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Polydopamine-Based All Solid-State Flexible Organic Neuromorphic Devices for Access Device-Free Artificial Neural Networks

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Recent developments in organic neuromorphic devices and biohybrid interfaces are promising examples that show potential to improve implantable devices toward organic adaptive brain-machine interfaces. However, fully integrated neuromorphic arrays still require relatively complex circuitry that includes multiple access devices to ensure synaptic weight stability and prevent sneak paths. Here, it is shown that polydopamine (PDA), the byproduct of dopamine autoxidation, promotes proton conductivity and can serve as a solid-state electrolyte. Slow kinetics and high energy barriers of the PDA solid electrolyte prevent loss of conductance state for the device with a three-terminal configuration without an access device, while partial dedoping of the conductive polymer channel by PDA simultaneously increases its stability in ambient environments. Fabricating the neuromorphic device on a flexible poly(styrene-block-isobutylene-block-styrene) substrate and the inherent bio-compatibility of PDA demonstrates its potential toward more sophisticated implantable neuromorphic circuits for advanced neuroprosthetics.

1. Introduction

Recent increasing interest in bioelectronics has resulted in successful applications ranging from sensors and actuators to chronic implants, bioinspired memristor devices, and brain-machine interfaces. For many of these applications, biocompatibility is crucial and as a result, there have been a broad range of studies investigating organic biocompatible materials. Of particular interests are organic mixed ionic and electronic conductors, which can conduct both ionic and electronic charges and have been successfully employed as sensors, amplifying signals, and ion-gated transistors. These materials can also carry electrical stimuli to activate cell functions or trigger cell response and sense the cell activity. Integrating these organic materials in neuromorphic systems has shown great promise in hardware-based machine learning applications and shows potential for integration with biomedical implants. A recently developed biohybrid synapse is a promising example toward future adaptive brain-machine interfaces, combining biosensing with brain-inspired signal processing. Sensing electrochemical activities of neuronal cells and translating those signals into short-term and long-term plasticity values stored within device memory, enables local optimization and training based on the biological or physiological environment. However, for applications like prosthetic implants, byproducts of electrochemical sensing of neurotransmitters can be undesirable, causing a blockade and reducing device sensitivity over a prolonged period of time. On the other hand, despite the successful demonstration of poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) in vitro and in vivo applications with artificial as well as naturally occurring electrolytes, neuromorphic circuits operating locally at the interface with biology can require dedicated and solid-state electrolytes to assure long-term performance stability and the elimination of interference with neighboring devices. At the same time, sophisticated hardware-based neural networks such as crossbar arrays require access devices to enhance stability and prevent undesired tuning and sneak currents, further complicating the systems. In this work, we demonstrate a solid-state electrolyte polydopamine (PDA) based on the dopamine oxidation byproduct, which can promote proton conductivity. Slow kinetics and high energy barriers of PDA solid electrolyte, simultaneously prevent unwanted dedoping and loss of conductance state for the device with a three-terminal configuration and without any access devices involved.

Inspired by the adhesion mechanism of natural mussels, PDA has been commonly employed as a robust coating material. Polydopamine as a biomaterial melanin is inherently biocompatible, which is essential to any viable organic electroconductive material. Previous studies have shown that PDA can be used in a wide range of applications. For example, PDA behaves as a multifunctional coating and shows remarkable adhesion to a variety of surfaces, regardless of surface properties such as chemical constitution, shape, and roughness thus rendering...
hydrophobic surfaces to promote adhesion and proliferation of biological cells.[27,28] Moreover, PDA can promote proton conductivity similar to Nafion.[29,30] A biocompatible solid-state electrolyte like PDA offers an ideal platform for developing stable biointerfaces, as well as benefiting neuromorphic hardware applications as a solid electrolyte facilitating enhanced state retention and the reduction of circuit interference. The flexible nature and the inherent biocompatibility of polydopamine offers a path toward more sophisticated implantable neuromorphic circuit for advanced neuroprosthetics.

2. Results and Discussion

2.1. Device Architecture

Organic electrochemical random access memory (EC-RAM) has previously been employed as building blocks in neuromorphic arrays[31] due to their beneficial characteristics such as symmetric and linear tunable conductance and low switching energy.[32] A mixed ionic and electronic organic polymer, PEDOT:PSS is implemented in a three-terminal configuration of an electrochemical neuromorphic organic device (ENODe), and the electronic conductance state, or synaptic weight, of the material is modulated by coupling the movement of protons from the gate to the source and drain channel via an electrolyte[14] see Figures 1a and 2a. Here PDA film is used as a solid electrolyte/proton exchange layer. Previous studies indicate that PDA is permeable to monovalent cations, and thus to protons, due to the presence of a continuous network of interconnected intermolecular voids within PDA. Moreover, ion conductivity within PDA was found to be independent of film thickness.[33]

PDA is obtained by autooxidation of dopamine under slightly alkaline conditions at pH 8.5 in Tris HCl buffer, see Figure 1c. To eliminate the effect of Tris buffer ions on the PEDOT:PSS conductance, after PDA polymerization the solution is centrifuged twice with the solvent discarded each time and the PDA precipitant transferred to Milli Q water. Dip coating the substrate with the PEDOT:PSS films in the PDA solution for 1–2 h forms a layer of PDA. The resistance of the PEDOT:PSS film was found to increase with an average of 87.7% ± 4.9%. This results highlights that PDA can serve as an reducing agent to dedope the PEDOT:PSS and a solid electrolyte simultaneously[30,34] since more than half of the phenyl ring positions remain protonated after polymerization.[35] Dedoping PEDOT:PSS with an amine has been found to increase stability.[14,36]

Similar to other solid electrolytes, proton conduction of PDA is sustained by hydration (see Figure S4, Supporting Information).[37,38] To eliminate experimental variability with varying environmental conditions, we performed all the measurements in a controlled environment with a relative humidity of 75% or above. These levels of humidity can be maintained at a very specific level with a saturated salt solution (e.g., NaCl will produce a relative humidity of 75.2%).

Upon applying positive and negative gate square pulses (Vg = ±2 V) and pulse duration of 1 sec, protons flow through the electrolyte and tune the conductance of the channel, see

Figure 1. a) Planner schematic representation of the EC-RAM device on a flexible substrate. b) Device conductance changes are controlled by applying gate pulses of ±2V and duration of 1 s without an access device. Negative bias at the gate was applied to increase the conductance and positive to decrease. The insets show a zoom-in with the individual states and the corresponding gate current. c) Dopamine solution at different time points (Vg = ±2 V) and pulse duration of 1 sec, protons flow through the electrolyte and tune the conductance of the channel, see
Figure 1b. In this figure, we show 200 discrete conductance states, and the insets show a zoom-in with the individual states and the corresponding gate current. Now based on Ohm’s law and by considering the values of applied voltage at the gate (Vg) and the gate current (Ig), the resistance between gate and source can be obtained \( R_{gs} = \frac{Vg}{Ig} = \frac{2(V)}{22(nA)} = 90 \, \text{M}\Omega \). Similarly, the gate-source resistance can be calculated when aqueous electrolyte is utilized \( R_{gs} = 2.63 \, \text{M}\Omega \) (see Figure S2, Supporting Information). Comparing these two values shows a significant increase. This reveals that there is a high energy barrier for protons to flow via the PDA solid electrolyte into the channel, and as a result traps protons in the film, see Figure 2b. Maintaining charge neutrality in the film, this high energy barrier subsequently prevents undesired dedoping of the PEDOT:PSS film and loss of conductance state. Additionally, the high energy barrier can be beneficial for directly interfacing with biology as it would ensure that the generated current does not damage biological cells or tissue.

To allow sufficient proton migration in the planar structure of the ENODEs, the gap between gate and channel should be as small as possible without sacrificing electrical separation, see Figure 3a. We achieved this by separating the gate and channel electrode with femtosecond laser ablation. With this technique, the electrodes are <5 µm apart and they have an ohmic resistance in the megaohm range.

2.2. State-Retention Measurements

To achieve long-term retention in three-terminal EC-RAM or ENODEs, a switch (access device) or series current limit resistor is commonly used.\(^{[39]}\) These devices prevent or limit electronic discharging of the channel and maintain its conductance level. In this study, state retention measurements are performed on the EC-RAM devices using PDA as the electrolyte without an access device and compared to a device with an aqueous electrolyte which is coupled to a current limiting resistor (see Figure 2a and Figure S1, Supporting Information). The tuning behavior and state retention of the device with PDA is found to be almost identical to the device with NaCl aqueous electrolyte and a series resistor of 100 M\(\Omega \), see Figure 2d,e. This demonstrates that the relatively high energy barrier for proton movement in PDA serves as a natural series resistor limiting discharging and loss of conductance state (Figure 2b). This allows the state retention of the EC-RAM to be materials-based rather than circuit limited, simplifying the electrical circuit and peripheral electronics for integration in an array. An array of these devices can be employed for online learning applications where a constantly changing data input requires regular updating of the weights, and thus state retentions in the order of minutes as presented here, are expected to be sufficient.
Moreover, the PEDOT:PSS used for the gate and channel is normally highly conductive and has a low oxidation potential once it is reduced, which significantly reduces its conductance state stability. To overcome this issue and enhance the conductance (state) retention, usually, an amine-based reducing agent is introduced to the channel.\textsuperscript{[36,40]} Immersing the device in PDA solution for PDA deposition allows some PDA to penetrate to the PEDOT:PSS film and partially dedope it and at the same time forms a layer of PDA covering gate, channel, and the gap in between. The presence of PDA in the PEDOT:PSS film and at the solid interface with the electrolyte reduces the diffusion of amines into the electrolyte leading to more stability and higher state retention, see Figure 2c.

2.3. Flexible Solid-State Neuromorphic Device

This study aims to take the first steps toward organic adaptive neural interfaces so consequently biocompatibility and flexibility are crucial. In order to match these requirements, the suggested EC-RAM device must be fabricated on a flexible and biocompatible substrate. Clinical investigation has shown that poly(styrene-block-isobutylene-block-styrene) (SIBS) is an ultra-biostable thermoplastic elastomer and by itself provokes insignificant inflammation when utilized as medical implants.\textsuperscript{[45]} Hence SIBS can be utilized as an ideal substrate for any implantable electronics. Therefore, we fabricated our solid-state EC-RAM device on a SIBS substrate and showed that the device is flexible (Figure 3b) and its conductance can be tuned while bent on a cylinder surface with a radius of 1 cm and bending angle of 45° (Figure S5, Supporting Information). This device shows a potential for further investigation of implanting this flexible EC-RAM device and integration of neuromorphic arrays interfacing with biological environments.

In summary, we demonstrated that polydopamine can serve as a solid-state electrolyte which significantly increases the energy barrier for ion/proton diffusion while maintaining an electrically disconnected gate and channel, thus eliminating the need for an access device and potentially significantly decreasing fabrication complexity when integrating in larger neuromorphic arrays. Simultaneously, the polydopamine solid electrolyte film has been found to partly dedope PEDOT:PSS which results in a higher film resistance and increased stability.

3. Experimental Section

Device fabrication consisted of cleaning glass slides while sonicating in isopropanol, acetone, and DI water each for 10 min. Gold electrode contacts were prepared by evaporation. The PEDOT:PSS solution was patterned and spun on the slide at 1000 RPM for 30 s and baked at 110 °C for 20 min. The device gate and the channel were then separated by femtosecond laser ablation (Pulse energy 80 nJ, Repetition Rate 1000 kHz, XY speed 0.5 mm s\(^{-1}\)).

Dopamine hydrochloride was purchased from Sigma–Aldrich and were added 2 mg ml\(^{-1}\) to Tris buffer (pH 8.5, 10 mM). The solution was stirred for 18 h and then centrifuged twice at 4000 rpm for 5 min. Every time the solvent was discarded, and precipitant was transferred to Milli Q water. For PDA deposition the device was dip coated in the PDA solution and rest for at least 1 h and then baked to remove excess water.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
organic neuromorphic devices, polydopamine, solid-state electrolytes

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