of this licence are available at: https://creativecommons.org/licenses/by-nc-nd/4.0/

Please cite the published version.
Dr Mark Platt
Tunable Nanopores: Resistive Pulses and Current Rectification
ELECTROCHEM 2016

SENIOR LECTURER
ANALYTICAL SCIENCE
LOUGHBOROUGH UNIVERSITY

m.platt@lboro.ac.uk
@Plattlb
Markplatt.yolasite.com
1. Overview of qNano - Tunable Resistive Pulse Sensors

2. Current Rectification (ICR) properties of Polyurethane Pores
   a) Modification of their surfaces with polymers.

3. Aptamer Modified Pore Walls

4. Compare Data from ICR to Resistive Pulse Sensor (RPS)

5. Combining ICR and RPS to detect Cu ions
Equipment and Pore size

- **TRPS**
- Detect 50 nm → 6 μm particles
- Thickness ~ 250 μm
- Zeta potential of ~ 8mV in PBS pH 7
- Zeta Potential Measurements
- Characterisation of virus, bacteria, nanomaterials, protein corona, bioassays

- **e.g.** NP200
  110 nm – 400nm
Current Rectification

**Negative Pore, and a Negative Bias within the Pore**

- The cations migrating from the electrolyte outside the pore in the opposite direction are free to traverse the pore opening.
- The anions are unable to approach the tip due to the migration of cations.
- A region of locally high KCl concentration builds up just inside the pore (compared to the bulk concentration).
- Increase in conductivity

\[
\text{Use the ratio } \frac{i_{-1.6v}}{i_{+1.6v}}
\]

Layer-by-Layer approach

<table>
<thead>
<tr>
<th>[KCl] mM</th>
<th>Unmodified Pore</th>
<th>PEI - Layer 1</th>
<th>PAAMA - Layer 1</th>
<th>PEI - Layer 2</th>
<th>PAAMA - Layer 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.38</td>
<td>0.46</td>
<td>2.41</td>
<td>0.37</td>
<td>2.86</td>
</tr>
<tr>
<td>10</td>
<td>1.09</td>
<td>0.67</td>
<td>1.69</td>
<td>0.29</td>
<td>2.44</td>
</tr>
<tr>
<td>50</td>
<td>1.09</td>
<td>0.90</td>
<td>1.10</td>
<td>0.73</td>
<td>2.09</td>
</tr>
<tr>
<td>PBS (pH 7.4)</td>
<td>1.15</td>
<td>0.81</td>
<td>1.10</td>
<td>0.93</td>
<td>1.29</td>
</tr>
</tbody>
</table>
Effects of Stretch and pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Unmodified Pore</th>
<th>PEI - Layer 2</th>
<th>PAAMA - Layer 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.83</td>
<td>0.31</td>
<td>0.83</td>
</tr>
<tr>
<td>7</td>
<td>1.40</td>
<td>0.52</td>
<td>1.98</td>
</tr>
</tbody>
</table>
DNA modified Pore walls

50 mM KCl

10 mM KCl
DNA modified Pore walls

5 mM KCl, pH 7
DNA modified Pore walls

![Graph showing current (nA) vs voltage (V) for different concentrations of VEGF, DNA, and BSA.]

<table>
<thead>
<tr>
<th>Concentration of VEGF</th>
<th>Rectification ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 pM</td>
<td>1.36</td>
</tr>
<tr>
<td>50 pM</td>
<td>1.93</td>
</tr>
<tr>
<td>0.5 nM</td>
<td>3.64</td>
</tr>
<tr>
<td>5 nM</td>
<td>11.60</td>
</tr>
<tr>
<td>50 nM</td>
<td>10.12</td>
</tr>
<tr>
<td>DNA</td>
<td>1.33</td>
</tr>
<tr>
<td>BSA</td>
<td>1.53</td>
</tr>
</tbody>
</table>
Resistive Pulse Sensing

\[ \Delta i_p = \text{Particle volume} \]

\[ J = \text{Pulse Frequency/ Rate (particles/unit time)} \]

\[ J = C \left( D + \frac{\varepsilon (\zeta_{\text{particle}} - \zeta_{\text{pore}})}{\eta} E \right) D_p + \Delta P \]

Duration = Particle velocity \sim zeta potential

Analytical Methods (2015)7, 8534-8538
Biosensors and Bioelectronics (2015) 68, 741
Analytical Chemistry (2014) 86 (2) pp1030-1037
Comparison between RPS and ICR

<table>
<thead>
<tr>
<th>Concentration of VEGF</th>
<th>Rectification ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 pM</td>
<td>1.36</td>
</tr>
<tr>
<td>50 pM</td>
<td>1.93</td>
</tr>
<tr>
<td>0.5 nM</td>
<td>3.64</td>
</tr>
<tr>
<td>5 nM</td>
<td>11.60</td>
</tr>
<tr>
<td>50 nM</td>
<td>10.12</td>
</tr>
<tr>
<td>DNA</td>
<td>1.33</td>
</tr>
<tr>
<td>BSA</td>
<td>1.53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ICR</th>
<th>RPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Easy to run</td>
<td>Easy to multiplex</td>
</tr>
<tr>
<td>Comparable sensitivities</td>
<td>Comparable sensitivities</td>
</tr>
</tbody>
</table>
Detection of Metal ions

pH 7

pH 5

pH 3

Relative Particle Speed (μm/ms)

KCl Concentration (mM)

Δ Silica-APTES-Cu

● Si-APTES
Selectivity and sensitivity

Complimentary ICP data
Velocity of particles of varying surface chemistry

- pH 7
- pH 5
- pH 3

The graph shows the relative particle speed (1/ms) as a function of pH (3, 5, 7). The graph indicates a decrease in particle speed with increasing pH, with the label 'Si-APTES-Cu' indicating a different behavior or condition compared to 'Si-APTES'.
White and coworkers showed that a negatively charged particle passing through a pore with a negative surface charge can create a conductive pulse prior to the resistive pulse at a negative polarity.

\[ \text{Negative Particle} + \text{Negative Pore} + \text{negative potential} = \text{Conductive and Resistive Pulse} \]

Conductive Pulse waves

- **Conductive pulse** = An indication of the Double layer Structure?
- **Resistive pulse** = Velocity data to confirm the Metal?
Double signal showing Cu binding

**pH 7**

- **Conductive**
- **Resistive**

**pH 3**

- **Conductive**
- **Resistive**
Summary and conclusions

1. Introduction to TRPS

2. LBL assembly on PU pores gives a pH, IRC.

3. DNA/ aptamer functionalised pore walls

4. Compare Data from ICR to Restive Pulse Sensor (RPS)

5. Conductive and Resistive pulses give a dual signal for metal ion detection
Acknowledgements

Group
Graduate Students;
Emily Billinge
Emma Blundell
Laura Mayne
Suchanuch Sachdev
Sarah Hampson
Chen Hu
Matthew Healey
Research Associate
William Rowe

Project students
Michael Lickorish
Rhushabh Maugi

Collaborators
Dr S. Christie (Chemistry)
Dr S Mastana, School of Sport, Exercise and Health Sciences
Prof R Harris (Additive Manufacturing Research Group)
Prof A Tok - Nanyang Technological University
Dr M Sivakumaran - Peterborough City Hospital
Dr R Vogel - The University of Queensland
Mr H van der Voorn, Dr Murray Broom - Izon Science Ltd
Prof Ewa Stepien - Jagiellonian University – Poland
Prof Paula Vanninen - University of Helsinki, Finland

@Plattlb
http://markplatt.yolasite.com/

Thank You