

Supplementary Materials

Effects of Monomer and Electrolyte Concentrations on Actuation of PPy(DBS) Bilayers

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1. Experimental

Table-SM 1. Experimental conditions. Headings indicate deposition solution concentrations, while numbers inside the table show the cycling conditions (current stimulation method, stimulation NaDBS concentration).

| | | NaDBS | | | | | | |
|---------|-------------|--------|------------|------------|------------|------------|------------|------------|
| | | Low | | Mid | | High | | |
| | | 0.01 M | 0.02 M | 0.04 M | 0.08 M | 0.16 M | 0.32 M | |
| Pyrrole | L o w | 0.01 M | 5 mC, 0.01 | 100%, 0.01 | 5 mC, 0.01 | 100%, 0.01 | 5 mC, 0.01 | 100%, 0.01 |
| | | 0.02 M | 5 mC, 0.08 | 100%, 0.32 | 5 mC, 0.08 | 100%, 0.32 | 5 mC, 0.08 | 100%, 0.32 |
| | M i d | 0.04 M | 5 mC, 0.04 | 100%, 0.04 | 5 mC, 0.04 | 100%, 0.04 | 5 mC, 0.04 | 100%, 0.04 |
| | | 0.08 M | 5 mC, 0.02 | 100%, 0.32 | 5 mC, 0.02 | 100%, 0.32 | 5 mC, 0.02 | 100%, 0.32 |
| | H i | 0.16 M | 5 mC, 0.16 | 100%, 0.16 | 5 mC, 0.16 | 100%, 0.16 | 5 mC, 0.16 | 100%, 0.16 |
| | | 0.32 M | 5 mC, 0.02 | 100%, 0.08 | 5 mC, 0.02 | 100%, 0.08 | 5 mC, 0.02 | 100%, 0.08 |

Duplicate samples were produced for several conditions, and not all combinations of deposition and stimulation conditions were employed. Some production conditions did not yield usable bilayers. In all, 17 samples were stimulated at 5 mC, and 19 were stimulated at 100% of charge capacity.

The PPy(DBS) sometimes grew around the edge of the bilayer and onto the back side of the Kapton. This was more prevalent at low total concentration levels. Bilayers with substantial backside growth were discarded.

2. Deposition Voltages

Fig.-SM 1 shows representative deposition chronovoltammograms as a function of pyrrole and NaDBS concentration, and Fig.-SM 2 shows the deposition potentials. The data in Fig.-SM 2 are averaged from all the samples.

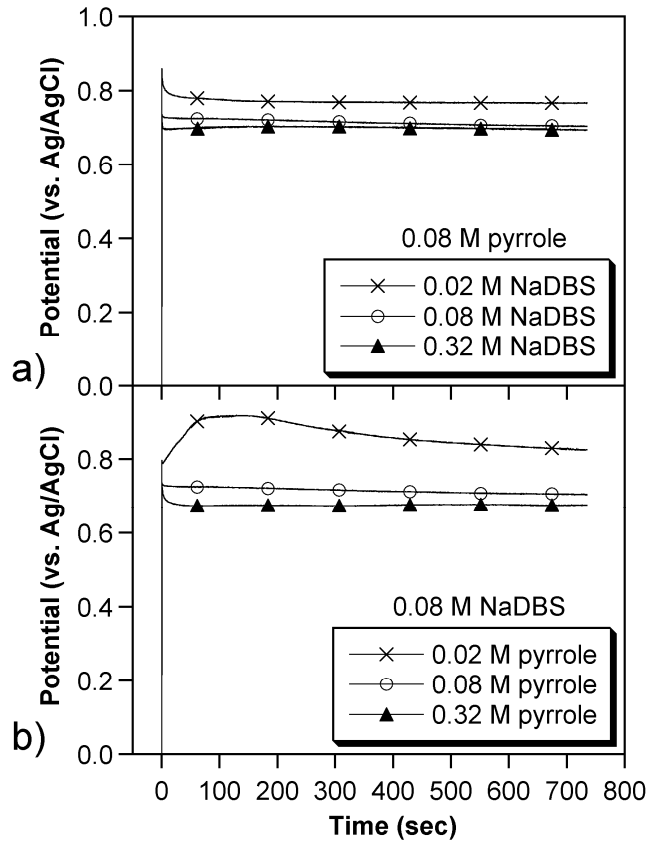


Fig.-SM 1. Typical deposition chronovoltammograms for different a) NaDBS and b) pyrrole concentrations, holding the other at medium (0.08M). Higher concentrations resulted in lower voltages in both cases.

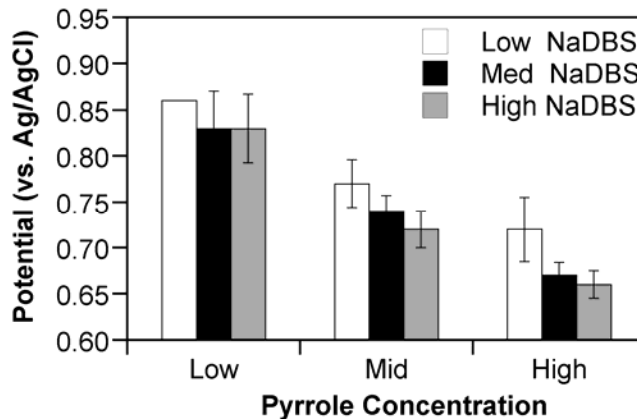


Fig.-SM 2. Effect of deposition solution concentrations on deposition potentials, averaging over all the data.

3. Cyclic Voltammograms



Fig.-SM 3. Cyclic voltammograms grouped by NaDBS concentration (columns), pyrrole concentration (rows), and stimulation NaDBS concentration (columns within columns). All y-axes are from -5 to 4 mA, and x-axes are from -1.5 to $+0.5$ V vs. Ag/AgCl. Labels on the lower right of each CV indicate the cycling NaDBS concentration, on the upper left the sample number.

4. Deposition Solution Concentrations

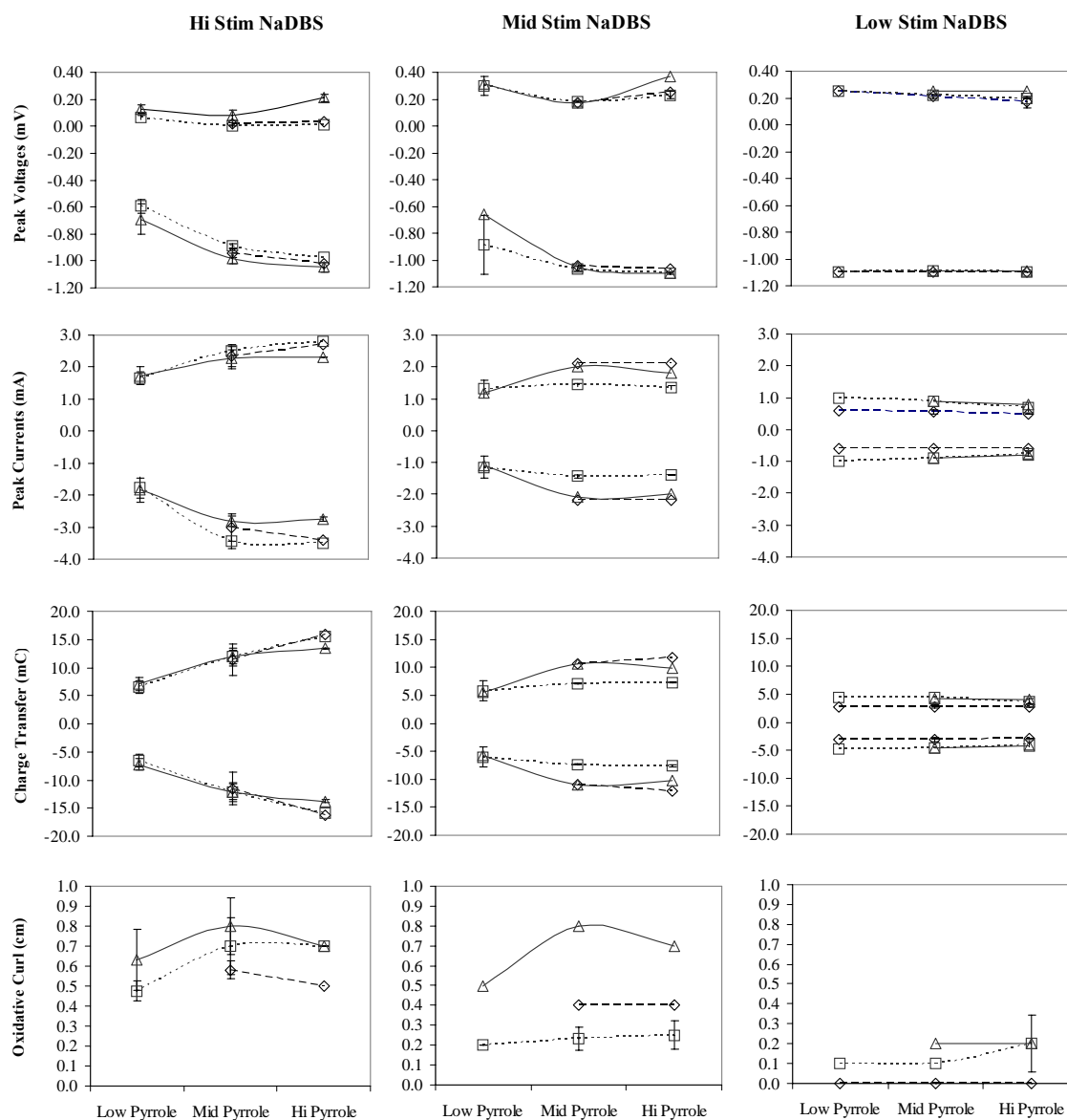


Fig.-SM 4. Peak voltages and currents, charge consumed, and bending movement during oxidation, by stimulation NaDBS concentration (the 3 columns of graphs), by deposition pyrrole concentration (the 3 columns within each graph), and by deposition NaDBS concentration (the 3 plots within each graph where Δ =high, \square =mid, and \diamond =low), for the 15th conditioning cycle.

The dependence of the cyclic voltammograms (CVs) on deposition NaDBS concentration is illustrated in Fig.-SM 5, and the CV metrics are summarized in Fig.-SM 6 (cycling electrolyte concentration was high in these figures because only these samples completely oxidized and reduced). High NaDBS concentrations in the deposition solution increased the hysteresis for all pyrrole concentrations (Fig.-SM 5), but this effect was small. Low and medium NaDBS concentrations resulted in similar CVs. The currents and charge exchanged were not affected by NaDBS concentration in the deposition solution (Fig.-SM 6).

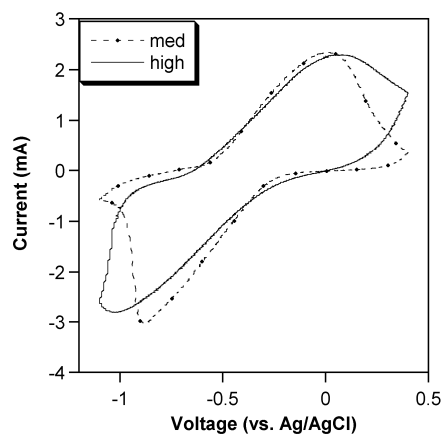


Fig.-SM 5. Cyclic voltammograms taken at 150 mV/sec in high concentration NaDBS electrolyte of PPy films grown in medium pyrrole concentration and medium and high NaDBS concentrations.

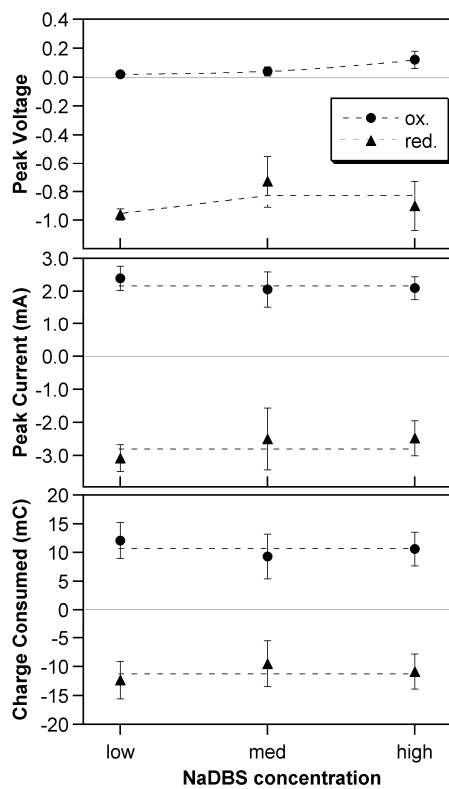


Fig.-SM 6. Peak voltages, peak currents, and charge exchanged during cyclic voltammetry in high NaDBS concentration electrolyte vs. NaDBS concentration during deposition. (Dashed lines are guides for the eye.)

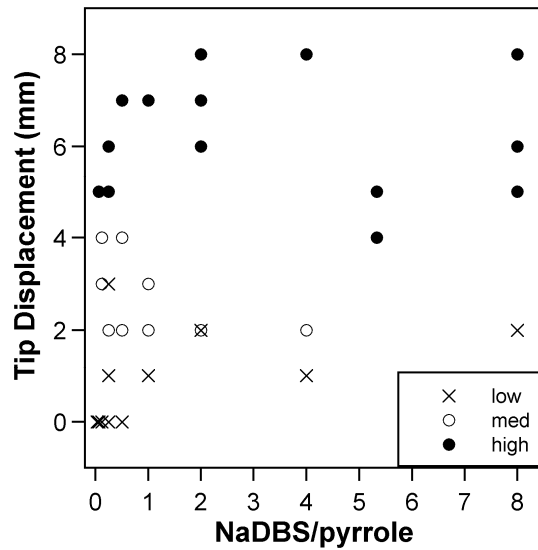


Fig.-SM 7. Movement as a function of the NaDBS to pyrrole ratio for different concentrations of cycling electrolyte concentration.

Movement to charge ratio is plotted in a 3D graph in Fig.-SM 8.

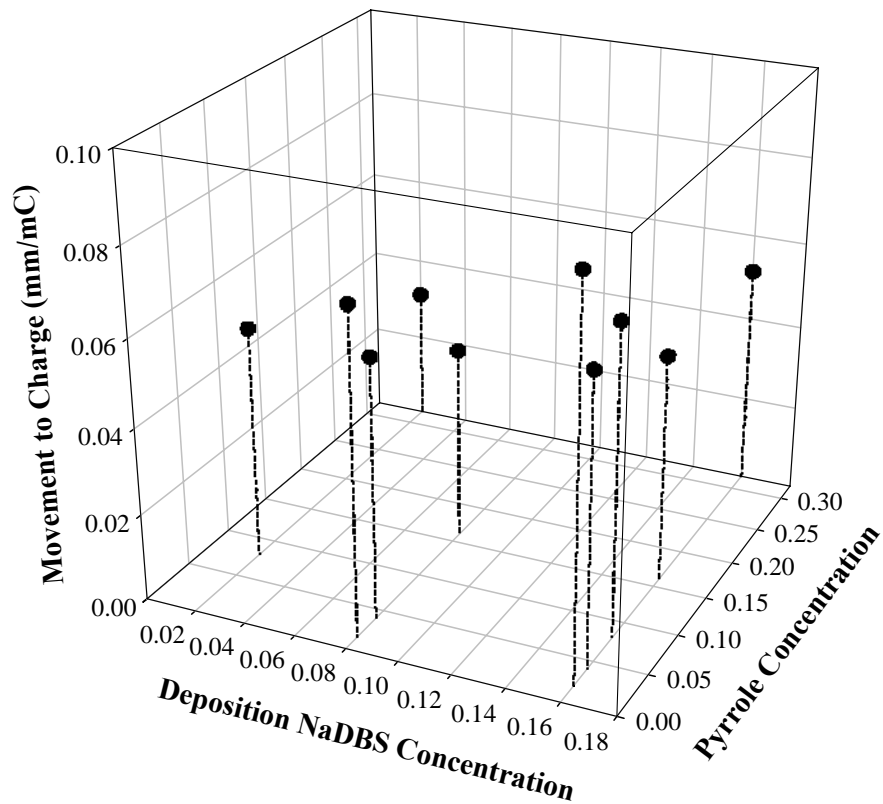


Fig.-SM 8. Movement to charge ratios as a function of pyrrole and deposition NaDBS concentrations (high NaDBS concentration in all cycling solutions).

In high NaDBS cycling concentration, there was a statistically significant average decrease in movement to charge ratio with pyrrole concentration, with this metric dropping by approximately 25% from low to mid pyrrole concentration and another 25% from mid to high (Fig.-SM 9).

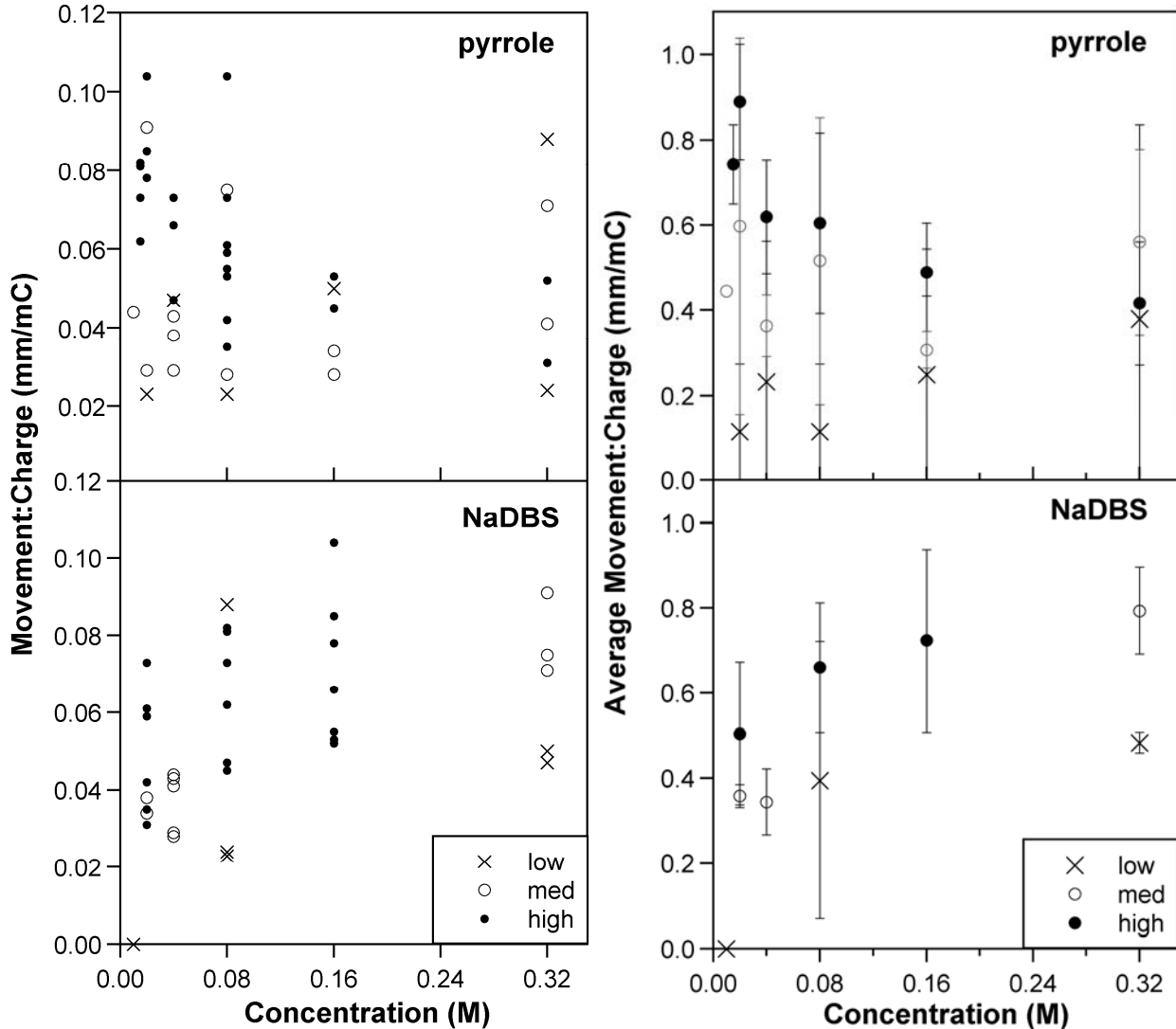


Fig.-SM 9. Movement to charge ratio (left) and average movement to charge ratio (right) as a function of deposition solution pyrrole and NaDBS concentrations, with different symbols representing different cycling NaDBS concentrations (x = low, o = med, and • = high)

5. Cycling Electrolyte Concentration

The oxidation peak positions are plotted vs. concentration in Fig.-SM 10; since the reduction peaks were outside the window of the cyclic voltammograms except in the high concentration range, these could not be plotted.

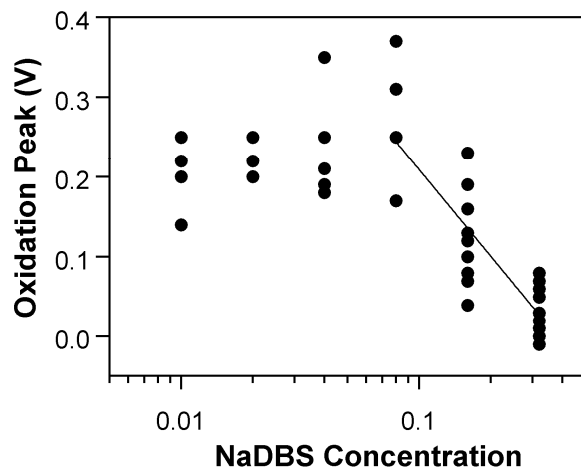


Fig.-SM 10. Oxidation peak potential as a function of NaDBS concentration in the cycling solution. A curve fit for the data ≥ 0.08 M gives a slope of approximately -360 mV/decade. Data points include all pyrrole and deposition NaDBS concentration combinations, neither of which had a clear systematic effect on the oxidation peak.

The peak shifts are *not* due to the Nernst equation, which relates the electrode potential to chemical concentrations [C] and the number of electrons in the reaction n : $E = E_o - \frac{RT}{nF} \ln[C]$, where $RT/F = 59$ mV at room temperature [58]. (The oxidation peak positions are plotted vs. concentration in Fig.-SM 6 of the Supplementary Materials.) The oxidation peak position was constant until 0.08 M NaDBS, and then it moved approximately -360 mV/decade. This would mean that approximately 6 Na^+ were involved per electron above 0.08 M, but none below that concentration, which does not make sense. The reduction peak was even more sensitive to concentration. The shifts were due to increasing resistance of the electrolyte and probably also mass transport limitations at low electrolyte concentrations.

The tip movement and charge exchanged are shown as a function of cycling electrolyte concentration in Fig.-SM 11. Predictably, based on **Error! Reference source not found.8**, which showed that only samples cycled in high concentration NaDBS underwent the full redox reaction, both were increasing functions of concentration. As expected, movement and charge exchanged were highly correlated. Many previous workers have found a linear relationship between charge exchanged and strain in individual devices, but this was not true *between* devices for these bilayers.

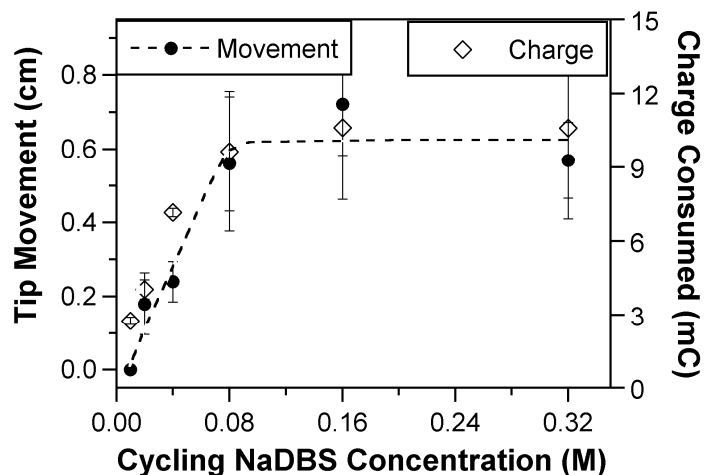


Fig.-SM 11. Effect of NaDBS concentration in cycling electrolyte on movement and charge (dashed line is a guide for the eye). Averages were taken over all samples.

There was also no correlation between movement to charge ratio and cycling NaDBS concentration during the conditioning cycles (Fig.-SM 12). There was, however, in the current stepping experiments, in which the total amount of charge exchanged was kept constant.

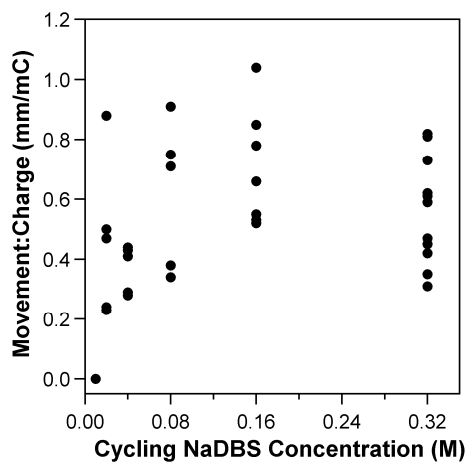


Fig.-SM 12. Movement to charge ratio as a function of cycling NaDBS concentration.

6. Voltage Stepping

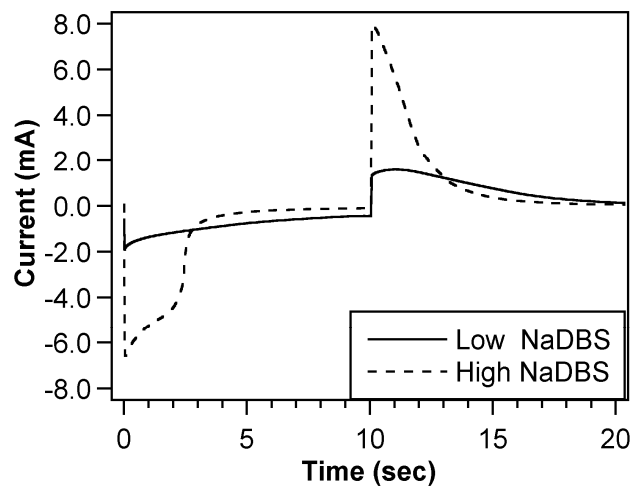


Fig.-SM 13. The effect of varying NaDBS concentration during stimulation (0.02 and 0.32 M). These samples were deposited in medium (0.08 M) pyrrole and NaDBS concentrations.