The Emerging Role of Electrodeposition in Additive Manufacturing

by *Trevor M. Braun and Daniel T. Schwartz*

Rapid prototyping has been used for creating three-dimensional objects from computer-aided design (CAD) files since the 1980s. There are a suite of technologies that underpin rapid prototyping, but a key advantage of many is their use of additive manufacturing (AM) processes; objects are created by placing material just where it is needed. AM processes use materials efficiently, reduce waste, and sometimes eliminate any post-processing steps. In recent years, the dropping costs and increasing availability of 3D-printing technologies (one class of AM methods) have driven widespread use and creative user communities. The easy-to-use, integrated software and hardware provides users with freedom in design that has created vast do-it-yourself/hobbyist markets. Software reconfigurable additive manufacturing technologies are empowering users by simplifying the way objects and devices are fabricated today.

Additive manufacturing has evolved over the past three decades to the point where current methods encompass lateral and vertical resolutions ranging from nanometers to centimeters, as shown in Fig. 1.[1-3] The first of these technologies commercialized was stereolithography (SL), which uses a photosensitive liquid polymer that hardens when an ultraviolet laser impinges on the resin.[4] The partially cured object is then lowered into the liquid to allow for curing of each subsequent additive layer. Stereolithographic resolutions are typically in the millimeter range, but the development of microstereolithography (MSL) has enabled additive manufacturing at sub-micron level resolution.[5,6] However, SL and MSL have limited material capabilities as they require photosensitive polymers. Selective laser sintering (SLS) is similar to SL, except a solid powder is sintered (fused) by the application of a high-energy carbon dioxide laser beam.[7] The primary advantage of SLS is increased material capabilities (polymers, metals, and composites), but the vertical and lateral resolutions are typically in the millimeter range due to laser focus diameter, powder granule size limitations, and thermal conduction beyond the laser focus. Similar technologies to SLS include electron beam melting (EBM) which uses an electron beam instead of a carbon dioxide laser to melt the powder and laser engineered net shaping (LENS) which injects the powder into a specific location before then heating it with a high powered laser.[2]

The 3DP process (developed at MIT) also uses powder as the material stock but instead applied inkjet nozzle technology to deliver liquid binder.[8] 3DP eliminates the need for high powered lasers or electron beams and achieves better resolution than SLS, but was originally limited to powdered polymer materials. Later, Prometal developed a steel powder and liquid binder to form metal features in a manner similar to 3DP.[2] However, Prometal-fabricated steel objects typically required high temperature sintering as a post-processing step to fuse the metals. Fused deposition modeling (FDM) processes have recently become the most commercially available additive manufacturing technology because of the inexpensive machinery and low materials cost. Ubiquitous machines like "Makerbot" rely on low melting point polymer filaments to transfer liquid polymer to the object, followed by solidification. Despite the low cost, commercial FDM systems are limited to printing thermopolymers and often have millimeter scale XY resolution as set by the diameter of the extrusion nozzle.

Stereolithography, selective laser sintering, 3DP, and fused metal deposition represent some of the most common methods for additive manufacturing. While each has attributes and limitations, taken in aggregate, AM technologies are seeing explosive growth. For example, Fig. 2a shows the publication trends for a topic search of "3D Printing" in the Web Of Knowledge search engine. Research publications on 3D printing grew slowly for years, but there has been an exponential increase in publications starting in 2012.

What role has electrodeposition played in the growing field of AM? Figure 2b shows the publication trend from a search in Web Of Knowledge for "3D printing AND (Electrodeposition OR Electroplating OR Plating)". Electrodeposition based 3D printing research has an almost identical growth trend as in Fig. 2a but is involved in a tiny fraction of the total 3D-printing publications. Electrodeposition based additive manufacturing technologies offer a possible solution to the material limitations of the technologies highlighted above (deposition capabilities include metals, alloys, semiconductors and polymers) while also improving the lateral and vertical resolution capabilities.[9] Electrodeposition is particularly unique in its ability to create films at sub-nanometer (monolayer) vertical resolutions, enabling an unexploited market for 3D-printing

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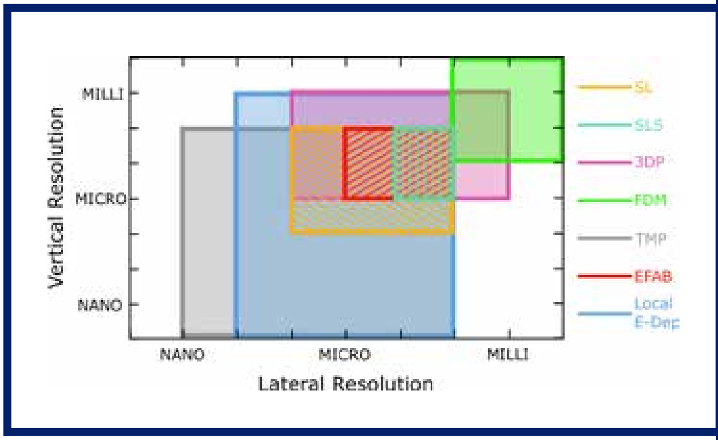

Fig. 1. *The lateral and vertical resolutions for various additive manufacturing techniques govern the kinds of objects that can be fabricated. Shown here is the approximate design space for seven different additive manufacturing methods. Abbreviations for each method are given in the text.*

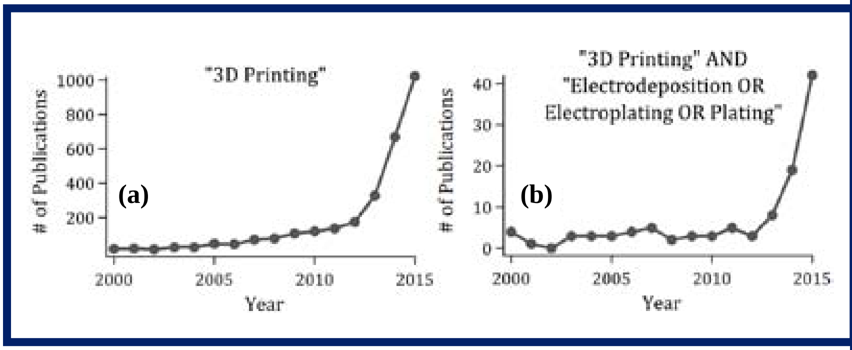

Fig. 2. *Publication trends involving 3D printing are revealed for topic searches involving the terms (a) "3D Printing" and (b) the subset of topics that also include "Electrodeposition OR Electroplating OR Plating".*

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AM. Clearly, electrodeposition additive manufacturing is a rich, untapped space for additional research efforts.

The standard for electrodeposition additive manufacturing and patterning is through-mask plating, which has been highly utilized for development of integrated circuits, printed circuit boards, and hard drive components. This technique requires a mask to create the patterned layer and typically needs several deposition and material removal steps to fully develop the pattern. Recent years have seen the development of new electrodeposition methods utilizing flexible masks and sacrificial material in an attempt to reduce fabrication steps and increase geometric complexity of the fabricated structure. One example from our lab uses flexible masks for through-mask plating of 3D shapes.[10] Pliant masks are laser cut to the desired shape and then adhered to nonplanar conductive substrates. After electrodeposition, the masks are removed, producing features such as the NiFe coil structure in Fig. 3a. Another method for layered manufacturing utilizes sacrificial material that is etched after electrodeposition to create 3D features.[11,12] In this system, varying mass transfer rates or current densities during deposition of NiFe alloys can produce sacrificial iron-rich layers and retained nickel-rich layers from a single bath. This manufacturing method is capable of producing 3D features such as the microgear in Fig. 3b, where a standard through-mask plated object (an extruded 2D shape) has embedded 3-D layers that can be partially or fully etched.[12]

The most sophisticated and commercially successful electrochemical technology utilizing sacrificial materials for 3D fabrication is electrochemical fabrication (EFAB) or MICA (a second generation form of EFAB), which has been commercialized by Microfabrica.[1,13] EFAB is a three-step process (per layer) consisting of sacrificial material deposition, structural material deposition, and surface planarization. First, a sacrificial material (normally copper) is deposited using a pre-fabricated negative micro-mold. Then, the retained material (normally nickel) is blanket deposited, filling in gaps left by the micro-mold and also depositing on top of the sacrificial material. Finally, both materials are planarized to the desired layer thickness. After repeating until all of the layers of the build are completed, the sacrificial material is etched leaving only retained structural material with micro-feature line rules down to 20 µm. Figure 3c shows an SEM image of a gyroscope consisting of 31 layers fabricated using the EFAB process.[14] Despite EFAB's success in microfabrication, it does not possess all of the traits for additive freeform fabrication, because there are hardware masks and layer-to-layer planarization. Through-mask plating and EFAB have some material selection advantages and better spatial resolution than SL, SLS, 3DP, and FDM but are not fully software-reconfigurable. Specifically, through mask plating and EFAB each use physical masks or stamps to develop their patterns. Direct write (DW) electrodeposition methods are needed to bridge the resolution and material capabilities in electrodeposition additive manufacturing with user friendly software reconfigurable techniques like FDM and SLS.

There have been several attempts to use localized electrochemistry for direct-write patterning as a software-reconfigurable solid freeform fabrication method. The use of microelectrodes to confine current density locally on a conductive substrate has shown growth rates on the order of µm s^{-1}.[9] Application of an electric field between a conductive substrate and a microelectrode in close proximity produces a highly localized current distribution at the substrate. The lateral resolution of the current distribution is dictated by the dimensions of the microelectrode. Highly developed scanning probe technology such as scanning electrochemical microscopy (SECM) and scanning tunneling microscopy (STM) have demonstrated nanometer scale patterning for both electrodeposition and etching.[15-17] Microelectrode direct-write electrodeposition addresses local control of current density and can easily achieve sub-micron resolution, but has diffusion limited mass transfer rates, which can limit material growth rates. Impinging jet electroplating systems address mass transfer limitations by providing controllable convective-diffusive mass transfer rates at the substrate. One of the first direct write jet-plating methods was developed by IBM in 1982 (laser-jet electroplating).[18-21] This technology is able to achieve deposition rates of 50 µm s^{-1} by combining jetted convection with a linearly-directed laser to further improve mass transfer and kinetic rates. Control of mass transfer and local current density enables a wide range of materials to be deposited, and can be software-reconfigurable.

Our laboratory expanded on impinging jet electroplating systems by implementing full software control of all electrodeposition and mass transfer parameters with a tool called Electrochemical Printing (EcP), enabling flexible electrodeposition of metals and alloys in a raster or vector drawing mode.[22-25] Figure 4 describes how EcP works. Software images (Fig. 4a, top) are used to define print locations and system operating conditions: Microjet fly-height (h, distance from microjet nozzle to substrate), electrolyte flow rate (v), and applied current and charge. These conditions are loaded into the custom software that controls each parameter (Fig. 4b). Figure 4c shows a schematic of the EcP print head and key features. A platinum anode is inserted upstream of the microjet outlet and the microjet nozzle diameter (d) and fly-height (h) are critical dimensions for deposit resolution. Full software control enables easily repeatable patterned deposition such as the copper on gold "Scale" pattern shown in the optical micrograph in Fig. 4d. Here, we see that decreasing fly-height clearly improves deposit resolution, as current is more localized at the substrate. The serial nature of local electrodeposition techniques presents a major barrier to commercial implementation of EcP. However, a U.S. Patent awarded in 2009 addresses the design rules for a multi-pixel print head which enables parallel patterning and increased throughput.[26]

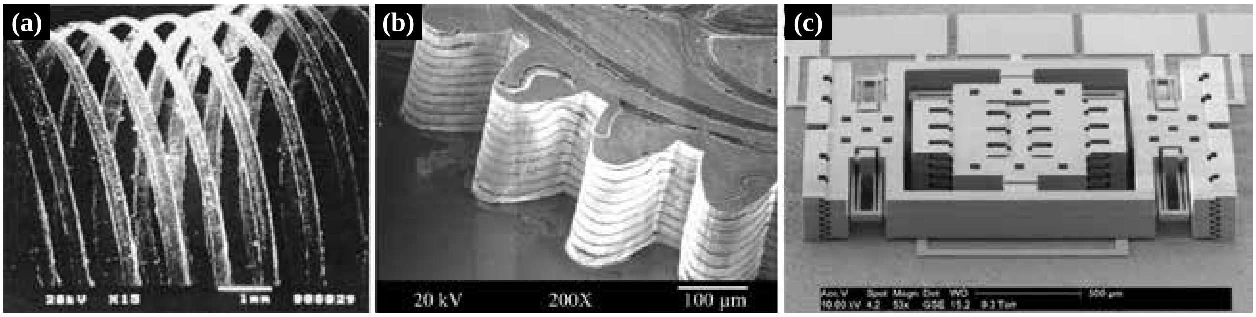

Fig. 3. *Examples of electrodeposition creating successively distinctive three dimensional objects. (a) Flexible laser-cut masks are used to create a 3D nickel coil structure.[10] (a) Embedded sacrificial layers can be placed within traditional 2D extruded through-mask plated objects.[12] (c) Repeated through-mask electrodeposition of sacrificial copper, blanket electrodeposition of retained nickel, and planarization, enables automated many-layer builds such as a gyroscope fabricated using EFAB.[14]*

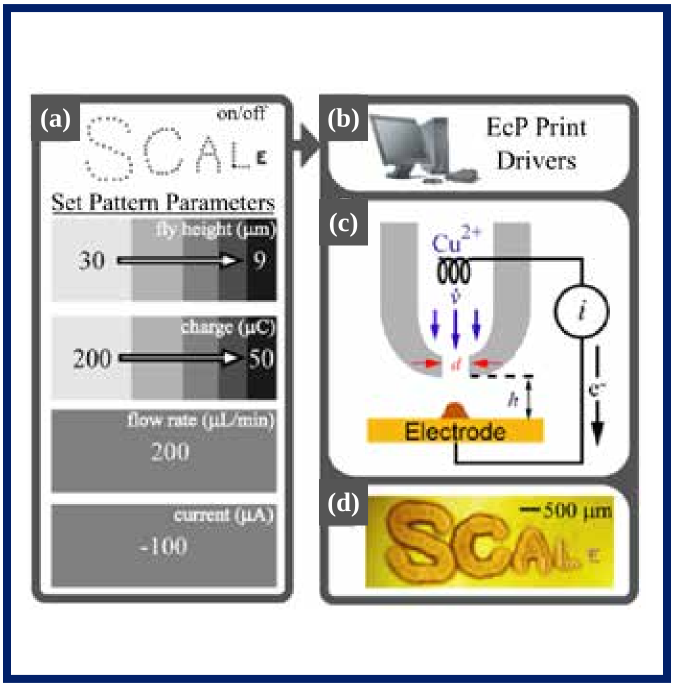

Fig. 4. *Shows a schematic for software reconfigurable operation of Electrochemical Printing. (a) A bitmap image indicating deposit location and process parameter selection is uploaded to a computer software program (b) with appropriate electrochemical and mass transfer operating conditions. This information is relayed to the EcP tool (schematic shown in (c)) which produces the corresponding copper pattern (d).*

Convective-diffusive mass transfer control allows deposition of a wide range of alloy materials from a single bath. This was first demonstrated with EcP through copper-nickel alloy deposition from a single bath (0.7 M $NiSO_4$, 0.004 M $CuSO_4$, and 0.500 M Na citrate). Figure 5a shows a 3D topographical map and a series of energy dispersive x-ray spectra (EDX), plots (a-f), for a 10 × 10 array of copper-nickel dots deposited under varying applied current and flow rates. EDX spectra show that copper-nickel alloy composition can be tailored by both the applied current and mass transfer conditions. The highest copper composition (plot b) occurs under low applied current and high mass transfer conditions, whereas the highest nickel composition (plot e) occurs at low mass transfer and high applied current conditions. These observations are consistent with kinetically limited nickel deposition and mass transfer limited copper deposition. These results show how EcP can be used to deposit both sacrificial (copper) and retained (nickel) materials from a single bath. This is the foundation for layered microfabrication from a software reconfigurable system.

EcP can be further modified to allow for much greater compositional control of the deposit by switching the electrolyte composition. This was achieved by adding a low volume micromixer upstream of the microjet nozzle outlet, providing rapid mixing of up to four individual bath streams. In this configuration, material composition is controlled by mixing individual bath components on the fly while printing, and then setting flow and current density that is optimal for that bath. Figure 5b shows an optical micrograph of a raster layer printed using EcP with on-the-fly mixing of baths in the micromixer. First, nickel raster dots were deposited at select locations from a 0.3 M $NiSO_4$, 0.004 M Na acetate, and 0.014 M acetic acid bath. After the nickel pattern finished, a copper bath (0.1 M $CuSO_4$ and 0.001 M H_2SO_4) was mixed on the fly, and another raster layer was printed, filling in the pattern. The Ni EDX image in Fig. 5c, clearly reveals the nickel-rich

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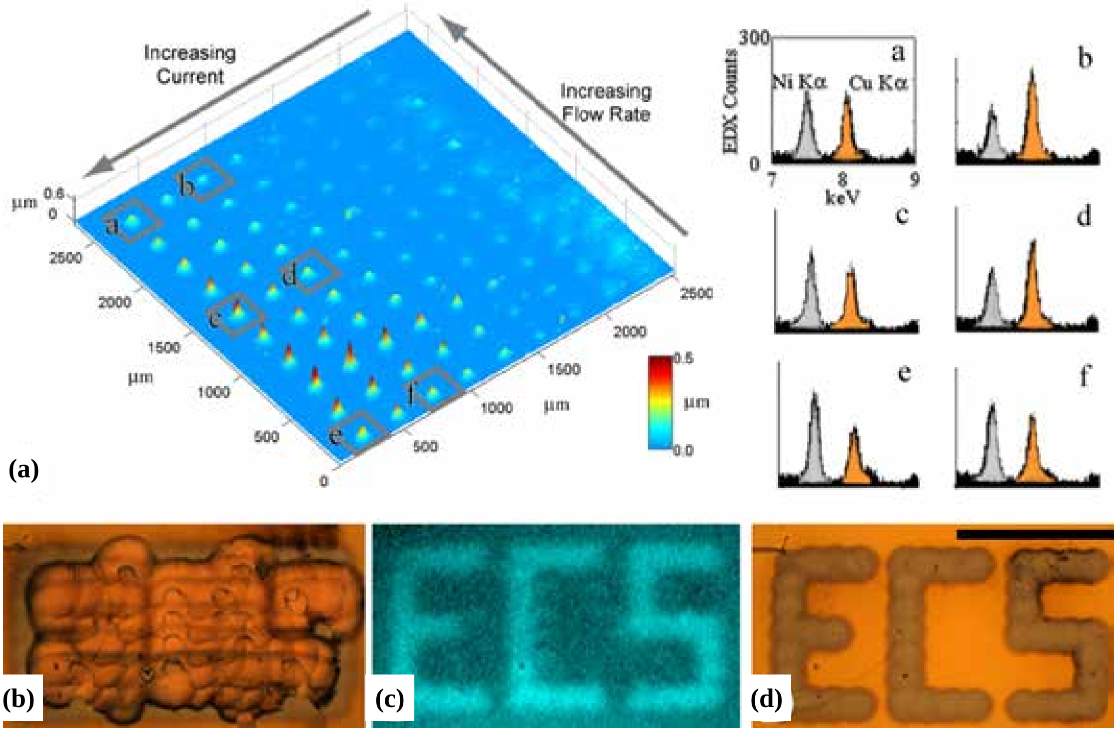

Fig. 5. *Local control of material composition using electrochemical printing (EcP). (a) Stylus profilometry (left) of nickel-copper alloy deposits in a 10 × 10 array of varying applied currents and electrolyte flow rates. EDX spectra (right) show copper and nickel Kα peaks indicating material composition for the deposits highlighted in the array. (b) Optical micrograph of nickel and copper material deposited in a single layer pattern using the EcP micromixer providing pure metal deposition control. (c) EDX map of the pattern in (b) showing nickel rich pattern within the single layer. (d) Optical micrograph of the pattern in (b) after chemical etching the sacrificial copper metal leaving only the nickel ECS logo remaining. Scale bar is 1 mm.*

material in the pattern "ECS." In Fig. 5d, the copper material in the layer was chemically etched with household ammonia cleaner, leaving only the nickel ECS pattern. The EcP micromixer provides rapid, local elemental material composition control demonstrating a proof-of-concept method for software-reconfigurable layered manufacturing using EcP. This one-layer build is the starting point for more complex, but fully software controlled, 3D printing in metal.

In recent years, we have simplified the EcP tool so it can operate using bipolar electrochemical reactions, making it possible to perform patterned electrodeposition without any need for an electrical connection to the substrate.[27-29] This configuration is potentially advantageous for additive manufacturing on surfaces that are difficult to connect electrically, at the expense of needing more sophisticated electrolyte engineering. We have so far demonstrated bipolar micropatterning of copper, nickel, silver, and gold using our software reconfigurable scanning bipolar cell (SBC).

We routinely perform EcP and the SBC in the micro to milli resolution regime. The scaling relationships for these microjet-based electrochemical systems have been studied and are well-understood.[27-29] The high mass transfer provided by the micro-jetted electrolyte eliminates concentration gradients at the substrate, allowing these systems to be approximated with a secondary current distribution (limiting current densities can exceed 10 A cm^{-2}).[23] Scaling of secondary current distribution systems are described by the dimensionless Wagner number, relating charge transfer resistances to ohmic resistances in the cell. Simple scaling relationships for these resistances as a function of operating parameters and geometric conditions provide insight for future scale-down to sub-micron patterning.

Additive manufacturing technologies have continued to evolve over the past three decades to meet the needs of manufacturing industries, researchers, and hobbyists alike. Techniques such as SL, SLS, 3DP, and FDM have been at the forefront of commercial additive manufacturing due to software control enabling greater design flexibility. FDM additive manufacturing has recently had great commercial success. Electrodeposition methods for additive manufacturing have also found significant commercial opportunities. Despite this, electrodeposition systems that are fully software controlled are just beginning to emerge. To bridge the advantages of techniques such as FDM with advantages of electrodeposition techniques like through-mask plating, localized electrodeposition methods have been explored. In our laboratory, electrochemical printing was developed for local electrodeposition, providing higher material growth rates to due to high convective-diffusive mass transfer. The full software control of mass transfer and electrochemical parameters in EcP provides excellent deposit composition control, an attractive feature for 3D fabrication that relies on patterning sacrificial and retained materials. Further software design and automation is necessary to drive this technology toward the sophisticated layered manufacturing displayed by methods such as EFAB/MICA. As 3D printing continues to grow, additional research efforts in software-reconfigurable, direct-write electrodeposition will create an alternative pathway for additive manufacturing, particularly at sub-micron resolutions.

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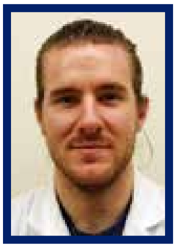

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