Microelectronic Engineering 193 (2018) 65–70

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Research paper

Organic memristive element with Chitosan as solid polyelectrolyte

Angelica Cifarelli [a,*], Antonella Parisini [a], Tatiana Berzina [b], Salvatore Iannotta [b]

[a] Department of Mathematical, Physical and Computer Sciences, University of Parma, Viale G. P. Usberti 7A, 43124 Parma, Italy
[b] CNR-IMEM, Parco Area delle Scienze 37A, 43124 Parma, Italy

ARTICLE INFO

Article history:
Received 31 May 2017
Received in revised form 18 February 2018
Accepted 21 February 2018

Keywords:
Organic memristor devices
Chitosan gel
Polyelectrolyte
Biocompatible materials
Solid state electrochemistry

ABSTRACT

The biomimetic devices such as the artificial synapses are of great significance because they can emulate the functions of biological systems. The development of memristive devices represents one of the most promising pathways towards adaptive and neuromorphic computing.
This study reports the characterization of the first organic memristive element based on polyaniline-Chitosan (PANI–CS) junction. The Chitosan is used as solid polyelectrolyte in the active area of organic memristive element. Its working principle is based on the significant variation of the resistance of PANI in the oxidized and reduced states in junction area. The experimental parameters that influence the memristive behavior of Chitosan-based devices were studied by means of voltage-current measurements.
The application of biocompatible material, the Chitosan, in organic memristive devices pave the way towards the application of organic memristor in bio-integrated systems.

1. Introduction

Sophisticated structures and functionalities of biological systems in nature have offered inspirations in the development of new classes of devices able to mimic biological functions and to be integrated in biological systems. Bio-inspired devices with properties for actuation, sensing, smart electronics, computation can sense and respond to environmental changes by mimicking human nervous system, muscles and skin [1].

Among these biomimetic devices, artificial synapses and resistive switching memories are of great significance because they can emulate the signal process and memory functions of biological synapses [2]. From this point of view, the development of memristive devices and systems is playing a very relevant role and represent one of the best, most promising, pathway towards adaptive and neuromorphic computing [3–5].

A variety of materials have been proffered for the developing of resistive switching devices that fall under the broader definition of memristors [6–9].

Strukov et al. [10] showed how memristive effects arise in materials, where there is a strong interaction between ionic and electronic transport.

Recently, various organic materials, including polymers, have been used in solid-state devices and which demonstrate performance similar to their inorganic counterparts [11].

Sreetosh Goswami and co-workers report an organic memory device that can compete in performance with oxide-based memristors [12]. Recently, cells based on Nafion and poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) have shown even more promising performance for neuromorphic operations [13].

Polyaniline (PANI) based memristive devices, proposed by Erokhin et al. [14], have emerged as promising candidates for hardware implementation of artificial synapses and memory systems due to their high flexibility, low cost, solution processability, three-dimensional stacking capability, and biocompatibility.

The organic memristive element consists of polyaniline-polyethylene oxide (PANI–PEO) junction; its working principle is based on the significant variation of the resistance of PANI in the oxidized and reduced states [15]. The most important characteristic of the memristive element is the gradual but slow increase in conductivity during a direct voltage sweep and a rather fast decrease in conductivity during a reverse voltage sweep, as well as a “memory” property of the system. Redox reactions occur in the contact zone between the PANI film and a solid electrolyte [16]. So the choice of solid polyelectrolyte seems crucial. This device is able to perform some information processing task, mimicking the processes in real neuronal circuits and the kind of plasticity found in synapses. In addition, it has been previously demonstrated that through the combination of this kind of memristive elements it is possible to realize logic elements (AND, OR, …) [16] or adaptive networks [17].

Several efforts were performed to improve PANI-based memristive devices performances, e.g. endurance, switching rate, etc. The reduction of the PANI active channel dimension and the miniaturization of

* Corresponding author.
E-mail address: angelica.cifarelli@fis.unipr.it (A. Cifarelli).

https://doi.org/10.1016/j.mee.2018.02.024
0167-9317/

memristive devices leads to the increase in the stability and applicability [18].

Recently, organic memristive devices have been used for the realization of elementary and bilayer perceptrons that are neural networks able to implement basic brain-inspired learning functionalities and parallel processing [19,20].

New research frontiers are not only orientated towards bio-mimetic or bio-inspired systems but also towards the developing of interfaces and electronic elements (e.g. biosensors) able to work together with natural ones (proteins, cells etc.) [21]. The use of biocompatible materials in organic memristor, in particular as interface layer, becomes a crucial issue in order to realize bio-integrated systems.

The Chitosan (poly-β(1,4)-D-glucosamine) is a linear amino-polysaccharide. It is an abundant, natural biopolymer. The distinguishing structural feature of chitosan is its primary amine at the C-2 position of the glucosamine residues. At low pH, these amines get protonated and become positively charged, that makes chitosan (CS) a water-soluble cationic polyelectrolyte. The use of Chitosan for lab-on chip and biodevices was not extensively reported in literature [22].

In this study we report the characterization of the first organic memristive element based on polyaniline-Chitosan (PANI–CS) junction. The Chitosan is used as solid polyelectrolyte in the active area of organic memristive element. In particular, the Chitosan solid polyelectrolyte was studied in comparison with PEO, generally used in organic memristive elements [14–17].

The dwell time between the voltage application and the readout of the current value, the Chitosan gel formulation (its concentration and the presence of lithium salts) are the parameters that could influence the electrochemical characteristics of devices and they were investigated in this study.

2. Materials and methods

2.1. Materials and reagents

Chitosan (poly-β(1,4)-D-glucosamine medium molecular weight (Mw ~ 100 KDa), from *Pandalus borealis*, 77% deacetylation), polyethylene oxide (PEO) (Mw ~ 8.000,000 Da), emeraldine base polyaniline (Mw ~ 100,000 Da), Lithium perchlorate ($LiClO_4$) were purchase from Sigma-Aldrich. *N*-methyl pyrrolidone (Sigma-Aldrich, anhydrous, 99.5%), toluene (Sigma-Aldrich, ACS reagent, ≥99.5%), acetic acid (Fluka, ACS reagent, 0 ≥ 99.7%), hydrochloric acid (Fluka, ACS reagent, 37%) were used without further purification. Water (for film deposition, solution preparation, washing) was purified by Milli-Rho-Milli-Q system (resistivity: 18.2 MΩ cm).

2.2. Preparation of devices

Chitosan (CS) gel was prepared in 2% acetic acid water solution. Several formulations of CS gel were tested. In particular, CS powder was solubilized in acetic acid (2% w/w) water solution, after 24 h of swelling and dissolution of the powders, the formation of a transparent gel was achieved (formulation 1). In the second formulation, $LiClO_4$ (0.1 M) water solution was acidified with acetic acid (2% w/w) and then CS powder was dissolved in it (formulation 2). Several concentrations of Chitosan were tested (20 g/L, 30 g/L, 50 g/L, formulation 3, 4 and 5 respectively).

The PANI Emeraldine base (MW 100,000) powder was dissolved in 1-methyl-2pirrolidone (NMP) at a concentration of about 0.1 mg/mL and filtered carefully. 10% of toluene was added to NMP solution of PANI in order to improve the solution spreading on water interface. Deposition of molecular layers was carried out using the KSV 5000 LB trough with a modified method of Langmuir-Schaefer (LS) (horizontal lifting). PANI monolayer was compressed at a rate of 0.5 cm/min to a surface pressure of 10 mN/m. Deionized water (resistivity of 18.2 MΩ × cm) was used as a subphase. The resulting PANI film (about 60 nm thick) was doped in 1 N hydrochloric acid (1 N HCl) for 1 min. A thin CS gel stripe of 1–2 mm width, was placed onto the central part of PANI layer between source (S) and drain (D) electrodes. The pH of gel was adjusted with HCl to pH 1 before the formation of physical contact between a stripe of CS gel and a layer of PANI. A silver wire (gate electrode, G) with a diameter of 50 μm was positioned above the polymeric gel stripe and covered with an additional layer of gel. The whole structure was dried at 25 °C overnight before the electrical characterization.

2.3. Electrical characterization

The electrical measurements were performed using a Keithley 236 source measure unit and a Keithley 6514 system electrometer. The 236 unit was used to apply a potential difference between the source (S) and the drain (D) electrodes of the device, keeping the source at the ground level, and to measure the total current ID passing through the device. The 6514 unit was used to measure the current passing from the gate to the drain electrode I_G, i.e. the ionic current. The subtraction of this value from the one measured by the 236 unit gives the value of electronic current passing through the PANI layer. A more detailed description of the experimental set up is reported in Ref. 14.

The voltage–current characteristics were measured between −1.2 V and +1.2 V Measurements started at 0 V applied to the drain electrode. The sampling period was 1 s. Voltage was applied in steps of 0.1 V. Readout of the current value was performed by waiting a time after the voltage application, in order to equilibrate the transient processes in the devices in each test, as highlighted in Refs. 14–17. Several experiments were carried out: at each voltage step, the delay time of 5, 10, 20, 60 or 180 s was kept. In this work, dwell time of 60–180 s are found as effective to observe memristive behavior. Electrical measurements of cyclic voltage-current (V-I) characteristics for each device (Fig. 1) described in par 2.2 were performed. Each experiment was performed at least in triplicate.

3. Results and discussion

3.1. Organic memristive device (OMD) with Chitosan

The devices were prepared using chitosan as a solid polyelectrolyte doped with HCl and without addition of any lithium salts. For dwell times shorter than 60 s, linear voltage-current characteristics were observed, without any memristive behavior: the switching of PANI in conductive state due to ionic drifting at the solid polyelectrolyte-PANI layer interface does not occur. The Fig. 2 represents typical cyclic I-V characteristics of the device recorded using a dwell time of 180 s. The Chitosan gel was prepared according to formulation 1 (par.2.2) adjusting the pH of gel with HCl, used as doping agent.

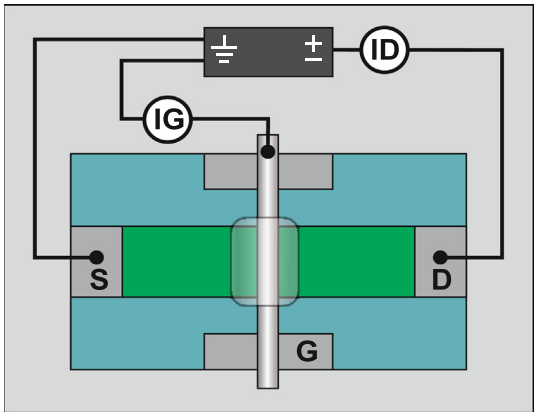

Fig. 1. Schematic representation of organic memristive device and circuit for measuring of its voltage-current characteristics.