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Characterization of gas diffusion electrodes for metal-air batteries

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HIGHLIGHTS

- 2D and 3D multiphase lattice-Boltzmann models are presented
- Simulations on high resolution FIB-SEM reconstructions of Ag GDEs are performed
- Efficient methodology for the screening of GDE saturation behavior
- Saturation-dependent correlations for structural and transport parameters

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ABSTRACT

Gas diffusion electrodes are commonly used in high energy density metal-air batteries for the supply of oxygen. Hydrophobic binder materials ensure the coexistence of gas and liquid phase in the pore network. The phase distribution has a strong influence on transport processes and electrochemical reactions. In this article we present 2D and 3D Rothman-Keller type multiphase Lattice-Boltzmann models which take into account the heterogeneous wetting behavior of gas diffusion electrodes. The simulations are performed on FIB-SEM 3D reconstructions of an Ag model electrode for predefined saturation of the pore space with the liquid phase. The resulting pressure-saturation characteristics and transport correlations are important input parameters for modeling approaches on the continuum scale and allow for an efficient development of improved gas diffusion electrodes.

1. Introduction

Metal-air batteries possess a very high theoretical energy density which makes them interesting for both mobile and stationary applications [1,2]. At the negative electrode, metals like Al [3], Li [4], Mg [5], Na [6,7], and Zn [8,9] were suggested in the literature [10]. In recent years Li-air batteries received the most attention in the battery community [11,12]. However, the only system which successfully reached the stage of mass production is the primary Zn-air battery. At the positive electrode oxygen is reduced and evolved during discharge and charge, respectively. Sufficient supply of O_2 during discharge is accomplished by the concept of porous gas diffusion electrodes (GDEs). The electrodes are commonly made of carbon materials. However, in aqueous systems carbon is known to dissolve ('carbon corrosion') and carbon-free GDEs were proposed [13–15]. Hydrophobic binder materials ensure the coexistence of gas and liquid phase in the porous structure of the GDE. The saturation behavior is characteristic for the porous material and can be described by capillary pressure saturation (p_c–s) curves. The amount and distribution of the liquid phase has a strong influence on transport processes. The transport in the gas phase ensures a good supply of O_2 and, thus, allows to draw high current densities. Moreover, the binder improves the mechanical stability of the electrode. During discharge the conditions in the GDE change due to the formation of solid discharge products (e.g. Li_2O_2 or Na_2O in

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non-aqueous Li-air and Na-air batteries, respectively). This will affect the electrolyte distribution and might eventually cause transport limitations of oxygen.

Due to their application in alkaline fuel cells the concept of gas diffusion electrodes was studied already in the 1960s. Design optimizations of the electrodes were mainly done by intensive experimental studies. In recent years the improvements in computational efficiency made computer simulations a common design tool in the engineering disciplines. However, traditional CFD (computational fluid dynamics) tools like the volume of fluid (VOF) method [16,17] have their limitations in the simulation of multiphase flow in complex geometries. In recent years the lattice Boltzmann method (LBM) [18–20] became increasingly popular for this class of problems because it is easy to implement and scales favorably. In LBM a probability distribution of discrete particle velocities is propagated on a computational lattice. Interactions between particles, boundaries, etc. are modeled by suitable collision operators. Several multiphase models were suggested in the literature for the simulation of immiscible fluids [21]. The most prominent ones are the Shan-Chen model [22,23], the free-energy model [24,25], and the color gradient or Rothman-Keller (RK) model [26–28]. A common problem of the methods is the numerical stability and accuracy in the simulation of systems with high density and viscosity ratios which also includes the air-water system. Recent publications present modifications of the models which are able to overcome this limitation [29,30]. This extends the applicability of the method to technical systems like gas diffusion media of polymer electrolyte fuel cells and the number of publications in the field increased rapidly [31–36]. However, to our knowledge this is the first publication of pore-scale LBM simulations of gas diffusion electrodes for metal-air batteries. In our work we use an RK type multiphase model to simulate multiphase flow in two and three dimensions. The model is based on the work of Leclaire [37–39] and Liu et al. [40]. In their publications the authors successfully demonstrated the simulation of high density ratios. In our study we focus on aqueous electrolytes, however, the presented methodology is not limited to this case. An important feature of our model is that we explicitly take into account the non-homogeneous wetting properties of the GDE which consists of hydrophilic electrode particles and hydrophobic binder fibers. This is an important step and has been barely pursued in previous pore-scale studies of electrochemical devices [34,41–45]. In general it is straightforward to extend our model to an arbitrary number of solids with different wetting properties. Therefore, we are also able to characterize structures with a given distribution of solid discharge products corresponding to varying depth of discharge. The position, size, and morphology of discharge products are not predicted by our simulations but subject of ongoing research.

The focus of our article is set on the development of a methodology for the characterization of gas diffusion electrodes for metal-air batteries. In order to demonstrate our approach we use a pristine electrode sample corresponding to the beginning of discharge. First, the structure of porous Ag model electrodes is reconstructed based on FIB-SEM tomography as explained in Section 2. The reconstruction serves as simulation domain for multiphase LBM simulations. Model equations and computational details are summarized in Sections 3 and 4. 2D and 3D simulations are performed to simulate the evolution of the phase distribution towards an energetic minimum (Section 5.1). The results are evaluated to obtain characteristic pressure-saturation curves (Section 5.2) and saturation dependent transport parameters (Section 5.3).

2. Electrode reconstruction

We use samples of Ag model electrodes which were characterized regarding their electrochemical performance in our previous article [46]. The focus of this work is set on the structural characterization and investigation of transport processes on the pore-scale. In this section we explain in detail the methodology which was developed for the reconstruction of gas diffusion electrodes using FIB-SEM tomography. The suggested procedure is schematically shown in Fig. 1.

2.1. FIB-SEM

To obtain the micro-structure for our simulations a dual-beam ZEISS N-Vision 40 SEM-FIB instrument is used. The SEM has a field-emission electron gun with an acceleration voltage between 5 and 30 kV and a vertical electron-optic axis. The FIB is based on a Ga^+ primary ion-beam with a 30 kV acceleration voltage. The ion-optic axis is at an angle of 54° to the electron-optic axis. The standard vacuum levels for the electron-gun and the sample chamber are 10^{-9} and 10^{-5} mbar, respectively. The serial sectioning of the sample is achieved using FIB and the images are acquired using the SEM at specified milling intervals.

Before the SEM imaging of the sample, it must be ensured that the SEM and FIB images correspond to the same region-of-interest of the sample. This condition is obtained in the following way: Firstly, we set the sample stage to the eucentric tilt position to avoid an offset in sample position with sample tilt. Secondly, the coincidence of the electron and ion beam has to be ensured. This is established by tilting the sample by 54° with a constant working-distance of about 5 mm and adjusting the Z-axis until the SEM image of the sample comes into focus. A trench is cut into the sample in the vicinity of the region-of-interest with a relatively intense ion-beam current of 6.5 nA such that the cross-sectional (CS) plane becomes visible. The CS plane is then gently polished with an ion-beam current of 300 pA. Subsequently, the total region for 3D tomography is selected for ion-milling. The two samples were filled with a low viscosity epoxy resin in order to improve the contrast of the images. This is an important step to facilitate the reconstruction process. The left panel of Fig. 1 shows a representative SEM image. We note that the resin has rather well impregnated the pore space of the GDEs. Horizontal and vertical dimension are in the following named x and y, respectively. The direction perpendicular to the x-y plane is denoted by z and represents the direction of the FIB cut. The total thickness of the cut is 10 μm. In order to optimize the total duration of milling and image-acquisition, the SEM images are obtained at every fifth FIB-slice which results in 84 images representing slices of 0.12 μm thickness. Note, that (x, y) values of the voxel-size are related by the relation $y = x/\sin(54^\circ)$, where the value of x is determined by the magnification of the image and the 54° origin from the tilt of the sample.

2.2. Structure generation

The second panel of Fig. 1 shows a representative binarized and cropped image of the electrode micro-structure (black). The images of different slices were aligned to account for the sample-drift during imaging. The perspective correction and pixel-size adjustments were done in the software package IMOD. The epoxy resin improves the contrast in the images and helps to identify solid particles. In spots where the impregnation of the electrode is incomplete the phases are assigned manually. Further details of the methodology of reconstruction is discussed in detail elsewhere [47]. Finally, the images were stacked to a virtual structure in the commercial software GeoDict [48]. The resulting geometry can be seen in the third panel of Fig. 1. The reconstructions are mirrored at the x–y plane in order to increase the simulation domain in the