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Continuous Extraction and Electrochemical Monitoring of Potassium Ions in a Plant Leaf Using a Wearable Ion Sensor

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To the best of our knowledge, this is the first study to show the minimally invasive extraction and continuous monitoring of potassium ions (K^+) in a plant leaf, which is one of the most important electrolytes in plant cells. By utilizing the leaching phenomenon, K^+ in a leaf was extracted using an extraction solution, which is composed of phosphate-buffered saline and a surfactant, TritonX-100. K^+ sensor films were placed in contact with the leaf surface via a membrane soaked in the extraction solution to detect K^+ extracted from the leaf into the extraction solution. This novel plant-wearable sensor is expected to enable the minimally invasive daily monitoring of the chemical compounds in leaves for advancements in plant healthcare in future agriculture.

1. Introduction

Recent developments in sensing technologies have enabled the development of various sensors for achieving smart agriculture. Useful data detected by such sensors include environmental data, such as temperature, humidity, and carbon dioxide levels; soil data, such as pH and ion conductivity; and crop image data.[1,2] These data are analyzed and fed back to cultivation management and harvest timing to improve the productivity and quality of crops. However, presently, it is difficult to constantly and noninvasively or minimally invasively monitor the chemical components inside plants, and to the best of our knowledge, no previous studies on the use of such data have been reported. If the chemical components inside plants can be constantly monitored, this would enable a more accurate quality control of crops and an early detection of plant diseases before they become apparent.

Spectroscopic analyses, such as fluorescent spectroscopy,[3] Raman spectroscopy,[4] and near-infrared spectroscopy,[5,6] have been utilized for the nondestructive detection of chemical components in plants. Although these analytical techniques are highly sensitive and quantitative, they require large and expensive analytical systems and a high degree of user expertise. Recently, the development of miniaturized and wearable sensors for human healthcare has been

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applied in the field of smart agriculture.[7–9] Thin, light-weight, and flexible devices can be placed on the surfaces of plant leaves and stems to monitor their growth using strain sensors,[10] water loss from plants using humidity sensors,[11] and volatile organic compound emissions from plants using gas sensors.[12,13] Some chemicals in plants have also been monitored destructively using chemical sensors, which are inserted into the plant body[14–20] and attached to artificially injured areas of plants.[21–25] Incorporating nanomaterial-based sensors into plant bodies is another strategy for monitoring the chemicals in plants.[26] However, there have been few studies on wearable sensors capable of noninvasively or minimally invasively and continuously monitoring chemical components in plants.

In our previous study, we proposed a new method for the noninvasive detection of blue-fluorescent substances in plant leaves.[27] Blue and green fluorescence in intact leaves is emitted by cinnamic acids, mainly ferulic acid, which are covalently bound to the cell walls of the epidermis, and other fluorescent secondary metabolites. Changes in the fluorescence intensity of blue-fluorescent substances have been utilized as indicators of plant stress and disease.[3] In our previous study, blue-fluorescent substances, including chlorogenic acid, were noninvasively extracted by placing a hydrogel film on the leaves of a cherry tomato plant, and we found that their fluorescence intensity increased owing to *Ralstonia solanacearum* infection. The mechanism of the release of blue-fluorescent substances from the inside of plants into the hydrogel was based on the leaching phenomenon, where the substances inside plants can be released externally through defects, such as micropores, micro-damaged areas, trichome bases, leaf tips, and edges.[28] The components extracted into the hydrogel using this technique include blue-fluorescent substances and a variety of chemicals within the plant.

In this study, we demonstrated the feasibility of extracting a potassium ion (K^+), which is one of the most important electrolytes in plant cell physiology, using the leaching phenomenon. Additionally, a wearable K^+ sensor film was placed in contact with the leaf surface via a membrane soaked with a phosphate-buffered saline (PBS)-based extraction solution to show the minimally invasive extraction and continuous monitoring of K^+ in a plant leaf for the first time.

2. Materials and Methods

2.1 Extraction of K^+ in a leaf

A branch of cherry tomatoes ("yellow-mimi", *Solanum lycopersicum* cv, or TY Chika; TTM106) was cut and placed in tap water. To evaluate the effects of the composition of the extraction solution on the efficiency of K^+ extraction from a leaf, a tomato leaf was immersed in 0.5 mL of the following extraction solutions for 1 h: ultrapure water (UW), 20 μM PBS (16.2 μM Na_2HPO_4, 2.9 μM KH_2PO_4, 274.0 μM NaCl, and 5.4 μM KCl; pH 7.4) (PBS), ultrapure water containing a surfactant, namely, 0.3 mg mL^{-1} TritonX-100 (Nacalai Tesque, Inc) (UW+T100), and 20 μM PBS containing 0.3 mg mL^{-1} TritonX-100 (PBS+T100). To extract K^+ absorbed into the leaf via the foliar absorption pathway, two adjacent leaves were used for subsequent extraction experiments. One leaf was immersed in 300 μL of extraction solution containing PBS+T100 and the other leaf was immersed in a foliar absorption solution composed of 0.3 mg

mL^{-1} TritonX-100 in 100 mM KCl aqueous solution. The extraction solution was collected every hour and replaced with a fresh solution. K^+ concentrations in the collected extraction solutions from both experiments were quantified using a K^+ meter (LAQUAtwin K-11, Horiba).

2.2 Cytotoxicity test of extraction solution

Cellulose membranes (Whatman™ 3001-861, cytiva) containing the extraction solution (PBS or PBS+T100) were attached to the surfaces of tomato leaves randomly selected in one tomato strain for 5 h. After detaching the membranes, the growth of each leaf was monitored by measuring the maximum vertical length and maximum width of the leaf. The test was performed using three different tomato strains (n = 3).

2.3 Fabrication of K^+ sensor film

A silver paste (TYPE; FA-323, FUJIKURA KASEI Co., Ltd.) was printed as a lead pattern on a polyethylene naphthalate (PEN; thickness: 125 μm) substrate using a stencil sheet and baked for 30 min at 150 °C to evaporate the silver paste solvent. Carbon–graphite ink, including a redox compound of Prussian blue (PB-carbon) (C2070424P2, SunChemical Co.), was painted on the active area using a stencil sheet, followed by drying at 60 °C for 30 min. A total of 1 μL of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS; Clevious P Jet700, Heraeus) was drop-casted onto the PB-carbon area as an interfacial ion–electron transducer to minimize the potential drift of the sensors, followed by annealing at 80 °C for 15 min. Finally, 10 μL of mixture solution for the K^+-selective membrane was drop-casted on the PEDOT:PSS/PB-carbon area and dried for 15 min at 60 °C. The mixture solution for the K^+-selective membrane was prepared by dissolving 2 mg of valinomycin (Nacalai Tesque), 0.25 mg of potassium tetrakis (4-chlorophenyl)borate (Sigma-Aldrich), 16.35 mg of poly(vinyl chloride) (Sigma-Aldrich), and 35.5 μL of bis(2-ethylhexyl) sebacate (Tokyo Chemical Industry) in 275 μL of tetrahydrofuran (Tokyo Chemical Industry). The resulting sensor electrode was immersed in a conditioning solution (100 mM KCl aqueous solution) for 1 h before use.

A liquid-junction silver (Ag)/silver chloride (AgCl) reference electrode was fabricated on the same substrate as the K^+-selective electrode by screen printing. The silver paste (TYPE; FA-323, FUJIKURA KASEI Co., Ltd.) was printed on a PEN substrate as a lead pattern and baked for 30 min at 120 °C to evaporate the silver paste solvent. Subsequently, Ag/AgCl paste (Code No. C2130809D5, Sun Chemical) was printed on the active area of the Ag-lead pattern and baked for 30 min at 120 °C. The internal electrolyte paste, 50 wt% of polyvinylpyrrolidone (molecular weight is 40,000; Kanto Kagaku), was mixed in a saturated KCl aqueous solution with dimethyl sulfoxide (Fujifilm Wako Pure Chemical) in a 1:3 ratio and screen-printed over the Ag/AgCl active layer and baked for 30 min at 30 °C in vacuum. Next, a nitrocellulose membrane was placed as a liquid junction on the internal electrolyte layer and the entire structure was covered, except for the tip of the liquid junction, with a screen-printed ultraviolet (UV)-curable insulator paste (JELCON, No. IN-15M, Jujo Chemical Co., Ltd.) and irradiated with 302 nm UV for 15 min.

The potentiometric response of the resulting K^+ sensor film was measured using the measurement solutions. Concentrated KCl solution was periodically added into the measurement solution and continuously stirred at 200 rpm while monitoring the potential difference between the working and reference electrodes using the electrochemical analyzer (ALS model 602E, BAS Inc.) operated in the open-circuit potential mode (input impedance: 1×10^{12} Ω).

2.4 Extraction and detection of K^+ in a leaf using K^+ sensor film

Tobacco (*Nicotiana tabacum L.* cv., Tsukuba ichi-gou, Japan tobacco) was grown indoors under illumination of a light-emitting diode (approximately 3000 lx) for 12 h per day in pots containing commercial potting soil (Tachikawa Heiwa Nouen). A tobacco leaf was cut, and two K^+ sensor films were placed on it separately. A cotton cellulose fiber (BEMCOT™ M-1, Asahi Kasei) containing 0.3 mg mL^{-1} TritonX-100 and 100 mM KCl aqueous solution was wrapped around the petiole of the tobacco leaf to introduce K^+ into the leaf. The K^+ sensor film was attached to the tobacco leaf such that the K^+-selective membrane was in contact with the leaf surface via a cellulose membrane (Whatman™ 3001-861, cytiva) containing the extraction solution. Each sensor was connected to different electrochemical analyzers to simultaneously detect the extracted K^+ in each area.

3. Results and Discussion

First, the effects of the composition of the extraction solution on the efficiency of K^+ extraction from leaves were investigated by immersing the tomato leaves in the extraction solutions for 1 h [Fig. 1(a)]. The concentration of K^+ in the PBS (8.3 μM) was designed to be less than the concentrations of K^+ in the tomato xylem sap (30–40 mM)[29] to maintain a concentration gradient that allows K^+ to diffuse out of the leaf. The extraction solutions were collected to quantify the extracted K^+ concentration using a commercially available potassium ion meter. Figure 1(b) shows the concentration of the extracted K^+ normalized by the weight of the leaf (indicated as μM/mg-leaf). The average values of the normalized K^+ concentration slightly increased when PBS was used instead of UW. Considering the high ion concentration in the leaf, when ultrapure water was used as the extraction solution, the ultrapure water would move into the leaf because the osmotic pressure was higher in the leaf, and this might prevent the extraction of K^+ using the concentration gradient. The use of PBS as an extraction solution slightly increased the amount of the extracted K^+ probably because of the slightly smaller difference in osmotic pressure between the leaf and the extraction solution.

Adding TritonX-100 into the extraction solution also caused a slight increase in the average values of the normalized K^+ concentration. TritonX-100 is a surfactant that can cause a cytotoxic effect on the cell membrane. Therefore, we tested the cytotoxicity of TritonX-100 by comparing the growth of the tomato leaves untreated and treated with the extraction solution as follows. The cellulose membranes containing the extraction solution (PBS or PBS+T100) were attached to the surfaces of tomato leaves randomly selected in one tomato strain for 5 h. After detaching the membranes, the growth of each leaf was monitored by measuring the maximum vertical length

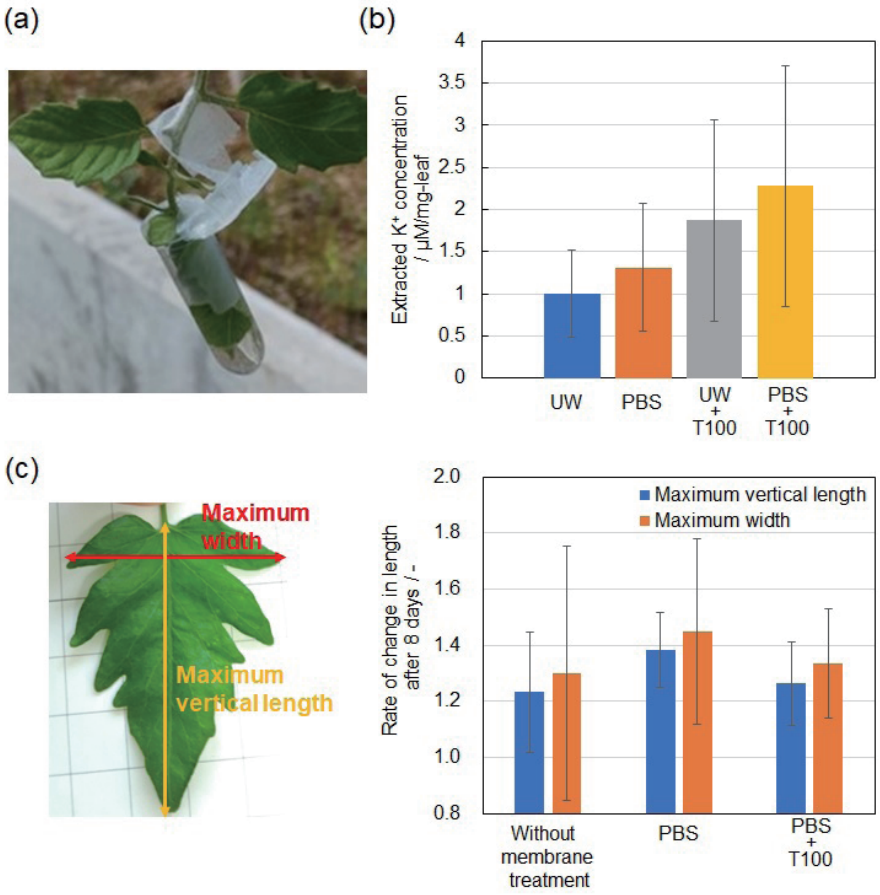

Fig. 1. (Color online) (a) Photograph of a tomato leaf immersed in extraction solution: ultrapure water (UW), 20 μM PBS (PBS), UW containing 0.3 mg mL^{-1} TritonX-100 (UW+T100), and 20 μM PBS containing 0.3 mg mL^{-1} TritonX-100 (PBS+T100). (b) Concentrations of extracted potassium ions normalized by the weight of the leaf (indicated as μM/mg-leaf) (n = 3). (c) Rates of changes in maximum vertical length and maximum width in tomato leaves before and eight days after detaching the membrane containing PBS or PBS+T100 (n = 3).

and the maximum width as shown in the photograph in Fig. 1(c). Figure 1(c) shows the rates of changes in maximum vertical length and maximum width in tomato leaves before and eight days after detaching the membrane containing PBS or PBS+T100. As a control experiment, the leaf without membrane treatment was also observed. In the Y-axis, 1.0 means no change in leaf length eight days after the treatment. There was little difference in leaf growth rate under all conditions (Rate = 1.2–1.4), suggesting the minimal cytotoxicity of TritonX-100. However, this needs further study. Therefore, we called this extraction technique "minimally invasive extraction". On the basis of these results, we used PBS+T100 as the extraction solution in the next experiments.

Figure 2(a) shows the setup for extracting K^+ from tomato leaves via leaching. Two adjacent leaves were used for this extraction experiment. One leaf was immersed in the extraction solution, PBS+T100, and the other leaf was in the foliar absorption solution containing 0.3 mg

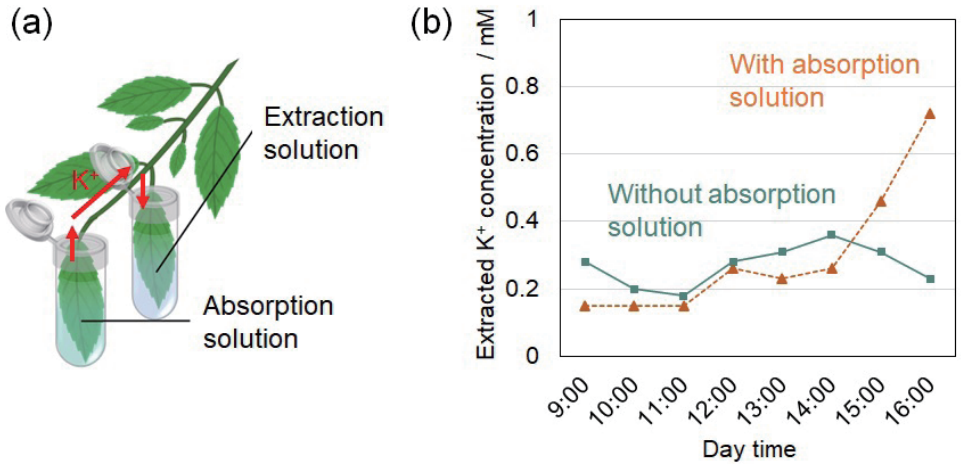

Fig. 2. (Color online) (a) Setup for potassium ion (K^+) extraction absorbed into leaf by foliar absorption pathway. (b) Change in K^+ concentration extracted into extraction solution with and without foliar absorption in a different leaf.

mL^{-1} TritonX-100 and 100 mM KCl aqueous solution. In this configuration, we expected that the K^+ absorbed by the leaf would be transported to the next leaf through the foliar fertilization pathway[30,31] and then extracted into the extraction solution. The extraction solution was collected every hour and replaced with a fresh solution. The K^+ concentration in the collected extraction solution was quantified using a commercially available potassium ion meter. Figure 2(b) shows the time course against the detected concentration of K^+ in the extraction solution. The concentration of the extracted K^+ gradually increased. However, when the next leaf was not immersed in the foliar absorption solution, no marked change in the concentration of the extracted K^+ was observed. This result suggested that the K^+ absorbed into the plant by the aforementioned pathway was extracted into the extraction solution via leaching. In other words, the K^+ extracted into the extraction solution was suggested to be derived from the K^+ in a tomato leaf.

The K^+ extracted into the extraction solution was continuously monitored using a wearable K^+ sensor film. Figures 3(a) and 3(b) show the structure and photograph of the K^+ sensor film, respectively. The valinomycin-based K^+-selective membrane was used to cover the active area of the carbon electrode via a PEDOT:PSS-based interfacial ion–electron transducer layer, which had the same structure as in our previous study.[32] The liquid-junction Ag/AgCl reference electrode composed of a Ag/AgCl electrode pattern covered with an internal electrolyte layer and an insulation layer was fabricated on the same substrate. The internal electrolyte layer was connected to the outer measurement solution through a nitrocellulose-membrane-based liquid junction. Figure 3(c) shows the representative potentiometric responses of the K^+ sensor film in the KCl aqueous solution and the extraction solution (PBS+T100). Both graphs were obtained using the same sensor film. The sensor showed a quick and stable response regarding the change in K^+ concentration in the concentration range from 0.1 to 10 mM even in the extraction solution. Figure 3(d) shows the relationship between the K^+ concentration and the detected potential. In

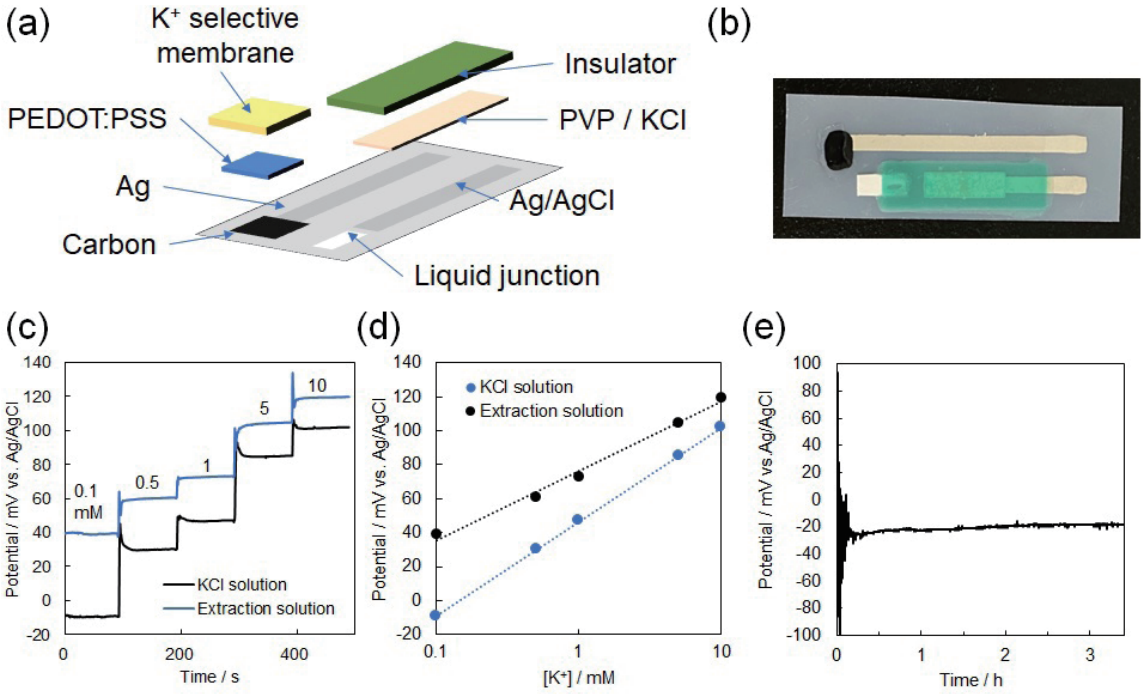

Fig. 3. (Color online) (a) Structure of potassium ion (K^+) sensor film. (b) Photograph of K^+ sensor film. (c) Potentiometric responses of K^+ sensor film in potassium chloride (KCl) aqueous solution and extraction solution. (d) Potentials against K^+ concentration were detected in the KCl aqueous solution and extraction solution. (e) Potential stability of liquid-junction Ag/AgCl electrode against a commercially available Ag/AgCl reference electrode.

the KCl aqueous solution, the slope was 52.2 ± 4.7 mV/dec (n = 4), which is almost the same as the theoretical Nernst slope. When TritonX-100 was added to the KCl aqueous solution, the slope decreased to 90.2% of that within the KCl aqueous solution. Additionally, in the extraction solution, the slope decreased to 73.5% of that within the KCl aqueous solution probably because the surfactant-mediated extraction of interfering ions affected the interfacial K^+ selectivity of the sensor membrane.[33]. Figure 3(e) shows the potential stability of the liquid-junction Ag/AgCl electrode against a commercially available Ag/AgCl reference electrode in 20 μM PBS. After approximately 15 min of setup, when the measurement solution gradually entered into the internal electrolyte layer through the liquid junction to ionically connect the inside and outside of the reference electrode, the electrode showed a stable potential for more than 3 h. The potential drift from 1 to 3 h was 2.1 mV/h, which is a sufficient operational time for the experiment described in Fig. 4.

The minimally invasive extraction and continuous monitoring of K^+ in plant leaves were demonstrated using a wearable K^+ sensor film. Figure 4(a) shows a photograph of the experimental setup. Two K^+ sensor films were separately placed on a tobacco leaf via a membrane containing the extraction solution. Tobacco leaves were used in this study because of their large surface area for examining the distribution of K^+ introduced into the leaves. A cotton cellulose fiber containing 0.3 mg mL^{-1} TritonX-100 and 100 mM KCl aqueous solution was wrapped around the petiole of the tobacco leaf to introduce K^+ from the cut surface of the petiole

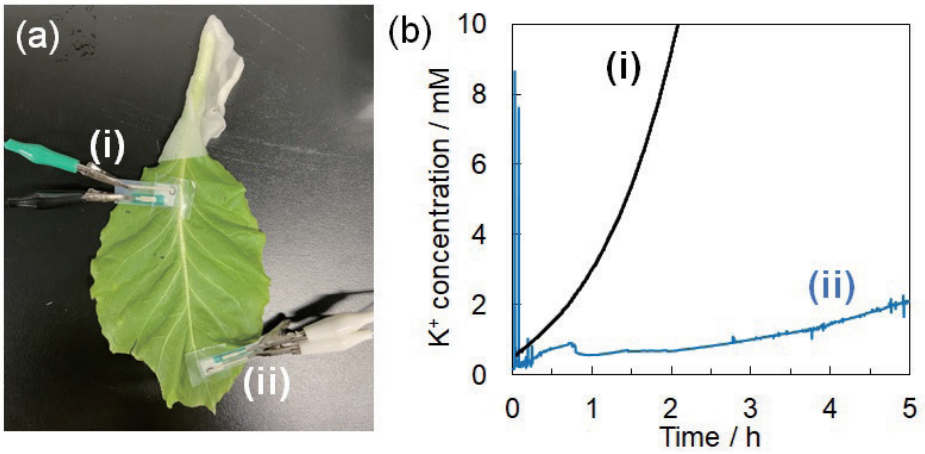

Fig. 4. (Color online) (a) Photograph of experimental setup. (b) Time courses of K^+ concentration detected at positions (i) and (ii) in (a) after introducing K^+ into leaf.

into the leaf. Each sensor was connected to different electrochemical analyzers to simultaneously detect the extracted K^+ in each area. Figure 4(b) shows the time course of the detected K^+ concentration after introducing K^+ into the leaf. The potentials were converted into K^+ concentrations using a calibration curve obtained from the extraction solution. The response of the sensor at position (i) increased gradually, suggesting the continuous extraction and detection of the K^+ introduced in the leaf. The response of the sensor at position (ii) showed a slow change probably because of the slow diffusion of K^+ in the complex transport pathways.[30] The slopes of the two sensors were evaluated in the KCl aqueous solution before and after the measurements of 51.9 and 55.5 mV/dec for position (i) and 53.4 and 54.6 mV/dec for position (ii), suggesting the stability of the sensor response during these experiments. To the best of our knowledge, this is the first study to show the minimally invasive extraction and continuous monitoring of chemical compounds in plant leaves utilizing the leaching phenomenon.

4. Conclusions

In this study, we found that K^+ in plant leaves can be extracted in a minimally invasive manner by utilizing the leaching phenomenon. The extracted K^+ was successfully and continuously detected using a K^+ sensor film that was in contact with the plant leaf via an extraction solution-soaked membrane. However, the present sensor has some limitations regarding long-term monitoring because the soaked extraction solution in the membrane gradually evaporated during measurements. Furthermore, it is unclear whether the concentrations of the extracted compounds quantitatively reflect their chemical composition in the leaves. Our further studies are focused on improving the wet interfacing materials and analyzing the relationship of the extracted (in the extraction solution) and unextracted compounds of the plant leaves to open up opportunities for the digital management of the cultivation and harvesting of crops in future agriculture.

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References

1 T. T. S. Lew, R. Sarojam, I. C. Jang, B. S. Park, N. I. Naqvi, M. H. Wong, G. P. Singh, R. J. Ram, O. Shoseyov, K. Saito, N. H. Chua, and M. S. Strano: Nat. Plants **6** (2020) 1408. https://doi.org/10.1038/s41477-020-00808-7
2 H. Yin, Y. Cao, B. Marelli, X. Zeng, A. J. Mason, and C. Cao: Adv. Mater. **33** (2021) 2007764. https://doi.org/10.1002/adma.202007764
3 H. K. Lichtenthaler: Photosynthetica **59** (2021) 364. https://doi.org/10.32615/ps.2021.020
4 S. Gupta, C. H. Huang, G. P. Singh, B. S. Park, N. H. Chua, and R. J. Ram: Sci. Rep. **10** (2020) 20206. https://doi.org/10.1038/s41598-020-76485-5
5 H. Itoh, K. Nomura, N. Shiraishi, Y. Uno, S. Kuroki, and K. Ayata: Environ. Control Biol. **53** (2015) 205. https://doi.org/10.2525/ecb.53.205
6 K. B. Beć, J. Grabska, G. K. Bonn, M. Popp, and C. W. Huck: Front. Plant Sci. **11** (2020) 1226. https://doi.org/10.3389/fpls.2020.01226
7 G. Dufil, I. Bernacka-Wojcik, A. Armada-Moreira, and E. Stavrinidou: Chem. Rev. **122** (2022) 4847. https://doi.org/10.1021/acs.chemrev.1c00525
8 G. Lee, Q. Wei, and Y. Zhu: Adv. Funct. Mater. **31** (2021) 2106475. https://doi.org/10.1002/adfm.202106475
9 C. C. Qu, X. Y. Sun, W. X. Sun, L. X. Cao, X. Q. Wang, and Z. Z. He: Small **17** (2021) 2104482. https://doi.org/10.1002/smll.202104482
10 W. Tang, T. Yan, J. Ping, J. Wu, and Y. Ying: Adv. Mater. Technol. **2** (2017) 1700021. https://doi.org/10.1002/admt.201700021
11 J. A. Barbosa, V. M. S. Freitas, L. H. B. Vidotto, G. R. Schleder, R. A. G. de Oliveira, J. F. da Rocha, L. T. Kubota, L. C. S. Vieira, H. C. N. Tolentino, I. T. Neckel, A. L. Gobbi, M. Santhiago, and R. S. Lima: ACS Appl. Mater. Interfaces **14** (2022) 22989. https://doi.org/10.1021/acsami.2c02943
12 Z. Li, Y. Liu, O. Hossain, R. Paul, S. Yao, S. Wu, J. B. Ristaino, Y. Zhu, and Q. Wei: Matter **4** (2021) 2553. https://doi.org/10.1016/j.matt.2021.06.009
13 Z. Liu, M. Wang, M. Wu, X. Li, H. Liu, N. Niu, S. Li, and L. Chen: Trends Anal. Chem. **158** (2023) 116872. https://doi.org/10.1016/j.trac.2022.116872
14 N. Coppedè, M. Janni, M. Bettelli, C. L. Maida, F. Gentile, M. Villani, R. Ruotolo, S. Iannotta, N. Marmiroli, M. Marmiroli, and A. Zappettini: Sci. Rep. **7** (2017) 16195. https://doi.org/10.1038/s41598-017-16217-4
15 J. Church, S. M. Armas, P. K. Patel, K. Chumbimuni-Torres, and W. H. Lee: Electroanalysis **30** (2018) 626. https://doi.org/10.1002/elan.201700697
16 C. Diacci, T. Abedi, J. W. Lee, E. O. Gabrielsson, M. Berggren, D. T. Simon, T. Niittylä, and E. Stavrinidou: iScience **24** (2020) 101966. https://doi.org/10.1016/j.isci.2020.101966
17 Y. Hu, J. Zhao, H. Li, X. Wang, P. Hou, C. Wang, A. Li, and L. Chen: RSC Adv. **8** (2018) 23404. https://doi.org/10.1039/C8RA03475C
18 J. Michela, C. Claudia, B. Federico, P. Sara, V. Filippo, C. Nicola, B. Manuele, C. Davide, F. Loreto, and A. Zappettini: Sci. Rep. **11** (2021) 18598. https://doi.org/10.1038/s41598-021-97872-6
19 H. Li, C. Wang, X. Wang, P. Hou, B. Luo, P. Song, D. Pan, A. Li, and L. Chen: Biosens. Bioelectron. **126** (2019) 193. https://doi.org/10.1016/j.bios.2018.10.041
20 D. Huo, D. Li, S. Xu, Y. Tang, X. Xie, D. Li, F. Song, Y. Zhang, A. Li, and L. Sun: Biosensors **12** (2022) 35. https://doi.org/10.3390/bios12010035
21 Q. Q. Ren, X. J. Yuan, X. R. Huang, W. Wen, Y. D. Zhao, and W. Chen: Biosens. Bioelectron. **50** (2013) 318. http://dx.doi.org/10.1016/j.bios.2013.07.001
22 A. S. Lima, K. R. Prieto, C. S. Santos, H. P. Valerio, E. Y. Garcia-Ochoa, A. Huerta-Robles, M. J. Beltran-Garcia, P. D. Mascio, and M. Bertotti: Biosens. Bioelectron. **99** (2018) 108. https://doi.org/10.1016/j.bios.2017.07.039
23 R. Pandey, O. Teig-Susshoz, S. Schuster, A. Avni, and Y. Shacham-Diamand: Biosens. Bioelectron. **117** (2018) 493. https://doi.org/10.1016/j.bios.2018.06.045
24 H. R. Wang, X. M. Bi, Z. J. Fang, H. Yang, H. Y. Gu, L. J. Sun, and N. Bao: Sens. Actuators, B **286** (2019) 104. https://doi.org/10.1016/j.snb.2019.01.119
25 K. C. He, H. R. Wang, H. Yang, L. J. Sun, W. Liu, and N. Bao: Anal. Chim. Acta **1120** (2020) 59. https://doi.org/10.1016/j.aca.2020.04.051

26 J. P. Giraldo, H. Wu, G. M. Newkirk, and S. Kruss: Nat. Nanotechnol. **14** (2019) 541. https://doi.org/10.1038/s41565-019-0470-6
27 S. Iwasa, Y. Kobara, K. Maeda, and K. Nagamine: Sci. Rep. **12** (2022) 13598. https://doi.org/10.1038/s41598-022-17785-w
28 H. B. Turkey, Jr.: Bull. Torrey Bot. Club **93** (1966) 385. https://doi.org/10.2307/2483411
29 V. M. Gallegos Cedillo, M. Urrestarazu, J. E. Álvaro: J. Soil Sci. Plant Nutr. **16** (2016) 991. https://doi.org/10.4067/S0718-95162016005000072
30 C. G. Corrêa, M. T. Rebouças, M. Diniz, and H. W. P. de Carvalho: ACS Agric. Sci. Technol. **1** (2021) 728. https://doi.org/10.1021/acsagscitech.1c00211
31 J. Niu, C. Liu, M. Huang, K. Liu, and D. Yan: J. Soil Sci. Plant Nutr. **21** (2021) 104. https://doi.org/10.1007/s42729-020-00346-3
32 R. Shiwaku, H. Matsui, K. Nagamine, M. Uematsu, T. Mano, Y. Maruyama, A. Nomura, K. Tsuchiya, K. Hayasaka, Y. Takeda, T. Fukuda, D. Kumaki, and S. Tokito: Sci. Rep. **8** (2018) 3922. https://doi.org/10.1038/s41598-018-22265-1
33 E. Malinowska and M. E. Meyerhoff: Anal. Chem. **70** (1998) 1477. https://doi.org/10.1021/ac970761t