Short communication

Characterization of pore network structure in catalyst layers of polymer electrolyte fuel cells

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Mohamed El Hannach [a,*], Tatyana Soboleva [b], Kourosh Malek [b,c], Alejandro A. Franco [a,1,2], Marc Prat [d,e], Joël Pauchet [a], Steven Holdcroft [b,c]

[a] CEA, LITEN, LCPEM, 17 rue des Martyrs, F-38054 Grenoble, France
[b] Department of Chemistry, Simon Fraser University, Burnaby, BC, Canada V5A 1S6
[c] National Research Council of Canada, Institute for Fuel Cell Innovation, 4250 Wesbrook Mall, BC, V6T 1W5 Vancouver, Canada
[d] University of Toulouse, INPT, UPS, IMFT, Avenue Camille Soula, 31400 Toulouse, France
[e] CNRS, IMFT, 31400 Toulouse, France

HIGHLIGHTS

- We build a comprehensive model of nitrogen adsorption isotherm.
- The results confirm the existence of different sorption regimes.
- We validate the representation of a catalyst layer porous media using a pore network.
- The effect of ionomer content on pore size distribution was successfully modeled.

GRAPHICAL ABSTRACT
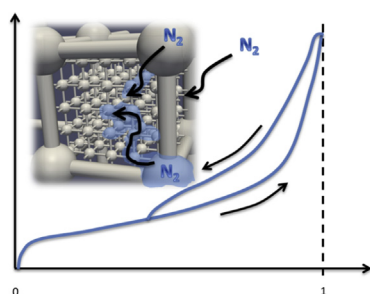
ABSTRACT

We model and validate the effect of ionomer content and Pt nanoparticles on nanoporous structure of catalyst layers in polymer electrolyte fuel cells. By employing Pore network modeling technique and analytical solutions, we analyze and reproduce experimental N_2-adsorption isotherms of carbon, Pt/carbon and catalyst layers with various ionomer contents. The porous catalyst layer structures comprise of Ketjen Black carbon, Pt and Nafion ionomer. The experimental pore size distributions obtained by N_2-adsorption are used as an input to generate porous media using the pore network approach. Subsequently, the simulated porous structures are used to produce simulated N_2-adsorption isotherms, which are then compared to the experimentally measured isotherms. The results show a good agreement in the prediction of the effect of the ionomer content on the microstructure of catalyst layers. Moreover, the analysis of the isotherms confirms the hypothesis of ionomer distribution on the surface of agglomerates as well as the existence of different sorption regimes in primary and secondary pores of fuel cell catalyst layers.

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* Corresponding author. Simon Fraser University, Mechatronic Systems Engineering, School of Engineering Science, 250-13450 102 Avenue, Surrey, BC, Canada V3T 0A3.
  E-mail address: melhannach@gmail.com (M. El Hannach).
[1] Laboratoire de Réactivité et de Chimie des Solides (L.R.C.S.), Université de Picardie Jules Verne, CNRS UMR 7314-33 rue Saint Leu, Amiens, France.
[2] Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France.

1. Introduction

In current and past physical models of Catalyst Layer (CL) in Polymer Electrolyte Fuel Cells (PEFCs), there has been a lack of clear CL nanostructure picture, in particular, structure and function of ionomer, nature and distribution of active interfaces, structure and composition of agglomerates, porosity, mixed

wettability, and water distribution [1]. Simulations of microstructure formation, including self-organization of components in CL, predict the interplay between fabrication parameters, structure and transport properties [2,3]. Moreover, understanding CL structure is imperative for development of novel materials and improvement of CL physicochemical properties. Nevertheless, in order to evaluate the impacts on "pseudo" steady state performance and durability, modeling efforts are needed to couple basic structural parameters obtained from modeling the CL microstructure formation to the fuel cell performance modeling [4,5].

In order to complete basic structural aspects, the remaining issues include establishing a relationship between composition and microstructure in terms of ionomer and Pt content, pore size distribution, and pore network characteristics. The Pore Network Modeling (PNM) approach is widely used to study the transport phenomena inside porous materials and its application has increased recently in the field of Proton Exchange Membrane Fuel Cell (PEMFC) materials. The main input of the PNM is the pore size distribution (PSD). Nitrogen physisorption is a common tool used to evaluate microstructures of porous materials and obtain pore size distribution curves. The PSD can be estimated either from adsorption or desorption isotherms using modified forms of Kelvin equation for capillary condensation.

In this work, we used the PSDs extracted from the nitrogen adsorption isotherms for various catalyst layer compositions as an input parameter for the PNM. The experimentally-derived isotherms were reported in Ref. [6] and explained in the Experimental section. Then the adsorption isotherms are simulated using the model described below to reproduce the experimental isotherms. The flexibility of the PNM allows for simulation of the nitrogen adsorption process with the consideration of pores blockage due to nitrogen condensation. A comparison between the experimental and simulated isotherms validates representation of the CL using the pore network model.

2. Experimental

In a previous study by Soboleva et al. [6], Ketjen Black carbon and a catalyst powder with 46 wt% Pt on Ketjen Black from Tanaka Kikinzoku Kogyo (TKK) [1,6] were used for N_2-adsorption studies and for fabrication of the catalyst coated membranes (CCMs). All CCMs were fabricated by spray-deposition of catalyst inks on Nafion 211 membrane, used as received. CCMs with 5, 10, 30 and 50 wt% of ionomer in the CL corresponding to 0.047 mg cm^{-2} (0.1 I/C), 0.094 mg cm^{-2} (0.2 I/C), 0.375 mg cm^{-2} (0.8 I/C), and 0.875 mg cm^{-2} (1.8 I/C) ionomer loadings were prepared. Carbon and Pt loadings were held constant at 0.475 mg cm^{-2} and 0.4 mg cm^{-2} respectively. The thickness of the catalyst layers was 12 ± 2.0 μm.

N_2-physisorption experiments, previously published in Ref. [6], were performed at 77 K on a 3100 Surface Area Analyzer (Beckman Coulter™). N_2 gas of ultra-high purity 99.999% was used. Carbon and Pt/carbon samples of ~100 mg were degassed at 160 °C for 12 h prior to the adsorption experiment to remove any residual water from the samples. CCMs of total 50 cm^2 were cut into thin strips, placed in the sample tube and degassed for 12 h at 105 °C. Adsorption experiments were performed immediately after degassing. A blank adsorption experiment on Nafion 211 membrane was performed and it was found that contribution of the membrane to N_2 adsorption of CCMs is negligible. Adsorption isotherms of Pt/carbon powders and CCMs were all re-plotted after normalizing by carbon content in each sample. BET surface areas were found from BET equation [7], by plotting left-hand side term of the equation against p/p_0 in the range from 0.05 to 0.2 p/p_0.

Monolayer volume, n_m, was found from the slope and the intercept of such a BET plot, Eq. (1):

$$n_m = \frac{1}{slope + intercept} \tag{1}$$

Surface area is then calculated from Eq. (2):

$$SA_{BET} = \frac{n_m \cdot N \cdot s}{V} \tag{2}$$

where N — Avogadro's number, s — cross-sectional area of the N_2 molecule (0.162 nm^2); V — molar volume of adsorbent gas.

Total pore volume was found at a partial pressure of 0.98 p/p_0 (STP) by converting to liquid nitrogen volume using the conversion factor of 0.001547 [8].

Pore size distributions (PSDs) were assessed using the Barret–Joyce–Halenda (BJH) method, which is based on the Kelvin equation and accounts for the formation of a condensed layer adsorbed on the pore wall prior to capillary condensation, which is accounted for using Harkins–Jura equation:

$$t_{N2} = \left(\frac{13.99}{0.034 - \log(p/p_0)} \right)^{1/2} (\mathring{A}) \tag{3}$$

where t_{N2} — thickness of the adsorbed layer on the pore wall, Å; p — partial pressure of N_2; p_0 — saturation pressure of N_2 at 77 K [9].

3. Model development

The PNM is based on using a network of pores and throats (links between adjacent pores) (Fig. 1) to represent the structure of a porous medium [10,11]. The pore network used in this work is constructed from spherical shape pores and cylindrical shape throats. The distance between two adjacent pores, i.e., network spacing, is constant. Thus, the pore network is regular. We use only 3D networks where every pore is connected to 6 adjacent pores (Fig. 1). The CL consists of agglomerated carbon/platinum particles. Two types of pores are considered: primary pores ($d < 5$ nm) representing pores inside agglomerates, and secondary pores ($d > 5$ nm) representing pores between agglomerates.

Secondary pores are represented by a 3D regular pore network with a network spacing equal to 150 nm. The value is chosen to be higher than the maximum pore diameter to avoid any overlap between two adjacent pores. The size of the network is measured by a number of pores in x, y, and z directions. The size of the main pore network is $15 \times 15 \times 15$, which is equivalent to 3375 pores and 10,800 throats. The size of the simulated domain is equivalent to
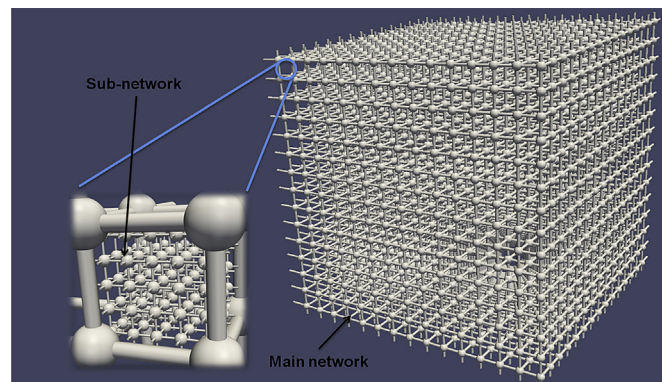

Fig. 1. Pore network representing the primary pores (sub-network in the left) and the secondary pores (main network in the right).