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Model of cathode catalyst layers for polymer electrolyte fuel cells: The role of porous structure and water accumulation

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Abstract

The cathode catalyst layer (CCL) is the major competitive ground for reactant transport, electrochemical reaction, and water management in a polymer electrolyte fuel cell (PEFC). Our model, presented here, accounts for the full coupling of random porous morphology, transport properties, and electrochemical conversion in CCLs. It relates spatial distributions of water, oxygen, electrostatic potential, and reaction rates to the effectiveness of catalyst utilization, water handling capabilities, and voltage efficiency. A feedback mechanism, involving the non-linear coupling between liquid water accumulation and oxygen depletion is responsible for the transition from a state of low partial saturation with high voltage efficiency to a state with excessive water accumulation that corresponds to highly non-uniform reaction rate distributions and large voltage losses. The transition between these states could be monotonous or it could involve bistability in the transition region. We introduce stability diagrams as a convenient tool for assessing CCL performance in dependence of composition, porous structure, wetting properties, and operating conditions.

Keywords: Polymer electrolyte fuel cells; Physical modeling; Cathode catalyst layer; Porous composite structure; Liquid water accumulation; Stability diagram

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are promising electrochemical devices for the direct conversion of chemical energy of a fuel into electrical energy. Enormous research programs worldwide explore PEFCs as power sources that could replace internal combustion engines in vehicles and provide power to portable and stationary applications. Generally, PEFCs operate below ∼80 °C. Anodic oxidation of H_2 produces protons that migrate through the polymer electrolyte membrane (PEM) to the cathode, where reduction of O_2 produces water. Meanwhile, electrons, produced at the anode, perform work in external electrical appliances or engines. Unrivalled thermodynamic efficiencies, high energy densities, and ideal compatibility with hydrogen render PEFCs primary solutions to the global energy challenge.

The key role of water for the operation of PEFCs has been recently reviewed in a feature article in *Physics Today* [1]: water is the reaction product of the oxygen reduction reaction (ORR) at the cathode; water acts as the proton shuttle in PEM and catalyst layers; excessive amounts of water, accumulating in pores, are an asphyxiant in gas diffusion media. Dehydration of anodic regions in the PEM due to the electro-osmotic drag of water molecules with the hydration shells of migrating protons could lead to the breakdown of proton conductivity [2]. The resulting large membrane resistance causes excessive Joule heating which could trigger structural degradation of the PEM. In catalyst layers poor wetting of the surface of Pt catalyst diminishes the apparent rates of current conversion, since essentially only Pt|water interfaces are supplied with protons that are needed for electrochemical reactions. Accumulation of water in the porous pathways of catalyst layers and gas diffusion media blocks the transport of gaseous reactants and products.

In any of these cases, too much or too little water in the components of a PEFC gives rise to rather non-uniform distributions

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Abbreviations: CCL, cathode catalyst layer; GDL, gas diffusion layer; MEA, membrane electrode assembly; ORR, oxygen reduction reaction; PEFC, polymer electrolyte fuel cell; PEM, polymer electrolyte membrane; PSD, pore size distribution.

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of reaction rates with detrimental impact on voltage efficiency and effectiveness of catalyst utilization. Such effects are indicated in current–voltage curves by the occurrence of limiting current behaviour [3–5]. Invariably, understanding of distribution and fluxes of water in all components is of vital importance for the operation of PEFCs; it provides guidelines for adjusting materials structures and operating conditions in view of high voltage efficiencies and proper water balance.

The toughest competitions between random composite morphology and complex coupled processes unfold in the CCL [6]. Reactions proceed at Pt nanoparticles, which are randomly dispersed on a high-surface carbon matrix. During fabrication, the colloidal solution of carbon/Pt and ionomer self-organizes into a phase-segregated composite medium with interpenetrating percolating phases for the transport of electrons, protons, and gases [7]. As explored in [7], the process of microstructure formation depends on the type of the supported catalyst (carbon, Pt), the type and amount of ionomer added, the type of dispersion medium used during ink preparation, and the fabrication conditions (temperature, pressure).

The purpose of the present publication is to evaluate how the emerging structure specified by composition, pore size distribution (PSD), and wetting properties of pores determines CCL performance, rated in terms of voltage efficiency, water handling capability, and catalyst utilization. The main focus will be on effects of the porous structure and liquid water accumulation on steady state performance.

This paper elaborates the structural picture and the corresponding framework model of catalyst layer operation that was explored in [6]. The previous work employed a highly simplified representation of the pore space by a bimodal δ-distribution and solutions were obtained in the limit of fast proton transport only. Here, we provide solutions for the full spatial coupling between porous structure, liquid water saturation, and performance. With this extension, we can calculate spatial distributions of water, oxygen partial pressure, oxygen diffusion coefficient, reaction rates, etc. Moreover, we can analyze relations between liquid water accumulation, reaction penetration depth, and global current–voltage performance. This represents a marked enhancement of diagnostic capabilities in catalyst layer and fuel cell research. As we will explain, the non-linear spatial coupling can give rise to bistability in the operation of CCLs, which has not been exploited before. Moreover, the full model allows systematic evaluation of the effects of varying compositions and pore size distributions, which are interesting in view of the structural design of CCLs.

We will briefly review the continuity equations that govern fluxes and transformations of oxygen, protons, and water. The method for solving these equations will be outlined. Thereafter, we will discuss different signatures due to blocking of gaseous transport by liquid water in CCLs and gas diffusion layers (GDLs). The general characteristics of the current–voltage response curve of a CCL, including the effect of liquid water formation in pores, will be discussed. It involves the transition from a state with low saturation and relatively uniform reaction rate distribution to the state with critical liquid water saturation in parts of the layer and rather non-uniform reaction rate distributions. Bistability can occur in the transition region. We will conclude with a parameter study and introduce stability diagrams as a useful tool for assessing catalyst layer performance for varying structures, compositions, and operating conditions.

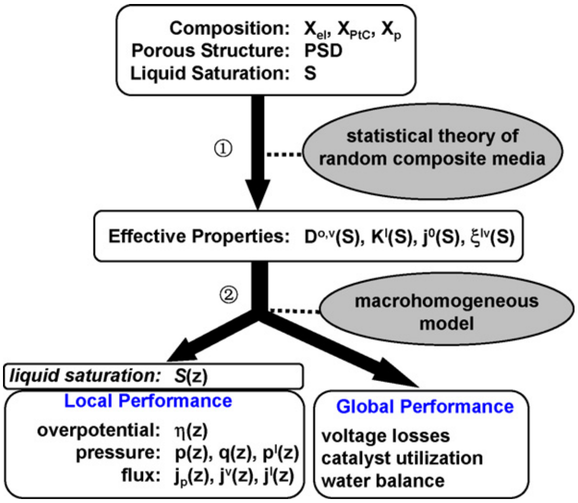

Fig. 1. Two-step modeling strategy for linking composite porous structure with effective properties, and performance.

2. The model

We employ the structural picture of random composite CCLs with agglomerated microstructure as described in detail in [6] (*cf*. Fig. 1 in [6]). We consider a 1D model of mass transport and reaction in through-plane direction under isothermal conditions. The model relies on stipulating the following two aspects of CCL operation in theory and experiment:

Local equilibrium of water in CCLs: How does the local water content in CCLs depend on materials morphology and operating conditions? By which mechanisms does it attain local equilibrium? We assume that capillary forces at the liquid–gas interfaces in pores equilibrate the local water content in the catalyst layer. We, thus, neglect surface film formation or droplet formation in pores. Ex situ diagnostics, probing porous structures and water sorption characteristics, is needed to relate equilibrated water distributions to structure and conditions in CCLs.

Processes involving water transport and transformation: What are the relevant mechanisms and transport coefficients of water fluxes (diffusion, convection, hydraulic permeation, electro-osmotic drag)? What are relevant mechanisms and rates of phase changes (between liquid water, water vapour, surface water, water in membrane)? These mechanisms and relevant parameters are related to evaluation by ex situ diagnostics. Here, we use relations from the statistical theory of random composite media [8–11] and percolation theory [12] to assess effective parameters of transport and interfacial processes. The relations employed have proven appropriate in a number of modeling studies [13–17]. They could consistently explain effects of structure and composition on performance in relevant experimental studies [18–21].