Development of Ion-Selective Electrode Fabrication Process Based-on Drop-On-Demand Printing Technique

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Abstract

Ion-selective electrodes (ISEs) have been applied across many fields. The typical fabrication often offers large size and expensive electrode. We develop a fabrication process using drop-on-demand (DOD) printing technique to produce a smaller sensor. The DOD printer utilizes a pneumatic-base print-head as drop generator of a polymer ink. Several groups of photopolymer are specifically formulated to use with our DOD printer. The polymer ink is printed to form a thin membrane that is the important part in the ISE. Operating parameters in printing process are identified to achieve good forming of the final film.

***Keywords**:* Drop-on-demand, Ion-selective electrode, Photopolymer.

1. Introduction

Research and development on ion-selective electrodes (ISEs) have been continued for quite sometimes. The fabrication trend of those electrodes is moving toward miniaturization in order to reduce cost and yield high volume production. Many research groups tried to devise fabrication techniques that offer simple processes. For example, Konchi et al. [1] used the screen-printing technique to fabricate sensors with copper ion-selective membrane. Cranny et al. [2] form silver-silver chloride electrodes for detecting chloride ions based-on thickfilm technology. Heng et al. [3] developed solid-state ion sensors by using a photocurable self-plasticised acrylic membrane. Uhlig et al. [4] produced a miniaturized ion-selective sensor chip to detect potassium in a biomedical application. Liu et al. [5] created a microsensor for soil moisture measurement.

The typical ISE fabrication process often engages a solvent casting of targeted polymers, and then attaches the formed polymer to the electrode tube. This process can be cumbersome when the size of the sensor is small. Since miniaturized ISE often consists of multi-materials putting layer-by-layer, we adopt a drop-on-demand (DOD) printing techniques that performs these manufacturing tasks naturally.

Drop on demand (DOD) is one type of inkjet printing technologies that ejects a micro-droplet at desired location. Three-dimensional objects are realized by printing another layer on top of others. The DODs have been recently applied to fabricate sensors. For example, Cho et al. [5] fabricated humidity sensors with photo-curable electrolyte inks using ink-jet printing technique. Huang et al. [6] improved ink-jet printing method to create $LiCoO_2$ thin film electrode.

This paper presents our ongoing development of the fabrication processes. We developed a DOD printing system to create three-dimensional parts. Drop-on-demand printing system is used with our propietary photopolymer formula to form certain layers of an ion-selective electrode. Droplets of a printing media are formed using pneumatic-based print-head. Several experiments were carried out to find appropriate parameters of fabrication processes. Those parameters include operating room temperature, pressures of pneumatic system, timing for pressure pulse, chemical composition, and curing time.

The paper is organized as following. Section 2 gives the overview of components of the DOD printing system comprises computer program, UV LED lamp and the chemical which is used for printing. The chemical composition and processes of chemical preparation are also elaborated in this section. Section 3 describes the experiment set up procedure, parameters and CMU printing program. Furthermore, the mechanism of pneumatic system and synchronizer are explained. Section 4 discusses the results of experiments. Finally, conclusions are given in section 5.

2. Drop-on-demand printing system

2.1 Drop-on-demand printing system

Our DOD printing system as illustrated in Fig. 1 consists of main components as following: a XYZ motion stage, a set of pneumatic-based droplet ejector, a synchronizer and a controlling computer.

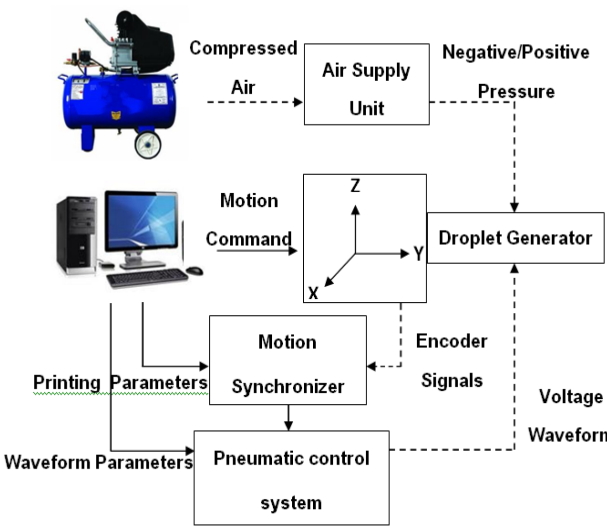

Fig. 1 An overview of the DOD printing system

The "CMU printer control" program, depicted in Fig. 2, controls and organizes the operating sequences of the printer system. As for curing process, the UV LED with the center of wavelength at 365 nm is used to cure the printed polymer which is shown in Fig. 3. For ease of installation, the glass fiber optic is used to guide the light to the printing stage

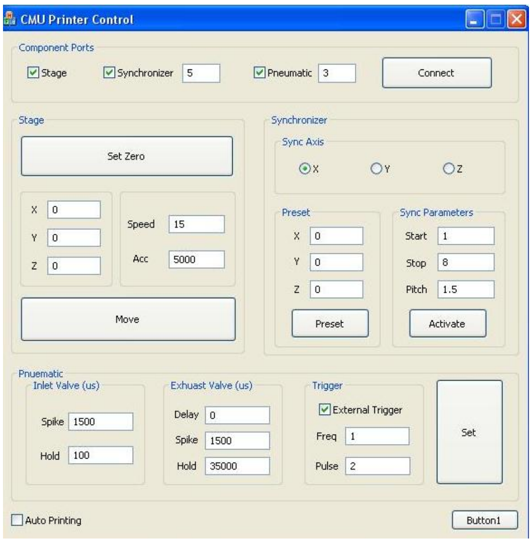

Fig.2 Controller program window

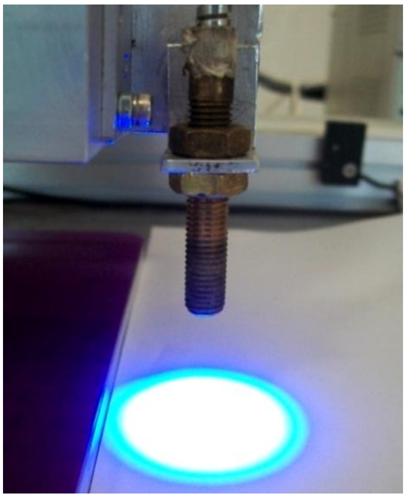

Fig. 3 UV LED Lamp

2.2 Chemicals

All chemicals used in our project are analytical grade. We formulate two chemical groups; the first chemical group prepare by mixing 1,6-hexanediol diacrylate (HDDA), ethyl-4-dimethylaminobenzoate (EDMAB) and thioxanthone-9-one (TXO) with the weight ratio is given in Table 1.

Table.1 Chemical composition of the supporting membrane polymer.

Chemical	Weight Ratio (%)
HDDA	94.4
EDMAB	4.7
TXO	0.9

The cocktail in Table. 1 is blended to methyl methacrylate (MMA) with the ratio 1:1. This photo-sensitive polymer will be used as a supporting structure of the membrane polymer.

The second chemical group is formulated to use as a stock for an ion-selective membrane. The chemicals are n-buthyl-acrylate (nBA), 1,6-hexanediol diacrylate (HDDA), ethyl-4-dimethylaminobenzoate (EDMAB), and thioxanthone-9-one (TXO). The weight ratio is illustrated in Table. 2.

Table.2 Chemical Composition of the Membrane Polymer

Chemical	Weight Ratio (%)
nBA	90.0
HDDA	0.5
EDMAB	8.6
TXO	0.9

3. Experimental Set Up

Experiments are conducted under various operating parameters to determine the proper setting in ISEs fabrication. Our DOD system is operated in the air-conditioned room. The temperature is controlled in the range of 23-27 degree Celsius. We used the polyester film (laser printer film) as the printing substrate. Various parameters of orifice size, droplet pitch and curing time are used for several tests. Orifice sizes for testing are varied from 75 - 150 μm and the droplet pitches 1.0 – 2.0 mm are used in the experiments.

The "CMU Printer Control" program acts as the brain of system. It controls and organizes the sequences of all printing tasks. In addition, the program specifies the motion of the XYZ stage, communicates with the synchronizer, and defines all timings of the pneumatic system.

The pneumatic system is operated through two solenoid valves; one for inlet and another for exhaust. The voltage supply to each valve is using spike and hold pattern as shown in Fig.4. The spike-voltage is fixed at 24 volts and the hold-voltage is set at 16 volts. The spike-time and hold-time are controlled using our proprietary pneumatic-driver hardware.

The synchronizer captured the motion of the XYZ stage and sending pulse command to the pneumatic-driver hardware once the position of the print-head (stage) is at the desired position as depicted in Fig.5. Hence, it closed the loop between motion and printing.

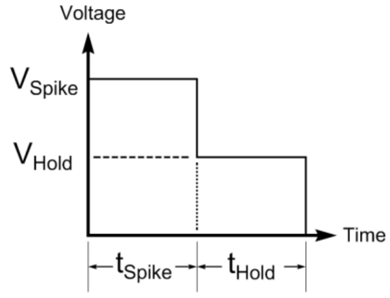

Fig. 4 Supply voltage pattern to the solenoid valve

The print-head comprises brass cylinder, nozzle and pneumatic connector as shown in Fig. 6. After installing the print-head, the nozzle and reservoir are cleaned with ethanol and using compress air purging through the print-head until it dries. The photopolymer is then load into the reservoir. The polyester substrate is prepared from the laser printer films.

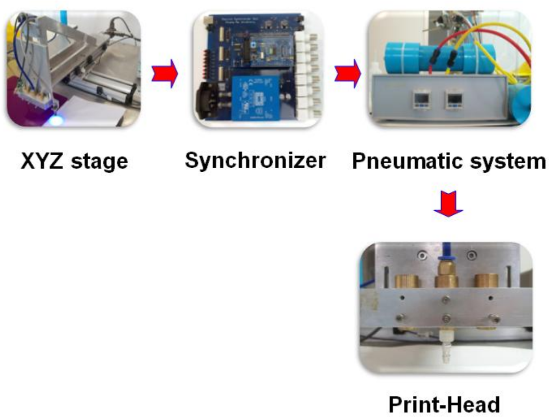

Fig. 5 The DOD system diagram

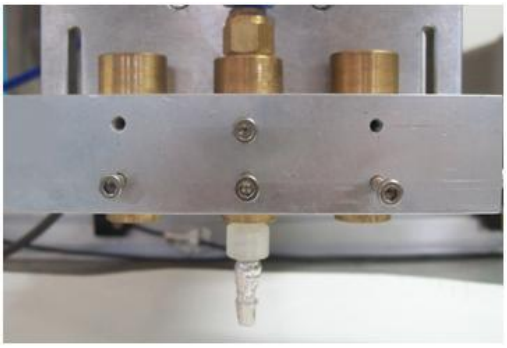

Fig. 6 The Print-head

When key-in all parameters to the CMU printer control program, the machine is printing the polymer automatically to the substrate. The UV lamp is manually turned on immediately after the printing process is completed. The UV light exposes only small area of the substrate. Therefore, we need to move the light spot back and forth in order to let the photo-polymer cured evenly. Once the curing process is completed, the substrate is washed with absolute alcohol to remove uncured residue. Similar experiment procedures are conducted on both groups of polymer. Several experiments lead us to obtain suitable parameters.

4. Result and Discussion

After printing the polymer with several sets of parameters, the results of printing the first chemical group are shown in Fig.7.

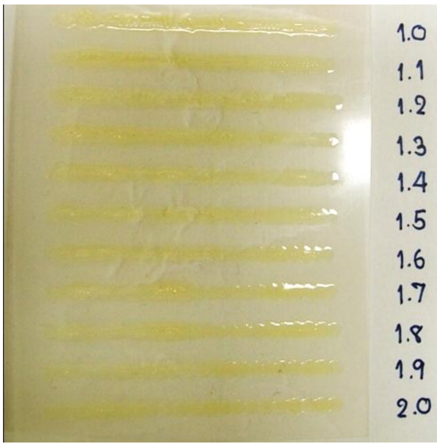

Fig.7 The printed lines of the first chemical group with droplet pitch 1.0 - 2.0 mm.

The line with 1.0 mm pitch was widest but the edge and the surface were not even. The line with 2.0 mm pitch was thinnest and the edge was clearly not even. The line with 1.5 mm pitch formed the smoothest line. The diameter of the orifice for this experiment was 150 µm. All printed lines were cured under UV exposure in the same conditions. The curing time and LED UV lamp speed were 4 seconds and 15 mm/s, respectively.The second experiment was performed to test the curing time for the second group of polymer, since the chemical composition of the second group was very different compared the first. The cured samples with various exposure times are illustrated in Fig. 8.

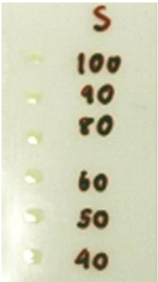

Fig.8 The curing time test 40-100 seconds

The membrane polymer that exposure to UV light less than 40 seconds was not cured; thus, the uncured polymer was washed away after rinse with absolute alcohol. As a result, the suitable curing duration was set 40 seconds.

The last experiment was to fabricate membrane using two chemical groups. The first chemical group was used as a supporting material for the membrane polymer group. The supporting material was printed in the rectangular grid 10X10 mm as shown in Fig. 9.

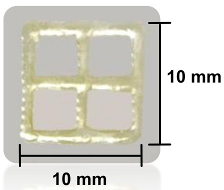

Fig.9 Rectangular grid 10X10 mm printed from the first chemical group.

After curing, we rinsed the printed substrate with absolute alcohol to remove uncured residue and let it dry at room temperature. After the printed structure dried, five microliters of the membrane polymer was dropped at the center of the each grid manually. The membrane was cured under UV exposure with the scanning rate of 10 mm/sec. The duration of curing was 400 seconds. The membrane film created by manual drop is shown in Fig. 10. To compare with the automatic printing, the membrane polymer was dropped on another structure grid using drop-on-demand printer and cured with the same condition as manual drop. The printed result is illustrated in Fig.11.

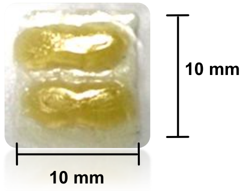

Fig. 10 The cure membrane film of manual drop.

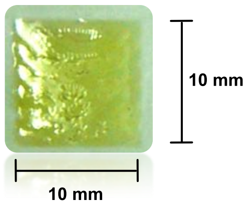

Fig. 11 The cured membrane film of automatic drop.

When the membrane polymer has cured, the tacky and flexible film was obtained which was a required characteristic of membrane for ISE. Although the membrane could be fabricated with the pneumatic-based print-head, the surface of the cured polymer film was not very smooth and the shape of the film was not very well defined. The shrinkage of photo-polymer after cured caused unsmooth and ill-defined shape of the membrane film. However this does not affect to the function of ISE.

5. Conclusions and Future Development

We present the development of ion selective electrode fabrication using drop-on-demand printer. The development includes the chemicals and the parameters during fabrication processes. The chemicals are formulated to minimize curing time and cured film shrinkage. The printed film shows desired characteristics of membrane polymer. The future development of our fabrication process is to complete the whole sensor that can be used to measure ion such as nitrate, ammonium and chlorine.

6. Acknowledgement

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7. References

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