Overpotential Identifiability for Electrode Characterization in Water Electrolysis

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Abstract

In water electrolysis, the kinetic overpotential of the oxygen evolution reaction leads to significant energetic losses. To reduce the kinetic overpotential, new electrode materials are frequently investigated. For the characterization of investigated electrodes in terms of performance, the different overpotentials in an experimental setup must be accurately estimated. Estimates of the overpotentials can be obtained by fitting a model of the setup to experimental data. However, the model estimates might have large uncertainty, which needs to be quantified. To this end, we perform parameter estimation and identifiability analysis based on a set-membership approach to determine confidence intervals for the overpotentials. As experimental data, we use chronopotentiometry measurements from a beaker cell setup. The results allow to get an impression of the uncertainty not only of the model parameters but also of the overpotentials themselves and hence of the relative importance of different loss mechanisms.

**Keywords**: modeling, parameter estimation, uncertainty, electrochemistry, hydrogen

* 1. Introduction

In water electrolysis, the operating voltage at a certain current, i.e., production rate, is a key factor influencing the system efficiency. The operating voltage is given by the sum of the equilibrium potential and several overpotentials. These represent the voltage losses caused by various phenomena. The kinetic overpotential needed to overcome activation energies required for the oxygen evolution reaction has a large contribution to the total voltage losses (Fabbri et al., 2014). Therefore, new electrode materials are frequently investigated (Wang et al., 2020). These materials are often tested in experimental setups that differ from industrial cell designs. To help transfer results from the experimental setup to industrial cell designs, the different overpotentials must be quantified as accurately as possible from the experimental data. To this end, a model of the experimental system can be used to get an estimate for each overpotential. To get an impression of how reliable the obtained estimates are, it is desirable to quantify the uncertainty in terms of confidence intervals. This allows to analyze if the uncertainty is sufficiently small, which is a requirement for reliably transferring the results to a model of the industrial cell design.

In this work, we aim at quantifying the uncertainty in parameters as well as overpotentials using methods from the field of identifiability analysis. Identifiability analysis aims at assessing whether parameter values can be estimated uniquely for a given model structure and data set (Guillaume et al., 2019). We adopt the set-membership method used by Jung et al. (2019), which allows to obtain confidence intervals by approximating the feasible parameter set and solving a constrained optimization problem. In contrast to local methods that compute the confidence intervals based on the Fisher information matrix, the method has the advantage that the identifiability analysis is global such that the whole parameter space is considered. The approximation of the feasible parameter set allows the method to be less computationally expensive than when an exact description of the feasible parameter set is used. Using the set-membership method, we derive confidence intervals for both parameters and overpotentials based on chronopotentiometry measurements from a beaker cell setup.

* 1. Methodology

To obtain confidence intervals for the overpotentials, we investigate an indirect and a direct approach. In the former, parameter confidence intervals are obtained using the set-membership approach described by Jung et al. (2019). The overpotential confidence intervals are then calculated by maximizing and minimizing the respective overpotential at each current density separately and restricting the parameters to be within the priorly obtained parameter confidence intervals. In the case of the direct approach, we directly use a set-membership approach to maximize and minimize each overpotential at each current density separately, while enforcing respective identifiability constraints.

We use experimental measurements for the oxygen evolution reaction at the anode side of alkaline water electrolysis in a beaker cell setup as described in Thissen et al. (2023). In the beaker cell, a reference electrode is used so that the contribution of the anode can be observed independently of the cathode. A 1 cm² industry-standard Ni mesh is used as both anode and cathode. Chronopotentiometry measurements at several current densities were conducted in a 30 wt.% KOH solution at 80°C.

We assume that a steady state is reached during chronopotentiometry and hence use a steady-state model to describe the system. The used model is comparably simple and includes a kinetic (ηkin) and ohmic overpotential (ηohm). Mass transfer and gas bubble effects are expected to be less pronounced at the present experimental conditions and due to continuous stirring, and are hence neglected. We model ηkin using the Tafel equation and the ηohm with a constant resistance. The steady-state model therefore includes three parameters: the ohmic resistance, the exchange current density, and the Tafel slope.

* 1. Results

The results show that both the indirect and the direct approach can be used to obtain overpotential confidence intervals. While the confidence interval for ηohm is the same for both approaches, the confidence interval for ηkin differs significantly and is much tighter for the direct approach. Assuming an experimental noise of 1 mV, the obtained confidence interval for ηkin at 1 A/cm2 is around ±10 mV and ±90 mV for the direct and indirect approach, respectively. While both approaches ensure the fulfillment of the identifiability constraints, the direct approach gives a tighter and therefore clearer picture of the overpotential confidence interval. The overpotential confidence intervals allow to get an impression of the uncertainty in the overpotential contributions and therefore show how accurately the contribution of the individual loss mechanisms can be identified. In the context of electrode characterization, this allows to analyze how reliable ηkin can be estimated.

* 1. Conclusions

In this work, we show how identifiability analysis can be employed to obtain confidence intervals for overpotentials and therefore analyze the uncertainty in the estimation of overpotentials. A low uncertainty in the estimation of overpotentials is necessary for the results to be reliably transferable from an experimental setup to a model of the industrial cell design. Certain estimates of the overpotentials further allow to assess the contribution of different phenomena (e.g., kinetics and mass transfer) to the overall cell potential and therefore identify levers for potential improvement. In case of a high uncertainty in the estimation of overpotentials, further measurements might help to achieve lower uncertainty. Either way, quantifying the uncertainty is a key first step. Such an approach is expected to be even more relevant when more complex models are used to describe the system and additional overpotential contributions are considered. Furthermore, these methods can be used to estimate overpotential confidence intervals based on different or multiple electrochemical measurements in the future.

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