On The Time Resolution of the Atomic Emission Spectroelectrochemistry Method

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The time resolution of the atomic emission spectroelectrochemical (AESEC) flow cell has been investigated by numerical simulations. The results demonstrate that the time resolution of the AESEC electrochemical flow cell may be simulated numerically based on the consideration of electrolyte flow patterns and ion transport in the cell. The residence time distribution (RTD) closely approximates a log-normal distribution for both experiment and simulation. Time resolution may be improved by increasing the flow rate; however, this also leads to marked heterogeneities in the flow field near the surface. An optimum flow rate of 3 cm³ min⁻¹ was determined. The problem may be avoided somewhat by using a mask to cover all the surface except for a small portion near the center of the flow cell.

Corrosion, dissolution and passivation occur spontaneously on the surface of metals in the presence of aggressive electrolytes. In order to accurately predict the evolution of these systems it is necessary to have real-time kinetic data so that the rate laws of the different elementary reactions may be identified. Atomic emission spectroelectrochemistry (AESEC) is an analytical technique that allows monitoring the dissolution of a large number of elements, simultaneously, in real time, during the reaction of a material with an aggressive electrolyte. References¹⁻¹¹ describe the history, the instrumentation, and typical applications of this technique. Briefly, an inductively coupled plasma atomic emission spectrometry (ICP-AES) is used to continuously monitor the concentration of dissolved elements downstream from an electrochemical flow cell. Within the time resolution of the system, the instantaneous concentration flowing out of the cell (C_m(t)) and the instantaneous dissolution rate at the working electrode/electrolyte interface (v_M(t)) are directly related to each other as follows:

\[ v_M(t) = f_e C_m(t) \]  

where \( f_e \) is the flow rate through the cell. The use of the technique is therefore very similar to that of a rotating ring disk electrode (RRDE) in which the electrochemical detection at the ring is replaced by the ICP-AES down stream from the flow cell. The major advantage of this technique is that we may simultaneously follow any number of species dissolving from the working electrode and usually with simplified quantification and sample preparation. On the other hand, as compared to the RRDE, AESEC has significantly lower time resolution.

Several other research groups have proposed similar couplings in recent years. A quasi-identical electrochemical flow cell was used by Mercier et al. to investigate the corrosion of Al¹³,¹⁴ also using ICP-AES detection. Voith et al.¹⁵ have proposed an electrochemical flow cell using atomic emission spectroscopy. Homazova et al.¹⁶,¹⁷ and Ott et al.¹⁸ proposed a capillary flow cell coupled to inductively coupled plasma mass spectrometer (ICP-MS) as a means of following multielement corrosion and dissolution with improved spatial resolution. Along similar lines, the scanning droplet cell has been coupled with an ICP-MS²⁰⁻²³ or with a UV-vis spectrometer²⁴,²⁵ to perform time and potential resolved dissolution analysis of different materials. A numerical simulation of electrolyte flow in the scanning droplet flow cell has been attempted to optimize the geometry of the flow cell²⁶ or to separate the contributions of diffusion and kinetically controlled reactions.²⁷

The poor time resolution mentioned above may be a problem for all of these techniques, for example when one would like to quantitatively compare elemental dissolution with electrochemical current transients. The latter are essentially instantaneous on the time scale of these experiments while the concentration transients are broadened due to the hydrodynamics in the flow cell. This comparison allows the determination of the rate of oxide film formation when the cathodic current is negligible,²⁻⁸ or the determination of the cathodic current when oxide formation is negligible.¹⁰,¹¹ The correlation of cathodic current and dissolution rates is also important for assessing the dissolution of oxides and/or conversion coatings induced by a cathodic current.²⁵

To this end, Ogle and Weber² proposed a numerical convolution method that puts the electrochemical data on the same time resolution as the spectroscopic data so that a point by point comparison could be made. The extensive diffusion layer and low convection rate make the dissolution rate measurement in a significant broadening of the concentration transients, C_M(t), with respect to the instantaneous dissolution rate transient at the working electrode surface, leading to a convolution integral relationship between \( v_M(t) \) and \( f_e C_M(t) \):

\[ f_e C_M(t) = \int_0^t v_M(x) h(t-x) dx \]  

where \( h(t) \) is the residence time distribution (RTD)²⁸,²⁹ of the electrochemical flow cell (which is equivalent to the transfer function between the electrochemical and the spectroscopic measurement).³⁰

As the electrochemical current is essentially instantaneous on the time scale of these experiments, Eq. 2 describes the relationship between the measured dissolution rate and the electrical current when only an anodic dissolution is measured. Recently a deconvolution routine has been proposed.¹¹

Eq. 2 is completely general for all of the coupled techniques mentioned above. The RTD \( h(t) \) however is specific for each flow cell design. It may be defined experimentally as the normalized concentration transient at the outlet of the cell following a delta function of dissolution at the working electrode/electrolyte interface.

\[ h(t) = C(t) / \int_0^\infty C(t) dt \]  

The delta function of dissolution was simulated by applying a short anodic pulse to a suitable electrode material such as copper or stainless steel in H₂SO₄ and HCl² and by Mercier et al.¹⁴ for Al in H₂SO₄. In all cases, the experimental \( h(t) \) was closely approximated by a simplified version of the log-normal function with two adjustable parameters:

\[ h(t) = \begin{cases} \sqrt{\frac{\pi}{2\tau}} e^{-\frac{\beta^2}{4\tau^2}} & \text{if } t > 0 \\ 0 & \text{if } t = 0 \end{cases} \]  

In Eq. 4, \( \tau \) is the time of the peak maximum and \( \beta \) is related to the peak width. These parameters are equivalent to the mean and standard

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deviation of an ordinary Gaussian distribution by simply substituting In(t) for t.

As the RTD is a key factor in the interpretation of AESEC data, it is of primary importance to understand the physical origin of this distribution. In previous publications, it was tacitly assumed that the broadening of the concentration transients was due entirely to the hydrodynamics of the flow cell. However, the electrochemical kinetics of anodic dissolution may also contribute to the experimental broadening as may the aspiration and nebulization system of the ICP spectrometer. An important application of AESEC is to precisely determine the contribution of electrochemical kinetics and this requires an independent knowledge of the contribution of hydrodynamics.

The objective of this work is therefore to compare the experimentally determined RTD obtained with the Cu/CuCl$_2$$^-$ system with that determined by numerical simulation assuming that mass transport in the flow cell is uniquely responsible for the broadening of h(t). These experiments and simulations were conducted as a function of flow rate so as to determine an optimum flow rate for an enhanced time resolution while maintaining the most uniform distribution of flow vectors at the surface of the working electrode to ensure the uniformity of diffusion controlled reactions. It will also be demonstrated that significant improvement in both factors may be obtained by using a mask to expose only a central area of the surface.

**Experimental**

*MATERIALS.—* Spectropure copper (Johnson Matthey, 99.9995%) was used as a working electrode. Prior to each experiment the surface of the sample was manually ground with 4000 grit SiC paper then rinsed with ethanol (analytical grade, VWR Prolabo) and purified water (Millipore system, 18 Ω cm$^2$). A flow of nitrogen was used to deaerate the solutions. The experiments were performed in deaerated 1 M HCl (analytical grade, VWR Prolabo) solutions in purified water (Millipore system, 18 Ω cm$^2$). A flow of nitrogen was used to deaerate the solutions. The deaeration started 1 hour prior to each experiment and was continued until the end of the experiment.

*AESEC parameters.—* The emission intensity for Cu was monitored at 324.754 nm. The detection limit defined as two times the standard deviation of the blank solution was 2.7±0.2 μg L$^{-1}$ under the conditions of these experiments.

Fig. 1 illustrates the basic design of the electrochemical flow cell. The cell is divided into a working electrode and a counter electrode compartment, labeled WEC and CEC respectively in Fig. 1. The two compartments were separated by a permeable membrane which allowed ionic current flow but prevented bulk mixing of the electrolytes. The membrane also promoted a uniform current density on the working electrode. The surface area of the working electrode exposed to the electrolyte was determined by the geometry of the o-ring and was measured as 0.51±0.01 cm$^2$ in the standard configuration. The volume, V, of the WE electrode compartment was determined experimentally to be 0.27±0.02 cm$^3$. In this work the flow rate was varied between f$_e$ = 1 to 5 ml min$^{-1}$ controlled by a peristaltic pump upstream from the flow cell. The minimum renewal time of the electrolyte in the cell (= V/f$_e$) varied between approximately 3 and 27 seconds. The electrolyte flow entered at the bottom of the cell and existed at the top so as to favor the removal of any gaseous species that may form during the experiment.

In a second configuration, only the central part of the surface was exposed to the electrolyte by using a mask consisting of an insulating and impermeable electroplating tape (3M 470, 0.18 mm thick) that covered the periphery of the working electrode but left uncovered a circle with 1.3±0.1 mm radius (or 0.053±0.005 cm$^2$) of the Cu working electrode. The areas of the surfaces in the standard and the masked configuration were measured from observation of the reactive zone of the Cu electrode obtained by optical microscopy after the experiment. The flow rate of the electrolyte was 1.1±0.1 cm$^3$ min$^{-1}$, 3.1±0.1 cm$^3$ min$^{-1}$ and 5.0±0.1 cm$^3$ min$^{-1}$.

The “standard” method of measuring h(t) for the AESEC flow cell was by approximating a delta function of Cu dissolution via a 1 s anodic, galvanostatic pulse of 1 mA to a pure Cu electrode and measuring the Cu concentration as a function of time downstream from the flow cell. (Note that the procedure was altered for Fig. 3, where an anodic potentiostatic pulse of 1.5 s was used. This should not change the measured distribution of h(t).) This experiment was performed under a variety of conditions including variable flow rate, with and without the use of a mask. Assuming a faradaic yield of 100%, this pulse would correspond to 10$^{-5}$ mol for Cu oxidation to CuCl$_2$. The n = 1 reaction has been well characterized in previous publications$^{2,3}$ and was verified in this work in the next section (Fig. 3). The concentration vs. time profiles were then normalized (Eq. 3) so that the area under the transient was equal to unity. These experimental h(t) distributions were then fitted to an empirical log-normal distribution, defined by Eq. 4. The time offset due to transport through the capillaries has been removed for all data. The t = 0 for the concentration transients was defined as previously described$^{2}$ as the data point immediately preceding the first point that rises above background.
Figure 2. Schematic of the electrochemical flow cell used for the simulation. A working electrode (WE) is placed at the bottom of the cell with or without a mask. The mask leaves uncovered a circle with 1.3 mm radius in the center of the WE. The $v$ and $h_1$ planes cross the cell through the center of the feed capillary in vertical and horizontal dimensions respectively. The $h_2$ plane lies 0.2 mm above the WE.

The application of the anodic pulses was performed with a Gamry Reference 600 potentiostat with Ag/AgCl saturated reference electrode and a Pt foil counter electrode. The analog potential and current signals were routed into the measuring circuit of the ICP-AES to guarantee the same time scale for the measurements of Cu current, potential and total current. The data acquisition rate of all signals from ICP-AES was 10 points per second for Fig. 3 and otherwise 1 point per second.

Numerical Model

For the simulation of the electrochemical process the experimental flow cell of Fig. 1 was modeled as shown in Fig. 2. The modeling approach combines numerical models for the electrolyte flow and ion transport. To describe the flow in the cell, the mass and momentum conservation of the electrolyte flow is modeled by the incompressible Navier-Stokes equations, solving for the fluid velocity $u$ and the pressure $p$:

$$\nabla \cdot u = 0$$\hspace{1cm}[5]

$$\frac{\partial u}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} + \frac{1}{\rho} \nabla p - \nu \nabla^2 \mathbf{u} = 0$$\hspace{1cm}[6]

where $\rho$ is the electrolyte density and $\nu$ is the kinematic viscosity. The Reynolds number ($Re$) of the system defined as

$$Re = \frac{\rho u L}{\nu}$$\hspace{1cm}[7]

with $L$ the characteristic length of the geometry. $Re$ is less than 1 indicating a laminar flow defined by the small cell geometry (Fig. 2) and the small (less than 5 cm$^3$ min$^{-1}$) rate of electrolyte flow.

We assume that the concentration gradients of the dissolved species in the flow and their evolution in time, do not in any way influence the hydrodynamic flow in the cell, in other words we assume dilute solution theory. Therefore, Eqs. 5 and 6 are decoupled from the species transport equations, and are solved for a stationary state solution. The density and viscosity of the electrolyte were assumed to be constant $\rho = 10^3$ kg m$^{-3}$ and $\nu = 10^{-6}$ m$^2$ s$^{-1}$ characteristic for water as a main electrolyte component.

For the solution of the species concentration in the electrolyte, based on the multi-ion transport and reaction model (MITReM),\textsuperscript{31,32}

we can state a balance equation for each species in the system:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + \sum_{r=1}^{R} s_{ir} v_r$$\hspace{1cm}[8]

where $C_i$ is the concentration of species $i$. The source term on the right hand side of Eq. 8 comes from the homogeneous reactions, where $v_r$ is the rate of reaction $r$ and $s_{ir}$ is the stoichiometric coefficient of species $i$ in this reaction. The flux $\mathbf{N}_i$ is given by convection, diffusion and migration as follows:

$$\mathbf{N}_i = -D_i \nabla C_i + z_i F D_i \nabla C_i$$\hspace{1cm}[9]

where $D_i$ is the diffusion coefficient, $z_i$ is the charge, $F$ is the Faraday’s constant, $R$ is the universal gas constant, $T$ is the temperature and $U$ is the potential. The flux perpendicular to an electrode is given by the

Figure 3. Experimental determination of the residence time distribution. (A) The variation of potential as a function of time showing the 1.5 s potentiostatic pulse at $t = 0$ simulating a delta function of Cu dissolution; followed by the return to the open circuit potential. (B) The normalized concentration transient of dissolved Cu downstream from the electrochemical flow cell. The dashed curve represents a non linear least squares fit to Eq. 3 with the fitting parameters given in the figure. (C) The data of Fig. 2B expressed on a log (t) axis to demonstrate the log-normal nature of the residence time distribution. (D) Integral of the Cu ICP transient (expressed as charge assuming $n = 1$) versus the integral of the electrochemical current transient. This result confirms the $n = 1$ dissolution mechanism.
heterogeneous reactions:

\[ N_i \cdot I_a = \sum_{e=1}^{E} s_e v_e \]  

The RTD experiment was simulated as a 1 s pulse of uniformly distributed species flux, injected perpendicular to the surface of the working electrode. Again, the 1 s duration is sufficiently short to be considered a Dirac delta function of dissolution. By injecting a mass pulse instead of applying a current pulse we avoid considering migration in Eq. 9. This pulse is integrated in time (time-accurate simulation) and over the surface of the electrode to obtain the total amount of the substance injected into the electrolyte. Following injection, the dissolved species undergo mass transport by diffusion when close to the electrode, and mainly by convection when further from the electrode until it is ultimately removed from the cell. For the diffusivity of the medium, \( D_1 \), is assigned to \( 10^{-6} \text{ m}^2 \text{s}^{-1} \). The total quantity of Cu dissolved during the experiment was determined by integrating the ICP-AES transient prior to normalization using Eq. 1. This quantity was expressed as electrical charge using Faraday’s law with the assumption of \( n_1 \) process consistent with thermodynamic calculations for this electrolyte.

Numerical simulation of the residence time distribution.— A schematic diagram of the electrochemical flow cell used for the numerical simulation is given in Fig. 2. This model is identical to the experimental flow cell in every respect except that the O-ring at the edge of the sample compartment is not taken into account. The working electrode (WE) is placed at the bottom of the cell with or without the mask. For the purpose of the numerical simulation, several different planes are defined in Fig. 2. The \( v \) and \( h_1 \) planes cross the cell through the center of the feed capillary in the vertical and horizontal dimensions respectively. The \( h_2 \) plane lies 0.2 mm above the WE.

A series of numerical simulations of the velocity distributions in the cell was performed at various flow rates as shown in Fig. 4. The “steady state” velocity vector distributions \( f \) was measured by the copper pulse dissolution experiment under galvanostatic conditions as described in the Experimental section, and compared with the simulated response to a pulse release from the working electrode, as shown in Fig. 5. The numerical simulation assumed the pulse to be perfectly distributed over the active surface area at \( t = 1 \text{s} \). A full 3D video of the simulation reproducibility of the experimental residence time distribution. Prior to \( t = 0 \), the background concentration of Cu is negligible demonstrating that the corrosion rate of Cu in deoxygenated 1 M HCl is very low. The dashed curve in Fig. 3B, gives a non linear least squares fit of Eq. 4, demonstrating that the data is well approximated by the empirical log-normal function with only two adjustable parameters. The fitted values of the parameters are given in the figure along with the estimated error. The quality of the approximation is clearly demonstrated by the symmetry of \( h(t) \) when plotted against a log time axis, Fig. 3C.

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Experimental determination of the residence time distribution.— Fig. 3 illustrates the experimental determination of \( h(t) \). The potential vs. time profile is shown in Fig. 3A. The results of four different experiments are overlaid. The delta function of dissolution was simulated by application of a potentiostatic anodic pulse for +1.5 s at 0.05 V vs. NHE. Fig. 3B gives the average value of the normalized transient for the four experiments. The light gray curves show the average value \( \pm \) one standard deviation. This result demonstrates the excellent reproducibility of the experimental residence time distribution. Prior to \( t = 0 \), the background concentration of Cu is negligible demonstrating that the corrosion rate of Cu in deoxygenated 1 M HCl is very low. The dashed curve in Fig. 3B, gives a non linear least squares fit of Eq. 4, demonstrating that the data is well approximated by the empirical log-normal function with only two adjustable parameters. The fitted values of the parameters are given in the figure along with the estimated error. The quality of the approximation is clearly demonstrated by the symmetry of \( h(t) \) when plotted against a log time axis, Fig. 3C.

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Figure 5. Experimental (circles) and simulated (lines) measurements of the residence time distribution, h(t), following a 1 s mole mass of $10^{-7}$ pulses without a mask for 1, 3 and 5 cm$^3$ min$^{-1}$ flow rate into the feed capillary ($f_e$). The areas of the curves have been normalized and the mean of two experimental curves for each flow rate is presented. Alternative plots on a linear time scale and in integral form are given in the supplementary materials.

Figure 6. (a) Simulated residence time distribution, h(t), for a 1 s, $10^{-7}$ mole pulses for 1.00, 1.25, 1.50, . . . , 5.00 cm$^3$ min$^{-1}$ flow rate into the feed capillary ($f_e$). The areas of the curves have been normalized. (b) shows the $\tau$ (circles) and $\beta$ (squares) parameters as a function of $f_e$. The filled points show experimental measurements while the empty points give the simulated residence time distribution from Fig. 6a.

Optimization by use of mask.—To avoid problems associated with a possible vortex at the entrance of the cell or the stagnant zones at the edges of the working electrode, an attempt was made to limit the active surface area to a small surface in the center of the flow cell, where the flow distribution is relatively constant. The results for the residence time distribution with and without the mask are shown in Fig. 7 with the fitting parameters for each curve in Table I for $f_e = 3$ cm$^3$ min$^{-1}$. The presence of the mask does not change the position of the peak maximum but reduces the half-width of the RTD thereby improving the time resolution of the experimental data. Obviously this does not completely eliminate the more stagnant areas in the flow cell, however it does create a situation where the reacting surface is not in contact with the stagnant electrolyte, which is probably of considerable benefit for the uniformity of the electrode reaction itself. It also prevents the dissolved species from diffusing into some of the stagnant areas at the entrance of the cell and along the edges, although clearly there is a stagnant zone at the outlet of the cell.

It is of interest to observe the concentration distribution at the active surface for the different times: $t_1$, $t_2$, and $t_3$ (3, 10 and 30 s), before, at, and after the maximum as indicated in Fig. 7. This is shown in Fig. 8 without the mask and in Fig. 9 with the mask. Marked heterogeneities are observed on the periphery of the flow cell without the injection and removal of ions in the cell for different flow rates is presented in the “supplementary materials” for this article. It is clear from Fig. 5 that the experimental results are in reasonably good agreement with the numerical simulation supporting the assumption that mass transfer in the flow cell does indeed control the residence time distribution. Note that Fig. 5 gives the residence time distribution on a log $t$ axis to better demonstrate the symmetry of the log-normal distribution. The same data is given on a linear time axis and in an integral format in the “supplementary materials” for this article.

Fig. 6 shows the simulated h(t) distribution in a wide range of flow rates in the feed capillary ($f_e$). Each curve in Fig. 6a was fitted to the log-normal distribution (Eq. 4). The results are shown in Fig. 6b. It is clear that the increase of $f_e$ from $f_e = 1$ cm$^3$ min$^{-1}$ to $f_e = 3$ cm$^3$ min$^{-1}$ results in a dramatic decrease of the position of the peak maximum, $\tau$ (in seconds), and the half-width, which is inversely proportional to $\beta$ (unitless). Further increase of $f_e$ up to 5 cm$^3$ min$^{-1}$ shows only modest enhancement of the time resolution yet leads to an increased significance of the vortex at the entrance of the cell. Therefore, we conclude that $f_e = 3$ cm$^3$ min$^{-1}$ is an optimum value of time resolution versus flow uniformity.
Table I. The parameters of $\tau$ and $\beta$ of log-normal residence time distribution shown in Fig. 7 for 3 cm$^3$ min$^{-1}$ flow rate in the feed capillary. Standart error of fitting for each data set was less than 0.1 for $\tau$ and 0.01 for $\beta$.

|          | $\tau$/s | $\beta$/unitless | $\tau$/s | $\beta$/unitless |
|----------|-----------|------------------|-----------|------------------|
| without the mask | Experimental | 9.9 | 1.21 | 1.33 |
|          | Numerical  | 12.5 | 1.82 | 1.82 |
| with the mask | Experimental | 9.5 | 1.82 | 1.82 |
|          | Numerical  | 9.9 | 1.82 | 1.82 |

the mask indicated by the stagnation of the substance near the input of the flow cell. The problem with the stagnation of the substance in the confined zones at the edge of the cell was resolved using the mask.

Discussion

Considering the flow rate, $f_e$, as a purely instrumental parameter, the sensitivity of the technique is inversely proportional to $f_e$ by Eq. 1, and in addition, the nebulization / aspiration system is more efficient at lower flow rates. However, the flow rate will also play a role in the reaction rate and mechanisms especially if certain electrode processes are diffusion limited. Therefore it is important to optimize sensitivity, time resolution and the uniformity of electrolyte flow on the surface.

The increase of the flow rate, $f_e$, increases the time resolution of the experiment by decreasing the time required to wash out dissolved species from the flow cell. However, it increases the heterogeneity in the velocity vector distribution visible by the propagation of the vortex like behavior of the flow at the input of the flow cell (Fig. 4). From the tested flow rates of 1.00, 1.25, . . . , 5 cm$^3$ min$^{-1}$, the optimal flow rate was found to be 3 cm$^3$ min$^{-1}$, balanced between the essential requirements of time resolution and homogeneity of the flow. Heterogeneities in the flow rate inside the cell may cause differences in the mass transport of species between the center and the periphery of the cell. This can result in composition gradients between the two zones of not only metal cation concentrations but other species involved in the electrochemical reactions such as $\text{pH}$, $\text{Cl}^-$, $\text{O}_2$, etc.

This work has not dealt specifically with the optimization of the flow cell geometry which is difficult to vary due to the use of an o-ring to define the active surface area. Some obvious improvements are imaginable, for example by making the outlet flush with the working electrode surface. However this is not possible when using an o-ring to define the active surface. Therefore in this work, we have focused on optimizing the flow rate and limiting the surface with a mask. It would be possible to make modifications using a 3D printing technique such as proposed by Kollender et al.\textsuperscript{26}

In this work, the use of the mask improves both the homogeneity of the flow at the active surface and the time resolution, however it may significantly reduce the sensitivity due to a lower surface area of the anode and therefore a lower absolute quantity of material dissolved for a given dissolution rate. The decrease of the anode area from 0.51 cm$^2$ without the mask to 0.053 cm$^2$ would reduce the sensitivity by a factor of 9.6 and that can be critical for low dissolution rates. Therefore, the mask can be used for active systems and/or if a significant impact of flow heterogeneities on the electrochemical behavior of the studied system is suspected.

Conclusions

The results demonstrate that the time resolution of the AESEC electrochemical flow cell may be simulated numerically based on the consideration of the electrolyte flow patterns and ion transport in the cell. The residence time distribution ($h(t)$) closely approximates a log-normal distribution for both the experiment and the simulation. Time resolution may be improved by increasing the flow rate, however this also leads to marked heterogeneities in the flow field near the surface. Based on both the experiment and the simulation, the optimal flow rate was determined as 3 cm$^3$ min$^{-1}$. The problem with flow heterogeneity may be improved by using a mask to cover all the surface except for

![Figure 8](image_url)

Figure 8. The substance distribution ($C$) in mole m^{-3} in $h2$ (on the left) and $v$ (on the right) cross sections for 3 cm$^3$ min$^{-1}$ flow rate into the feed capillary without the mask for $t_1$, $t_2$ and $t_3$ (3, 10 and 30 s) times after a $10^{-7}$ mole mass pulse corresponding to an imposed mass flux on the surface of $1.67 \times 10^{-3}$ mole m$^{-2}$ s$^{-1}$. Animation of the evolution of the substance distribution with time is given in supplementary materials.
Figure 9. The substance distribution (C) in mole cm$^{-3}$ in h2 (on the left) and v (on the right) cross sections for 3 cm$^{-3}$ min$^{-1}$ flow rate into the feed capillary with the mask for $t_1$, $t_2$ and $t_3$ (3, 10 and 30 s) times after a 10$^{-3}$ mole mass pulse corresponding to an imposed mass flux on the surface of 18.8 × 10$^{-7}$ mole m$^{-2}$ s$^{-1}$. Animation of the evolution of the substance distribution with time is given in supplementary materials.

a small portion near the center of the flow cell where the flow is relatively more uniform.

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