Appendix A: Fit curve for chronopotentiometry

To compare the chronopotentiometric series quantitatively with each other, the chronopotentiometric series can be fitted with a theoretical function. Using such a universal function, the chronopotentiometric series can be described using the ohmic resistance (derived from the initial jump in voltage when a current starts or stops), the non-ohmic resistance (derived from the latter stationary voltage) and the time scale thereof.

As indicated in the main text, the chronopotentiometric series are too complicated for an analytical solution. An empirical function is used to fit the experimental data. As the chronopotentiometric series approach asymptotically an equilibrium value for each current, an exponential or hyperbolic function is most probable.

Such an exponential function is given by:

$$U = \beta_1 \cdot e^{-t/\tau} + \beta_2 \qquad \text{(eq. A1)}$$

And a suitable hyperbolic function is given by:

$$U = \beta_1 \cdot \left(\frac{1}{t/\tau + 1} \right) + \beta_2 \qquad \text{(eq. A2)}$$

In which U is the electrode voltage (V) is the time after the start or stop of the electrical current (s) and β_1, β_2, and τ are parameters to fit each stage of the experimental series. The parameter β_1 acts as the amplitude of the non-ohmic overpotential (V), β_2 acts as the voltage at the start or stop of the electrical current (V) and τ is the time scale for the non-ohmic resistance (s).

An example of (part of) a chronopotentiometric series is given Fig. A1, together with two possible fitted functions according to eq. A1 and A2.

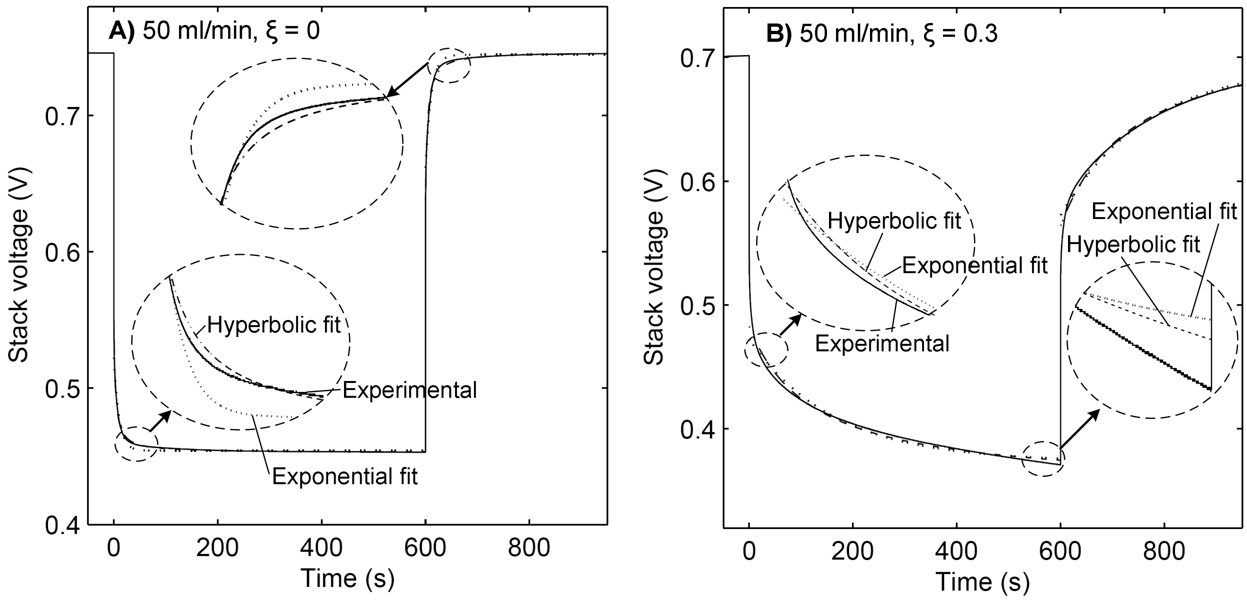

Figure A1: Chronopotentiometric series for a stack with a feed water flow rate of 50 ml/min, in case none of the channels is blocked (A) and in case 30% of the channels is blocked (B). The solid line represents experimental data, the dotted line indicates the exponential fit (eq. A1) and the dashed line indicates the hyperbolic fit (eq. A2). A current density of 10 A/m^2 was applied between 0 and 600 s, while open circuit was applied at the other time. The sections near t = 0 s and t = 600 s are zoomed.

As demonstrated in Fig. A1, the hyperbolic fit describes the experimental data better than the exponential fit. The difference is most pronounced in the case where no preferential channeling occurs (Fig. A1A), but also the case with preferential channeling fits better to a hyperbolic function than to an exponential function (Fig. A1B). Therefore, we use a hyperbolic function to fit the experimental data and calculate the parameters β_1, β_2, and τ for each stage.