17.4 Environmentally-Friendly Disposable Circuit and Battery System for Reducing Impact of E-Wastes

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The era of Internet of Things (IoT) is arriving as electronic devices have become ubiquitous. Engineers have incorporated various harmful substances and scarce elements into electronic devices for improving their performance. Disposable uses cases, such as moisture sensors or thermometers, are also increasing. As a result, a large amount of electronic devices causes electronic and electrical wastes (e-wastes), and this has become a global environmental problem. When the electronic devices are discarded without recycling, the harmful substances in them pollute the soil and water (Fig. 17.4.1). In addition, the use of scarce elements deplete resources, causing economic conflicts. For a sustainable society, disposable electronic devices should use only materials that do not harm the environment or deplete resources.

Up to now, there has been no global consensus on materials in electronic devices that do not harm the environment or deplete resources. In addition, since previous studies on environmentally friendly devices focused only on single components such as circuits [1][2] or batteries [3][4], they were not able to operate as electronic devices. Therefore, this paper suggests harmful substances and scarce elements that should not be used as a first step towards forming a consensus on environmentally friendly materials. Then, to meet the material suggestion, a newly developed organic transistor with carbon electrodes and a battery composed only of soil fertilizer elements are presented. Lastly, a moisture-sensor system is demonstrated to verify their feasibility. This is the world's first demonstration of an environmentally friendly battery and circuit system.

First, the scarce elements and harmful substances that should not be used are discussed. The definitions of scarce elements differ among countries and organizations and cover critical materials, strategic mineral resources, and critical minerals. Thus, at least the common elements among these definitions, such as precious metals, should not be used. In this paper, the circuit and battery were developed with only 7 kinds of elements (H, C, N, O, Mg, Al, S) listed within top 20 elements in the earth's crust. On the other hand, in addition to the differences among countries and organizations in definitions of hazardous materials, there is no list of common substances that are non-hazardous to the environment. Therefore, this paper refers to lists containing more than 2000 chemical substances that are regulated by Japanese law because they may have adverse effects on the atmosphere, soil, water, etc. These regulations meet the European Union's Restriction of Hazardous Substances (RoHS) and the Stockholm Convention on persistent organic pollutants. The circuit and battery in this paper were developed without these regulated substances (Fig. 17.4.2).

To meet the material requirements above, an organic semiconductor was selected as a basic component of the circuit instead of silicon semiconductors that contain several scarce elements and harmful substances. In conventional organic semiconductors [5], gold (a scarce element) and halogen elements (harmful substances) are often contained in the electrode and insulator, respectively. A technique of forming carbon electrodes has recently been reported [6]. In this paper, carbon-electrode organic semiconductors with a halogen-free insulator (aluminum oxide and cyclo-olefin polymer) were fabricated (Fig. 17.4.3). Although the carbon has a high resistance, it is adequate to operate the organic electronic devices. The effective carrier mobility of p-TFT was 2.9 $cm^2V^{-1}s^{-1}$ and n-TFT was 0.26 $cm^2V^{-1}s^{-1}$. These transistors were designed as a complementary circuit to reduce power consumption for the developed battery in this paper.

A battery composed only of soil fertilizer elements (C, H, O, Mg) was newly developed as the power source of the system (Fig. 17.4.4). This battery is based on a magnesium-air battery. This is because the electrodes of the magnesium-air battery are carbon and magnesium, which are not harmful or scarce. Conventionally, the cathode of a magnesium-air battery often uses an electrode in which carbon particles are mixed with fluororesin (a harmful substance) to form a three-dimensional porous body structure. Therefore, we have developed the battery cell without fluororesin by making the carbon electrode from bacterial cellulose that has a three-dimensional porous structure. This battery cell generates electrical power by obtaining a 1M magnesium acetate aqueous solution ($(CH_3COO)_2Mg$) with air (O_2). Since a voltage of 10V or higher was required to operate the organic circuit, 12 series-connected cells were fabricated. This battery could maintain the voltage of more than 10V at a current of 100μA for more than 3 hours.

The developed circuit and battery system was validated and evaluated in a moisture-sensor application. The block diagram of the system is illustrated in Fig. 17.4.4. In this system, the developed battery acts as both power source and sensor. When the battery detects moisture, it generates electricity and power on the sensor circuit. Then, the sensor circuit transmits a detection signal with its own 3-bit ID assigned to each device. The signal is transmitted from a speaker with amplitude-shift keying (ASK) modulation by sound waves.

Figure 17.4.5 depicts the sensor circuit. This circuit modulates a carrier frequency (f_c) with a 4-bit input signal ("D0" =detection signal, "D1, D2, D3" =3-bit ID). This circuit was designed as a digital circuit except for the oscillator (Osc) to obtain tolerance against variations of transistors. This circuit uses 2 types of Osc. One generates clock frequency (f_{clk}) for the digital circuit, and the other generates carrier frequency (f_c) for sound waves. These Oscs were based on ring oscillators that can oscillate only with transistors since it is difficult to make resistors and inductors with only the required materials. The digital block of this sensor circuit consists of a parallel-to-serial convertor (P/S) and a modulation circuit (Mod). The P/S serializes the 4-bit parallel input signal by using a 2-bit counter and a selector (Sel). To reduce the number of transistors, the 2-bit counter was implemented with gray code and the Sel. was designed with transfer gates. The serialized signal from the P/S is modulated by AND logic with the carrier signal (f_c) in Mod. The sensor circuit was manufactured by dividing it into 6 chips (#1 to #6) for debugging. #1 is the Osc for the sound wave, #2 is the Osc for the clock, #3 and #4 are Flip Flop (FF) in the 2-bit counter, #5 is the Sel, and #6 is Mod.

To demonstrate the effectiveness of the system, the sensor circuit and battery were fabricated and verified (Fig. 17.4.6). The developed battery and the sensor circuit (divided into 6 chips) were connected to an oscilloscope through a breadboard. The waveforms of the oscilloscope were shown when the moisture was put into the battery. The battery voltage was stable in the range of 14.8 to 15.6V, and the current ranged from 3 to 20μA. The OSCs for the carrier (#1) and clock (#2) generated 140 and 6.7Hz frequency, respectively. According to the clock, the sensor circuit successfully generated the detection signal and ID with ASK modulation. This system could generate the modulated sound waves when the circuit was connected to a speaker (the speaker was powered by another stabilized DC power supply). These results demonstrate that the environmentally-friendly circuit and battery system can operate as electrical devices.

Figure 17.4.7 displays photos of 6 chips fabricated. Furthermore, we have integrated the sensor circuit on one chip and validated (the number of ID is restricted to 2). This enables systems at practical levels of size and performance by using integration. In addition, the developed transistors and batteries are cheaper than silicon transistors and commercial batteries. Thus, they are suitable for disposable use cases from the viewpoint of not only the environment but also cost.

References:
[1] Y. Gao et al., "Moisture-triggered physically transient electronics," Sci. Adv., Vol. 3, 1-8, Sept. 2017.
[2] R. Martins et al., "Papertronics: Multigate paper transistor for multifunction applications," Applied Materials Today, Vol. 12, 402-414, Sept. 2018.
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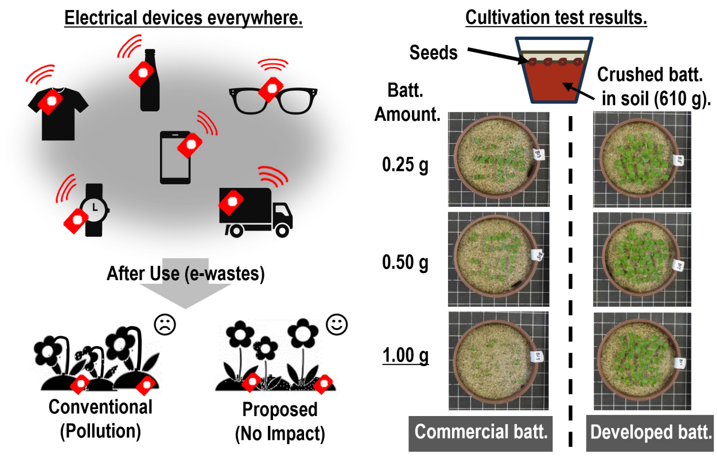


Figure 17.4.1: Concept of the disposable circuit and battery system. Cultivation test results show that just 1.00 gram of crushed commercial battery has a significant effect on plant growth unlike the developed battery.

Green: "NOT" regulated substance or scarce elements Red : Regulated substance or scarce elements

		This work	[1] Only Circuit	[2] Only Circuit
Circuit	SC	C_9-DNBDT-NW PhC_2-BQQDI	Indium gallium zinc oxide	Indium gallium zinc oxide
	Electrode	Carbon	Nickel, Aluminum	Aluminum
	Insulator	Aluminum oxide, Polycycloolefin		Cellulose Paper
	Pad/Wire	Carbon	Cupper	
	Substrate	Polyimide		

		This work	[3] Only Battery	[4] Only Battery
Battery	Cathode	Carbon	Molybdenum	Silver
	Anode	Magnesium	Magnesium	Aluminum
	Electrolyte	Magnesium acetate aqueous	Phosphate-buffered saline	Gelatine, Graphene
	Current Collector	Carbon	-	-
	Separator	Cellulose	-	-
	Housing	Polylactic acid	Polyanhydride	Polyanhydride

Figure 17.4.2: Comparison of circuit and battery materials.

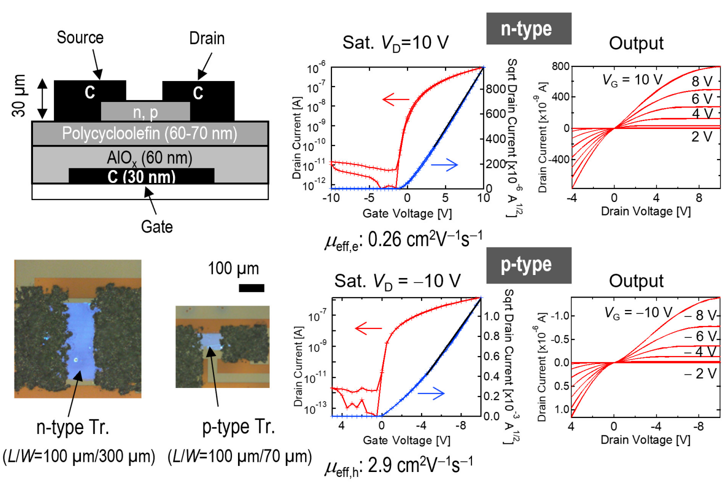


Figure 17.4.3: Developed transistors and its static performance used in this demonstration.

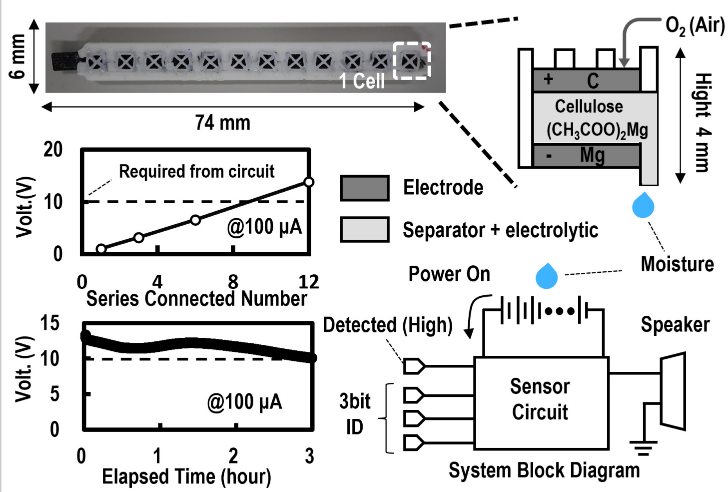


Figure 17.4.4: The developed battery and system block diagram of the moisture-sensor system. The system utilizes the characteristics of the battery that it generates electricity with moisture.

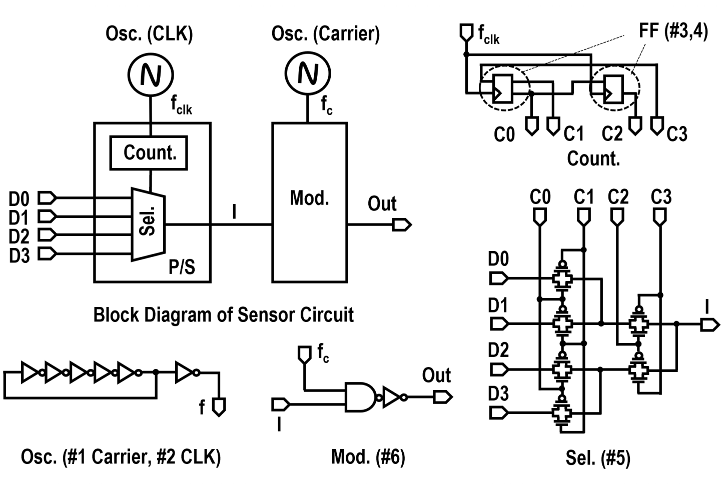
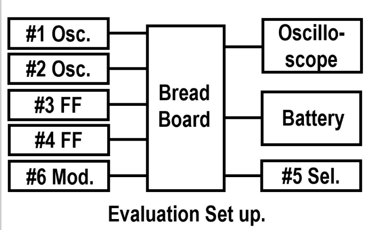


Figure 17.4.5: Diagram of the sensor circuit. The sensor circuit was manufactured by dividing it into 6 chips (#1 to #6) in the demonstration.



Performance Summary.

Carrier [Hz]	140
Clock [Hz]	6.7
Voltage [V]	14.8-15.6
Current [μA]	3-20
Date Rate [bps]	6.7
# of ID.	3

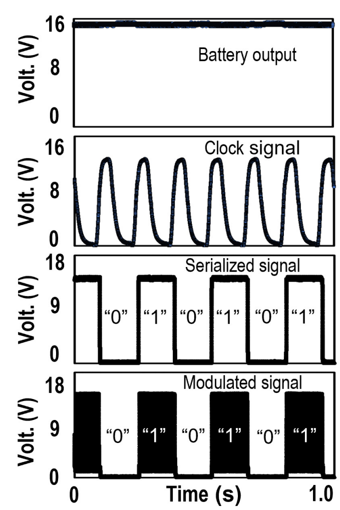
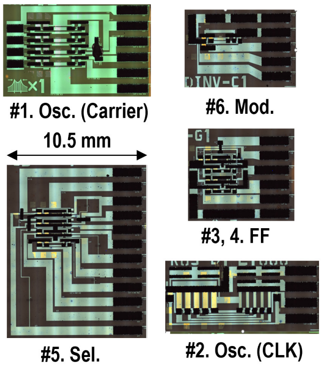
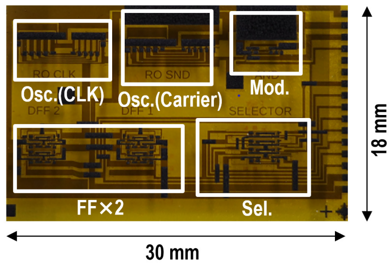


Figure 17.4.6: Evaluation set up and experimental results of the demonstration.





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# of Tr.	82	N/A	1

Figure 17.4.7: Micrographs of 6 chips fabricated for the demonstration. Micrograph of integrated chip and measured waveforms.