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Highly customisable scanning droplet cell microscopes using 3D-printing

Jan Philipp Kollender [a,b], Michael Voith [b], Simon Schneiderbauer [c], Andrei Ionut Mardare [a,b], Achim Walter Hassel [a,b,*]

[a] Christian Doppler Laboratory for Combinatorial Oxide Chemistry Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria
[b] Institute for Chemical Technology of Inorganic Materials (ICTAS), Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria
[c] Department of Particulate Flow Modelling, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria

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ABSTRACT

3D printing was applied for the first time to produce highly customised flow type scanning droplet cell microscope heads which combine electrochemical measurements with downstream analytics of the electrolyte. The main advantages are the optimised fluid dynamics, the homogeneous and laminar mass transport along with the simplicity of the production at low costs. An improved design is presented that is hard to be machined in a classical way. This flow-type scanning droplet cell microscope (FT-SDCM) combines features from older versions of the techniques, the classical theta capillary based version and V-shaped microscopes. Different versions are compared and fluid dynamic simulations were performed to reveal their particularities in terms of electrolyte flow and surface wetting. Fabricating of the complex design of the flow cell was realised using a rapid prototyping approach. The newly proposed prototype is tested under various experimental conditions for assessing its stability, wetting and sealing performances. Both chemical and electrochemical dissolution experiments have shown a perfect electrolyte confinement within the cell and a complete wetting of the addressed area together with high throughput experimentation capabilities due to the robust design and ease of use in combination with a gantry robot.

1. Introduction

The working principle of the Scanning Droplet Cell Microscopy (SDCM) was firstly developed in 1997 by Hassel et al. for electrochemical investigations of nanostructured oxide films on aluminium [1]. The central idea behind SDCM is to address only a small area of the investigated surface (working electrode) which results in a strong localisation of the electrochemical reactions. This strong localisation has been achieved by bringing an electrolyte droplet at the tip of a glass capillary in contact with the working electrode (free droplet mode) or by pressing a soft plastic capillary or silicone-sealing terminated glass capillary against the working electrode (contact mode). Spot sizes down to a few micrometers can be achieved with excellent reproducibility in contact mode [2]. With SDCM all common electrochemical measurements such as cyclic voltammetry, chronoamperometry, potentiometry and electrochemical impedance spectroscopy can be performed [3]. Within the last 15 years various types of SDCMs such as flow-type SDCM (FT-SDCM) [4] and V-shaped SDCM [5] for electrochemical flow-through experiments or photoelectrochemical SDCM (PE-SDCM) [6] for local photoelectrochemistry have been developed. Until now SDCM has been applied for example for high-throughput screening of thin film material libraries [7,8], microstructuring of surfaces [9], local anodisations for plastic electronics [10], direct writing of anodic oxides [11], localised measurements on bulk samples [12–15], impedance measurements on the microscale [16] and online monitoring of reaction products by connecting the output of a FT-SDCM to external analytics such as ICP-MS [17,18] or ICP–OES [19,20]. Essentially a FT-SDCM is a mobile electrochemical flow-through cell that can be easily moved to another spot on the sample. Additionally it addresses only a small part of the working electrode. This allows for example high throughput screening of thin-film material libraries which is nearly impossible using conventional flow cells. One drawback of any capillary based approach is that additional expensive equipments e.g. capillary puller, high precision polishing machine and an optical microscope

* Corresponding author at: Christian Doppler Laboratory for Combinatorial Oxide Chemistry, Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria. Tel.: +43 732 2468 8700; fax: +43 732 2468 8905.
E-mail address: achimwalter.hassel@jku.at (A.W. Hassel).

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for manufacturing and assembly are needed. Additionally, the used capillaries are rather fragile and great care is needed when handling them. Therefore, a robust and easy way to manufacture an alternative to the capillary based-SDCM is of high interest and would make SDCM more easily accessible for other researchers. The most obvious approach would be to fully machine a SDCM from bulk material using high-precision 5-axis machining centres as done in some commercially available [21,22] and previously reported solutions [23]. Unfortunately, using this approach, the cost even of a simple SDCM can substantially rise.

During the last 10 years significant advances have been made in 3D-printing in terms of available materials, printing resolution and price. Today, materials with good chemical stability for most electrochemical applications e.g. acrylonitrile butadiene styrene (ABS), epoxy, polycarbonate (PC), polypropylene (PP), titanium and stainless steel are available [24]. Printing resolutions down to 100 μm are available on commercial 3D-printers. A clear advantage of 3D-printing is that even very complex geometries including undercuts and embedded curved channels can be easily realised since the object is built layer by layer without needing mechanical tools. The price of the printed object is essentially only determined by the amount of consumed building material independent of how complex the object is and the time need to print the object if something like a depreciation of the printer is calculated. Today, even no ownership of a 3D-printer is required since 3D-printing service companies are available offering various materials and printing techniques combined with instant online quoting [25,26]. This eliminates the high investment costs for a 3D-printer and need of specifically trained staff. Prices for 3D-printing have dropped dramatically for selected materials which makes 3D-printing a relatively cheap method compared to CNC-milling. CAD-drawings required for 3D-printing can be easily made using low-cost and user-friendly CAD-programs [27,28]. This combination of user-friendly CAD-programs and availableness of 3D printing service companies makes it very easy to obtain highly customized SDCMs at low cost. An expensive in-house mechanical workshop is therefore no longer needed.

An attempt for 3D-printing of electrochemical flow cells was already made in 2010 [29]. However this 3D printed cell has not been coupled with online downstream analytics of reaction products and has no scanning capabilities. Therefore in this paper a 3D printed FT-SDCM with a complex geometry specifically optimised for online downstream analytics of reaction products is presented. Additionally the presented FT-SDCM can also be used for automated high-throughput experimentation on thin film material libraries. The cell was characterised using computational fluid dynamics (CFD) simulations and tested under different experimental conditions.

2. Experimental and theoretical approaches

2.1. Theoretical simulations and previous FT-SDCM designs

Two previous designs of the FT-SDCM are presented in this work and their particularities in terms of electrolyte flow are calculated and compared for a better understanding of possible design drawbacks which can be improved. All simulations shown in this publication were carried out in 3D space using the ANSYS FLUENT software (Ansys Inc., U.S.A). The flow is assumed to be steady, incompressible and isothermal. Thus, the steady incompressible Navier–Stokes equations are solved [29]. Furthermore, the influence of possible dissolved species is neglected and the calculation uses, therefore, the properties of water at room temperature. For the discretisation of the convective term in the momentum equation, a second-order upwind scheme is used. The derivatives appearing in the diffusion term are computed by a least squares method and the pressure–velocity coupling is achieved by the SIMPLEC algorithm. The face pressures are computed as the average of the pressure values in the adjacent cells (linear interpolation). A flow rate of 3 mL min^{-1} was used in the calculations which can be considered laminar since the channel as well as the gap Reynold numbers are between 10 and 100 depending on the droplet cell geometry. At the flow guide separating the in- and outflow channels a no-slip boundary condition was applied while at the inflow boundary condition the mass flow rate is set. At the outflow boundary the pressure has to be prescribed, which is set to the surrounding pressure. Finally, a polyhedral mesh was used with a grid spacing of approximately 5 % of the local channel diameter, which leads to a much finer grid in the gap than in the in- and outflow regions of the FT-SDCM.

Until now basically two different types of FT-SDCMs are used. The first one is the theta capillary based approach (see Fig. 1a) [4]. A glass capillary is split into two channels by a vertical wall which is partially removed at the cell tip for allowing the electrolyte flow. In this case the electrolyte is streaming from one compartment of the cell into the other. Typically a silicone gasket at the tip of the capillary is used to seal the wetted area. The micro-reference and counter electrodes are inserted from the top part in one of the electrolyte channels, while the investigated area becomes the working electrode. This design ensures wetting of the sample even at low flow rates. The CFD simulation presented in part (a) of Fig. 1 was calculated using a flow rate of 3 mL min^{-1} exemplifying this aspect. Starting from the point of highest velocity positioned at the centre of the wetted area, the calculations show a radial decrease of the fluid velocity with more than 50% along a distance equivalent to a channel diameter. The fluid velocity mapping shows a U-shaped profile for velocities higher than 75% (considered as a minimum useful limit) from the maximum achievable velocity. This rather sharp vectorial profile indicates that removing gas bubbles formed on or particles released from the surface may be accentuated in the centre of the wetted region and not as effective toward the edges. Apart from this, a major drawback of the theta capillary approach is the fragility of the cell and the long manufacturing time required. Additionally, the process of manually removing the separating wall may not be very reproducible so the geometry of the flow channel near the working electrode can greatly differ between various cells. This can be overcome if all geometrical values are exactly known and a calibration series of dip etching in hydrofluoric acid is performed from which the tips are reproducibly prepared. Nevertheless, it remains laborious.

The second type of flow cell is typically manufactured from a polymer block by drilling two channels into the block [23]. The two channels are intersecting each other under a certain angle at the tip of the cell creating an elliptical opening. The sealing at the tip of this V-cell is typically applied manually. The CFD simulations of this type of cell are presented in part (b) of Fig. 1. In order to allow a direct comparison with the theta-capillary cell, the same flow rate and the same inner diameter of the flow channels were used. Also, the distance between the investigated surface and the lower point of the wall, separating both channels is identical with the previous case. The maximum fluid velocity calculated within the V-cell is approximately 3 times larger than the one found for the theta-capillary, but the velocity profile is very different. The distribution of the velocities higher than 75% from the maximum achievable velocity is in this case more located at the tip of the cell. A certain elongation of this profile along the outlet channel (right side) is accompanied by the presence of a vertex where a dramatic velocity drop can be seen. From this simulation it can be concluded that the probability that this type of cell produces vortexes is higher as compared to the theta-capillary type. Each