Numerical simulation of gas-diffusion-electrodes with moving gas–liquid interface: A study on pulse-current operation and electrode flooding

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ABSTRACT

In gas-diffusion-electrodes of electrochemical systems, the interface between gas and liquid electrolyte can move with operation time. It is challenging to mathematically assess moving interfaces, especially if the transient and spatial distribution of species are of interest. We mathematically model a gas-diffusion-electrode and apply a finite volume method with moving grid to solve the model equations. The step-size of the finite volume method is coupled to the moving gas–liquid interface, which is coupled to the current density applied. In detail, we study pulse-current operation and flooding of the electrode, and investigate parameters that influence the oxygen distribution in the electrode. The results obtained emphasize the benefit of the moving grid method applied. This method is able to assess the accurate diffusion resistance for oxygen in the gas-diffusion-electrode. Based on this work, possible limitations of gas-diffusion-electrodes can be derived for their usage in metal air batteries.

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1. Introduction

Secondary zinc air batteries might be the upcoming alternative to state-of-the-art lithium-based battery systems due to their higher theoretical energy density (Caramia and Bozzini, 2014). One key-part of zinc air batteries is the gas-diffusion-electrode. There, the transport of gaseous species, and the electrochemical reactions of gaseous and liquid species occur. Since species transport limits the electrochemical performance at high current densities, the reaction and transport processes as well as their interaction have to be investigated intensively before novel electrode structures and innovative operation strategies can be proposed.

Existing model approaches consider the gas-diffusion-electrode in zinc air batteries as zero-dimensional with sufficient supply of reactants (Deiss et al., 2002; Schröder and Krewer, 2014). Thus, these approaches are limited to describe spatial concentration distributions in the electrode and electrode-specific phenomena, such as flooding of the gas-diffusion-electrode with liquid electrolyte. Flooding can be caused by a volume expansion of anode material in zinc air batteries (Schröder et al., 2014; Arlt et al., 2014). This leads to an increased liquid level in the gas-diffusion-electrode, and shifts the gas–liquid interface with operation time. A model-based description of a gas-diffusion-electrode can help to widen the insight into the flooding mechanism and its impact on the oxygen distribution inside the electrode.

In this novel work, we set up a one-dimensional model of a gas-diffusion-electrode. The model contains partial differential equations for species concentrations, e.g. Fick's second law, and electrochemical relations. Due to the nature of the problem considered, i.e. changing liquid volume in the gas-diffusion-electrode, we aim to directly track the gas–liquid interface position during the numerical simulation. Thus, the one-dimensional model is discretized in space for this work with a moving grid finite volume method as suggested by Ferziger and Perić (2002) (chapter 12.4, p. 375–378). Primarily, this method is chosen because it can be used without violating mass conservation (Ferziger and Perić, 2002; Cao et al., 2003; Brio et al., 2010). There are multitudes of other approaches to solve the underlying partial differential equations: analytically (Crank, 1975), with various discretization methods (Eymard et al., 2000), or with volume-of-fluid methods, which require to implement momentum conservation equations and thus require additional computational effort (Hirt and Nichols, 1981).

Considering the large amount of extensive numerical studies for two-phase flows (Tryggvason et al., 2001; Muradoglu and Kayaalp, 2006; Dong et al., 2014; Balcázar et al., 2014), it is evident that

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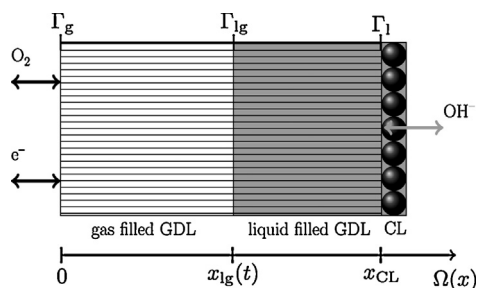*E-mail address:* u.krewer@tu-braunschweig.de (U. Krewer).

Fig. 1. Schematic of the gas-diffusion-electrode investigated, with gas-diffusion-layer (GDL), catalyst layer (CL), and the parts filled with liquid electrolyte and gas phase. The time-dependent position of the gas–liquid interface, Γ_{lg}, is situated at x_{lg}. The boundary interfaces are indicated with Γ_l and Γ_g, respectively. The position of the catalyst layer is at x_{CL}; it marks the end of the domain considered in this work.

moving grid methods become more and more important for a variety of engineering applications. In general there are several moving grid methods with numerous variations reported in literature. Koltakov and Fringer (2013) state that there are mainly two classes of moving grid methods: the first class of methods dynamically adds grid points during the simulation in regions where an increased resolution is necessary, and then removes grid points in regions that are not of interest. To identify cells which need modification requires high computational effort and dealing with variable sized data structures. The second class of methods leaves the number of grid points unchanged, but dynamically moves them during the simulation. Their movement is based on a certain strategy or physical phenomena in grid regions of interest. Since the number of grid points is thereby fixed, this method might be easier to implement than for methods with adding or removing grid points. Furthermore, grid points at the interface of two phases normally align with mesh elements of the exact solution of the mathematical problem, so that moving mesh methods improve simulation accuracy (Koltakov and Fringer, 2013; Huang et al., 1994).

In the following, we first will describe the mathematical model of the gas-diffusion-electrode, and then briefly explain the finite volume method with moving grid applied. Subsequently, we compare efficiencies of moving grid and standard finite volume method with fixed grid by means of specific test cases. Furthermore, we investigate parameters that influence the oxygen distribution in the gas-diffusion-electrode, and implement pulse-current operation and flooding of the electrode as test cases. This analysis will help to further understand the diverse reaction and transport processes in gas-diffusion-electrodes, which in the end helps to optimize such electrodes and operation strategies applied.

2. Gas-diffusion-electrode model

In the following, the gas-diffusion-electrode (GDE) considered in this work is described. Furthermore, it is explained where a moving gas–liquid interface is expected.

The GDE is composed of a porous gas-diffusion-layer (GDL) and an attached porous catalyst layer (CL). Both are partly filled with air and liquid electrolyte (KOH-solution), respectively. A schematic of the GDE is given in Fig. 1. At the CL, the following electrochemical reaction takes place

$$\frac{1}{2}O_2 + H_2O + 2e^- \overset{r(t)}{\rightleftharpoons} 2OH^- \tag{1}$$

with $r(t)$ being the reaction rate of reaction (1).

This reaction is reversible, and enables either oxygen reduction or oxygen evolution, which implies that oxygen can either be consumed or produced in the GDE. For oxygen reduction, gaseous oxygen needs to diffuse through pores of the GDE, dissolves in the liquid phase, and subsequently diffuses through the liquid filled

part of the GDE in order to reach the CL, where it reacts electrochemically.

2.1. Model domain

All governing equations are considered for the one-dimensional space-domain $\Omega(x)$, which is illustrated in Fig. 1. The GDE is situated in $\Omega(x)$ and ranges from 0 to x_{CL}. $\Omega(x)$ contains the gas filled and liquid filled sub-domains Ω_g and Ω_l, respectively. Each sub-domain is confined by two interfaces that are indicated with Γ. Thus, there are four interface boundaries: one outer interface boundaries to ambient air, Γ_g, one inner interface boundary, Γ_l, and two inner interface boundaries, Γ_{gl} and Γ_{lg}, at the same position in between Ω_l and Ω_g. The inner gas–liquid interface between both domains is discussed in more detail in Appendix A.

2.2. Governing equations

2.2.1. Mass balances and charge balance
Species concentrations in gas phase ($j = O_2$) and in liquid phase ($j = O_2, OH^-$) are calculated with Fick's second law and a source term (Wang et al., 1998), so that

$$\frac{\partial c_j(t,x)}{\partial t} = \nabla \left(-D_{j,h}^{eff} \cdot \nabla c_j(t,x) \right) + Q_j(t,x) \tag{2}$$

This equation is a parabolic partial differential equation. Therein, c_j is the molar concentration of a species, $D_{j,h}^{eff}$ the effective diffusion coefficient of a species through the fluid h, which is corrected for the porosity of the GDL, ε_{GDL}, so that

$$D_{j,h}^{eff} = \varepsilon_{GDL} \cdot D_{j,h} \tag{3}$$

where $D_{j,h}$ is the diffusion coefficient for species j in fluid h. For fluid h being a liquid, i.e. liquid KOH-electrolyte, the diffusion coefficient for O_2 is implemented as a function of c_{OH^-} in this work, as given by (Davis and Horvath, 1967).

$Q_j(t, x)$ is a source or sink term for species j, which is determined by chemical or electrochemical reactions taking place. For this work, solely the electrochemical reaction (1) is considered to occur at x_{CL} directly at the catalyst. Consequently, Q_j becomes zero for all $x < x_{CL}$. Directly at x_{CL}, Q_j is described as product of the volume specific reaction rate, $r(t)/A \cdot d_{CL}$, and the stoichiometric coefficient of species j in reaction (1), ν_j, so that

$$Q_j(t, x) = \begin{cases} 0 & \text{if } x < x_{CL} \\ \nu_j \cdot \dfrac{r(t)}{A \cdot d_{CL}} & \text{if } x = x_{CL} \end{cases} \tag{4}$$

where A is the cross-sectional area of the GDE, d_{CL} is the catalyst layer thickness.

$r(t)$ is expressed by a Butler–Volmer expression, as proposed by Mao and White (1992), so that

$$\begin{aligned} r(t) = \quad & k_{forw} \cdot \frac{c_{H_2O}}{c^{ref}} \cdot \left(\frac{c_{O_2}^*}{c^{ref}} \right)^{\frac{1}{2}} \cdot \exp \left(\frac{-(1-\alpha) \cdot F}{R \cdot T} \cdot \eta \right) \\ - \; & k_{backw} \cdot \left(\frac{c_{OH^-}}{c^{ref}} \right)^2 \cdot \exp \left(\frac{\alpha \cdot F}{R \cdot T} \cdot \eta \right) \end{aligned} \tag{5}$$

where c^{ref} is a reference concentration of $1000\ \text{mol m}^{-3}$, k_{forw} and k_{backw} are reaction rate constants for the anodic and cathodic reaction of reaction (1), respectively. α is the charge transfer coefficient for the electrochemical reaction, F is Faraday's constant, R is the universal gas constant, and T is the temperature in the GDE.