Electronic Supplementary Material (ESI) for Faraday Discussions.


# Functionalised Microscale Nanoband Edge Electrode (MNEE) Arrays; the systematic quantitative study of hydrogels grown on nanoelectrode biosensor arrays for enhanced sensing in biological media

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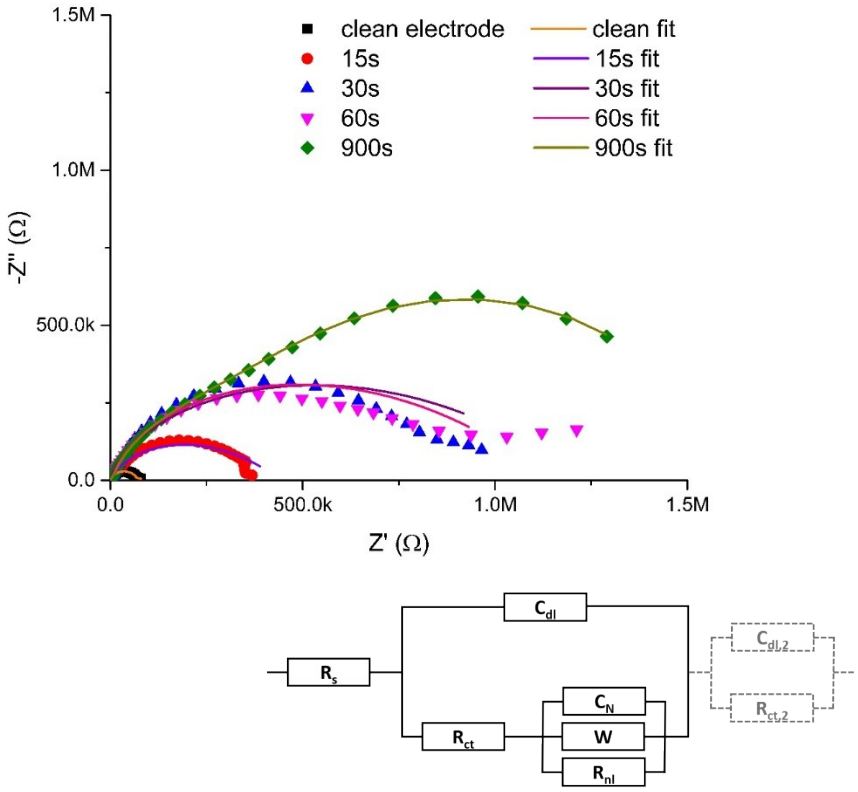



**Figure S1** Nyquist plots of the EIS data obtained from hydrogel grown for different time periods on a 30 µm 3D MNEE array and the corresponding circuit fits to the equivalent circuit shown. The experimental (point) and corresponding fits (solid lines of the same colour) are shown. The fitted values can be found in table S1.

**Table S1** Fitted circuit element values and the associated error in each fit for hydrogels grown for different time periods on a 30 µm 3D MNEE array. Unless otherwise stated the gels were grown at 100 µA.

| Parameter | Hydrogel Growth Time (s) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **0** | **5** | **10** | **15** | **20** | **30** | **60** | **900** | **15 (50µA)** |
| $R_s$ (Ω) | 173 ± 9 | 164 ± 3 | 170 ± 6 | 179 ± 45 | 163 ± 21 | 178 ± 17 | 173 ± 32 | 176 ± 17 | 158 ± 17 |
| $C_{dl}$ (nF) | 21.3 ± 0.5 | 21.9 ± 0.3 | 23.0 ± 0.3 | 19.1 ± 0.3 | 18.4 ± 0.6 | 59.6 ± 8.9 | 23.4 ± 0.8 | 40.2 ± 10.2 | 12.7 ± 0.4 |
| $R_{ct}$ (kΩ) | 15.7 ± 0.3 | 14.5 ± 1.5 | 19.9 ± 1.7 | 14.9 ± 0.7 | 22.1 ± 1.8 | 16.0 ± 5.8 | 18.8 ± 2.0 | 23.2 ± 8.6 | 18.0 ± 1.7 |
| $C_N$ (nF) | NA | 22.5 ± 0.3 | 15.6 ± 1.8 | 35.6 ± 1.9 | 21.3 ± 0.9 | 55.4 ± 10.4 | 23.1 ± 1.6 | 49.8 ± 7.9 | 22.7 ± 1.7 |
| $Y_o$ (nS) from W | 14400 ± 1772 | 513 ± 18 | 302 ± 29 | 428 ± 20 | 140 ± 9 | 192 ± 26 | 293 ± 16 | 490 ± 18 | 150 ± 2 |
| Calculated $D$ using $Y_o$ ($\times 10^{-6} cm^2 s^{-1}$) | 7.228 ± 0.89 | 0.258 ± 0.009 | 0.152 ± 0.015 | 0.215 ± 0.010 | 0.070 ± 0.005 | 0.096 ± 0.013 | 0.147 ± 0.008 | 0.246 ± 0.009 | 0.075 ± 0.001 |
| $R_{nl}$ (kΩ) | 9.0 ± 0.3 | 73 ± 1 | 101 ± 3 | 366 ± 4 | 1778 ± 67 | 737 ± 68 | 1030 ± 45 | 715 ± 40 | 1983 ± 128 |
| Calculated $D$ using $R_{nl}$ ($\times 10^{-6} cm^2 s^{-1}$) | 7.244 ± 0.241 | 0.893 ± 0.012 | 0.646 ± 0.019 | 0.161 ± 0.016 | 0.037 ± 0.001 | 0.089 ± 0.008 | 0.063 ± 0.003 | 0.091 ± 0.005 | 0.033 ± 0.002 |
| $C_{dl,\,2}$ (nF) | - | - | - | - | - | - | - | 938 ± 28 | - |
| $R_{ct,\,2}$ (kΩ) | - | - | - | - | - | - | - | 874 ± 23 | - |
| $\chi^2$ | 0.0651 | 0.0239 | 0.0561 | 0.0238 | 0.0792 | 0.0995 | 0.1560 | 0.0105 | 0.0463 |

The expression used to calculate $D$ from $Y_o$ was

$$D = \left(\frac{2RT\sqrt{2}.Y_0}{n^2F^2A\sqrt{2}\,c}\right)^2 \quad \text{(Equation S1)}$$

where $Y_0$ is the admittance at a frequency of 1 Radian $s^{-1}$, $D$ is the diffusion coefficient, $R$ is the universal gas constant, $T$ is the temperature, $n$ is the number of electrons being transferred, $F$ is Faradays constant, $A$ is the area of the electrode array and $c$ is the bulk concentration of the redox agent.

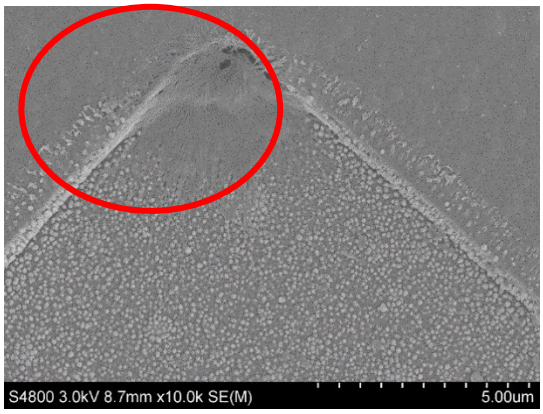
The expressions used to calculate $D$ from $R_{nl}$ were;

$$i_l = \frac{4RT}{FR_{nl}} \quad \text{(Equation S2)}$$

and

$$i_l = \frac{0.96nFDcL}{N} \quad \text{(Equation S3)}[1]$$

where $i_l$ is the limiting current, $R_{nl}$ is the resistance attributable to non-linear diffusion in the EIS fit, 0.96 is a correction factor previously reported for electrodes with this recessed architecture[13], $L$ is the edge length of a single square in the array and $N$ is the number of squares in the array.



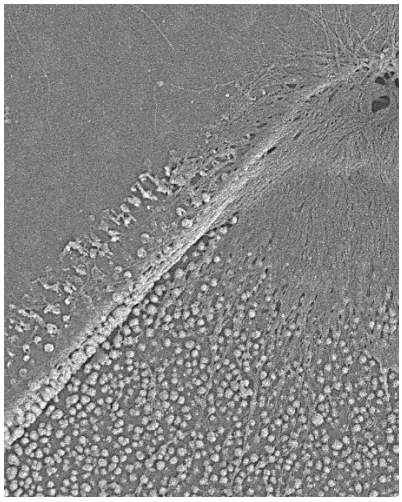



**Figure S2** Close up of the SEM image of 5 s growth at 100 µA on a 30 µm 3D MNEE array (region denoted by red circle in Figure 6a) to display the enhanced hydrogel growth in the corners of the cavity.

**Table S2** corresponding values to those in Table S1 for the fits in Figure 9a.

| **Parameter** | **Clean** | **PNA Probe** | **Hydrogel** | **DNA Target** |
|---|---|---|---|---|
| $R_s$ **(Ω)** | 233 ± 33 | 210 ± 21 | 233 ± 22 | 334 ± 103 |
| $C_{dl}$ **(nF)** | 71 ± 2 | 54 ± 1 | 54 ± 1 | 51 ± 1 |
| $R_{ct}$ **(Ω)** | 4349 ± 117 | 9988 ± 203 | 16650 ± 763 | 25991 ± 239 |
| $C_N$ **(nF)** | - | - | 427 ± 269 | 405 ± 71 |
| $Y_0$ **(nS), from W** | 17671 ± 1033 | 8376 ± 705 | 3376 ± 2437 | 3638 ± 753 |
| $R_{nl}$ **(kΩ)** | 7558 ± 122 | 6837 ± 184 | 10302 ± 902 | 10614 ± 616 |
| $\chi^2$ | 0.0369 | 0.0049 | 0.06475 | 0.044493 |