



## Short communication

## Common inconsistencies in modeling gas transport in porous electrodes: The dusty-gas model and the Fick law



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## HIGHLIGHTS

- Common inconsistencies in modeling gas transport in SOFC electrodes are discussed.
- Assuming uniform pressure in dusty-gas model is inconsistent with stoichiometry.
- Use of Bosanquet formula in Fick model does not allow diffusive fluxes to sum up to 0.
- Dusty-gas model must be used without isobaric assumption for multi-component mixtures.
- Fick model can be used for binary mixtures considering ordinary diffusion only.

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## ABSTRACT

The paper shows as two assumptions typically made in modeling gas transport in solid oxide fuel cell electrodes, i.e., a) uniform pressure in the dusty-gas model, and b) validity of the Bosanquet formula in the Fick model, may lead to serious inconsistencies (such as molar fractions that do not sum up to one or fluxes that do not obey reaction stoichiometry), thus nullifying the efforts of the mechanistic modeling of transport phenomena. The nature of the inconsistent use of the models is explained with clear examples, then the correct implementation of the gas transport models is discussed. The study aims to promote a coherent physically-based modeling of gas transport phenomena in porous electrodes in order to assist their rational design.

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## 1. Introduction

One of the current trends in solid oxide fuel cell (SOFC) research is the development of more efficient and stable electrodes and cells. In electrode-supported designs, a significant contribution to voltage losses may arise from gas transport resistances through porous electrodes [1]. The correct modeling of gas transport phenomena is important to predict the partial pressure profiles within a porous electrode, which allow us to evaluate local reaction rates [2], the occurrence of detrimental redox conditions [3], concentration overpotentials and limiting current densities [4] or to infer unknown parameters [5].

Modeling gas transport in SOFC electrodes requires the

description of viscous multi-component gas mixtures moving within a porous medium in transition regime (i.e., Knudsen number between 0.01 and 10). Therefore, a gas transport model must encompass, at least, transport mechanisms such as ordinary diffusion, Knudsen diffusion and viscous flow. Typically, thermal and surface diffusion are neglected. Several gas transport models have been adopted in SOFC modeling: Fick model (FM) [6], Maxwell–Stefan model (MSM) [7,8], dusty-gas model (DGM) [7,9], binary friction model (BFM) [10,11], cylindrical pore interpolation model (CPIM) [12,13]. By far, FM and DGM are the most frequently used.

However, unfortunately a large number of good modeling studies are partly flawed by incompatible assumptions or incorrect applications of these models, which lead to serious inconsistencies such as molar fractions that do not sum up to 1 or fluxes that do not obey reaction stoichiometry. In such a case, the gas transport model fails to predict partial pressure profiles, thus potentially affecting

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not only concentration losses, but also activation and ohmic losses because transport and reaction phenomena are intrinsically coupled [14].

The aim of this paper is to summarize the typical inconsistencies found in the literature in the application of DGM and FM, which are the assumption of uniform pressure and the use of the Bosanquet formula, respectively. Proofs of the inconsistencies are shown and the correct implementation of the models is remarked in order to avoid an incorrect use. The paper is thus concerned with the formal consistency of the model implementation: the inherent soundness of the gas transport models, their mutual comparison and the quantification of how their incorrect use may affect the prediction of partial pressure profiles are out of the scope of the paper, for which the reader is referred to specific studies [1,7,10–13,15].

## 2. Mathematical background on gas transport modeling in SOFC electrodes

The core of a continuum electrode-level or cell-level model consists in a set of mass balance equations within the porous electrodes. For simplicity, let us consider a 1D geometry, although the discussion can be easily extended to 2D and 3D. Let us also assume isothermal conditions, ideal gas behavior and homogeneous electrode microstructure, because most of the gas transport models are valid under these assumptions.

The molar balance (i.e., continuity equation) for a generic gas species  $i$  is as follows:

$$\frac{\phi}{RT} \frac{\partial(Py_i)}{\partial t} + \frac{\partial N_i}{\partial x} = s_i \quad (1a)$$

$$N_i = y_i \frac{P}{RT} v + N_i^{diff} \quad (1b)$$

where  $\phi$  is the porosity,  $R$  the gas constant,  $T$  the temperature,  $P$  the total pressure,  $y_i$  the molar fraction,  $x$  the coordinate ( $x = 0$ : electrode-gas chamber/channel interface,  $x = L$ : electrode-electrolyte interface),  $N_i$  and  $N_i^{diff}$  the total and diffusive molar fluxes,  $v$  the molar average velocity and  $s_i$  is the source term, which is due to the sum of chemical and electrochemical reactions involving the species  $i$ . Typically, a Dirichlet boundary condition is set on one side (e.g., at  $x = 0$ ,  $P = P^{ch}$  and  $y_i = y_i^{ch}$  are specified) and a Neumann boundary condition is set on the other side (e.g., if the electrochemical reaction is assumed to occur at the electrode-electrolyte interface only,  $N_i = -\nu_i j^S / F$  is set at  $x = L$ , where  $\nu_i$  is the stoichiometric coefficient and  $j^S$  the current density per unit surface).

For  $n$  gas species, the problem is solved once evaluated the dependent variables, which are the velocity and  $n$  independent state variables (for example, given the algebraic constraint  $\sum_{i=1}^n y_i = 1$ ,  $n$  independent state variables are  $P$  and  $y_i$  for  $i = 1, \dots, n-1$ ). In general, the complete description of the system requires: a)  $n$  molar balances as Eq. (1a), b) the momentum balance (i.e., equation of motion), c) the equation of state (e.g., the ideal gas law, as assumed in this study), and d) constitutive equations (i.e., gas transport models, as those mentioned in Section 1) to link the fluxes  $N_i$  to the state variables and the velocity field [16]. Note that some gas transport models as DGM, BFM and CPIM already comprise the momentum balance, thus the momentum balance must not be explicitly included in the set of equations.

If a flawed gas transport model is used, an inconsistency is created. The inconsistency can be  $\sum_{i=1}^n y_i \neq 1$  or one of the fluxes may not obey the corresponding molar balance (some examples are given in Sections 3.2 and 4.2).

## 3. The dusty-gas model (DGM)

### 3.1. DGM equations

The dusty-gas model is an implicit expression among fluxes, pressure and molar fractions as follows [9]:

$$\sum_{j \neq i}^n \frac{y_j N_i - y_i N_j}{D_{ij}^{B,eff}} + \frac{N_i}{D_i^{K,eff}} = -\frac{P}{RT} \frac{dy_i}{dx} - \frac{y_i}{RT} \left( 1 + \frac{BP}{\mu D_i^{K,eff}} \right) \frac{dP}{dx} \quad (2)$$

$D_{ij}^{B,eff}$  and  $D_i^{K,eff}$  are the effective binary and Knudsen diffusivities, corrected by porosity  $\phi$  and tortuosity factor  $\tau$  as  $D_{ij}^{B,eff} = (\phi/\tau) \cdot D_{ij}^B$  and  $D_i^{K,eff} = (\phi/\tau) \cdot D_i^K$  [17]. Binary diffusivities  $D_{ij}^B = D_{ji}^B$  can be evaluated with kinetic-theory-based methods (e.g., Chapman-Enskog [18]) or correlations (e.g., Fuller et al. [19]) while the Knudsen diffusivity is equal to:

$$D_i^K = \frac{1}{3} d_p \sqrt{\frac{8RT}{\pi M_i}} \quad (3)$$

where  $d_p$  is the mean pore size and  $M_i$  the molecular weight of species  $i$ . In Eq. (2),  $\mu$  represents the dynamic gas viscosity and  $B$  the electrode permeability, typically calculated as  $B = (\phi/\tau) \cdot d_p^2/32$ .

A large number of experimental studies have satisfactorily validated the DGM in porous media with and without reaction [8,20]. The superiority of the DGM has been proven in SOFC applications too [7,10,12], although we must agree with Bhattacharyya and Rengaswamy [21] that the same set of experimental data [22] has been considered in all these studies. For the sake of completeness, it must be mentioned that some criticisms have been raised about the formal derivation of the DGM [11,13,23]. On the other hand, comparisons with much sounder models like BFM and CPIM performed by Wang et al. [12] and Vural et al. [10] show that there is no significant difference among these models.

By summing up Eq. (2) for all the  $n$  species we obtain [8,10,12,15]:

$$\frac{dP}{dx} = -\frac{RT \sum_{i=1}^n \frac{N_i}{D_i^{K,eff}}}{\left( 1 + \frac{BP}{\mu} \sum_{i=1}^n \frac{y_i}{D_i^{K,eff}} \right)} \quad (4)$$

which shows that in the DGM the pressure gradient is related to Knudsen diffusion and viscous flow.

### 3.2. Assumptions inconsistent with the DGM

Once specified the gas transport model as in Eq. (2), the mathematical problem is determined since it consists of  $n$  molar balances as Eq. (1a) in  $n$  state variables (remember that the DGM already includes the momentum balance, thus the molar average velocity is implicitly calculated). Any additional relationship among  $P$ ,  $y_i$  and  $N_i$  makes the problem overdetermined, thus leading to an inconsistency in its solution.

The typical inconsistent assumption made in the DGM application is the assumption of uniform pressure [6,24–35], which is an additional constraint on the state variable  $P$ . In such a case, by considering the definition of  $D_i^K$  in Eq. (3), Eq. (4) becomes [8,15]:

$$\sum_{i=1}^n N_i \sqrt{M_i} = 0 \quad (5)$$

Eq. (5) is the Graham's law of effusion, which correctly describes the diffusion behavior in a confined system in the absence of

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