Additive Manufacturing of Electrodes: Innovative Applications and Opportunities

Mike T. Hauschultz^{1*}, Maria H. Friedo¹, Torsten Döhler¹, Andrea Böhme¹, Maria Richetta², Andreas H. Foitzik¹

1 Technical University of Applied Sciences Wildau, Hochschulring 1, 15745 Wildau, Germany 2 Department of Industrial Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy

* Correspondence: mike.hauschultz@th-wildau.de

Abstract

Additive manufacturing, also known as 3D printing, has gained tremendous importance in recent years. One of the areas where additive manufacturing is particularly useful is in the fabrication of electrodes. Electrodes are an important component of a wide range of applications, including electrochemistry, biomedical engineering, energy storage, analytics, electronics as well as life sciences. Traditionally, electrodes have been manufactured through costly processes such as etching, electroplating or cutting and milling. Additive manufacturing offers a new way to fabricate electrodes by depositing materials layer by layer (Yap et al., 2015). This opens up new possibilities for designing electrodes with complex geometries and structures that would not be possible using conventional methods. As a result, 3D printed electrodes are gaining interest in fields such as electromobility, water disinfection, manufacturing, and life sciences, which will be presented in this paper.

Introduction

The purpose of this paper is to provide an overview of several innovative applications where 3D printing is, or could be, used in the manufacture of electrodes. Since electrodes are mostly metallic, this work focuses mainly on applications where selective laser melting could be used. There are other 3D printing techniques that would also be applicable, but they are not the focus of this work. These are among others fused filament fabrication (FFF), printing of conductive materials or post-processing of regular filament prints, binder jetting and sintering and direct metal laser sintering (DMLS).

Selective Laser Melting (SLM)

Selective Laser Melting (SLM) is a technology that can be used to create threedimensional metal objects. This process uses a layer-by-layer approach to manufacturing. At the beginning of the process, a thin layer of metal powder (pure metal or alloy) is deposited on the print bed. Then a laser, directed by a galvo mirror system, melts the metal powder locally where a 3D object is to be built. The print bed is lowered by the height of one layer before this process is repeated layer by layer to form a 3D object. This allows for overhangs, bridges and complex internal structures that would not be possible with 2.5D milling or subtractive manufacturing. As many SLM printers allow recycling of excess powder, the process is environmentally friendly compared to conventional manufacturing techniques. To enable recycling, the formation of metal oxides must be avoided, so the printing process is performed under inert gas. This also prevents burning and combustion effects. The manufacturing process is also easier to learn and automate than traditional techniques. These factors, along with the freedom of design, are why this process is widely used in prototyping and lightweight manufacturing. (Yap et al., 2015)

Electric Field Forming Applications

The applications of electric field forming, 3D printed electrodes could be divided into two categories: life science applications and electronics applications.

Application in Electronics and Fabrication

Starting with electronics, there are already many applications using 3D printed parts, such as printing entire circuits using conductive filaments on an FFF 3D printer (Nassar & Dahiya, 2021). This makes it possible to better fit a circuit board into small spaces with special requirements. These applications are compact and flexible in their use cases. Other applications in this area include the fabrication and tuning of specific millimeter-wave antennas, as demonstrated by Zhang's research team (Zhang et al., 2016).

Besides applications in electronics, there are several applications for 3D printing in electrochemistry, as Browne's team reports. In addition to developing energy storage based on supercapacitors and batteries, there are prospects for creating energy conversion systems based on 3D printed electrodes for water splitting applications. Since SLM 3D printed electrodes have higher conductivity, they see more opportunities in using them over FFF printed electrodes. (Browne et al., 2020)

There are technologies that are highly dependent on the shape of the electric field. Even though they used subtractive manufacturing fabricated electrodes in their research, their work could be extended and followed up by using 3D printed electrodes because they have more freedom of shape. Two of these technologies are plasma forming and electrodeposition. In plasma forming, 3D electrodes were used to improve NOx removal (Takaki et al., 2004). In electrolytic deposition, the thickness of the deposited material is directly dependent on the strength of the electric field. The so-called "dog-bone effect" has been used in reverse to influence the deposition by structuring the electrode, which changes the electric field as to be seen in Figure 1 (Döhler, Böhme, Geissler, et al., 2022; Döhler, Böhme, Neumann, et al., 2022). To extend this work, a 3D-printed electrode can be evaluated that offers more possibilities in shaping the electric field.

Another technology based on the electric field is EDM (electrical discharge machining), which is used to create negatives of 2.5-dimensional electrodes, even with high aspect ratios. The use of 3D printed electrodes is already state of the art for complex structures that can't be produced by subtractive manufacturing. Different 3D printing techniques are used for this process in the literature, including an FFF process combined with washing and sintering (Bordón et al., 2022) or a DMLS process comparable to the SLM process (Reddy et al., 2020).

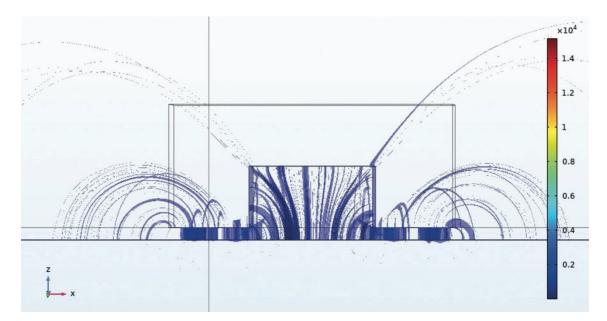


Figure 1: Simulated density function of electric field lines as a function of electrode shape. The results show the usefulness of the electrode shape for applications where electric field tuning can be exploited. (Simulation in Comsol Multiphysics, Module Electrodeposition) (Döhler, Böhme, Neumann, et al., 2022)

Application in Life Sciences

With 3D printed structures already being studied and tested for bone-replacement implants in the human body (Chacón et al., 2022; Luo et al., 2018), the idea of using 3D printing in other life science applications does not seem too far-fetched.

Many of these life science applications have been performed by Pumera's research group, which has demonstrated improvements in biosensing applications using a helical metal 3D-printed electrode (Ambrosi et al., 2016). Using this type of electrode, promising qualities could be shown in measuring the electrochemical properties of samples in solution of metal ions such as Pb and Cd (Lee et al., 2017) and biomolecules such as phenols (which are found in plastics, pharmaceuticals, dyes, etc.) (Cheng et al., 2017), acetaminophen (also known as Paracetamol) and the neurotransmitter dopamine (Liyarita et al., 2018).

Similarly, 3D structured electrodes can be used to remove pollutants in water using the electrocoagulation process. This process dissolves metal hydroxides from the electrode, which bind and precipitate most substances in the water. Research has shown that the efficiency of this process depends on the shape and surface structure of the electrode (Khandegar & Saroha, 2016). Therefore, the shape of printed electrodes can be further improved to maximize the efficiency.

Cooling Applications

In addition to field forming applications, cooling applications can also be divided into electronics and manufacturing applications and life sciences applications, which appear to be in the minority in this case.

Application in Electronics and Fabrication

Since 3D printing has the ability to form internal structures in addition to external structures, it is possible to use it for complex cooling channels, which will be the focus of this section. The applications presented aim to improve the efficiency and/or lifetime of electrodes by improving existing cooling channels.

The basis for this cooling application was created by cooling batteries with Tesla valve structured cooling channels, which results in a lower temperature gradient and therefore better cooling performance (Monika et al., 2021). Combining such cooling structures with battery electrodes could further improve efficiency, which would be important for applications in electric vehicles.

Cooled electrodes have been shown to increase the lifetime of production electrodes in electric discharge machining and welding (Hirsch & Leibovitz, 2019). While water-cooled welding electrodes have been commercially available for some time, cooled EDM electrodes are still a research topic. The integration of a simple cooling structure for use with liquid nitrogen has been shown to reduce tool electrode wear by up to 27% (Abdulkareem et al., 2010). A combination of such electrode cooling with Tesla mixing structures and conformal cooling channels through additive manufacturing is expected to provide a greater overall reduction in electrode wear.

Application in Life Sciences

In addition to field forming applications, there are life science applications for cooled electrodes. An important example is water-cooled electrodes for radiofrequency ablation (RFA). This technique is used to destroy cancer cells inside the living organism using high-frequency currents. By cooling such electrodes, secondary indirect damage can be avoided (Shi et al., 2019). There are also cooled wet electrodes that additionally deliver saline into the body to increase the coagulation volume (Miao et al., 2000). All of these features could be included without the use of 3D printing, which raises the question of what further improvements in cooling capability and functionality could actually be achieved with 3D printing.

Conclusion

This paper provides an overview of three-dimensional electrodes, their use cases and future opportunities. These include millimeter wave antennas, applications in electroplating and plasma, biosensors and EDM, as well as various cooling implications to improve the lifetime and efficiency of electrodes or secondary damage in RFA applications. In addition, electrodes with high surface-to-volume ratios and flow-through characteristics can be produced. Therefore, future use may focus on applications in hydrogen catalysis and flow-through reactors for sensing and temperature control.

References

- Abdulkareem, S., Ali Khan, A. & Konneh, M. (2010). Cooling effect on electrode and process parameters in EDM. *Materials and Manufacturing Processes*, *25*(6), 462–466. https://doi.org/10.1080/15394450902996619
- Ambrosi, A., Moo, J. G. S. & Pumera, M. (2016). Helical 3D-printed metal electrodes as custom-shaped 3D platform for electrochemical devices. *Advanced Functional Materials*, *26*(5), 698–703. https://doi.org/10.1002/adfm.201503902
- Bordón, P., Paz, R. & Monzón, M. D. (2022). Evaluation of the Performance of Atomic Diffusion Additive Manufacturing Electrodes in Electrical Discharge Machining. *Materials*, 15(17). https://doi.org/10.3390/ma15175953
- Browne, M. P., Redondo, E. & Pumera, M. (2020). 3D Printing for Electrochemical Energy Applications. *Chemical Reviews*, *120*(5), 2783–2810. https://doi.org/10.1021/acs.chemrev.9b00783
- Chacón, J. M., Núñez, P. J., Caminero, M. A., García-Plaza, E., Vallejo, J. & Blanco, M. (2022). 3D printing of patient-specific 316L–stainless–steel medical implants using fused filament fabrication technology: two veterinary case studies. *Bio-Design and Manufacturing*, *5*(4), 808–815. https://doi.org/10.1007/s42242-022-00200-8
- Cheng, T. S., Nasir, M. Z. M., Ambrosi, A. & Pumera, M. (2017). 3D-printed metal electrodes for electrochemical detection of phenols. *Applied Materials Today*, *9*, 212–219. https://doi.org/10.1016/j.apmt.2017.07.005
- Döhler, T., Böhme, A., Geissler, U., Hallmann, P., Foitzik, A., Hofmann, M., Bochem, R. & Neumann, J. (2022). *Apparat und Verfahren zur Aufbringung einer strukturierten Beschichtung sowie Metallgegenstand mit einer strukturierten Beschichtung* (Patent No. DE102020127401).
- Döhler, T., Böhme, A., Neumann, J., Bochem, R., Hoffmann, M., Foitzik, A. H. & Geissler, U. (2022. July). Mikrogalvanische Methode zur Abscheidung von lateral verteilten Schichtdicken unter Verwendung einer galvanischen Beschichtungstechnologie. *IMaps Deutschland Plus*, 984–987. www.imaps.de
- Hirsch, R. B. & Leibovitz, R. (2019). *Influence of Water Temperature and Flow on Electrode Life*.
- Khandegar, V. & Saroha, A. K. (2016). Effect of Electrode Shape and Current Source on Performance of Electrocoagulation. *Journal of Hazardous, Toxic, and Radioactive Waste, 20*(1). https://doi.org/10.1061/(asce)hz.2153-5515.0000278
- Lee, K. Y., Ambrosi, A. & Pumera, M. (2017). 3D-printed Metal Electrodes for Heavy Metals Detection by Anodic Stripping Voltammetry. *Electroanalysis*, *29*(11), 2444– 2453. https://doi.org/https://doi.org/10.1002/elan.201700388
- Liyarita, B. R., Ambrosi, A. & Pumera, M. (2018). 3D-printed Electrodes for Sensing of Biologically Active Molecules. *Electroanalysis*, *30*(7), 1319–1326. https://doi.org/https://doi.org/10.1002/elan.201700828

- Luo, J., Jia, X., Gu, R., Zhou, P., Huang, Y., Sun, J. & Yan, M. (2018). 316L Stainless Steel Manufactured by Selective Laser Melting and Its Biocompatibility with or without Hydroxyapatite Coating. *Metals*, *8*(7), 548. https://doi.org/10.3390/met8070000
- Miao, Y., Ni, Y., Yu, J. & Marchal, G. (2000). A Comparative Study on Validation of a Novel Cooled-Wet Electrode for Radiofrequency Liver Ablation. *Investigative Radiology*, *35*(7). https://journals.lww.com/investigativeradiology/Fulltext/2000/07000/A_Comparati ve_Study_on_Validation_of_a_Novel.7.aspx
- Monika, K., Chakraborty, C., Roy, S., Sujith, R. & Datta, S. P. (2021). A numerical analysis on multi-stage Tesla valve based cold plate for cooling of pouch type Liion batteries. *International Journal of Heat and Mass Transfer*, *177*, 121560. https://doi.org/https://doi.org/10.1016/j.ijheatmasstransfer.2021.121560
- Nassar, H. & Dahiya, R. (2021). Fused Deposition Modeling-Based 3D-Printed Electrical Interconnects and Circuits. *Advanced Intelligent Systems*, *3*(12), 2100102. https://doi.org/10.1002/aisy.202100102
- Reddy, L., Krishna, L., Kumar, S. & Pinninti, R. R. (2020). A Comparative Study on Performance of 3D-Printed EDM Electrode with Conventional EDM Electrode (pp. 217–225). https://doi.org/10.1007/978-981-15-1124-0_19
- Shi, X., Pan, H., Ge, H., Li, L., Xu, Y., Wang, C., Xie, H., Liu, X., Zhou, W. & Wang, S. (2019). Subsequent cooling-circulation after radiofrequency and microwave ablation avoids secondary indirect damage induced by residual thermal energy. *Diagnostic and Interventional Radiology*, *25*(4), 291–297. https://doi.org/10.5152/dir.2019.17455
- Takaki, K., Shimizu, M., Mukaigawa, S. & Fujiwara, T. (2004). Effect of electrode shape in dielectric barrier discharge plasma reactor for NOx removal. *IEEE Transactions on Plasma Science*, *32*(1 I), 32–38. https://doi.org/10.1109/TPS.2004.823973
- Yap, C. Y., Chua, C. K., Dong, Z. L., Liu, Z. H., Zhang, D. Q., Loh, L. E. & Sing, S. L. (2015). Review of selective laser melting: Materials and applications. In *Applied Physics Reviews* (Vol. 2, Issue 4). American Institute of Physics Inc. https://doi.org/10.1063/1.4935926
- Zhang, B., Zhan, Z., Cao, Y., Gulan, H., Linnér, P., Sun, J., Zwick, T. & Zirath, H. (2016). Metallic 3-D Printed Antennas for Millimeter- and Submillimeter Wave Applications. *IEEE Transactions on Terahertz Science and Technology*, 6(4), 592– 600. https://doi.org/10.1109/TTHZ.2016.2562508