Additive Manufacturing for Electrochemical (Micro)Fluidic Platforms

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Hydrodynamic Electrochemistry

Many electrochemical experiments involve relatively large volumes (>50 mL) of electrolyte, conducted in a stationary solution, but there are significant advantages to be gained by making the measurement under controlled flow and shrinking the electrode and cell volume down to the microscale. To consider why, it is first important to discuss what controls the electrochemical current, I, in a dynamic electrochemical measurement.

As Eq. 1 shows, I is directly proportional to the rate of the electrochemical reaction, expressed as the flux, \( \jmath \):

\[ I = nAF \jmath \]  

(1)

where \( n \) is the number of electrons transferred per redox event, \( A \) is the area of the electrode (cm\(^2\)) and \( F \) is Faraday’s constant. The flux, \( \jmath \), can either be limited by electron transfer or mass transfer, the latter which is described by the Nernst-Planck equation, 1 which outlines the contributions of diffusion, convection and migration to \( \jmath \).

In the presence of excess supporting electrolyte and under stationary conditions, diffusion is the only form of mass transport. However, by adding a (quantitative) convective term to diffusion it is possible to (significantly) increase transport of species to the electrode surface. This has the advantage of both increasing \( I \) (extremely useful for low concentration detection) and accessing faster electron transfer reactions. Operation of electrochemical cells with convective-diffusive transport has traditionally been carried out by either rotating the electrode (rotating disk electrode) 2 or flowing solution onto the electrode, e.g., the impinging or wall jet electrode (WJE), 3,4 or flowing solution over the electrode surface, e.g., channel or tubular flow cell. 5 To make \( I \) quantitative, it is important that the convective–diffusion process is controlled and well-defined; thus laminar flow is much preferred over turbulent flow.

By shrinking down the dimensions of the electrode and the electrochemical cell, it is possible to (i) increase the diffusional flux of species to the electrode surface, increasing current to noise ratios, and (ii) reduce sample volume requirements. Practically, miniaturisation is much easier when dealing with electrochemical flow systems than with rotating electrodes. Although tubular flow electrodes have been utilised for a variety of applications, 6,7 they are nowadays infrequently observed in literature, possibly because they are more difficult to fabricate and miniaturise than other electrochemical flow systems.

Flow electrodes, due to the enhanced mass transport from convection, typically produce steady state voltammetric behaviour. 8 Quantitatively, mass transport can be solved leading to analytical equations which describe the relationship between the limiting current, \( I_{\text{lim}} \), and volumetric flow rate, \( V_f \). For example, for a band electrode in a channel flow cell under laminar flow conditions, as shown in Fig. 1a, the Levich equation holds where: 5

\[ I_{\text{lim}} = 0.925nFCD^{3/2}V_f^{1/2}w^{-3}h^{-2/3}x_e^{-2/3} \]  

(2)

where \( w \) is the channel width, \( 2h \) is the channel height, \( x_e \) is the electrode width, and \( C \) and \( D \) are the concentration and diffusion coefficients, respectively, of the species of interest. Channel flow electrodes (CFE) have a wide range of uses, for example in flow injection analysis (FIA), 9 dissolution studies, 10 kinetic studies 11 and reaction mechanism investigations, 12 electro-osmotic flow 13 and trace detection of a range of analytes. 12 The history and theory of CFE’s has been reviewed by various authors. 14-16

Figure 1b depicts the general schematic of a WJE. For this system under laminar flow conditions, \( I_{\text{lim}} \) is given by: 17,18

\[ I_{\text{lim}} = 1.597nFk\alpha^{3/4}R^{5/12}D^{3/2}V_f^{1/2}a^{1/2}C^{1/4} \]  

(3)

where: \( k \) is a numerical constant describing the momentum flux, \( R \) is the disk electrode radius, \( \alpha \) is the kinematic viscosity, and \( a \) is the nozzle diameter. WJE’s are commonly used for trace analyte determination, 19 anodic stripping analysis, 20 kinetic studies, 21 and as end of column detectors in High Pressure Liquid Chromatography (HPLC). 22 They have been reviewed by various authors. 23-25

Conventional Fabrication of Electrochemical Flow Cells

Channel Flow Electrochemical Cells  •  Channel flow electrochemical cells can generally be classified as either two- or three-part cells. For the two-part cell, typically the channel inlet and outlet are built into a single insulating component, attached through adhesive 26 or mechanical force 27 to a second component — a flat plate containing the working electrode, as shown in Fig. 2ai. In the case of a three-part cell, as shown in Fig. 2a(ii), the channel dimensions are determined via the use of a gasket, e.g. Teflon, 28 thermoplastics, 29 or an O-ring, 30 which is held between the upper unit, containing the inlet and outlet, and the working electrode.

(continued on next page)

Fig. 1. Schematic of (a) a band electrode in a typical channel flow cell and (b) a 2D cross section of a WJE. Flow profiles for each are displayed in blue.
and the electrode-containing base plate. For Eq. 2 to strictly apply it is important there is a co-planar arrangement of the electrode and its insulating casing, which can be difficult to achieve depending on the fabrication methodology adopted. Typical methods of electrode fabrication include lithographic patterning of Au or Pt on an insulating material or sealing of metal foils in an epoxy based insulator. Other methods of encapsulation do exist for more challenging electrode materials such as carbon nanotubes and conducting diamond. The reference and counter electrodes are typically inserted into the inlets/outlets to form a three-electrode cell.

The vast majority of flow cells are fabricated using either precision micromachining or lithography. Precision micromachining involves the machining of solid blocks of appropriate materials, e.g., PMMA, PTFE, polyethylene, polypropylene or silica, to form channels and inlets/outlets. A combination of machining techniques, such as milling, drilling, tapping, turning are employed. To produce smaller channels, smoother walls or more complicated internal geometries, an increase in precision and tooling complexity is required, which results in manufacturing costs increasing significantly. Precision machining can achieve feature sizes of hundreds of μm with roughness of tens of μm. With optimization of machining parameters and the use of a computer controlled milling machine, parts can be fabricated in tens of seconds.

Lithographic techniques are also routinely used to fabricate flow cells. Smaller (micro-scale) dimensions result from lithography when compared to precision machining. Lithography also enables the use of harder materials (e.g., glass) that can be difficult to precision machine. For example, features tens of nm in size can be reliably fabricated, although this is well below the typical dimensions of microfluidic channels. Lithography can be used to make the flow cell either directly, typically in silicon, or by replica moulding. Patterned photoresist can be used as the walls of a channel, analogous to a machined gasket, or as a mask for substrate etching. Patterned photoresist and etched silicon can also be used as a replica mould in combination with the casting of PMMA or PDMS. A PDMS flow cell, sitting on a quartz slide containing the electrode(s), is shown in Fig. 2ai. Although the preparation and etching processes are multiple-step and can take multiple hours, the replica moulding process is relatively rapid, with parts being fabricated in tens of minutes. However, lithography in general is a multi-stepped process which requires clean-room facilities. It is thus capital intensive and not viable for the majority of users.

To date, it is almost impossible to form a one component channel flow cell where the electrode is already integrated into the host material using lithography or precision machining. This is due to the difficulties associated with the creation of internal geometries (voids) within a single component structure. One example exists of a tubular flow electrode formed by machining a hole through a monolithic structure consisting of three layers of insulating diamond, conducting diamond and insulating diamond.

Wall Jet Electrochemical Cells Early designs of the impinging or WJE involved close approach of a nozzle, typically a = 0.25–1 mm, to a large electrode, typically r ≈ 1–3 mm, as shown in Fig. 2bi. This arrangement is very similar to that used today in HPLC with electrochemical (EC) detection. Common cell materials include Teflon, PVC and Perspex. These cells are often fabricated through precision machining, with screws or magnetic clamps used to hold the cell together, as shown in Fig. 2bi. Modern designs typically employ faster solution flow rates, smaller nozzle diameters and a wider variety of electrode configurations.

There are various designs for wall jet cells that are used both commercially and in academic laboratories. For example, BASi produce a three-part flow cell intended for HPLC-EC, in which the electrode, gasket, and top plate are held together with a clamp. This design has also been used for FIA-EC. Similarly, DropSens produces a range of flow devices which have been used in a variety of FIA-EC studies. The wall jet cells (typically 2h = 400 μm, r = 250 μm, a = 4 mm) are fabricated from methacrylate by precision machining and use O-rings and magnetic clamps to complete the flow cell.

Additive Manufacture of Microfluidic Flow Cells Additive manufacturing (AM) is the process of building up a structure by adding successive layers (bottom up) as opposed to removing material subtractively from a larger block (top down). AM is a broad and rapidly developing category of manufacturing techniques that takes 3D objects designed in silico, converts them to layers of 3D pixels (voxels) and then directs a device to form the object by selective addition of patterned layers. Several methods of AM are currently available. Here we aim to provide a brief overview of those most pertinent to building flow cells for electrochemical measurements. A more comprehensive description of the various types of AM can be found in recent review articles.

For simplicity, the field of AM can be broadly split into two categories: stereolithography apparatus/selective laser sintering (SLA/SLS), and extruded droplet/filament technologies, as shown in Fig. 3. SLA involves the light-mediated curing of layers or voxels within a vat of liquid resin using either a digital micro-mirror device (similar to those found in commercial projector systems) or a directed laser beam. SLS (here grouped with selective laser melting; SLM) involves...
the use of lasers to cure beds of plastic or metal powders. Both SLS and two photon SLA are “direct write,” sequentially curing voxels to build up a part, whereas in SLA whole layers are formed simultaneously. For example, the EnvisionTec SLA machines use UV light to cure successive layers of a liquid acrylate resin, while 3D systems’ ProX series uses a SLS machine which employs a laser to pattern layers by selective melting of a bed of granulated plastic beads.

In extruded droplet/filament AM, typified by methods more broadly known as fused deposition modelling (FDM) and 3D printing (3DP), a 3D part is made by layers formed from a printing nozzle extruded as a continuous filament or as single droplets from a nozzle. Thermoplastics (e.g., ABS) are most commonly used, but UV-cured acrylate resins are also prevalent. Instead of directly printing the plastic itself, a binder can be jetted onto a bed of powder, setting the granulated bed into the appropriate form. For example, the RepRap family of machines uses extruded filaments of ABS to build parts onto a build platform, while the Stratasys’ PolyJet systems use inkjet technology to build multimaterial/multi-coloured parts.

A breakdown of the pertinent parameters for the different AM methods discussed is presented in Table I. It should be noted that there are usually several commercial examples available for each method and the figures quoted in the table are representative of the best achievable by any one example in each class.

Build time for AM varies widely with method and machine. Generally, it takes around 1 minute to form a single layer with total time depending on the final device height and the layer thickness. Build times in the hours are usual. Post-build curing is recommended for some methods (e.g., UV curing of acrylate resins and sintering of metal parts) to improve part strength, adding tens of minutes to hours to the process.

3D voxel size defines the smoothness of the resulting part. Small voxels produce smooth parts, but also require potentially longer build times for an arbitrarily large part. Extruded filament methods generally have the poorest resolution (voxel sizes of 100-200 µm as a lower bound), with the size defined by the nozzle aperture and the properties of the material being extruded. The resolution in most SLA/SLS methods is different in the XY and Z dimensions as the XY smoothness is defined by the distance between neighbouring voxels and the Z smoothness is defined by the thickness and uniformity of the build layer. Obviously, liquids can be more uniform and flat than a powder bed, so SLA methods generally provide a higher resolution limit than SLS methods. As a result, SLA can provide high resolution in all three dimensions, but is typically limited in build area (tens or hundreds of mm in XY and several tens of cm in Z, depending on the machine). For small devices, like flow cells for electrochemistry, this is not an issue. Resolutions of 25 µm are achievable with roughness of <10 µm RMS in XY dimensions with layer-by-layer building, where whole layers are cured simultaneously by sequential projection of the appropriate images. Extremely high voxel resolution is possible with two photon stereo-lithography which uses a steered laser beam to cure specific spots and has the highest resolution in all three dimensions, with voxel sizes of hundreds of nanometers possible. However, only a limited build area (<10 mm) is feasible due to the focal length of the laser systems employed.

An early example of AM for fabrication of electrochemical microfluidic flow cells was carried out by Macpherson, Unwin and co-workers, who developed a SLA method for the fabrication of the channel/outlet/inlet component of a 2-part flow cell, aimed at continuous flow voltammetry. The cells were 10 mm × 10 mm × 10 mm and contained a 200 µm height channel. An EnvisionTec Perfactory Mini machine was used to fabricate up to 8 cells in one build (about 3 hours) based on computer aided design structures and using an acrylate resin. The same flow cells were later used for the analysis of ascorbic acid oxidation and the dissolution kinetics of gypsum and calcium sulphate. The flow cells were further optimised for FIA-EC by reducing the inlet and flow cell volume, reducing the channel height from 200 µm to 25 µm and smoothing the fluid pathways by minimising inlet-channel geometry changes. These factors all assisted in favourably reducing analyte dispersion. The resulting flow cell and analytical signals for the FIA-EC detection of dopamine are shown in Fig. 4. The same flow cell has also been employed for trace FIA-EC analysis of dissolved hydrogen sulphide. Other groups have also developed CFE and WJE flow cells using AM. One advantage of the AM approach, as shown above, is that designs can be readily altered and that even in one build, several different structures can be fabricated.

Traditional methods, such as lithography and precision machining, are essentially 2.5D, meaning that a 2D shape is extruded/swept into the third dimension. The key differentiating feature of AM compared...
to more traditional methods is that AM allows the formation of internal voids in a single piece of material. This capability is especially valuable for microfluidic cells, for which cracks or seals between different parts create risks of leaking solution. Furthermore, some geometric features such as true right angle corners and undercuts are difficult to achieve with traditional methods. By contrast, most AM techniques are well-suited for creating such features.

The advantage of being able to fabricate internal voids with AM is demonstrated by comparing a precision machined commercial wall jet cell (Fig. 5a) with that produced by SLA (Fig. 5b, c). As shown schematically in Fig. 5ai, the commercial cell has a single outlet, positioned to one side of the centrally located inlet. Note, the electrode sits symmetrically beneath the inlet nozzle and is always larger in diameter. Finite element simulations of the resulting flow profile illustrate the consequence of one off centre outlet; flow deviates from the ideal case of being radially symmetric. To achieve radially symmetric flow it is necessary to place the outlets around the edge of the electrode and equalise the pressure of each outlet path. While traditional fabrication methods generally require 2.5D channels, AM allows the construction of complex internal voids—as shown in Fig. 4bi—that would be impossible to fabricate by alternative methods. As shown in Fig. 5bii, this structure results in a much more uniform flow profile away from the inlet nozzle. The corresponding SLA fabricated WJE cells are shown in Fig. 5c.

One way to improve performance is to coat the flow cell, post-build, with a resistant polymer to enhance stability. Another method is to add small particles of non-reactive materials to the mixture to produce build parts with significantly altered properties. Most development work in this area is focused on developing stable, printable plastics with hard, stiff, strong, or flexible properties simulating polycarbonate, polypropylene, and ceramics. This can have a positive impact on solvent stability, as indicated in Table II, where two resins—methylacrylate and a high temperature (HT) resin—are compared for their stability in different common solvents. The HT resin is a proprietary blend of acrylate and a microparticle additive that confers improved temperature and chemical stability. Although lifetime was improved, significant swelling or leaching was observed, which would affect the long-term performance of a continuous flow sensor. To date, there is no systematic study investigating solvent stability of common AM materials which would profitably serve researchers in this field.

An area of particular interest to electrochemists is the solvent stability of AM materials. Machined stainless steel components, Teflon, or diamond will have much greater solvent stability than many polymeric based AM or PDMS/PMMA lithographically fabricated microfluidic flow cells. FDM requires the plastic to melt, flow and set and is therefore limited to thermoplastics such as ABS and PLA. In terms of chemical stability, ABS is relatively stable in alkali/water solutions while PLA is more stable in acid and neutral solutions. SLA is dominated by acrylate monomers that are polymerised with light-activated cross-linking reagents, which are generally stable in water, but unstable in organic solvents such as acetone.

Fig. 4. SLA-fabricated flow cell for FIA-EC detection of dopamine using a carbon nanotube electrode. (a) 3D (left) and side views (right) of a 25 μm height flow cell (key dimensions are given in mm unless stated otherwise). (b) Schematic (cut-away) illustrating placement of the flow cell on the electrode support (flow direction indicated by blue arrows). (c) FIA-EC data for dopamine detection, a LOD of 5 pM was obtained in PBS buffer. Adapted from reference 9.

Fig. 5. (a,b) (i) Internal geometry (not to scale) and (ii) finite element modelling simulation of flow within (a) a commercial WJE cell and (b) a WJE cell built using SLA. (c) Photographs indicating the internal geometry enabled by AM-SLA, copyright Jonathan Newland. Scale bars = 3 mm. The fluid velocity profiles shown in (a,b) are taken 50 or 100 μm from the base of the chamber for the commercial and SLA WJE cells respectively, the color bar indicates the flow rate in mL/s.
Future Perspectives for Additive Manufacture in Electrochemistry

There is significant development work underway to increase the number of buildable materials. Recent work demonstrated use of a pre-ceramic composite which was converted to a non-porous ceramic by firing post-build.22 This work is expected to continue and is largely driven by engineers who aim for specific physical properties rather than chemists who are primarily interested in chemical properties. By highlighting the potential benefits that an AM approach can yield for electrochemists in flow, it is hoped that a significant new driver for the development of chemically resistant materials will develop.

Multi-material AM (MM-AM)68 allows the monolithic fabrication of parts composed of materials of different properties. For example, it is possible to produce conducting feedstock material by impregnating parts composed of materials of different properties. For example, it is possible to produce conducting feedstock material by impregnating with conducting particles such as carbon black69 or silver.70 Thus, it should be possible to fabricate flow cells that have the electrodes fully integrated. The near term benefit of this approach would be that no sealing of the flow cell with the electrode substrate is necessary, hopefully minimising possible solution leakage. The longer term benefit is that it will be possible to directly incorporate sensing functionality into devices without complicated multi-component assembly lines. Monolithic devices composed of integrated electronic components have already been successfully built using MM-AM.71,72 In the near future, the world of manufacturing, where devices are assembled in centralized factories, could undergo significant restructuring as AM technologies allow the fabrication of sophisticated and bespoke devices directly in the home of the end user.

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Table II. Solvent stability tests with AM resins for flow cell fabrication.46

| Solvent        | Methacrylate resin, % Δ mass | HT resin, % Δ mass |
|----------------|-----------------------------|-------------------|
| Acetone        | –*                          | 6.6               |
| Acetonitrile   | –*                          | 3.5               |
| Ethanol        | 2.8                         | 0.8               |
| Butan-1-ol     | –*                          | 0.5               |
| Distilled water| 0.6                         | 0.1               |
| Dodecane       | 0.2                         | 0.1               |
| Paraffin oil   | 0.2                         | 0.0               |
| Dimethyl sulfoxide | –*                    | –1.3              |
| Toluene        | 1.1                         | –9.5              |

*Material infested with cracks such that cell was broken into multiple pieces, or complete dissolution of the material.
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