

Dendritic Network Implementable Organic Neurofiber Transistors with Enhanced Memory Cyclic Endurance for Spatiotemporal Iterative Learning

Soo Jin Kim, Jae-Seung Jeong, Ho Won Jang, Hyunjung Yi, Hoichang Yang, Hyunsu Ju,* and Jung Ah Lim*

Dendritic network implementable organic neurofiber transistors with enhanced memory cyclic endurance for spatiotemporal iterative learning are proposed. The architecture of the fibrous organic electrochemical transistors consisting of a double-stranded assembly of electrode microfibers and an iongel gate insulator enables the highly sensitive multiple implementation of synaptic junctions via simple physical contact of gate-electrode microfibers, similar to the dendritic connections of a biological neuron fiber. In particular, carboxylic-acid-functionalized polythiophene as a semiconductor channel material provides stable gate-field-dependent multilevel memory characteristics with long-term stability and cyclic endurance, unlike the conventional poly(alkylthiophene)-based neuromorphic electrochemical transistors, which exhibit short retention and unstable endurance. The dissociation of the carboxylic acid of the polythiophene enables reversible doping and dedoping of the polythiophene channel by effectively stabilizing the ions that penetrate the channel during potentiation and depression cycles, leading to the reliable cyclic endurance of the device. The synaptic weight of the neurofiber transistors with a dendritic network maintains the state levels stably and is independently updated with each synapse connected with the presynaptic neuron to a specific state level. Finally, the neurofiber transistor demonstrates successful speech recognition based on iterative spiking neural network learning in the time domain, showing a substantial recognition accuracy of 88.9%.

1. Introduction

As society faces the era of big data and artificial intelligence, neuromorphic computing capable of massively parallel information processing has garnered intensive attention as the most promising computing architecture for overcoming the limitation of the current von Neumann architecture.^[1] One of the keys for realizing a neuromorphic device is the ability to reliably emulate synaptic plasticity, which means regulating and memorizing the strength or amplitude (i.e., synaptic weight) of a synaptic connection between two neurons, corresponding in biology to the influence that the signal firing of one neuron exerts on another neuron.^[2] Regarding the synaptic transmission mechanism in biology, it is generally understood that signaling between the neurons is related to the ion migration at the end of the cell in electrolyte medium and the changes in membrane potential of the neuron cell.^[3] For example, when the action potential reaches axon terminal

S. J. Kim, Dr. H. Ju, Dr. J. A. Lim Center for Opto-Electronic Materials and Devices Korea Institute of Science and Technology Seoul 02792, Republic of Korea E-mail: hyunsuju@kist.re.kr; jalim@kist.re.kr S. J. Kim, Prof. H. W. Jang

Department of Materials Science and Engineering Seoul National University Seoul 08826, Republic of Korea

J.-S. Jeong Center for Neuromorphic Engineering Korea Institute of Science and Technology Seoul 02792, Republic of Korea

J.-S. Jeong, Dr. J. A. Lim Division of Nano and Information Technology University of Science and Technology of Korea Daejeon 34113, Republic of Korea

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Prof. H. W. Jang Research Institute of Advanced Materials Seoul National University Seoul 08826, Republic of Korea Dr. H. Yi Post-Silicon Semiconductor Institute Korea Institute of Science and Technology Seoul 02792, Republic of Korea Dr. H. Yi Department of Materials Science and Engineering YU-KIST Institute Yonsei University Seoul 03722, Republic of Korea Prof. H. Yang Department of Chemical Engineering Inha University Incheon 22212, Republic of Korea







Figure 1. a) Schematic of biological presynaptic and postsynaptic neurons and a synapse (inset). b) Illustration of the device architecture for neurofiber-OECT, schematic of the doping mechanism by ions in a permeable semiconductor (inset) and photograph of OECT-neurofiber. c,d) Molecular structures of poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly[3-(6-carboxyhexyl)thiophene-2,5-diyl] (P3CT) (c) and of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) (d).

and depolarizes the membrane, a voltage-gated calcium ion (Ca²⁺) channel is activated in the cell membrane and Ca²⁺ influx allows synaptic vesicles to release neurotransmitter molecules at the dendritic end of the presynaptic neuron, as shown in Figure 1a. Binding of the neurotransmitters to the receptors at the postsynaptic neuron causes newly localized changes in the membrane potential. The continuous potential changes driven at different synapses or timings are integrated in an excitatory or inhibitory manner in this postsynaptic neuron and lead to decide whether its action potential would fire. Structurally composed of cell bodies, long slender axons, and dendrites, neurons have a fibrous shape with numerous branches. At the end of the dendrites, synaptic communication occurs in several channels between neurons. Given the biological synaptic communication mechanism and dendritic structure of a neuron, a neuromorphic electronic device should ultimately be an integrated device capable of multichannel communications with the synaptic-weight controllability and spatiotemporal signal summation functionality of a neuron.

Recently, organic electrochemical transistors (OECTs) based on electrochemical interactions between conjugated semiconductor polymers and ions in an electrolyte gate insulator have attracted remarkable attention as the most promising neuromorphic platform that best mimics biological synaptic plasticity on the basis of a voltage-gated ionic channel.^[1] The intrinsic advantages of OECT devices, which include good biocompatibility, excellent tunability, low-energy switching, simple implementation of multiple channels, and low-cost fabrication, are irresistibly attractive for neuromorphic device applications.^[1,4–6] The synaptic weight function can be defined as the active channel conductance tunable via variation of the strength of a pulsed gate bias. According to the conditions of the gate-bias pulses (corresponding to the presynaptic stimulations), the formation of an electrical double layer at the conjugated polymer/ electrolyte insulating layer interface or the penetration of ions into the conjugated polymer active channel occurs, which results in different short- or long-lasting drain-current characteristics.^[4,7] On the basis of this principle, synaptic functionalities such as short-term plasticity and long-term plasticity, including paired-pulse facilitation (PPF), excitatory postsynaptic current (EPSC), and/or inhibitory postsynaptic current (IPSC), have been successfully demonstrated by several research groups using various neuromorphic OECT devices.^[8-15] Basic circuit simulations for learning, such as handwritten(MNIST) classification and Pavlov associative based on the synaptic functions of OECTs, have demonstrated preliminary feasibility of using the OECT neuromorphic devices in applications.^[12,16] Even though such significant advances in OECT-based neuromorphic devices have been reported, the electrochemical doping mechanism of conjugated polymers in an OECT synaptic device-including how the ionic species at the conjugated polymer/electrolyte interfaces interact with the conjugated polymer under synaptic functional conditions-has not been fully elucidated. Understanding this mechanism is essential for further improving the performance of OECT neuromorphic devices.

One of the most important concerns for the potential application of OECT neuromorphic devices to artificial intelligence technologies such as machine learning is the cyclic endurance ADVANCED SCIENCE NEWS _____ www.advancedsciencenews.com

of the devices, i.e., the ability of the devices to reliably perform for extensive numbers of repetitive write-read-erase-read (W-R-E-R) cycles. Typically, a spiking neural network (SNN)based learning process follows a Hebbian rule that requires the repetitive correction on the synaptic weights according to the incoming stimuli. The corresponding synaptic weights are represented by the conductance of the synaptic device and the conductance should be repeatedly increased or decreased for the synaptic weight correction.^[17] For example, the synaptic weight (W_{ij}) is generally defined as $W_{ij} = \frac{g_{ij} - g_{min}}{z}$, where g_{ij} is the $g_{\max} - g_{\min}$ conductance of the synaptic device between the i^{th} and j^{th} neurons, and g_{min} and g_{max} are the minimal and the maximal conductance states of the device, respectively. The relative change in the synaptic weight is iteratively calculated and updated during the learning. If the conductance levels of the programmed and/ or the erase states vary at every repeated cycle, the individual conductance at every operation, gij, changes; in addition, the memory window, $g_{max} - g_{min}$, is also variable, resulting in a distorted normalization factor. Therefore, the synaptic weight difference, ΔW , from the previous status is inevitably updated erroneously. Ultimately, this unreliable updating deteriorates the learning itself through the synaptic weight updates. Only a few studies on the cycling characteristics of organic neuromorphic devices have been reported,^[7,9] and studies on the cyclic endurance of neuromorphic OECT devices are even less common.

Here, we propose dendritic network implementable neuromorphic fibrous OECTs with enhanced memory cyclic endurance for spatiotemporal iterative learning. As a novel approach to the construction of neuromorphic devices that mimic nerve fiber architecture, a fibrous OECT comprising a doublestranded assembly of electrode microfibers (DSA-microfibers) and an iongel electrolyte, referred to as a neurofiber-OECT, is demonstrated. The proposed neurofiber-OECT facilitates the dendritic network implementation with simple physical contact of the gate-electrode microfibers on the DSA-microfiber structure, as well as a higher current response for the gate-bias stimuli compared with the current responses of the conventional planar devices. From the technological point of view, it is worth noting that fiber electronic device is a key component of a freely deformable, and adaptive electronic textile platform for smart wearable devices.^[18,19] Development of fiber-based textile neuromorphic devices can be an important step toward future wearable technologies capable of computing and learning about human senses like wearable robots.^[20,21]

In the present work, carboxylic-acid-functionalized polythiophene-poly[(3-(6-carboxyhexyl)thiophene)-2,5-diyl] (P3CT) is especially proposed for neuromorphic OECT devices with improved memory retention and cyclic endurance characteristics. Unlike poly(3-hexylthiophene) (P3HT), which has been intensively demonstrated as a conjugated polymer semiconductor for neuromorphic OECT devices that exhibit a short retention time and unstable cyclic endurance under repeated potentiation and depression processes, the neurofiber-OECT based on P3CT exhibits highly stable cycling reliability. Through fundamental studies of the electrochemical reactions of the P3CT and ions under cyclic operation, we found that the balanced charge state involving the carboxylic acid group of the P3CT side chain facilitates the reversible redox reactions in the P3CT channel, leading to the stable long-term potentiation (LTP) and long-term depression (LTD) cyclic endurance of the device. By contrast, the doped state of P3HT cannot be reversibly recovered to the initial state because of the presence of anions that penetrated the film, which leads to the degradation of the retention and cyclic endurance of the device. Finally, a P3CT neurofiber-OECT device implementing a dendritic network with plural presynaptic neuron gates and one postsynaptic neuron channel enables the unit neural network to be configured more efficiently for complex computation, leading to the successful imitation of leaky integrate-and-fire behavior and synaptic behavior. As a proof of concept, we demonstrate that the P3CT-neurofiber device with improved cyclic endurance can be applied to speech recognition of the TI-46 speech corpus,^[22] with a substantial recognition accuracy of 88.9%, through tempotron-based iterative SNN learning.^[23]

2. Results and Discussion

Figure 1b illustrates the device structure of the neurofiber-OECT device based on DSA-microfibers. In previous work, we demonstrated the performance and characteristics of the fibrous organic transistors based on the DSA-microfibers structure, where a high output current at low operating voltages was achieved through utilization of a high-capacitance iongel gate insulator and a short channel length.^[24] We also demonstrated that the electrical performance of the DSA-microfiber transistor was almost maintained after they have been woven into the textile and subjected to repeated bending deformation. A holistic view of the process and a detailed explanation of the fabrication of the neurofiber-OECT are described in Figure S1 (Supporting Information). This architecture enables multiple implementations of synaptic junctions, similar to the dendrite structure of biological neurons, through simple physical contact of gate-electrode microfibers on the surface of the iongel coating without requiring additional interconnect junctions. Figure 1b shows the cross-sectional structure of the neurofiber-OECT device. In principle, when a negative bias is applied to the gate microfiber of the neurofiber-OECT, electrochemical doping of polythiophene at the source microfiber occurs via interaction with the bis(trifluoromethane)sulfonimide (TFSI) anions in the iongel; the induced charge carriers in the polythiophene active channel can be trapped or transported to the drain microfiber according to the applied electric-field conditions.^[4] Molecular structures of the important components (P3HT, P3CT, 1-ethyl-3-methylimidazolium (EMIM) cation, and (TFSI) anion) are depicted in Figure 1c,d. The neurofiber-OECT devices based on P3HT and P3CT are hereafter referred to as P3HT-neurofiber and P3CT-neurofiber devices, respectively.

Unlike a typical planar P3HT-OECT device, the P3HT-neurofiber device exhibits a 1.94-fold greater postsynaptic current response under the same presynaptic gate pulse (-0.7 V, 100 ms) compared with the planar device with the same channel length (2 μ m) and channel width (1 cm), as shown in Figure S2a (Supporting Information). This greater current response might be due to the enlarged area of the semiconductor channel that can interact with the ionic species of the iongel insulator. Because





Figure 2. a,e) Transfer characteristics of neurofiber-OECTs based on P3HT (a) and P3CT (e) at $V_{DS} = -0.2$ V. b,f) Drain current as postsynaptic current induced by V_{GS} as a presynaptic stimulus varying from -0.7 to -1.5 V in P3HT-neurofiber (b) and P3CT-neurofiber (f). c,g) 50 W–R–E–R cycles of devices based on P3HT (c) and P3CT (g) by using $V_{GS} = -1.5$ V, 10 s duration for the programming pulse (V_{PGM} and T_{PGM}) and $V_{GS} = 1.8$ V, 5 s duration for the erasing pulse (V_{ER} and T_{ER}). After each pulse, I_{DS} values were recorded with $V_{GS} = 2$ mV at 2 s intervals. d,h) Retention characteristics of the P3HT-neurofiber (d) and P3CT-neurofiber (h).

ions in the iongel can easily migrate under the applied electric field, an electrochemically active channel can presumably be induced at both sides of the DSA microfibers, as shown in Figure S2b,c (Supporting Information). This possibility implies that the device geometry of the neurofiber-OECT may promote a high signal-to-noise ratio of the neuromorphic device for such weak presynaptic stimulation.

The transfer characteristics $(I_{DS}-V_{GS})$ of the P3HT-neurofiber device under a repeated gate-bias ($V_{\rm GS}$) sweep are shown in Figure 2a. The V_{GS} sweep range was gradually changed from (+1.8 to -0.7 V) to (+1.8 to -1.8 V) under six repeated forward/ reverse cycles. Increasing the negative V_{GS} resulted in an increase of the ON-state drain current (I_{on}) and an enlargement of the memory ratio, indicating that the P3HT-neurofiber OECT exhibits gate-field-dependent memory characteristics. When the negative $V_{\rm GS}$ was applied below -0.7 V, bistable current state was not observed. At $V_{\rm GS}$ biases more negative than –1.0 V, a hysteresis window with an $I_{\rm on}/I_{\rm off}$ current ratio greater than 10^1 began to appear; the maximum value was $\approx 10^2$ at $V_{GS} = -1.5$ V. This behavior indicates that the short-term plasticity and longterm plasticity properties can be controlled via the applied presynaptic gate bias. In fact, Figure 2b shows the shift of the synaptic plasticity from short-term to long-term memory with increasing presynaptic V_{GS} bias. This result is comparable to that for the previously reported planar P3HT-based OECT neuromorphic devices.^[16] Notably, an increase of the OFF-current $(I_{\rm off})$ state with repeated operation cycles was unexpectedly observed. This increase of $I_{\rm off}$ during cyclic operation was also observed in the typical planar P3HT-OECT devices, as shown in Figure S3 (Supporting Information), which indicates that this phenomenon is not attributable to the neurofiber-OECT device architecture.^[25] Consequently, the P3HT-based OECT device exhibits unstable cyclic endurance and the long-term potentiation state of the device did not return to its initial state. Figure 2c shows the endurance of the P3HT-neurofiber device for 50 repeated W-R-E-R switching cycles. In fact, the programmed ON-state current was degraded by more than 55% from the initial current and the erased OFF-current level gradually increased, leading to substantial degradation of the $I_{\rm on}/I_{\rm off}$ memory ratio after 50 operation cycles. The retention characteristics of the P3HT-neurofiber, as shown in Figure 2d, also indicate a definite increase of the OFF-current state by a factor of 3.6 during the initial 250 s, even under the extreme erasing condition of V_{GS} = +2.5 V, which is the maximum voltage that can be applied without electrochemically degrading the EMIM and TFSI ions(see Figure S4 in the Supporting Information).^[26]

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A possible mechanism of this unstable endurance of the P3HT device is discussed in detail later.

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Notably, the P3CT-neurofiber exhibited stable gate-fielddependent memory characteristics during repeated cyclic operation with a progressively increasing V_{GS} . As shown in Figure 2e, the Ion gradually increased with increasing maximum negative $V_{\rm GS}$ bias, however, the current value returned to the initial $I_{\rm off}$ state at $V_{GS} = 0$ V for six repeated cycle sweeps. The P3CTneurofiber showed a memory ratio 10 times larger than that of the P3HT-neurofiber. Like the P3HT-neurofiber, the P3CTneurofiber also showed the synaptic transition from short-term to long-term synaptic plasticity, as shown in Figure 2f. This enhanced cyclability of the P3CT-neurofiber compared with that of the P3HT-neurofiber is confirmed in Figure 2g. The programmed ON- and erased OFF-current states were maintained even after 50 W-R-E-R repeated operations. Figure 2h clearly shows that the bistable conductivity of the P3CT-neurofiber device maintained a 10³ current window much more stably, unlike the P3HT-neurofiber device. Additionally, the multilevel retention was examined for different 5 programming voltages (Figure S5a, Supporting Information) and with the same programming voltage bias varying the number of the programming pulses (Figure S5b, Supporting Information). It explicitly shows the nonvolatile multilevel behavior of the device. These results clearly indicate that the P3CT with carboxylic acid functional groups led to a substantial improvement in the cyclic endurance of the neuromorphic OECT devices.

To gain deep insight into the origin of this difference in the cycling behaviors of the P3HT- and P3CT-OECT devices, the electrochemical doping and dedoping processes of the P3HT interface with [EMIM][TFSI] ions under an applied electric field were first investigated. Figure 3a shows a cyclic voltammogram of the P3HT film in [EMIM][TFSI] ionic liquid, as recorded under repeated oxidation and reduction cycling conditions.^[27] Oxidation peaks of P3HT are observed at 0.3 and 0.6 V in the first cycle; these peaks originate from the formation of positive charges at the polythiophene chains by removal of the electrons.^[28] Interestingly, the oxidation peak at 0.38 V was found to be distinctively enhanced in the second and third scan cycles (Figure 3a, inset). This result implies that, because a certain amount of positive charges remained after the reduction process in the first scan cycle, more positive charges were induced in the P3HT film in the continuous second cycle.

Molecular interactions of P3HT and [EMIM][TFSI] ions were investigated by Fourier transform infrared (FT-IR) and Raman analysis using the P3HT films of which electrochemical state was controlled by using cyclic voltammetry. As shown in Figure 3d, the C-H out-of-plane bending absorption in the thiophene ring, which originally appeared at 821 cm⁻¹, was substantially shifted to 881 cm⁻¹ when P3HT was oxidized at 2.0 V. This result is attributable to the reinforcement of C-H bonding by the deficiency of electrons in the thiophene ring, which is related to the formation of positive polarons in the polythiophene backbone at the oxidation potential.^[29] In addition, we observed the characteristic peaks of TFSI anions in the FT-IR spectrum of the oxidized P3HT film (Figure 3c). These peaks are direct evidence of the penetration of TFSI anions into the P3HT film during the oxidation process. The stretching vibrations of the S-N-S and SO₂ bonds of TFSI anions distinctly shifted from 1063 and 1143 cm⁻¹ to 1017 and 1115 cm⁻¹, respectively, during the oxidation process, indicating weakening of the bond stretching stabilized by counter charges.^[30,31] In addition, two split SO₂ peaks at 1112 and 1136 cm⁻¹, which correspond to the transoid structure of TFSI, newly appeared in the spectrum of the oxidized P3HT (see Figure S6 in the Supporting Information). Given that the transoid structure of the TFSI anion preferably interacts with counter ions because of the lower steric hindrance resulting from the exposure of its negatively charged N atom, this result is evidence that TFSI anions interacted with positively charged species. Because the EMIM cations did not penetrate into the P3HT during the oxidation process (no characteristic peaks of EMIM cations were observed in the FT-IR spectrum of the oxidized P3HT film, see Figure 3b), we reasonably conclude that the TFSI anions played a role in stabilizing the polarons generated in the oxidized P3HT backbone. These analysis results show that the programmed state of the P3HTneurofiber device with high conductivity is attributable to this stabilization of the generated polarons in the oxidized P3HT film by penetrated TFSI anions.

To understand the dedoping state of P3HT under a reduction potential, we subjected oxidized P3HT to a reduction process by applying -2.0 V. FT-IR analysis of the dedoped P3HT film shows that the peaks of the P3HT and the TFSI anions did not completely return to their initial peak positions (Figure 3d). The bending vibration peak of C-H in the thiophene ring of P3HT was observed at a slightly higher wavenumber than its original position in the spectrum of the pristine P3HT film. Furthermore, the S–N–S and SO₂ stretching peaks of the TFSI anions appeared at lower wavenumbers than in the spectrum of TFSI itself. These results strongly indicate that, even after a strong reduction bias was applied, a certain amount of penetrated TFSI anions remained in the P3HT film and still interacted with the polarons induced in the P3HT backbone. The doping and dedoping state of P3HT according to the oxidation and reduction conditions was further confirmed by Raman spectroscopic analysis (see Figure S7a in the Supporting Information). Conclusively, P3HT channel can be easily doped and the generated polarons can be stabilized by the penetrated TFSI anions under an applied oxidation potential. However, the doped-state P3HT did not recover to its initial neutral state because TFSI anions remained in the film even under reduction conditions, which finally led to the observed degradation in the retention and cyclic endurance properties of the P3HT-based OECT neuromorphic devices. Figure 3e is a schematic summarizing the possible molecular interactions of the P3HT and the TFSI ions, along with the expected charge distribution in the P3HT-OECT device according to the redox process.

In comparison with P3HT, P3CT exhibited completely different electrochemical redox behavior. Figure 3f shows the cyclic voltammograms of P3CT under repeated oxidation and reduction cycling. Interestingly, the inset of the oxidation peak at 0.69 V shifted to -0.23 V after the second oxidation process and no further shift was observed under repeated oxidation processes. These results indicate that the oxidation potential of P3CT was lowered after the first redox cycle by a structural change of the P3CT. Under FT-IR analysis, we investigated changes in the chemical structures of P3CT and [EMIM][TFSI] ions under oxidation and reduction conditions, as shown in ADVANCED SCIENCE NEWS _____





Figure 3. a,f) Cyclic voltammograms of P3HT (a) and P3CT (f) in [EMIM][TFSI] at 50 mV s⁻¹. b–d,g–i) Changes in the FT-IR transmittance spectra of P3HT (b–d) and P3CT (g–i) films upon doping and dedoping during cyclic voltammetric cycling. e,j) Schematics representing the interaction between P3HT and TFSI anion (e) and that between P3CT and [TFSI][EMIM] (j) upon electrochemical doping.

Figure 3g–i. In a typical spectrum, pristine P3CT shows two bands at 936 and 1700 cm⁻¹, which are assigned to the C–O and C=O bonds in carboxylic acid groups, respectively. When the P3CT was first oxidized, the C–O band shifted to a higher wavenumber (954 cm⁻¹), whereas the C=O band shifted to a

lower wavenumber (1694 cm⁻¹) (Figure 3g,h). These results provide strong evidence that carboxylic acid (COOH) groups were changed to carboxylate (COO⁻) groups with resonance coupling between C–O single bonds and C=O double bonds.^[32] Additionally, i) reduced absorption at the 3500–2500 cm⁻¹ broad



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band corresponding to the O-H stretching and hydrogen bonding of the dimer^[33] and ii) appearance of strong absorption at 1300 cm⁻¹ and 1398 cm⁻¹ by (COO⁻) group in FT-IR^[34] as well as (iii) X-ray photoelectron spectroscopy analysis results support the removal of hydrogen from carboxylic acid groups in the oxidized P3CT (see Figures S8 and S9, Supporting Information). This behavior is consistent with previously reported results showing that the dissociation of protons in carboxylic acid groups induced a charge balance with the polarons under an applied oxidation potential, leading to a long-term memory state.^[35] After the reduction of this first oxidized P3CT film, the change in absorption associated with the C=O band (944 cm^{-1}) and the C-O band (1697 cm⁻¹) when compared with their initial absorption values in the spectrum of pristine P3CT was still observed. This means that a certain amount of carboxylate anions and protons remained even after the first redox reaction was completed. The change of the functional group in P3CT from electron-withdrawing carboxylic acid (COOH) to electrondonating carboxylate (COO⁻) might enhance the stability of the oxidized polythiophene backbone of P3CT, resulting in a lower oxidation potential after the first redox cycle. In addition, the shifted absorption band for C-H out-of-plane bending in the thiophene ring from 821 to 841 cm⁻¹ in the spectrum of oxidized P3CT returned to its initial wavenumber after redox cycling, as shown in Figure 3i. This result shows behavior that differs from that observed in the FT-IR results of the P3HT, as previously mentioned (Figure 3d). This difference implies that the positively charged state of the polythiophene backbone in the P3CT can be fully recovered to its initial state after repeated redox cycles. In fact, this result was verified by Raman spectroscopic analysis of the P3CT films under continuous oxidation-reduction cycles (see Figure S7b in the Supporting Information). Based on these results, we can conclude that electrochemical doping and dedoping process of P3CT interfacing with [EMIM] [TFSI] ions is reversible, unlike the doping and dedoping process of P3HT; in addition, this reversibility of P3CT leads to good cyclic endurance of the P3CT-neurofiber device.

Interestingly, the characteristic absorptions of the EMIM cation as well as those of the TFSI anion were observed in the spectra of the redox-cycled P3CT films (Figure 3g,h). This indicates that both TFSI and EMIM ions penetrated to the P3CT during the oxidation reaction and that a certain amount of both ions remained after the reduction process. In particular, the two split TFSI peaks in the spectrum of the reduced P3CT film (green line in Figure 3h) indicate the existence of TFSI anions with the transoid structure, which is favorable for ionic interaction. Given that almost no polarons remained in the reduced P3CT backbone, we inferred that the remaining TFSI anions interacted with the protons dissociated from carboxylic acid (Figure 3j). Furthermore, the absorption peak at 1575 cm⁻¹ corresponding to CH₂N/CH₃N stretching of EMIM shifted to 1568 cm⁻¹ in the spectrum of the reduced P3CT film, indicating stabilization of the positively charged imidazole ring by the anion.^[36] That is, even though the EMIM and TFSI ions that penetrated to the oxidized P3CT films remained in the films after the electrochemical reduction process, the charges of both ions could be screened by counter ions of protons and carboxylate anions of the P3CT. Therefore, a reversible change in the doping and dedoping state of P3CT was achieved, which ultimately led to the stable cyclic endurance of the P3CT-neurofiber device. The chemical interactions between EMIM, TFSI, and P3CT molecules and the charge distribution in the P3CT-based OECT device according to the redox process are schematically illustrated in Figure 3j.

Different redox mechanisms of P3HT and P3CT in the electrochemical reaction can affect the morphology and crystalline structure of the films. Figure 4a shows atomic force microscopy (AFM) images of P3HT films. When the P3HT films were oxidized, the nanofibril structure of the pristine P3HT film swelled because of the penetration of the TFSI ions. However, such swelled P3HT morphology did not recover to the initial nanofiber structure even after the reduction process, implying that the physical penetration and ejection of TFSI anions during electrochemical reactions resulted in reorganization of the P3HT chains. The crystalline structure of P3HT films subjected to electrochemical redox reactions was investigated using 2D grazing-incidence X-ray diffraction (2D-GIXD) (see Figure S10a in the Supporting Information). Figure 4b shows the out-of-plane (200) and in-plane (010) diffraction plot extracted from the 2D-GIXD pattern of P3HT. After oxidation of the P3HT film, its crystallinity substantially decreased. The lamellar stacking distance (a-axis) of P3HT increased from 1.61 to 1.88 nm because of the penetration of ions into the P3HT film; however, the π - π stacking distance (*b*-axis) decreased. These results are consistent with those of Guardado et al., who reported that ions injected into P3HT resulted in reduced crystallinity with increased lamellar stacking spacing and reduced π - π stacking originating from lattice strain.^[37] They found that the crystallinity and deformation of the molecular stacking structure were not fully recovered to the state of the pristine P3HT film despite the reduction process. When the oxidative potential was applied to the P3HT and [EMIM][TFSI] interface, TFSI ions penetrated into the stacked alkyl side chains and the nanofibril structure consisting of interconnected crystallites transformed into the nanogranule structure (Figure 4c). This supports the results of the electrochemical study showing that the doped state of P3HT was not recovered to its initial neutral state during continuous redox cycles because TFSI anions remained in the film.

In the case of P3CT films, a different tendency was observed for the morphological and crystalline structural changes under the redox conditions. When the P3CT was electrochemically oxidized and reduced in the [EMIM][TFSI], the nanogranular morphologies of pristine P3CT swelled and then returned to the initial structure (Figure 4d). Compared with the results for the P3HT films, this suggests that P3CT retains its initial structure under repeated penetration/removal of ions. Figure 4e shows the out-of-plane and in-plane GIXD results for the P3CT films according to the electrochemical redox reaction state. After the first oxidation reaction, the decrease of the crystallinity and the enhancement of the amorphous halo peak were prominent in the out-of-plane lamellar stacking, unlike the P3HT case, where the interlamellar distance increased (see Figure S10b in the Supporting Information).^[38] These results indicate disruption of the side-chain stacking during doping, accompanied by the penetration of ions and the transformation of carboxylic acid groups to carboxylate groups in the side chains of P3CT (Figure 4f). Deprotonation of the carboxylic acid groups in the







Figure 4. a,d) AFM topography images for P3HT, doped P3HT, and dedoped P3HT (a) and for P3CT, doped P3CT, and dedoped P3CT (d) films. b,e) Outof-plane and in-plane grazing-incidence X-ray diffraction (GIXD) patterns of P3HT (b) and P3CT (e) upon electrochemical doping. c,f) Schematics showing the change in the polymer structure under doping/dedoping by ions in P3HT (c) and P3CT (f).

polymer backbone is known to result in conformational transitions such as the rotation of the polymer backbone because of electrostatic repulsion forces between negatively charged polymer chains.^[39] In fact, Raman analysis of P3CT films supports the reduced planarity of polythiophene backbone by tiling or rotation of the thiophene moieties.^[40,41] (see Figure S11 in the Supporting Information) In this state the π - π stacking of the P3CT along the in-plane direction almost collapsed, and it was not recovered after the reduction process. The rotated thiophene backbone structure might provide sufficient free volume in the P3CT, where the ionic species can reversibly penetrate and retract during the redox reaction without substantial





morphological changes. Therefore, it can be concluded that the reversible ionic movement in the P3CT film as well as the balanced charge state of P3CT leads to the highly stable and durable properties during cyclic operation.

A key feature of the demonstrated neurofiber device is that the reversible doping and dedoping effect can be locally controllable by each gate. This facilitates the implementation of a unit neural network composed of multiple presynaptic neurons connected to single postsynaptic neurons. In terms of the functionality, the presynaptic spikes pass through the gates of the neurofiber as if it happens at axon terminal in biological neural network. Each gate separately defines the local channel area to change the conductance by doping and dedoping and correspondingly contributes to the source-drain current acting as an artificial synapse. The response current to the incoming spikes through each gate is integrated in a leaky way, such as a signal integration manner in the postsynaptic neuron. (see Figure S12 in the Supporting Information). To act as an artificial neuron device for neural response transmission in an SNN, response spikes of the P3CT-neurofiber's drain current denoting the postsynaptic neuron's membrane potential should mimic the expected neural behavior depicted by the leaky integrate-andfire (LIF) model.^[42] The incoming spikes' frequency determines the magnitude of the response spikes in neurons' rate coding. Figure 5a shows that the response spikes in the drain current are integrated according to the time interval (Δt) between the input pulses into the P3CT-neurofiber, representing LIF behavior. Different frequencies of the input spikes lead to the

drain current's distinguishable integration behaviors to reach the threshold (blue line). The P3HT-neurofiber also shows the same integration behavior responding to the input spike frequency (see Figure S13 in the Supporting Information). The minimum energy consumption observed in the P3CT-neurofiber device is estimated as 2 pJ per spike (Figure S14, Supporting Information). This energy consumption is comparable to that of previously reported neuromorphic devices, which is on the order of 2.68 pJ per spike on average.^[43]

During the learning process, the synaptic weights need to be appropriately adjusted depending on the potentiation and depression cases. In the P3CT- and P3HT-neurofibers, various program states function as the synaptic weights of the artificial synapses between the gate (presynaptic neuron) and the source-drain (postsynaptic neuron). Typical potentiation and depression behaviors of the neurofiber device are shown in Figure 5b, and each drain-current level of the potentiation and the depression corresponds to the synaptic weight. In greater detail, the program states of the P3HT-neurofiber (red dots) exhibit a relatively large deviation compared with those of the P3CT-neurofiber (black dots). Thus, the P3HT-neurofiber results in an inaccurate learning process because of the inaccurate synaptic weight responding to the spike stimuli and the overlap between the synaptic weights. A comparison of the program-state reliability between the P3HT- and the P3CT-neurofibers (Figure 5c) explicitly shows that the P3CT-neurofiber maintains the state levels during 46 repetitions of the potentiation and depression processes, whereas the state levels of the



Figure 5. a) Postsynaptic current (PSC) of a P3CT-neurofiber as a function of the time difference (Δt) between applied voltage spikes ($V_{GS} = -0.7 \text{ V}$, 100 ms). b) Long-term potentiation ($V_{DS} = -0.2 \text{ V}$, $V_{PGM} = -1.5 \text{ V}$, $T_{PGM} = 1 \text{ s}$) and long-term depression ($V_{DS} = -0.2 \text{ V}$, $V_{ER} = 1.8 \text{ V}$, $T_{ER} = 0.5 \text{ s}$) in the P3CT- and P3HT-neurofibers. c) Cycle test of long-term potentiation and long-term depression in P3CT- and P3HT-neurofibers over 45 cycles. d) Reproducible and discrete channel conductance of the P3CT-neurofiber defined by each gate programmed/erased (P/E) pulses ($V_{DS} = -0.2 \text{ V}$, $V_{PGM} = -1.5 \text{ V}$, $T_{PGM} = 1 \text{ s}$, $V_{ER} = 1.8 \text{ V}$, $T_{ER} = 0.1 \text{ s}$). Red, green, and blue sections show the conductivity of the channel controlled by gate1, gate2, and gate3, respectively; the number of each gate pulse is presented on the graph. e) Integration operation and value comparison for response spikes according to gates and program combinations in the P3CT-neurofiber.



P3HT-neurofiber continuously increase during cycle tests and differ from the initial program state level. This indicates that the P3CT-neurofiber is more reliable for implementing the neuromorphic learning operation by repetitively changing the program states as an artificial synaptic device.

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In addition, each synaptic weight in the unit neural network represented by the multigate P3CT-neurofiber should be controlled independently by the corresponding gate to process the spatiotemporal spike patterns incoming from the presynaptic neurons. We investigated the independent synaptic behavior of the multigate P3CT-neurofiber by measuring the reproducible and discrete channel conductance defined by each gate (Figure 5d). The synaptic weight levels labeled as a number were controlled and reproduced back and forth by one gate at a time when the other synaptic weights were programmed at a specific level in advance (gate1-red, gate2-green, and gate3-blue in Figure 5d). From this measurement, the synaptic weights of the multigate P3CT-neurofiber could be independently updated to a specific state level for the individual synapses connected with the presynaptic neuron to a specific state level. Specifically, the multigate structure P3CT-neurofiber enables a dendritic neural network to be readily configured via the implementation of both neuron and synapse behavior. Figure 5e shows how the multigate structure P3CT-neurofiber can distinguish the spatiotemporal spikes according to the synaptic weights for input signals having the same time interval. The left two plots among the subplots in Figure 5e show that the initial or low-level programmed states in gate1 make it difficult for the integrated response spikes to reach the threshold (dashed line). However, increasing the programmed state levels of gate1 and gate2 reduces the input pulses required for the integrated response spikes to cross the threshold, as shown in the right two plots among the subplots in Figure 5e. These results show that the integrated response spikes can be classified according to the combination of the programmed state levels and the spatiotemporal signals from the specific gates by utilizing the characteristics of the multigate P3CT-neurofiber for the same input.

To confirm the feasibility of P3CT-neurofiber for practical textile artificial neural network system, an array comprising 100 distinct synapses with 10 presynaptic neurons and 10 post-synaptic neurons connected was demonstrated, as shown in **Figure 6**a. This neural network array was simply fabricated by weaving the 10 P3CT-neurofibers with 10 gate-microfibers. The transfer characteristics ($I_{DS}-V_{GS}$) of the 10 synapses marked with red circle in the array show uniform memory window with I_{on}/I_{off} current ratio over 10³ at $V_{GS} = 0$ V (Figure 6b). The performance of 100 neurons is shown in Figure S15 (Supporting Information), which indicates that the P3CT-neurofibers can be reproducibly fabricated to form a neural network operating with distinct memory states.

In order to confirm whether the P3CT-neurofiber operates as a neuromorphic device in the spatiotemporal SNN learning, speech recognition based on the neuronal characteristics of the P3CT-neurofiber was demonstrated. As shown in Figure S12 (Supporting Information), the source–drain current (I_{DS}) of the P3CT-neurofiber responds to the incoming stimuli through each gate and was modeled as the postsynaptic neuron's

membrane potential. The local channel area defined by each gate represents the corresponding synapse between the preand the postsynaptic neurons by regulating the synaptic weight. Thus, the incoming spatiotemporal stimuli with the same voltage bias result in the different partial I_{DS} for the individual gate to be integrated in a leaky way. Therefore, the response I_{DS} of the P3CT-neurofiber represents the membrane potential in the spatiotemporal SNN learning method. In this work, the response spikes of the P3CT-neurofiber, which are expressed as an integration of the product of the synaptic weights and the LIF neuron signals, are especially simulating the membrane potential in the spatiotemporal SNN learning method known as tempotron.^[23,42] This model straightforwardly mimics the spatiotemporal spike signal process of biological neural network and its synaptic weights sensitive to the gate bias stimuli are suitable to implement the SNN learning method. The speech recognition process with the tempotron model using the neuronal characteristics of the P3CT-neurofiber is described in Figure 6c. (The detailed learning task is explained in Figure S12, Supporting Information) The input data, taken from the TI-46 database,^[22] consists of isolated audio waveforms of spoken digits, zero to nine, pronounced by different females. The waveform data are converted into spatiotemporal patterns, and the converted data in a series of spikes are then fed to the gates, the presynaptic neurons, through the corresponding synaptic weights into 10 P3CT-neurofibers designated to each spoken digit as the output. The response input spike from the gate (presynaptic neuron) is modeled with the corresponding synaptic weight and the time constants for leaky behavior (see Figure S16 in the Supporting Information). During the training process, the channel regions specified by the gates and corresponding to the synaptic weights are updated to classify one digit among ten digits according to the tempotron learning rule. Afterward, in the test process, the P3CT-neurofiber's I_{DS} distinguishes the input spoken digits by firing or remaining silent, following the LIF behavior. In the unit neurofiber, as a binary classifier, firing is interpreted as "target" and remaining silent indicates "null" for prediction. For example, in the case of the spoken digit "zero," the prediction is correct when the device designated as the zero classifier fires and the other devices corresponding to other digits remain silent. Through the training and testing processes, the results of classification test accuracy for ten devices trained for each digit are depicted as a 2D map in Figure 6d; the overall average test accuracy was 88.9%. In Figure 6e, the P3CTneurofiber successfully operates as a neuromorphic device by showing the saturated accuracy according to the iterative learning process. However, when the neuronal characteristics of the P3HT-neurofiber are used to perform speech recognition in the same way, unlike in the case of the P3CT-neurofiber, classification accuracy cannot be developed for the iterative training process because the weight value cannot be updated to the correct value as a consequence of the programmed/erased state's degradation identified in Figure 5b,c. In this unstable conductance states for iterative operation, some conductance states cannot be expressed as the synaptic weights because its conductance level is out of the effective conductance range defined by the g_{max} and g_{min} values. This finally results in the absence of the available synaptic weight in the learning process.

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Figure 6. a) Schematic of biological neural network and neurofiber transistor network. Photograph of a 10×10 array of P3CT-neurofibers. b) Overlaid plots of transfer characteristics for red circle regions in the 10×10 array. c) Process of speech recognition with the tempotron using the P3CT-neurofiber. d) 2D map of the classification test accuracy for 10 digits. e) Comparison of the accuracy with iterations of learning for speech recognition between the P3CT-neurofibers.

3. Conclusion

In the present work, dendritic network implementable neuromorphic fibrous OECTs with enhanced memory cyclic endurance were demonstrated using double-stranded assembly of electrode microfibers coated with carboxylic-acid-functionalized polythiophene (P3CT) and an iongel electrolyte gate insulator. The proposed P3CT-neurofiber organic transistor showed gate-field-dependent multilevel memory characteristics with good long-term stability and stable cyclic endurance, as well as synaptic plasticity, which was controllable via the presynaptic gate bias. These properties are substantially improved compared with those of neuromorphic OECTs based on conventional P3HT, which exhibited a short retention time and unstable cyclic endurance under repeated potentiation and depression processes. In the present work, fundamental studies on the electrochemical reactions of the polythiophenes and ionic species under cyclic operation revealed that the

anions that penetrated into the P3HT active channel under doping conditions and caused long-term plasticity were not completely removed from the P3HT active layer even under strong dedoping. This irreversible redox behavior of P3HT resulted in a continuous increase in the OFF-state current and in unreliable endurance under repeated cyclic operations. By contrast, the carboxylate anions and protons dissociated from the carboxylic acid groups of P3CT remained after the dedoping process, which effectively stabilized the residual cations and anions that penetrated the P3CT film during the doping process. This balanced charge state facilitates the reversible redox reactions in the P3CT channel, resulting in stable cyclic endurance of the device. P3CT-neurofiber transistor exhibited LIF behavior suitable for an SNN and maintained stable state levels during numerous repeating potentiation and depression processes. The synaptic weight of multigate P3CT-neurofiber transistors with a dendritic network was independently updated for easy synapse connection with the presynaptic ADVANCED SCIENCE NEWS _____



neuron to a specific state level. Finally, the high classification accuracy in speech recognition as an iterative learning simulation was successfully demonstrated with P3CT-neurofiber transistors. This work demonstrates that the cyclic endurance of the organic neuromorphic devices is important for iterative learning applications and that reversible electrochemical reactions of the organic semiconductor channel and ionic species are a critical factor for improving the memory and endurance properties of the device.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

artificial neural networks, cyclic endurance, fiber-shaped electronic devices, neuromorphic devices, organic electrochemical transistors, polythiophene, redox mechanism

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