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Design of capillary flows with functionally graded porous titanium oxide films fabricated by anodization instability

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ABSTRACT

We have developed an electrochemical fabrication method utilizing breakdown anodization (BDA) to yield capillary flows that can be expressed as functions of capillary height. This method uses anodization instability with high electric potentials and mildly acidic electrolytes that are maintained at low temperature. BDA produces highly porous micro- and nano-structured surfaces composed of amorphous titanium oxide on titanium substrates, resulting in high capillary pressure and capillary diffusivity. With this fabrication technique the capillary flow properties can be controlled by varying the applied electric field and electrolyte temperature. Furthermore, they can be expressed as functions of capillary height when customized electric fields are used in BDA. To predict capillary flows on BDA surfaces, we developed a conceptual model of highly wettable porous films, which are modeled as multiple layers of capillary tubes oriented in the flow direction. From the model, we derived a general capillary flow equation of motion in terms of capillary pressure and capillary diffusivity, both of which can be expressed as functions of capillary height. The theoretical model was verified by comparisons with experimental capillary flows, showing good agreement. From investigation of the surface morphology we found that the surface structures were also functionally graded with respect to the capillary height (i.e. applied electric field). The suggested fabrication method and the theoretical model offer novel design methodologies for microscale liquid transport devices requiring control over propagation speed.

1. Introduction

Capillary flows through thin porous media have been widely utilized for small volume liquid manipulation systems such as chromatographic analyzers, biosensors, microchemical reactors, and paper-based microfluidic devices [1–8]. These devices are generally cheap and simple because additional pumping systems are not necessary to achieve transport. Capillary flows are predictable and effectively scale to miniature flows; therefore, they are appropriate for developing small-scale flow devices requiring precise liquid delivery. To take advantage of capillary flows, different porous substrates have been applied because capillary flows are media dependent; examples include capillary tubes and wedges, microfabricated structures, porous media composed of small particles or fibers, and sponges [9,10]. However, in most porous media it is difficult to tailor the capillary flow for a given application because it is challenging to realize arbitrary shapes and spatially functionalized porous structures. Therefore, most of the porous media mentioned above can only be used for conventional capillary flows obeying Washburn's equation and the modifications thereof [11–13]. New types of porous media and fabrication techniques with corresponding capillary flow equations of motion must be developed for more demanding applications.

In the literature, equations of motion for capillary flows have been derived from the Navier–Stokes equations or modifications thereof [11–15]. These approaches result in Washburn's classical equation for one-dimensional capillary flows assuming uniform capillary pressure, no inertial-effects, and constant channel cross section [15]. This equation can be used to estimate capillary flows through wetting porous media with uniform porous structures and surface energy. However, Washburn's equation cannot be used to estimate the capillary flows for porous media with spatial variations in surface energy, pore radius, and cross sectional area. Reyssat et al. recently developed an imbibition model aimed at studying capillary flows for porous media with varying circular cross-section, demonstrating that shape variations affect the dynamics of the capillary rise [16].

Recently, we developed a method to produce highly wetting porous surfaces using anodization instabilities [17]. During conventional anodization, oxide film thickness increases linearly with

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time [18]. However, when the anodization potential exceeds a critical value, the anodized films burst due to ionic shear stress that exceeds the surface tension of the films, resulting in irregular structures on the substrate [19]. This fabrication method is known as breakdown anodization (BDA). Surfaces produced by BDA on titanium plates show extremely low effective contact angles (nearly zero) and fast water spreading. These properties result from the highly porous surface composed of amorphous titanium dioxide, which provides high surface energy. It is well known that surface roughness enhances the intrinsic wetting behavior [20,21]. As a result, rough surfaces can show perfect wetting while the flat surfaces show partial wetting [20]. In addition, structured surfaces can show superwetting and the wetting behaviors can be altered by the morphology [21,22]. Recently, we have shown that capillary flows on surfaces produced by BDA can be expressed by Washburn's equation [17]. However, if porous structures of the surface are non-uniform, the capillary pressure changes locally, resulting in varying propagation speeds. In this case, the capillary flows do not follow Washburn's equation. Therefore, we modify the equations of motion to account for local variations in capillary properties.

In this work, for the first time, an electrochemical fabrication method using anodization instability is presented for the design of capillary flows with functionally graded porous films controlled by electric fields. Additionally, we derive capillary flow equations of motion to predict the transport in these systems. First, we suggest a simplified conceptual model of highly wetting porous surfaces. Then, we derive a general capillary flow equation of motion from the conceptual model for predicting capillary speeds on heterogeneous surfaces. Finally, the capillary flows are expressed as functions of the local properties such as capillary pressure and capillary diffusivity, which are functions of capillary rise height. With the fabrication method and the theoretical model, we show that various capillary flows can be designed by BDA with spatially variable electric fields.

2. Theory

From the Navier–Stokes equations, if inertial effects are negligible and the flow is laminar, Poiseuille's law gives the average flow velocity in a single cylindrical tube:

$$V_{avg} = -\frac{r^2}{8\mu}\left(\frac{\partial P}{\partial y} + \rho g\right), \tag{1}$$

where V_{avg} is the average flow velocity over the entire cross sectional area of the tube, r is the tube radius, $\partial P/\partial y$ is the pressure gradient in the flow direction y, g is the gravitational acceleration constant, and μ and ρ are the liquid viscosity and density, respectively.

From Eq. (1), one-dimensional capillary flow in a uniform cylinder of radius r_c can be described by Washburn's equation [15],

$$\frac{dh}{dt} = \frac{1}{h}\frac{r_c^2}{8\mu}\left(\frac{2\gamma\cos\theta}{r_c} - \rho g h\right), \tag{2}$$

where h denotes the height reached by the liquid in the capillary, t the time, θ the surface contact angle and γ the air–liquid surface tension. This equation typically credited to Washburn is sometimes called the Lucas-Washburn or Bell-Cameron-Lucas-Washburn equation in honor of work by Lucas (1918) and Bell & Cameron (1906) that preceded Washburn's original publication in 1921. From Eq. (2), when the height h of the liquid is small, the hydrostatic pressure can be neglected, and we can obtain a simple expression of the capillary rise height as a function of time,

$$h^2 = \frac{r_c\gamma\cos\theta}{2\mu}t = \frac{1}{2}D_{cap}t. \tag{3}$$

Here, we introduce the capillary diffusivity $D_{cap} = r_c\gamma\cos\theta/\mu$, which has units of m^2/s. When the properties of the material are uniform in the capillary, the surface contact angle remains constant and D_{cap} remains constant. Similarly, the capillary pressure, P_{cap}, can be calculated from the maximum capillary rise height, h_{max}. At equilibrium, the gravitational force on the liquid column balances the capillary force. Thus, the capillary pressure can be calculated as

$$P_{cap} = \frac{2\gamma\cos\theta}{r_c} = h_{\max} g\rho. \tag{4}$$

From Eqs. (3) and (4), the capillary tube radius (r_c) and surface contact angle (θ) can be obtained as follows: $r_c = (2\mu D_{cap}/P_{cap})^{1/2}$ and $\cos\theta = (\frac{1}{2}\mu D_{cap}P_{cap}/\gamma^2)^{1/2}$.

We model highly wetting porous films as layered capillary tubes oriented in the flow direction, as shown in Fig. 1. Similar capillary tube models have been employed to simplify flows in porous media [23] but here we suggest a capillary tube model for wettable porous films with varying surface width and capillary properties. The hypothetical capillary tube has an effective radius r_c. The number of capillary tubes ($N_{c,y}$) present at the capillary height, y, can be obtained using,

$$N_{c,y} = \frac{2R_y}{2r_c}\frac{H_c}{2r_c} = \frac{R_yH_c}{2r_c^2}. \tag{5}$$

where R_y and H_c are the half width and the thickness of the film, respectively, at capillary height y. Therefore, the total cross-sectional area of capillary tubes (A_y) can be expressed as $A_y = \pi r_c^2 N_{c,y}$. The volumetric flow rate at a given cross-section of the porous film can be calculated as

$$\dot{V} = V_{avg}\pi r_c^2 N_{c,y} = \frac{\pi R_y H_c}{2}V_{avg}. \tag{6}$$

Combining Eqs. (1) and (6), the relation between the pressure gradient and the volumetric flow rate can be found to be:

$$-\frac{r_c^2}{8\mu}\left(\frac{\partial P_y}{\partial y} + \rho g\right) = \frac{2\dot{V}}{\pi R_y H_c}. \tag{7}$$

From mass conservation, we know that the volumetric flow rate is not a function of capillary height. In addition, the local capillary radius can be expressed as a function of the capillary pressure and

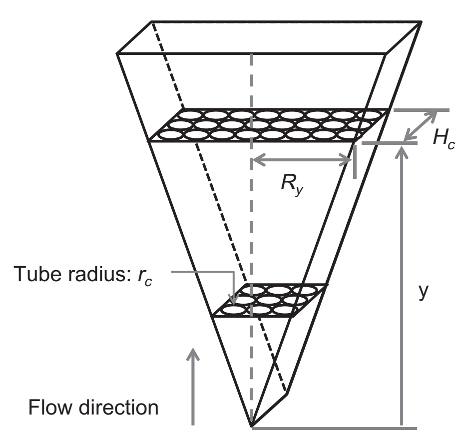

Fig. 1. Schematic illustration of the conceptual model for wettable porous films with varying cross sectional area. The porous film has constant height, H_c, and varying half width, R_y. The porous film can be modeled as layers of capillary tubes vertically oriented. The number of capillary tubes in the x-direction and y-direction varies according to the radius of a single capillary tube, r_c, and the width R.