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Dang, W., Manjakkal, L., Lorenzelli, L., Vinciguerra, V. and Dahiya, R. (2017) Stretchable pH Sensing Patch in a Hybrid Package. In: IEEE Sensors 2017, Glasgow, UK, 30 Oct - 01 Nov 2017.

This is the author accepted manuscript.

The published version is available:
DOI: 10.1109/ICSENS.2017.8234297

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Deposited on: 27 October 2017

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Stretchable pH Sensing Patch in a Hybrid Package

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***Abstract*— This work presents a novel stretchable pH sensing patch to detect the pH in body fluid which is one of the most important parameters in human health monitoring. The sensing patch is a hybrid package comprising of polyimide/gold-based stretchable interconnects and graphite composite-based flexible pH sensor. With the integration of stretchable interconnects, the patch is able to withstand external stretching up to 50% longer than its original length. Moreover, the electrical behavior of the patch does not degrade as studied by the real-time resistance investigation. In order to protect the connecting electrodes and wirings from direct contacting with solution under analysis, the sensing patch is encapsulated with elastic polymer with the active sensing area exposed. The fabricated patch reveals a high pH sensitivity of 36.2 µA/pH in the pH range between 5 and 9 which is validated through electrochemical and electroanalytical studies.**

Keywords—hybrid package, stretchable interconnects, pH sensor, electrochemistry, graphite composite

I. INTRODUCTION

Rapid growth in flexible and stretchable electronics have opened new avenues for health monitoring. The conformability or the stretchability in healthcare technologies is vital because it allows the sensing device to conform to human body and thus enable robust measurements. However, such devices must have electrically and mechanically robust connection over certain degree of bending, twisting and stretching movements [1, 2]. This calls for suitable packages, especially with soft materials. In this paper we present a pH sensor patch with stretchable interconnects packaged in soft polydimethylsiloxane (PDMS). The pH sensor has been used here to demonstrate the utility of proposed packaged patch in healthcare applications. Amongst various physiological parameters, the pH value of body fluid is most important due to its strong relationship with the human activity. For example, the status of human body can be reflected in pH through sweat [3, 4], diseases [5], drug delivery [6] and wound monitoring [7] etc. The pH value in sweat can reflect the status of skin dehydration level and even detect the skin disease [4]. The pH value of wound indicates the wound healing status where the pH of healthy skin is around 5-5.5 and infected wounded skin will show a slightly basic pH (7-8.5) due to bacterial colonization [7]. A few works in literature have reported conformable or stretchable devices for health monitoring. These include stretchable electrochemical patch with the pH, humidity, glucose and temperature sensing [5] and stretchable skin-mountable device to measure the concentration of sodium chloride and pH [8]. While interesting sensing mechanisms have been demonstrated in literature, the packaging is largely ignored. For health applications the packaging plays a crucial role in the acceptance of new technology. The packaging in these application also has specific requirements. For example, the electrochemical sensing device requires its active area to be exposed to the fluid and rest of the components to be packaged in soft substrates to enable flexibility or stretchability. The electrical connects in the device should be encapsulated against any corrosive solution and aggressive solvent. Furthermore, the materials for packaging have to be chemically, electrically and thermally stable. Conventional packaging often realized in microfluidic channels [4], molded blocks [9] and multi-layered lamination [7, 10] is insufficient for health applications. These techniques are either difficult to be implemented in real-time electrochemical sensing due to the fully sealed structure or difficult to be stretchable due to its rigidity.

This work was supported by the European Commission under grant agreement PITN-GA-2012-317488-CONTEST and Engineering and Physical Sciences Council (EPSRC) Fellowship for Growth – Printable Tactile Skin (EP/M002527/1).

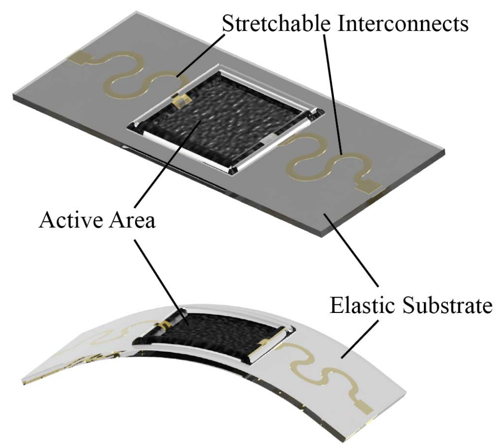

Figure 1: Schematic of the stretchable pH sensing patch with hybrid packaging that can be conformably attached to unconventional surface.

This paper presents a novel stretchable pH sensing patch packaged in soft PDMS. The package is an elastic polymer PDMS with all the electrical connection protected against solution under analysis. The sensing electrode, which is based on graphite composite, is sensible to pH values ranging from 5 to 9. The sensing electrode is flexible and has been integrated with serpentine-shaped stretchable interconnects with silver adhesive. The overall patch is packaged in a hybrid structure as depicted in *Figure 1* where stretchable interconnects provide the stretchability in the system, flexible electrode actively sense the signal, silver adhesive electrically connects sensing electrode with stretchable interconnects and solid epoxy mechanically bonds all the connection area. In this way, the

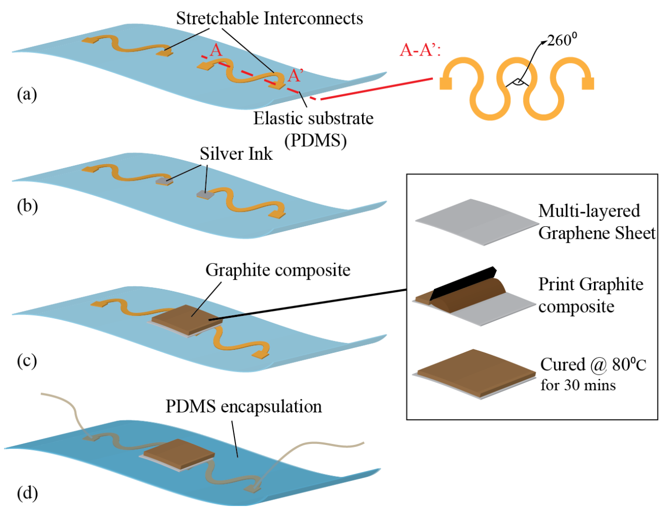

Figure 2: The assembly steps of prototype device including (a) transferring prepared stretchable interconnects to PDMS substrate, (b) applying silver inks on the contact electrode, (c) transferring pH sensing electrode and (d) final encapsulating with electrical wirings.

realized pH sensing patch can withstand around 50% external stretching and conformably attached to any arbitrary surface.

II. Experiments

The overall fabrication process of the pH sensing patch can be separated into three phases which comprise the stretchable interconnect fabrication phase, pH sensing electrode fabrication phase and final device packaging phase.

A. Stretchable Interconnects fabrication

The stretchable interconnects were fabricated on silicon carrier wafer based on polyimide (PI) and gold. The design of interconnects has the serpentine shape in order to provide a high stretchability to the patch [11]. The serpentine-shaped interconnects in our work has a curved arc of 260° and a width of 500 µm as illustrated in *Figure 2(a)*. The fabrication process started from spin-on PI precursor on silicon carrier wafer. The serpentine shape pattern was realized through photolithography and dry etching followed by gold metal deposition on cured PI film. After this the interconnects were transferred via water soluble tape (3M, US) to the elastic PDMS (Sylgard®, Dow Corning) substrate which has a thickness of 180 µm and prepared with a pre-polymer/ cross link ratio of 10:1.

B. pH sensing electrode fabrication

The sensing electrode is composed of a commercial multi-layered graphene sheet (Graphene Supermarket, US) covered with printed graphite composite [12]. After printing, the graphite composite was cured in the oven at 80°C for 30 mins as described in *Figure 2(c)*.

C. Stretchable pH sensing patch packaging

The final pH sensing patch was assembled through steps as illustrated in *Figure 2*. Silver ink were first applied to the contact pads from stretchable interconnects. Then the sensing electrode was transferred to bridge the two interconnects. Afterwards, the integration area was encapsulated by epoxy adhesive. In the end, the overall structure was encapsulated by PDMS with the sensing area opened.

III. Results and Discussion

The electrochemical performance of the pH sensitive electrode was evaluated by electrical impedance spectroscopic (EIS) analysis in the AC frequency range between 10 mHz and 1 MHz using Metrohm Autolab. Buffer solution for testing the performance of pH sensing were used as received from Sigma-Aldrich. They have a pH value ranging from 5 to 9. Electrochemical experiments were performed using a two electrode system with an external glass Ag/AgCl reference electrode. Analytical performance of the device was performed by using the cyclic voltammetry (CV) with a sweeping the potential from -1 V to 1 V at a sweep rate of 0.05 V/s. Electromechanical experiments were performed on the vibration-resist table with a custom-made uniaxial stretching setup based on two linear step motors (Micronix, US). Simultaneously, the variation in electrical resistance of the prototype was recorded through multimeter (Agilent 34461A, US).

The complex impedance data of the electrode observed from EIS analysis is represented as a Nyquist plot in *Figure 3(left)*. The variation of complex impedance with pH of solution is due to the change of electrical properties of electrochemical double layer (EDL) formed between the graphite electrode-pH solution interface [10, 13]. The straight line in Nyquist plot represent the ion diffusion across the sensitive electrode from the pH solution. We observed that the angle for the straight line changes with the variation of H^+/OH^- ionic concentration in solution. As shown in *Table 1*, the slope of the angle increases along with the increase in pH values. Due to the conductive nature of the graphite electrode, the charge transfer resistance at high frequency range is negligible (represented in the *Figure 3(right)*). However, due to the variation in conductivity of buffer solution, there is a shift in the resistance R_s (shown in *Table 1*). The variation in R_s is due to influence of electrolyte resistance and other minor ohmic resistance of the material.

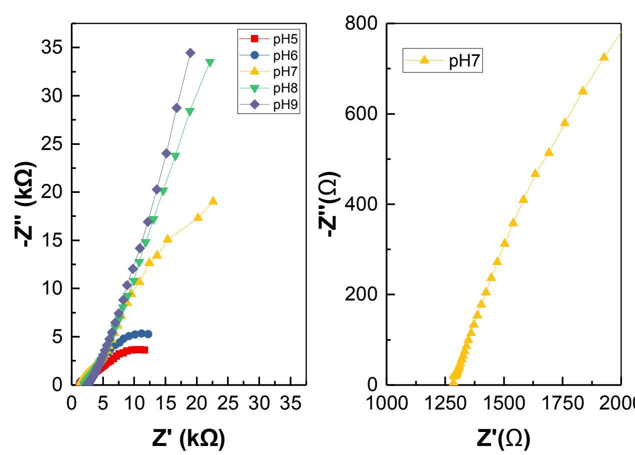

Figure 3: EIS spectrum of fabricated pH sensing patch corresponding to each pH values (left) and magnified image in high frequency range from EIS spectrum for pH 7 (right).

TABLE I. COMPARISION IN SOLUTIION RESISTANCE AND SLOPE ANGLE BETWEEN DIFFERENT PH VALUES.

pH value	R_s (Ω)	*Slope (°)*
5	1314.3	23.44
6	1309.3	33.05
7	1283.1	46.45
8	2115	61.4
9	2496.7	68.29

The pH sensitivity of the electrode was measured by using electroanalytical CV measurements. *Figure 4(left)* indicates the relationship between the measured current and swept potential between -1 V and 1V. It is observed that the corresponded output current at 1 V decreases when the pH is increasing. In the meanwhile, oxidation and redox peaks can be noticed in the curve of pH 7 which may due to the impurity in the solution. Hence, the data point of pH 7 was not evaluated. The measured data points can linearly fit in curve with a slope of 36.2 µA/pH. The straight line confirms that the ionic diffusion at the electrode surface with changing pH value of solution [14].

The electrical behavior of the fabricated device was mechanical stable when stretched at a ratio of 50% as depicted in *Figure 5*. The device shows a maximum change in 6% under 50% stretching. The change in overall resistance of the device is attributable to (a) the deformation in conductors, (b) change in contact resistance and (c) bending effect of composite. The effective contributions of these factors are illustrated in *Figure 5*.

IV. CONCLUSION

In this work, a stretchable pH sensing patch with soft PDMS package was fabricated and characterized through electrochemical and electromechanical measurements. The fabricated sensing patch has a pH sensitivity of 36.2 µA/pH. The hybrid package structure allows the overall patch withstand a stretchability of 50%. Furthermore, the electrical behavior of pH sensing patch shows to be stable against external stretching.

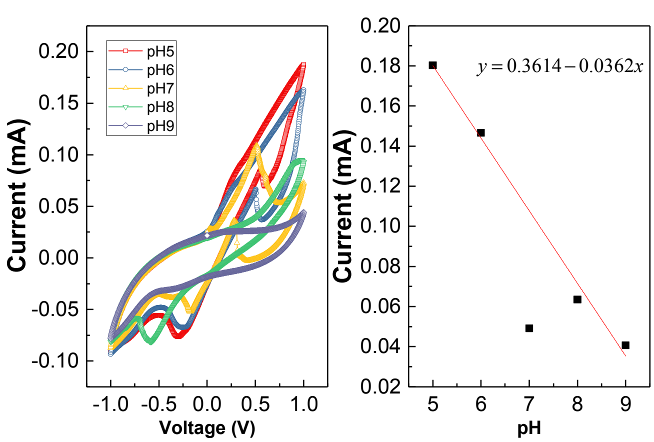

Figure 4: The cyclic voltammetry sweep for the fabricated pH sensing patch. (left) and the pH sensitivity of fabricated patch with the linear fitting.(right).

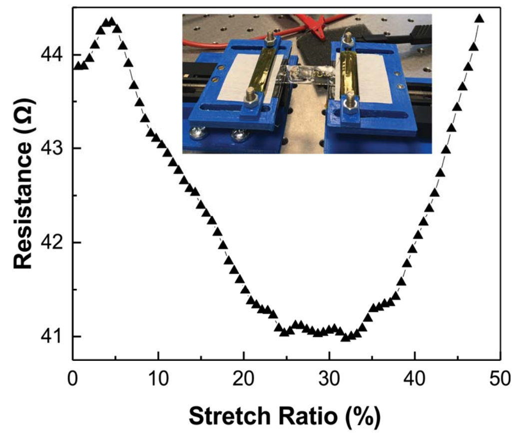

Figure 5: Electromechanical characterization on the stretchable pH sensing patch.

REFERENCES

[1] W. Dang, V. Vinciguerra, L. Lorenzelli, and R. Dahiya, "Printable stretchable interconnects," *Flexible and Printed Electronics,* vol. 2, pp. 1-17, 2017.

[2] N. Yogeswaran, W. Dang, W. T. Navaraj, D. Shakthivel, S. Khan, E. O. Polat, *et al.*, "New materials and advances in making electronic skin for interactive robots," *Advanced Robotics,* vol. 29, pp. 1359-1373, 2015.

[3] V. F. Curto, S. Coyle, R. Byrne, N. Angelov, D. Diamond, and F. Benito-Lopez, "Concept and development of an autonomous wearable micro-fluidic platform for real time pH sweat analysis," *Sensors and Actuators B: Chemical,* vol. 175, pp. 263-270, 2012.

[4] V. F. Curto, C. Fay, S. Coyle, R. Byrne, C. O'Toole, C. Barry, *et al.*, "Real-time sweat pH monitoring based on a wearable chemical barcode micro-fluidic platform incorporating ionic liquids," *Sensors and Actuators B: Chemical,* vol. 171–172, pp. 1327-1334, 2012.

[5] H. Lee, T. K. Choi, Y. B. Lee, H. R. Cho, R. Ghaffari, L. Wang, *et al.*, "A graphene-based electrochemical device with thermoresponsive microneedles for diabetes monitoring and therapy," *Nat Nano,* vol. 11, pp. 566-572, 2016.

[6] H. Lee, C. Song, Y. S. Hong, M. S. Kim, H. R. Cho, T. Kang, *et al.*, "Wearable/disposable sweat-based glucose monitoring device with multistage transdermal drug delivery module," *Science Advances,* vol. 3, 2017.

[7] T. Guinovart, G. Valdés-Ramírez, J. R. Windmiller, F. J. Andrade, and J. Wang, "Bandage-Based Wearable Potentiometric Sensor for Monitoring Wound pH," *Electroanalysis,* vol. 26, pp. 1345-1353, 2014.

[8] X. Huang, Y. Liu, K. Chen, W.-J. Shin, C.-J. Lu, G.-W. Kong, *et al.*, "Stretchable, Wireless Sensors and Functional Substrates for Epidermal Characterization of Sweat," *Small,* vol. 10, pp. 3083-3090, 2014.

[9] C.-P. Hsu, P.-C. Chen, *et. al.*, "A Package Technology for Miniaturized Field-Effect Transistor-Based Biosensors and the Sensor Array," *ECS Journal of Solid State Science and Technology,* vol. 6, pp. 63-67, 2017.

[10] M. Simić, L. Manjakkal, K. Zaraska, G. M. Stojanović, and R. Dahiya, "TiO_2-Based Thick Film pH Sensor," *IEEE Sensors Journal,* vol. 17, pp. 248-255, 2017.

[11] M. Gonzalez, F. Axisa, M. V. Bulcke, D. Brosteaux, B. Vandevelde, and J. Vanfleteren, "Design of metal interconnects for stretchable electronic circuits," *Microelectronics Reliability,* vol. 48, pp. 825-832, 2008.

[12] S. Khan, L. Lorenzelli, and R. S. Dahiya, "Technologies for Printing Sensors and Electronics Over Large Flexible Substrates: A Review," *IEEE Sensors Journal,* vol. 15, pp. 3164-3185, 2015.

[13] L. Manjakkal, C. L. Pascual, and R. Dahiya, "Electrochemical Sensors with Screen Printed Ag/AgCl/KCl Reference Electrodes," IEEE Sensors 2017 (Accepted), Glasgow, UK, 2017.

[14] F. S. Semaan, E. M. Pinto, É. T. G. Cavalheiro, and C. M. A. Brett, "A Graphite-Polyurethane Composite Electrode for the Analysis of Furosemide," *Electroanalysis,* vol. 20, pp. 2287-2293, 2008.