Voltage Regulated Uptake and Release of L-Glutamate from a Molecularly Selective Switch for Physiological Applications

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In this paper results are presented on the development of a device demonstrating the uptake and release of L-glutamate in solutions with neutral pH. A device which selectively regulates the concentration of biomolecules, such as the primary neural transmitter L-glutamate, could be useful for many biological and medical applications. In the literature it has been demonstrated that polypyrrole (PPy) is a promising material for the recognition basis of molecularly selective devices [1, 2]. In this study we investigated the feasibility of the PPy based "glutamate switch" for the voltage dependent uptake and release of L-glutamate for physiological applications.

Key words: Polypyrrole; Molecular Selective Polymer; L-Glutamate.

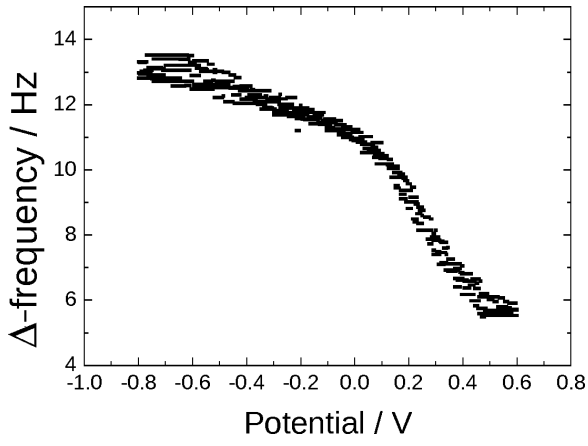

Fig. 2. Frequency vs. voltage characteristics of overoxidized PPy in a 0.1 M sodium L-glutamate solution with neutral pH phosphate buffer.

Glutamate doped PPy films were potentiostatically deposited on Au working electrodes in a 3-electrode cell using an aqueous solution containing sodium L-glutamate salt and the pyrrole monomer. Reproducible, smooth polymer films were achieved using optimized deposition parameters [3]. To create glutamate selective films, the PPy is galvanostatically overoxidized after deposition by electrically degrading the polymer using phosphate buffer solutions. During this process the glutamate ions are ejected from the polymer, while oxygen rich groups are incorporated into the polymer backbone forming cavities selective for L-glutamate [1]. The exact mechanism of the cavity formation is not understood in the literature.

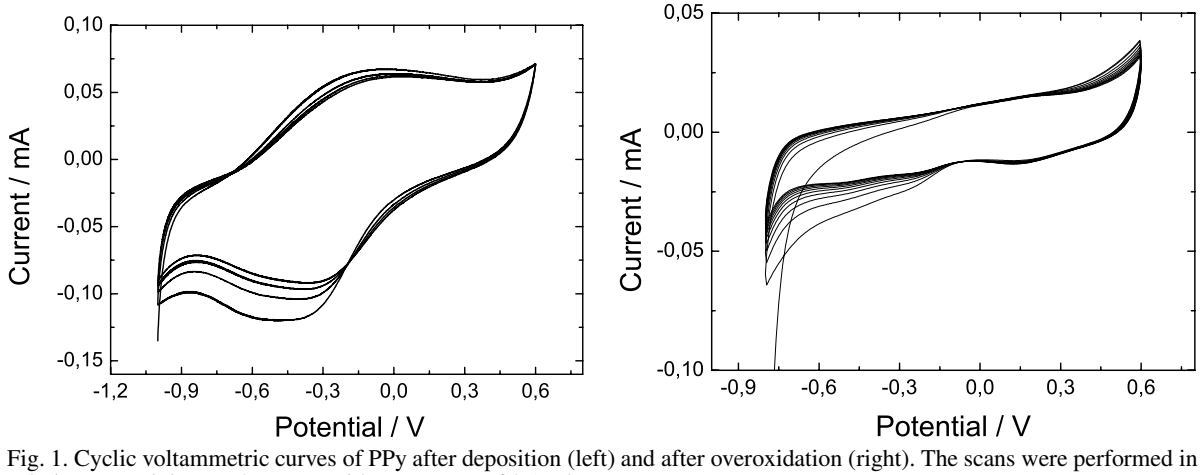

Fig. 1. Cyclic voltammetric curves of PPy after deposition (left) and after overoxidation (right). The scans were performed in solutions containing L-glutamate with a scan rate of 0.1 V/s.

Overoxidizing the PPy films leads to a change in the film properties. This can easily be seen in Figure 1, which shows cyclic voltammetric curves taken before (left) and after (right) the overoxidation process, respectively, using solutions containing L-glutamate. Prior to the overoxidation process a pronounced oxidation and reduction peak is apparent, which correlates to the uptake and release of glutamate, respectively. The current voltage (CV) curves were observed to be very stable over many cycles, indicating stable PPy films. After the overoxidation process, these peaks vanish, due to the low conductivity of the overoxidized PPy. The resulting film is porous and insulating.

The voltage dependent uptake and release of glutamate from the overoxidized PPy was investigated using electrochemical quartz crystal microbalance (EQCM) techniques. Au coated quartz crystals were used as the working electrodes in these experiments, and the frequency of the crystal was monitored during the voltage sweeps. The results are shown in Figure 2. Experiments were performed in a neutral pH phosphate buffer solution to avoid local pH variations in the solution. It was seen that the frequency decreases during the positive scan, corresponding to an increase in mass of the PPy film. The increase in frequency in the negative scan direction corresponds to a decrease in the mass of the PPy film. This indicates that the glutamate anion is incorporated into the polymer backbone during the positive scan direction, while it is ejected during the negative scan direction.

Reference measurements were performed in buffer solution without glutamate in order to investigate the effect of the buffer on the voltage dependent frequency changes. These data showed comparably small changes in the mass of the polymer film.

These results indicate that devices based on overoxidized PPy can be fabricated for the regulation of L-glutamate under physiological pH.

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