

Supplementary Information



Experimental Investigation of the Gas/Liquid Phase Separation Using a Membrane-Based Micro Contactor

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1. State of the Art

In 2003, Meng et al. [1] presented the first inorganic membrane based micro contactor in a μ DMFC for the gas/liquid phase separation. The inorganic membrane was made of a [100] silicon wafer with venting holes integrated by etching and modified by a hydrophobic coating. By using capillary forces, known since 1830 and described by the Young-Laplace equation, the liquid was kept in the channel while the gas are vented via the pores. In later works from Lee et al. [2], Amon et al. [3] and Alexander et al. [4], the gas/liquid phase separation using a micro contactor with a similar inorganic and modified membrane was independently confirmed.

Kraus et al. [5] studied a membrane based micro contactor for the gas/liquid phase separation. For the liquid separation a hydrophilic membrane was used, while for the gas separation a hydrophobic membrane was applied. Furthermore, the dependence of the separation efficiency with the orientation, system and environmental temperature, system pressure for the liquid separation, liquid-to-gas ratio, and environmental humidity was studied. Based on the work of Meng et al [1], the author assumed the capillary pressure as a driving force for the gas separation.

Meng's subsequent works [6–8] however, investigated the active gas/liquid phase separation with commercially available hydrophobic polytetrafluoroethylene (PTFE) and polypropylene (PP) porous polymeric membranes by using a pressure gradient as the driving force for the separation process. Mainly, their research was focused on the liquid entry pressure, confirming the efficiency of this separation method for different methanol concentrations. Furthermore, an optimized design of the separation structure and a successful integration into a μ DMFC system was reported.

Xu et al. [9] and David et al. [10] also examined independently the active gas/liquid phase separation using porous and non-porous polymeric membranes with one or different pore sizes. In addition, both authors introduced Darcy's law as a model to describe the pressure gradient driven active gas/liquid phase separation in a membrane based micro contactor. Moreover, Xu et al. [9] developed four criteria for the successful removal of gas bubbles when using a membrane based micro contactor:

- Bubble length needs to be larger than the channel height
- Bubble traveling time on the membrane should be sufficient
- Bubble speed should be lower than a critical value
- The transmembrane pressure should be lower than the water entry pressure

In addition, Fazeli et al. [11] studied experimentally the effect of differential pressure across the membrane, flow velocity, and flow channel dimensions on the separation process using also a

membrane based micro contactor. The high impact of the differential pressure across the membrane in the separation performance was a main result of their work.

2. Capillary Forces

In the 19th century Thomas Young and Pierre-Simone Laplace described mathematically the relationship between surface tension, surface curvature, and pressure difference at the interface between two fluids -with wetting and non-wetting behaviour- also known as capillary pressure [12,13]. The above mentioned relationship is defined by the Young-Laplace equation:

$$p_{cap} = p_{nw} - p_w = 2 \cdot \sigma_{lg} \cdot H \tag{1}$$

 σ_{lg} stands for the surface tension, whereas H represents the resulting mean curvature between two fluids mainly gas and liquid. The mean curvature H can be generally calculated by Equation (2):

$$H = \frac{1}{n} \sum_{i=1}^{n} k_i$$
⁽²⁾

where n represents the enclosed areas of the bubble in micro channel and k_i the resulting curvature of a spherical surface calculated by the reciprocal radius of the sphere as shown in Equation (3).

$$k_i = \frac{1}{r_i} \tag{3}$$

Various spherical radii could appear by using different micro channel geometries e.g., rectangular, square or circular, as well as uniform or diverse surface wetting behaviours. Due to the manufacturing process by micro machining and etching technologies, micro channels presents ideally a rectangular geometries. In case of the etching process elliptical micro channels are common. Various sphere radii are shown in Figure S1 for a rectangular channel with a hydrophilic wetting behaviour.



Figure S1. Sketch of a gas bubble in a hydrophilic channel adopted by Kraus et al. [8]

With the known radius R_i and the wetting behaviour expressed by the contact angle φ_i , the radius r_i of the sphere can be calculated using Equation (4), assuming that the front and rear calotte are equal and not affected by the surrounding liquid.

$$r_{i} = \frac{R_{i}}{\cos(\varphi_{i})} \tag{4}$$

Substituting Equations (2), (3) and (4) in Equation (1), the occurring capillary pressure in a micro channel can be calculated for a rectangular, square, and circular geometry using Equation (5). In general this pressure can be seen as a force acting for or against the pore wetting. The effective direction of the force is characterized by a positive or negative value.

$$p_{cap} = \frac{1}{2} \cdot \sigma_{lg} \cdot \left(\frac{\cos(\varphi_t)}{R_t} + \frac{\cos(\varphi_b)}{R_b} + \frac{\cos(\varphi_l)}{R_l} + \frac{\cos(\varphi_r)}{R_r} \right)$$
(5)

Assuming constant geometry and a homogenous wetted perimeter Equation (5) can be simplified, as shown below with Equation (6) for circular and with Equation (7) for rectangular geometries:

$$p_{cap} = \frac{4 \cdot \sigma_{lg} \cdot \cos(\varphi)}{h}$$
(6)

$$p_{cap} = 2 \cdot \sigma_{lg} \cdot \left(\frac{\cos(\varphi)}{h} + \frac{\cos(\varphi)}{w}\right)$$
(7)

In Equation (4) the sphere radius and thus in Equation (5) the capillary pressure, can be influenced by the wetting properties of the surface, which depend on the material and surface. For ideal solid surfaces, the cosine of the contact angle φ_i at a given temperature and pressure can be expressed by Young's equation:

$$\cos(\varphi_{\rm i}) = \frac{\sigma_{\rm sg} - \sigma_{\rm sl}}{\sigma_{\rm lg}} \tag{8}$$

where the interfacial energies are denoted by solid-gas interfacial specific energy σ_{sg} (free surface energy), solid-liquid interfacial specific energy σ_{sl} (interfacial tension), and liquid-gas interfacial specific energy σ_{lg} (surface tension).

Every interfacial specific energy characterises the strength of one of the interactions between solid-gas, solid-liquid, and liquid-gas interface. In addition, the strength of the interactions can be influenced by the temperature [14], the pH values of the surface and liquid respectively [15], and by the size of the liquid droplets [16]. Furthermore, the contact angle is not constant over time due to liquid evaporation [17]. In addition, by surface saturation processes, the strength of the interaction between the solid and liquid interface, is influenced by the amount of e.g. hydroxyl groups at the surface [17].

The above mentioned temperature dependence mainly refers to the surface tension. Vázques et al. [18] provide a data set for the following linear expression of the surface tension for pure liquid water and liquid water-methanol mixtures in air as surrounding gas:

$$\sigma_{\rm lg} = \left(K_1 - \frac{K_2}{^{\circ}\rm C} \cdot \vartheta \right) \, \rm mN/m \tag{9}$$

where K_1 and K_2 are the provided parameters. Values for water and relevant methanol concentration are given in Table S1.

Table S1. Fitted parameters for the temperature dependency of the surface tension provided by Vázques et al. [22].

Mass fraction ω _{CH3OH} in [-]	Mole fraction x _{CH3OH} in [-]	K ₁ in [-]	K ₂ in [-]
0.000	0.000	76.0114	0.1609
0.050	0.029	66.6950	0.1584
0.100	0.059	59.7657	0.1457
0.150	0.090	54.6635	0.1407

The gas/liquid phase separation can be achieved by exploiting the effect of capillary pressure in sufficiently small pores, to exclude liquid from entering the pores. In aqueous systems, hydrophobic surfaces with a contact angle in the range of $90^{\circ} < \phi \le 180^{\circ}$ lead to negative capillary pressure. On the other hand, hydrophilic surfaces with a contact angle in the range of $0^{\circ} \le \phi < 90^{\circ}$ have a positive capillary pressure. Figure S2 shows the capillary pressure calculated by Equation (5) for four different micro channel configurations and pores (round capillary) depending on a scaling factor s dividing the starting values width and/or height of the channel geometry.



Figure S2. Capillary Pressure p_{cap} for water at 20 °C, $\sigma_{H_2O} = 0.07275$ N/m, dependent on channel geometry, surface properties, and material combination. **Rectangular I** (wall contact angle: 60°, width: 1 mm, height: 0.5 mm) without hydrophobic membrane on the top of the micro channel. **Rectangular II** (wall contact angle: 60°, width: 1 mm, height: 0.5 mm) with hydrophobic membrane made of PTFE (contact angle: 120° [19]) on the top of the micro channel. **Round Capillary I** (wall contact angle: 60°, diameter: 1 mm). **Round Capillary II** (wall contact angle: 60°, diameter: 0.5 mm)

In Figure S2, it is clearly visible that homogenous wetted micro channels with a width of 1 mm and a height of 0.5 mm have always the highest positive capillary pressure with an increasing scaling factor. Furthermore, heterogeneous wetted micro channels, as they can occur in a membrane based micro contactor (see Figure S3), have the lowest positive capillary pressure due to the high influence of the hydrophobic membrane. To utilize the capillary pressure as a driving force for the passive gas/liquid phase separation, the size of the channel plays a major role and must be taken into account if a passively operated gas/liquid separation is the main objective.

Furthermore, it is evident that the capillary pressure is negative proportional if the contact angle of the walls becomes hydrophobic. If the wall contact angle reaches a value of 120° and a hydrophilic membrane with a contact angle of 60° is used as a separation layer, Figure S2 can be mirrored on the x-axis and the capillary pressure has negative values as expected.

By using hydrophobic porous membranes with hydrophobic coated pores ($d_P \sim 200$ nm), the liquid can be retained in the micro channel, while the gas can flow through the membrane. This behaviour is in general caused by the hydrophobic nature of the membrane material creating a high negative capillary pressure in the pores as previously described. In the reverse case, i.e. with a hydrophilic porous membrane with hydrophilic coated pores, the gas is retained in the micro channel while the liquid flows through the porous membrane.

However in this last case, the pressure drop generated by the liquid flowing through the pores becomes the limiting factor for the separation. This is due to the greater density and viscosity -factor of 1000- compared to the gas. To achieve higher volumetric flow rates consequently, larger differential pressures as a driving force or larger membrane areas are required for the separation of the same amount of liquid, making this type of separation unattractive for a compact and portable µDMFC.

In addition, the anode side of the μ DMFC is mainly fed actively with a water-methanol mixture by an external pump, causing a forced mass transfer. Moreover, the generated gas raises the average flow velocity in the system resulting in a total system pressure increase. In that case, the active gas/liquid phase separation with a porous membrane based micro contactor takes place and the passive gas/liquid phase separation with the capillary pressure as a driving force plays no longer a role for the separation process.

However, to ensure the portability of portable energy systems or applications, the gas/liquid phase separation must be independent of orientation, which can be ensured by the capillary forces in the micro channels. In macroscopic channels, gravitational forces have a considerable influence on the behaviour of the two-phase flow (TPF), since buoyancy forces exceed the capillary forces. The influence of capillary forces increases with a decreasing channel diameter as shown in Figure S2. To quantify the ratio of capillary and gravitational forces, the Confinement number (Co) calculated by Equation (10) .The Eötvös number (Eo), related to the Confinement number, can be calculated by Equation (11).

$$Co = \frac{1}{d_h} \sqrt{\frac{\sigma_{lg}}{g \cdot (\rho_l - \rho_g)}}$$
(10)

$$E\ddot{o} = \frac{1}{8 \cdot Co^2}$$
(11)

where d_h represents the hydraulic diameter, g the gravitational acceleration, ρ_l the liquid density, and ρ_g the gas density. For a rectangular or square channel, the hydraulic diameter can be calculated using the cross-section area A and wetted perimeter U_w as shown in Figure S2 by using the following equation:

$$d_{h} = \frac{4 \cdot A}{U_{w}} \tag{12}$$

According to Huh et al. [20], Serizawa et al. [21], Suo et al. [22] and Brauner et al. [23] the capillary forces become predominant over the buoyancy forces if $Co \ge 3.3$ or $E\ddot{o} < 0.01$. Using the data for a micro channel with a height of 0.5 mm and a width of 1.0 mm with water + air at 20 °C, a Confinement number of $Co \approx 4$ and an Etövös Number of $E\ddot{o} \approx 0.0075$ are obtained. In both cases, the capillary forces are predominant over the gravitational forces and an orientation independent separation can be assumed.

3. Equipment

The specifications of the mini CORI-FLOW™'s and MFC's are summarized in Table S2.

Name	Тур	Medium	Output	Deviation
FIC 1	MFC	Syn. air	0-100 NmL/min	± (0.5 % Rd + 0.1 % FS)
FIC 2	MFC	Syn. air	0-500 NmL/min	± (0.5 % Rd + 0.1 % FS)
FIC 3	MFC	CO ₂	0-1000 NmL/min	± (0.5 % Rd + 0.1 % FS)
FIC 4	mini CORI-FLOW	Methanol	0-200 g/min	± (0.2 % Rd + 0.02 g/h)
FIC 5	mini CORI-FLOW	Water	0-2000 g/min	± (0.2 % Rd + 0.5 g/h)

Table S2. Specifications of deployed mini CORI-FLOW's and MFC's.

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