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Electrochemical characterisation of a microfluidic reactor for cogeneration of chemicals and electricity

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Abstract

A microfluidic fuel cell type reactor based on the co-laminar flow cell design has successfully been constructed. This reactor provides the advantages of electrosynthesis in terms of selectivity, but does not require electricity to operate as classical electrochemical reactors do and it is capable of generating a small amount of electricity instead. Due to the microfluidic design, no membrane is needed for this reactor cutting down the costs. The feasibility of this reactor is examined in this study, and it is characterised electrochemically using linear sweep voltammetry. As a case study for microfluidic cogeneration, the hydrogenation of nitrobenzene is chosen as this reaction provides many valuable products such as aniline and azoxybenzene. The methanol oxidation is taken as a counter reaction. The highest conversions were observed at the lowest flow rate and lowest concentration of nitrobenzene. As expected, the highest currents were observed at the highest concentration, but the flow rate did not have a high influence on the current, due to self-poisoning nature of the methanol oxidation, i.e., the surface was gradually covered with CO molecules. At a certain amount of CO coverage the anode was found capable of self-regeneration. The highest power density obtained was 0.542 mW cm^{-2} at a cell potential of 0.217V and a

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current density of -2.498mA cm^{-2} . A conversion of 37% has been achieved at a flow rate of $5\mu\text{L min}^{-1}$ with an average power density of 0.062mW cm^{-2} .

Keywords: microfluidic reactor, co-laminar flow cell, electrochemical cogeneration, nitrobenzene, methanol oxidation

1. Introduction

Classical chemical production processes, especially those that involve oxidation and reduction reactions, are often inefficient. This inefficiency has two main reasons, the first being heat generation in the common case of exothermic reactions. In most cases this heat cannot be fully recuperated, due to low efficiency of heat exchangers [1]. The second reason is the production of by-products due to low selectivity of the catalyst used in the reactor. This leads to a loss of raw materials and the need for additional purification steps, which can be expensive and time consuming [2].

The electrochemical production of products in a fuel cell type reactor [3, 4] has the potential to greatly increase the efficiency of these processes. In an electrochemical reactor, the selectivity can be controlled in two separate ways, as both the electrocatalyst and the operating potential have an influence towards selectivity [5–7]. As fuel cells are very efficient devices [8], the second problem, waste heat, is mostly overcome. The co-generated electricity of the fuel cell can be viewed as energy savings, further increasing the efficiency of the process.

In recent years, an innovative new type of fuel cell is emerging: the laminar flow fuel cell (LFFC), also known as the microfluidic fuel cell [9]. This fuel cell uses features of laminar flow to form a stable interface between the anolyte and the catholyte, removing the need of an expensive semi-permeable membrane. Besides this reduced cost, the absence of the membrane has additional advantages, such as simple and flexible assembly [10–12], easy water management [11, 12] and electrolyte pH flexibility [10–15]. This pH flexibility not only entails that the fuel cell is compatible with both acidic and alkaline supporting electrolyte solutions, but it includes the ability to alter the pH of both the anolyte and the

catholyte separately, greatly increasing the potential difference and the fuel cell performance, at the expense of the consumption of electrolyte [16, 17].

The performance of LFFCs is however still limited by a number of factors, such as the high Ohmic losses [18, 19] and low fuel utilisation [12, 18] at higher flow rates, which are needed for the elimination of reactant mixing [19] and transport limitations [12, 19]. Reactant mixing should be avoided to reduce reactant crossover [19, 20] and to enhance reactant recirculation possibilities [20].

Because of the interesting features of a LFFC described above, cogeneration of useful end-products and electricity could benefit from using a LFFC-type reactor. A general name for devices that use the LFFC concept is co-laminar flow cell (CLFC). To the best of our knowledge cogeneration in this type of reactor has not been reported before. The objective of this paper is to find out whether cogeneration is possible using this reactor type, and to study the basic parameters that influence its electrochemical behaviour. As a case study for cogeneration, the hydrogenation of nitrobenzene is used. The feasibility of cogeneration of cyclohexylamine and electricity using nitrobenzene was previously proven by Yuan et al. [21] in a PEM fuel cell reactor. Besides cyclohexylamine, the electrochemical hydrogenation of nitrobenzene provides access to many other high-value products, including aniline [6], p-aminophenol [22, 23] and azoxybenzene [22, 24].

The electrochemical reduction of nitrobenzene proceeds in three steps, each involving two electrons and two protons, given in eq. 1 [22, 25]. Depending on the working potential and the electrocatalyst, either phenylhydroxylamine [24] or aniline [6] can be obtained. The unstable phenylhydroxylamine can re-oxidise to nitrosobenzene, and condense with a second phenylhydroxylamine molecule to form azoxybenzene [22, 24] or, in acidic medium, recombine via the Bamberger rearrangement to p-aminophenol [23] or p-ethoxyaniline [25], depending on the solvent. The standard reduction potential, calculated from the difference in Gibbs free energies of formation [26], of the 6-electron reduction towards aniline is 0.784V vs SHE at pH 0.

The methanol oxidation to CO_2 in alkaline solution is used as anodic reaction. The half-reaction of the methanol oxidation is given in eq. 2 and has a standard reduction potential of -0.81V vs SHE at pH 14 [27]. As electrocatalyst for the methanol oxidation, a Pt-Ru nanoparticle catalyst is used.

The overall cell reaction in combination with the nitrobenzene reduction in acidic medium towards aniline is given in equation 3. Since the two electrolytes have a different pH, the consumption of electrolyte is seen in this equation, in the production of H_2O from H^+ and OH^- . The E_{cell}^0 is 1.59V, given the catholyte and anolyte have a pH of 0 and 14, respectively.

2. Experimental

2.1. Reactor construction

The CLFC was constructed based on the design of the Ferrigno fuel cell [9]. The different parts of the fuel cell were machined using a CNC milling machine (Datron M7 Kompakt). An exploded view of the cell is depicted in figure 1. The flow channels, together with space to put the electrodes, are milled in a Delrin[®] polyoxymethylene (POM) piece (no. 1 in figure 1). Afterwards the graphite electrodes, which are coated with catalyst ink (see section 2.2), are put in their designated areas. The resulting flow channel is of a y-shaped form; consisting of two channels of 0.5x0.5x10mm intersecting, each at a 30° angle, and a main channel of 1x0.5x30mm with 28mm long electrodes at each side (no. 2). These electrodes are glued to electrical wires (shown at no. 1) with silver epoxy glue (circuitworks[®] CW2400). The main channel has one exit.

The top of the channel is closed by a Topas[®] cyclic olefin copolymer (COC) cover (no. 3) with three small perforations to allow the flow to pass through at the two inlets and the outlet. A rubber seal is placed between this seal and the COC piece to make the construction leakage-free. The seal is covered by a polymethylmethacrylate (PMMA) plate that has threads for inserting nanoports (no. 4). The cover and the top plate are made of transparent polymers to be able to look inside the reactor. The different pieces are held together by an aluminium holder (no. 5), the two parts of which are screwed tight.

FIGURE 1

2.2. Electrode preparation

As electrocatalyst for the methanol oxidation, a commercial 50m% Pt - 25m% Ru nanoparticle catalyst supported on carbon black (Alfa Aesar[®], particle size 2.4nm) was used. The cathode catalyst is a 20m% Cu nanoparticle catalyst supported on Norit[®] activated carbon, prepared by wet impregnation and reduction by H₂ [28]. The electrocatalytic behaviour of this catalyst for nitrobenzene and oxygen can be found in the supporting information of this paper. Electrocatalyst inks were prepared using 8.0mg of catalyst and 300µL of a 1m% polystyrene solution in toluene. After 90 minutes of sonication 20µL of the ink was used to coat the electrodes, which have an available surface of 4x28mm before entering the Delrin[®] support. The resulting coating has a catalyst loading of 4.8µg mm⁻² for both anode and cathode. Although the catalyst loading is the same, because of the difference in metal content the metal nanoparticle loading for the anode and cathode will be different. The polystyrene in the ink acts as a binder, ensuring the catalyst remains attached to the graphite.

2.3. Electrochemical measurements

The electrochemical measurements were carried out using a BioLogic VMP3 multichannel potentiostat. Linear Sweep Voltammetry (LSV) measurements were performed to assess the performance of the CLFC. The cell open circuit potential (OCP) between the cathode and the anode was measured for 10 minutes,

after which the potential was scanned from OCP till 0V using a scan rate of 5mV s^{-1} . The anode and cathode potentials were measured separately with two different channels of the potentiostat, using a Ag/AgCl (sat. LiCl in ethanol, Autolab) reference electrode ($E = 0.142\text{V}$ vs SHE) in a recipient at the exit of the fuel cell. All potentials in this paper, except for cell potentials, are referred to this reference electrode. As the reactor does not have a temperature controller, all measurements were performed under room temperature, which varied between 20 and 25°C .

The catholyte that has been used in the setup is a 0.3M perchloric acid solution (VWR, Analar Normapur, 70%) in absolute ethanol (VWR, Analar Normapur, 99.9%). Nitrobenzene (Merck, 98%) was added to this solution to obtain concentrations of 0.0125M, 0.025M and 0.0375M. Ethanol is used as a solvent because of the low solubility of nitrobenzene and its derivatives in aqueous solutions. The anolyte consists of 0.1M methanol (VWR, Analar Normapur, 99.9%) in an aqueous solution of 1M sodium hydroxide (VWR, Analar Normapur, 99%). Both electrolytes are purged with nitrogen for 20 minutes before the measurement to remove oxygen.

The flow rates were set using New Era NE-1000 and NE-1010 programmable syringe pumps. For the measurements, the control of the flow rates was automated: a range of flow rates was set, and each flow rate was applied for 63.3 minutes. This coincides with the time needed to complete five measurements, as described above. Both Terumo[®] 10mL and BD Plastipak[™] 50mL Luer-Lok[™] syringes have been used.

It should be mentioned that in order to operate the fuel cell, it has to be tilted 90° into a vertical position with the cathode on top. This is done to avoid the interference of gravity [29]: the significantly lighter ethanolic solution floats on top of the aqueous solution. If the fuel cell is oriented horizontally, the laminar flow interface is effectively formed perpendicular to the electrodes. However, with vertical orientation, gravity is instead helping to establish and maintain a stable interface between the electrolytes.

2.4. Product conversion measurement

For the product conversion measurement, a constant load of 1000Ω was connected to the CLFC. This allowed the CLFC to operate spontaneously. The flow rate of both electrolytes was set at $5\mu\text{L min}^{-1}$. The catholyte was 0.3M HClO_4 in ethanol with 0.025M nitrobenzene. The anolyte was 1M NaOH with 0.1M methanol. The measurement was run for 1000min. During the experiment the cell, cathode and anode potential were monitored using a BioLogic VMP3 multichannel potentiostat. The current densities and power densities were then calculated using Ohm's law.

The solution obtained at the end of the experiment was diluted 60 times before being analysed using UV-Vis spectroscopy with wavelengths varying from 220nm to 400nm. A HP 8452A UV-Vis spectrometer was used to measure the spectrum. The resulting spectrum was fitted using the Lambert-Beer equation per wavelength, with attenuation coefficients calculated from calibration curves.

3. Results and discussion

3.1. Proof of concept

The first matter that needs to be determined is whether the nitrobenzene reduction is occurring in the CLFC. For this purpose, two LSV measurements were performed, one without and one with nitrobenzene present in the reactor. The results of these two LSV experiments are given in figures 2 and 3. In these measurements, the potential was scanned from OCP to 0V as this is the range in which the reactor operates as a fuel cell. The green lines depict a single measurement where nitrobenzene was present in the electrolyte, whereas the blue lines correlate to a measurement where no nitrobenzene was added to the catholyte. In figure 2 the cell potential (full line) and power density (dashed line) are given as a function of the current density. These two quantities were chosen since both of them can be used as a criterion for optimisation. As both the anodic and cathodic potential are monitored during potential cycling, the individual reaction kinetics of both the anodic and cathodic reaction can be obtained, as shown in figure 3. The potentials in this figure relate to the cell

potential in figure 2 as $E_{\text{cathode}} - E_{\text{anode}} - IR_u = E_{\text{cell}}$. The measured current at this potential is plotted on the y-axis, and it is inverted for the anode. R_u is the Ohmic resistance, which is 30Ω as determined by electrochemical impedance spectroscopy at high frequencies. For the Ohmic drop calculation, the resistance of both the anolyte and the catholyte were assumed to be equal at 15Ω .

The flow rate in this particular set of experiments was set at $25\mu\text{L min}^{-1}$. The OCP of the measurement without nitrobenzene is 0.696V , and the obtained maximum current and power densities are 0.911mA cm^{-2} and 0.140mW cm^{-2} , respectively. Because this measured current density is not negligible, this indicates the presence of a reaction at the cathode. As can be noticed from the solid blue line in figure 3, this reaction has a very low reaction rate. This is also clear when comparing the differences between the start and the stop potentials of the anode and the cathode: $\Delta E_{\text{cathode}}$, the amount the cathodic potential has changed during the measurement, has a value of 0.510V , whereas $\Delta E_{\text{anode}} = 0.165\text{V}$. The low reaction rate could be due to a low concentration of reagent, or low catalytic properties of the Cu nanoparticle catalyst for the reaction. When looking at the possible electrochemical reactions based on the present reactants, the most plausible cathodic reaction is the oxygen reduction reaction. Residual oxygen can still be present in both electrolytes since the fluids have to be transferred into the syringes after the purging with nitrogen.

For the experiment depicted by the green lines, the concentration of nitrobenzene was 0.025M . The OCP of the measurement was 0.739V , which is higher than the OCP of the measurement without nitrobenzene, a first indication that indeed the nitrobenzene reduction is taking place at the cathode. It is however significantly lower than the calculated ΔE_{cell}^0 of 1.59V . To understand the reasons for this discrepancy, the individual potentials of the anode and cathode have to be considered: $E_{\text{cathode}} = 0.123\text{V}$ (0.265V vs SHE) and $E_{\text{anode}} = -0.616\text{V}$ (-0.474V vs SHE). The difference between these values and the standard reduction potentials are -0.528V and 0.339V , respectively. This is due to the slow kinetics of both half-reactions [30–34], and fuel crossover can also have a significant effect. Indeed, a low cell potential can even be an indication of fuel

crossover [20]. There are other minor reasons that may affect the cell potential, namely the low product concentration, low reactant concentration and the pH of the catholyte.

The maximum current density of 4.81mA cm^{-2} was obtained at $E_{\text{cell}} = 0\text{V}$ (short circuit conditions). The maximum current density being obtained at short circuit conditions is logical, as per the Butler-Volmer equation [35]. At this operating conditions the reactor will not cogenerate electricity as the power density is 0 (cf. figure 2), but the conversion of products will be maximal. The maximum power density of 0.482mW cm^{-2} at $E_{\text{cell}} = 0.221\text{V}$ and $j = 2.18\text{mA cm}^{-2}$. From these currents, together with the elevated cell potential, it can be concluded that indeed the nitrobenzene reduction is taking place at the cathode.

The exponential nature of the electrochemical kinetics of the nitrobenzene reduction as a function of potential are demonstrated in figure 3. The cathode potential starts at 0.121V and ends at -0.298V ($\Delta E_{\text{cathode}} = 0.419\text{V}$), and the anode potential shifts from -0.619V to -0.318V ($\Delta E_{\text{anode}} = 0.291\text{V}$). Both potential intervals are similar, but the higher $\Delta E_{\text{cathode}}$ indicates that the cathodic reaction proceeds at a lower rate. This behaviour is intended, since the formation of products from the nitrobenzene reduction should not be limited by the counter reaction. It is most likely due to the lower concentration of nitrobenzene compared to methanol. As the measurement in the presence of nitrobenzene is performed under the same circumstances as the one in absence of nitrobenzene, the oxygen reduction is also expected to occur as a parasitic reaction in this case. This has as consequence that not all the measured current is used to reduce nitrobenzene, resulting in a lower current efficiency.

The methanol kinetics for the experiment in presence of nitrobenzene also varies from that in the absence of nitrobenzene. This is most likely related to the state of the anode, as will be discussed further in section 3.4.

FIGURE 2

FIGURE 3

3.2. Influence of flow rate

The influence of flow rate on the electrochemical behaviour of the reactor was studied via automated experiments in a solution of 0.0125M of nitrobenzene where the flow rates of both the anolyte and catholyte were changed simultaneously every 63.3 minutes. During this time, five LSV measurements were completed per flow rate. The consecutive measurements are performed to study the influence of time. The results of these measurements are given in figure 4. The x-axis in these scatter plots is the measurement time, i.e., the time when the single LSV measurement started relative to the start of the experiment. Six quantities are displayed in this plot, coming from separate LSV measurements, similar to the ones described in section 3.1. Markers at the same time in the plot represent the same LSV measurement. The flow rate is varied randomly between 5 and 95 $\mu\text{L min}^{-1}$ to avoid systematic time evolution. Since the flow rate of both the anolyte and the catholyte are set at this value, the flow rate in the main channel of the fuel cell will be twice this value. Flow rates of 5 $\mu\text{L min}^{-1}$ and 95 $\mu\text{L min}^{-1}$ correspond to residence times in the main channel of 90s and 5s, respectively.

The cell OCP at the start of each measurement and the maximum power density obtained during the measurement are displayed in figure 4A. In figure 4B, anode, cathode and ending potentials are indicated. Anodic and cathodic potentials were measured at the start of the measurement. Anode potentials are found at the bottom of the plot and cathode potentials at the top. The ending potential represents the last potential of both the cathodic and anodic scan (when $E_{\text{cell}} = 0\text{V}$), without any IR_u compensation. The relative location of this ending potential, as explained in the single LSV measurement above, is an indication of which reaction is rate determining: the longer the distance between the cathodic and end potentials $\Delta E_{\text{cathode}}$ relative to the distance between the anodic and end potentials ΔE_{anode} , the more rate determining the cathodic reaction.

At $t = 10\text{min}$, the OCP starts at a high value of 0.826V at a flow rate Φ_V of 55 $\mu\text{L min}^{-1}$. When the flow rate is decreased to 10 $\mu\text{L min}^{-1}$ (indicated as zone I in figure 4) the OCP suddenly drops to 0.599V, and when the flow rate

is increased again it rises back to a value of 0.793V. The power density starts at a somewhat lower value of 0.321mW cm⁻², after which it follows the same behaviour as the OCP. At the time of the drop in cell potential, the cathodic potential also drops significantly from 0.138V to -0.066V. The ΔE_{cell} of 0.219V between the last measurement of $\Phi_V = 55\mu\text{L min}^{-1}$ and the first measurement of $\Phi_V = 10\mu\text{L min}^{-1}$ can thus be explained by the drop in cathodic potential. Since the anodic potential does not indicate a sudden drop, this behaviour is not likely due to the loss of the laminar flow interface, since it seems to be specific to the cathodic reaction. It might be due to fuel crossover, since it happens at lower flow rate, however when the flow rate is even lower ($\Phi_V = 5\mu\text{L min}^{-1}$, zone IIIa in figure 4) the cathode potential does not drop significantly. During the rest of the experiment, the cathodic potentials are reasonably stable.

From $t = 132\text{min}$ to $t = 367\text{min}$, zone II in figure 4, the cell potential and the power density decrease gradually over time, unaffected by the different flow rates. When looking at the anodic potential, and to a lesser extent the end potential, a similar behaviour is observed. This loss of cell potential cannot be attributed to fuel or oxidant crossover, since it is unaffected by the flow rate. Considering it is dependent on the measurement time, this loss in potential is dependent on the previous state of the electrode. This leads to the conclusion that the measurement is effectively influencing the state of the anode. This influence is so large that it almost completely masks the influence of the flow rate. This phenomenon is further investigated in section 3.4 of this paper.

After the decline of anode activity, it does not remain stable. At $t = 391\text{min}$, when the flow rate is changed to $5\mu\text{L min}^{-1}$, two different observations can be made. The first one is that the anode potential increases towards a value that corresponds to the ones at the beginning of the measurement. The second observation is that the end potential shifts a similar amount. This means that the cathodic reaction is a lot more rate limiting than before. This rate limitation makes sense: the concentration boundary layer near the electrode will increase in size [36], decreasing the mass transport limited current. The anode, methanol having a higher concentration, suffers less from mass transport limitations.

Apart from an increased cell potential, the performance of the fuel cell is also greatly increased: the last measurement with $\Phi_V = 65\mu\text{L min}^{-1}$ has a maximum current density of -2.33mA cm^{-2} and a maximum power density of 0.199mW cm^{-2} , whereas at the first measurement of $\Phi_V = 5\mu\text{L min}^{-1}$ these values are -3.01mA cm^{-2} and 0.303mW cm^{-2} , respectively. This increase in performance, and in anode potentials, after the decrease in flow rate, is most likely due to another change in the state of the electrode. For the rest of the measurement (zone III), the behaviour of the anode open circuit potential becomes erratic, since both the lowest value (-0.513V , indicated as point 1) and the highest value (-0.694V , point 2) of the anode potential are measured in a time span of 62 minutes, after which the potential drops again. The explanation for this behaviour is given in section 3.5.

To summarise, the influence of the flow rate on the reactor performance seems limited: it only seems to have a severe effect at low flow rates, where the cathode activity drops due to nitrobenzene depletion. The anode appears to be unaffected by the flow rate, but severely affected by the measurement itself.

FIGURE 4

3.3. Influence of nitrobenzene concentration

The second parameter that can have an influence on the performance of the CLFC is the concentration of reactant, in this case nitrobenzene. To examine this influence, two additional concentrations of nitrobenzene were measured, specifically 0.025M and 0.0375M . Figure 5 shows the experiment performed with a nitrobenzene concentration of 0.025M . In this experiment the flow rate was varied between $1\mu\text{L min}^{-1}$ and $40\mu\text{L min}^{-1}$ in a random order. In figure 6, the concentration of nitrobenzene has been further increased to 0.0375M . For this concentration, the flow rates were varied between $1\mu\text{L min}^{-1}$ and $95\mu\text{L min}^{-1}$. For both measurements the concentration of methanol remained the same at 0.1M , so it is still present in excess. In both figures 5 and 6 the cell potential and the power density are not shown as these parameters do not provide any additional information. The cell potential can still be derived from these figures

as $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$, and the power density follows the same trends as the cell potential (similar to figure 4A).

In the measurement of 0.025M nitrobenzene much of the same phenomena observed in the measurement of 0.0125M can be found. Initially an increase of anodic potential is observed, indicating a change in electrode state. This increase seems to be independent of flow rate, and only dependent on time. At the same time the maximum power density and current density remain stable, although there is a slight decrease in both at the lower flow rate of $9\mu\text{L min}^{-1}$. Similar to the measurement at $10\mu\text{L min}^{-1}$ with 0.0125M nitrobenzene, at the low flow rate of $4\mu\text{L min}^{-1}$ (indicated by zone Ia in figure 5), the cell potential collapses due to a heavy decrease in cathode potential. This is then quickly restored at a higher flow rate. It is worth noting though that such a steep potential drop does not happen at every flow rate lower than $10\mu\text{L min}^{-1}$, although it happens frequently.

As seen in the previous measurement, the cell potential and power density decrease again over time (zone I), a behaviour that can be attributed to an anode potential drop. After a certain amount of time, the anode potential begins a periodic behaviour of higher and lower potentials (zone II). As before, this is probably due to a change in the state of the anode. In this particular measurement it is clearly noticeable that the potential never decreases below approximately -0.51V: after the anode potential reaches this value, it increases again. This is a similar potential as found in figure 4.

FIGURE 5

Interestingly, the experiment with a concentration of 0.0375M of nitrobenzene, depicted in figure 6, shows a different picture. Until $t = 198\text{min}$ the anodic potential increases, after which it declines, but much more slowly than the previous experiments. The relative values of $\Delta E_{\text{cathode}}$ and ΔE_{anode} indicate that the cathode reaction is still the rate limiting reaction. For first measurement with a flow rate of $95\mu\text{L min}^{-1}$, this difference in ΔE is as high as 0.44V for the cathodic and 0.33V for the anodic reaction. A second observation from this

measurement is the increased current: apart from the measurements of $1\mu\text{L min}^{-1}$ and one measurement of $2.5\mu\text{L min}^{-1}$, the maximum current densities, measured at $E_{\text{cell}} = 0\text{V}$, are always higher than 4.25mA cm^{-2} , the average current density being 4.68mA cm^{-2} . Compared to the experiment with a lower concentration of nitrobenzene (0.0125M), these values were 2.33mA cm^{-2} and 3.13mA cm^{-2} , respectively (disregarding the measurement of $\Phi_V = 10\mu\text{L min}^{-1}$).

The higher currents are of course expected, since the concentration of nitrobenzene is higher the reaction kinetics will also increase. However, considering the end potentials of each potential scan in both experiments are similar, or even a bit lower in the case of the higher concentration, indeed both the anode as well as the cathode kinetics have increased. This is most likely related to the anode potentials not dropping as severely over time as seen in the other experiments. The anode is not completely unaffected by measurement time however.

Apart from this influence of the measurement time, for the first time in these experiments, a clear influence of the flow rate is noticeable for the cell potentials. This is in contrast to the measurements performed at a lower nitrobenzene concentration described in section 3.2. Looking at figure 6, this influence can for the most part be linked to the potential drop of the cathode. At lower cell potentials, the cathode potential is lower, which can be associated with fuel crossover. This crossover towards the cathode can provide an explanation why the potential drops so severely in some cases with low flow rates when the concentration of nitrobenzene is lower than 0.0375M . As the supply of nitrobenzene on the surface is depleted, it will be refreshed at a lower rate due to the slower diffusion. The methanol oxidised at the surface of the cathode will therefore have a larger relative influence if the concentration of nitrobenzene is lower. The anode does not seem to be affected that much, apart from the extreme cases of flow rates, 1 and $2.5\mu\text{L min}^{-1}$ (indicated as zone I). This is presumably due to the lower concentration of nitrobenzene compared to methanol, lowering the diffusion rate. At $1\mu\text{L min}^{-1}$ (zone II) however the anodic potential drop is severe, indicating that the nitrobenzene reduction proceeds more easily on the Pt-Ru catalyst than the methanol oxidation on the Cu one.

FIGURE 6

The results of the experiments with different nitrobenzene concentrations indicate that reactant concentration is affecting the performance of the CLFC more heavily than the flow rate, especially at higher concentrations where the measurement does not affect the state of the anode so severely, which leads to increased anodic reaction kinetics. As expected, the cathodic reaction kinetics are also increased by the concentration of reactant.

3.4. Decline of anode activity

To understand what is going on at the anode in zone II of figure 4, in zone I of figure 5 and to a lesser extent from $t = 198\text{min}$ on in figure 6, the reaction mechanism of the methanol oxidation towards CO_2 on a Pt-Ru nanoparticle catalyst has to be considered. The high activity of Pt-Ru for methanol oxidation is considered to be due to the bifunctional mechanism [37]. First, methanol chemisorbs on the Pt surface and undergoes a consecutive dissociative electrosorption [38] (eq. 4). An intermediate of adsorbed CO on Pt is formed, which can be on-end, bridge, or multi-bonded depending on the surface orientation. The difficulty here is that this adsorbed CO is very difficult to remove, and in many cases it is the rate determining step for methanol electrocatalysis. If the adsorbate is not adequately removed, the reaction is self-poisoning [39]. On Ru-alloyed Pt the adsorption of OH^- occurs on the Ru sites (eq. 5) [40]. This adsorption occurs much faster than on pure Pt. The adsorbed OH^- and CO then react towards adsorbed COOH. In alkaline media, this chemical step can be the rate determining step [41]. The COOH is then removed by reacting with OH^- to form CO_2 and H_2O (eq. 6). Next, the CO_2 reacts with the OH^- in solution to form CO_3^{2-} , carbonating the electrolyte.

Adsorbed CO is thus an important intermediate during this oxidation, and it can become a rate determining step. A gradual covering of the Pt surface with CO molecules might provide an explanation for the gradual decrease in anodic potentials seen in the experiment.

A possible explanation as to why the self-poisoning behaviour is observed in a much lesser extent with higher concentrations (figure 6) can be found looking at figures 4 and 5: the time it takes until the lower value of the anode potential is first reached for the experiment of 0.025M nitrobenzene is approximately double that of the measurement of 0.0125M nitrobenzene. Apart from the lower flow rates reducing the supply of methanol, this might also be due to reactant crossover: as the nitrobenzene encounters the anode, it gets additional current which it can use to oxidise the CO to CO₂. This effect is also present during the waiting periods between the measurements, and can therefore be observed separately, e.g. with the first measurement of 5µL min⁻¹ of 0.0125M nitrobenzene (zone IIIa in figure 4), where the OCP already increased prior to any measurement at this flow rate. As the concentration of nitrobenzene is increased, reactant crossover augments, explaining the slower poisoning witnessed in figure 6. Looking back at figure 3, the difference between the anode kinetics in presence and in absence of nitrobenzene are most likely also related to decreased CO adsorption when nitrobenzene is present in the catholyte.

3.5. Periodic behaviour of reactor performance

As the decline in anode potential is attributed to the adsorption of CO on the surface, the increase in potential is most likely linked to the desorption of said adsorbate. An explanation can be found in the fact that the anode potential

never drops below -0.51V . This lower limit of potential can indicate that at this potential, the anode is almost completely covered with CO. If that is the case, the only reaction happening on the anode will be the oxidation of CO to CO_2 . Due to this being the only reaction, the surface is cleaned so the oxidation of methanol to CO can take place again. The anode potential behaviour can be fully explained using this conclusion: at the beginning of the experiment, the anodic surface is clean and the only reaction happening is the oxidation of methanol to CO. After a while, the surface begins to fill with adsorbed CO. Being the rate determining step, the oxidation of this adsorbate towards CO_2 happens at a more positive potential than the first step of the oxidation of methanol. As after a while both reactions begin to take place, due to the lack of free Pt on the surface for methanol to adsorb to, the anodic potential becomes a mixed potential, which is indicated by a the gradual decrease in potential as CO oxidation takes up a higher relative share.

As the CO is adsorbing on the surface at a faster rate than it is removed, the potential will continue to decrease until it reaches its lowest value. At this value, the surface will be almost completely filled with adsorbed CO molecules. Then the cycle begins again, as now the CO oxidation is the most important reaction taking place the surface is wiped clean again. The periodic behaviour of increase and decrease in anodic potential after the lower limit is first reached can be explained by the fact that not all the CO is removed from the surface: once the methanol oxidation is taking place at a sufficient rate it will become the fastest reaction again, covering the surface with CO molecules. This theory also explains why the regeneration of the anode is usually found at lower flow rates: the supply of methanol drops, allowing the surface to be freed as the adsorption reaction proceeds at a lower rate.

Oscillations occurring during the oxidation of methanol have been observed before in literature, both in potentiostatic [42] and galvanostatic [43, 44] conditions. In galvanostatic conditions, due to the absorption of CO the electrode potential increases to maintain a constant current, and this increase in potential leads to the increase of CO oxidation. Because of this the surface is cleaned and

a new cycle is started [45]. This can be linked to the nitrobenzene crossover and consecutive reduction at the anode, which supplies a constant current to the anode.

3.6. Conversion of nitrobenzene

A last quantity that has to be considered comparing different flow rates and concentrations of nitrobenzene, is of course the conversion. In this study, the fuel consumption is of secondary importance compared to this quantity, as the goal is to use the fuel cell as a chemical reactor for the hydrogenation of nitrobenzene. Table 1 lists theoretical conversions for nitrobenzene, purely based on the measured current. Faraday’s law has been used to calculate the amount of nitrobenzene converted every second, and this amount divided by molar flow rate of nitrobenzene gives the theoretical conversion (eq. 7). The assumption has been made that all nitrobenzene converts to aniline ($n = 6$). The presence of residual oxygen has not been taken into account for these calculations. The Faraday efficiency of the nitrobenzene reduction may also not be 100%. Because of these issues these calculations will provide an overestimation of the conversion. The conversion has been calculated on two points, namely at the maximum current density ($X_{j_{\max}}$) and at the maximum power output ($X_{P_{\max}}$). Due to the slow cathode kinetics (cf. figure 4) the results of $c_{\text{NB}} = 0.0125\text{M}$ and $\Phi_V = 10\mu\text{L min}^{-1}$ are an outlier and are not shown in this table.

$$X_{\text{NB}} = \frac{\frac{I}{n \cdot F}}{c_{\text{NB}} \cdot \Phi_{V,\text{NB}}} \quad (7)$$

Table 1: Average theoretical conversions, calculated via the current and the flow rate (eq. 7). For the calculation of $c_{\text{NB}} = 0.025\text{M}$ and $\Phi_V = 5\mu\text{L min}^{-1}$, only the last three measurements are used.

c_{NB}	$5\mu\text{L min}^{-1}$		$10\mu\text{L min}^{-1}$		$25\mu\text{L min}^{-1}$	
	$X_{j_{\max}}$	$X_{P_{\max}}$	$X_{j_{\max}}$	$X_{P_{\max}}$	$X_{j_{\max}}$	$X_{P_{\max}}$
0.0125M	74.0%	32.6%	-	-	14.3%	6.34%
0.025M	47.0%	20.6%	26.8%	11.7%	12.0%	8.06%
0.0375M	38.5%	16.7%	20.5%	9.01%	8.81%	3.90%

It is immediately noticeable that the theoretical conversion decreases rapidly when the flow rate is increased. The figures imply that a flow rate of $25\mu\text{L min}^{-1}$ is too high from a conversion point of view. In fact, to increase the conversion, the flow rate should be as low as possible, especially if there is to be any power drawn from the system, as indicated by the low figures in the column of $X_{P_{\max}}$. As for the concentrations, due to the influence of the concentration over the measured current being rather limited, the highest conversions are seen at the lowest concentration.

As a final proof for cogeneration, the actual conversion of the reactor under a constant load was measured. For this a load of 1000Ω was connected to the cell and the flow rate was set at $5\mu\text{L min}^{-1}$ for 1000min. The nitrobenzene concentration was 0.025M. Product analysis results are depicted in table 2. The table shows that nitrobenzene is converted into aniline and the intermediate nitrosobenzene in this reactor. The total conversion of nitrobenzene is 37%. The average power delivered through the system was 0.062mW cm^{-2} with an average cell potential of 0.093V and an average current density of -0.665mA cm^{-2} .

Table 2: Products formed in the cogeneration CLFC. Concentrations of nitrobenzene (NB), phenylhydroxylamine (PHA), aniline (AN), azoxybenzene (AOB) and nitrosobenzene (NOB) are determined by UV-Vis analysis. The flow rate of the anolyte and catholyte was set at $5\mu\text{L min}^{-1}$ for 1000min.

V mL	c_{NB} mM	c_{PHA} mM	c_{AN} mM	c_{AOB} mM	c_{NOB} mM
10.5	7.2	0.0	2.7	0.0	1.6

Aside from the desired products, the electrolyte contains many other components such as methanol, NaOH and ClO_4^- . It is clear that to function as a proper reactor, the CLFC has to be optimised further and downstream processing of the end products is needed.

4. Conclusions

A fuel cell type reactor, based on the laminar flow fuel cell design, has been successfully constructed. This reactor provides a means for hydrogenation of

nitrobenzene while generating a small amount of power. The highest power density of 0.542mW cm^{-2} has been obtained at a concentration of nitrobenzene of 0.0375M and a flow rate of $55\mu\text{L min}^{-1}$. The highest theoretical conversion of nitrobenzene, 74.0% , has been observed at the low flow rate of $5\mu\text{L min}^{-1}$ and at the lowest measured concentration of 0.0125M . The conversion of this measurement at the point of maximum power density was 32.6% . These are not the actual conversions, for the presence of residual oxygen in the system induces a parasitic current that is not taken into account. The actual conversion measured in the reactor using a load of 1000Ω with 0.025M nitrobenzene and a flow rate of $5\mu\text{L min}^{-1}$ was 37% with an average power density of 0.062mW cm^{-2} .

The electrochemical behaviour of the CLFC is influenced by nitrobenzene concentration, the flow rate and the measurements themselves. A higher nitrobenzene concentration increases the reactant crossover and decreases the effect of fuel crossover. Although it is overshadowed by the effect of the measurements, the flow rate has an influence: at low flow rates the cathode kinetics can collapse due to the combined effect of nitrobenzene deficiency and fuel crossover. The measurements themselves are influencing the electrochemical behaviour due to the intermediate of adsorbed CO on the surface of the anode, which acts as a catalyst poison. After the reactor has reached a certain coverage of CO the surface is freed and the anode kinetics are increased again.

With these measurements the concept of cogeneration in a microfluidic reactor is proven. In further research the conversions need to be confirmed by the detection of the formed products and at a later stage further optimisation can be considered.

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Figures

Figure 1: Exploded view of the cogeneration CLFC. (1) POM piece with milled flow channels. (2) Electrocatalyst coated graphite electrodes placed in the POM piece and glued to the electrical wires with conductive epoxy. (3) COC plate and rubber seal covering the channel. (4) PMMA piece with holes for nanoports for tubing. (5) Aluminium plates that hold the construction together.

Figure 2: Polarisation plot and corresponding power density plot of two LSV measurements with $\Phi_V = 25 \mu\text{L min}^{-1}$. Both a measurement in presence (green lines) and in absence (blue lines) of 0.025M nitrobenzene is shown. Full lines represent the cell potential (left-hand axis) and the dotted lines represent the power densities (right-hand axis).

Figure 3: Electrochemical reaction plot of the LSV measurements that are shown in figure 2. Both the anodic (dotted line) and the cathodic (full line) voltammogram are shown. The voltammograms are compensated for the Ohmic resistance of the fuel cell of 30Ω . The same colours are used as in in figure 2.

Figure 4: Experimental data of the automated LSV measurements with $c_{NB} = 0.0125\text{M}$. In figure A, the cell potential (●) and the maximum power density (■) for every LSV measurement are depicted. The x-axis represents the starting time of the single LSV measurement relative to the start of the experiment. In figure B, the anode potential (●), the cathode potential (▲) and the end potential (◆) of each LSV measurement is shown. The flow rate setting per measurement (■) is also indicated in this plot. Three zones are marked in the figure; (I) zone of $10\mu\text{L min}^{-1}$, (II) cell potential decline zone, (III) erratic cell potential behaviour zone with $5\mu\text{L min}^{-1}$ zone.

Figure 5: Experimental data of the automated LSV measurements with $c_{NB} = 0.025M$. The same markers are used as in figure 4B. Two zones are marked; (I) Cell potential decline zone with Ia: $4\mu L \min^{-1}$ zone, (II) erratic cell potential behaviour zone.

Figure 6: Experimental data of the automated LSV measurements with $c_{NB} = 0.0375M$. The same markers are used as in figure 4B. Two zones are marked; (I) $2.5\mu L \min^{-1}$ zone, (II) $1\mu L \min^{-1}$ zone.