Direct ink writing for electroresponsive human machine interfaces

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SINGAPORE

**DIRECT INK WRITING FOR ELECTRORESPONSIVE HUMAN
MACHINE INTERFACES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2021

DIRECT INK WRITING FOR ELECTRORESPONSIVE HUMAN MACHINE INTERFACES

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2021

Statement of Originality

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Authorship Attribution Statement

This thesis contains material from 1 paper submitted in the following peer-reviewed journal and is currently under review, in which I am listed as an author.

Work regarding tactile responsive device from Chapter 5 and Chapter 6 is submitted as *Ankit; Febby Krisnadi, Shreyas Pethe, Kwang Jen Ryan Lim; Mohit Rameshchandra Kulkarni, Dino Accoto.,Nripan Mathews, "MXene Incorporated Polymeric Hybrids for Stiffness Modulation in Printed Adaptive Surfaces."*

The contributions of the co-authors are as follows:

Ankit conceived the idea with the guidance from Nripan Mathews.

Ankit designed and led the research under the supervision of Nripan Mathews., carried out the experiments, and analysed the experimental data.

Ankit and Febby Krisnadi fabricated the composite and actuators and performed their characterization.

Shreyas Pethe performed the Direct-Ink-Write of Ag, PEG and PDMS.

Shreyas Pethe prepared the MXene dispersions.

Kwang Jen Ryan Lim prepared the screen-printed Ag heaters.

Mohit Rameshchandra Kulkarni helped in designing electrical circuit for all-printed haptic device.

Dino Accoto helped with mechanical characterization of bulk composites.

Ankit & Nripan Mathews wrote the manuscript. All the authors contributed in reviewing the manuscript.

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Pethe Shreyas Dinesh

Abstract

To aid with efficient and reliable communication with machines, Human-Machine Interfaces (HMIs) are crucial. Current approaches for HMIs rely on rigid, non-compliant devices. This structural non-compliance with inherently soft, curvilinear human body makes interfaces non-intuitive and limits widespread applications of HMIs. Hence, it is necessary to develop newer, compliant form factors for HMIs via development of soft sensors and responsive devices.

Existing methods for fabrication of soft devices require high temperature processing and are hence not suitable for large scale devices made with soft polymeric materials. Extrusion based additive manufacturing methods such as Direct Ink Writing (DIW) show great potential for this application. This work focuses on optimization and modification of DIW system to handle various viscosities of inks, and special functional materials, to fabricate all-printed HMI devices.

Initially, a custom DIW setup was assembled in-house. 3 axis motion stage was used for moving the dispensing head. Syringe pump and peristaltic pumps were used for low-viscosity inks. Pneumatic ink dispenser was used for highly viscous shear thinning inks. The Syringe-pump system was modified to accommodate Phase Change Material (PCM) ink for tactile response devices.

Formulations of various composite material systems were optimized for printing via DIW systems. First, a low viscosity conducting ink of PEDOT:PSS and MWCNT aqueous suspensions was prepared. 2 different dilutions of MWCNT, 0.5mg/ml and 1mg/ml were prepared and mixed with PEDOT:PSS in varying volume ratios. 1:3 ratio of PEDOT:PSS to 0.5 mg/ml MWCNT suspension was found out to have lowest resistivity. Subsequently, Acetylene black nanoparticles were mixed with PDMS to form viscous conducting composite ink. Percolation threshold for the network is found out to be at $\sim 13\%$ (w/w). To maintain printability, loading was limited to 15% and ink was prepared by adding crosslinker and thinner to the mixture. Further, Polyethylene glycol (PEG) was dispensed

using a modified setup to keep it molten. Ti_3C_2 MXene was intercalated using LiBr and DMSO and delaminated to prepare 10mg/ml suspension which was added to PEG. The PEG-MXene composite had higher amount of nucleation sites. This helped in speeding up the phase transformation of printed patterns.

For the sensing part of HMI, various tactile sensors were printed using the developed conducting inks. PEDOT:PSS-MWCNT composite was used to fabricate bending angle sensor, and strain sensor. The bending angle sensor shows fast, highly linear response with up to 10° resolution, and a range of $0-180^\circ$. The strain sensor successfully measures small strains with $\Delta R/R_0=15$ measured for 5% strain. Further, Acetylene black – PDMS ink was utilized for fabrication of proximity sensor. Material differentiation and water content detection using these sensors is demonstrated. Different sensor geometries were tested and upto 2% of $\Delta C/C_0$ was achieved for metallic object. PEG-MXene PCM ink was used along with silver joule heater to fabricate flexible hardness modulation based tactile response devices. A thermally modulated transition resulting in 10 times change in hardness of the material was obtained as a response. A 3×3 array of such devices was printed to demonstrate display of letters via hardness modulation

Finally, future scope of this project is discussed. Challenges for printing inks such as MXene dispersions and Liquid Metal are presented. Results of initial experiments carried out for newer printing paradigms such as 3D printing of stretchable materials and multi-material printing is discussed. Further, newer devices such as all printed stretchable electroluminescent devices and printed active devices such as TFTs are proposed.

Lay Summary

Communication with machines such as computers and robots is crucial in today's technology -based world. Exchange of data between humans and machines can be facilitated by Human-machine interfaces. This research explores the possibility of 2D and 3D printing of such interfaces using a technique called direct ink writing, where, liquid inks are dispensed along computer-sketched paths and drawings. A custom built system was assembled to do so using 3-axis robot and different pumps to move ink through the printing nozzle.

Various inks were developed for different purposes. Conducting polymer called PEDOT:PSS and carbon nanotubes were mixed to form highly conductive ink. This ink was used to make sensors which can sense degree of stretching and bending angle.

Conducting particles of carbon were mixed with silicone to form stretchable paste like conducting ink. Proximity sensors were printed using this ink, and various geometries were compared. Highly sensitive spiral shape of sensor was used to demonstrate detection of presence of water and differentiate between metal and plastic to sort objects based on their materials.

Polyethylene glycol, a wax like material which can change phase when heated at lower temperatures was used to make a device which generates different hardness on demand. The softness or hardness of patterns can be felt by touching it. An emerging nanomaterial called MXene is used to increase the speed of solid-liquid transition. This material is used to prepare devices that change hardness on demand, to give feedback to humans.

For future scope, 3D printing of stretchable conductors, printed stretchable displays and printed transistors are discussed, along with newer ink formulations.

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Abbreviations

3D	3-dimentional
2D	2-dimentional
DIW	Direct ink writing
DMSO	Dimethyl Sulfoxide
EL	Electroluminescence
FDM	Fused deposition modelling
FFF	Fused filament formation
HMI	Human Machine Interface
MWCNT	Multiwalled Carbon Nano Tubes
LM	Liquid Metal
PCM	Phase Change Material
PEDOT:PSS	Poly(3,4-ethyldioxythiophene) : Polystyrene sulphonate
PDMS	Polydimethylsiloxane
PEG	Polyethylene glycol
SEM	Scanning electron microscopy/micrograph
SLS	selective laser sintering
SVG	Scalable vector graphic

Chapter 1

Introduction

This chapter describes the motivation for the research project and provides a background for the topic. Importance of development of newer interfaces between machines and physical worlds is emphasized. Reasons for choice of direct ink writing technique is briefly discussed. Objective of this study is to explore and expand the capabilities of DIW printing technique for fabrication of soft interface devices such as sensors and actuators. Various novel functional inks are developed and optimized. Soft sensors for sensing strain, bending angle and proximity fabricated. Novel all-printed soft tactile response device is reported.

1.1 Research motivation

Human machine interfaces (HMIs) are the systems that enable exchange of information between humans and machines. For information exchange, machines need to interact with the environment and sense various stimuli such as touch, pressure, temperature, proximity etc. Various specialized sensors are used to convert these physical stimuli to digital signals which can be read and processed by computers. Response from machines can be produced using various actuators, which convert digital signal into output perceivable by human sensory receptors. These include light, sound, and displacement / deformation. [1] HMIs are critical for their role in applications such as robotics[2], medical devices and health monitoring [3]–[5], prosthetics[6], and virtual and immersive reality[5], [7], [8]. However, conventional HMIs are rigid and non-compliant. Furthermore, the traditional HMIs simulate the tactile experience rather than producing actual physical changes. This limits their widespread application. [9] Hence, to improve the interaction between humans and physical systems, compliant and soft interfaces need to be developed. [10].

Figure 1. 1 Various application where HMIs play crucial role.

To this end, focused research has been done on developing soft sensors and actuators. Variety of soft sensors have been fabricated including strain sensors[11], [12], pressure sensors[12],[13],[14], and proximity sensors[15], [16]. To generate tactile response, soft actuation technologies like DEAs[17] pneumatics[18], piezoelectric materials[10], [19] magnetic materials[20], shape memory polymers / alloys [21] have been explored. These

responsive surfaces comprising of soft sensors and actuators are currently being fabricated using methods such as thermal deposition [3][7][22] (Chemical and physical vapor deposition, sputtering, etc.), spray pyrolysis, lithography[23], [24], and solution processing (casting, blade coating, spin coating, etc.)[25] for electrodes and active layers (responsive matrix). However, these fabrication techniques have certain limitations. (1) Most of these techniques are suitable for small scale devices (μm to cm scale). (2) Some of these techniques involve high temperatures which may not be suitable for organic molecules (polymers). (3) Few methods for electrode deposition rely on thermal deposition and high-energy processing, which may not be suitable for soft, elastomeric substrates. (4) The human interfaces need to be customized according to the requirements of the user for optimized use. These fabrication techniques do not allow for large customized human interfaces. (5) Finally, these methods do not allow for multi-material processing required for complete device fabrication.

Additive manufacturing techniques like DIW (direct ink writing) aim to mitigate these shortcomings. DIW is an extrusion based system which utilizes computer controlled dispensing of liquid inks. DIW offers advantages of handling variety of materials (viscosity, rheology, post processing) , [26]–[28] printing in 2 dimensions and 3 dimensions[27], [29], and ability to print multiple materials at the same time [30], [31] on top of the advantages such as large scale fabrication, patterning, and low temperature processing offered by any other printing process. Generally high viscosity inks have been dispensed using DIW setups and low viscosity inks have rarely been tried. Furthermore, phase change materials (PCMs) (solid to liquid) have not been patterned previously. Patterning of PCMs along with printed heaters will allow for novel responsive devices. Additionally, different surface textures can be created by patterning of PCM. Finally, an all-printed tactile responsive device is also demonstrated which, to the best of our knowledge, has never been reported previously.

1.2 Problem Statements

- (a) Owing to the working principle of DIW system, it becomes challenging to dispense low viscosity inks. However, for a truly versatile system, the setup should be capable of handling materials across the spectrum of viscosities.
- (b) Phase change materials which undergo thermally driven solid to liquid transitions pose challenge in terms of patterning, via any fabrication technique. This is a result of different mechanical, morphological and surface wetting behaviors in solid and liquid phase.
- (c) Different fabrication techniques used for individual layers of a device necessitates moving the substrate to different stations and time consuming alignment processes . This increases the fabrication complexity and in turn, the cost.

1.3 Objective and Scope

The objectives of this dissertation are as following :

- To optimize the DIW system for printing of ink formulations with wide range of viscosities.
- To design a customized module for patterning of PCMs.
- To fabricate all printed HMI devices using DIW system.

The scope of this dissertation are as follows :

- Development and optimization of ink formulations (conductive inks).
- Electrical and morphological characterizations of DIW printed ink formulations (conductive inks).
- Customization of DIW setup for printing PCMs.
- Formulation and characterization of PCM ink.

- Printing resistive and capacitive sensors for tactile and proximity sensing.
- Generation of haptic response through all-printed flexible rigidity modulation device.
- Electrical, thermal and mechanical evaluation of the devices.

1.4 Dissertation Overview

Chapter 1 provides a motivation and background for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning strategies for fabricating stretchable electronics and e-skins. Various printing methods and inks are discussed in this chapter.

Chapter 3 discusses the details of experimental procedure and principles of characterization methods.

Chapter 4 describes the assembly of the custom built DIW system and the operation principles of various components in it.

Chapter 5 elaborates the results of experiments regarding ink formulations and optimization.

Chapter 6 provides a detailed overview of all the devices that were fabricated using DIW setup and inks described in earlier chapters.

Chapter 7 concludes the study and elaborates on the future scope for the project.

1.5 Outcome and Novelty

A custom DIW setup was assembled. Low viscosity PEDOT:PSS - MWCNT aqueous composite ink was successfully printed using DIW setup. Strain and bending angle sensors were successfully printed using this ink. Additionally, high viscosity Acetylene black-

PDMS composite ink was developed and dispensed using same setup. Proximity sensors were fabricated using this ink. PCM ink of Polyethylene glycol - MXene composite was also formulated and successfully printed. Modifications were made to the system for dispensing PCM ink. Fabrication of an all-printed tactile response device using printed joule heaters, PCM ink and PDMS encapsulation is reported.

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Chapter 2

Literature Review

Recent developments in the field of stretchable electronics for making soft HMIs are discussed in this chapter. Various mechanical and material based approaches for making stretchable, compliant devices are explained briefly. Different printing methods used to fabricate these stretchable conductors are evaluated. Inkjet printing, Direct ink writing and Screen printing are discussed in detail to determine their suitability for the application. Process capabilities, applications, and limitations for these three techniques are considered and an attempt is made to compare them. Further, the process parameters for direct ink writing such as ink rheology, print speed, nozzle height etc., and their effects on printing are explained in detail. Metallic, carbon-based, and organic ink systems are discussed briefly based on their stretchability, printability, and electrical properties towards the end of the chapter.

2.1 Human-Machine Interfaces and tactile sensing

As discussed in previous chapter, devices that facilitate exchange of information between a human and a machine can be classified as human-machine interfaces. These include sensors which convert physical stimuli to digital signal, and actuators, which convert digital data to human-perceivable output. Various types of sensors including touch and proximity sensors, temperature sensors [1], humidity sensors[2], [3], photosensors and cameras, vibration sensors, accelerometers, microphones etc. are used to collect physical information and convert it to digital form.

However, for an active interaction with computer, humans still largely rely on physical input devices like keyboards, mice, and trackpads. In the last decade resistive and capacitive touch screens have largely augmented and replaced the conventional devices. [4] Since touch is the most primitive way humans and animals interact with each other, it is intuitive to use tactile input for communication with machines.[5]

On the other side, tactile output devices are still under-explored. Commercial output devices are still limited to motor-based haptics and vibration actuators. However, newer manufacturing techniques and materials are now being studied for fabrication of new forms of tactile outputs. These include wearable soft haptics, piezo-electric based devices and surface and texture modulation devices[6][7][8].

For seamless transitions between physical and virtual worlds, its important for these input/output devices to conform with all types of objects and human body. This is possible with the help of specialized materials and design approaches to make flexible and stretchable electronics. Thus, this study will mainly focus on fabrication of soft tactile interfaces. This includes strain, proximity, touch and bending sensors on the input side and surface modulation device on the output side.

2.2 Stretchable Electronics for Soft Interfaces

The recent development of e-skins for robotics and human machine interface has opened new avenues for materials research. Efforts have been made to fabricate multifunctional sensing skins and interfaces.[9]–[11] The main focus area for materials science in this field is that of fabricating devices that can not only conform, but mechanically behave like human skin.

For this application, stretchable and flexible electronics have been widely studied in the recent years, owing to their advantages over conventional electronics. As most of the components required for fabrication are polymeric materials, they can be processed without clean room requirements and highly specialized equipment. Digital and transfer printing techniques can easily take advantage of this and cheaply produce them for applications such as flexible displays, f-PCBs, bioelectronic implants and e-skins[12].

There are several strategies used for making stretchable electronics, which can be categorized into two approaches, mechanical/structural and materials. Under structural approach, design elements such as serpentine patterns[13], mesh[11], kirigami[14], printing on pre-stretched membrane etc. can be implemented. On the other hand, materials based approach uses intrinsically stretchable conducting materials like PEDOT:PSS, CNTs[15] / AgNW[16] and their percolation networks, liquid metals[17], ionic conductors[18] etc. Table 2.1 taken from [19] summarizes these different approaches.

Table 2. 1 Comparison of structures and materials implemented for making stretchable conductors. (Taken from Matsuhisa et. al [11])

Structure / Material	Conductivity (S/cm)	Sheet Resistance (Ohm / sq.)	Stretchability (%)	Young's Modulus	Processes
Serpentine	~400,000	5-20	20-1600	-	Photolithography, laser, mechanical cutting
Mesh	~400,000	20	20-1000	-	Photolithography, laser, mechanical cutting
Microcracks	~400,000	10	30-350	-	Vacuum deposition
Longitudinal wave	~400,000	2	20-400	-	Pre-stretching, heating, hydration
Liquid metal	34,000	0.01	>1000	<1kPa	Fluidics, Nozzle printing, stencil printing
Ionic conductor	~0.001	100-1000	>1000	1kPa-1MPa	Fluidics, nozzle printing
Conducting Polymers	0.1-1000	~10	80-800	10kPa-10MPa	Spin coating, Inkjet printing
CNTs	~1000	~300	>150	~1MPa	Spray coating, spin coating
AgNWs	~10,000	0.1-20	100-200	~1MPa	Spray coating, spin coating
Printable elastic conductors	100-70,000	0.01-0.1	100-400	1-10MPa	Screen printing, nozzle printing

As it can be seen from table 2.1, most techniques for forming intricate patterns involve high energy processes like laser cutting, thermal evaporation, CVD etc. Others include invasive chemicals. These techniques damage soft surfaces and thus limit the substrates greatly. Moreover, as they are subtractive / masked deposition processes, substantial

amount of material is wasted. Thus additive manufacturing techniques like printing are being investigated for this purpose.

2.3 Printing Techniques for Electronics

The development of printed electronics started with the use of screen printing for making silver contacts, in 1984. Further advancements in digital printing techniques like inkjet printing made it possible for functional silver inks to be deposited at higher resolutions and more complex patterns could be achieved. During the last decade, a major progress in the field of carbon nanomaterials lead to development of inks made from graphene and CNTs. Transfer printing techniques such as stamping, gravure printing as well as inkjet printing and direct dispensing were demonstrated for the inks. Transistors and logic elements have also been reported[20]. Recently, effort is also being made to print out composite materials, 2D materials like MXenes and TMDCs as well as functional polymers. Electrically conducting polymers provide a high degree of mechanical flexibility and stretchability for making stretchable circuits and components.

Figure 2. 1 Overview of printing processes

At present there exists a wide array of materials printing techniques. A wide range of structural and functional materials can be printed to achieve intricate geometries and designs using the techniques described in (but not limited to) Figure 2.1.

Printing processes can widely be classified in 3 groups, based on the dimensionality of their printing.[21] For dot printing, Inkjet printing is widely used and studied for the fabrication of electronics, while powder-based 3D printing is used for manufacturing ceramics. For processes which use continuous line, extrusion-based processes like FDM have been commercialized for 3D printing of solids. Direct Ink Writing is used for handling low viscosity and shear-thinning viscoelastic inks. Robocasting is a similar method, primarily studied for making ceramic green bodies. In the planar printing, one layer of the material is printed at a time. Digital Light Processing is commercialized for 3D printing laser parts, while for electronic materials, screen printing is used to make flexible printed silver circuit boards. Following chapter will discuss one representative technique from each group, viz. Inkjet printing, Direct Ink Writing and Screen printing.

2.4 Inkjet Printing

Inkjet printing has been an established technique for digital printing. The technology relies on dispensing drops of volumes in picolitres, with diameters as small as $15\mu\text{m}$. Combined with functional inks, a wide variety of devices can be printed using inkjet printer. *Beedasy and Smith* [22] have summarized the technologies, inks and modifications for inkjet printing of electronics. The printers can be operated in one of the two modes : continuous mode and drop-on-demand [23].

In the continuous inkjet mode, a stream of droplets is generated continuously using electrostatics. The orifice through which the droplets travel has opposite polarity as

that of a pair of charged plates. The electric field attracts and directs the stream for printing. Unused droplets are directed towards an ink gutter to catch and recycle them.

Figure 2. 2 Schematic of Inkjet printing in (a) continuous mode (b) drop on demand mode, taken from [15]

In Drop on Demand (DOD) mode, the ink droplets are only generated where necessary. This removes the necessity to deal with the unused droplets. Two different droplet generation mechanisms, thermal and piezo-electric crystals are used for DOD printing. The thermal inkjet head (also known as bubblejet) works by heating ink chamber to vaporize the ink and produce bubbles. These bubbles push the ink out of the orifice. However, industrial and commercial printer heads mainly use piezo-electric crystal. The actuation of crystal is used to produce the pressure pulse which dispenses the ink. The pulse can be customized and tweaked to a great deal to best suit the ink by controlling the actuation voltage and timing. The voltage waveform affects the size and frequency of the droplets. [22]

Problems such as misfiring of jets, nozzle wetting and satellite droplets can be rectified by optimizing waveform and voltage of the jetting nozzle. *Liou, Chan and Shih* have identified various parameters affecting print quality. According to the study, increase in voltage results in increase of both, droplet velocity as well as size. Critical values of nozzle diameter, fluid viscosity and surface tension limit the use of inks and obtainable resolution, while avoiding the problems[24].

Inkjet printing is a versatile process despite its specific requirements for ink properties. The application of inkjet in printing of functional materials range from conducting circuits [25],

to sensors [26] [27] , and from perovskite solar cells [28], to thin film transistors and displays [29].

2.4.1 Screen Printing

Use of mesh screens for transferring and patterning ink on to various substrates dates to early 1900s, and is widely used for making printed textiles and clothing, decals, labels, signboards etc. The same technique is used with functional ink to produce perovskite solar cells [30], Organic LEDs [31], and flexible circuits [32].

Figure 2. 3 Schematic of screen printing process. Taken from [25]

The basic screen printing setup includes a stencil screen, squeegee and clamps to clamp the screen and substrate together. Silk screen mesh with desired pattern to block the ink from the blank regions. Negative image of the pattern to be printed is etched into a photocurable resin applied over the screen. Different screens can be used on the same substrate to print different inks and form multi-layered devices. The process can be manual or automated depending on the screen size and desired throughput. [33]

The print quality depends on majorly 2 factors, mesh size and ink properties. Very fine mesh sizes can be used to achieve line widths of $20\mu\text{m}$ [34]. Mesh size depends on factors such as mesh count, wire diameter, and mesh thickness.

Screen printing varies from other digital printing techniques in a sense that it requires a pre-formed mesh for unique design. Thus, this process is suitable for mass production. However, it cannot be efficiently used for prototyping or custom printing as every design change requires the screen to be prepared from scratch.

2.4.2 Direct Ink Writing

Direct Ink Writing is a digital printing technique which dispenses the ink in the patterns directly on the substrate. It is analogous to FDM for polymer 3D printing and robocasting for ceramics, only difference being the inks. DIW uses viscoelastic or shear thinning ink formulations to print various structural/functional components. The inks are pushed through a nozzle by maintaining pressure on the one side. The nozzle is moved across the print area using a 3-axis motion system in order to trace the path

Figure 2. 4 Schematic of a direct ink writing system. Taken from [29]

The line width and print resolution depend on the ink properties, print speed, nozzle diameter and other properties. This study will focus on DIW and section 2.3 will discuss the printing technique and the affecting parameters in detail.

Direct ink writing process is customizable and can be fine-tuned to best suit the ink. Due to which, all printed devices can be made on the same setup. These include hydrogel based structures, biosensors, micro-electrode arrays[35], supercapacitors[36] and energy storage devices[37]. [38] Direct ink writing provides more robust and flexible system for printing. Wide variety of materials can be dispensed with the same setup with minimal additives in the material. Changes in viscosity can be compensated by adjusting other parameters such as write speed and nozzle height. This type of flexibility is not offered by inkjet printing. At the same time rapid prototyping, customization and modularity of the system makes it an attractive choice for development of all-printed electronic systems. Table 2.2 summarizes and compares the three printing systems.

Table 2. 2 Comparison between inkjet printing, DIW and Screen printing

Parameter	Inkjet Printing	Direct Ink writing	Screen Printing
Dimensionality	0 (dot)	1(line)	2(plane)
No of passes required	High (>~50)	Medium (~10-20)	Low (1-5)
Print speed	Very low	High	Very High
Digital designing	Possible	Possible	Screen masks only
Multi material printing	Possible	Possible	Possible (usually separate passes required)
Ink viscosities	10-15 cp (Newtonian)	1(aqueous) – >100 cp (shear thinning)	>100 cp (shear thinning and thixotropic)
Initial cost	High	Moderate	Low
Operational cost	Low	Low	High

2.4.3 Parameters Affecting DIW

As with any process, direct ink writing has several variables. These need to be optimized for the best quality of printing and achieving desired resolution. The identified parameters

are the ink delivery, the gap between printing nozzle and the substrate, surface properties of substrate and nozzle, properties of ink and the printing speed. Commonly, the inks used for extrusion based printing are viscous and form a continuous filament when pushed out of nozzle.

Lewis et. al. have categorized the ink delivery systems in two types : constant pressure and constant displacement. In printing methods like robocasting, where a viscous slurry needs to be extruded, the constant displacement mode is implemented, with the help of a mechanically/pneumatically driven plunger pushes the ink out. Constant pressure mode requires high control over ink rheology and a slight change in the properties might change the extrusion dynamics, as the extrusion is carried out by maintaining uniform pressure at the reservoir.

The inks flow with a radially varying shear stress profile through the nozzle, which can be described as

$$\tau_r = \frac{\Delta P r}{2l}$$

Where ΔP is the pressure gradient, r is the radial position within the nozzle and l is the length. For uniform extrusion, the shear stress has to be above the yield stress of the inks throughout the nozzle. [39]

Yuk and Zhao have shown that with the right combination of the parameters, it is possible to print line widths smaller than the size of the nozzle. Figure 2.5 (a) shows different parameters taken into consideration to achieve the desired thickness and line width for printing viscoelastic inks. The two governing factors, dimensionless nozzle speed V^* and nozzle height H^* have been calculated as follows :

$$V^* = \frac{V}{C}$$

$$H^* = \frac{H}{\alpha D}$$

Where V is print speed, C is the speed of ink extrusion, H is nozzle height and αD is the extrudate diameter after die swelling.

The printing can be done in equi-dimensional mode ($V^* = \alpha^2$) or thinning mode ($V^* > \alpha^2$) in order to print lines with width equal to or smaller than the nozzle diameter. The velocity and height of the nozzle both have inverse relation with the line width, and can be fine-tuned to suit the application. [40]

Figure 2. 5 Effect of printing parameters (a) Schematic of a printing nozzle, (b) Different printing modes with changing velocity (c) Phase diagram for the printing modes , from [27]

Low-viscosity inks, such as aqueous suspensions and dispersions, however, behave in a different manner. Nozzle wetting and surface spreading is prominent in this case, unlike the high viscosity shear thinning inks. *Cordonier and Sierros* [41] have exploited this behavior for printing micro-patterned films with just the capillary action, i.e. without applying any back-pressure.

Low-viscosity ink formulations are easier to prepare and use, as compared to high viscosity. Thickening additives or viscous ink base are not required, and the curing or drying time can be reduced significantly. *Friedrich and Begley* studied the wetting phenomena for low viscosity inks by taking in-situ images of the process. 3 regimes of wetting : droplet, balanced and overflow were identified. (Figure 2.6)

Figure 2. 6 Contact angle vs Contact line position w.r.t. nozzle with 3 wetting regimes. Images : 3 different phenomena in wetting. It is desirable to have balanced flow. Taken from [31]

Best quality of printing can be achieved by keeping the contact angle and contact-line position combination in the balanced regime. Accordingly, surface tension of the ink and print speeds need to be adjusted. They conclude that low flow rate to print speed ratios, lower viscosities and surface energies, and smaller nozzle to substrate distances are necessary to print uniform, continuous filaments of desired width. [42]

2.5 Ink Formulations

Ink writing is most versatile when it comes to variety of printable materials. On the structural materials side, FDM printing of plastic 3D printing with Polylactic Acid (PLA), Polyvinyl Alcohol (PVA), Acrylonitrile butadiene styrene (ABS) are already commercialized. Ceramic slurries can be printed into green bodies using robocasting. Various biomaterials have been printed to serve as scaffolds for ex-situ organ growth. [39] , The inks used for printable electronics can be categorized as per their active materials into 3 classes as metallic inks, nanomaterial inks and organic inks. All ink systems have their own advantages and disadvantages pertaining to stretchability, printability and conductivity.

2.5.1 Metallic Inks

Metallic inks for printed electronics are one of the most mature ink systems. Various commercial silver paste formulations are available. These include silver paints, epoxy adhesives and special screen printing inks. Copper, Aluminum, Gold etc. are used to make various grades of conducting ink, usually implemented to make flexible RFID tags, textile electronics and printed electronics

Typically, highest conductivities are attained by metal nanomaterial-based inks. These include Ag nanoparticles[43], Ag nanowires[16], [44], Au nanoparticles and Cu nanoparticles. However, most of these inks require an additional high temperature sintering step in order to remove the solvent, surfactants and dispersant phases. The printed metallic films are usually not stretchable and rupture after straining. To make the silver inks stretchable, silver flakes are dispersed in rubber matrix. *Matsuhisa, N. et al* show that introducing surfactant drastically increase both stretchability and conductivity of rubber-silver flakes composite, via self-assembly and surface modification[45]. *Tan H.W. et. al.* have compared various metallic inks, including single component inks, alloy inks, metal-oxide based inks and core-shell bimetallic nanoparticle inks.[46] Silver nanowires provide the best combination of conductivity, cost effectiveness, and ease of dispersion. They can also form percolation networks for highly stretchable and healable conductors, and thus are desirable as soft electrodes for HMI applications[47].

Figure 2. 7 Silver nanoparticle ink (A) before sintering and (B) After sintering. Taken from [35]

Liquid metals have recently emerged as an alternative high conductivity metal inks for printing applications in e-skins, soft robotics and wearables. These are usually alloys of Gallium, with other metals such as Indium, Tin etc., which have very low melting point. Compositions suitable for direct write techniques such as inkjet printing[48], and direct ink writing[49] have been reported.

Figure 2. 8 (a) Microcontact printed capacitive pattern on Ecoflex substrate, from [41] (b) Optical microscope image of 3D printed CNT - liquid metal composite wires scalebar = 100 μm , from [42]

Various additives such as Carbon nanotubes, metal nanoparticles are added to liquid metal to enable 3-D printing [50]. *T. Neumann and M. Dickey* have summarized various methods for printing of stretchable conductors using liquid metals[51].

2.5.2 Carbon Based Inks

Conducting properties of carbon allotropes such as amorphous carbon, graphene, multiwalled and single walled nanotubes have been widely exploited for making printing inks. As carbon is a non-toxic earth abundant element, its use for electrical applications is studied for long time. Low cost and high-quality conducting carbon-nanomaterials can be

prepared by various methods, ranging from mechanical exfoliation to arc-synthesis and chemical routes. Two main contenders – 1 dimensional carbon nano-tubes (CNT) and 2 dimensional graphene are currently explored for ink formulations. Both standalone and composites [52] inks are prepared from CNTs and Graphene.

Figure 2. 9 SEM micrographs at various zoom levels for DIW CNT-Graphene composite ink pattern, taken from [44]

Carbon nanotubes are inherently hydrophobic. Thus, various surfactants are needed to prepare aqueous solution of CNTs. SDS, Sodium benzoate, Triton X-100 are some of the commonly used surfactants [53],[54]. Alternatively, they can be functionalized by adding organic ligands, attaching functional groups or inducing charge for better dispersion. [55] Graphene and its other forms are also studied for preparing printing inks. Due to the high surface area, graphene finds applications into printed flexible micro-supercapacitors [56]. Graphite flakes, graphene nanoplatelets (GNPs), reduced graphene oxide (rGO) etc. are used for preparing inks for inkjet printing and DIW. [57]

2.5.3 Conducting Polymer Inks

Conducting polymers are a class of polymers which conduct electricity through the movement of conjugated π – bonds. Depending on the molecular structure, the polymers can exhibit conductivity (e.g. PEDOT-PSS, Polypyrrole etc.), or semi-conducting and photoconducting behavior (e.g. P3HT). Some polymers can also be electroluminescent (PPP, PPV etc.) and are used to prepare PLED devices.

However, only few provide the ease of handling to prepare inks. PEDOT:PSS is a mixture of two polymers : poly(3,4-ethelnynedioxythiophene) and polystyrene sulphonates.

PEDOT:PSS is readily soluble in solvents such as DI water and DMSO. Various commercial PEDOT:PSS based inks are used for making transparent conducting coatings for solar cells and Display devices. Development OLEDs, Stretchable interconnects and flexible circuits is reported using roll-to-roll, gravure and inkjet printing methods.[58]

H. Yuk, B. Lu, S. Lin *et.al.* reported cryogenic lyophilization (freeze-drying) of PEDOT:PSS solutions and re-dissolution to prepare viscous shear thinning 3D printable ink. The study also reports dispersion of PEDOT:PSS into hydrogels for preparing self-supporting 3D structures, using Direct Ink Writing.[35]

Figure 2. 10 Molecular structure of EDOT and sulphonated styrene monomers.

PEDOT:PSS can also be used to prepare hybrid composite inks, by dispersing graphene, CNTs and other conducting nanomaterials in it. The use of polymer avoids agglomeration of functional nano-material and the conductivity is improved significantly[59], [60].

This study aims to combine various ink systems in order to prepare stretchable, skin conformable sensing and response devices. An effort will be made to use Direct Ink Writing to print all the layers of the device to prepare all-printed responsive e-skin.

2.6 Chapter summary

Human machine interfaces are bi-directional communication devices for information transfer. As humans mainly interact with their surroundings with touch, it is important to facilitate tactile interactions between computers and humans. Moreover, these interfaces need to be compliant and conformable. Stretchable and flexible electronics can help with fabrication of such devices. There are 2 main approaches for making electronics stretchable

and flexible - materials based and design based. Both approaches can benefit for non-conventional manufacturing techniques to handle complicated patterns and materials that are difficult to handle by conventional methods. The 3 main processes for fabrication include inkjet printing, DIW, and screen printing. Among these, DIW printing is the most versatile method. DIW can handle inks with various viscosities easily. This is used for printing variety of conducting inks including liquid metals, conducting polymers, and carbon based composite inks.

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Chapter 3

Experimental Methods and Materials

The chapter describes equipment, methods and materials used for the study. Conductive Ink formulations were prepared utilizing MWCNT, MWCNT-PEDOT:PSS composite, Acetylene black - PDMS composite and commercially available silver epoxy paste. PEG-MXene composite ink was utilized for phase change matrix. Details of Ink preparations are discussed. Electrical, mechanical, optical, and morphological characterization of the samples were performed. Custom setup built for characterization of proximity sensor is described at the end of the chapter.

3.1 Printing Equipment

The setup used in this study employs 3 **Zaber X-LSQ A 150™** linear motor stages controlled by a custom python 3 code, with the help of PySerial library for ASCII communication with the device. The pattern to be printed is first designed in **Inkscape**, and G-Code is extracted from .SVG files using **AllToGCode™** software. Later, file handling algorithms are used to save the code as a list of co-ordinates. The co-ordinates are then transferred to the stage and the pattern is traced by the nozzle/dispensing head.

For the controlled dispensing of the fluid, **Masterflex L/S peristaltic pump™** and controller were used, along with the tubing provided by the manufacturer. The pump was controlled manually for setting the volume flow rate in continuous mode. Customized setup, as described in next chapter using **NewEra NE1000™**, was set up for printing molten PEG for fabrication of haptic response device.

For viscous inks, a commercial system from **Nordson EFD™** is used. **UltimusPlusII™** air pressure controller was used for driving the piston, which was connected to an air compressor. Input to the controller was maintained at 60psi. The output was controlled within the range of 0.3-15psi. Nordson EFD **E2V™** 3-axis robot was used for motion control. **Optimum®** series syringe barrels were mounted on the robot, in which ink was filled and dispensed via Optimum® general purpose needles.

Optimum® tips of **gauge size 18** (for PEG), **21** (for coarse printing of CNT, PEDOT:PSS), **25** (for fine printing and complicated shapes and devices) were used for dispensing with custom built systems as well. For Ag paste ink, nozzle diameter was selected based on required thickness of pattern.

3.2 Materials and inks

3.2.1 MWCNT-PEDOT:PSS inks

An aqueous suspension of **PEDOT:PSS – PH1000** from **Heraeus, Germany** was used as the conducting polymer base for composite inks. Multiwalled CNTs with $\sim 100\text{nm}$ diameter and $\sim 3\mu\text{m}$ from **Cheaptubes USA** were used to prepare this ink.

Figure 3. 1 Chemical structures of two component ionomers, Poly (styrene sulphonate) i.e., PSS and poly(3,4-ethylenedioxythiophene) i.e. PEDOT, which forms PEDOT:PSS

For preparing aqueous CNT ink, multi walled carbon-nanotubes were dispersed in DI water by using the **SONICS probe-sonicator** with 13mm probe. The concentration was kept at 0.5mg/ml. Triton X-100 was used as the surfactant, as it has been reported to have best performance for MWCNTs [1]. Amplitude was kept at 40% with a 1:3 on/off ratio for 15 min. to prevent rupture of CNTs. CNT ink was then printed on glass slide with copper tape contact for resistance measurement.

To form intertwined network of PEDOT:PSS and CNTs, the two components, viz. aqueous suspension of PEDOT:PSS and dispersion of MWCNT was mixed in various ratios using vortex machine and ultrasonicated for 15 min. The resulting Inks were used to print 1,5 and 10 layers for study.

Table 3. 1 Mixing ratios for inks and resulting MWCNT concentration

For CNT dispersion of 0.5mg/ml			For CNT dispersion of 1mg/ml		
Ink	Ratio of PEDOT:PSS susp. to CNT disp., (v/v)	CNT (mg/ml)	Ink	Ratio of PEDOT:PSS susp. to CNT disp., (v/v)	CNT (mg/ml)
A	2:1	0.167	A*	2:1	0.333
B	1:1	0.250	B*	1:1	0.5
C	1:2	0.333	C*	1:2	0.667
D	1:3	0.375	D*	1:3	0.750
E	1:4	0.4	E*	1:4	0.8

Figure 3. 2 Images of PEDOT:PSS-MWCNT composite inks of various concentrations

Two different concentrations of starting CNT suspension were used for the study, viz. 0.5mg/ml (hereafter referred to as ink A, B, C, D and E) and 1mg/ml (hereafter referred to as ink A*, B*, C*, D* and E*). To study the effect of CNT loading, inks were prepared by mixing the two components in different volume ratios as given in table 3.1. It was found out that ink D has lowest resistance, as discussed in chapter 5. This ink was thus prepared in larger quantities.

3.2.2 Acetylene Black – PDMS composites

Viscous, shear thinning thixotropic ink [2] was prepared by mixing PDMS and Acetylene black nanoparticles. **Sylgard 184™** from **Dow Corning** was used as the PDMS matrix and **Super P acetylene black** carbon nanoparticles (avg. Particle dia. 42nm) from **Alpha Aesar** was used as the conducting filler.

Acetylene Black powder was weighed according to the required composition. PDMS elastomer base was then mixed with the powder using **Thinky ARE-310™** mixer for 6 minutes, at 2000 rpm. This mixture was stored at room temperature. As and when needed, crosslinker was added to the mixture in 1:10 v/v ratio of monomer along with **DOWSIL™ OS2** silicone cleaner as thinner. This ink was then mixed thoroughly inside the syringe barrel using thinky mixer for 12 mins at 2200 rpm.

Figure 3. 3 Chemical structure of Polydimethylsiloxane (PDMS)

To find out percolation threshold, inks of Acetylene black concentrations of 1, 5, 7.5, 10, 12.5 and 15 % w/w of PDMS A were prepared and cast in 3d printed mould of 1cm×1cm×1mm dimensions. The flat square samples were cured and then used for measuring conductivity across the corners. Since the ink became too thick to be extruded beyond this loading, 15% was used for printing proximity sensors.

3.2.3 PEG-MXene composites as PCM ink

Polyethylene glycol (M.W. 2000), Sigma Aldrich was melted at 80°C and filled in glass syringe. Pristine PEG patterns were printed using a modified system which kept PEG molten throughout dispensing period.

Figure 3. 4 Chemical structure of Polyethylene glycol (PEG)

Ti₃C₂T_x HF-etched multi-layered MXene was purchased from **Laizhou Kai Kai Ceramic Materials Co., Ltd**, China. The flakes were then delaminated by co-intercalation of DMSO and Li followed by ultrasonication in DI water. The process is discussed in detail

in section 5.4.2. This produced 10 mg/ml suspension of few-layer MXenes in DI water which was then mixed with molten PEG by magnetic stirring. This ink was then filled in glass syringe and used with the modified syringe pump system for printing patterns.

3.2.4 Silver epoxy

Heraeus Sol560 conductive silver epoxy was used for printing joule heaters. The viscous ink was prepared by thinning the epoxy paste with butyl acetate in 0.5ml/g ratio. The components were mixed in THINKY ARE-310 centrifugal mixer for 3 mins at 2000 rpm without degassing step.

Since the ink required higher temperatures for curing, a low temperature cure formulation was used with temperature sensitive substrates such as PDMS. **DuPont™ PE827** which cures within the range of 60°C-100°C was used in place of Sol560 for such applications.

3.3 Characterizations

3.3.1 General Characterizations

The inks were electrically characterized using two-terminal resistance program on **Keithley 4200 SCS** Semiconductor Characterization System. For the composite inks, the patterns were printed on cured, plasma treated PDMS films, with 1, 5, and 10 layers, and the resistance was measured. All the patterns printed for ink and print parameter characterizations were at least 2 cm long in order to avoid the effects of bullet heads and dripping at the end of the pattern. The most uniform length of the pattern was selected for measurement.

Hardness measurements were done using a hand-held Shore A scale hardness tester.

Primary optical characterization was done using **Olympus polarizing microscope**.

3.3.1.1 Scanning electron microscopy

Figure 3. 5 (a) Components inside a typical SEM column (b) Ray diagram for electron beam travelling through the column [4]

Scanning electron micrographs were obtained on **JEOL 7600 F FESEM** at various zoom levels. A scanning electron microscope can obtain highly magnified images by using an electron beam to scan the surface of an object.

The electron beam is produced using electron guns, which work either by thermionic emission or field emission. FESEM uses field emission guns, which contain W hairpin filament with LaB_6 crystal.

Large voltages applied across the filament and cathode pull out the electrons from the filament and accelerate them. These electrons are then focused into a beam using electromagnetic lenses and raster scanned across the sample surface using a scanning coil. This generates an interaction volume on the surface of specimen and various signals are produced via electron-specimen interaction. The signal used primarily for visualizing the topography include secondary electrons, which are electrons emitted by sample after absorbing primary electrons. Sensors positioned between the objective lens and sample stage detect these signals. The topography of the sample, along with a large depth of field

of electron beam produces a characteristic 3-dimensional image. [3],[4]

Since the samples need to be conducting to avoid electron charge buildup, all samples were coated with a conductive Pt coating using a sputtering machine.

3.3.1.2 Zeta potential measurement

Zeta potential of MXene suspension was measured using **Horiba SZ-100** to gauge the stability of colloidal suspension, which was an indicative of successful delamination. Zeta potential is the electrical potential on a particle at the slipping plane.

Figure 3. 6 (a) schematic of the interaction between colloidal particle and suspending liquid. (b) Schematic of DLS based Zeta potential measurement system. Taken from [5].

In a colloidal system, the stability is achieved due to the charges on particles repelling each other. Such a charged particle moves with a specific velocity under the influence of an electric field. The velocity of particle is directly related to viscosity and dielectric constant of the suspending liquid, as well as the potential at the junction between particle and liquid. If the suspending liquid is kept constant, the velocity of particles can give out the potential. This velocity is measured using dynamic light scattering.

In DLS measurements, optical laser is shined on the suspension placed in a cuvette. As the light interacts with particles in the suspension, it gets scattered at various angles. This scattered light is detected by photodetectors in the instrument. [5],[6]

MXene nanosheets have -ve charge on them. With higher degree of delamination, the charge increases, and eventually the dispersion becomes stable. With higher amount of single/few layer thick nanosheets, the absolute value of zeta potential increases. Thus Zeta

potential was used to judge the amount of delamination of the MXene.

3.4 Device characterizations

A custom made uniaxial stretching device was used to apply strain to the resistive sensors. It was also used to obtain strain response of the Acetylene Black-PDMS ink. The pattern or sensors were fixed between two moving platforms using clamps.

Figure 3. 7 Uni-axial stretcher used for recording strain response of sensors and patterns.

The part behind the clamp did not get stretched and hence it was used for making stable contacts with the sensor. The strain was increased step-wise and resistance was measured at every step. The proximity response of sensors printed using Acetylene black was tested using a custom setup shown in the fig. 3.8(a). Zaber motion stage was used to move and hold objects above the sensor with accurate distances. Various objects were attached to the clamp and moved above the sensors.

To record the response from sensor, an ADC board, **AD7150 from Analog Devices** was used with the provided software. For distance vs response test, objects were moved from 50mm to 5mm distance from the sensor in steps of 5mm. Object was held at every step for 500 readings and an average of middle 300 readings were taken, in order to filter EM noise during the movement of the motors.

Figure 3. 8 (a) Setup for testing of proximity sensor showing motion stage with Al block, plastic platform for sensors, various objects used, ADC board and software running on screen showing data. (b) Weights used for metal/non-metal differentiation (c) Glass vial without and with water.

For testing general sensor response, a square aluminium block was used as a standard measurement. For metal non-metal response, a commercial steel weight was used. To minimize the effects of parameters such as shape and surface area of the object an identical weight was 3D printed out of PLA and used as a plastic object. For the water content experiment, an empty 20ml glass vial was first used and then was completely filled with water, as shown in figure 3.8 (b) and (c) .

Thermal characterization of joule heaters was done using thermocouple. Thermal images for tactile response device were taken using **Fluke thermal TI401 pro** and the images were edited using fluke proprietary software.

Data from all the experiments was processed using **MS Excel** and was plotted using **Origin Pro** for this report.

3.5 References

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Chapter 4

Design and Setup of a Direct Ink Writing System

Custom setup for Direct Ink Writing (DIW) of different ink formulations was assembled. The chapter describes design processing and control system, XYZ movement within printing space and ink dispensing mechanisms. Development of printing designs, conversion of these drawings into cartesian coordinates via G-code, and execution of the codes through customized program has been explained in detail. Assembly of XYZ system allowing for movement within the printing space and different ink dispensing mechanisms to accommodate for various ink formulations have been discussed. Customizations done in the printing setup to accommodate different materials for dispensing have also been explained. Commercial compressed air based system used for viscous ink is discussed in brief at the end of the section

.

Principles of design for a Direct Ink Writing (DIW) setup

Figure 4. 1 Block diagram of a generic automated printing system

An automated printing system requires following basic blocks : An XYZ movement system to move the printhead or the substrate, an ink dispensing system and a central control to command the previous two.

For the system used in this work, a combination of 3 linear motor stages is used for the movement in the print space. The dispensing system comprises of three components : a pump, a reservoir and a nozzle : which may or may not be separated by tubing depending on the type of pump. A desktop computer is used for controlling the stages and the pump through python scripts.

Two strategies can be implemented for tracing the pattern by the nozzle – moving substrate bed while keeping the nozzle stationary or moving the nozzle and keeping the substrate stationary. Although the parameters are only dependent on the relative motion, moving the nozzle is preferred for the ease of design and gives greater flexibility in the terms of substrates, in this system.

The parameters affecting the print quality are ink dispensing rate, printing height, print speed and the rheological properties of the ink. Figure 4.2 shows the schematic of the

printing nozzle. The print speed is kept constant in this study, and the dispensing rate was varied to change the line width, hence changing the resolution. A meniscus is formed on the outer side of the tip due to the surface tension of the ink. To minimize this wetting, the printing height is kept equal to the ID of the tip.

Figure 4. 2 Schematic of printing nozzle showing the various factors affecting the process

To print variety of materials with the same system, high amount of adjustment needs to be done to tweak and optimize these printing parameters. Custom built system allows modifications in motion control and dispensing, which is able to handle multi-material printing and combining multiple printing methods. Hence for low viscosity inks, which are not traditionally used for DIW, the custom setup is used

For more viscous, thixotropic inks commercial dispensing systems are useful. These systems are typically designed and optimized for dispensing sealants and glues onto complex mechanical parts, or applications such as dispensing soldering metal mixture at exact points. All such compositions are shear thinning and Acetylene Black + PDMS mixture ink from this study has similar behavior. Thus, a commercial system was used for patterning this ink

4.1 Assembly of the custom built DIW system

Figure 4. 3 Visual representation of the printing system

A visual representation of the printing setup is shown in shown in the figure 4.2. The computer-pump and computer-motion stage communication is carried out via USB serial ports on computers and RS232 ports on the pumps and stage. Tubing from pumps is directly attached to the nozzle.

A combination of 3 independent Zaber X-LSQ A150 linear stages is used to achieve the required spatial positioning and 3-dimentional motion of the printhead. The high resolution ($0.09\mu\text{m}$) and high accuracy ($<45\mu\text{m}$) provided by the system is capable of fine printing of large area devices. The motion is controlled by a python script run on the computer via an RS232 cable for ASCII communication.

The printing head uses a custom 3D-printed Luer-Lock fixture for the printing tip and tubing. Standard fluid dispensing tips with gauge 18 to 26 were used for dispensing different line widths

For dispensing of material, Syringe pump and Peristaltic pumps were used alternatively,

depending on the flow-rate requirements and ink properties. For printing PEG, a syringe pump with glass syringe and silicone tubing was wrapped in resistive heating element and kept at $>70^{\circ}\text{C}$ for printing. For the inks which required stirring, Masterflex L/S series peristaltic pump was used, with an ink reservoir kept on magnetic stirrer

Viscous inks are better dispensed using a pressure driven system, unlike volume displacement mechanisms of peristaltic pump and syringe pump. Thus, for printing Acetylene black + PDMS ink, compressed air based commercial system was used. This system is briefly discussed in section 4.6

4.2 Designing and motion control

4.2.1 File processing and code for printing

Printing techniques usually implement one of the two approaches for printing : Dot printing or line printing. Droplet based printing techniques, such as inkjet implement the first. Usually, the printhead scans across the complete substrate area, dispensing material where necessary. For this approach, the file is divided into pixels, and raster scanned (figure 4.4 b). The line printing methods, however, trace the path (figure 4.4 c), as the flow of printing material is continuous. Robocasting, FDM and DIW are some examples of printing of this type.

Figure 4. 4 (a) A 4*6-pixel version of letter 'A'. (b) Raster scanning and (c) Vector tracing

The file formats handled by these two approaches are different from each other. Dot-printing techniques require a ‘bitmap’ image. Material is not dispensed at pixels with values 0, while depending on the printer capabilities, different volumes are dispensed as per non-

zero pixel values. Most of the materials printers require the bitmap to be monochrome, as the dispensing is binary. On the other hand, the systems with line printing require ‘scalable vector graphics (.svg)’ formats for printing. These files store the image as paths and objects, rather than storing the pixels. Thus, the images can be scaled infinitely without pixellation

Figure 4.5 Processing of print file

These paths can be converted to set of co-ordinates to be followed using conversion algorithms. Laser-cutting machines, CNC lathes and milling machines use the G-Codes, which comprise of these co-ordinates and machine codes such as on/off, tool change etc. Many commercial and open source software are available to convert vector files to custom G-Codes. All-to-GCode converter, was used for this study as it was easy to use, fast and accurate.

The output from the conversion is given as a .tap file, readable using a text reader. The file contains sequential rapid positioning code in the syntax 'G0 X__Y__'. Beginning and end

of each path is marked by a positioning code for Z axis. The .tap file can be saved as a text file to be edited using file handling python scripts. These scripts save the co-ordinates followed by X and Y into two separate lists (arrays) of numerical values, which are then fed to the X and Y axes of the stage respectively

After calibration is done, printing procedure starts, as the positioning loop traverses through the 'list of lists'. The Z-axis is moved away from the substrate at the end of every list, which marks the end of the path, and brought back to the initial position for the first value of next list. The positioning loop is run till the end of last set of co-ordinates. For multiple layers, the same process is repeated with delay between subsequent prints

4.2.2 Z-axis calibration

Figure 4.6 Schematic for the calibration process, with cross-section of the tip. 1: The head is manually moved towards substrate, 2: Stopped when the tip touches the surface 3: tip is lifted to printing position. d is the inner diameter of the nozzle.

Distance between printing tip and substrate is one of the parameters affecting the width of printed line. The recommended distance between the substrate and the tip is equal or close to the internal diameter of the tip itself [1]. To maintain this, the calibration procedure for the Z axis position is carried out at the beginning of printing

As shown in the schematic, the Z-axis is manually brought down till the tip touches the substrate, and the position value is recorded. Tip diameter is subtracted from position of the Z stage and the updated value is used for printing thereafter. A meniscus is formed before the print is started to ensure that pattern is printed completely

4.3 Ink Dispensing

Due to the modular nature of the system, it is possible to use different pumping systems for different inks. Syringe pump and Peristaltic pump were used to dispense materials in this study. These two fluid displacement technologies work with different principles and thus vary in their capabilities.

Syringe pump or syringe drive moves fluid by mechanically displacing the plunger in the syringe. The net volume dispensed is equal to the distance travelled by plunger multiplied by cross-section of syringe. The syringe can be connected to a hose to carry the fluid to the desired location. Figure 4.7 (a) shows the working principle of syringe pump.

Figure 4.7 Schematics for working principles of (a) syringe pump and (b) peristaltic pump. Arrows show the motion of the ink (blue gradient)

Peristaltic pump, on the other hand is a type of positive displacement pump, which moves a fixed amount of fluid per cycle. As shown in Figure 4.7(b), rollers driven by a rotating fixture squeeze the tubing to capture and push the liquid in the direction of rotation. This creates a vacuum behind the roller and the liquid is pulled in. This process takes place n times in one rotation, where n is the number of rollers. The pump is completely isolated from the fluid, causing minimum contamination. Moreover, the pump can draw liquids from a reservoir, and run practically endlessly

Peristaltic pumps have faster response time as compared to syringe pump, as only a small

volume of liquid is displaced at a time. Syringe pumps, on the other hand, have to move the entire volume of in in syringe as well as tubing. This causes a pressure lag, and drooling or dripping occurs

4.4 Modifications to print PEG -MXene PCM ink

PEG 1000 is solid at room temperature, but melts into a viscous liquid when heated at $>60^{\circ}\text{C}$. To keep PEG from solidifying, a resistive heating element was wound on the Glass syringe and dispensing tube in helical manner. 1A current was maintained in the element by connecting it across a DC power source.

Figure 4. 8 Modified apparatus for printing PEG.

The flow rate for printing PEG was optimized to $45\mu\text{l}/\text{min}$, to achieve line width of around 1mm. More complex patterns were printed at slower write speed and $10\mu\text{l}/\text{min}$ flow rate. Higher flow rates cause features to merge with each other before solidification, while lower flow rate cause discontinuous printing and solidification at the tip

18, 21, 25 26 gauge flat fluid dispensing tips were used for dispensing inks depending on the viscosity of ink and desired line width of the pattern

4.5 Air pressure based dispensing for Acetylene Black + PDMS ink

While dispensing inks with relatively high viscosity and shear-thinning behavior, hydrostatic lag becomes significantly prominent. The delay between movement of the dispensing system and material leaving the nozzle increases with viscosity of material. For this reason, these inks have commonly been dispensed using an air-piston based system. As shown in the schematic in fig. 4.9, controlled air pressure is maintained on a plunger which pushes the ink forward in a syringe. The entire syringe can be mounted on the motion stages and moved along the pattern. With the syringe being directly attached to the needle, the lag would be avoided.

Figure 4. 9 Schematic of a pneumatic fluid dispensing printhead

Compressed air based commercial system from Nordson EFD™ was used in this work to dispense viscous composite of PDMS and Acetylene Black. The system comprises of UltimiusPlus II™[2] which is capable of controlling pressure within the range of 0.3 psi to 15 psi. The syringe is mounted on Nordson E2V™ [3] robot. .dxf files were prepared using Autocad™ software. Pressure, velocity and printing gap were adjusted according to the print requirements. Commercial Syringes provided with the equipment were used as cartridges and EFD needles of gauge 18,20,25,32 were used for printing different line widths.

Figure 4. 10 Nordson E2V 3- axis robot and UltimiusPlus dispensing system

Usage of compressed air based system allows material to be stored right above the dispensing nozzle. This greatly reduces the travel length of material and reduces problems arising due to it. Materials with higher viscosity can be handled easily. In case of peristaltic pumps, the gaps between wheels cause an oscillating flow of material at lower prints. This is less than ideal for continuous printing. Air pressure drives the material in smooth continuous motion, giving the best results. This system would be used and optimized for future projects according to needs and exploited for its versatility and convenience of use.

4.6 Chapter Summary

Direct ink writing systems comprise of an XYZ movement system to move the printhead or the substrate, an ink dispensing system and a central control to command the previous two. An algorithm was designed to use vector graphics paths for controlling XYZ-stage and system was programmed using python. For ink dispensing, a syringe pump and peristaltic pump were initially used. To dispense phase change materials, a modification was done to the syringe pump system by adding a heating element. Although syringe pump and peristaltic pump worked well for dispensing low viscosity inks, for thicker ink, a commercially available pneumatic based system was implemented.

4.7 References

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Chapter 5

Ink Formulations and Characterizations

This chapter discusses ink formulations used in this study. Printing of pristine MWCNT suspension is briefly discussed. Effect of variation of concentration for PEDOT:PSS-MWCNT composite ink is investigated. Results of electrical and morphological characterizations of this ink are used for optimization of mixing ratios. Commercial silver nanoflakes paste is printed to form joule heaters. Percolation threshold is obtained for Acetylene black-PDMS composite ink by electrical characterization of various concentrations of Acetylene black particles. Strain response for this ink is presented. Effect of change in printing parameters on the line width is given. Finally, delamination of MXene is discussed followed by formulation and characterization of PEG- MXene composite phase change material ink.¹

¹ Section 5.4 is submitted as Ankit, F.Krisnadi et. al., "MXene Incorporated Polymeric Hybrids for Stiffness Modulation in Printed Adaptive Surfaces", Nano energy 2021. (Written permission is not required from Elsevier).

5.1 Problem Statements

5.1.1 Printing of MWCNT aqueous suspension

Figure 5. 1 (a) Serpentine pattern printed using aqueous MWCNT suspension. Scalebar = 1cm (b) SEM of a single carbon nanotube

Aqueous suspension of 0.5 mg/ml MWCNT could be printed out using 0.25 mm tip. Multiple layers were required to printed conducting patterns. Random alignment of printed nanotubes resulted in lower conductivity.

Figure 5.1 (a) shows single layer of serpentine pattern printed on 3M VHB acrylic. For studying the effect of multiple passes, a straight line of length 4cm was printed. The very high initial resistance dropped with subsequent passes. The rate of reduction of the resistance was high for initial 5 passes. The difference reduced with further layers, as illustrated in the Figure 5.2

Figure 5. 2 Resistivity of printed CNT line vs number of layers

After 20 consecutive layers, the resistivity was lowered down to around $15\text{k}\Omega/\text{cm}$. However, the print could not be used for making conducting circuits. The high resistance of the pattern can be attributed to the local agglomeration of the MWCNTs. During the process of ink curing/drying, the dispersant and surfactant evaporate at different rates. The Van der Waals forces cause the CNTs to stick together and agglomerate again, producing a localized coffee ring effect. [1]

5.1.2 Formulation of PEDOT:PSS and MWCNT Composite Inks

To overcome the issue of agglomeration of CNTs, a stable dispersant is required, which can form conducting films after drying. PEDOT:PSS was tested for this purpose

Figure 5. 3 (a) Entrapment of separated MWCNTs by PEDOT:PSS polymer chain to form percolation networks. Taken from J. Mannayil et. al. [2] (b) Drop cast films of PEDOT:PSS, CNT suspension and composite ink. (c) Micrograph of PEDOT:PSS film cracked after stretching (d) SEM of PEDOT:PSS film and (e) composite films (ink D, 20000x)

As shown in the schematic (figure 5.3 (a)) the mixing of PEDOT:PSS suspension along with CNT dispersion provides a matrix for CNTs to be embedded in and avoids agglomeration after drying. An overall improvement in conductivity, stretchability and flexibility of the films was achieved. MWCNTs have been studied for forming films in by spin coating and blade coating.[2] Pure PEDOT:PSS films are flexible after drying,

however, stretchability of the films is limited. This can be seen in fig. 5.3 (c), which shows discontinuity in the film after stretching. Adding CNT to the films enhances the mechanical properties of the films and prevents cracking.

Aqueous suspension of PEDOT PSS was printed without any changes as a control for the study. Despite the good printing quality, the sheet resistance of the prints was as high as $10\text{k}\Omega/\text{mm}$ for 10 layers. Moreover, stretching the PEDOT:PSS films resulted in rupture, even at low strains. High thickness of the film, achieved by multiple passes did not improve the results significantly, and made the film more brittle.

As discussed in experimental chapter, 5 different ratios of MWCNT suspension and PEDOT:PSS were mixed, with 2 different dilutions of CNT suspension. For 0.5mg/ml MWCNT suspension, the resulting inks showed lowest resistance, $\sim 277\ \Omega/\text{cm}$, for the ratio 1:3. Figure 5.4(a) plots the measured resistance values for the inks A, B, C D and E for different number of layers printed on top of each other. A similar trend was observed in the inks prepared using CNT suspension with concentration 1 mg/ml .

Figure 5. 4 Resistance for printed pattern for PEDOT:PSS and CNT composite ink, at different number of layers and mixing ratios. The CNT suspension used has concentration 0.5 mg/ml in (a) and 1 mg/ml in (b)

Figure 5. 5 Scanning Electron Micrographs for films D10 (left) and D*10 (right). The former shows individual CNTs dispersed in the PEDOT:PSS sheet (encircled) while the later shows randomly oriented clusters of CNTs

Overall, the resistivity was substantially higher for the second ink system as compared to the first one, despite having higher concentrations of CNTs. The significant difference between the resistivities of the two ink systems can be attributed to the degree of dispersion of CNTs. SEM images show clumps and clusters of nanotubes for the films having higher amounts of CNTs.

Lesser density of CNTs with better dispersion has higher conductivity as compared to poorly dispersed clusters of CNTs, as the orientation of the CNTs in isolated clusters is random. Due to the directionality of CNTs, non-aligned CNTs from the clusters do not contribute to the conduction of the current. On the other hand, regardless of random orientations, isolated CNTs dispersed in the sheet of PEDOT:PSS act as alternative pathways of lower resistance for charge carriers, thus electrically shorting the sheet

The ratio of mixing of PEDOT:PSS and MWCNT dispersion changes the resistivity of inks substantially. Initially, as the amount of CNTs increases the resistance of the ink drops. However, with addition of higher amount of dispersion, dilution of the ink occurs. Thus, even if the amount of MWCNTs increases with respect to the PEDOT:PSS, overall concentration in the ink decreases, as more solvent gets added in the ink. This causes the resistance to increase again. This is seen in fig. 5.4 where inks E and E* have higher resistance as compared to inks D and D*.

As the composition D (1:3) achieved lowest resistance per unit length, it was used for printing devices and specimens of stretchable conductors. Section 6.2 discusses the stretchability matters of printed PEDOT:PSS patterns. To enhance stretchability, printing on pre-stretched substrates is proposed. Initial trials were conducted for printing on a stretched VHB acrylic film. The film was stretched to 400% and 10 layers of serpentine pattern was printed on it. After the print dried, the film was relaxed and brought back to the original dimensions.

SEM of the pattern after relaxation shows high degree of folding and coiling (Figure 5.6). Such a print maintains its conductivity value after being stretched, as it only gets unfolded and ruptures are avoided even at large values of strains. As relaxation causes de-scaling of printed elements, better print resolution and density can be achieved.

Figure 5. 6 SEM of serpentine pattern printed on pre-stretched film.
Inset: magnified image of one fold

5.2 Printing of Silver paste

Commercially available silver epoxy pastes use silver flakes embedded with binders that cure by heating to formulate screen printable inks. High conductivity and easy handling make them a suitable choice of inks for printed electronics. Many such formulations have

been used for printed electronics on cloth and other flexible substrates. Single layer patterns with resistance as low as $0.4 \Omega/\text{cm}$ were printed.

Figure 5. 7 Image of printed joule silver heater. Scalebar = 2cm (b) SEM image of Ag Paste, 2000x

Depending on the formulation, the inks need to be cured at various temperatures and timings in order to form continuous conducting layers. The pastes used in this study were suitable for screen printing, which requires highly viscous pastes. Hence butyl acetate was added to the pastes and mixed thoroughly before printing.

Despite the good flexibility, the cured films of Ag are not very stretchable and develop cracks after very small strain. Thus, the stretchability of these printed patterns is limited and can only be enhanced to certain extent by geometrical designing.

5.3 Acetylene Black-PDMS conductive ink

5.3.1 Printing of Pristine PDMS

Figure 5. 8 Printed spiral pattern of PDMS spreading before curing

Pure PDMS was printed as an encapsulation for tactile devices as well as printed strain sensors with PEDOT:PSS + CNT ink. However, due to low viscosity and relatively high times for curing, well defined structures of PDMS could not be printed, neither was 3D printing possible.

This is demonstrated in figure 5.8. A spiral pattern was printed on glass slide. The gap between adjacent lines of the pattern was kept to be 1 mm. However, after 1 hour, the lines merge. This flowing of PDMS coupled with longer cure times makes it difficult to print finer patterns but makes it ideal for forming thin uniform sheet at desired locations, mainly as encapsulation

Figure 5. 9 AFM of PDMS, left – drop cast sample, right – area fill sample

In contrast to drop casting, the continuous films formed by area-fill dispensing, i.e. printing lines close enough so that they merge and form continuous lines has two effects. On the positive side the dispensed encapsulations can be controlled more precisely, in terms of location and thickness. On the other hand, surface roughness of these films is significantly higher than the drop cast films, as seen in fig. 5.9. Measured RMS roughness value for drop cast sample is 1.95nm, while that for area-fill film is 4.078nm.

5.3.2 Acetylene black- PDMS composite

Acetylene black was mixed with PDMS using thinky mixer, as described in section 3.2. The nanoparticle enhanced the viscosity of the material and filaments of the ink could be extruded. Since acetylene black is a conductive filler, this ink can be used for printing stretchable conductive patterns. The percolation threshold for it was found out by measuring conductivity for cast samples from 1% to 15%. Here, percolation threshold refers to the minimum concentration below which a conducting path of connected filler

particles does not exist. It was observed to be between 11-13% loading, as the slope of the graph changes dramatically in this section

Figure 5. 10 (a) Filament of Acetylene black + PDMS ink extruded from nozzle. (b) Samples with different loading of Acetylene Black (c) Concentration vs. Conductivity of the samples

As it can be seen from fig. 5.10 (c), the samples with concentrations upto 7.5% are non-conducting. The conductivity shoots up beyond ~13%. Ink with 15% loading was used for all further prints. Increasing the loading beyond 15% increases the viscosity of the ink substantially and makes it impossible to dispense through needle. OS2™ silicone cleaner was used to thin down the ink for using it with smaller nozzles. Fig. 5.11 shows SEM images for 1% and 15% samples, where the white particles are of Acetylene black and grey matrix is PDMS.

Figure 5. 11 SEM of PDMS-acetylene black ink with (a) 1% loading (b) 15% loading, 5000x

The strain response of printed patterns was measured by measuring resistance within 2 points while stretching it uniaxially using the contraption shown in chapter 3. The strain

response was linear. This ink thus can be used for making resistive strain sensors with high sensitivity and large range

Figure 5.12 Change in resistance vs strain

Printing parameters influence the size of printed features significantly, which further changes the applications of the ink. Effect of various printing parameters on the size of printed feature width are shown in fig. 5.13

Figure 5.13 Effect of various printing parameters on line width - Pressure, Print gap, Speed vs line width

As observed, the printing parameters affect the print quality in following manner :

Increase printing pressure / flow rate increases the line width. ($W \propto P^b$)

Increasing the printing gap decreases the line width (while increasing the thickness i.e. height of printed filament). ($W \propto 1/H^c$)

Increase in velocity of printing decreases the line width. ($W \propto 1/V^a$)

In total, it can be written,

$$W \propto k \frac{P^b}{V^a H^c} \quad \dots eq. 5.1$$

Where k is the constant depending on viscosity of ink, nozzle diameter, etc.

5.4 Polyethylene glycol (PEG) + MXene Composite as PCM

5.4.1 Printing of PEG

For generating tactile response by selective rigidity modulation, PEG was used as a phase change material. As shown in previous chapter, a customized setup was used to print PEG by melting it at temperatures higher than 50°C. After dispensing, PEG was able to hold its shape and solidify. Low wetting of the substrate ensured that the printed lines do not spread. Various pseudo-auxetic patterns were printed on PDMS and 3M VHB acrylic sheets. Thickness gradation was achieved by 2 methods – superimposing multiple layers on top of each other and changing the flow rate. The first method provides a vertical change of dimensions while the later provides an overall volumetric change with variation in thickness as well as line width. The transitions in patterns can be perceived by touch and thus can be utilized for fabricating haptic response devices with higher functionalities and conveying tactile information with varying intensity.

Figure 5.14 (A) and (B) shows printed Peano and Hilbert space filling curves, respectively. (C) and (D) are the pseudo-auxetic patterns printed on elastomeric substrates. The patterns behave like auxetics for very low values of strains, however, brittle nature of PEG does not

allow high stretchability. In Figure 5.14 (E) and (F), two different approaches for gradient printing are shown. In (E), 1,3 and 5 layers of PEG are superposed for a stepwise gradient across the Peano curve geometry. For each printing iteration, nozzle height was re-calibrated on the previous layer. In (F), variation in line width was obtained by changing the deposition rates to 10, 20, 30 40, 50 and 60 μ l/s.

Figure 5. 14 Printing of PEG into representative fractal motifs, Peano curve (A) and Hilbert curve (B), and Pseudo auxetic patterns (C) & (D). Creating hardness gradients by deposition of superposing layers of PEG (E) and by varying the deposition rate (F) Scale Bar=1cm

PEG is further used to print tactile response devices. The printability of PEG can be utilized to print various layered structures, hardness domains and phase-change devices. The ability of PEG to absorb heat and change phases at relatively lower transition temperature is exploited in making a tactile device with on-demand hardness modulation

5.4.2 MXene delamination and dispersion

MXene is a new family of 2D materials which have unique properties and are advantageous over conventional materials like TMDCs and Graphene. One of the biggest advantage is the hydrophilicity of MXenes. Most MXenes have hydrophilic groups as surface terminations. This makes it easier to disperse in water and formulated in inks

Figure 5. SEM images of Ti₃C₂ MXenes (a) As received powder showing accordion structure (10,000x) (b) Few layer thick sheet of MXene obtained by delamination (14000x)

MXenes are usually etched from parent MAX phase inorganic compounds by eliminating 'A' phase. The most studied MXene is Ti₃C₂, which is prepared from Ti₃AlC₂. Single/few layer thick Ti₃C₂ is a highly conductive 2D material

To etch the Al from parent phase Ti₃AlC₂, 2 routes have commonly been applied. Initial attempts involved use of various concentrations of HF to etch away the phase. Newer methods such as MILD, are taking over it, which use LiF/HCl to form in-situ HF, reducing the hazards of HF. After etching the Al, 'accordion structure' of sheets is obtained which needs to be delaminated to get MXene. Figure 5.15(a) shows the accordion structure while 5.15(b) shows delaminated few layer thick nanosheet. In LiF/HCl route, lithium ions intercalate into the spacing between the sheets, expanding it. Thus vigorous shaking or quick ultrasonication is sufficient for separating the sheets. In this study however a commercially available, pre-etched powder was used. Since it was etched using HF, a separate step of intercalation was required

Previous studies use small molecules such as DMSO for intercalation. However, it was followed by high-energy probe sonication which resulted in smaller sheets, thus reducing the conductivity. To simulate Li intercalation various amounts of LiBr salt were added along with DMSO.

Figure 5. 15 Co-intercalation with Li and DMSO (a) Zeta potential vs concentration. Yellow zone shows concentrations of Li reported in literature for LiF/HCl process (b) Processing chemistry vs stability

The as-purchased powder was stirred with DMSO and LiBr for 24h at 37C for intercalation. DMSO and LiBr was later removed by solvent exchange by washing and centrifuging with DI water multiple times at 7-8C. Required quantity of DI water was then added to the dispersion to prepare desired concentrations and the dispersion was ultrasonicated in ice bath for 1 hr to delaminate the MXene sheets. Fig.5.15 shows the effect of various concentrations of LiBr on Zeta Potentials of resulting dispersions. Zeta potential (modulus) increases with higher surface charge. Thus, more negative Zeta potential signifies higher degree of delamination

5.4.3 Pristine PEG vs PEG-MXene composite

To enhance the speed of melting and solidification of PEG for faster response times of tactile device, additional nucleation sites were required. This was achieved by mixing an aqueous suspension of MXene (10mg/ml) nanoflakes in PEG. The water from aqueous

suspension interacts with PEG by forming hydrogen bonds. MXene flakes with very high surface area provide large number of nucleation sites. This helps speed up the sluggish melting/solidification of pure PEG, which happens over a range of $\sim 30^{\circ}\text{C}$.

As seen in fig. 5.17, the pure PEG sample has only a few nucleation sites and takes over 390 seconds to completely solidify. On the other hand, composite shows starting of nucleation at multiple sites simultaneously and completely solidifies within 90s. This rapid solidification is highly desirable for the melting based tactile device discussed in next chapter

All the inks discussed in these sections were utilized individually or in combination for

Figure 5. 16 Micrographs of nucleation in pure PEG (top row) vs PEG- MXene-water composite (bottom row) making various sensors and devices, which are discussed in the next chapter, with characterizations of sensors.

5.5 Chapter Summary

PEDOT:PSS and MWCNT were mixed in various ratios to prepare a conductive, low viscosity ink. 2 different dilutions of MWCNT, 0.5mg/ml and 1mg/ml were prepared and mixed with PEDOT:PSS in varying volume ratios. 1:3 ratio of PEDOT:PSS to 0.5 mg/ml MWCNT suspension was found out to have lowest resistivity.

Acetylene black-PDMS composite was made using thinky mixer. Percolation threshold for the network is found out to be at ~13%(w/w). 15% loading of Acetylene Black in PDMS was used as a viscous ink for printing proximity sensors. The line width for this ink was found out to be directly proportional to printing pressure and inversely proportional to printing gap and speed.

Further, modified setup with heating element wound across syringe and tubing was used to print PEG phase-change ink. Ti₃C₂ MXene was intercalated using LiBr and DMSO and delaminated to prepare 10mg/ml suspension which was added to PEG. The PEG-MXene composite had higher amount of nucleation sites. This helped in speeding up the phase transformation of printed patterns.

5.6 References

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Chapter 6

Printed Sensors and Responsive Systems

*This chapter describes the sensors and actuator devices fabricated using DIW printing of inks formulated in chapter 5. Mechanism for resistive and capacitive sensing is discussed in brief. PEDOT:PSS-CNT composite ink is used to fabricate strain sensors and bending angle sensors. Acetylene black-PDMS ink is used for fabricating proximity sensors. Various geometries for proximity sensors are tested based on their sensitivity. It is observed that spiral geometry produces largest response and hence is chosen for further studies. Detection of water content and differentiation of metal and plastic materials is demonstrated. A hardness modulation based tactile response device is fabricated using silver paste joule heaters and PEG-MXene composite ink as phase change material. Tactile display of letters using 3*3 pixel device is demonstrated.²*

² Section 6.4 is submitted as Ankit, F.Krisnadi et. al., "MXene Incorporated Polymeric Hybrids for Stiffness Modulation in Printed Adaptive Surfaces", Nano energy 2021. (Written permission is not required from Elsevier for thesis purposes).

6.1 Mechanisms for sensors

A wide variety of sensors can be fabricated by printing passive components, using conductive inks. The sensors can be classified primarily as capacitive, resistive, and inductive.

The resistive sensors are implemented for strain / displacement sensing. Output of the resistive sensor corresponds to physical deformation of the sensor. The physical deformation can result in 2 phenomena – change in dimensions of the sensor and change in concentration of conductive elements in a given cross section.

Figure 6. 1 Working of a resistive strain sensor

For a conductor of length L and cross section A ($H \cdot W$), resistance R is given by

$$R = \frac{\rho L}{A} \quad \dots \text{eq. 6.1}$$

Where ρ is the resistivity of the material.

As the formula indicates, changes in any of the dimensions or resistivity of the material. The first effect results in change cross sectional area and length of the resistor, thus changing the value of it, while the second results in a change in bulk resistivity of the material.

The value of capacitance C for a capacitor with electrode area A and distance between the plates d is given by

$$C = \frac{\epsilon_0 k A}{d} \quad \dots \text{eq. 6.2}$$

Where ϵ_0 is permittivity of free space and k is dielectric constant of a material.

As shown in fig. 6.1 (left top and bottom), capacitive sensors can also be used for sensing pressure, which works similar to resistive sensors. As the two faces of a capacitor made out of stretchable materials are pressed together, the distance between them changes and it results in change in capacitance.

Figure 6. 2 Schematic of working principle of capacitive pressure sensor (left) and proximity sensor (right)

However, this study uses capacitive sensors for sensing proximity of the object, as well as material of the object. A capacitive proximity sensor resembles a flattened or open parallel plate capacitor. Variations in geometries can result in different capacitance which will be discussed further. Since the gap between the electrodes is not sealed off like a traditional capacitor, electric field lines emerge out of the plane of the sensor, as shown in image 6.0. These lines can be intersected by objects in the vicinity, which changes the capacitance of the sensor. More lines are intersected when an object is closer, and the difference is more pronounced. Furthermore, higher the dielectric constant k of object, greater the change in C , as indicated in eq. 6.2. This property can be used for detecting and differentiating between material of an object.

6.2 PEDOT:PSS – CNT printed sensors

Both resistive and capacitive sensors were printed using MWCNT + PEDOT:PSS ink. Fig. 6.3 shows micrographs of a printed resistor as it is uniaxially stretched.

Figure 6. 3 Micrographs of cracks forming in PEDOT:PSS + CNT film after stretching.

The strain causes cracks in the film, which greatly increases its resistivity by limiting conductive pathways for the current. This phenomenon can be used in 2 ways – to measure bending on a flexible but non-stretchable substrate, and to measure stretching on a stretchable substrate.

6.2.1 Bending Angle Sensor

Soft robotic actuations are usually driven from a single point using pressurized fluids. Often, it is difficult to predict the exact motion of actuators like gripper, since they conform to the object they are gripping. This makes it important to know the radius of bending as a form of feedback.

Bending angle sensors were thus printed on a flexible PET substrate as shown in fig. 6.4 (a). 6.4 (b) shows the schematic of the sensor pattern. This sensor could be implemented as an additional layer to the gripper for self-sensing of motion.

Figure 6. 4 (a) photograph of printed bending angle sensor (b) Schematic of the sensor (c) Resistance vs angle of bending (d) Resistance values while cyclic bending at increasingly higher angles

As shown in fig. 6.4(c), linear response was obtained from the bending sensor as it resistance was measured at every 10° . The resistance/time graph was captured while bending the sensor increasingly higher at steps of 10° , holding for 5 seconds and taking back to original position repeatedly. Although fairly consistent, there is a slight variation in the original resistance reading at 0 bend. This can be attributed to factors such as change in contact resistance and relaxation of the polymer chains

To demonstrate application of a bending angle sensor, it was attached on a finger to sense movement of the finger. Resistance of the sensor was measured at various positions of finger, as shown in fig 6.5 . The resistance is proportionally higher at higher bending radii. This can be potentially used for gesture recognition and hand motion tracking in real time.

Figure 6. 5 Using bending angle sensor to measure curving of a finger

6.2.2 Strain Sensor

A resistor was printed on top of plasma treated PDMS substrate, and then encapsulated with contacts to form a strain sensor. Fig 6.6 (a) shows the linear response of the device. While 6.6 (b) shows schematic and (c) the actual device being stretched. As seen in the response graph, the value of resistance changes linearly with the strain. A large change in resistance is observed at a very low strain of 5%.

Figure 6. 6 (a) Response of printed strain sensor, change in resistance vs strain. (b) Schematic of the sensor (c) image of actual sensor being stretched.

The sensor is highly sensitive over smaller strains. However, beyond 5% strain, continuity of the pattern is lost, and it no longer conducts. This greatly limits the applications of this sensors to very small range, over which it is linear.

Miniaturization of this sensor was attempted by printing smaller features using higher speeds and smaller nozzle diameters. As shown in fig. 6.6, the smallest sensor printed was $6\text{mm} \times 6\text{mm}$. A proposed use for the miniaturized version is as a pressure sensor on fingertips of gripper / prosthetics as a part of e-skins.

Figure 6. 7 Miniaturized version of the printed strain sensor

6.2.3 Capacitive touch Sensor

Capacitive pressure/touch sensors were prepared using same method. The schematic of the device is shown in fig. 6.8, along with the response generated by touching the sensor. The capacitance value drops significantly with touching and continues to decrease further by pressing down on the sensor. However, the output from the sensor was noisy and non-repeatable.

Figure 6. 8 (a) Capacitance vs Time graph for capacitive touch sensor (b) dimensions of printed sensor

Major factors for this were low conductivity of the ink, top encapsulation, and difficulty in forming contacts with the printed pattern due to adhesion issues. Thus, the sensor was not characterized further, and acetylene black/pdms mixture was used instead of PEDOT:PSS-CNT composite ink for capacitive sensors.

6.3 Acetylene Black – PDMS proximity sensors

As described in previous chapter, conducting nanoparticles of acetylene black were mixed with PDMS along with curing agent and thinner to prepare shear thinning, viscous ink. It was used to print stretchable sensors directly on fingers of a soft robotic gripper. At times, vision based sorting system is not sufficient alone. There are cases when it is not feasible to use camera due to visual noise / obstructions. A non-visual sensory system to recognize position of an object as well as material can be useful for augmentation or as an alternative in these cases. Capacitive proximity sensors were designed, optimized and fabricated for this purpose

6.3.1 Sensor design considerations

Figure 6. 9 Images of various designs of the printed proximity sensor. Right - generalized schematic of the sensor

Performance of a proximity sensor depends on the base value of capacitance. This is affected by geometry of the sensor. For this study 4 different geometries of sensors were identified. Fig 6.9 shows images of the 4 printed sensor geometries and a generic schematic of the sensor. For the comparison, the sensors were printed with same active area and distance between adjacent electrode lines. (25mm $\times$ 20mm, and 1mm center to center, respectively.)

Figure 6. 10 (a) absolute capacitance for various designs with object at different distances from the sensor. (b) Sensor response for aluminium block

In design 1 and 2, the interdigitated electrodes act as individual capacitors connected in parallel, which greatly increases the total capacitance. Whereas in design 3 and 4, both the electrodes comprise of a single line intertwined in different ways.

It was observed that the capacitance was highest for design 1 (17.1 pF), followed by 2 (10.5 pF), while 3 and 4 had similar capacitance values ($\sim$ 3-4 pF). The $\Delta C/C_0$ was highest for design 3 and 4 and lowest for 1. Design 3 and 4 produced nearly 2% change in capacitance. Design 4 was selected for further applications due to this high sensitivity, along with simplicity of printing.

Sensors with higher capacitance have better noise tolerance, but the sensitivity is significantly less. On the other hand, if noise is controlled or digitally filtered out, sensors with lower capacitance give large change in output giving better readability. This is

especially important in case of material identification

6.3.2 Sensor Performance

Figure 6.11 (a) Repeatability of printing with response of 3 sensors. (b) cyclic testing of a sensor (c) durability testing with repeated bending

During intended operation, the sensor undergoes bending as the gripper fingers curl (see 6.3.4) . To quantify the changes in geometry due to bending, capacitance response was measured at 3 different bending radii.

$\Delta C/C_0$ reduces on bending, as shown in fig. 6.11. The difference is significant as compared to flat sensor; however, it does not reduce much by further bending the sensor.

The repeatability of printing was tested by printing 3 identical sensors of spiral geometry and testing the response. Furthermore, cyclic testing for 1 sensor was done by repeatedly moving the block to 50mm and 5mm, 10 times. The results for these are shown in fig. 6.12. fig 6.12 (c) further shows durability test for the sensors.

The sensor was bent repeatedly at radius of 50 mm and the change in base capacitance value was measured. It can be seen that the capacitance drops initially and stabilizes after first 50 cycles. This can be attributed to changes due to changes at rigid contacts.

Figure 6.12 (a) Repeatability of printing with response of 3 sensors. (b) cyclic testing of a sensor

6.3.3 Material differentiation using proximity sensor

Proximity response was recorded for empty vial and vial filled with water. Since the dielectric constant of water is significantly higher than that of air, very high proximity response is seen for filled vial. The difference between response was observed for 4 designed mentioned 6.3.1. Designs with lower base capacitance showed highest difference between the response for empty and glass vial. Highest difference was observed for spiral design while interdigitated geometry gave lowest response.

Figure 6.143 Response of different designs with empty and filled vial. (a) Design 4, (b) Design 3, (c) Design 1 and (d) Design 2.

Different materials have different permeability which changes how they interact with electric fields. Metal The response for metal was recorded using a commercial steel weight. An identical weight was 3D printed using PLA and used for recording response for plastic.

Figure 6.14 (a) Sensor response for metal and plastic. (b) Plastic object (orange) and metal object

Metal gives very high response in comparison with plastic, which can be used for sorting metallic and non-metallic objects.

6.3.4 Integration with robotic fingers

To demonstrate the use, these sensors were printed on soft robotic fingers as shown in fig 6.15(a). A robotic gripper equipped with these fingers can be used to augment camera based systems for recognizing objects that are visually similar. For example, for differentiating between a real and a toy mandarin, as shown in fig. 6.15(b). The difference between water content of the real and plastic mandarin is causes the difference in respective capacitances.

Further, using a combination of 3 sensors, an object can be located in space for efficient gripping, as shown in fig. 6.15(c). The relative changes in the capacitance values of sensors can be compared and used for triangulating an object. Outputs of 3 sensors, (front, right and left) corresponding to different positions of object are shown.

Figure 6. 155 (a) Soft capacitive sensor printed on a robotic finger, (b), (c) applications of soft capacitive sensors on a gripper - object differentiation and object triangulation

Detection and identification of materials of objects would be extremely useful for augmented reality and real time object detection. Objects can be modelled along with their material properties. This will help machines interact with the physical objects similar to the way humans do.

6.4 Tactile Response Device

The construction of the device comprised of 4 components : Substrate, Joule heater, PEG pattern and top encapsulation layer. These layers were printed on top of each other one by one

Figure 6. 16 Process for direct ink writing of tactile response device on a PI substrate.

The silver joule heater is printed in the pattern as shown and the contacts are made using copper tape, later a layer of PEG is deposited exactly on top of the pattern to optimize the heating. Later the PDMS encapsulation is made by area-fill dispense of PDMS.

Figure 6. 16 Heating graphs for silver patterns at different voltages (a) and after bending (b).

Silver paste was printed to fabricate joule heaters for the tactile response devices. The ink was printed in patterns and then cured at 80°C for 15 mins. As the epoxy in the ink crosslinks, it forms continuous films that are highly flexible. Good quality prints with resistance values as low as 0.085 Ω/mm could be printed out. The patterns printed on PI substrates were flexible and bendable, however, lower adhesion of the inks made it difficult to use with the elastomeric substrates such as PDMS. The SEM of these films shows a dense network of silver nanoflakes embedded in epoxy matrix.

Figure 6. 18 A 3x3-pixel array of response devices

The printed joule heaters were heated using a DC power supply. At 3V, substantial amount of heating was achieved and temperatures in the range of 120°C were achieved within 4 minutes. It was seen that after bending the heater, current drawn was slightly lesser for the same voltage, due to slight increase in resistance. Consequentially, the heating curve shifted slightly downwards. Nevertheless, the heaters worked sufficiently well for melting PEG, which has melting point ~60°C.

Figure 6. 19 Hardness variation (A) and temperature variation (B) for a printed 3×3 array device to form letters N,T and U*. Shore A hardness measured for devices in ON state gives low values (>10) while for non-actuated devices gives high values (~50).

A 3×3 array of devices was printed on PI sheets. By electrically actuating the devices in particular combinations, any pattern letters N, T, and U were formed as hardness variation patterns. Fig.6.19- shows thermal image and hardness graphs for the devices.

Only the activated pixels get heated when the current is applied. The temperatures reach upto 90°C, which results in melting of PEG only at those pixels. The substrate, PI is a poor conductor of heat, and along with PDMS encapsulation, it prevents “off” pixels from melting. The hardness drops from 50 to 3-4 on shore A scale as a result of melting. This

change is perceivable by human touch.

With a higher resolution in printing, the devices can be used as tactile pixels or taxels to print haptic response skins, braille displays etc.

6.5 Chapter summary and conclusions

Soft printed sensors can implement various mechanisms for measurements. Change in dimensions of a sensor causes change in its resistance. This can be used in a resistive sensor. Objects interfere with electrical field lines emerging from a capacitor. This can be used for detecting touch and proximity.

Resistive sensors fabricated using PEDOT:PSS- CNT composite ink can be used for sensing strain and bending angle. The bending angle sensor shows fast, highly linear response with up to 10° resolution, and a range of 0-180°. The strain sensor successfully measures small strains with $\Delta R/R_0=15$ measured for 5% strain.

Proximity sensors were fabricated using Acetylene Black-PDMS composite. Different sensor geometries had different base capacitance values and sensitivities. These sensors can individually be used for differentiating metals and non-metals and sensing water content. A combination of 3 sensors mounted on a gripper can be used for locating and triangulating objects.

A stack of patterned PEG-MXene PCM ink and silver joule heater can be used to fabricate tactile response devices. A 3*3 array of such devices was printed to demonstrate tactile display of letters via hardness modulation.

Chapter 7

Conclusions and Future Scope

A summary for this study and conclusions drawn from the experiments are presented in this chapter. Following a brief concluding section, Future avenues are stated. Challenges for printing of EGaIn and oxidation issues of MXene inks are discussed in detail. Suggestions regarding future work related to this study are presented. Extension of printing in 3D, and fabrication of EL devices as well as active devices like TFTs is proposed

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7.1 Summary and Conclusions

This study successfully demonstrates the viability of direct ink writing technique for fabrication of flexible and stretchable electronic devices for sensing as well as responsive e-skin.

A direct ink writing system typically consists of a robot to move printhead along pre-defined path, an ink dispensing system and an interfacing computer. The ink dispensing systems can implement various mechanisms for moving fluids. A syringe pump, a peristaltic pump and a pressurized air based system are investigated in this study. A syringe pump was modified by adding resistive heating element to melt a phase-change material and print. However, all three systems have their advantages as well as shortcomings. Syringe pump is easy to use and interface with the system. However, since the ink must travel through the length of tubing, issues such as dripping and hydrodynamic lag become prominent. The peristaltic pump is useful in cases where inks require constant stirring. However, the oscillating motion of ink makes the pump less than ideal for printing at lower dispensing rates. Air pressure based system addresses these issues by eliminating the tubing between syringe barrel and printing needle. However, a separate source of pressurized air has to be maintained and controlled for this system.

In terms of print resolution, the printed feature width depends on the printing parameters. Width of a printed line increases with increased rate of volume dispensed / applied pressure, while it decreases with increase in printing gap as well as printing speed.

A total of 5 ink formulations were optimized and used separately or in combination to fabricate various devices in this work. PEDOT:PSS and MWCNT mixture shows higher conductivity and better printability as compared to its components. The inks made by mixing aqueous suspensions of PEDOT:PSS and MWCNT are highly conducting and show lowest resistance at the optimum composition with PEDOT:PSS suspension to MWCNT suspension ratio of 1:3, with dilution of MWCNT dispersion kept at 0.5 mg/ml. Higher ratios of MWCNT decreases the overall concentration of active components in the

ink, as the solvent volume goes up, while higher concentration of MWCNT dispersion reduces the degree of separation of individual CNTs. Highly sensitive strain sensors and bending angle sensors could be successfully printed using PEDOT:PSS-MWCNT composite ink.

To print proximity sensors, Acetylene Black and PDMS were mixed along with thinner in a planetary mixer. The as formed ink was highly viscous, and filaments could be extruded. Percolation threshold for formation of conductive network of acetylene black filler in PDMS matrix was found out to be ~13%. To make highly conducting ink, 15% w/w filler was added, beyond which the ink became too viscous to be extruded. 4 different geometries of proximity sensor were printed using this ink, and spiral design was chosen based on its high sensitivity and ease of printing. It was demonstrated that different response is obtained for different materials using these sensors, which can be used to differentiate and sort materials.

The silver ink has highest conductivity, however, as the formulation requires curing at higher temperature, the choice of substrates is limited. The printed silver patterns can act as joule heaters and reach temperatures as high as 123°C for 3V.

High molecular weight Poly-ethylene-glycol is a phase change polymer which melts above roughly 50°C and thus can be printed by heating the apparatus. A PEG-MXene composite ink, in which MXene nanoflakes were separated and added to PEG to aid with nucleation, was also developed. This drastically reduced its melting and solidification time. PEG-MXene composite was printed on the printed joule heater and Pristine PDMS was used for encapsulation to form a hardness variation based tactile response device.

7.2 Unresolved issues and Recommendations

Current study focuses solely on printing of 2-D devices for applications in e-skins. However, the capabilities of direct ink writing go further and many novel applications can be handled provided printing optimization is performed and correct ink system is used.

One of the major issues with current research is lack of highly stretchable conductor for connecting various devices on stretchable form factors. Most existing inks change resistance substantially on stretching and deformation and hence are only useful for sensing applications. However, for interconnects, truly stretchable inks need to be developed. EGaIn, a eutectic alloy of Indium and Gallium is being investigated for such an application[1]. Novel 2D materials can be investigated for making additive-less inks in order to form a stretchable network. MXenes, discussed briefly in chapter 5.4.2, are a promising class of materials for such an application [2], although various challenges need to be overcome before implementing these materials.

7.2.1 Printing challenges for EGaIn

Substantial work is being done in the field of patterning EGaIn for making highly stretchable conductors. DIW of EGaIn is a powerful way of achieving this. However, low viscosity coupled with non-Newtonian behavior of EGaIn calls for implementation of special strategies.

Attempts to print EGaIn were made during the course of this study. A major challenge for printing EGaIn was difficulties in breaking the oxide scale formed on the droplet before it touches the substrate. The thin layer of oxide on droplet prevents the metal from adhering to the substrate and instead the droplet grows bigger and bigger over the tip of needle. Recently a few methods are described for overcoming this issue in literature[1], as summarized in fig. 7.1.

Figure 7.1 Strategies to break oxide scale during DIW of EGaIn, taken from [1]

2 methods involving mechanical rupture of the scale rely on shear and tensile forces respectively. However, in case of shear rupture, the tip needs to be maintained extremely close to the substrate surface, and thus the surface needs to be very flat. Additives can be added to the film to change its flow behavior, although careful selection of materials would be required to make sure electrical properties of EGaIn are preserved. Dropwise dispensing is also possible, where the dispensing system is a hybrid of DIW and inkjet printing.

Figure 7. 2 Successful print of EGaIn printing on PDMS. The spiral sensor pattern is shown.

Nevertheless, EGaIn remains a very promising material owing to its tolerance for stretching while producing minimal change in resistance and can be developed and optimized for printing with a DIW system.

7.2.2 Oxidation of MXenes

MXenes are a class of novel 2D materials which are being widely studied for their chemical, electrical and thermal properties. Ti_3C_2 MXene is one of the most common material used for making highly conducting aqueous inks. However, its high surface area coupled with its hydrophilicity makes it prone to rapid oxidation in aqueous medium. This poses a major issue for processing of aqueous inks with MXene and drastically reduces shelf life.

Literature suggests that MXene flake starts oxidizing from its edge. To prevent oxidation, blocking contact of oxygen with open edges of the MXenes is important. Thus, various additives are currently being explored, which include chelating compounds and antioxidants. Protecting the edges of sheet slows down the oxidation by curbing the initiation of the reaction. Citric acid is a promising reagent for this as it acts by attaching to the edges of sheet while further enhancing protection by acting as an antioxidant.[3] A

comparative study of various additives can be done to elicit the actual mechanism behind the oxidation and subsequent prevention of it. The understanding of this will help in developing the formulation which will prevent the oxidation of MXenes while preserving their electrical properties.

MXenes as a family of materials is not limited just to conducting nanosheets. Novel materials from this class are being discovered rapidly, which involve novel 2D semiconductors, photoconductors and topological conductors. Study of such materials and their properties can help formulate inks for printed active devices.

7.3 Future Scope

7.3.1 3D printing and multimaterial printing for integrated HMIs

DIW is not only limited to 2 dimensional patterns of conductive inks. It can be exploited to print 3D structures of functional inks by tweaking and tuning the rheological behaviour of the inks. Shear thinning inks can be dispensed into 3D structures by stacking multiple

Figure 7.3 3D printed samples (a) PDMS-Acetylene black ink, during print (b) after curing (c) Printed ceramic green body (d) After setting the ceramic

layers on each other. As the shear force on ink reduces to zero after it is dispensed, the inks stop flowing and stacking becomes possible. This is demonstrated in figure 7.3(a,b) where a square pattern of Acetylene black - PDMS composite ink was printed successively on top of each other while increasing the print gap with each layer. These could further be

cured to form conductive stretchable 3D structures.

3D printing such systems via DIW can be explored for printing novel architectures for various sensors. With increased conductivity they can be used for fabricating truly 3D printed multi layered circuits which are flexible and stretchable. They can also be implemented for preparing soft actuators with fine-tuned movements.

The printing capabilities can be further increased by printing multiple materials in the same layer to create intricate non-homogenous patterns for various applications. Slurries of chemically bonded phosphate ceramics (CBPCs) can be optimized for printing green bodies. An attempt at printing ceramics is shown in fig. 7.3(c,d).

By implementing various material combination it is possible to closely mimic complex biological structures. For example, printed ceramics can form bones, i.e. structural components, micro-actuators made of soft materials can be then printed around it, and finally a sensor laden e-skin can be printed as final layer.

7.3.2 Electroluminescent devices for optical response

Electroluminescence is a phenomenon in which materials emit light when electrical field is applied across them. EL displays have long been commercialized and have created a niche in applications. A generic EL device is structured similar to a capacitor, where the dielectric layer comprises of electroluminescent materials, such as Zn based phosphors.

In recent years, stretchable composites of conductors and EL materials have been widely

Figure 7. 4 Schematic for various layers of EL device

explored for fabrication of stretchable EL displays. [4]

To further this study on DIW for e-skins, an all printed electroluminescent display would be an excellent avenue to explore. As shown in fig.7.4, the structure of an EL device comprises of substrate, transparent electrodes and EL layer. PDMS can be used as substrate as well as printed encapsulation. An ink comprising of dilute, highly conducting suspension of Ag nanowires can be printed to form transparent electrodes. PDMS and EL phosphor layer can be readily mixed to form an EL dielectric layer.

A visual response from printed e-skins would be extremely useful for soft robotics applications, in order to make human-machine interface highly integrated and intuitive for use.

7.3.3 Printed Active Devices

Most of the current research on printed stretchable devices is focused on sensors or electrodes. However, with the advances in solution processed transistors, improved formulations are being developed. These solutions can be modified to be used as printing inks. Metal oxide based TFTs are one such avenue which can be readily adapted to printing. Controlled dispensing of various layers of TFT would help simplify fabrication of devices as opposed to spin coating, which require photolithography for device definition. It would also enable producing TFTs with varying properties on the same wafer by in-situ adjustments in concentration. Such an approach can also be helpful for high throughput development of functional materials and is worth exploring.

7.4 Chapter summary

Two promising materials for stretchable electronics include liquid metal and MXene inks. However, due to the surface tension of liquid metal, special adjustments and strategies need to be explored for reliable and repeatable printing of it. MXene dispersions have a problem of rapid oxidation and thus have limited

shelf life and usability, which needs to be addressed.

The newer paradigms like 3D printing and multi-material printing are promising avenues for DIW printed electronics and devices. Initial experiments are done towards these. Also, newer devices can be explored for printing, which include electroluminescent displays and active devices like TFTs.

7.5 References

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