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Red-Ox front propagation in polyaniline-polymer electrolyte system as a basis for spiking and rate-based neural networks and multibit ReRAM

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ABSTRACT

We observed and studied the phenomenon of the redox front propagation in different polyaniline (PAni) deposited samples interfaced with liquid or solid polymeric electrolyte. The front of electrochemical conversion, in which the insulator and the conductor parts of PAni are interfaced, is studied observing the temporal evolution of the conductivity of PAni samples. The propagation of redox front was studied in electrochemically obtained thick (2 μm) and in thin (50 nm) polyaniline films, obtained using Langmuir-Blodgett (LB) method. In the configuration that we tested, the speed of the red-ox front propagation for the thin LB films was found to be 200 μm/sec opening the way for the manufacturing large neural networks, realized using PAni based memristive devices, in which the memristance can be quickly changed in the programmable manner. The prototypes of the spiking neuron connections were manufactured on the basis of lithographically developed gold contacts, bridged by electrochemically grown polyaniline and placed under polymer electrolyte layer with only one counter electrode (gate) for the whole manifold of pseudo-two-terminal memristor bridges. The spike propagation was studied in such gold-polyaniline systems. The research opens the possibility of miniature spike or rate-based neural network circuits manufacture, based on metal pads and polyaniline.

1. Introduction

In the area of polymer science, the propagation of conductivity (redox) front in conductive polymers, immersed into electrolytes, was studied quite intensively. Olle Inganas [1] with coauthors studied the propagation of conductivity (redox) front from conductive electrode and through the film, immersed in the electrolyte solution, in polythiophenes, using change of their absorbance. The front propagation was found to be caused by the red-ox processes in polymers, changing their oxidative state, which can propagate along the polymer film to very long distances due to electron conductivity, transferring charge carriers (mainly electrons, but locally ions to counter-balance the electron transfer red-ox processes) to or from the front, where reduction or oxidation processes, involving electrons, are taking place. They found propagation speed to be quite high and distances, to which front propagated, to be quite long (up to several centimeters).

They also found the dependencies of speed of front propagation on electrode potential and suggested a theoretical model, describing front propagation, based on polymer electrochemistry.

Aoki et al. [2] for the first time observed the propagation of Red-Ox front in polyaniline in liquid electrolyte using optical microscope, observed the red-ox front propagation in polythiophene [3] and polypyrrole and suggested a descriptive model based on the percolation theory [4]. Aoki and co-authors further observed the change of mechanism of front movement from propagation control to the diffusion control with the change of the solvent [3].

At the same time some theoretical papers [5,6] suggested the analytical models behind the conductive red-ox front propagation, based on ion diffusion into or from the film and electron transport along the polymer. In [5] it was found that the limiting process, which determines the speed of front propagation, is the diffusion of anions out of or into the film, balancing the electroneutrality in the process of cations involved in the red-ox processes inside the polymer. Similar optical approach was currently used also to reveal resistance variation.

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