Inkjet Printing of Fuel Cell Electrodes: Spreading and Evaporation of Particle-Laden Drops

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Abstract

Proton exchange membrane fuel cells (PEMFC) are seen as potential candidates of environmentally friendly power sources for a wide range of fields. The durability and production cost are the main shortcomings limiting the large scale development and commercialization of this technology. In this paper we report both experimental findings on PEMFC fuel cell electrodes manufacturing by inkjet printing as well as theoretical modeling of the impact of particle-laden drops and their evaporation which in final lead to the printed electrodes. The experiments highlight that deposit patterns which may be in the form of coffee rings and affect electrochemical performance. The form of the deposits is strongly influenced by four main parameters: solvent composition, solid content, substrate properties and temperature. A numerical model is developed for better understanding and predicting the spreading of one or more drops and the resulting coffee ring formation. The model is based on the lubrication approximation taking into account contact line motion of the drops, solvent evaporation, viscous and Marangoni effects which all play a critical role in the enhancement or limitation of coffee ring formation. This work may be considered as a first step to better control catalyst ink deposit patterns during manufacturing of fuel cells by fluid jetting.

Introduction

Proton exchange membrane fuel cells (PEMFC) offer the prospect of zero emission energy production for applications ranging from stationary power generation to automotive transportation. The future success and competitiveness of this technology are highly related to the advance on manufacturing and design of the Membrane-Electrodes Assembly (MEA). The competitiveness should be addressed by decreasing production costs and increasing performances and durability. A key to these issues is the optimization of catalyst layers which consists in reducing Pt loading and improving its use within the layer.

The versatility, adaptability and reproducibility of inkjet printing has been extensively used in a wide range of applications [1] and may be considered as a promising process candidate for fuel cell electrodes manufacturing. This technique possess, several advantageous features like low ink consumption or direct writing of patterns. Nevertheless besides these features, the decrease of Pt loading requires a fine control of colloidal particle deposits forming the catalyst layers. Dried inkjet spots may lead to various and complex patterns, as the coffee ring structures, evidenced by Deegan et al. [2], and which have been observed in many inkjet applications such as organic thin-film transistors, light-emitting diodes or conductive deposits [1]. The deposit coffee ring results from the non-uniform evaporative flux, maximum at the contact line of the drying droplets. The particles transport is driven by the mutual actions of contact-line pinning and evaporation enhancement of solvent near the contact line. This phenomenon of non-uniform distribution of ink particles affects fuel cell performances, as we will show, and a simple model enabling to control that coffee stain is of great interest for optimizing the manufacturing of PEMFC electrodes by inkjet printing. This paper aims to address this issue by a relevant lubrication model account for contact line motion, particles content, and Marangoni effect as well as substrate temperature. Comparisons with experiments are given for a number of cases.

Electrode Manufacturing by Fluid Jetting

Evidence of Coffee Ring Formation

Catalyst inks were prepared from carbon-supported catalyst (46% w/w platinum on Vulcan XC-72R; Tanaka) and Nafion® solution (DuPont DE2020, 20wt% in alcohol and water), dispersed in water and a suitable mixture of solvents. This mixture of solvents and the solid contents were adapted for the inkjet process and the nature of substrates. The problem of wetting due to hydrophobicity of the substrates was solved by adding a suitable surfactant.

The formulated inks were printed with a laboratory piezoelectric inkjet printer developed by Siliflow ™ and composed of a single nozzle of 150 μm diameter. Due to its single nozzle, the printing time is rather long, but this equipment presents the benefits of being quite robust and reliable. Moreover, thanks to its ability to purge the ink whenever the nozzle is clogged and to change the ink very easily, it enables to develop catalyst inks that could not be used in conventional inkjet printer due to poor dispersion and quick sedimentation.

Droplets were deposited on membranes (Nafion® NRE 211) and gas diffusion layers (GDL SGL 24BC). Different morphologies were examined, when varying the inks and the substrate temperature, with optical microscopy and scanning electron microscopy images. As shown in Figure 1, the addition of ethylene glycol to the ink leads to different patterns, which may hinder the formation of coffee stain even. However the coffee stain is present without the ethylene glycol, so that its control has to be evaluated relatively to the fuel cell performance.

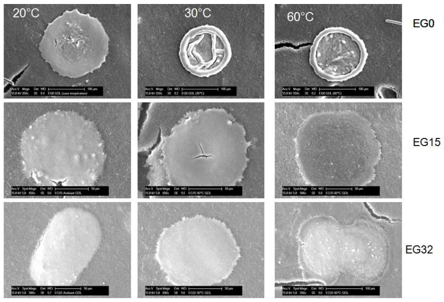

Figure 1. *Coffee ring formation during spreading on PEMFC GDL at different ethylene glycol (EG%) concentration.*

Coffee Ring and Single Cell Performance

Two different inkjet printed cathodes (100µgPt/cm²): with a pronounced coffee ring (ratio ring/drop of 0,4) and with almost homogeneous spots (ratio ring/drop of 0,9) were tested. The single cell performances of these two inkjet printed cathodes present very favorable performances for these Pt loadings compared to other manufacturing processes. Nevertheless, the coffee ring seems to negatively affect the PEMFC performance as highlighted by the polarization curves (Figure 2)

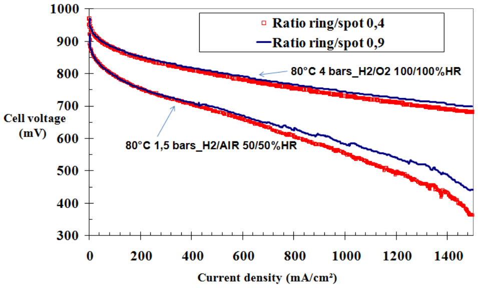

Figure 2. *Polarization curves under air (Cathode/Anode = Air/H_2, T = 80°C, RH = 50% and P = 0.15MPa) comparing inkjet printed catalyst layers with pronounced coffee ring effect and with homogeneous printing.*

The obvious effect of coffee ring formation on fuel cell performance leads us to propose a relevant numerical modeling to better understand the main underlying mechanisms. This is detailed in the following section.

Lubrication Approximation: Drop Evaporation and the Coffee Ring Modeling

We consider a droplet of a volatile liquid on a uniformly heated horizontal substrate as sketched in Figure 3. The liquid vapor interface is given by $h(r,t)$ with contact angle θ_E, the evaporative mass flux through the interface is J. The drop liquid is assumed to be composed of a catalyst ink dissolved in a volatile solvent with the associated concentration equation. For simplicity, we have neglected gravity, which is a good approximation for drops smaller than the capillary length $l_c=(\sigma/(\rho g))^{1/2}$.

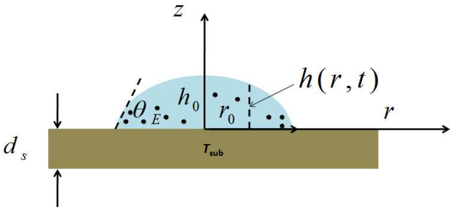

Figure 3. *Geometry of the physical system and problem description.*

The model accounts for two partial differential equations solved simultaneously for the drop non-volatile 'solute' fraction c and droplet height h. In fact we consider the liquid used to consist of a solvent phase, which evaporates, and a solute phase containing particles which does not.

The dimensionless equation in cylindrical coordinates for $h(r,t)$ of the problem could be rewritten in the following form [3]:

$$\frac{\partial h}{\partial t}+\frac{1}{r}\frac{\partial}{\partial r}\left\{rh^3\frac{\partial P}{\partial r}+rh^2\frac{\partial\tilde{\mathrm{T}}}{\partial r}\right\}+EJ=0 \qquad (1)$$

where P and $\tilde{\mathrm{T}}$ express respectively:

$$P=-\frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{\partial h}{\partial r}\right]+\Pi \quad \text{and} \quad \tilde{\mathrm{T}}=-\frac{M_a}{P_r}(h+W)J$$

We adopt the following formulation for the disjoining pressure (n=9, m=3):

$$\Pi=A(1-\sigma\cos\theta_E)\left[\left(\frac{h^*}{h}\right)^n-\left(\frac{h^*}{h}\right)^m\right] \qquad (2)$$

where $A=(1-n)(1-m)/\varepsilon^2h^*(n-m)$ and h^* are constants accounting for the precursor film, $\varepsilon=h_0/r_0$.

Note that the disjoining pressure term is zero for a fully wetting substrate where $\theta_E=0$.

The dimensionless number, $E=(k_l\Delta T/\rho\varepsilon L_{at}h_0U_0)$ which represents the ratio of the viscous time scale to the evaporative time scale, enables to impose the temperature variation of the substrate. $\Delta T=T_{sub}-T_{sat}$ is the temperature increase of the substrate with respect to the saturation temperature (T_{sat}). The liquid is of density ρ, kinematic viscosity ν, thermal conductivity, k_l and latent heat of vaporization L_{sat}. Π corresponds to the dimensionless disjoining pressure modeling the wettability. Since we assume a linear variation in the surface tension σ due to temperature T, we have $M_a=\gamma\Delta Th_0/(2\mu\kappa U_0r_0)$ and $P_r=\nu/\kappa$, the thermo-capillary Marangoni and Prandtl numbers, respectively. The time scale being $t_0=3\mu r_0^4/(\sigma_0h_0^3)$, the velocity scale $U_0=r_0/t_0$. $\gamma=-d\sigma/dT$, $\kappa=k_l/\rho c_p$, where c_p is the heat capacity. $W=k_ld_s/k_sh_0$, where k_s, k_l, d_s, h_0 are the substrate and liquid thermal conductivities, the substrate thickness and droplet height, respectively.

For simplicity purpose, we use the assumption that the concentration of the solute depends only on the radial position $c(r,t)$. The solute conservation leads to satisfy the following equation:

$$\frac{\partial(hc)}{\partial t}+\frac{\partial}{r}\left[rh^2cQ\right]=0 \qquad (3)$$

where $Q = h\frac{\partial P}{\partial r}+\frac{\partial \tilde{\mathrm{T}}}{\partial r}$.

We take into account the variation of the viscosity of the fluid due to the evaporation of the solvent. The effect of evaporation could be expressed using [4] as follows:

$$\frac{\mu}{\mu_0}=\exp\left[a_v(c-c_0)\right] \qquad (4)$$

where c_0 is the initial solute fraction and a_v a constant.

To account for the presence of particles, we make use of the Krieger-Dougherty equation:

$$\mu_0=\mu_s(1-\varphi/\varphi_m)^{-B\varphi} \qquad (5)$$

μ_s is the liquid viscosity without particles, φ_m the maximum packing fraction, B a constant close to 2.5.

We use the following expression for the evaporative flux mainly due to the temperature increase imposed by the substrate [5]:

$$J=\frac{(1-c)}{h+W+K} \qquad (6)$$

with $K=\left(2\pi R_g\right)^{1/2} k_{th}T_{sat}^{\,3/2}/\alpha h_0\rho_v L_{at}^{\,2}$ which is linked to the liquid volatility.

Single Drop Spreading and Evaporation

For validation purpose of the lubrication model, we consider the drop evaporation and spreading on a horizontal wetted substrate. In the spreading case, we carry out the modeling of a water drop spreading from an intial contact angle of 50° to an equilibrium contact angle of 5° for 50µl drop. Figure 3(a) shows the center height evolution during the spreading, which verifies the well-known power law behavior referred to as Tanner's law $h = at^{\beta}$. We observe very good agreement between our numerical results and Tanner's law. Moreover, the coefficients, β=0.202~1/5, are very close to those reported elsewhere for water droplets.

In the evaporation case, we perform both an experimental and numerical modeling of the evaporation of a drop of water of 15nl on a glass substrate of contact angle 30°. We obtain through our model a quite good prediction of the drop volume evolution. The experimental limitations prevent to measure the volume evolution up to complete disappearance of the drop which fortunately can be followed through numerical simulation. It is unlikely that the physics of drop evaporation change too much when the drop becomes smaller and smaller and moreover, at least from an applied point of view, this has not profound consequences on the final results. The numerical model predicts an evaporation time of almost 2.2s which compares quite well with the characteristic evaporative time as shown in Figure 3(b).

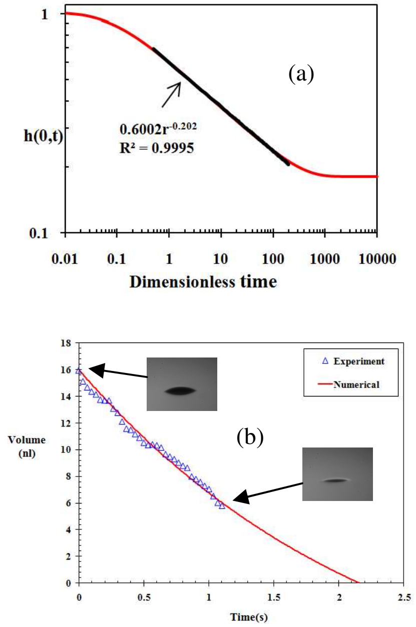

Figure 3. *(a) Simulated drop spreading (b) Experimental and numerical prediction of drop during evaporation on a glass substrate at 60°C.*

Coffee ring Modeling

Single Drop

The model which has been established allows modeling the evaporation of a binary component containing particles. The evaporation of such a mixture leads to the formation of the coffee ring. The model is used here for controlling the coffee ring phenomenon involved in applications such as fuel cell manufacturing (Figure 4).

The evaporation of a drop of 170µm of diameter containing 3% of solid particle on the PEMFC fuel cell GDL (gas diffusion layer) is performed at 20°C and 60°C.

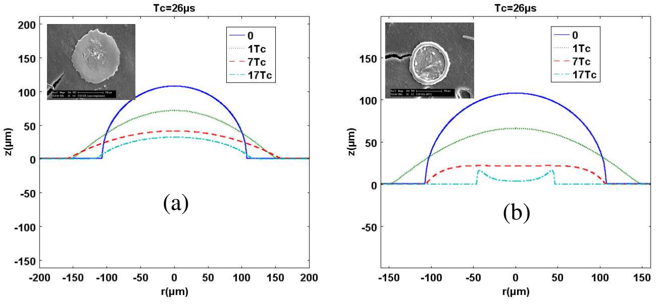

Figure 4: *Temperature effect on the coffee ring formation at (a) 20°C and (b) 60°C.The insert represent experimental results of coffee ring formation on PEMFC fuel cell GDL (Gas diffusion layer) at the prescribed temperature.*

For this modeling, since the ink on the GDL substrate has a contact angle of around 100°, we use as an initial profile a spherical cap deposited drop [5] which evaporates when spreading from 90° on the heated substrate. Due the presence of particles and the binary-mixture nature of the fluid the coffee ring formation occurs at a rate which is controlled by the temperature and the particle concentration.

We numerically retrieve the fact that a heated substrate leads to greater evaporation which in turn yields an enhanced coffee ring deposit (Figure 4). We also obtain that the final contact diameter is $0.5r_0$ which is comparable with the experimental result. Conversely, a cooled substrate diminishes largely the edge evaporation from the drop and one may hinder or even prevent coffee ring formation through this mechanism. An evident drawback in this case is the rate of evaporation which may be too long for practical purposes.

To test the prediction capability of the model, a sensitivity study is performed with the Marangoni effect and the ink volatility, i.e, the resistance to phase change from liquid to vapor, accounted for by the parameter *K*. We obtain that the higher the Marangoni number, the less is the coffee ring formation, as observed in [6]. Also, the larger is *K* the lesser the volatility of the liquid. Thus for large value of *K* or low volatility liquid, the model indicates the possibility to limit the coffee ring formation, as shown below in Figure 6. This is in full agreement with the experimental observation of Figure 1.

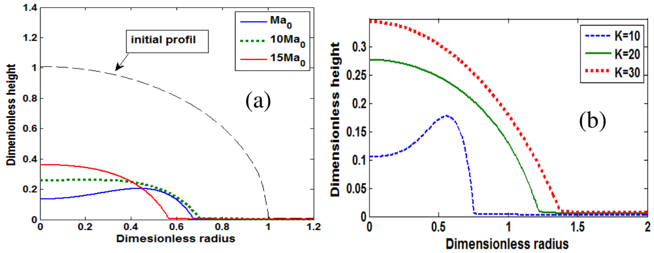

Figure 6. *Sensitivity to the (a) Marangoni and (b) ink volatility.*

Coalescing drops

By extending the previous equations in 2D [5], we carry out the coffee ring formation with a coalescing drop as shown in Figure 5.

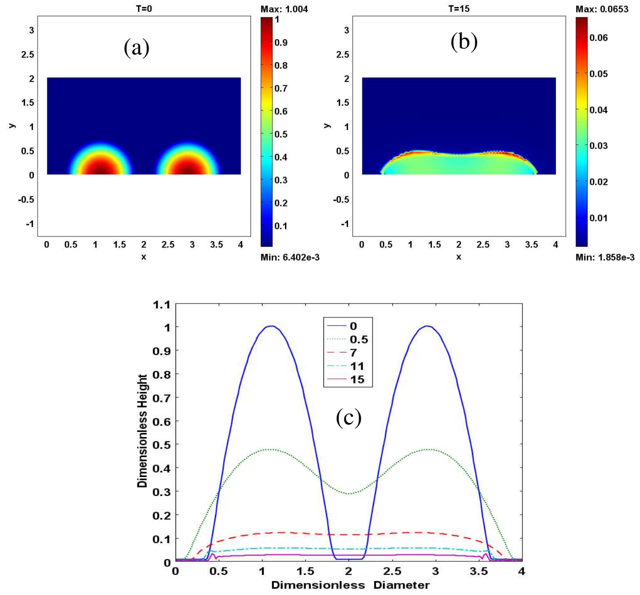

Figure 5. *Simulated coalescing drops and evaporation at (a) initial, (b) final height contour plots and (c) the free surface profile.*

The simulation shows that even though the coffee ring may be observed its intensity seems to be limited by the coalescence configuration. This may be due to the distance for the particles transport inside the merging drops. Also the merging of drops may hinder or even inhibit coffee ring formation. This has to be checked by appropriate experiments. This is the first time, to the best of our knowledge, that the formation of such patterns is studied numerically through drop coalescence and evaporation. This numerical study paves the way for better understanding and controlling the coffee ring formation which may impact on fuel cell performance as demonstrated in Figure 2.

Conclusion

In this paper, the effect of coffee ring formation on the PEMFC fuel cell performance is demonstrated. The importance of the operating conditions and ink properties on coffee ring formation has been highlighted as well. For a better understanding of the phenomenon, a lubrication model is proposed accounting for most of the relevant physics involved in single and multiple drops dynamics. The main results for spreading and evaporation have been validated through judicious experiments. The model, as it stands, is able to predict coffee ring both in case of a single and two coalescing drops. It may of course be extended to multiple drops.

Acknowledgments

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Author Biography

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