## 論文の内容の要旨

(Summary of the dissertation)

論文題目 Printable Elastic Conductors for Large Area Stretchable Electronics

(大面積伸縮性エレクトロニクスのためのプリンタブル伸縮性導体)

氏 名 松久 直司

Stretchable electronic devices are essential for applications in many fields, such as wearables, healthcare, robotics, and human computer interfaces. For example, stretchable wearable sensors conform to large deformations of skins and joints and enable daily diagnosis without sacrificing the patients' daily lives. Stretchable sensors, or indicators on the surface of robots help their precise movements and improve the safety when they interact with human.

To realize these stretchable electronic devices, large stretchability is required. For example, human skins and joints have stretchabilities of ~20% and >100%,<sup>[1]</sup> respectively. Robots are designed to exceed human, requiring higher stretchability. The internal electrical connections are one of the solutions to place sensors around the joints, but the harmonic designs with mechanical systems are difficult. Furthermore, soft robots have been recently developed.<sup>[2]</sup> They have a soft bodies like octopus. Sensors employed on them also should be soft, thus the necessity of soft, stretchable devices are clear.

A stretchable wiring is the most important component to realize stretchable electronic devices. One of the approaches to realize them is thin conducting films can gain with structures such as serpentine, [3] accordion, [4] and mesh. [5,6] Another approach is utilization of intrinsically stretchable materials such as liquid metals, [7] ionic conductors, [8] and conducting polymers. [9] Composites of elastomer and conducting fillers is also one of the approaches. This methods are advantageous in terms of their printability. High performance elastic conductors have been realized by employing conducting fillers such as single or multi

walled carbon nanotubes (SWCNTs or MWCNTs),<sup>[10,11]</sup> Ag nanowires (Ag NWs),<sup>[12]</sup> Polyaniline (PANI),<sup>[13]</sup> Au nanoparticles (Au NPs),<sup>[14]</sup> and Ag flakes.<sup>[15]</sup> These show the high conductivity without strain, but it has been difficult to achieve high conductivity at strain higher than 100%. The focus of this research is to overcome this issue with low cost materials and simple printing materials.

Herein this dissertation, elastic conductors with high conductivity at large strain are demonstrated with two different concepts. The first elastic conductor inks consist of Ag flakes, fluorine rubbers, methylisobutylketone (MIBK), fluorine surfactant, and water. [16] Ag flakes are conducting fillers in the printed materials. Fluorine rubbers give the elasticity to the composite and are dissolved by MIBK. Function of fluorine surfactant and water is explained later. The ink can be printed on elastomeric substrates using stencil printing process.

Figure 1a shows the conductivity strain characteristics. The initial conductivity is 738 S cm<sup>-1</sup>, and the stretchability is as high as 215% while keeping the conductivity of 182 S cm<sup>-1</sup>. Compared with the other studies, this material showed the highest conductivity at strains of >150%. This high conductivity at high strain is achieved by utilizing hydrophilic-hydrophobic phase separation during drying process. Figure 1b shows the SEM images of the elastic conductors with and without surfactant and water. Without surfactant, Ag flakes are uniformly dispersed in elastomer. On the other hand, with surfactant, Ag flakes are aggregated at the top of the trace. Despite of the low volume fraction of Ag flakes, these materials show similar initial conductivity. The introduction of surfactant and water initiates the alignment of Ag flakes in the composites, resulting in that Ag flakes form conducting paths without reinforcing the elastomer.

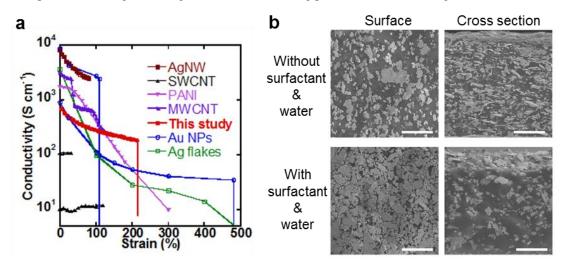


Figure 1. Printable elastic conductors with a phase separation assembly of Ag flakes. a, Conductivity-strain characteristics and comparison with the previous studies. [10–16] b, Surface/cross sectional SEM images of elastic conductors without/with surfactant and water. [16] Scale bars,  $10 \mu m$ .

The elastic conductors can be printed on textiles, enabling electronic textiles (e-textiles) applications. The first demonstration is electromyogram (EMG) measurement systems [16] (Figures 2a-c).

The elastic conductors printed in the side of human body work as vital electrodes to record EMGs. These are wired to organic transistor amplifier circuit through elastic conductors printed on the other side. Figure 2c clearly shows the recorded EMG signals generated when the wearer closed his hand. Patients or athletes can conduct their health monitoring just by wearing this device. Another application is touch sensors. (Figures 2d-f) Two sheets of textiles with printed traces are faced, forming mechanical switches. Without touch, fuzzes on the surface of textile disturb the connection of elastic conductors, but, with touch, these are short. Figure 2f demonstrates the LED operation by turning on these touch sensors.

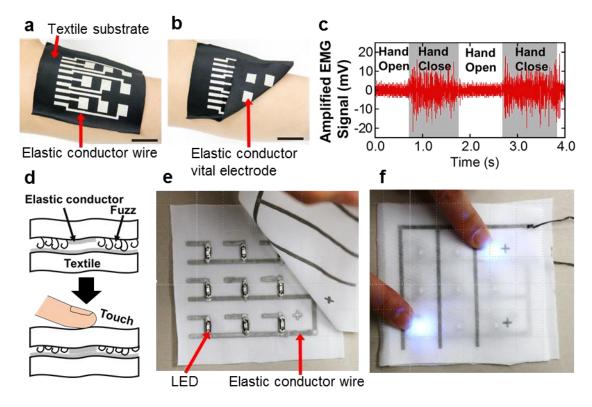


Figure 2. E-textiles enabled by printed elastic conductors. a-c, EMG sensors. d-f, Touch sensors. a,b, Pictures of EMG sensors. Scale bars, 2 cm. c, EMG signals amplified by organic amplifiers. d, A mechanism of touch sensor. e,f, Pictures of touch sensors.

Elastic conductors with another mechanism have been developed and exhibited even higher stretchability and conductivity. The details and their applications will appear in patent and journal papers in 5 years.

In this dissertation, the following things were achieved.

- Highest conductivity (>100 S cm<sup>-1</sup>) at strain higher than 100%.
- Proposal of new concepts to develop printable elastic conductors.
- Demonstration of e-textiles enabled by printed elastic conductors.

The developed printable elastic conductors have a large potential to realize large area stretchable electronics

in a very low cost manner. Future research can focus on the more careful choice of the materials to improve the cyclic durability or environmental stability.

## References

- Y. Menguc, Y.-L. Park, H. Pei, D. Vogt, P. M. Aubin, E. Winchell, L. Fluke, L. Stirling, R. J.
  Wood, C. J. Walsh, *Int. J. Rob. Res.* 2014, 33, 1748.
- [2] M. Wehner, R. L. Truby, D. J. Fitzgerald, B. Mosadegh, G. M. Whitesides, J. A. Lewis, R. J. Wood, *Nature* 2016, 536, 451.
- [3] D.-H. Kim, N. Lu, R. Ma, Y.-S. Kim, R.-H. Kim, S. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T. -i. Kim, R. Chowdhury, M. Ying, L. Xu, M. Li, H.-J. Chung, H. Keum, M. McCormick, P. Liu, Y.-W. Zhang, F. G. Omenetto, Y. Huang, T. Coleman, J. a. Rogers, *Science* 2011, 333, 838.
- [4] M. Kaltenbrunner, T. Sekitani, J. Reeder, T. Yokota, K. Kuribara, T. Tokuhara, M. Drack, R. Schwödiauer, I. Graz, S. Bauer-Gogonea, S. Bauer, T. Someya, *Nature* 2013, 499, 458.
- [5] T. Someya, Y. Kato, T. Sekitani, S. Iba, Y. Noguchi, Y. Murase, H. Kawaguchi, T. Sakurai, Proc. Natl. Acad. Sci. 2005, 102, 12321.
- [6] M. Vural, A. M. Behrens, O. B. Ayyub, J. J. Ayoub, P. Kofinas, ACS Nano 2015, 9, 336.
- [7] R. C. Chiechi, E. A. Weiss, M. D. Dickey, G. M. Whitesides, *Angew. Chemie Int. Ed.* **2008**, 47, 142.
- [8] C. Keplinger, J.-Y. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides, Z. Suo, *Science* **2013**, *341*,
- [9] S. Savagatrup, E. Chan, S. M. Renteria-Garcia, A. D. Printz, A. V. Zaretski, T. F. O'Connor, D. Rodriquez, E. Valle, D. J. Lipomi, Adv. Funct. Mater. 2015, 25, 427.
- [10] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya, *Nat. Mater.* 2009, 8, 494.
- [11] K. Chun, Y. Oh, J. Rho, J. Ahn, Y. Kim, H. R. Choi, S. Baik, Nat. Nanotechnol. 2010, 5, 853.
- [12] J. Liang, K. Tong, Q. Pei, Adv. Mater. 2016, 28, 5986.
- [13] H. Stoyanov, M. Kollosche, S. Risse, R. Waché, G. Kofod, Adv. Mater. 2013, 25, 578.
- [14] Y. Kim, J. Zhu, B. Yeom, M. Di Prima, X. Su, J.-G. Kim, S. J. Yoo, C. Uher, N. A. Kotov, *Nature* 2013, 500, 59.
- [15] T. Araki, M. Nogi, K. Suganuma, M. Kogure, O. Kirihara, *IEEE Electron Device Lett.* **2011**, *32*, 1424.
- [16] N. Matsuhisa, M. Kaltenbrunner, T. Yokota, H. Jinno, K. Kuribara, T. Sekitani, T. Someya, *Nat. Commun.* **2015**, *6*, 7461.