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Two-phase model of hydrogen transport to optimize nanoparticle catalyst loading for hydrogen evolution reaction

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ABSTRACT

With electrocatalysts it is important to be able to distinguish between the effects of mass transport and reaction kinetics on the performance of the catalyst. When the hydrogen evolution reaction (HER) is considered, an additional and often neglected detail of mass transport in liquid is the evolution and transport of gaseous H₂, since HER leads to the continuous formation of H₂ bubbles near the electrode. We present a numerical model that includes the transport of both gaseous and dissolved H₂, as well as mass exchange between them, and combine it with a kinetic model of HER at platinum (Pt) nanoparticle electrodes. We study the effect of the diffusion layer thickness and H₂ dissolution rate constant on the importance of gaseous transport, and the effect of equilibrium hydrogen coverage and Pt loading on the kinetic and mass transport overpotentials. Gaseous transport becomes significant when the gas volume fraction is sufficiently high to facilitate H₂ transfer to bubbles within a distance shorter than the diffusion layer thickness. At current densities below about 40 mA/cm² the model reduces to an analytical approximation that has characteristics similar to the diffusion of H₂. At higher current densities the increase in the gas volume fraction makes the H₂ surface concentration nonlinear with respect to the current density. Compared to the typical diffusion layer model, our model is an extension that allows more detailed studies of reaction kinetics and mass transport in the electrolyte and the effects of gas bubbles on them.

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Introduction

The production of hydrogen by the electrolysis of water could enable the storage of large amounts of solar energy over long

time periods. Both solar cells connected to a separate electrolyzer and integrated devices, such as photoelectrochemical cells, could accomplish this at high efficiency [1]. While the integrated devices could benefit from their smaller number of components and lower current density at the electrodes, they

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are also technically more challenging than connecting a solar panel to an electrolyzer [2,3].

One of the challenges has been to find efficient, stable and cheap catalyst materials. The total reaction of the electrolysis consists of two half-reactions: the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Several catalyst materials have been studied for both reactions, but so far no HER catalyst has shown a performance comparable to that of platinum (Pt) [4,5]. In fact, the charge transfer kinetics of HER on Pt are so fast that the total overpotential comes almost entirely from mass transport losses, which are consequently sometimes mistaken for reaction kinetics [6–9]. Therefore, understanding the effects of mass transport on the total reaction overpotential, so that they can be reliably distinguished from the kinetics of the charge transfer reactions, is important in order to avoid misinterpretations of measurement results, since the kinetics are the primary focus of attention in performance optimization and mechanistic studies of new HER catalysts.

In our recent feasibility study of ultra-low Pt loadings for use in photoelectrochemical H₂ production we combined experiments with numerical simulations to determine the minimum Pt loading necessary to drive HER in an integrated photoelectrolysis cell [10]. The numerical simulations agreed well with the experiments and showed that Pt loading as low as 100 ng/cm² is enough to drive HER at a 10 mA/cm² current density and a 50 mV overpotential [10]. While this already demonstrated the feasibility of ultra-low Pt loadings, the simulation results also clearly confirmed mass transport effects as the main factor limiting the performance of Pt-based photocathodes, which calls for further attention to this topic.

In this article we develop the single-particle model used in Ref. [10] to provide a more detailed description of H₂ mass transport at the photocathode. For the sake of simplicity, H₂ transport in gaseous form was excluded from the previous version of the model [10], because simulations with the more detailed model presented here had shown that, at the current densities generated by un-concentrated sunlight, H₂ mass transport appears similar to diffusion and can therefore be accurately treated by considering only dissolved H₂. Here, we report the model in its extended version that also takes into account gaseous H₂, as well as the dissolution kinetics between the gaseous H₂ in the bubbles and the dissolved molecular H₂ in the liquid phase.

Describing mass transport as a diffusive process is very common, because with some measurement setups (e.g., nano- and microelectrodes [11,12]) mass transport is indeed diffusive, and in other cases, such as with rotating disc electrodes (RDEs) [13], as long as the surface concentration depends linearly on the current density, the surface concentration and mass transport limitation can be described with diffusion, regardless of the actual mass transport process.

Our mass transport model describes both H₂ gas bubbles and H₂ dissolved in water as individual molecules. This is a worthwhile detail to pay attention to because experiments indicate that only the hydrated H₂ molecules in liquid can react at the electrode, whereas the gaseous H₂ is only a passive spectator of the electrode reactions, although most of the H₂ in water actually exists in the gaseous form (bubbles) [14].

When H₂ is generated, these nanobubbles (diameter ≈ 440 nm [14]) act as the nucleation centers for the growth of bubbles [15]. Moreover, it has been observed that increasing the amount of gas bubbles in liquid electrolyte may enhance mass transport, i.e., reduce the thickness of the diffusion layer [16]. Therefore, it is important for a detailed description of mass transport to consider both hydrated molecules and gas, as well as the dissolution kinetics of H₂ between the liquid and gaseous phases.

Our model is an attempt to describe the effects of the H₂ bubbles on the mass transport within the diffusion layer methodology. Practical simulations often use the diffusion layer approximation because of its simplicity and relatively good accuracy when its thickness is sized correctly. However, with gas bubbles the mass transport of H₂ varies with the current density [16], and therefore the diffusion layer thickness would also need to be adjusted. Several models for the effect of the bubbles on mass transport exist, but they may be quite elaborate [17]. The purpose of our model is to formulate a simple mass transport model that would consistently take the effects of the gas bubbles into account, so that an accurate estimate of the mass transport near equilibrium together with the dynamics of the mass transfer from the liquid to the bubbles would correctly adjust the overall mass transport conditions to the current density.

Although our model has to be solved numerically, we also develop a simplified version of it that can be solved analytically. Later we will discuss the properties of these models, with most of the attention being paid to a comparison between the numerical simulations and the analytical approximation to study the validity of the simplified model compared with the full numerical model. Since the diffusion of H₂ molecules is a typical approximation for their mass transport and our model is based on the diffusion layer approximation, we also discuss the properties of our model in comparison with the pure diffusional transport of a single chemical species. We also discuss details of the reaction kinetics, especially how the hydrogen coverage of the catalyst affects its current–overpotential curve.

The insights obtained in this study help to provide an understanding of the details of H₂ transport in liquid and the role of the related properties. Although the model assumes a low gas concentration, it serves as a step towards including gas bubbles and their interactions with the liquid electrolyte in the mass transport models used for performance modeling and the simulation of photoelectrochemical devices.

Model of the reaction kinetics and mass transport

In this section we describe our model of HER reaction kinetics and mass transport. Our model of the HER reaction kinetics is based on an earlier model by Wang et al. [18] and was described in detail in our earlier article [10], so here we discuss only its essential parts. The most important difference between our model and theirs is that we consider the effect of mass transport on all concentrations and the surface hydrogen coverage, whereas in the model of Wang et al. proton transport and the effect of mass transport on the

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