Modeling Oxygen Gas Diffusion Electrodes for Various Technical Applications

Fabian Kubannek[1], Thomas Turek[2], and Ulrike Krewer[1,*]

In gas diffusion electrodes (GDEs), electrocatalysts are in contact with gas and electrolyte ensuring a large active three phase boundary. GDEs are used for important technical applications in energy transformation and chemical synthesis. This review gives an introduction into the vast range of existing models for GDEs and their specific purpose, with an emphasis on oxygen reduction electrodes. After introducing the processes occurring in GDEs, modeling approaches are described according to their dimensionality (from 0D to 3D to multiscale) and perspectives for future research are discussed.

Keywords: Gas diffusion electrodes, Mathematical models, Oxygen reduction, Reaction transport interaction

1 Introduction

Gas diffusion electrodes (GDEs) are porous electrodes in which the solid electrocatalyst is simultaneously in contact with a gas phase and a liquid or solid electrolyte (Fig. 1). The reason for using this configuration is the strong enlargement of the active three phase boundary with direct contact between electrocatalyst and reactants compared to a completely dry or wetted electrode, where the activity would be only determined by the geometric electrode area. On the other hand, the gaseous educts and products are only able to enter and leave the electrode through diffusion. Gas evolving electrodes, such as those employed in water or chlor alkali electrolysis, are usually not classified as GDEs since

Figure 1. Schematic of gas diffusion electrode.

convective transport of gases is the predominant mechanism. The decisive role of diffusion in GDEs necessitates that very thin electrodes with typical thicknesses between 10 and a few hundred µm are employed. GDEs have to meet further requirements for successful operation. These include chemical and electrochemical stability for the given application, sufficient mechanical stability, especially in large scale electrochemical cells, high electronic conductivity, and, in most cases, also a hydrophobic/hydrophilic pore structure for easy access of both gases and liquids. GDEs can be freestanding, uniformly composed electrodes. The active material can be supported on current collectors, such as nets or fabrics, or the GDE might be subdivided into functional units, e.g., catalyst layer, microporous layer, and gas diffusion layer in fuel cells.

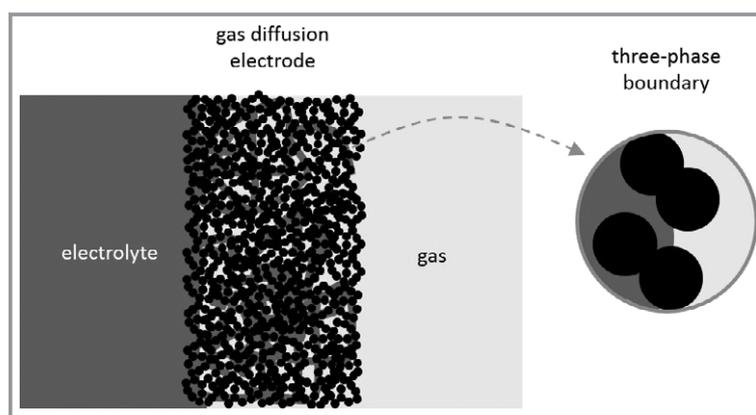GDEs are required for many important technical applications in energy transformation and chemical synthesis and were proposed for several further potential uses being under development (Tab. 1). It can be seen that especially oxygen reduction with its complex kinetics and corresponding high losses is often carried out over GDEs because high catalytic activity and large electrochemically active surface area are of utmost importance for this particular reaction.

The history of GDEs for fuel cells has been summarized by Kurzweil [7], while Li and Dai [8] give a good overview about GDEs for zinc air batteries. In 1902, Reid already

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Table 1. Examples of processes utilizing GDEs. ODC, oxygen de polarized cathode.

Application	GDE	Reaction
PEM fuel cell	anode	hydrogen oxidation
	cathode	oxygen reduction
Metal air battery	cathode	oxygen reduction
Chlor alkali electrolysis with ODC [1]	cathode	oxygen reduction
HCl electrolysis with ODC [2]	cathode	oxygen reduction
Anhydrous HCl electrolysis [3]	anode	chlorine evolution
	cathode	oxygen reduction
H_2O_2 synthesis [4]	cathode	oxygen reduction
Advanced salt splitting [5]	anode	hydrogen oxidation
CO_2 electrolysis [6]	cathode	carbon dioxide reduction

described an alkaline fuel cell with porous electrodes in con tact with gaseous reactants and liquid electrolyte [9]. The principle of GDEs was discussed by Schmidt in his early book from 1923 [10]. In 1925, Heise introduced an im proved alkaline zinc air battery using carbon electrodes treated with wax to prevent flooding [11]. A breakthrough in the manufacture of stable electrodes for alkaline electro lyte was achieved by the introduction of polytetrafluorethy lene (PTFE) as hydrophobic component and binder. On the other hand, the invention of sulfonated tetrafluoroethylene based copolymers, e.g., Nafion®, discovered by DuPont in the late 1960s allowed for the development of modern poly mer electrolyte membrane (PEM) fuel cells with an acidic solid electrolyte [12].

Properly parameterized, GDE models replace lookup ta bles to predict the performance of the electrode or cell and give an insight into limitation due to single processes. Mathematical models for GDEs were first developed for liq uid alkaline electrolytes. Austin et al. introduced a simple 1D pore model where the electrolyte fills the pores to a cer tain depth at which a meniscus is formed [13]. However, this assumption leads to very small three phase boundaries and corresponding low limiting current densities. For a more appropriate description, a second spatial domain had to be introduced, either by extending the meniscus by addi tion of a thin liquid film on the pore walls [14 16] or by dividing the electrode into hydrophilic regions filled with electrolyte and hydrophobic pores for the gas [17, 18]. In a final version, these approaches were combined in the so called thin film flooded agglomerate (TFFA) model [19]. This model allows to describe true limiting current densities and can be also employed for PEM fuel cells with solid elec trolyte.

After decades of development, modeling of GDEs for sev eral purposes has now reached a relatively mature state, albeit with important questions still remaining open. The most advanced state of GDE modeling has been achieved for PEM fuel cells. In this field, textbooks [20] and several recent reviews are available [21 23]. Especially the critical review by Weber et al. [22] gives an excellent overview about the field, with special emphasis on multiphase flow, and the most important areas for future research. For the case of modeling metal air batteries, Li et al. [24] as well as Clark et al. [25] discuss the present state and future require ments including the specific requirements for metal air GDEs.

The present review gives a comprehensive introduction into GDE modeling from an engineering rather than an electrochemical perspective. It concentrates on the oxygen reduction as the most demanding and difficult to describe reaction presently carried out over GDEs. Specific and com mon challenges of batteries, electrolyzers, and fuel cells are pointed out and discussed comparatively. After a brief introduction of the processes occurring in a GDE and their interaction, the developed approaches are systematically discussed according to their dimensionality (from 0D to 3D to multidimensional). Finally, the remaining open questions and perspectives for future research will be summarized.

2 Processes in Gas Diffusion Electrodes

2.1 Overview

In this chapter, an overview on processes that determine the electrochemical performance of GDEs is given. Fig. 2 sche matically shows the most important processes. Next to the desired main reaction, side reactions can occur. Conduction of electrons in the electrode and conduction of ions in the electrolyte determine the ohmic losses of the electrode. Mass transport resistances occur in the gas phase, where
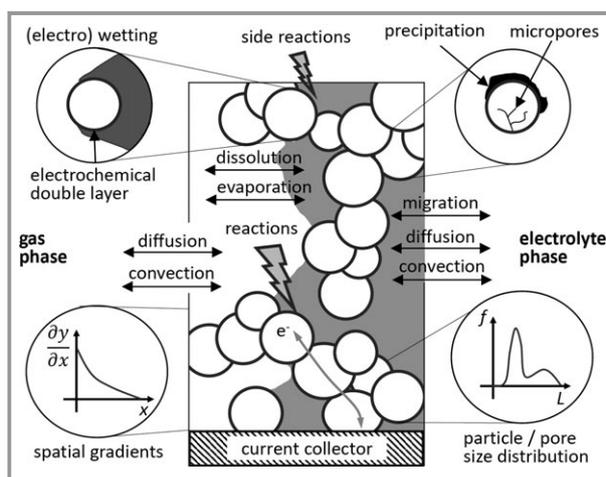
Figure 2. Schematic of processes in gas diffusion electrodes.

transport is driven by diffusion and sometimes convection, and in the electrolyte phase, where diffusion, convection, and migration are relevant. Transport processes result in spatial gradients of concentrations and potential that may be considered as well. Phase equilibria govern the dissolution of gas into the electrolyte and the evaporation of the electrolyte into the gas phase. The location of the gas liquid phase boundary is determined by capillary forces, the electrode's wetting properties, and the hydrostatic pressure of both phases. In some cases, the electrode properties that govern the processes and performance losses in the GDE are strongly inhomogeneous so that particle or pore size distributions have to be considered. If solid products precipitate in the electrode, the electrode's properties may also change over time.

In Tab. 2, common and specific challenges in the design and operation of oxygen reducing GDEs are summarized for three important fields of application. In all these applications oxygen transport and distribution play a key role. Even though the solid electrolyte in PEM fuel cells fundamentally differs from the liquid electrolyte in metal air batteries and in oxygen depolarized cathodes (ODCs), the changes in the local activity of the electrolyte are a challenge in all three systems because also the properties of the solid electrolyte strongly depend on the relative humidity that changes locally and in time. Product removal is an important factor in metal air batteries as well as in PEM fuel cells. In metal air batteries, often a solid product precipitates and blocks pores, i.e., transport pathways, and active electrode surface. In PEM fuel cells, the reaction product water might condensate and block the gas channels. In the following sections, the approaches to model the processes outlined above will be summarized.

Table 2. Common and specific challenges of oxygen reducing GDEs for different applications.

Property	PEM fuel cell	Metal air battery	Chlor alkali electrolysis with ODC
Reactant supply			
Oxygen transport and distribution	+	+	+
Electrolyte distribution			
Local distribution of liquid electrolyte		+	+
Local activity of solid electrolyte as a function of humidity	+		
Product formation			
Solid precipitation (pore and surface blocking)		+	
Liquid condensation (pore clogging)	+		

2.2 Electrochemical Reaction

The electrochemical reactions in GDEs occur at those parts of the electrode surface, where the gaseous or dissolved reactant is in contact with electrolyte and electroactive catalyst. This so called electroactive area as well as the activity/concentration of reactants, the temperature, and the local potential difference across the electrolyte/electrode interface determine the resulting reaction rate and current. If any of these variables shows a significant spatial distribution, e.g., due to slow transport processes, then local reaction rates and current densities differ, and spatially discretized models are required.

The dependency of the reaction rate on these variables is usually described with concentration dependent rate equations which contain an exponential dependence on overpotential η, i.e., the deviation of potential difference across the interface to the potential difference at zero current. The most important one is the Butler Volmer equation

$$r = \prod a_i^{|\nu_i|} k_f \exp\left(\frac{\alpha z F \eta}{RT}\right) \quad \prod a_i^{|\nu_i|} k_b \exp\left(\frac{(1 \quad \alpha) z F \eta}{RT}\right)$$

(1)

with activities a_i of species i involved in the reaction, the forward rate constant k_f, the backward rate constant k_b, the charge transfer coefficient α, the number of transferred electrons z, the Faraday constant F, and the ideal gas constant R.

The first term of Eq. (1) corresponds to the oxidation reaction of the reactants, and the second term to the reduction with the corresponding reactants. For irreversible reactions or operation far from open circuit potential, one of the terms can be omitted. This is equivalent to using the Tafel equation instead of the classical Butler Volmer equation.

Many models of oxygen reduction electrodes lump the complex elementary reaction steps to an overall reaction and reaction rate [26 28]. The elementary reaction steps depend on various factors such as catalyst material, electrolyte, potential, and surface properties. Detailed descriptions of oxygen reduction reaction (ORR) kinetics often involve H_2O_2 or adsorbed intermediates like O_2H_{ad} [29, 30] for aqueous cells as well as adsorption and desorption steps. An overview on the microkinetic reaction steps and species during ORR is given in [31] for PEM fuel cells, in [32] for alkaline fuel cells, and in [33] for metal air batteries.

Where relevant, chemical reaction steps, degradation, and side reactions in GDEs are modeled together with the main electrochemical reaction steps [34, 35]. Further aspects are kind and state of catalyst as, e.g., Pt may form electrochemically less active oxides at high potential, and redox mediators in Li air batteries to facilitate electrochemical reactions locally [36].

2.3 Mass and Heat Transport

Although, in principle, it would be possible to capture real material structures and all transport processes in porous electrodes from atomistic over nano to microscales using molecular dynamics calculations, the computational effort is still too high and, therefore, continuum models are preferred [37]. These models typically lead to a set of differential equations for the transport processes, which can be solved with conventional discretizing techniques taking appropriate boundary conditions into account. The basic mass transport mechanisms are diffusion, pressure driven convection as well as migration and electroosmotic drag, which is another convective mechanism transporting uncharged molecules together with ions in an electrical field. The driving force for all these transport processes is the electrochemical conversion of species, which is described with Faraday's law and appropriate kinetic models.

In the gas filled pores of a GDE, diffusion is the predominant mass transfer mechanism, for which different models might be used. One difficulty arises from the fact that multicomponent mixtures might be involved requiring the application of the more sophisticated Maxwell Stefan approach instead of Fick's law. To include wall collisions in narrow pores (Knudsen effect) and viscous friction, extended models such as the binary friction model (BFM) were developed [38]. Another problem is related to the required effective diffusion coefficient of the transported species, which must take into account not only bulk and Knudsen diffusion, but also the electrode porosity, the pore size distribution, and the tortuosity of the pathways. In [37], a good overview of the available procedures and correlations for estimating tortuosities and effective diffusivities in porous systems is given. In lithium air batteries, the situation is complicated by the fact that solid products precipitate in the pore system during discharge, which may lead to oxygen limitation [39].

In the electrolyte filled part of the GDE, the non ideality of the species may need to be considered for the description of diffusion. In that case, it is necessary to formulate the diffusion model with chemical potentials [40] rather than with concentrations, and appropriate relationships for the activity coefficients are required. In addition, migration of ions and electroosmotic drag of uncharged species may contribute to the overall mass transport. For a simple, ideal, and one dimensional case in steady state without convection, the flux J of an ionic species can be described with the following form of the Nernst Planck equation

$$J = -D\frac{dc}{dx} - zuFc\frac{d\varphi}{dx} \qquad (2)$$

where D is the diffusion coefficient, c the species concentration, z the valency of the ion, u the ionic mobility, F the Faraday constant, and φ the potential. The potential gradient is usually obtained from Ohm's law and inversely proportional to the effective ionic conductivity of the electrolyte.

Heat transport in GDEs can be described with model equations taking the heat source or sink of the electrochemical reaction and effective thermal conductivities into account for which again details of the porous GDE structure are required. Since GDEs are thin electrodes often made of materials with relatively high thermal conductivity, the approximation of isothermicity over the thickness of the electrode can be used in many cases. However, temperature gradients along the channels in flow fields or in the stack have to be considered.

2.4 Phase Transition and Wetting

In the GDE, gases are in contact with liquid or solid electrolyte. For the here discussed case of oxygen reduction, O_2 needs to be dissolved in the electrolyte before the reaction can occur at the electrolyte covered catalyst surface. Hence, the equilibrium concentration of oxygen has to be calculated with suitable relationships. In many cases, Henry's law can be used since the solubility of oxygen in important electrolytes is very low. On the other hand, the solvent of the electrolyte, e.g., water in aqueous systems, will evaporate and typically thermodynamic equilibrium is again assumed. For solid polymer electrolytes, swelling phenomena occur, which have an influence on transport properties and thermodynamics [41].

Important remaining questions for the case of a liquid electrolyte are to which extent and where exactly the pore system is filled with liquid, and which parts remain accessible for the gas phase. The mechanical equilibrium for a pore filled with liquid is described with the Laplace equation:

$$p = \frac{2\gamma\cos\theta}{r} \qquad (3)$$

where p is the pressure, γ the surface tension of the liquid, θ the contact angle, and r the pore radius. Depending on the local properties of the pores, part of the pore system will become accessible to the liquid. The effect of this phenomenon on the performance of silver based GDEs for oxygen reduction was investigated by Wang and Koda [42] assuming a uniform pore size. Pioneering work on the wetting of a GDE with liquid based on a realistic 2D and 3D reconstruction of the electrode structure has been recently published by Latz and co workers [43]. An important further effect that has not yet received particular attention in GDE research is electrowetting [44], where surface tension and wetting properties depend on the electric potential. This phenomenon could lead to markedly changed wetting conditions in working GDEs.

2.5 Steady State and Dynamic Interaction of Processes

Reaction, transport, and phase transition are coupled in GDE models; they strongly interact and determine the performance of the electrode. GDE performance is usually assessed by plotting the steady state electrode (over)potential vs current per geometrical area of electrode, for a certain temperature, inlet concentrations including relative humidity, and inlet flow rate or excess ratio. Especially for operation in dynamic applications or environments, for degradation or state estimation or for in depth analysis of the (interaction of) reaction, phase change, and transport processes, dynamic models are required [45]. Here, depending on the dynamics of interest, dynamic species balances, dynamic charge balances, or dynamic energy balances are required. Usually, phase change processes are assumed to be in equilibrium. For dynamics in the upper millisecond range, detailed kinetics and surface coverages of intermediates that vary over time need to be considered; mass transport processes are slower, followed by even slower heat transport processes. During dynamic load changes in the range of milliseconds to seconds, a significant proportion of the current dynamics can result from double layer charging and discharging. For GDEs which contain gaseous and liquid species in the electrode, e.g., due to formation of product water during oxygen reduction, formation of droplets, and blocking of pores or inlet/outlet channels may cause random and difficult to control behavior [46], ranging from fluctuations in the seconds to minutes range. When modeling GDEs in batteries, dynamics always needs to be considered because the state of the battery electrodes always changes with time.

kinetics at GDE surfaces, and for integration into cell [47] up to system [48] models or even application models, such as dynamic fuel cell car models. For GDEs for oxygen reduction, such lumped models can be found especially in fuel cells with solid electrolyte and in metal air batteries with liquid electrolyte.

Electrochemical reactions and their kinetics are classically studied by rotating disc electrodes using flat electrodes or depositing single catalyst particles at a flat support [49]; however, the results are often not representative for the reaction in GDEs, e.g., suggesting products that are not found in GDEs [50]. Thus, it is advisable to conduct such studies at the GDE level, where optionally transport effects are minimized with a tailored setup [51]; model based kinetic identification can then be conducted using lumped or one dimensional GDE models with detailed kinetic steps [29].

In methanol or hydrogen fed alkaline membrane fuel cells, understanding and improving water management at each GDE is a challenging task as water is consumed at the cathode during ORR, dragged to the anode, and diffuses back from the anode. Here, scenario based analysis using a set of lumped electrode models with different assumptions for water transport, e.g., with/without drag, with different humidity or diffusivity, allowed to identify how the needs of the electrodes can be satisfied by modifying material properties, geometries, or inlet conditions [47]. The studies revealed the necessity of tailoring the water diffusion flux from anode to cathode and the corresponding required membrane properties to be able to operate the GDE, because water supply for ORR via humidity at cathode inlet is insufficient (Fig. 3). The small model size and limited number of differential equations allowed even to derive handy analytical solutions.
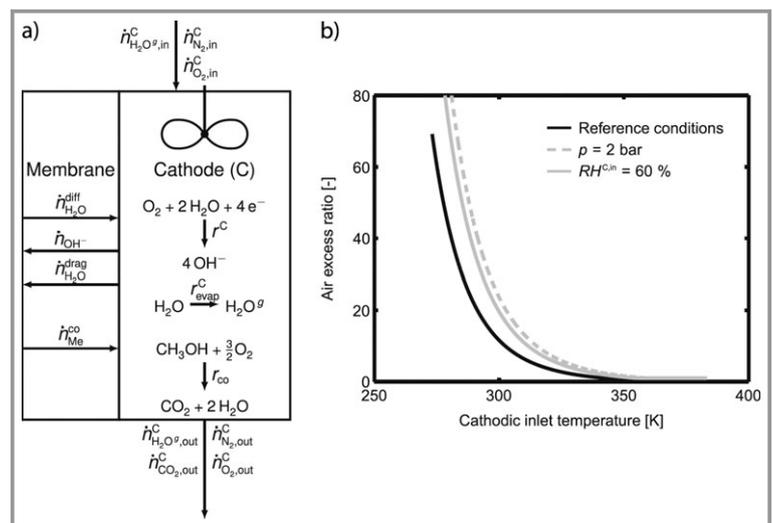
3 Gas Diffusion Electrode Models from 0D to 3D

3.1 Zero-Dimensional GDE Models

The smallest GDE models are zero dimensional (0D) in space. Such spatially concentrated GDE models generally do not account for potential, concentration, or temperature gradients inside the electrode. This makes simulation of transport processes computationally simpler and less expensive than in multidimensional models. Such models allow to focus on interaction of processes at a more general level or system level by neglecting spatial distribution in the GDE. Lumping the GDE may also be justified when comparing the thickness of the diffusion layer ($> 100\,\mu m$) to that of the electroactive GDE containing the catalyst, which is often only a few micrometers. Thus, 0D electrode models are mostly employed for fundamental studies on


Figure 3. Zero dimensional model for the oxygen electrode of an alkaline membrane fuel cell. a) Model structure, b) required minimum air excess ratio of (fully) humidified inlet to satisfy water demand when neglecting membrane transport. Adopted from [47] with permission from Elsevier.

Lumped GDE models are also used for analysis and optimization of GDEs with liquid electrolyte [52]. These are more intricate because location of the gas liquid phase boundary, and as such electroactive area, may change. Furthermore, lumped GDE models for metal air batteries may need to account for morphology or electrolyte level changes in the GDE during cycling due to metal deposition or dissolution. In Li/O_2 batteries with organic electrolyte, the main discharge reaction (Eq. (4)) yields a solid discharge product that precipitates in the pores of the cathode, changing the porosity and the available surface area:

$$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_{2(s)} \tag{4}$$

Early metal air battery models predicted the capacity based on GDE pore volume, that limits the amount of solid precipitate. In [3], transport was not considered but detailed reaction thermodynamics and energy balance for the whole cell. Wang [53] simulated the discharge curves and maximum attainable capacity of a Li/O_2 battery for different shapes of the solid discharge product as shown in Fig. 4.
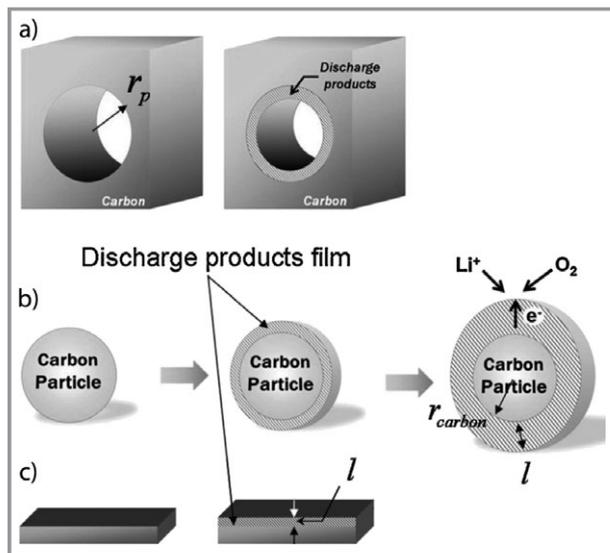
Figure 4. Three different discharge product morphologies in Li/O_2 batteries, reprinted from [53] with permission from Elsevier.

Tafel kinetics were used to describe the current potential relationship. Here, the overpotential available for the ORR is reduced by a linear voltage drop resulting from a finite conductivity of the discharge product film

$$\eta = \phi^s - \phi^{el} - E^0 + R^{prod}i \tag{5}$$

with the solid potential ϕ^s, the electrolyte potential ϕ^{el}, the equilibrium potential E^0, the current density i, and the product film resistance R^{prod} that depends linearly on the film thickness. Thus, the current potential relationship is time dependent.

It can be concluded that 0D GDE models are versatile and allow to address research questions at a general or basic level via focusing on the main effects and interactions of interest and without additional effects from spatial distribution. However, quantitative reproduction of large scale GDE behavior will be difficult.

3.2 One-Dimensional GDE Models

Lumped models neglect that under many realistic operating conditions, GDEs contain significant concentration gradients, which lead to spatially distributed reaction rates and potential. One dimensional (1D) spatial discretization can cover some of these effects; depending on the application, discretization may be through plane, i.e., between the electrolyte layer/separator and gas channel [34, 45, 51], or along the channel, i.e., from gas inlet into the cell to outlet [29]. The respective other dimension is considered again via a lumped approach.

As a result of this versatility and the still low numerical complexity and required computing power, 1D GDE models are applied for a wide range of tasks to achieve a better understanding of the bottlenecks in increasing the power density, i.e., power per geometric active area, and as such the local utilization of catalyst or volumetric current density. Studies range from designing thicknesses and other GDE parameters to analyzing and optimizing the effect of reactant distribution in the GDE. Reactant distribution is often of special interest due to two phase phenomena, e.g., water accumulation in low temperature fuel cell GDEs, or due to changes in the level of electrode flooding or solid species deposition in metal air batteries.

Along the channel models are useful especially for cells with large geometric area and low stoichiometry or risk of flooding. In [29], nonlinear frequency response of a PEM fuel cell cathode was modeled to determine if a multistep Damjanovic ORR mechanism containing an electro chemisorption or a chemisorption step would reproduce experimental data better. Gradients in oxygen partial pressure along the flow channel of the electrode were considered here and a comparatively simple convective transport mechanism was employed. However, along the channel models are mostly two dimensional, combining in and through plane approaches to account for the reactant gradients in both directions (see Sect. 3.2). Most one dimensional GDE models with solid electrolyte as well as most metal air battery models discretize in through plane direction only.

Highly used one dimensional GDE model approaches for a PEM fuel cell cathode are that of Bernardi and Verbrugge [54] and of Eikerling and Kornyshev [55]. The first model accounts for electric and ionic potential gradients, two phase flow and reaction using a concentration dependent Butler Volmer approach. More detailed 1D models may contain descriptions for flooded agglomerates in the catalyst

layer, different wettability properties within the layer and temperature balances, so that they can describe the experimentally observed performance hysteresis [56]. The model of Eikerling and Kornyshev [55] accounts for proton transport resistance, diffusion of oxygen, and the electrochemical reaction using a Tafel term and was purposely kept small as this enabled them to derive analytical solutions for certain limiting cases. The approach was extended to analytical solutions which cover a broader operating range, and it was shown to enable monitoring degradation parameters [57]. Lately, water effects were also addressed [58].

One dimensional GDE models for metal air batteries usually consider local concentration and potential gradients over the electrode thickness [34, 45, 59 61]. Along the channel or in plane models are presently barely found, as present metal air batteries have small geometric electrode areas and no active air supply, and thus, no large in plane inhomogeneity is expected.

Several models proposed for metal air battery GDEs consider the electrolyte displacement due to precipitation of a solid reaction product [45, 59]. In this case, change in porosity does not only influence transport properties like the local effective diffusion coefficient but also induces convective transport and a movement of the three phase boundary. Schröder et al. [45] and Yoo at al. [59] used a moving grid to model the volume change phenomena in an air electrode for a Zn air cell (Fig. 5). In this approach the number of discretized volume elements remains constant but the mesh size changes, requiring comparatively complex numerical solution schemes.

Other approaches put a focus on reaction mechanisms and surface passivation rather than volume changes due to precipitation. Grübl et al. [34] presented a model for a Li_2/O_2 battery with a detailed multistep reaction mechanism with the species O_2^-, LiO_2, and Li_2O_2. The solid reaction product forms a layer of constant thickness on the GDE surface and the end of discharge is reached when the electroactive surface area is zero. Additionally, the influence of a redox mediator is included to facilitate the charging process. Sahapatsombut et al. [62] compared the performance of a Na/O_2 battery with a flooded GDE to that with a partially flooded GDE. Also, here, the discharge product Na_2O_2 is assumed to form a film that allows for different discharge product morphologies. Exemplary cycling behavior is displayed in Fig. 6.

Also, for metal air batteries, wide model variations are possible, e.g., to determine maximum power for certain material parameters [60], to account in detail for nucleation processes [63] or for effects of external humidity or CO_2 accumulation [52], or to derive handy analytical models for special cases [64].

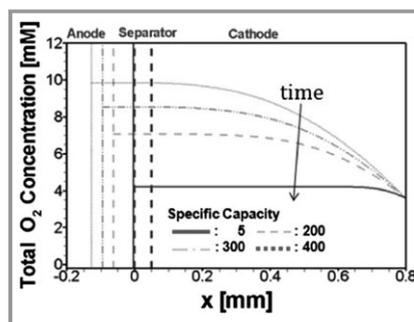All in all, 1D GDE models are similarly versatile as 0D models, but they allow to address cer

Figure 5. Oxygen concentration and position of anode/separator/cathode interfaces during discharge of a Li/O_2 battery, reprinted from [59] with permission from Elsevier.

tain spatial variations in one direction with still limited numerical complexity, and they still allow for analytical solutions.

3.3 Pseudo-Two-Dimensional GDE Models

As discussed earlier, models for GDEs should account for the large three phase boundary between gas, electrolyte, and electrocatalyst, which cannot be captured with a simple pore meniscus approach. For this reason, the meniscus was extended through addition of a thin liquid film on the pore walls (Fig. 7a) by Will [16], a model which was later also used by other groups [14, 15] for GDEs in alkaline electrolyte. An alternative approach for enhancing the three phase boundary was suggested by Newman and Tobias who divided the electrode into hydrophilic micropores filled with electrolyte and hydrophobic macropores for the gas [17]. In a similar manner, the flooded porous electrode model,
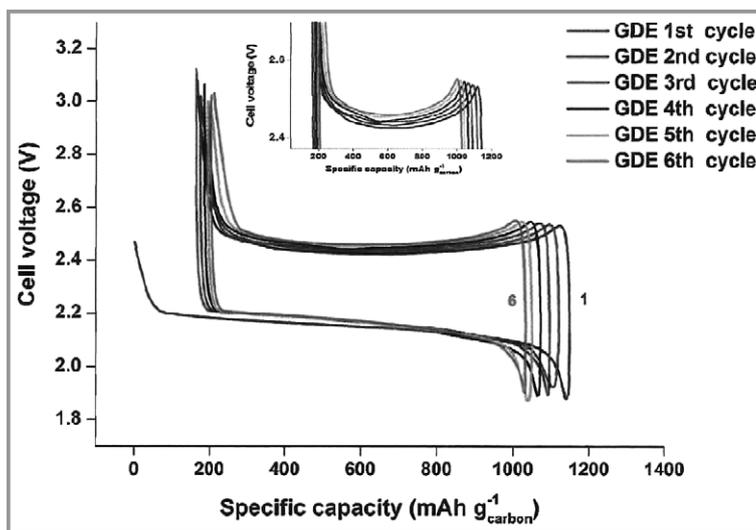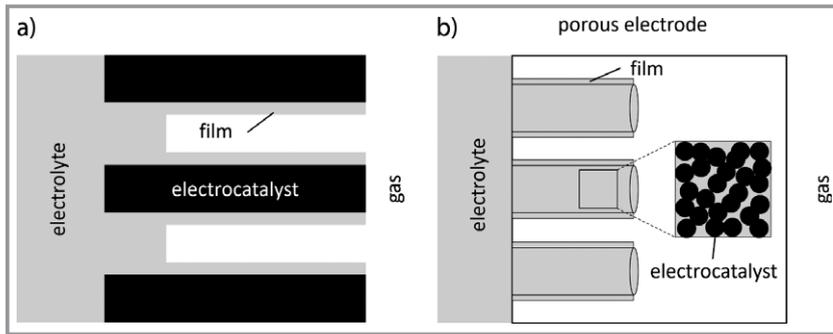

Figure 6. Simulated cycling behavior of a Na/O_2 battery. The capacity fade over cycle number is caused by side reactions with carbon dioxide and electrolyte decomposition. Reprinted from [62] with permission from Elsevier.

Figure 7. a) Thin film and b) thin film flooded agglomerate models for GDEs in contact with liquid electrolyte.

sometimes also called flooded agglomerate model, introduced by Giner and Hunter assumes that the electrode consists of two parts [18], which are either filled with gas or flooded with electrolyte. Finally, Cutlip combined these approaches in the so called thin film flooded agglomerate (TFFA) model in which the liquid filled agglomerates are coated by an additional film [19] (Fig. 7b). This extension allows to describe true limiting current densities as discussed by Pinnow et al. [65].

From Fig. 7, it becomes evident that the GDE has to be discretized in the through plane direction but that a second domain — film thickness and/or dimension of liquid filled regions — has to be additionally considered. For this reason, this type of model is considered as pseudo two dimensional (p2D). With these models, the performance of GDEs during oxygen reduction under isothermal and differential conditions could be accurately described. One example is the study of silver based GDEs in concentrated NaOH electrolyte by Pinnow et al. [65]. Fig. 8 shows that both the kinetic region and the overvoltage at industrially relevant current densities could be precisely captured. The increase of overvoltage with decreasing oxygen concentration was shown to be caused by limited oxygen diffusion inside the liquid filled parts of the electrolytes at the very low O_2 equilibrium con

centrations. Recent results by Botz et al. for the same electrode showed that the local hydroxide and water activities have an additional important influence on the GDE performance [66]. The p2D model for the Ag PTFE electrode developed by Pinnow et al. was later extended to ac count for the distribution of concentra tions and temperature along the height of the electrode [27].

Besides assuming a cylindrical geome try for the liquid filled GDE parts, a spherical shape might be used alterna tively. Svensson et al. [67] set up a dy namic model for the alkaline ORR on Pt in a GDE to derive electrochemical impedance spectra. In their flooded agglomerate model, catalyst agglomerates are completely filled with the liquid electrolyte and surrounded by gas filled pores as shown in Fig. 9. Potential variation and transport of oxygen were considered along the elec trode direction and in radial direction inside the agglomer ates.

Similar models have also been successfully employed for PEM fuel cells with solid electrolyte [28, 68, 69] and molten carbonate fuel cells [70]. A very good overview and a com parison of p2D agglomerate models for electrodes in con tact either with liquid or polymeric electrolytes can be found in the work of Perry et al. [71]. On the one hand, the fixed distribution of the electrolyte in PEM fuel cells facili tates simulation of the electrode performance, whereas the distribution of a liquid electrolyte under reaction conditions remains unknown and geometric assumptions in TFFA models cannot yet be validated in these cases. On the other hand, modeling of PEM fuel cell electrodes is extremely sophisticated given the existence of several functional layers with different properties and especially the dynamic forma tion and movement of liquid water in the pore systems.
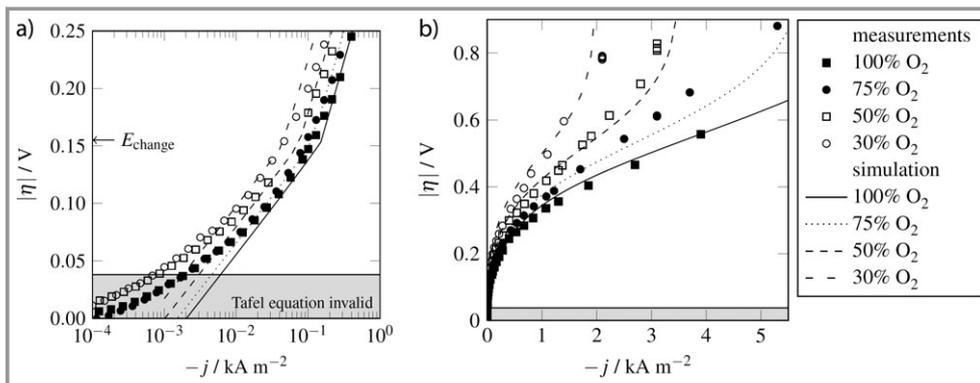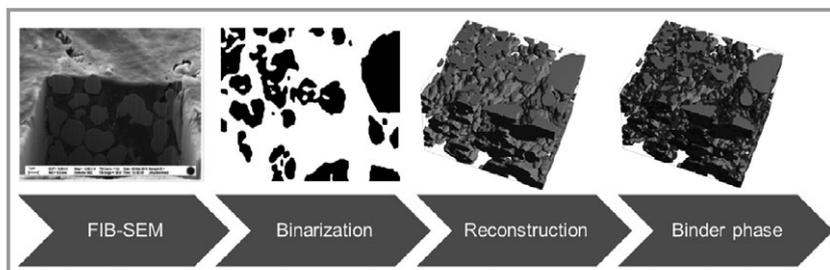

Figure 8. Overvoltage as a function of current density at different oxygen concentrations. Ag PTFE elec trode with $300\,\mu m$ thickness at $80\,°C$ in $11.25\,M$ NaOH. a) Kinetic region in logarithmic representation, b) linear graph of full overvoltage range. Reprinted from [65] with permission from Springer Nature.
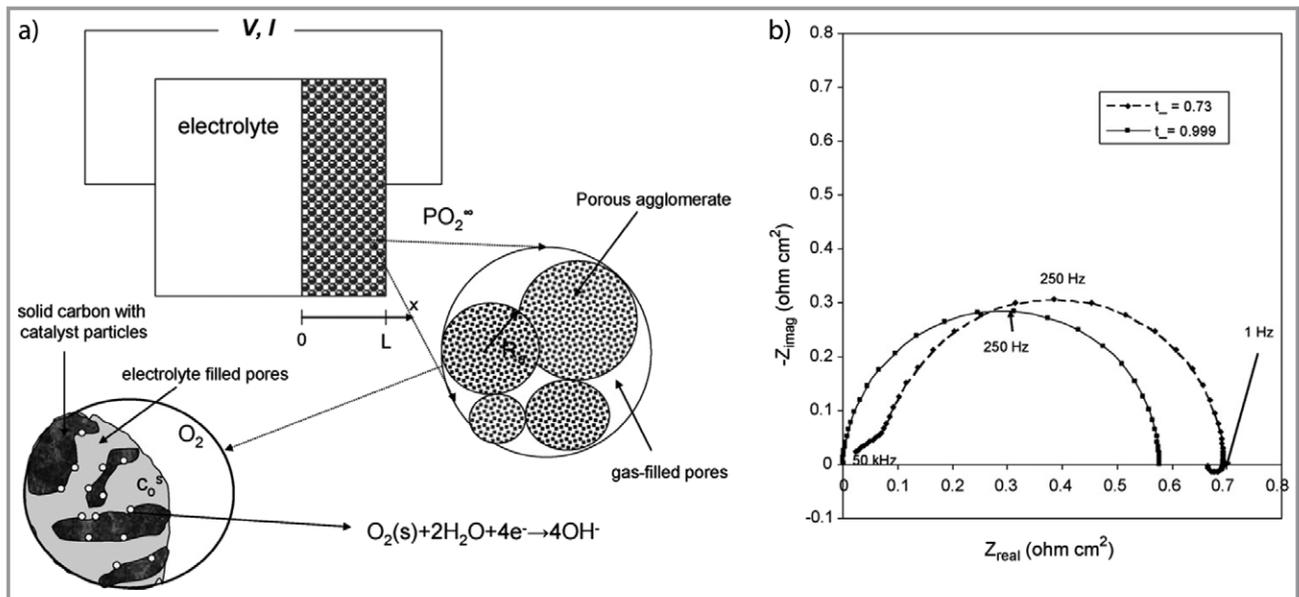
Figure 9. a) Flooded agglomerate model where the ORR takes place inside porous catalyst agglomerates that are surrounded by gas filled pores. b) Simulated EIS spectra for two different OH^- transference numbers. Reprinted from [67] with permission from Elsevier.

3.4 Three-Dimensional GDE Models

While three dimensional (3D) models for fuel cell stacks or other electrochemical devices have been used for quite some time, the development of such models for GDEs or porous electrodes in general is relatively new. 3D models on electrode scale require an appropriate representation of the complex and often distinctively anisotropic electrode structure. Until now, this approach is often restricted to the study of transport phenomena in the absence of electrochemical reactions. Hutzenlaub et al. reconstructed the cathode catalyst layer of a PEM fuel cell electrode three dimensionally with nanometer scale resolution [72]. The filling degree with liquid water and the oxygen diffusivity were calculated taking the pore size distribution and the hydrophilicity of the pore system into account. The wetting of a silver based GDE for metal air batteries with liquid based on a realistic 2D and 3D reconstruction of the electrode structure has been studied by Latz and co workers [43]. Fig. 10 shows the suggested procedure based on focused ion beam milling/scanning electron microscopy (FIB SEM) followed by digital processing.

Molaeimanesh and Akbari [73] as well as Zhang et al. [74] employed 3D lattice Boltzmann models for liquid water transport and oxygen diffusion in the cathode of PEM fuel cells. In both papers, the structure of the GDL was reconstructed based on cylindrically shaped carbon fibers. The electrochemical reaction in the adjacent catalyst layer was also taken into account as driving force for oxygen reduction and water formation. Thus, these models do not combine reaction and transport in an electrochemically active three dimensional electrode. Such a model has been presented by Bao et al. [75] who used a multiscale approach for their study of the discharge performance of Li/O_2 batteries. After reconstruction of the oxygen electrode structure through a particle packing method, the governing equations for oxygen reaction and diffusion in the porous electrode were numerically solved with an implicit finite volume scheme. Additionally, the formation of solid Li_2O_2 particles inside the pore structure (see also Sect. 3.4) was taken into account, and good agreement between simulated and measured discharge curves was achieved. The same approach was later used by Pan et al. [76] to study the optimal design of air electrode micro structures for Li/O_2 batteries.

3.5 Multiscale and Computational Chemistry GDE Models

All models outlined above are macroscopic continuum models which require to extract kinetic parameters from experi

Figure 10. Methodology to reconstruct the lattice Boltzmann simulation domain from FIB SEM images. Reprinted from [43] with permission from Elsevier.

ments, and which assume that electrode properties and state variables can be averaged within a volume element. Computational chemistry models based on first principles, density functional theory calculations, and Monte Carlo simulations do not rely on these requirements and assumptions.

The models with computational chemistry approaches are motivated by the significant advances in molecular simulations including density functional theory and molecular dynamics, promising ab initio descriptions, and more predictive modeling without experimental parameterization. They also have in common to be computationally highly demanding and to allow to simulate only up to very short time and length scales, typically below ms and nm, respectively, which is of low relevance for practical GDE operation. Also, a systematic variation of range of operating or design parameters and mathematical optimization of these parameters is prohibitively expensive presently. Consequently, these techniques have been applied to investigate certain properties of GDEs especially on a microscopic level, where the mean field assumption often does not apply. The models may come as stand alones, with detailed surface descriptions but short length and time scales, or as multiscale approaches by combining macroscopic with computational chemistry approaches to enable simulating typical GDE dimensions in the mm range and longer time spans. For example, Malek et al. [77] used coarse grained molecular dynamics simulations to investigate the morphology and transport properties of the solid electrolyte Nafion in a fuel cell GDE. Fig. 11 shows the simulated shape of a pore inside the hydrated ionomer.
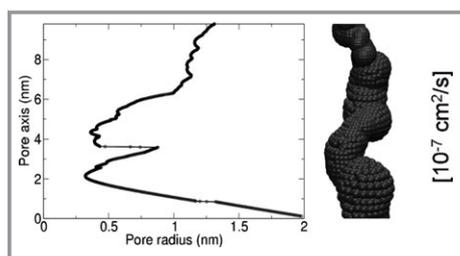
Figure 11. Pore shape and profile of the pore radius along the pore axis inside the hydrated ionomer simulated by coarse grained molecular dynamics. Reprinted from [77] with permission from AIP Publishing.

Because of their complex geometries, the large influence of transport phenomena, and various non idealities, the computational demand required by such approaches is still too high for the simulation of an entire GDE. However, some studies employ multiscale approaches that use a continuum model for the overall transport inside the GDE and that resolve phenomena of specific interest with more detailed, microscopic descriptions. Multiscale models may be entirely deterministic with continuum approaches but containing specific models for each scale. In these cases, the selection of processes that need to be resolved on microscale as well as the coupling of micro and macroscale is highly important [78].

Franco and Gerard [79] simulated the long term performance of a PEM fuel cell by coupling a macroscale model for transport and electrochemical performance with a nano scale model for prediction of carbon corrosion. Here, both models are solved simultaneously. Later on, Malek and Franco presented an extended multiscale model for aging phenomena in PEM fuel cell electrodes where parameters for the macroscale model are calculated by coarse grained molecular dynamics [35].

Bao et al. [75] link a one dimensional continuum model, that describes mass transfer and electrochemical reaction kinetics in a Li/O_2 battery, with a nano scale model, that describes the development of the active surface area during discharge. In Fig. 12a, the three dimensional reconstruction of the electrode microstructure that is used to calculate the fraction of blocked surface as a function of the amount of solid discharge product is shown. The resulting relationship (Fig. 12b) is coupled to the continuum reaction and transport model. It is clear that such approaches are very powerful but require a significant effort in model development to be able to describe the reaction transport interaction covered by macroscopic models.

4 Perspective and Open Questions

The investigation of GDEs is a vivid and active field of research with many open questions remaining at macro and microscale. The focus of future studies depends on the application and cell chemistry at hand. Generally, it can be expected that more accurate three dimensional reconstructions of GDE structures that can be obtained from experimental techniques such as FIB SEM or CT and X ray tomography [80] will give important inputs to the field of GDE modeling in future. Measuring pore sizes, transport paths, and the location of catalyst, electrolyte and binder materials ideally in operando will improve the quality of GDE models. A further barely addressed field is to account for parameter uncertainties; instead of three dimensional models with explicit structures, lower dimensional models containing distributed parameters and using stochastic approaches promise to address parameter uncertainties and fluctuations numerically more efficiently and provide more generalizable conclusions.

For metal air batteries, where a solid discharge product precipitates, the morphology and distribution of the discharge product is of crucial importance for the accessible cell capacity; this holds especially for practically relevant high currents. In future, relationships between electrode material, electrolyte properties and concentrations, operating conditions, and product morphology have to be established to increase the GDE performance. Here, modeling can contribute valuable insights into interaction of or limitation by processes and hints for improvements.

In most systems with a liquid electrolyte, such as oxygen depolarized cathodes for chlor alkali electrolysis, the location of the phase boundary and the size of the active (three
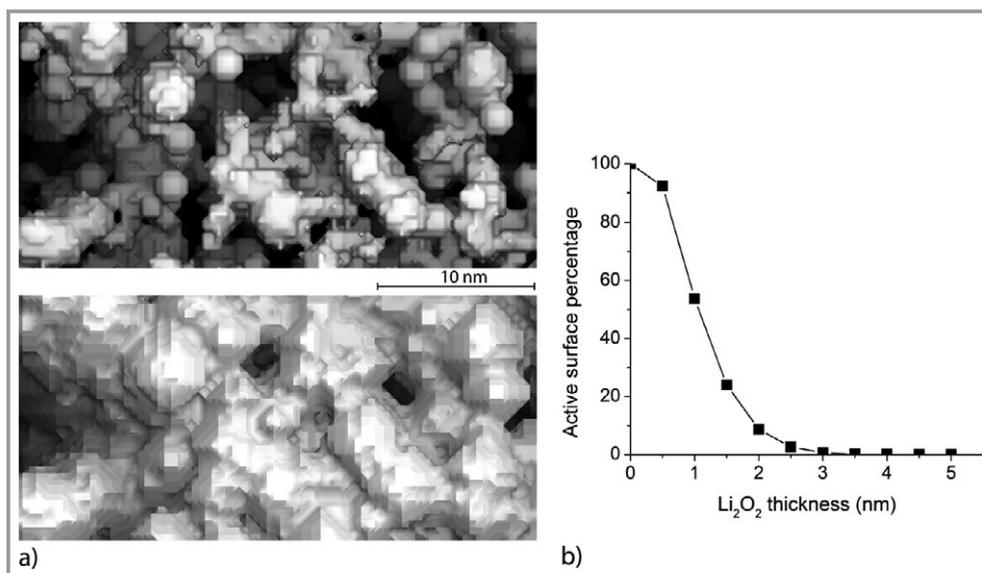
Figure 12. a) Cross sectional images of the constructed cathode nanoscale structure of before discharge (top) and after deposition of a 1 nm thin film of Li_2O_2 (bottom). b) The calculated remaining percentage of active surface area as a function of the thickness of the Li_2O_2 film. Reprinted with permission from [75]. Copyright (2015) American Chemical Society.

phase) boundary is a crucial question that needs to be addressed. The same is true for the emerging electrochemical reduction of carbon dioxide. In case of fuel cell electrodes, the distribution of water and reactants and factors fostering an optimal catalyst utilization and catalyst degradation are key questions that will continue to be in the focus of future modeling studies.

Finally, especially multiscale models including molecular modeling are expected to contribute significantly to allow more predictive modeling and a better microscopic understanding, including also degradation issues. Here, a vast combination of models is possible.

are needed to obtain proper structure performance relationships, which are the basis for knowledge driven improvement and tailoring of GDEs. The high complexity of the problem and the difficulty to measure and correlate processes clearly requires using in depth mechanistic modeling to unveil the relationships and reaction transport interactions. They also allow to step forward to efficient, digitalized GDE design. Here, models on various scales (0D to 3D as well as multi scale) have been successfully used for different purposes. Tab. 3 gives an overview via selected publications that illustrates the variety of dimensions, kinetics, and further assump

5 Conclusions

GDEs are an important class of electrodes for several technically relevant processes ranging from fuel cells over metal air batteries to electrochemical syntheses. Since GDEs are complex porous structures often containing different materials and reactants in several phases, the performance of these electrodes is governed by complex interactions of kinetic effects and transport phenomena. GDE microstructure and macrostructure both define the electrochemical properties and significant efforts

Table 3. Categorization of selected references by model structure and included processes. BV, Butler Volmer.

System	Dimensions	Reaction kinetics	Dynamic	Flooded electrode	Activity based	Solid precipitate	Ref.
Li O_2 battery	0D	BV	No		Yes	Yes	[26]
Alkaline direct methanol fuel cell	0D		No	Yes	No	No	[47, 81]
Li O_2 battery	0D	Tafel	No	Yes	No	Yes	[53]
PEM fuel cell	1D	BV	Yes	Yes	No	No	[29]
Na O_2 battery	1D	BV	Yes	Both	Yes	Yes	[62]
Li O_2 battery	1D	BV	Yes	Yes	Yes	No	[59]
ODC	P2D	Tafel	No	No	Yes	No	[65]
Li O_2 battery	Multiscale 3/1D	BV	Yes	Yes	No	Yes	[75]
PEM fuel cell	3D/molecular dynamics		No	No	(Yes)	No	[77]

tions used in GDE models. While simplified models are sufficient to study the GDE performance on the cell or system level or the general interaction of processes, significant progress towards a quantitative understanding of working GDEs is expected from 3D models. After reconstructing the spatial distribution of GDE materials and electrolyte, the locally resolved interplay of electrochemical reaction and transport processes within the pore system can be studied. Further, multiscale models including molecular modeling are expected to contribute to predictive modeling. It can be expected that improved models will allow to enhance GDE performance significantly in the future and finally to digitalize GDE design.

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Thomas Turek is full professor of Chemical Reaction Engineering at TU Clausthal. He studied Chemical Technology and Chemical Engineering in Dortmund and Karlsruhe and obtained his doctoral degree at Karlsruhe University in 1992. After a postdoctoral stay at the University of New South Wales in Sydney, Australia, he went back to Karlsruhe and completed his habilitation. From 2000 to 2004, he worked with Bayer Technology Services, before he was appointed professor at TU Clausthal. His current research focuses on reactors for chemical and electrochemical processes with the main emphasis on energy transformation and storage.

Ulrike Krewer is an expert for model based analysis and design of electrochemical cells and dynamic analysis from surface to system level. Since completing her studies in Chemical Engineering in Erlangen in 2001, she has strived to understand the processes and limitations in electrochemical cells. Starting with Ph.D. studies at the Max Planck Institute in Magdeburg on the dynamics of fuel cells, she moved to South Korea to develop fuel cell systems with Samsung SDI. Back in Germany in 2008, she extended her portfolio to batteries as head of an Otto Hahn research group and assistant professor in Magdeburg. Since 2012, she is full professor, director of the Institute of Energy and Process Systems Engineering at the TU Braunschweig and board member of the Battery Labfactory Braunschweig.

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