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# Deterministic contact mechanics model applied to electrode interfaces in polymer electrolyte fuel cells and interfacial water accumulation

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## HIGHLIGHTS

- Deterministic contact mechanics model applied to catalyst layer|MPL interface.
- Direct imaging of sample surface topology for true morphology.
- The cracked CL|MPL interface can store more water than the uncracked.
- Cracks cover little contact area and cause minimal interfacial resistance.
- van Genuchten water retention correlation shows a good agreement.

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## ABSTRACT

An elastic deterministic contact mechanics model is applied to the compressed micro-porous (MPL) and catalyst layer (CL) interfaces in polymer electrolyte fuel cells (PEFCs) to elucidate the interfacial morphology. The model employs measured two-dimensional surface profiles and computes local surface deformation and interfacial gap, average contact resistance, and percent contact area as a function of compression pressure. Here, we apply the model to one interface having a MPL with cracks and one with a crack-free MPL. The void size distributions and water retention curves for the two sets of CL|MPL interfaces under compression are also computed. The CL|MPL interfaces with cracks are observed to have higher roughness, resulting in twice the interfacial average gap compared to the non-cracked interface at a given level of compression. The results indicate that the interfacial contact resistance is roughly the same for cracked or non-cracked interfaces due to cracks occupying low percentage of overall area. However, the cracked CL|MPL interface yields higher liquid saturation levels at all capillary pressures, resulting in an order of magnitude higher water storage capacity compared to the smooth interface. The van Genuchten water retention curve correlation for log-normal void size distributions is found to fit non-cracked CL|MPL interfaces well.



## 1. Introduction

Polymer electrolyte fuel cells (PEFC) are promising power source devices for a wide variety of portable, automotive, and stationary applications. To achieve cost-effective mass-production of these low-emission devices, certain technological challenges have to be resolved [1]. Ohmic and mass transport losses at the interface of catalyst layer (CL) and micro-porous layer (MPL) have not been studied widely but recent experimental studies show that this interface plays a critical role in electrode structure and performance [2–6]. The imperfect interfacial contact of the CL and MPL can create high resistance pathway for electron transport, whereas the resulting interfacial voids can lead to liquid water pooling. Water accumulation at the CL|MPL interface is not desirable due to a hindrance of reactant gas transport to the electrode's active reaction sites and the resulting loss of fuel cell performance. Gaining a further insight into Ohmic and mass transport limitations of the interface requires better understanding of the morphologies of the CL and MPL as well as the CL|MPL interface topologies under varying compression.

Due to the minute length scales and experimental limitations, mathematical models are valuable tools often used in evaluating multiphase transport phenomena in PEFC materials. Modeling

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water transport through porous carbon substrates, such as diffusion media (DM) and MPL typically requires water retention curves. These are the correlations that relate capillary pressure to saturation; the most common correlations are reviewed by Gostick et al. [7] and Litster and Djilali [8]. These water retention curves include the Brooks-Corey [9], van Genuchten [10] and Udell [11] correlations, where the van Genuchten correlation is based on the reasonable assumption of a log-normal void size distribution. There is also a family of empirical correlations for water retention curves, such as Udell [11] functions, which are derived based on empirical data obtained by Leverett. There have been several experimental and computational studies reporting water retention curves for the DM and MPL [7,12,13] but none for the CL|MPL interface. Although, some researchers have previously included finite computational region for the MPL|DM interface [14–16], the interface between the MPL and CL is treated as an infinitely thin layer in most modeling studies.

There have been several experimental [17,18] and one analytical work [19] done to investigate the CL|MPL contact resistance. Kleemann et al. [17] used a 4-point device applying current across the CL|MPL interface and measured potential drop. They back-calculate the contact resistance using an electrical finite element simulation with the measured electric potential difference across the device as an input. They showed decreasing trend of contact resistance with increasing compression pressure, however they were not able to separate the MPL resistance from the contact resistance. Swamy et al. [19] developed an analytical model that computes contact resistance and estimates the maximum capacity for water accumulation at the interface at different compressions. They used statistical approach where key interfacial model parameters, such as summit density, standard deviation, and radius of the summit, were extracted from their optical profilometry data. To the best of our knowledge, there is no prior work on using actual CL and MPL morphology to computationally reconstruct the three-dimensional interfacial morphology under varying compression.

There have been numerous theoretical studies focused on understanding the interfacial roughness in the field of tribology [20–29]. Historically, two major frameworks (i.e., statistical and deterministic) have been developed to model the elastic–plastic interfacial contact. The statistical framework was pioneered by Greenwood and Williamson [30] (GW) to elucidate the relationship between the applied load and average gap for rough materials. Typically, the statistical approach approximates the surface summits using average parameters for their density, radius and curvature. The advantages of the statistical approach include its computational efficiency and the ease of calculating area-averaged interfacial parameters. However, the statistical models do not provide information about local gap, surface deformation and asperity contact pressure.

In contrast to the statistical approach, deterministic models use actual measured or generated surface profile data and predict local and area-average interface properties. Johnson et al. [20] developed an asymptotic three-dimensional solution to an interface featuring a sinusoidal surface pressed against a flat surface. In the following decades, the contact mechanics problems of real rough surfaces were solved using a matrix of influence coefficients, which relates contact pressure and deformation [24,25,27]. However, for three-dimensional surfaces the matrix's computational and storage expense were high- pressing for an alternative solution methodology. Solution procedures based on minimization of total complementary energy [28] utilizing a fast Fourier transform (FFT) [25,28,29] and convolution theorem has proved to be economic in data storage and efficient in computation.

Here we present a numerical elastic deterministic contact mechanics model that predicts average properties as well as local deformation, pressure and separation distance at the three-dimensional CL|MPL interface under different compressions. We image two different sets of CLs and MPLs using an optical microscope, characterize surfaces roughness, and then input three-dimensional CL and MPL surface profiles into the contact mechanics model. Water retention curves are generated based on the model predictions for the void size distributions of the two sets of interfaces.

## 2. Contact mechanics model

We use deterministic contact mechanics modeling approach proposed by Hu et al. [28] to resolve the local deformation of contacting asperities under applied pressure. The following assumptions were used in the present contact mechanics model:

- the surfaces deform elastically: the local strains are small and plastic deformation is neglected;
- the surfaces of MPL and CL are large enough to be treated as half-spaces;
- the magnitude of normal contact pressure is assumed to be much higher than the tangential forces because the MEA is very thin and the area of compression is large;
- zero intrusion is assumed between the CL and MPL surfaces.

Fig. 1 is a two-dimensional schematic of the MPL and CL surfaces prior and after deformation. In the figure, $\bar{\delta}$ is the separation distance between the two undeformed surfaces when a load is applied, whereas $\delta$ is the gap between the deformed surfaces. Based on a half-space Boussinesq solution, the composite vertical surface displacement, $u(x,y)$, at a point $(x,y)$ of two surfaces under the normal pressure field $p(x',y')$ is given by:

$$u(x,y) = \frac{2}{\pi E_{eq}} \iint_{\Omega} p(x',y')K(x'-x,y'-y)\mathrm{d}x'\mathrm{d}y' \tag{1}$$

where $K(x,y)$ represents surface deformation distribution under an applied contact unit load acting at the origin. For the elastic half-space surfaces, the kernel $K(x,y)$ is given by Boussinesq solution:

$$K(x',y') = \frac{1}{\sqrt{x'^2+y'^2}} \tag{2}$$

and where $E_{eq}$ is the equivalent Young's modulus of the two surfaces defined as:

$$E_{eq} = \left[\frac{1}{2}\left(\frac{1-\nu_{CL}^2}{E_{CL}} + \frac{1-\nu_{MPL}^2}{E_{MPL}}\right)\right]^{-1} \tag{3}$$

where $\nu$ is Poisson's ratio.

The force–displacement relation of Eq. (1) can be solved with matrix multiplication: $u = C \cdot p$, where $C$ is the matrix of influence coefficients. This matrix has to be determined in advance by

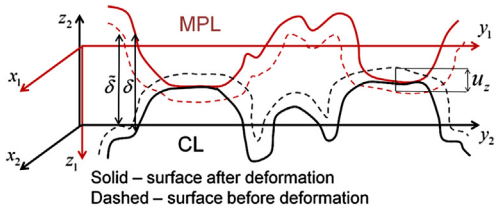


**Fig. 1.** Schematic of asperities and model parameters at the CL|MPL interface.