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**DOI**

[10.1021/acs.iecr.9b06925](https://doi.org/10.1021/acs.iecr.9b06925)

**Publication date**

2020

**Document Version**

Final published version

**Published in**

Industrial and Engineering Chemistry Research

**Citation (APA)**

Pérez-Gallent, E., Sánchez-Martínez, C., Geers, L. F. G., Turk, S., Latsuzbaia, R., & Goetheer, E. L. V. (2020). Overcoming Mass Transport Limitations in Electrochemical Reactors with a Pulsating Flow Electrolyzer. *Industrial and Engineering Chemistry Research*, 59(13), 5648-5656. <https://doi.org/10.1021/acs.iecr.9b06925>

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# Overcoming Mass Transport Limitations in Electrochemical Reactors with a Pulsating Flow Electrolyzer

Elena Pérez-Gallent,<sup>\*</sup> Carlos Sánchez-Martínez, Leon F. G. Geers, Susan Turk, Roman Latsuzbaia, and Earl L. V. Goetheer<sup>\*</sup>

**Cite This:** *Ind. Eng. Chem. Res.* 2020, 59, 5648–5656

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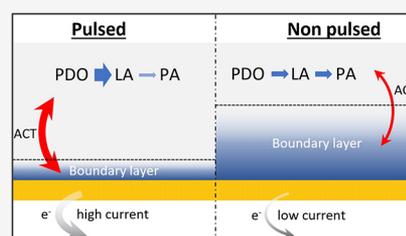
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**ABSTRACT:** Electrochemical processes are a promising technology for industrial production of chemicals. One of the major drawbacks of electrochemical systems is the low mass transfer of reactants toward the active surface area of the electrode. In this paper, an approach is presented to enhance the mass transfer and increase the overall performance of the reactions. The strategy comprises introduction of a pulsed electrolyte flow in the electrochemical flow cell. This pulsating behavior results in an improved mass transfer of electroactive species due to a higher instantaneous velocity driven by the pulsations. Though the net residence time of the reactants will not be altered due to the pulsation, the resulting enhancement of mass transfer leads to an increase of the conversion. The oxidation of 1,2-propanediol to lactic acid and pyruvic acid mediated by 4-acetamido-(2,2,6,6-tetramethylpiperidin-1-yl) oxidanyl (ACT-TEMPO) was chosen to study the influence of the pulsed flow. Under the pulsating regime, a yield increase of lactic acid of a factor of two and a 15–20% gain in selectivity to a total of 95% toward lactic acid can be achieved by tuning the process parameters.



## INTRODUCTION

Electrosynthesis is a promising technology for the transition toward a carbon-neutral chemical industry. The two main features of electrosynthesis are the fact that it is driven by electricity and the possibility of dynamic operation, which means that it can follow a fluctuating energy generation profile,<sup>1</sup> functioning on demand only when there is an excess of electricity in the grid. These systems can therefore store enormous amounts of energy from renewable sources in chemical products with a low carbon footprint.<sup>1</sup> Electrosynthesis is also a green process with reduced energy requirement in comparison to thermochemical conversion routes due to their milder process conditions.<sup>2</sup>

The main challenge for the development of electrochemical systems on an industrially relevant scale is the mass transport limitation of most reactions, often caused by low solubility of reactants (organic compounds in particular) in the electrochemical reaction medium. Hence, selectivity toward the desired product, productivity, and the energy efficiency of the process are affected. To overcome the difficulty of mass transfer limitations, researchers have come up with different designs and suggestions, including an increase of specific electrode area<sup>3</sup> (3D expanded foams electrodes,<sup>4</sup> packed and fluidized beds<sup>5</sup>), turbulence and mixing promoters,<sup>5–7</sup> increased linear fluid velocity,<sup>7</sup> increased pressure operation<sup>8</sup> (for solubilized gaseous species like CO<sub>2</sub>), and optimized designs of electrochemical cells (serpentine flow paths,<sup>9</sup> microfluidic,<sup>10</sup> rotating/moving electrodes,<sup>3,5,11</sup> ultrasound,<sup>12</sup> and plug-flow fluid orthogonal with mesh electrodes,<sup>13</sup> among

others). Some of these techniques require a complex reactor design, i.e., moving parts cause wear and tear on the reactor, increasing the need for regular maintenance, which increases costs.

The present study describes a pulsed flow reactor as a solution to enhance mass transfer without the need of a complex reactor design. The literature on this approach is scarce for electrochemical processes. However, it is a common approach for extraction processes and emulsion polymerizations in packed columns.<sup>14</sup> Despite the different reaction processes, the effect of pulsation on the axial dispersion will be similar. Cognet et al.<sup>4,15</sup> investigated mass transfer in porous percolated electrochemical reactors incorporating pulsed flow, demonstrating an increase in the mass transfer coefficients and changes in selectivity for electro-organic reactions.

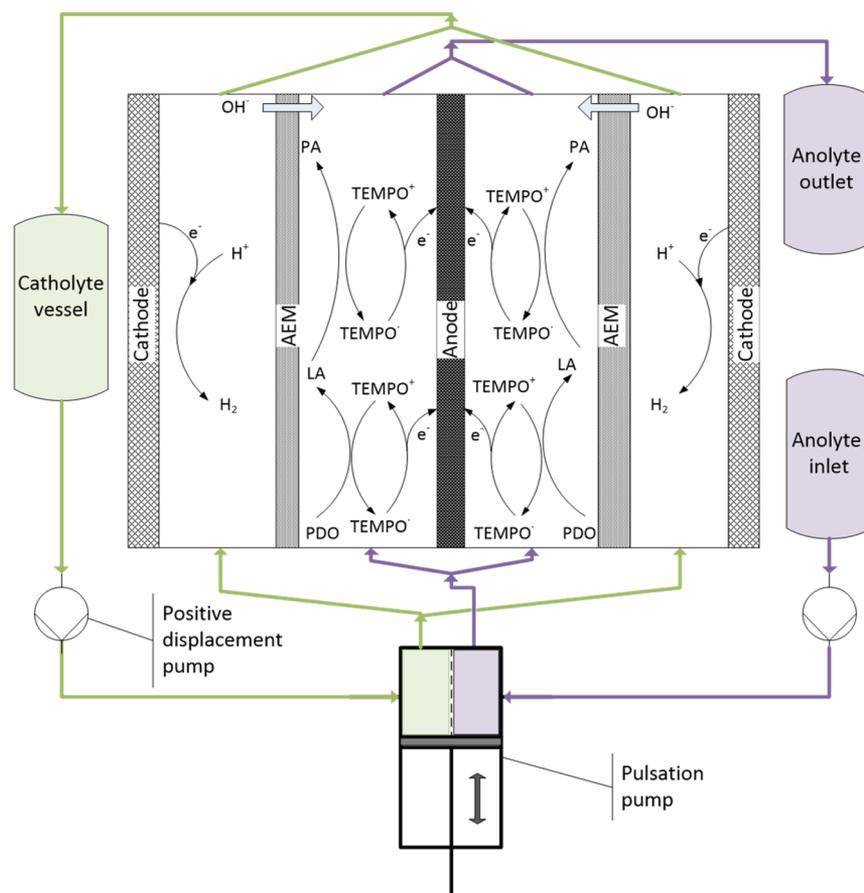
To exemplify the potential of pulsed flow in electrochemistry, the conversion of 1,2-propanediol (PDO) to lactic acid (LA) and further to pyruvic acid (PA) mediated by ACT-TEMPO was used as a test reaction.<sup>16</sup> The use of mediators such as TEMPO-based molecules presents some advantages for organic electrosynthesis due to its fast kinetics.<sup>17,18</sup> These two reactions take place in the bulk electrolyte in the cell, while

**Received:** December 18, 2019

**Revised:** February 24, 2020

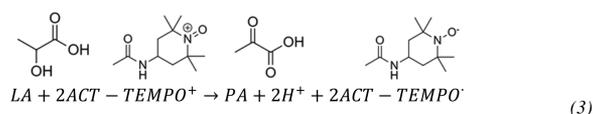
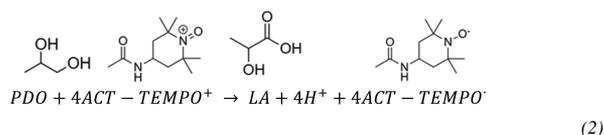
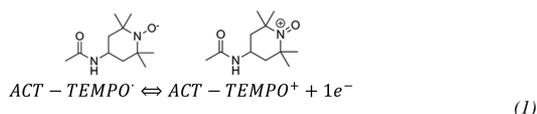
**Accepted:** March 11, 2020

**Published:** March 11, 2020



**Figure 1.** Schematic representation of the setup used for the oxidation of 1,2-propanediol (PDO) to lactic acid (LA) and pyruvic acid (PA) mediated by ACT-TEMPO.

the regeneration (i.e., oxidation) of the ACT-TEMPO<sup>•</sup> takes place on the electrode surface. The chemical reaction equations are shown below in eqs 1–3. This reaction was selected for its economic potential since lactic acid can be used as a building block for biodegradable polymers.<sup>19</sup> A parametric study of flowrates, pulsation frequency, and amplitude in the different compartments of the electrolyzer has been carried out in order to assess the performance of the electrolysis process. In addition, a phenomenological mathematical model has been developed to investigate the effect of the pulsed flow on the mass transfer in the process.



## EXPERIMENTAL SECTION

Figure 1 shows a schematic representation of the experimental setup used in this study. A picture of the setup used can be

found in the Supporting Information, Figure S1. The electrochemical cell employed contained two Ni foams plates as cathodes and one graphite plate as the anode that was used on both sides. Ni foam was selected as a cathode for water electrolysis in alkaline conditions due to its high stability<sup>20</sup> and high performance.<sup>21</sup> In addition, a foam structure was selected for its high surface area, which avoids current limitations by the cathodic reaction. A graphite plate was selected for its high performance in ACT-TEMPO oxidation.<sup>22</sup> The electrochemical reactor contains four liquid compartments (two for the anolyte and two for the catholyte, all 2.7 mm in height) separated by two anionic exchange membranes. The catholyte was recirculated through the cell, while the anolyte flowed through the cell in a single pass to guarantee preset concentrations of species at the inlet of the reactor. Two positive displacement pumps serve as feed pumps to provide a net flowrate of electrolytes in the range of 5–35 L·h<sup>-1</sup>. A diaphragm pump provides the pulsations with a total volume of 20 mL in the anolyte compartment and 20 mL in the catholyte compartment. The pulsation frequency of the pump can be adjusted in a range of 0–3 Hz. The net flow provided by the feed pumps was constant and independent from any pulsations provided by the diaphragm pump. However, the velocity corresponding to the pulsation is higher than in the net flow (see section Effect of the pulsation in the net flowrate, Figure S2 in the Supporting Information). With each stroke of the pulsating pump, the flowrate increases by an amount of 238 L·h<sup>-1</sup> for a frequency of 1.05 Hz and 588 L·h<sup>-1</sup> for a frequency of 2.6 Hz. Therefore, in the pulsed configuration, the net flowrate

is insignificant with respect to the maximum velocity due to the pulsations.

The electrochemical measurements were carried out using a Delta SM 120–50 power supply in potentiostatic mode applying a cell potential of 2.5 V. A filter press cell from ElectroCell was used for electrolysis of PDO to LA and PA. Two Ni foam plates ( $13.7 \times 29.5$  cm,  $404.15$  cm<sup>2</sup>) were used as the cathode. A graphite plate ( $13.7 \times 29.5$  m,  $404.15$  cm<sup>2</sup>) was used as the anode. The anode and cathode sides were separated by an anion exchange membrane (AEM) (Fumasep FAA-3-PK-130, FuMA-Tech). The currents reported here are normalized per geometric area.

The anolyte solution was prepared using a 0.5 M KHCO<sub>3</sub> (Sigma Aldrich, ACS reagent, granular, 99.7% purity)/0.5 M K<sub>2</sub>CO<sub>3</sub> (Acros, ACS reagent, anhydrous, 99 + % purity) buffer solution with 20 mM ACT-TEMPO (ABCR, 98% purity) as a mediator and 0.1 M PDO (Sigma Aldrich, >99.5% purity) as a reactant. A 0.5 M KOH (VWR, 85.3% purity) solution was used as the catholyte. All electrolyte solutions were prepared using MilliQ water.

An Agilent 1260 Infinity high-performance liquid chromatograph (HPLC) unit, running on an Aminex HPX-87H (390 x 7.8 mm) column using 5 mM H<sub>2</sub>SO<sub>4</sub> as eluent with a flow rate of 0.5 mL/min with RI-detector working at 35 °C, was used to analyze the liquid products. The retention time of the compounds analyzed were 11.6 min for pyruvic acid, 15.6 min for lactic acid, and 20.2 min for propanediol. The gases produced during the measurement were not analyzed.

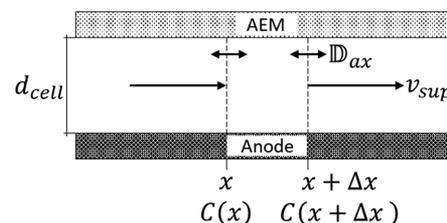
## THEORETICAL MODEL

The modeling approach for the present system covers the two main phenomena that determine the performance of the electrochemical process: the pulsation of the electrolyte and the mass transfer through the boundary layer in the anode compartment.

Prior to describing the modeling strategy, the effect of pulsation of the electrolytes' flow in the system must first be understood. Both the amplitude and the frequency of the pulsations play a role. The non-dimensional Strouhal (*Sr*) number is often used to characterize the regimes in oscillatory flow phenomena. It is the ratio of the velocity scale associated with flow (i.e., convection velocity) and the velocity scale associated with the oscillation (i.e., the pulse intensity, product of frequency and amplitude). When a pulsated flow for the electrolyte is introduced and the pulsation (with a given pulse volume, typically larger than the cell volume, meaning the full contents of the reactor are passing into and out of the cell on each stroke) is carried out at a low Strouhal number ( $Sr \leq 1$ ), the flow is dominated by convection through the cell. In this case, the oscillations are too weak to induce enhanced mixing, resulting in a flow regime resembling plug-flow. At high Strouhal numbers (when  $Sr \gg 1$ ), the flow is dominated by the oscillations that strongly enhance mixing. In addition, this will affect the boundary layer on the electrode and reduce the mass transfer limitation. This results in a flow regime that is losing its plug-flow character with increasing pulsation intensity, and the cell behaves more as a stirred tank reactor than a plug-flow reactor. In that case, the products and reactants will mix, effectively reducing the concentration of the reactants and decreasing the reaction rate. However, it must be stressed that the residence time inside the reactor will be the same regardless of the presence of pulsation, as the net flowrate is not altered by the pulsation.

A convenient way to account for pulsation-induced mixing in a model of the electrochemical cell is introducing an axial dispersion term for a plug-flow reactor model, as stated by Hoedemakers.<sup>14</sup> This axial dispersion term has the advantage that only the time-averaged effect of the pulsations is considered, which means that the model is a steady-state representation of the cell (i.e., no time-resolved calculations necessary).

Figure 2 represents a control volume of a portion of fluid in the flow cell, and outlines the mass balance terms for the



**Figure 2.** Simplified drawing of a portion of fluid of thickness  $\Delta x$ . In this sketch, meshwire or other design features present in the flow cell have not been depicted. AEM is the anion exchange membrane,  $d_{\text{cell}}$  is the compartment thickness (from anode to AEM),  $x$  is the longitudinal position within the reactor,  $C(x)$  is the concentration of an arbitrary species at position  $x$ ,  $v_{\text{sup}}$  is the superficial velocity of liquid in  $x$  direction, and  $D_{\text{ax}}$  is the axial dispersion coefficient.

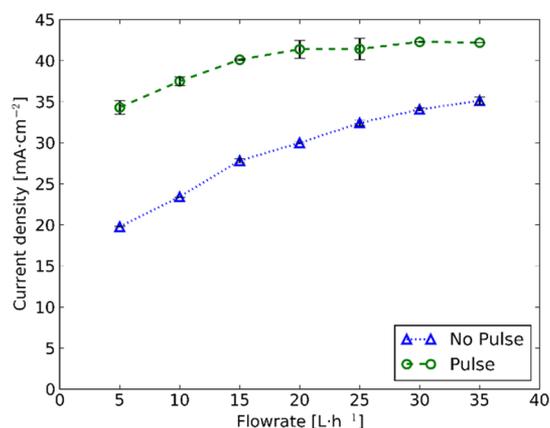
abovementioned plug-flow model with axial dispersion. Here, an arbitrary substance of concentration  $C(x)$  is convected through the reactor at superficial velocity  $v_{\text{sup}}$ , experiencing axial dispersion characterized by the axial dispersion coefficient,  $D_{\text{ax}}$ . This axial dispersion term is dependent on the liquid velocity, internal cell geometry, frequency, and displaced volume (amplitude) of pulsation, and will govern the degree of back-mixing within the flow cell when pulsations are present. In case of low dispersion, when the dispersion coefficient is comparable to the molecular diffusivity, the main mechanism for mass transfer at an electrode surface is molecular diffusion. Due to the slow rate of this process, mass transfer limits the oxidation reaction of ACT-TEMPO<sup>•</sup> at the anode. As a result, the reaction of ACT-TEMPO<sup>•</sup> with PDO and LA in the bulk of the liquid electrolyte will also be limited. In case of high dispersion, convection and mixing are the dominating mechanisms in mass transfer between the anode and the bulk. In that case, mass transfer will be significantly improved with respect to the diffusive case.

The second major aspect to be covered is the mass transfer of the electroactive species through the boundary layer developed at the anode surface. The boundary layer is modeled as a stagnant layer of fluid on the electrode surface in which the mass transfer of any species is dominated by diffusion. Quantifying mass transfer for the mediator (ACT-TEMPO) is necessary to model this process, as it mediates the oxidation reactions of PDO and LA. Determination of the mass transfer coefficient can be performed using correlations dependent on the flow regime and reactor internal geometry. Da Costa et al.<sup>23</sup> provided a method to estimate mass transfer coefficients for *spacer-filled channels*, a system that very much resembles the wire mesh present in this experimental study.

More detailed information of the developed model can be found in the [Supporting Information](#), section Theoretical Model.

## RESULTS AND DISCUSSION

In order to test the effect of the pulsation in an electrochemical reactor, the oxidation of PDO to LA and further to PA mediated by ACT-TEMPO<sup>+</sup> was studied at different flowrates without and with a pulsation of 2.6 Hz. Figure 3 shows the



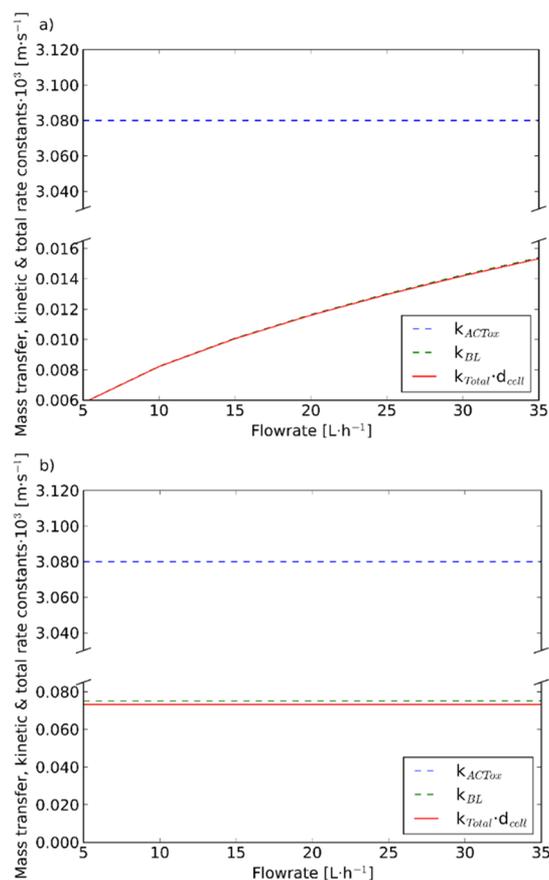
**Figure 3.** Current density measured during oxidation of 0.1 M PDO to LA and PA mediated by 20 mM ACT-TEMPO at a cell voltage of 2.5 V as a function of the electrolyte flowrate for a pulsating system (green circles) and for a non-pulsating system (blue triangles).

current density measured during the electrochemical reaction as a function of the electrolyte flowrate for a cell voltage of 2.5 V. For a non-pulsating system (blue triangles), the current density increases with increasing the flowrate of the anolyte and catholyte. This demonstrates mass transfer limitation. With increasing flowrate, the boundary layer on the electrode diminishes, and the reactants in the cell are continuously replenished. Both effects stimulate mass transfer, as expressed in the increased current density. At the lowest flowrate tested (5 L·h<sup>-1</sup>), the current density without a pulsation is  $\sim 20$  mA·cm<sup>-2</sup> compared to 35 mA·cm<sup>-2</sup> when a pulsation of 2.6 Hz is introduced ( $\sim 75\%$  increase). The pulsations enhance mass transfer of ACT-TEMPO<sup>+</sup> to the electrode, enhancing the oxidation reaction and leading to an increase in current.

Another important phenomenon that is shown in Figure 3 is that the current density reaches maximum value for flowrates exceeding 20 L·h<sup>-1</sup> in the pulsed flow situation. It is conjectured that this is caused by the fact that the bulk reactions (i.e., oxidation of PDO to LA and then LA to PA) become rate limiting at high flowrates. With increasing flowrate, the residence time of the reactants in the cell decreases. In addition, the pulsations enhance mixing. When residence time is decreased, all reactions have less time to run to completion, so the conversion decreases. This means that the conversion of ACT-TEMPO<sup>+</sup> to ACT-TEMPO<sup>•</sup> is also decreasing, effectively lowering the concentration of ACT-TEMPO. Another effect of pulsation is that the better mixing causes concentration gradients over the reactor to minimize, so there are no local zones with high concentrations for the pulsed case. Eventually, a lower concentration of ACT-TEMPO<sup>•</sup> will result in a limitation of the current density.

An alternative hypothesis of this current limitation is the ACT-TEMPO<sup>•</sup> oxidation being the rate-limiting step. However, this phenomenon is covered by the kinetic rate constant of the ACT-TEMPO<sup>•</sup> oxidation that was determined in the rotating disk electrode (RDE) experiments (see section Rotating disk electrode experiments in the Supporting

Information), which was shown to be much higher than the boundary layer mass transfer coefficient. Therefore, the most likely explanation for the current limitation is the kinetics of the bulk reaction becoming rate limiting at high flowrates (see Figure 4). Additional experiments will need to be performed to corroborate this theory.



**Figure 4.** Calculated rate constants for the (a) non-pulsed and (b) pulsed flow situations for mass transfer of ACT-TEMPO in the boundary layer ( $k_{BL}$ , dotted green line), for the electrochemical oxidation of ACT-TEMPO<sup>•</sup> ( $k_{ACTox}$ , dotted blue line) and the overall rate constant and a combination of both ( $k_{Total} \cdot d_{cell}$ , solid red line) as a function of electrolyte flowrate for a pulsation frequency of 2.6 Hz and a displaced volume of 20 mL. More information about the calculation of the rate constants can be found in the section Theoretical model of the Supporting Information document.

To evaluate the effect of the net flowrate and the pulsations on the overall reaction rate, the overall rate constant in the boundary layer needs to be calculated. It consists of two contributions: the electrochemical reaction on the electrode and the boundary layer mass transfer coefficient. The electrochemical reaction rate constant is retrieved from RDE experiments. The mass transfer can be evaluated from a Sherwood correlation for the flow configuration of the electrochemical cell with spacer mesh, as employed in the present work (see the section Theoretical model in the Supporting Information).

Tables 1 and 2 show the Sherwood ( $Sh$ ) numbers calculated for different flowrates for the non-pulsating and pulsating system, respectively. For the non-pulsating configuration, Sherwood numbers are low, illustrating the mass transfer limitation in this case.  $Sh$  in a pulsating system is 5 to 13 times higher

**Table 1. Summary of Process Parameters and Coefficients for the Non-Pulsed Configuration of the Electrochemical Conversion of 1,2-Propanediol to Lactic and Pyruvic Acid at a Cell Voltage of 2.5 V as a Function of the Electrolyte Flowrate<sup>a</sup>**

flowrate [L·h <sup>-1</sup> ]	$D_{a,x} \cdot 10^6$ [m <sup>2</sup> ·s <sup>-1</sup> ]	Sh [-]	Sr [-]	residence time [s]	$k_{BL} \cdot 10^6$ [m·s <sup>-1</sup> ]	$k_{Anode} \cdot 10^3$ [s <sup>-1</sup> ]	$v_{pulse} \cdot 10^3$ [m·s <sup>-1</sup> ]	$v_{int} \cdot 10^3$ [m·s <sup>-1</sup> ]	$v_{tot} \cdot 10^3$ [m·s <sup>-1</sup> ]
5	5.83	11.7	0.00	120	5.82	2.15	0.00	2.47	2.47
10	11.7	16.6	0.00	59.8	8.23	3.04	0.00	4.94	4.94
15	17.5	20.3	0.00	39.8	10.1	3.72	0.00	7.41	7.41
20	23.3	23.4	0.00	29.9	11.6	4.29	0.00	9.87	9.87
25	29.2	26.2	0.00	23.9	13.0	4.80	0.00	12.3	12.3
30	35.0	28.7	0.00	19.9	14.2	5.25	0.00	14.8	14.8
35	40.8	31.0	0.00	17.1	15.4	5.67	0.00	17.3	17.3

<sup>a</sup>Parameters  $k_{BL}$  and  $k_{Anode}$  are covered in the Supporting Information, section Theoretical model.

**Table 2. Summary of Process Parameters and Coefficients for the Pulsed Configuration of Electrochemical Conversion of 1,2-Propanediol to Lactic and Pyruvic Acid at a Cell Voltage of 2.5 V as a Function of the Electrolyte Flowrate for a Pulsation Frequency of 2.6 Hz<sup>a</sup>**

flowrate [L·h <sup>-1</sup> ]	$D_{a,x} \cdot 10^6$ [m <sup>2</sup> ·s <sup>-1</sup> ]	Sh [-]	Sr [-]	residence time [s]	$k_{BL} \cdot 10^6$ [m·s <sup>-1</sup> ]	$k_{Anode} \cdot 10^3$ [s <sup>-1</sup> ]	$v_{pulse} \cdot 10^3$ [m·s <sup>-1</sup> ]	$v_{int} \cdot 10^3$ [m·s <sup>-1</sup> ]	$v_{tot} \cdot 10^3$ [m·s <sup>-1</sup> ]
5	327	151	470	120	75.0	27.1	581	2.47	411
10	329	151	235	59.8	75.0	27.1	581	4.94	411
15	332	151	157	39.8	75.0	27.1	581	7.41	411
20	335	151	118	29.9	75.0	27.1	581	9.87	411
25	338	151	94.1	23.9	75.0	27.1	581	12.3	411
30	341	151	78.4	19.9	75.1	27.1	581	14.8	411
35	344	151	67.2	17.1	75.1	27.1	581	17.3	411

<sup>a</sup>Parameters  $k_{BL}$  and  $k_{Anode}$  Are Covered in the Supporting Information, section Theoretical model.

than in the non-pulsating system, indicating a significantly higher mass transfer rate of ACT-TEMPO<sup>•</sup> toward the electrode for the pulsating situation.

For pulsating systems, the total velocity (see  $v_{tot}$  in Tables 1 and 2) has two terms: net flow velocity ( $v_{int}$ ) and a fluctuating velocity caused by the pulsation ( $v_{pulse}$ ). The latter component is taken into account by calculating its root mean square (RMS) value. This RMS pulsation velocity is determined by the pulsation amplitude and frequency; it can be seen as a measure for the time-averaged effect of pulsations on the flow. Because of the selected pulsation conditions,  $v_{pulse}$  is two orders of magnitude greater than  $v_{int}$  for the pulsed configuration (see Table 2), rendering  $v_{tot}$  almost independent of the flowrate. The consequence is that  $Sh$ , and therefore the mass transfer, increases with total fluid velocity, which is dominated by the pulsation-induced velocity in the pulsed configuration. Hence, mass transfer is independent from the net flow in this case. The expression to determine each component of the flow velocity can be found in the section Theoretical model, in the Supporting Information.

To determine the rate limiting step in the mass transfer and oxidation process of ACT-TEMPO<sup>•</sup> to ACT-TEMPO<sup>+</sup>, the overall rate constant (see the section Theoretical model in the Supporting Information) in the boundary layer was plotted against the net flowrate for both pulsed and non-pulsed configurations. Figure 4 shows the mass transfer, kinetic, and overall rate constants for ACT-TEMPO. From both figures, it appears that the overall rate is determined primarily by the boundary layer mass transfer rate since the kinetic rate constant of the ACT-TEMPO<sup>•</sup> oxidation is one or two orders of magnitude higher than the boundary layer mass transfer constant (depending on the presence of the pulsations) and therefore does not limit the overall rate. It is important to note that, even though the mass transfer rate in the pulsed

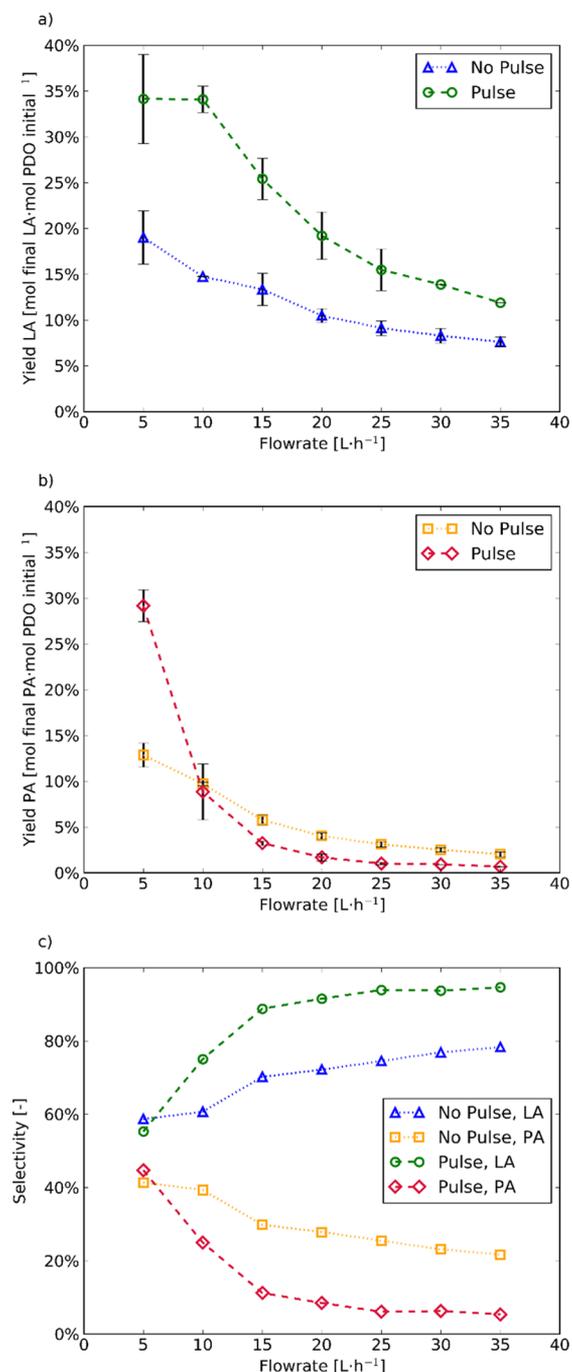
configuration is much higher than for the non-pulsed configuration, the process is still mass transfer limited.

## ■ LA AND PA YIELD

During the electrochemical reaction, the liquid products formed at the anode were collected and analyzed by HPLC. The LA and PA yields are shown in Figure 5 as a function of the net electrolyte flowrate without and with a pulsation of 2.6 Hz. For both pulsed and non-pulsed configurations, both yields decrease with increasing flowrate due to the lower residence time of the active species in the reactor at higher flowrates.

Introduction of pulsations doubles the LA yield with respect to the non-pulsating situation due to the induced mixing created by the pulsations and therefore increased dispersion in the flow. The effect of increased dispersion causes an increase in the Sherwood number and hence a better mass transfer of ACT-TEMPO<sup>•</sup>, causing a higher LA formation rate.

LA can be further oxidized to PA according to reaction eq 3. Figure 5b shows the yield of PA as a function of the electrolyte flowrate with and without pulsation. For low flowrates (5 L·h<sup>-1</sup>), the yield of PA is 60% higher for the pulsating system compared to the non-pulsating system. However, at higher flowrates, the yield of PA sharply decreases and becomes lower than the PA yield for the non-pulsed configuration at flowrates higher than 10 L·h<sup>-1</sup>. For flowrates over 35 L·h<sup>-1</sup>, the PA yield is even approaching 0%. The higher initial yield of PA at low flowrates is due to higher availability of LA (Figure 5a) and, in particular, for the pulsed situation, due to the higher mass transfer of ACT-TEMPO<sup>•</sup>, as explained before. The residence time appears to offer enough time for both oxidation reactions (PDO to LA and LA to PA) to take place. The sharp drop of the PA yield at higher flowrates is mostly due to the lower residence time. The formation of PA can only take place when LA is formed first, so the formation of PA is delayed with



**Figure 5.** Yield of (a) lactic acid and (b) pyruvic acid and (c) the selectivity of the reaction toward lactic and pyruvic acids for the oxidation of 0.1 M PDO mediated by 20 mM ACT-TEMPO at a cell voltage of 2.5 V as a function of the electrolyte flowrate in a pulsating system and in a non-pulsating system. The selectivity values in graph (c) were calculated as the quotient of the yield of lactic acid or pyruvic acid by the sum of the yields of lactic acid and pyruvic acid for each value of flowrate.

respect to LA. This causes the selectivity of the reaction to shift toward LA. This effect is amplified by the back-mixing generated by the pulsations. LA will mix with fresh feed, which effectively lowers the concentration of LA, resulting in a reduced reaction rate toward PA. Additionally, ACT-TEMPO is more selective for oxidation of primary alcohols than secondary alcohols, i.e., PDO oxidation over LA oxidation.<sup>24</sup>

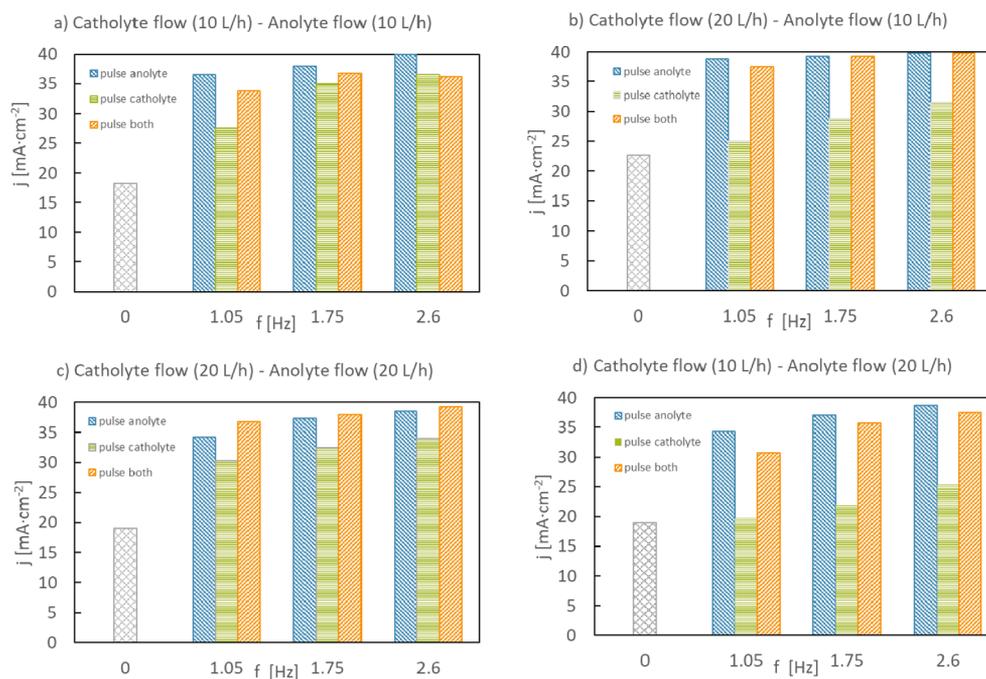
Figure 5c shows the selectivity of the reactions toward LA and PA as a function of the electrolyte flowrate for a non-pulsating and for a pulsating system with a frequency of 2.6 Hz. The highest selectivity for LA (~95%) can be achieved at a high flowrate (e.g., 35 L·h<sup>-1</sup>) and with a pulsating electrolyte.

The results of product yield and selectivity can be complemented with the calculated values of Faradaic or current efficiency (FE) for reaction eqs 2 and 3 (see the section Faradaic or current efficiency calculation, Figure S4, in the Supporting Information). The trends observed in the FE values with respect to the flowrate, both for pulsed and non-pulsated situations, are in agreement with the results of the yield of LA and PA in Figure 5a,b, i.e., an increase in FE for LA from ~50 to 75% in the non-pulsated situation and a decrease of the FE value for PA as the flowrate increases from ~15 to 10% without pulse. Importantly, the introduction of the pulsed flow increases the FE for LA production from 75 to 100% for a flowrate of 35 L·h<sup>-1</sup> and reduces the FE for the PA production from 10 to almost 0% for the same flowrate. The increase in FE with the introduction of pulsations also has a positive impact on the specific energy consumption (SEC) of the PDO oxidation to LA, leading to a decrease of the SEC to 30% with respect to the non-pulsated situation (see the section Specific energy consumption of the electrochemical process in the Supporting Information).

## FREQUENCY STUDY

In order to understand the effect of the pulsation, the electrochemical conversion of PDO to LA and PA mediated by ACT-TEMPO was studied in a system where the pulsation frequency can be changed, and the pulsation can be present only in the anolyte flow, only in the catholyte flow, or in both electrolyte flows. In addition, different flowrates were set independently for the anolyte and catholyte flows. Figure 6 shows the current density associated to the electrochemical reaction as a function of the pulsation frequency for different flowrate combinations.

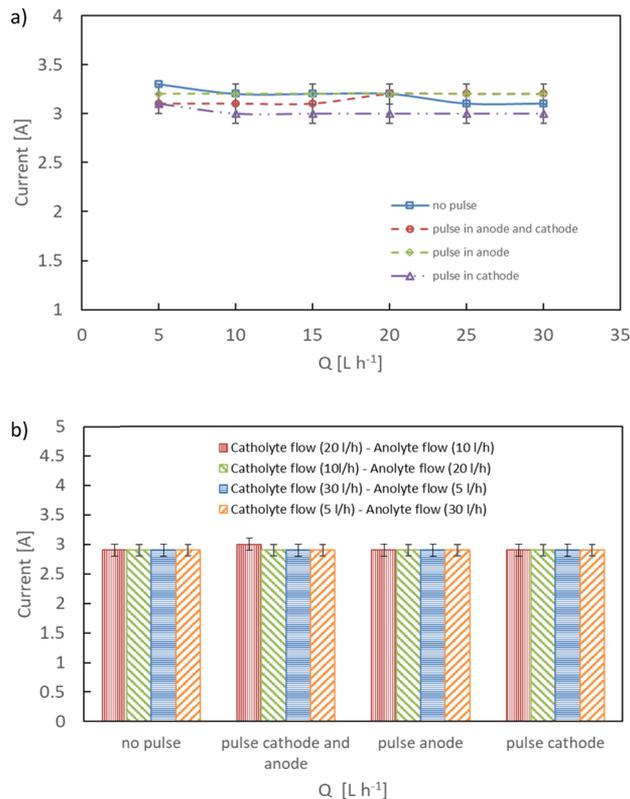
The most significant increase in current density is caused by the presence of a pulsation in the system above 1 Hz. The frequency of the pulsation has a much smaller effect on the current density. Higher frequencies lead to slightly higher current density, but the effect is not significant compared to the presence or absence of pulsations. This is in accordance with the predicted boundary layer mass transfer constant as a function of pulsation frequency (see the section Influence of pulsation frequency on mass transfer and overall rate constants, Figure S5 in the Supporting Information). Secondly, imposing pulsations on the anolyte flow results in a significantly higher current density than pulsations on the catholyte flow. This can be understood from the fact that the reaction of PDO to LA and PA takes place on the anode side, so there is a direct effect of the pulsations on the mass transfer of ACT-TEMPO. Pulsations on the catholyte side have an indirect effect since they could affect the mass transfer of OH<sup>-</sup> over the membrane. Nevertheless, pulsations on the catholyte side still cause up to 100% increase of current density, depending on pulse frequency and catholyte and anolyte flowrates. This effect may be explained by the stimulated mass transfer of OH<sup>-</sup> over the membrane since it is likely there is also a mass transfer limitation to and from the membrane. Another possible explanation is enhanced mixing due to membrane deformation and stimulated bubble transport.



**Figure 6.** Current density measured during the oxidation of 0.1 M PDO mediated by 20 mM ACT-TEMPO at a cell voltage of 2.5 V as a function of the pulsation frequency at different electrolyte flowrate combinations and the location of the pulsation.

The pulsation can induce a faster removal of gas bubbles on the electrode surface, which can block active electrochemical sites. These bubbles might be generated by the oxygen evolution reaction (OER) in the anode, and the hydrogen evolution reaction (HER) in the cathode. The removal of gas bubbles can induce a better mixing of species in the cell. Given that the cathodic reaction is based upon a non-mass transfer-limited reaction (HER), the removal of the bubbles would only affect the increase of availability of the active electrochemical sites for this reaction, while a better mixing of species will not play a significant role. Alternatively, the bending of the membrane that separates the cathode and the anode compartments can influence the reaction performance. Although the membrane is fixed in between two meshes in the catholyte and anolyte flow chambers, small bending of the membrane in the direction normal to electrode surface occurs when the flowrates in both compartments are not equal. When the flowrate of the catholyte is higher than the anolyte, the catholyte compartment expands slightly, decreasing the thickness of the anolyte compartment. This induces a higher flowrate in the compartment, resulting in a decreased thickness of the boundary layer and a higher mass transfer of the active species to and from the electrode.

In order to test these hypotheses, a control experiment (see Figure 7) was carried out where both cathodic and anodic reactions were based on non-mass transfer limited reactions, i.e., HER and OER. Figure 7a shows the current associated with the electrochemical process as a function of the flowrate for four configurations: non-pulsating, only pulsations of the anolyte, only pulsations of the catholyte, and pulsations of both the anolyte and the catholyte. First, the current is independent of the flowrate, indicating that the reaction is not mass transfer-limited for any of the four configurations. Noteworthy, the current also does not change significantly when pulsations are applied or not, regardless of the side they are applied upon. Figure 7b shows the current associated to the electrochemical



**Figure 7.** (a) Current measured during HER and OER at a cell voltage of 2.5 V as a function of the flowrate without pulsations, with pulsations in the anode, with pulsations in the cathode, and with pulsations in both anode and cathode compartments. (b) Current measured during water-splitting reaction at a cell voltage of 2.5 V for different electrolyte flowrate combinations for non-pulsed and pulsed configurations in either one or both compartments.

process for the four configurations and different ratios of anolyte and catholyte flows. These results suggest that there is no significant change in the performance of these electrochemical reactions (HER and OER) due to the pulsation induced removal of gas bubbles. In addition, it is conjectured that the increase in current depending on the position of the pulsation and depending on the relative flowrate of the catholyte versus the anolyte during the conversion of PDO to LA and PA is not caused by the removal of gas bubbles.

Knowing that pulsation parameters (displacement volume and frequency) have an effect in the performance of the oxidation of PDO to LA and PA mediated by ACT-TEMPO different reactor conditions should be tested, changing not only the frequency of the pulse but also the displacement volume in order to see the changes in yield toward products and selectivity. However, results of this work are not yet available for the present publication.

## CONCLUSIONS

It has been shown that the introduction of a pulsating flow in an electrochemical reactor shows several advantages in the performance of the conversion in the showcase of PDO to LA and PA mediated by ACT-TEMPO. A pulsating flow leads to an increase in the current associated to the reaction compared to a non-pulsating system. The conversion of PDO to LA in the presence of pulsation exhibits an increase in LA yield of a factor two compared to the non-pulsed system. More importantly, the selectivity for the products of PDO oxidation (LA and PA) can be tuned by adjusting the flowrates and the pulse frequency of the electrolytes for a given displacement volume. A high selectivity of LA (~95%) was obtained when the reaction of PDO mediated by ACT-TEMPO was performed at high flowrates (higher than 20 L·h<sup>-1</sup>) and a pulse frequency of 2.6 Hz. Compared to the non-pulsed case, this is an increase between 15 and 20%. The presence of a pulsation has two effects in the electrochemical system. First, the pulsation has a strong effect on the mass transfer of species to and from the electrode. The theoretical calculations show that the Sherwood number of the system with a pulsation is significantly higher than in the non-pulsating system due to the high instantaneous velocity caused by the pulse. Second, the pulsation induces back mixing which leads to dilution of species, thereby having a significant effect on the selectivity of the different products.

The overall rate of PDO oxidation is mainly determined by the boundary layer mass transfer rate since the kinetic rate constant of the oxidation of the mediator is two orders of magnitude higher than the mass transfer rate despite the presence of pulsations that significantly increase the mass transfer rate. Hence, the process is still mass transfer-limited.

Moreover, it was shown that the presence of pulsation in the catholyte and its relative flowrate with respect to the anolyte have a small influence on the performance of the ACT-TEMPO mediated reaction in terms of conversion. For reactions such as HER and OER, which are not mass transfer limited, the pulsation does not influence the current or conversion associated to the electrochemical process. It is concluded that there is no significant change in the performance of the HER and OER reactions due to the pulsation induced removal of gas bubbles at studied current densities. Therefore, it can be assumed that the removal of gas bubbles does not play an important role either in the ACT-TEMPO mediated reaction.

The studied reaction served as an example of the promising potential of introducing a pulsating flow with a view of improving the performance of mass transfer limited electrochemical reactions.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.9b06925>.

Picture of the set-up, Effect of pulsation in the net flow, rotating disk electrode experiments, theoretical model, Faradaic or current efficiency calculation, specific energy consumption of the electrochemical process, and influence of pulsation frequency on mass transfer and overall rate constants (PDF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors acknowledge VoltaChem for the financial support.

## REFERENCES

- (1) Vennekoetter, J. B.; Sengpiel, R.; Wessling, M. Beyond the Catalyst: How Electrode and Reactor Design Determine the Product Spectrum during Electrochemical CO<sub>2</sub> Reduction. *Chem. Eng. J.* **2019**, *364*, 89–101.
- (2) Frontana-Uribe, B. A.; Little, R. D.; Ibanez, J. G.; Palma, A.; Vasquez-Medrano, R. Organic Electrosynthesis: A Promising Green Methodology in Organic Chemistry. *Green Chem.* **2010**, *12*, 2099–2119.
- (3) Kovács, L. Electrochemical Mass Transfer in Active and Passive Fluidized Beds. *Period. Polytech., Chem. Eng.* **1980**, *24*, 171–187.
- (4) Cognet, P.; Berlan, J.; Lacoste, G.; Fabre, P.-L.; Jud, J.-M. Application of Metallic Foams in an Electrochemical Pulsed Flow Reactor Part I: Mass Transfer Performance. *J. Appl. Electrochem.* **1995**, *25*, 1105–1112.
- (5) Houghton, R. W.; Kuhn, A. T. Mass-Transport Problems and Some Design Concepts of Electrochemical Reactors. *J. Appl. Electrochem.* **1974**, *4*, 173–190.

(6) Leitz, F. B.; Marinčić, L. Enhanced Mass Transfer in Electrochemical Cells Using Turbulence Promoters. *J. Appl. Electrochem.* **1977**, *7*, 473–484.

(7) Walsh, F.; Reade, G. Design and Performance of Electrochemical Reactors for Efficient Synthesis and Environmental Treatment. Part I. Electrode Geometry and Figures of Merit. *Analyst* **1994**, *119*, 791–796.

(8) Ramdin, M.; Morrison, A. R. T.; De Groen, M.; Van Haperen, R.; De Kler, R.; Van Den Broeke, L. J. P.; Trusler, J. P. M.; De Jong, W.; Vlugt, T. J. H. High Pressure Electrochemical Reduction of CO<sub>2</sub> to Formic Acid/Formate: A Comparison between Bipolar Membranes and Cation Exchange Membranes. *Ind. Eng. Chem. Res.* **2019**, *58*, 1834–1847.

(9) Pillai, I. M. S.; Gupta, A. K. Performance Analysis of a Continuous Serpentine Flow Reactor for Electrochemical Oxidation of Synthetic and Real Textile Wastewater: Energy Consumption, Mass Transfer Coefficient and Economic Analysis. *J. Environ. Manage.* **2017**, *193*, 524–531.

(10) Kotb, Y.; Fateen, S.-E. K.; Albo, J.; Ismail, I. Modeling of a Microfluidic Electrochemical Cell for the Electro-Reduction of CO<sub>2</sub> to CH<sub>3</sub>OH. *J. Electrochem. Soc.* **2017**, *164*, E391–E400.

(11) Granados-Mendoza, P.; de Groot, M. T.; Keurentjes, J. T. F.; Schouten, J. C.; van der Schaaf, J. Intensification of Electrochemical Processes by Enhancing the Mass Transfer and Promoting Efficient Bubble Removal Using the Rotor-Stator Spinning Disc Reactor. In *ECCE10+ECAB3+EPICS : September 27th - October 1st, 2015, Nice, France*; Nice, France, 2017; pp 2–3.

(12) Coleman, S.; Roy, S. Effect of Ultrasound on Mass Transfer during Electrodeposition for Electrodes Separated by a Narrow Gap. *Chem. Eng. Sci.* **2014**, *113*, 35–44.

(13) Wang, J.; Li, T.; Zhou, M.; Li, X.; Yu, J. Characterization of Hydrodynamics and Mass Transfer in Two Types of Tubular Electrochemical Reactors. *Electrochim. Acta* **2015**, *173*, 698–704.

(14) Hoedemakers, G. F. M. *Continuous Emulsion Polymerization in a Pulsed Packed Column*, Technische Universiteit Eindhoven, 1990.

(15) Belmant, C.; Cognet, P.; Berlan, J.; Lacoste, G.; Fabre, P. -L.; Jud, J. -M. Application of an Electrochemical Pulsed Flow Reactor to Electroorganic Synthesis: Part I: Reduction of Acetophenone. *J. Appl. Electrochem.* **1997**, *28*, 185–191.

(16) Pérez-Gallent, E.; Turk, S.; Latsuzbaia, R.; Bhardwaj, R.; Anastasopol, A.; Sastre-Calabuig, F.; Garcia, A. C.; Giling, E.; Goetheer, E. Electroreduction of CO<sub>2</sub> to CO Paired with 1,2-Propanediol Oxidation to Lactic Acid. Toward an Economically Feasible System. *Ind. Eng. Chem. Res.* **2019**, *58*, 6195–6202.

(17) de Nooy, A. E. J.; Besemer, A. C.; van Bekkum, H. Highly Selective Tempo Mediated Oxidation of Primary Alcohol Groups in Polysaccharides. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 165–166.

(18) Rafiee, M.; Konz, Z. M.; Graaf, M. D.; Koolman, H. F.; Stahl, S. S. Electrochemical Oxidation of Alcohols and Aldehydes to Carboxylic Acids Catalyzed by 4-Acetamido-TEMPO: An Alternative to “Anelli” and “Pinnick” Oxidations. *ACS Catal.* **2018**, *8*, 6738–6744.

(19) Komesu, A.; de Oliveira, J. A. R.; da Silva Martins, L. H.; Maciel, M. R. W.; Filho, R. M. Lactic Acid Production to Purification: A Review. *BioResources* **2017**, *12*, 4364–4383.

(20) Garat, A.; Gras, J. Corrosion Study of Nickel for Alkaline Water Electrolysis. *Int. J. Hydrogen Energy* **1983**, *8*, 681–688.

(21) Hall, D. E. Electrodes for Alkaline Water Electrolysis. *J. Electrochem. Soc.* **1981**, *128*, 740–746.

(22) Cha, H. G.; Choi, K. S. Combined Biomass Valorization and Hydrogen Production in a Photoelectrochemical Cell. *Nat. Chem.* **2015**, *7*, 328–333.

(23) Da Costa, A. R.; Fane, A. G.; Wiley, D. E. Spacer Characterization and Pressure Drop Modelling in Spacer-Filled Channels for ultrafiltration. *J. Membr. Sci.* **1994**, *87*, 79–98.

(24) Ciriminna, R.; Ghahremani, M.; Karimi, B.; Pagliaro, M. Electrochemical Alcohol Oxidation Mediated by TEMPO-like Nitroxyl Radicals. *ChemistryOpen* **2017**, *6*, 5–10.