A Modified Koutecký-Levich Equation for the Analysis of Electrochemical Flow Cells with Complex Geometries

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Abstract

Electrochemical flow cells have found widespread use in analytical chemistry due to their short response time, high sensitivity and selectivity [1, 2]. The geometrical flexibility and therefore, the ease of coupling the electrochemical to other experimental techniques has attracted considerable interest for applications in electrocatalytic research as well. Such coupling is far more cumbersome with the rotating disk electrodes (RDEs) often used in this field, which on the other hand have proven their long-standing value as an analytical tool mostly due to their unique laminar flow profile with a uniform distribution of the reacting species' concentration across the electrode surface [3]. Being the only uniformly-accessible electrode known to date, the Koutecký-Levich (KL) equation can be applied to separate mass transport and kinetic related currents during a polarization RDE-experiment [4]. While similar KL-type equations have been proposed for wall-jet [5] and channel [6] electrodes, their applicability is limited to idealized cell geometry. In this work, we present a numerical approach to obtain a modified KL equation for electrochemical flow cells with complex geometries containing elements of both fluid profiles of wall-jet and channel electrodes.

We use COMSOL Multiphysics® software to model laminar flow velocity profiles of electrochemical flow cells described previously [7] featuring flow profile elements from both channel and wall-jet electrodes. The above is coupled to the Nernst-Planck equation describing the transport of diluted species towards an electrode surface represented as an equation based species flux following the Butler-Volmer equation.

By segmentation of the electrode into two parts described by a 'wall-jet to channel' ratio, a parametric sweep of the latter reveals an optimal partitioning where each part closely follows the relation between mass transport limited current (Ilim) and inlet flow rate (Vin) expected for wall-jet and channel electrodes, respectively. Thus, a modified KL equation is proposed by averaging the respective KL equations for channel and wall-jet electrodes according to the ratio obtained by numerical simulation.

In conclusion, we will present a novel approach to obtain a Koutecký-Levich type equation for electrochemical flow cells based on a geometrical combination of wall-jet and channel electrodes. These findings allow the application of highly flexible flow cells with nearly arbitrarily complex flow profiles in cases where the derivation of kinetic data is of prime importance. Experimental verification of the presented model is currently in progress, and
preliminary results will also be presented.

Reference