Numerical Partitioning Model for the Koutecký-Levich Analysis of Electrochemical Flow Cells with a Combined Channel/Wall-Jet Geometry

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We present numerical studies of the flow profile and electrode currents for the hydrogen oxidation and oxygen reduction reactions in an electrochemical flow cell. Koutecký-Levich type equations are obtained by partitioning the electrode surface into flow profile regimes and their correlation to idealized wall-jet and channel electrode geometries. The precision of several Koutecký-Levich type equations is evaluated and it is shown that differences between the most commonly applied equations are negligible within the range of flow rates studied and are surpassed by experimental errors.

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Controlled experimental conditions are of prime importance in electroanalytical chemistry, be it battery, corrosion, electrocatalysis (e.g., reactions occurring in fuel cells or electrolyzers), and electrodeposition related research, respectively. Especially for the latter two, a defined transport of reacting species in the electrolyte to the electrode surface is crucial. In both fields, rotating electrodes such as the rotating disk electrode (RDE) and the rotating cylinder Hull cell (RCH), respectively, have been the standard tool for electroanalytical investigations, due to their well-established mass transport conditions. Whereas the RCH exhibits a distinctly inhomogeneous current distribution similar to that of industrial electroplating baths, the RDE’s uniformly accessible electrode surface enables the study of kinetic parameters and reaction pathways of multistep reactions such as the technologically relevant oxygen reduction and hydrogen oxidation reactions (ORR and HOR, respectively). Drawbacks of rotating electrodes, however, lie in the substrate geometry being limited to circular shapes, the need for bulk sample conductivity, and in the difficulties associated to their combination with online monitoring tools of great interest in electroanalytical chemistry. For such purposes, electrochemical flow cells based on different geometries have found widespread use in flow analysis due to their fast response time, high sensitivity and selectivity.1–4 Also in electrocatalysis, flow cells have been employed offering the possibility to work at elevated temperature and pressure,5–7 further enhanced by the coupling to spectroscopic tools.3,5–11 Other designs emphasize gas dosing by upstream mixing of two electrolytes,12,13 implementation of quartz crystal microgravimetry14,15 or the combination with in-situ X-ray absorption spectroscopy16–20 or scattering techniques.20–25 Recently, a new class of electrochemical flow cells emerged from scanning electrochemical microscopes24,25 and scanning droplet cells,26–28 termed scanning flow cells (SFCs) or scanning droplet cell microscopes (SDCMs).29,30 A notable advantage is their ability to perform localized electrochemical measurements, thus greatly increasing throughput for the combinatorial screening of catalysts. Regardless of their wide range of application and advantages over RDEs, flow cells often involve complex flow velocity profiles and, thus, analytical solutions for the mass transport limited current as a function of flow rate are available only for generalized systems.31–36

While numerical methods can provide approximations for more complex cell designs,37–41 the commonly applied Koutecký-Levich (K-L) analysis to derive kinetic information from RDE experiments is rendered unusable, due to the non-uniformity of the diffusion layer thickness and, thus, current density distribution across the electrode surface.31,42

With this motivation, we present an electrode partitioning method to obtain a numerical description of the current distribution at an electrochemical flow cell combining elements of wall-jet and channel flow profiles. We apply this method to an electrochemical flow cell used by our group43 and compare the K-L type equation obtained by numerical partitioning to the one commonly applied for the rotating disk electrode.

Experimental Setup and Numerical Model

Cell geometry.—A detailed description of the electrochemical flow cell and its comparison to the RDE has been published elsewhere.43 In brief, the cell consists of a copper plate into which the electrode is placed flush and an electrical contact is obtained via the top of the working electrode (WE) surface (see Figure 1). The WE compartment

Figure 1. Sketch of the electrochemical flow cell. (1) Inflow from tube-in-tube (deaeration system), (2) outlets, (3) RE compartment, (4) CE compartment, (5) WE compartment with O-ring sealing and top-contact to copper plate. Dimensions are not to scale for clarity of presentation.

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of the cell consists of a 0.5 mm diameter inlet nozzle and four 1 mm diameter outlet channels machined in a polyether ether ketone (PEEK) part placed 0.5 mm above the surface of the electrode embedded in a second PEEK part. The inlet is connected via high-performance liquid chromatography (HPLC) fittings to a syringe pump that supplies fresh electrolyte from an inert gas purged reservoir. Additionally, a tube-in-tube (de-) aeration system (based on devices applied in flow synthesis) is connected upstream of the cell providing continuous, highly controllable gas dissolution into the electrolyte across a gas-permeable Teflon AF-2400 tubing, used for polarization experiments in different dissolved gas concentrations. Four outlets are arranged in a circular way around the inlet, two of which are intersected by compartments for reference and counter electrode (RE and CE), respectively. The placement of both RE and CE downstream of the WE prevents the former two from acting as a source of contamination and eliminates the need for diffusion barriers. A Kalrez perfluoro elastomer O-ring sandwiched between WE and the upper PEEK part defines the cell volume and prevents the electrolyte from wetting the top-contact, thus eliminating it as a source of contamination. The distance between nozzle and electrode (i.e., the cell height) is fixed at 0.5 mm by spacers machined directly into the fluidic PEEK part of the cell, independent from O-ring compression. While several designs of the electrochemical flow cell suitable for different substrate sizes are in operation, the calculations presented herein are based on a design with a 9.25 mm O-ring inner diameter and a corresponding wetted area of approx. 100 mm² typically used for 15 × 15 mm² substrates. Another cell geometry for 10 × 10 mm² samples is presented in the Supplementary Information.

**Theoretical background.**—The reciprocal total (i.e., measured) current ($1/\text{I}_{\text{tot}}$) of an irreversible faradaic reaction of first order with respect to the reactant’s concentration, as measured on a uniformly accessible electrode, can be described as a sum of the reciprocal of the kinetic current ($1/\text{I}_{\text{kin}}$, i.e., the current that one would measure in the absence of mass transport limitations) and the reciprocal of the mass transport limited current ($1/\text{I}_{\text{lim}}$), according to the well-known Koutecký-Levich equation:

$$ \frac{1}{\text{I}_{\text{tot}}} = \frac{1}{\text{I}_{\text{kin}}} + \frac{1}{\text{I}_{\text{lim}}} \tag{1} $$

The only electrode to date fulfilling the need for uniform accessibility implied in the above equation is the rotating disk electrode (RDE). While Wakabayashi et al. applied Eq.1 also to channel electrodes, its use for these has been scrutinized and, in agreement with experimental data, Scherson et al. later published a modified K-L type equation also for channel electrodes:

$$ \frac{1}{\text{I}_{\text{tot}}} = \frac{1}{\text{I}_{\text{kin}}} + 0.93 \frac{1}{\text{I}_{\text{lim}}} \tag{2} $$

Similarly, a K-L type relation was proposed for wall-jet electrodes by Albery and later applied for kinetic studies. If $\text{I}_{\text{tot}} < \text{I}_{\text{lim}}/2$, the wall-jet electrode’s accessibility is sufficiently uniform to obtain:

$$ \frac{1}{\text{I}_{\text{tot}}} = 1.06 \frac{1}{\text{I}_{\text{kin}}} + \frac{1}{\text{I}_{\text{lim}}} \tag{3} $$

Both modified K-L type relations (Eq.2 and 3), however, have been derived for certain cell geometries, preventing their direct application to a generic electrochemical flow cell.

**Governing equations.**—The model was split into fluid dynamics and mass transport parts, each reflected by their governing equations and boundary layer properties. The fluid flow can be described by the incompressible Navier-Stokes equation under the assumption of constant temperature and electrolyte density throughout the cell:

$$ \rho \frac{\partial \text{u}}{\partial t} = \mu \nabla^2 \text{u} - \nabla p + \rho \text{F} \tag{4} $$

where $\rho$ is the density, $\text{u}$ is the velocity tensor, $t$ is the time, $\mu$ is the fluid’s dynamic viscosity, $p$ is the pressure tensor and $\text{F}$ is the external force tensor. Further, assuming a steady-state velocity profile ($\frac{\partial \text{u}}{\partial t} = 0$) and negligible external force ($\text{F} = 0$), Eq. 4 reduces to:

$$ \mu \nabla^2 \text{u} = \nabla p \tag{5} $$

The mass transport can be described by the Nernst-Planck equation. Using a supporting electrolyte providing sufficient conductivity and an abundance of spectator ions, the migration term can be neglected. The convective term takes advantage of the solution of the above fluid dynamics part, thus introducing the need for a coupling solver scheme:

$$ \frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \text{u} \cdot \nabla c + r \tag{6} $$

where $c$ is the concentration of the reacting species, $D$ is its diffusion coefficient and $r$ describes an external chemical reaction rate. Under the assumption of a steady-state concentration profile ($\frac{\partial c}{\partial t} = 0$) as above and the absence of a chemical reaction rate term ($r = 0$), Eq. 6 reduces to:

$$ \nabla \cdot (D \nabla c) = \text{u} \cdot \nabla c \tag{7} $$

**Boundary conditions.**—The geometry and boundary conditions of the numerical simulation are summarized in Figure 2. To solve Eq. 5 for the fluid dynamics a linear flow velocity condition was assumed at the inlet (shown in red in Figure 2). For comparison with the measured polarization currents obtained using a syringe pump to drive the electrolyte in real experiments, the flow velocity was implemented as an average volumetric flow rate. For the outlets (shown in green in Figure 2), a pressure boundary condition was established with a value of $10^5$ Pa, reflecting atmospheric pressure. Furthermore, the symmetrical design of the flow cell was exploited to reduce the computational domain to one-eighth of the original model by applying symmetry boundary conditions at the symmetry lines (shown in blue in Figure 2). All other boundary layers including the electrode were implemented as no-slip walls with a fluid velocity of zero relative to
the wall. The initial velocity of the fluid body across the model was also set to zero.

For the mass transport problem introduced with Eq. 7, the inlet was described as an inflow boundary condition with an inlet concentration \( c_{in} \), whereas the outlet was implemented as an outflow boundary condition. Again, the symmetry lines were implemented as symmetry boundary conditions with a mass flux equal to zero in the direction normal to the boundary. To describe electrochemical reactions taking place at the electrode surface, a vanishing flux of reactive species was chosen as the boundary condition. For reversible electrochemical reactions (like the hydrogen oxidation/evolution reactions (HOR/HER) considered below) the flux \( N \) can be described using the form of the Butler-Volmer equation below:

\[
N = \frac{i_0}{F n} \left[ c_{surface}^{f} \exp \left( \frac{\alpha_f F}{RT} \eta \right) - c_{bulk}^{f} \exp \left( - \frac{\alpha_r F}{RT} \eta \right) \right]
\]

where \( i_0 \) is the exchange current density, \( F \) is the Faraday constant (96 485 C mol\(^{-1}\)), \( n \) is the number of transferred electrons per reacting molecule, and \( c_f \) and \( c_r \) are the concentrations of reacting species for the forward and the reverse reaction, respectively, at the electrode surface (\( c_{surface}^{f} \)) and in the electrolyte bulk (\( c_{bulk}^{f} \), which is identical to \( c_{in}^{f} \)). Additionally, \( \alpha_f \) and \( \alpha_r \) are the transfer coefficients for the forward and the reverse reaction, respectively, \( \eta \) is the overpotential, \( R \) is the ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the temperature. The roughness factor, customarily a part of this equation, has been assumed to be unity in this study, with the exchange current densities accounting for this.

On the other hand, for irreversible reactions proceeding at high overpotentials (like the OOR, also regarded herein) Eq. 8 simplifies to:

\[
N = - \frac{i_0}{F n} c_{surface}^{f} \exp \left( \frac{\alpha F}{RT} \eta \right)
\]

In this work Eq. 8 was used to describe the HOR, assuming an equal concentration of protons at the electrode surface and in the bulk of the solution (\( c_{surface}^{f} = c_{bulk}^{f} = 1 \)), while Eq. 9 was used without changes to model the OOR. All other boundary layers were implemented as no flux walls, for the mass transport problem being identical to the symmetry boundary condition. The initial concentration of the reacting species within the fluid body across the model was set to zero.

It should be noted that this numerical model does not hold for turbulent flow: while the Reynolds number \( Re \) can be used to characterize the flow based on velocity, density, and viscosity of the electrolyte, the geometry’s characteristic length changes along the fluid pathway, resulting in different values across the whole cell. However, within the nozzle where the characteristic length is at its smallest and the flow velocity largest, \( Re \) is in the order of 20 – 100, well below the transition to a turbulent flow regime at \( Re \approx 2000 \).

Meshing.—The model geometry was constructed with the computer-aided design (CAD) software CATIA V6 and transferred to the finite element method (FEM) software COMSOL Multiphysics 5.2, where the geometry was refined and discretized within three regions. A “Free Triangular” mesh was applied to the electrode surface, whereas a “Free Tetrahedral” mesh was applied to the fluid body of the model. A “Boundary Layer” mesh was applied to all no-slip walls to increase the accuracy of the computation fluid dynamics calculations at the interface. At the interface between triangular and tetrahedral mesh close to the electrode surface, the number of boundary layer mesh elements was increased, thus increasing the resolution of the model in close vicinity of the electrode. In order to distinguish wall-jet and channel type electrode parts, the electrode surface was split into a center disk and a peripheral ring part, described by an areal ratio parameter \( R_A = A_{center} / (A_{center} + A_{periphery}) \), corresponding to the disk-type fraction (i.e., \( A_{center} \)) of the whole electrode surface (i.e., \( A_{center} + A_{periphery} \)). Furthermore, a 2-step mesh refinement study was conducted, firstly decreasing the thickness of the first “Boundary Layer” mesh element by increasing the total amount of the latter until the local electrode current remained stable. Successively, the mesh element size for the “Free Triangular” mesh was decreased and chosen such that the total electrode current was steady upon a further change of the element size. Due to the partitioning mentioned above, the “Free Triangular” mesh was split into center and periphery parts as well and would change slightly upon variation of \( R_A \). Therefore, the difference in total electrode current for \( R_A = 0.005 \) and 0.25 was also assessed to assure a stable mesh. Details of the mesh refinement have been summarized in Table SI-1 and the results thereof are presented in Figure SI-1 of the Supplementary Information.

### Results and Discussion

In the following sections, the results of the computational simulations and a comparison of the model to experimental results will be presented. The reactions of choice were the HOR/HER and the OOR on platinum, both in acidic electrolyte. Kinetic and experimental parameters used for the numerical simulations were extracted from the literature and are summarized in Table I above.

#### Diffusion limited region.—In a first step, an overpotential \( \eta \) sufficiently high to yield a concentration of the reacting species equal to zero at the electrode surface was chosen for Eqs. 8 and 9 (see overpotential for diffusion control in Table I). The resulting flow profiles - obtained by solving Eq. 5 - at a volumetric inlet flow rate of 2 ml min\(^{-1}\) are shown in Figure 3a. Due to the small inlet nozzle diameter, the electrolyte enters the reaction compartment at high velocity, spreads over the electrode surface expanding and subsequently slows down. This behavior has been observed by Fuhrmann et al. for similar cell geometries. Solving Eq. 7 yields the total flux \( N \) of reacting species flowing over the electrode surface, and the multiplication of \( N \) by \( F \) and \( n \) results in the local current density \( \text{i}_{\text{loc}} \) shown in Figure 3b.

As expected from the velocity distribution, the highest concentration of reactive species is supplied to the center of the electrode with the smallest diffusion layer thickness and the highest local current density. Towards the outlets - shown as white circles in Figure 3b - the electrolyte velocity decreases, the supply of fresh reactants diminishes and the concentration boundary layer increases. Considering the
boundary layer as an array of finite resistors with a value proportional
to the boundary layer thickness, the electrode current is highest in the
electrode center and almost negligible in the region of stagnant
electrolyte. This leads to a highly non-uniform current density distribution
and highly localized probing of the electrode’s surface. Measurements
on not perfectly homogeneous electrodes are, therefore, difficult to in-
terpret with the presented cell design and efforts have been directed at
the optimization of the cell geometry via numerical modelling studies
not shown herein.

Subsequently, integration of $i_{loc}$ across the whole electrode surface
yields the current density $i_{tot}$, corresponding to the measured current
density in an experiment. The former is shown in Figure 3c as a func-
tion of the volumetric inlet flow rate for HOR conditions according
to Table I. A power fit $i_{tot} = p \cdot V_{in}^q$ in the range 0.5 to 5 ml min$^{-1}$
reveals an exponent $q$ of 0.40, lying in-between the values of 0.33
and 0.5 that would be expected for a channel or a thin layer flow cell,
respectively.$^{32,34}$ Therefore, the application of either Eq. 2 or Eq. 3
to obtain a pure kinetic current $I_{kin}$ does not appear appropriate for
the cell geometry considered herein. On the other hand, upon closer
examination of the flow profile in the plane of the in- and outlet cross-
section, one can distinguish two different flow regions depending on
inlet flow rate (cf. Figure 4a). A layered flow profile indicative of lam-
inar flow is observed in the region far from the inlet nozzle, whereas a
wall-jet-like flow profile forms at the inlet and extends into the chan-
nel region with increasing $V_{in}$. At $V_{in} \geq 4$ ml min$^{-1}$, a recirculation
region becomes apparent at the inlet nozzle due to the constriction
of an ideal wall-jet flow profile in the present case. In Figure 4b, the
concentration of the reactive species is plotted normalized to the inlet
concentration ($c_{in}$); it is apparent that, under these flow conditions, the
diffusion boundary layer thickness is sufficiently small to not interfere
with the height of the cell.

**Electrode partitioning.**—Subsequently, the electrode surface
was partitioned in a center (“wall-jet”) and a periphery (“channel”) part, described by the areal ratio parameter $R_s = A_{center}/(A_{center} + A_{periphery})$ mentioned above. Calculating $i_{tot}$ for

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**Figure 3.** (a) Computed streamlines of the fluid velocity $U$ with color bar representing the velocity magnitude under HOR conditions at a flow rate of 2 ml min$^{-1}$. (b) Computed local current density $i_{loc}$ across the electrode surface for the same parameters. In- and outlets are shown as white ellipses. (c) Computed $i_{tot}$ for the HOR at $\eta = 0.5$ V as function of $V_{in}$.

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**Figure 4.** Computed flow velocity profile (a) in the center plane at different volumetric inlet flow rates $V_{in}$. Contour lines for comparison drawn at $U = 40, 80, 120,$ and 160 mm s$^{-1}$, respectively. (b) The corresponding concentration plots under the same conditions.
both center and periphery parts for volumetric inlet flow rates of 0.5–5 ml min\(^{-1}\), separate \(i_{\text{tot,center}}\) and \(i_{\text{tot,periphery}}\) values were obtained. Reproducing the approach followed above, the exponents \(q_{\text{center}}\) and \(q_{\text{periphery}}\) of the power fit \(i_{\text{tot}} = p \cdot V_m^q\) were obtained for each ratio \(R_A\) using a least squares method, and are displayed in Figure 5. The summation of \(i_{\text{tot,center}}\) and \(i_{\text{tot,periphery}}\) yields \(i_{\text{tot}}\) for the whole electrode area as function of \(R_A\). The exponent \(q\) thereof was employed to verify the stability of the mesh for every partitioning step by comparison with the expected value for the non-partitioned model of 0.40.

From Figure 5 it is apparent that an areal ratio of \(R_A = 0.025\) (corresponding to a disk radius of 860 μm) results in an excellent match between \(q_{\text{periphery}} = 0.34\) and the expected value of 0.33 for a channel electrode.\(^{32}\) At the same \(R_A\), \(q_{\text{center}} = 0.67\), which is smaller than the value of 0.75 expected for an ideal wall-jet electrode,\(^{33}\) possibly due to the inability of a pure wall-jet flow profile to be formed due to the small distance between electrode and nozzle discussed above. The decrease of \(q_{\text{center}}\) for \(R_A < 0.025\) can be explained considering that, approaching a center diameter in the order of the inlet nozzle’s diameter, a wall-tube electrode arrangement is effectively formed. The flow profile thereof has been studied by several authors\(^{35,64,65}\) and a correlation of \(I_{\text{lim}}\) to \(V_m^{1/2}\) has been proposed.

In a first approximation, the velocity profile at \(R_A = 0.025\) can therefore be interpreted as a superposition of wall-jet and channel flow profiles. Considering \(I_{\text{lim}}\) in the mass transport limited region to be infinite and inserting the corresponding equations for \(I_{\text{lim}}\) in the inverse of the total current plotted against the inverse of the flow rate to the respective power (cf. Table I) is expected to yield a line with an intercept of zero. Therefore, a plot of the reciprocal current computed at \(\eta = 0.5\ V\) for the HOR at the center and the periphery parts as functions of \(1/V_m^{3/4}\) and \(1/V_m^{1/3}\), respectively, can be used to verify the applicability of the partitioning method, as shown in Figure 6 for \(R_A = 0.025\).

For the electrode partitioned at \(R_A = 0.025\), the intercept of the linear fit for the peripheral part in Figure 6b is close to zero, which would correspond to \(I_{\text{lim}}\) approaching infinity for large values of \(V_m\), according to Eq. 2 and the obtained current being truly diffusion limited. On the other hand, the corresponding intercept for the center part in Figure 6a does not reach zero within the fitted range, which is expected as the corresponding exponent \(q_{\text{center}} = 0.68\) (cf. Figure 5) is significantly below the value of 0.75 assumed for an ideal wall-jet flow profile. Nevertheless, a linear summation of Eq. 2 and 3, weighted by \(R_A\) according to Figure 5, leads to the following equation separating kinetic and mass transport determined currents:

\[
\frac{1}{I_{\text{tot}}} = R_A \cdot \left( \frac{1.06}{I_{\text{kin}}} + \frac{1}{I_{\text{lim}}} \right) + (1 - R_A) \cdot \left( \frac{1}{I_{\text{kin}}} + \frac{0.93}{I_{\text{lim}}} \right) \tag{10}
\]

which, after simplification, yields:

\[
\frac{1}{I_{\text{tot}}} = \frac{1}{I_{\text{kin}}} + \frac{1 + 0.06 \cdot R_A + 0.93 + 0.07 \cdot R_A}{I_{\text{lim}}} \tag{11}
\]

The proposed equation can be validated in the limiting cases of \(R_A\); for \(R_A = 0\), Eq. 11 yields Eq. 2 for the channel electrode and in the opposite case of \(R_A = 1\), Eq. 3 for the wall-jet electrode is obtained. The non-zero intercepts pointed out in Figure 6 introduce an error regarding the accuracy of Eq. 11, and its order of magnitude is discussed below. With \(R_A\) being very small for the flow cell geometry studied herein, Eq. 11 resembles Eq. 2 for the channel electrode. These findings agree with the correlation of \(I_{\text{lim}}\) to \(V_m\) with the power of 0.40, which is closer to the correlation expected for a channel rather than a wall-jet flow profile, which has also been shown in Figure 6.

### Koutecký-Levich analysis.

A combined parametric sweep of the overpotential \(\eta\) and the inlet flow rate \(V_m\) was performed to obtain the computed HOR polarization plots shown in Figure 7. The curves match the Nernstian diffusion current \(i_{\text{diff}}\) plotted as solid gray lines, which is observed for reactions with extremely fast kinetics and can be calculated using the equation below:\(^{36}\)

\[
i_{\text{diff}} = i_{\text{lim}} \left[ 1 - \exp \left( \frac{-2F}{RT} \eta \right) \right] \tag{12}
\]

It is well known that, due to these ultra-fast kinetics, the study of the HOR in acidic electrolytes on Pt-surfaces requires tools enabling extremely high mass transport rates such as the H\(_2\) pump,\(^{5,6,7}\) scanning electrochemical microscopy\(^{9,70}\) or micro-electrodes,\(^{71}\) with a recent review given in Reference 72. Thus, while the model accurately represents the diffusion-controlled polarization curves expected for
measurements carried out in a limited mass transport regime (such as
the RDE), the impossibility to derive kinetic information from these
computed polarization curves makes these unsuitable to demonstrate
the application of Eq. 11 for a complete K-L analysis.

Instead, ORR polarization curves were modelled applying Eq. 9
at the electrode surface and using the corresponding parameters listed
in Table I. Comparison of Figure 8a with literature studies of the
ORR on platinum reveals a good match of the current onset at an
overpotential of ≈0.27 V (corresponding to a measured potential of
≈0.95 V vs. RHE, based on an equilibrium potential of 1.23 V vs.
RHE). However, the limiting currents are significantly lower upon
comparison with RDE studies (e.g., ≈2 mA cm⁻² at 5 mL min⁻¹ in
Figure 8a, vs. ≈6 mA cm⁻² in an RDE rotating at 1’600 rpm); a
discrepancy that can be attributed to a weaker source of convection in
the flow cell considered in this study.

From the polarization curves, Tafel plots were obtained for both
the non-corrected currents and after application of Eq. 11, shown in
Figures 8b and 8c, respectively. It is apparent that, at low overpo-
tentials in which the total current is barely affected by mass transport
limitations (i.e., \( \eta_{\text{ORR}} \leq 0.35 \) V), the Tafel slope \( b \) can be obtained with
sufficient accuracy without applying a diffusion correction. To report
catalyst ORR-activities, a similar approach is conventionally used,
that is, by comparing the kinetic currents at potentials in the range of
\( \approx 0.85 \) to \( \approx 0.95 \) V vs. RHE, instead of deriving \( i_0 \) via extrapolation
of \( i_{\text{kin}} \) over several orders of magnitude. The overlapping polarization
currents in the kinetically controlled region at potentials of \( E > 0.85 \) V
vs. RHE for different inlet flow rates in Figure 8a and the Tafel plots
in Figure 8b to 8d confirm that this approach would also be suit-
able for comparison of catalysts tested with the presented flow cell,
validating our previous assumptions. To further verify this point,
experimental data of the surface-specific ORR-activity of polycrys-
talline platinum (PtPoly, circles) and platinum nanoparticles supported
on a high surface area carbon (PtHSAC, diamonds) at 0.9 V vs. RHE
derived from RDE-measurements in perchloric acid electrolyte are
also plotted in Figure 8c for comparison. It should be noted that,
for the model, sulfuric acid was used regarding input values of \( \mu, \rho, c_{\text{in}}, D \) (cf. Table I), whereas the experimental data used for this
comparison was obtained in perchloric acid. While it is well-known
that (bi-)sulfate species partially block the active sites in platinum
and lead to lower ORR activities in sulfuric vs. perchloric acid, this
effect is not accounted for in the simple Butler-Volmer equation
applied in the numerical model (cf. Eq. 9), rendering these computed
results comparable to experimental data obtained in a non-adsorbing
electrolyte such as the perchloric acid used in those studies. Furth-
more, the kinetic parameters \( (i_0, \alpha) \) in Table I were derived from fuel
cell measurements using platinum nanoparticles supported on a high

Figure 7. Computed HOR polarization curves obtained based on the para-
eters listed in Table I for different inlet flow rates. The corresponding diffusion
currents \( i_{\text{diff}} \) calculated according to Eq. 12 are shown as solid gray lines.

Figure 8. (a) Computed ORR polarization curves. (b) Corresponding Tafel plots for the non-corrected total currents and (c) kinetic currents after diffusion
correction applying Eq. 11, and (d) in the same graph at a flow rate of 1 ml min⁻¹ for ease of comparison. Experimental data at 0.9 V vs. RHE for platinum
nanoparticles supported on a high surface area carbon (PtHSAC) and polycrystalline platinum (PtPoly) from the literature are shown as black diamond and a black
circle, respectively.
surface area carbon as the cathode catalyst instead of polycrystalline platinum due to the lack of reliable exchange current densities thereof, which explains the excellent match of the computed $i_{0,model}$ value at 0.9 V vs. RHE with the corresponding experimental data for PtHSAC. This discrepancy between the specific activities for Pt-based catalysts with different dispersions/surface areas has been observed before and correlated to the ECSA in an experimental master curve, as well as supported by earlier DFT calculations.

If, as in this study, a complete K-L analysis is to be considered, the application of Eq. 11 extends the range in which a linear fit yields $b$ and $i_0$, increasing its reliability. However, since K-L type equations are not applicable within the region of complete mass transport limitation (i.e., at $\eta > 0.6$ V) due to insufficient current resolution, it is interesting to assess the maximum value of $I_{tot}/I_{tot,max}$ at which a Tafel fit yields $b$ and $i_0$ with sufficient accuracy. In Figures 9a and 9b these values are shown as solid red lines after diffusion correction with Eq. 11; $b$ and $i_0$ as obtained from the non-corrected (mass transport limited) currents are shown as black lines. For comparison, the currents were also corrected applying the equations for channel and wall-jet electrodes (cf. Eqs. 2 and 3), which appear plotted as solid and dash thick gray lines, respectively. As expected from the similarity of Eqs. 11 and 2, the accuracy of the respective Tafel fits matches as well. Following diffusion correction with Eq. 3, though, the Tafel fit yields a less accurate $i_0$ (Figure 9b) even for low ratios of $I_{tot}/I_{tot,max}$; however, $b$ (Figure 9a) is more accurate. It should be noted that, contrary to the common experimental practice referred to above, the extension of the fitting region to $I_{tot}/I_{tot,max}$ values $> 0.5$ still yields $b$ and $i_0$ with high accuracy. This can in part be attributed to the fact that the computed currents at low overpotentials are therefore not affected by mass transport losses and are much more accurate in the numerical simulation as compared to experimental studies. Nevertheless, the precision at $I_{tot}/I_{tot,max} > 0.5$ is adversely affected by $V_{in}$, which has been chosen as 2 ml min$^{-1}$ for the results presented in Figure 9 and the results need to be scrutinized in view of the application to experimental data.

**Comparison to the rotating disk electrode.**—Previous experimental and modelling studies on channel flow cells and SFCs found that the application of Eq. 1 for the rotating disk electrode results in sufficiently accurate diffusion correction for the K-L analysis of the ORR, regardless of cell geometry. While Wakabayashi et al. did not present any explanation for applying Eq. 1 to their channel flow double electrode cell, Kulyk et al. performed numerical simulations similar to those in this work that demonstrated the applicability of the general K-L equation with a ±6% precision across the complete current range. However, the authors did not provide an analogous study for the K-L type equation of a channel electrode, which, considering the geometry of their SFC, would be a more reasonable choice. Applying Eq. 1 and assessing the accuracy of $b$ and $i_0$, as shown in Figures 10a and 10b, these observations are confirmed to extend to the geometry modelled in this study. In fact, a comparison with the kinetic parameters obtained after diffusion correction with Eq. 11 shows that the K-L equation for the rotating disk yields more accurate results than any of the other K-L type equations studied herein. Considering that the equations for the channel and the wall-jet electrode (Eqs. 2 and 3, respectively) are based on the general K-L equation and contain approximations implying numerical errors that were not discussed in the respective references, it is reasonable to assume that the linear combination of the aforementioned equations into Eq. 11 will result in error propagation. Regardless of this aspect, for the ensemble of cell geometry, range of flow rates, and kinetic parameters studied herein, we propose that the application of Eq. 1 is sufficient for the K-L analysis, for which errors are generally dominated by experimental factors.

**Conclusions and Outlook**

Fluid profile and mass transport in an electrochemical flow cell were studied via numerical simulation. A simple model was developed to accurately calculate the electrode current of the ORR and HOR both in the mass transport limited regime and upon consideration of electrode kinetics. A novel method to obtain K-L type equations for electrochemical flow cells with superimposed flow profiles of channel and wall-jet electrodes was presented and verified by assessing the precision of $b$ and $i_0$ for the ORR on platinum in acidic electrolyte obtained by the K-L analysis. While the method can be applied to any kind of such cells, the partitioning ratio $R_k$, determining the weight of the channel and wall-jet electrode parts for a linear combination to obtain a K-L type equation, is expected to differ for different cell geometries. One such geometry with different O-ring diameter and outlet channel angle is presented in the Supplementary Information. Similarly, extending the range of calculated flow rates will modify the...
value of \( R_f \) obtained by the electrode partitioning method. For EFCs of arbitrary geometry, the model could be applied to calculate the corresponding polarization curves and, by variation of the numerators of a K-L type equation and assessment of its precision (cf. Figures 9 and 10), a K-L type equation for any EFC geometry could be obtained. It was shown that, for commonly used experimental conditions, the ORR currents at 0.85–0.95 V vs. RHE are largely unaffected by mass transport, confirming earlier assumptions to compare the catalysts' specific activities without the need for a complete K-L analysis.\(^{63,74}\) Furthermore, the applicability of the well-known K-L equation for the RDE was confirmed for the electrochemical flow cell presented herein and compared, over a large current range, to the respective equations for the channel\(^{19}\) and wall-jet\(^{20}\) electrodes, as well as for their linear combination regarded herein (cf. Eq. 11). It was found that the general K-L type equation for the RDE produces the most accurate results, similar to results presented by Kulyk et al.\(^{37}\) We assume this behaviour to be related to error propagation from the K-L equations for the channel and wall-jet electrodes.

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