

## Supporting information

# Overcoming mass transport limitations in electrochemical reactors with a pulsating flow electrolyzer

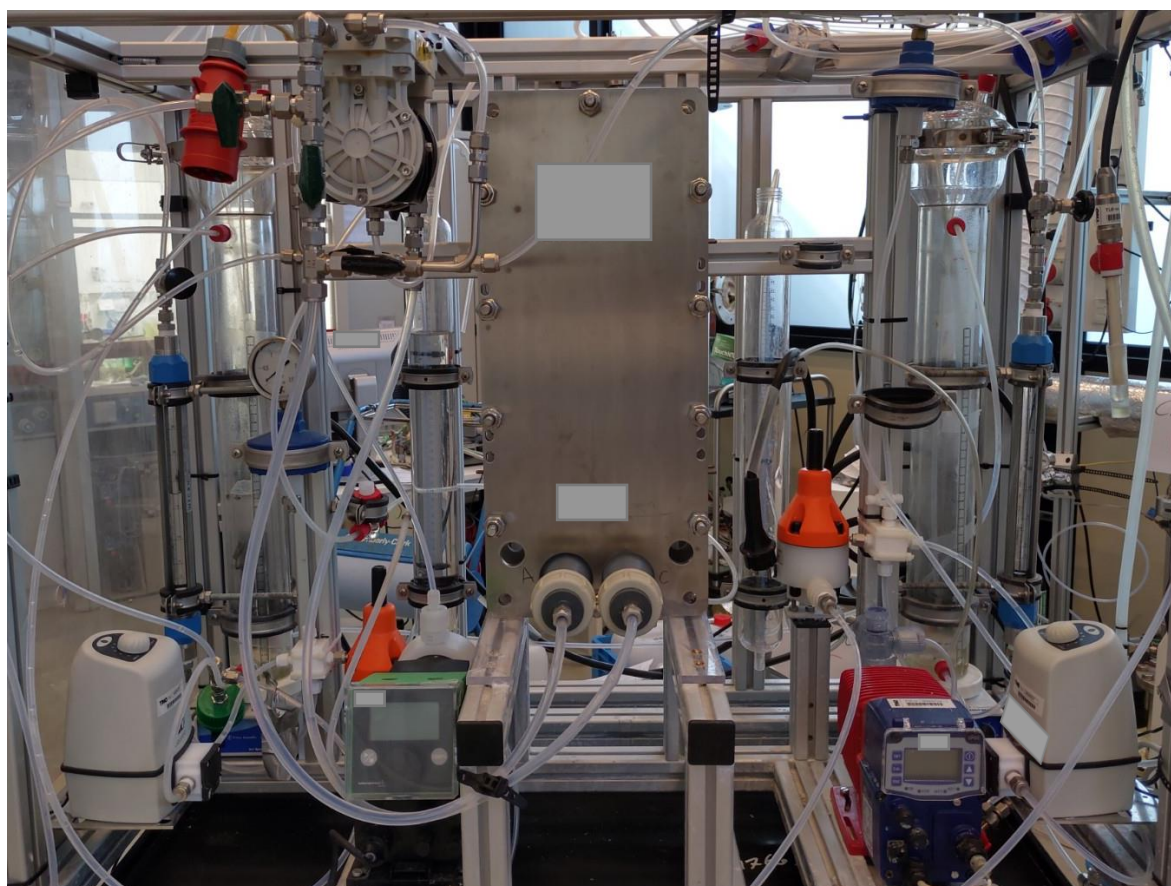
Elena Pérez-Gallent<sup>\*1</sup>, Carlos Sánchez-Martínez<sup>1</sup>, Leon F. G. Geers<sup>1</sup>, Susan Turk<sup>1</sup>, Roman Latsuzbaia<sup>1</sup>, Earl L. V. Goetheer<sup>\*1,2</sup>

<sup>1</sup>Department of Sustainable Process and Energy Systems, TNO, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

<sup>2</sup>Process and Energy, Delft University of Technology, Leeghwaterstraat 39, 2628 CB Delft, The Netherlands

[\\*elena.perezgallent@tno.nl](mailto:elena.perezgallent@tno.nl), [\\*earl.goetheer@tno.nl](mailto:earl.goetheer@tno.nl)

### 1. Picture of the setup



**Figure S.1.** Picture of the pulsating flow setup.

## 2. Effect of the pulsation in the net flow

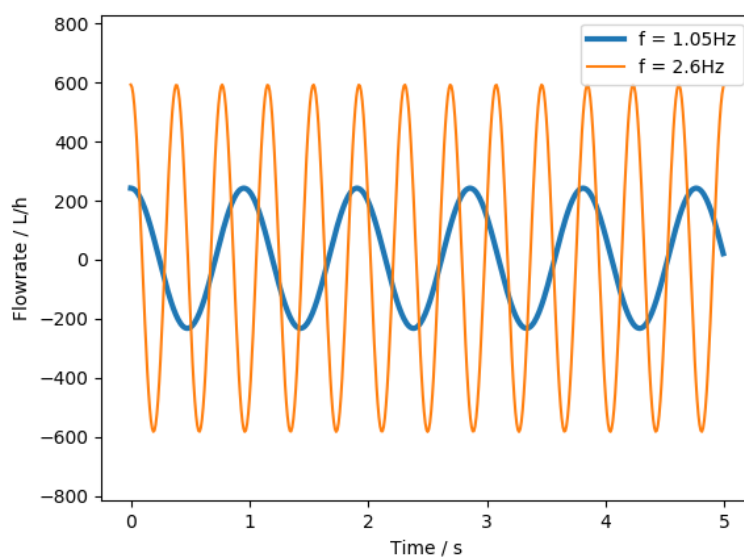
The total flowrate through the cell in a pulsed configuration is given by Equation (1) as the sum of the (constant) net flow through the cell and the time-dependent pulsating flowrate. Equation (2) gives the expression for the pulsating flowrate.

$$\Phi_{v,total}(t) = \Phi_{v,pulse}(t) + \Phi_{v,net}(t) \quad (1)$$

$$\Phi_{v,pulse}(t) = \pi \cdot V_0 \cdot f \cdot \cos(2\pi ft) \quad (2)$$

In which  $\Phi_{v,total}(t)$  is the total flowrate,  $\Phi_{v,pulse}(t)$  is the pulsating flowrate,  $\Phi_{v,net}(t)$  is the net convection flowrate through the cell,  $V_0$  is the total displaced volume of the pulsation (in the current setup this equates to 20 mL for each of the anolyte and catholyte),  $f$  is the frequency and  $t$  is time.

Figure S.2 presents the total flowrate as a function of time for two values of the pulsation frequency for a flowrate of 5 L/h in the setup as presented in the publication. As can be seen in the figure, the net flowrate is insignificant in comparison to the extremes of the pulsating flowrate: the maximum value of the pulsating flowrate is 238 L/h ( $\pi \cdot V_0 \cdot f$ ) for 1.05 Hz and 588 L/h for 2.6 Hz, compared to a net flowrate of 5 L/h.



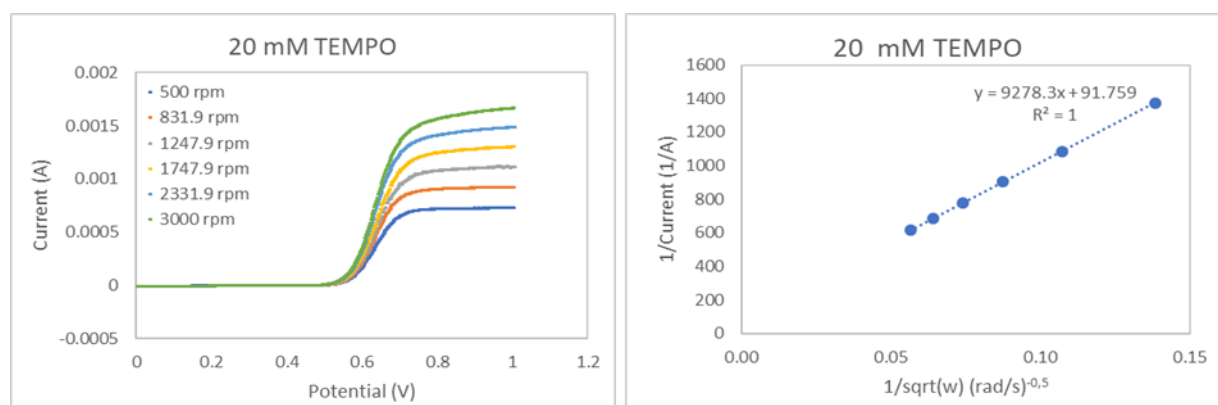
**Figure S.2.** Relative flow rate depending on the pulsation frequency for a net flow rate of 5 L/h.

### 3. Rotating disk electrode experiments

In order to study the kinetics of the interfacial process of ACT-TEMPO<sup>•</sup> oxidation, rotating disk electrode (RDE) experiments were carried out. Linear sweep voltammetry (LSV) of a graphite disk electrode in a 0.5 M KHCO<sub>3</sub> / 0.5 M K<sub>2</sub>CO<sub>3</sub> buffer solution containing 20 mM of ACT-TEMPO<sup>•</sup> was carried out in a single cell with different rotation rates and at a scan rate of 1 mV/s. The LSV results are shown in Figure S.3. From the limiting current observed at 0.9 V in Figure S.3a, the Koutecký-Levich plot (Figure S.3b) was constructed and Equation (3) was fit to the data to retrieve the kinetically controlled rate constant and the diffusivity of the ACT-TEMPO<sup>•</sup>.

$$\frac{1}{I} = \frac{1}{i_k} + \frac{1}{0.201FAD_0^{2/3}\nu^{-1/6}C_0\omega^{1/2}} \quad (3)$$

where  $I$  is the measured current at 0.9V,  $i_k$  is the kinetically controlled current that would be obtained for the limiting case of  $\omega^{-1/2} \rightarrow 0$ ,  $F$  is Faraday's constant,  $A$  the surface area of the disc electrode,  $D_0$  the diffusivity of ACT-TEMPO<sup>•</sup> in the solution,  $\nu$  the kinematic viscosity of the solution,  $\omega$  the rotation rate of the electrode and  $C_0$  the starting concentration of ACT-TEMPO<sup>•</sup>.



**Figure S.3.** a) Linear sweep voltammetry of a graphite electrode in a 0.5 M KHCO<sub>3</sub> / 0.5 M K<sub>2</sub>CO<sub>3</sub> buffer solution with 20 mM ACT-TEMPO performed at 1 mV/s at different rotation rates b) Koutecký-Levich plot.

The linear fit through the curve of  $1/I$  vs.  $1/\sqrt{\omega}$  in Figure S.3b shows a very strong correlation ( $R^2=1$ ). The intercept of the curve is equal to the reciprocal kinetic current, from which the kinetic rate constant of the electrochemical reaction  $k_{ACT_{ox}}$  at the electrode can be derived. Its value appeared to be  $1.07 \times 10^{-3}$  m/s. The diffusivity of ACT-TEMPO can be calculated from the slope of the curve and equated to  $2.22 \times 10^{-9}$  m<sup>2</sup>/s.

#### 4. Theoretical model

Before the model is described in detail, the definition is given of the Strouhal number, a non-dimensional quantity to characterize the different regimes in oscillatory flow phenomena.

$$Sr = \frac{f \cdot D}{U} \quad (4)$$

where  $f$  is the frequency of pulsation,  $D$  is a characteristic diameter (here the electrochemical cell thickness), and  $U$  is the convection velocity in the cell.

Referring to Figure 2 from the main article, the mass balance over a portion of fluid for the plug flow model with axial dispersion can be described with Equation (5):

$$\frac{\partial C_i}{\partial t} = \mathbb{D}_{ax} \cdot \frac{\partial^2 C_i}{\partial x^2} - \frac{v_{sup}}{\varepsilon} \cdot \frac{\partial C_i}{\partial x} + r_i \quad (5)$$

where  $C_i$  [ $\text{mol}/\text{m}^3$ ] is concentration of species  $i$  at instant  $t$  and position in reactor  $x$ ,  $t$  [s] is time,  $\mathbb{D}_{ax}$  [ $\text{m}^2/\text{s}$ ] is the axial dispersion coefficient,  $x$  [m] is the position along the reactor in the flow direction,  $v_{sup}$  [ $\text{m}/\text{s}$ ] is the superficial velocity of the liquid,  $\varepsilon$  [–] is the fraction of open space in the cell due to the spacer and  $r_i$  [ $\text{mol}/\text{m}^3 \cdot \text{s}$ ] is the reaction and transfer term of the species  $i$ .

The model is a one dimensional transport equation with axial dispersion. The bulk reactions are modeled by a reaction term and the electrochemical reactions (oxidation of ACT-TEMPO $\cdot$ ) are modeled by a diffusion-reaction term that covers both transport between the bulk and the anode and the reaction at the anode, reflected in Equation (6).

$$r_{ACT-TEMPO \cdot \text{ at electrode}} = k_{anode} [ACT - TEMPO \cdot] \quad (6)$$

where  $r_{ACT-TEMPO \cdot \text{ at electrode}}$  [ $\text{mol}/\text{m}^3 \cdot \text{s}$ ] is the oxidation rate of ACT-TEMPO $\cdot$  at the anode, given by the product of the overall rate constant  $k_{anode}$  [1/s] and the concentration of ACT-TEMPO $\cdot$ .  $k_{anode}$  is given by Equation (7).

$$k_{anode} = \frac{1}{\frac{d_{cell}}{k_{BL}} + \frac{1}{k_{ACT_{ox}}}} \quad (7)$$

where  $d_{cell}$  [m] is the thickness of the anolyte compartment (2.7 mm as stated in the main article), from electrode to membrane,  $k_{BL}$  [m/s] is the mass transfer coefficient of ACT – TEMPO $^+$  and ACT – TEMPO $\cdot$  through the boundary layer at the anode surface and  $k_{ACT_{ox}}$  [m/s] is the surface reaction constant for oxidation of ACT – TEMPO $\cdot$  at the anode (determined from RRDE experiments). From this equation it is clear that the overall rate constant is determined by the ratio between  $k_{BL}$  and  $k_{ACT_{ox}}$ .

Prior to determining the mass transfer constant, the terms that characterize the flow in a pulsed flow system, must be defined.

$$v_{sup} = \frac{\Phi_{vol}}{A_{cross}} \quad (8)$$

$$v_{int} = \frac{v_{sup}}{\varepsilon} \quad (9)$$

$$l_{stroke} = \frac{V_{pulse}}{A_{cross}} \quad (10)$$

$$v_{pulse} = \frac{\pi \cdot l_{stroke} \cdot f_{pulse}}{\varepsilon} \quad (11)$$

$$v_{tot} = \sqrt{v_{int}^2 + \frac{1}{2}v_{pulse}^2} \quad (12)$$

$$\tau = \frac{L_{cell}}{v_{int}} \quad (13)$$

where  $v_{sup}[m/s]$  is the superficial velocity of the fluid across the length of the anolyte compartment,  $\Phi_{vol}[m^3/s]$  is the volumetric flowrate in the anolyte compartment,  $A_{cross}[m^2]$  is the cross-section area of the anolyte compartment, given by the product of thickness of anolyte compartment,  $d_{cell}$ , and width of anolyte compartment,  $W_{cell}$ ,  $v_{int}[m/s]$  is the interstitial velocity of the fluid across the length of the anolyte compartment, through the voids left by the wire mesh,  $l_{stroke}[m]$  is the equivalent length of the anolyte compartment displaced when a pulsation is introduced,  $V_{pulse}[m^3]$  is the volume displacement introduced by the pump for pulsation ( $20 \cdot 10^{-3}m^3$  for the anolyte chamber),  $v_{pulse}[m/s]$  is the instantaneous velocity of the fluid through the anolyte compartment when pulsation is introduced,  $f_{pulse}[1/s]$  is the pulsation frequency introduced by the pump,  $v_{tot}[m/s]$  is the total averaged velocity of the fluid in the anolyte compartment, accounting for pulsation and no pulsation situations,  $\tau[s]$  is the net residence time of the fluid in the anolyte compartment,  $L_{cell}[m]$  is the total height of flow cell, in the direction of the flow of anolyte compartment.

To calculate  $k_{BL}$ , an adequate correlation is necessary to describe the mass transfer in a channel with a wire mesh flow distributor. The present work uses the correlation proposed by Da Costa et al.<sup>1</sup>, who give a Sherwood correlation specific for ‘*spacer-filled channels*’, a geometry very similar to the present wire mesh. The equations stated in that paper also allow to calculate the porosity for the wire mesh or ‘*voidage*’.

$$S_{vsp} = \frac{2}{d_f} \quad (14)$$

$$\varepsilon = 1 - \frac{\pi d_f^2}{2 \cdot l_m \cdot h_{sp} \cdot \sin(\theta)} \quad (15)$$

$$d_{hyd} = \frac{4\varepsilon}{\frac{2}{h_{sp}} + (1 - \varepsilon) \cdot S_{vsp}} \quad (16)$$

$$k_{dc} = 1.654 \cdot \left(\frac{d_f}{h_c}\right)^{-0.034} \cdot \varepsilon^{0.75} \cdot \left(\frac{\sin(\theta)}{2}\right)^{0.086} \quad (17)$$

$$Re = \frac{\rho \cdot v_{int} \cdot d_{hyd}}{\eta} \quad (18)$$

$$Sh = 0.664 \cdot k_{dc} \cdot Re^{0.5} \cdot Sc^{0.33} \cdot \left(\frac{2 \cdot d_{hyd}}{l_m}\right)^{0.5} \quad (19)$$

where  $S_{vsp}[1/m]$  is the specific surface area of wire mesh/spacer,  $d_f[m]$  is the diameter of a single fiber of the wire mesh ( $1.40 \cdot 10^{-3} m$  in this work),  $\varepsilon[-]$  is the porosity or ‘voidage’ of the anolyte compartment with wire mesh,  $l_m[m]$  is the distance between fibers in the wire mesh ( $6.31 \cdot 10^{-3} m$  in this work),  $h_{sp}[m]$  is the thickness of the wire mesh (top fiber to bottom fiber,  $2.10 \cdot 10^{-3} m$  in this work),  $\theta[rad]$  is the hydrodynamic angle or major angle of the mesh between fibers (experimentally determined to be  $1.82 rad$  for the present mesh),  $d_{hyd}[m]$  is the hydraulic diameter of the wire mesh channel,  $k_{dc}[-]$  is a correction factor applied for spacer-filled channels for the Sherwood correlation,  $h_c[m]$  is the height of the flow channel in the anolyte compartment ( $2.7 \cdot 10^{-3} m$  in this work),  $Re[-]$  is the Reynolds number of the flow through the anolyte compartment,  $\rho[kg/m^3]$  is the density of the fluid through the anolyte compartment ( $998 kg/m^3$  in the present work),  $v_{int}[m/s]$  is the interstitial velocity of the fluid across the length of the anolyte compartment,  $\eta[Pa \cdot s]$  is the kinematic viscosity of the fluid ( $1 mPa \cdot s$  in the present work),  $Sh[-]$  is the Sherwood number and  $Sc[-]$  is the Schmidt number given by Equation (20).

$$Sc = \frac{\eta}{\rho \cdot D_{ACT-TEMPO^+}} \quad (20)$$

In which  $D_{ACT-TEMPO^+}$  is the molecular diffusivity of ACT-TEMPO<sup>+</sup>.

The boundary layer mass transfer coefficient is then retrieved from the Sherwood number, as stated in Equation (21).

$$Sh_{ACT-TEMPO^+} = \frac{k_{BL} \cdot d_{cell}}{D_{ACT-TEMPO^+}} \quad (21)$$

The addition of a pulsating component on top of the (constant) convection velocity will result in a complex time-dependent set of differential equations. In case one would only be interested in the time averaged concentrations in a steady state, the equations can be simplified by incorporating the effect of pulsations in the dispersion coefficient and eliminating the transient term. Hoedemakers<sup>2</sup> studied a configuration very similar to the electrochemical cell with spacer discussed here. His work focused on emulsion polymerization in a pulsed packed column.

Hoedemakers<sup>2</sup> derived an expression for the axial dispersion coefficient,  $\mathbb{D}_{ax}$ , combining a term for the local convection coefficient in packed beds, and another term for the pulsation behavior, yielding the final Expression (22). In the present case, and according to the given geometry of the flow cell, the case that better resembles the wire mesh of the anolyte compartment will be

the Sulzer SMV8-DN50 packing from Hoedemakers, as it is a structured packing type, in which the fluid is forced to go through non-random geometric channels.

$$\mathbb{D}_{ax} = \varphi_1 \cdot v_{int} \cdot d_{mesh} + \varphi_2 \cdot l_{stroke} \cdot f_{pulse} \cdot d_{mesh} + \frac{\kappa_2 \cdot v_{int}^2 \cdot d_{mesh}^2}{\varphi_1 \cdot v_{int} \cdot d_{mesh} + \varphi_2 \cdot l_{stroke} \cdot f_{pulse} \cdot d_{mesh}} \quad (22)$$

$$\varphi_2 = 0.1 + 0.04 \cdot \frac{l_{stroke}}{d_{mesh}} \quad (23)$$

where  $\varphi_1[-]$ ,  $\varphi_2[-]$  and  $\kappa_2[-]$  are packing dependent coefficients,  $v_{int}[m/s]$  is the interstitial velocity of the fluid across the length of the anolyte compartment,  $d_{mesh}[m]$  is the diameter of the wires that make up the mesh in the cell,  $l_{stroke}[m]$  is the pulsation amplitude in the anolyte compartment and  $f_{pulse}[1/s]$  is the pulsation frequency. In this work, the values of 0.80 and 0.71 are used for  $\varphi_1$  and  $\kappa_2$ , respectively. These values were used by Hoedemakers for the Sulzer SMV8-DN50 packing with 10 mm packing diameter.

## 5. Faradaic or current efficiency calculation

The Faradaic or current efficiency (FE) for the present process is calculated assuming that the PDO oxidation reaction to LA (Reaction Eq. (2) from main manuscript) and subsequent LA oxidation reaction to PA (Reaction Eq. (2) from main manuscript) are electrochemical processes with an associated current and FE. In reality, the only electrochemical process taking place is the ACT-TEMPO oxidation (Reaction Eq. (1) from main manuscript), but this assumption can help to determine the electric current associated with either PDO to LA reaction or LA to PA reaction.

To calculate the FE, an electrochemical oxidation reaction in which component  $X$  reacts to give the oxidized form  $X^{n_e-+}$  is considered. In a continuous electrochemical flow cell, as the one depicted in Figure S.1, with a certain electrode area, and a certain flow compartment thickness (membrane-electrode distance), Faraday's Law can be applied to determine the rate of disappearance or consumption of  $X$ . The result can be seen in Equation (24).

$$\frac{dC_X}{dt} = \frac{j \cdot FE(X \rightarrow X^{n_e-+})}{n_{e-} \cdot F \cdot thickness} \quad (24)$$

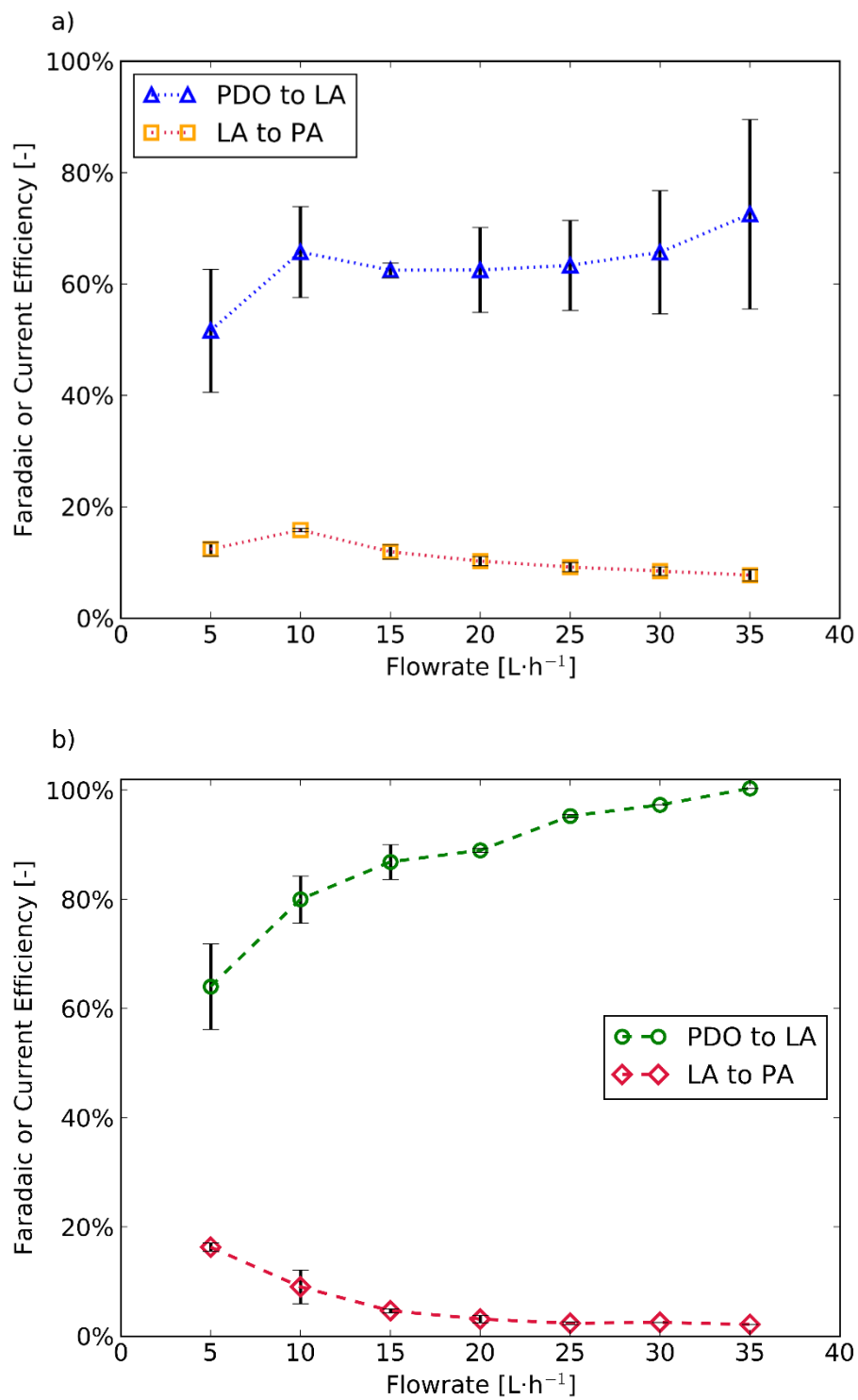
where  $C_X \left[ \frac{mol}{m^3} \right]$  is the concentration of  $X$  in the flow compartment at instant  $t$ ,  $t[s]$  is time,  $j \left[ \frac{A}{m^2} \right]$  is current density, referred to the electrode area,  $FE(X \rightarrow X^{n_e-+})[-]$  is the FE value for the specified reaction,  $n_{e-}[-]$  is the number of exchanged electrons in the mentioned electrochemical reaction,  $F \left[ \frac{C}{mol} \right]$  is the Faraday constant, and  $\cdot thickness$  is the thickness of the flow compartment of the electrochemical cell, i.e., the distance between the membrane and the electrode distance.

Integrating then Equation (24) over the whole residence time of the reactor, and assuming that both current density and FE are constant over the reactor, FE can then be calculated using Equation (25).

$$FE(X \rightarrow X^{n_e-+}) = \frac{|C_X|_{t=\tau} - C_X|_{t=t_0}|}{\tau - t_0} \cdot \frac{n_{e-} \cdot F \cdot thickness}{j} \quad (25)$$

where  $C_X|_{t=\tau} \left[ \frac{mol}{m^3} \right]$  is the concentration of  $X$  at the exit of the reactor, i.e., after residence time  $\tau$ ,  $C_X|_{t=t_0} \left[ \frac{mol}{m^3} \right]$  is the initial concentration of  $X$  at  $t_0$ ,  $\tau[s]$  is the residence time of the medium in the reactor, and  $t_0[s]$  is the initial time at which reaction starts, taken to be 0.

In Figure S.4, the calculated values of FE are shown, both for the PDO to LA reaction and for the LA to PA reaction, in the non-pulsed, Figure S.4a, and pulsed situations, Figure S.4b. For the PDO to LA reaction, the PDO concentration is used to calculate the associated FE to this reaction; for the LA to PA reaction, the final PA concentration is used.



**Figure S.4.** Faradaic or current efficiency of the oxidation reactions of PDO to LA, and of LA to PA, for a) Non-Pulse and b) Pulse situation.

## 6. Specific Energy Consumption of the electrochemical process

The Specific Energy Consumption (SEC) represents the energy per unit of mass of product in an electrochemical process. This quantity can be calculated for the oxidation reaction of PDO to LA (Reaction Eq. (2) from main manuscript) with Equation (26).

$$SEC_{LA} = \frac{n_{e^-} \cdot F \cdot \Delta V_{cell}}{FE \cdot M_{LA}} \quad (26)$$

where  $SEC \left[ \frac{kWh}{kg \text{ LA}} \right]$  is the Specific Energy Consumption of LA production,  $n_{e^-} [-]$  is the number of exchanged electrons in the reaction, 4 for PDO to LA,  $F \left[ \frac{C}{mol} \right]$  is the Faraday constant, 96500  $\frac{C}{mol}$ ,  $\Delta V_{cell} [V]$  is the total cell voltage applied, 2.5 V experimentally (see section Experimental from the manuscript),  $FE [-]$ : is the Faradaic efficiency of the PDO to LA reaction, and  $M_{LA} \left[ \frac{kg}{mol} \right]$  is the molecular weight of LA,  $90.08 \cdot 10^{-3} \frac{kg}{mol}$ ;

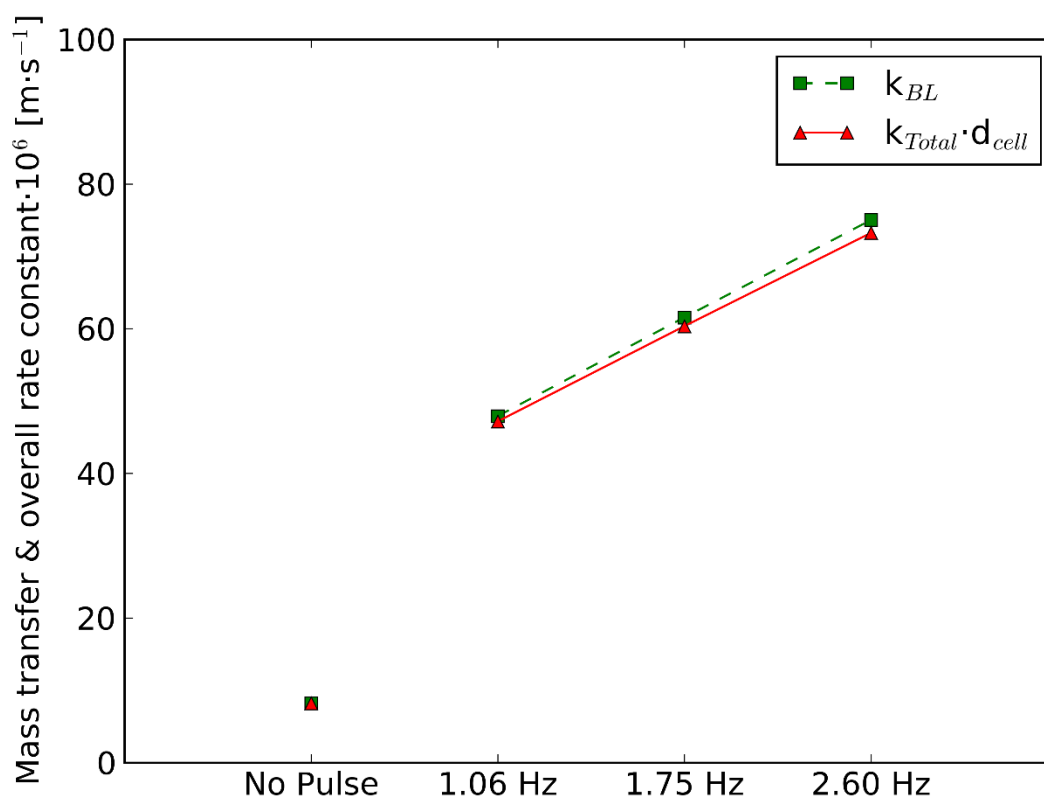
Since the process is performed potentiostatically, the total cell voltage remains the same for both pulsed and non-pulsed situations. The major difference is in the FE values, which are greater for the pulsed flow, thus making SEC lower. In Table S. 1, the SEC values for both pulsed and non-pulsed experiments are displayed as a function of the flowrate. The FE values are taken from Section 8. It can be concluded that, in principle, introducing a pulsation also enhances the energy efficiency of the electrochemical process for the production of LA.

**Table S. 1.** Specific Energy Consumption for the PDO to LA oxidation reaction for both pulse and non-pulse situations, referred for the production of LA.

Flowrate [L·h <sup>-1</sup> ]	SEC (No Pulse) [kWh·kg LA <sup>-1</sup> ]	SEC (Pulse) [kWh·kg LA <sup>-1</sup> ]
5	5,766	4,693
10	4,527	3,740
15	4,764	3,430
20	4,761	3,377
25	4,699	3,161
30	4,531	3,059
35	4,103	2,967

## 7. Influence of pulsation frequency on mass transfer and overall rate constants

The effect of the pulsation frequency on the mass transfer constant for the ACT-TEMPO through the boundary layer, and its effect on the overall rate constant can be observed in Figure S.5. For an electrolyte flowrate of  $10 \text{ L}\cdot\text{h}^{-1}$ , the mass transfer constant rises from  $8.2\cdot 10^3$  to  $47.9\cdot 10^3 \text{ m}\cdot\text{s}^{-1}$  at a value of pulsation frequency of 1.06 Hz, reaching the mass transfer coefficient a value of  $75.0\cdot 10^3 \text{ m}\cdot\text{s}^{-1}$  at 2.60 Hz. This behavior indicates that the presence or absence of pulsation has a stronger effect than the pulsation frequency, given the chosen range of frequencies. Similarly, the overall rate constant follows the same trend as the mass transfer constant, indicating that the process is mass transfer limited.



**Figure S.5.** Calculated rate constants of mass transfer ACT-TEMPO in the boundary layer ( $k_{BL}$ , dotted green line with green squares), and the overall rate constant, combination of both ( $k_{Total} \cdot d_{cell}$ , solid red line with red triangles), as a function of the pulsation frequency, for a displaced volume of 20 mL, and a electrolyte flowrate of  $10 \text{ L}\cdot\text{h}^{-1}$ .

### References

- (1) Da Costa, A. R.; Fane, A. G.; Wiley, D. E. Spacer Characterization and Pressure Drop Modeling in Spacer-Filled Channels. Pdf. *J. Memb. Sci.* **1994**, 87, 79–98.
- (2) Hoedemakers, G. F. M. Continuous Emulsion Polymerization in a Pulsed Packed Column, Technische Universiteit Eindhoven, 1990.