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Constitutive model development and micro-structural topology optimisation for Nafion hydrogel membranes with ionic clustering

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Abstract—The deployment of electroactive ionic polymer hydrogel–metal composites in artificial muscle and BioMEMS applications has recently been intensively investigated. In order to analyse their electromechanical responses to externally applied electrical fields, it is critical to develop a constitutive model linking the macro-mechanical moduli with the micro-mechanical characteristics, and to determine the geometric size and shape of the micro-structural cluster and investigate the effect of cluster morphology on the effective electro-elastic moduli of the polymer hydrogels. As a typical ionic polymer-based hydrogel, the Nafion membrane is studied in this work. Based on the Biot poroelasticity theory, a multi-scale constitutive model which includes both macro and micro characteristics is developed using an asymptotic homogenisation method. The effect of water-volume fraction on the effective elastic moduli of the hydrogel membrane is examined for different equivalent weights. Numerical investigations show that the simulated effective constitutive moduli agree well with experimental data. The presently developed constitutive model is thus validated. In order to determine the micro-structural shape of the polymer skeleton subject to fluid pressure, a representative volume element (RVE) is designed by topology optimisation of the periodic microstructures of the Nafion hydrogels, through the minimisation of the electro-elastic interaction energy between the polymer-based fluorocarbon matrix and the surrounding fluid. This optimal RVE correctly predicts the geometric shapes of the clusters.

Key words: Nafion hydrogel membrane; constitutive modeling; cluster; micro-structural topology optimisation; homogenisation method; computational BioMEMS; multi-scale simulation.

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INTRODUCTION

A Nafion membrane can be described as an ionic polymer hydrogel–metal composite consisting of two thin metal plates, such as platinum, and sandwiched thin polymer hydrogels. It is able to function as electro-active smart sensor/actuator-like materials for a wide range of applications such as in artificial muscles and BioMEMS devices. It also has excellent chemical and mechanical stability, high ionic conductivity and gas impermeability. In order to have a sound understanding of its electromechanical response to an applied voltage [1], the geometric size and shape of the microstructure of Nafion hydrogel membrane and the micro-structural effect on the effective electro-elastic moduli of the polymer-based hydrogel membrane must first be determined. Li and Nemat-Nasser [2] used the multi-inclusion and Mori–Tanaka models to simulate the effective elastic moduli and conductivity, and employed a simplified theoretical analysis to determinate the microstructure shape for a water-swollen Nafion hydrogel membrane. However, as their constitutive model is based on the assumption of volume averages, the analysis was highly approximate and thus unable to accurately predict the micro-structural geometries and mechanical properties.

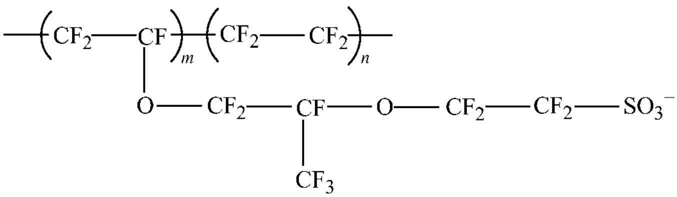
In order to develop a more accurate constitutive model and determine both the macro-mechanical and micro-structural characteristics for the Nafion hydrogel membrane, this paper presents a multi-scale analysis of the electromechanical responses of the Nafion membrane. This model employs the asymptotic homogenisation method [3], which is superior to the multi-inclusion model since it can predict both macro- and micro-mechanical properties. The presently developed model is also validated numerically by comparison of the present simulated results with experimental data, where very good agreement is observed.

Further, the present work also employs a topology optimisation technique to tailor the shape of the micro-structural cluster, instead of an empirical evaluation for both the cluster surface energy and the electro-elastic interaction energy between the ionic clusters and fluorocarbon matrix, as in Li and Nemat-Nasser [2]. The present topological optimisation technique includes the features of both size and shape optimization for the determination of optimal spatial material distribution. In other words, for a given load and boundary condition, the optimal redistribution of the material in the design domain is carried out to minimise the objective function [4]. This paper presents numerically the two-dimensional optimal results that indicate the shape of micro-structural cluster is almost circular when no electric field is applied externally. The numerical simulation agrees well with both the empirical evaluation [2] and experimental data [5].

CONSTITUTIVE MODEL DEVELOPMENT FOR NAFION MEMBRANE

Developed constitutive model of the Nafion membrane

Nafion, a perfluorinated membrane, can be schematically described as



It contains certain sulfonic ionic functional groups. This linear fluorocarbon polymer has the phase-separation morphology of discrete hydrophobic and hydrophilic regions, and can be strongly affected by water content and cations. The polytetrafluoroethylene in this material provides the three-dimensional structured backbone system with regularly spaced long perfluorovinyl ether pendant side chains terminating in ionic sulfonate groups [1, 2]. Due to the electrostatic dipole interactions and elastic forces, these ionic groups tend to aggregate to form tightly packed regions referred to as clusters. These interconnected clusters are readily saturated by water, and exert a distinct effect on the elastic and transport properties of Nafion. More information on this is available in the excellent review articles by Mauritz [6] and Heitner-Wirguin [7].

The swollen Nafion hydrogel membrane studied here comprises of a connected solid phase and an embedded porous phase, which forms the skeleton. The solid phase is linear elastic with constant tensor. The porous phase is saturated with a fluid of pressure p. It is reasonably assumed that the pores are connected and the pressure is uniform. Small angle X-ray scattering [8] and neutron scattering experiments [5] have clearly indicated that ionic clustering occurs in Nafion. A schematic representation of the micro-structure of water-saturated Nafion hydrogel membrane in the electrically neutral state is presented in Fig. 1 [1]. The clusters, as porous phases, are assumed to periodically distribute in the hydrophobic polymer-backbone continuum. All the water is assumed to exist only within the clusters, with no water in the channels connecting the clusters being assumed. The water in the channels is neglected here since the amount is very small.

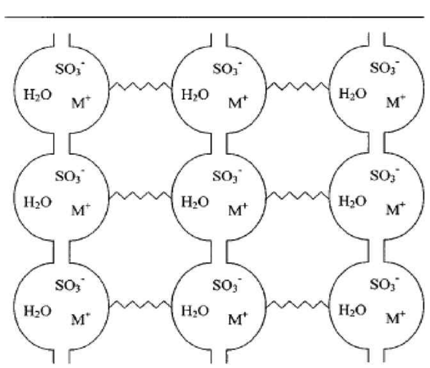


Figure 1. Micro-structural model for the Nafion hydrogel membrane.

Based on experimental data, Grot *et al.* [9] and Hsu and Gierke [10] obtained the following empirical relation for the effective tensile modulus of Nafion hydrogel membrane as a function of water volume fraction,

$$Y(c_{\mathrm{w}}) = Y_0 \exp\left(-\alpha \left[\frac{100 c_{\mathrm{w}} \rho_{\mathrm{w}}}{(1 - c_{\mathrm{w}})\rho_{\mathrm{d}}} + \frac{1200 - M_{\mathrm{e}}}{20} \right] \right), \tag{1}$$

where M_{e} is the equivalent weight of the Nafion hydrogels, c_{w} the water volume fraction of the hydrogels, ρ_{d} the density of the dry membranes (taken as 2.1×10^3 $\mathrm{kg/m^3}$ in this work). Y_0 is the reference modulus and taken as 275 MPa, and the empirical coefficient $\alpha = 0.0294$.

Li and Nemat-Nasser [2] analytically simulated the Nafion membrane effective elastic moduli and conductivity by the multi-inclusion and Mori–Tanaka models, and also carried out a simplified analytical study to determine the cluster morphology of a water-swollen Nafion hydrogel membrane. Their constitutive model is based on the assumption of volume averages such that it becomes very approximate, and presents difficulties when predicting the micro-structural geometries and mechanical properties.

Most works published to date [2, 9, 10] only predict approximately the constitutive moduli. In order to determine both macro-mechanical and micro-structural characteristics for the Nafion hydrogel membrane, a multi-scale analysis is carried out in this paper, for the electromechanical response of Nafion membrane by the asymptotic homogenisation method [3]. In general, the analysis of boundary value problems is extremely difficult for multiphase mixtures with numerous heterogeneities. The asymptotic homogenisation method, which employs an equivalent material model to represent the composites with numerous heterogeneities, is an alternative approach to compute the effective properties of the equivalent homogenised materials [3], whereby a representative volume element (RVE) distributed periodically is constructed. The method can predict both macro- and micro-properties of the composites, and for simple microstructures it may be implemented analytically. When the microstructures are more complex, numerical methods such as the finite element method (FEM) may then be employed.

In this paper, the asymptotic homogenisation method is employed to compute the constitutive moduli of the Nafion hydrogel membrane based on the Biot poroelasticity theory [11]. The method is based on the assumption that the RVE contains all the required information for the full description of the Nafion hydrogel membrane. According to the schematic model by Nemat-Nasser and Li [1] (see Fig. 1), the three-phase model developed by Yeager [5], and the cluster-network model by Gierke [8], a two-dimensional RVE, as shown in Fig. 2, is constructed for the present FEM analysis. Thus we have the generic form of the constitutive model of Nafion hydrogel membrane as [11, 12]

$$< \sigma_{ij}^{\mathrm{T}} > = C_{ijkl}^{\mathrm{H}} e_{kl}(\boldsymbol{u}) - \alpha_{ij} p, \tag{2}$$

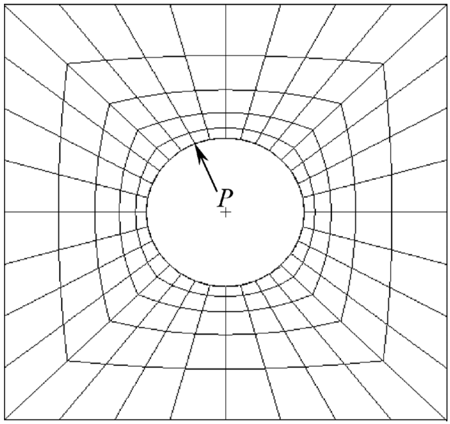


Figure 2. Finite element model of RVE for the Nafion hydrogel membrane subject to pore fluid pressure p.

where $< \sigma_{ij}^{\mathrm{T}} >$ are the components of macroscopic total stress tensor, $e_{kl}(u)$ the components of macroscopic strain tensor associated with the macroscopic displacement vector $\boldsymbol{u}$. p denotes the liquid pore pressure, C_{ijkl}^{H} the effective elastic stiffness tensor and α_{ij} the Biot-type effective stress coefficient tensor [11]. For a swollen Nafion hydrogel membrane, if C_{ijkl}^{S} represents the constitutive moduli tensor of the solid-phase elastic polymer, α_{ij} can be given by [13]

$$\alpha_{ij} = \left[I_{ij}^{kl} \left(1 - \frac{C_{ijkl}^{\mathrm{H}}}{C_{ijkl}^{\mathrm{S}}} \right) \right] \delta_{kl} \quad \text{or} \quad \boldsymbol{\alpha} = \boldsymbol{\delta} : \left(\boldsymbol{I} - \left(\boldsymbol{C}^{\mathrm{S}} \right)^{-1} : \boldsymbol{C}^{\mathrm{H}} \right), \tag{3}$$

in which $\boldsymbol{I}$ is a fourth-order identity tensor, $I_{ij}^{kl} = (1/2)(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$, and $\boldsymbol{\delta}$ is a second-order Kronecker Delta identity tensor. $\boldsymbol{C}^{\mathrm{S}}$ is the solid-phase polymer constitutive moduli tensor and $\boldsymbol{C}^{\mathrm{H}}$ the effective elastic stiffness tensor. It is noted that one of the objectives here is to compute the homogenised constitutive moduli C_{ijkl}^{H}, and also such that the same solution approach can be used to compute the effective conductivity and electrical constants.

Asymptotic homogenisation

In order to study the microstructural characteristics of the Nafion hydrogel membrane, a RVE, as shown in Fig. 2, is used to represent the Nafion microstructures with the requirement of periodic distribution. The asymptotic homogenisation method is based on the fact that the micro-structural representative size d is much smaller than the macro-structural one D. The relation between the global coordinate system $\boldsymbol{x}(x_i)$ for macrostructure and the local coordinate system $\boldsymbol{y}(y_i)$ for the RVE is written as

$$y_i = \frac{x_i}{\varepsilon} \quad (i = 1, 2), \tag{4}$$

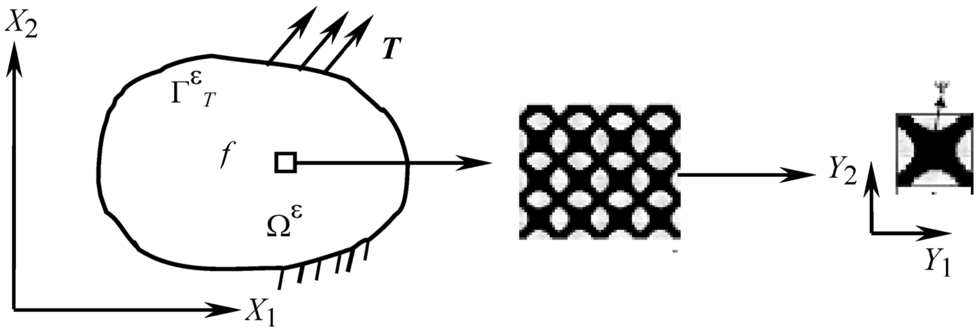


Figure 3. Illustration of transformation between macro- and micro-structures with two length scales.

where ε is a very small positive number representing a scaling ratio between the two coordinate length scales, as shown in Fig. 3. Thus, the displacements, strains and stresses are defined in both coordinate systems, the macro scale by coordinates $\boldsymbol{x}(x_i)$ and micro scale by coordinates $\boldsymbol{y}(y_i)$, i.e.

$$u_i^{\varepsilon}(\boldsymbol{x}) = u_i^{(0)}(\boldsymbol{x}, \boldsymbol{y}) + \varepsilon u_i^{(1)}(\boldsymbol{x}, \boldsymbol{y}) + \varepsilon^2 u_i^{(2)}(\boldsymbol{x}, \boldsymbol{y}) + \cdots, \tag{5}$$

$$e_{ij}^{\varepsilon}(\boldsymbol{x}) = \varepsilon^{-1} e_{ij}^{(-1)}(\boldsymbol{x}, \boldsymbol{y}) + e_{ij}^{(0)}(\boldsymbol{x}, \boldsymbol{y}) + \varepsilon e_{ij}^{(1)}(\boldsymbol{x}, \boldsymbol{y}) + \cdots, \tag{6}$$

$$\sigma_{ij}^{\varepsilon}(\boldsymbol{x}) = \varepsilon^{-1} \sigma_{ij}^{(-1)}(\boldsymbol{x}, \boldsymbol{y}) + \sigma_{ij}^{(0)}(\boldsymbol{x}, \boldsymbol{y}) + \varepsilon \sigma_{ij}^{(1)}(\boldsymbol{x}, \boldsymbol{y}) + \cdots. \tag{7}$$

The constitutive relation is thus expressed as

$$\sigma_{ij}^{-1} = C_{ijkl} e_{kl}^{-1}, \tag{8}$$

$$\sigma_{ij}^{0} = C_{ijkl} e_{kl}^{0}, \tag{9}$$

$$\sigma_{ij}^{1} = C_{ijkl} e_{kl}^{1}, \tag{10}$$

where

$$e_{ij}^{(-1)} = \frac{1}{2}\left(\frac{\partial u_i^{(0)}}{\partial y_j} + \frac{\partial u_j^{(0)}}{\partial y_i}\right), \tag{11}$$

$$e_{ij}^{(0)} = \frac{1}{2}\left(\frac{\partial u_i^{(0)}}{\partial x_j} + \frac{\partial u_j^{(0)}}{\partial x_i} + \frac{\partial u_i^{(1)}}{\partial y_j} + \frac{\partial u_j^{(1)}}{\partial y_i}\right), \tag{12}$$

$$e_{ij}^{(1)} = \frac{1}{2}\left(\frac{\partial u_i^{(1)}}{\partial x_j} + \frac{\partial u_j^{(1)}}{\partial x_i} + \frac{\partial u_i^{(2)}}{\partial y_j} + \frac{\partial u_j^{(2)}}{\partial y_i}\right), \tag{13}$$

in which the unknown displacement u_i, strain e_{ij} and stress σ_{ij}, are obtained by the equilibrium, geometric deformation and constitutive equations as

$$\sigma_{ij,j}^{\varepsilon} + f_i = 0, \qquad \text{in } \Omega^{\varepsilon}, \tag{14}$$

$$e_{ij}^{\varepsilon} = \frac{1}{2}\left(u_{i,j}^{\varepsilon} + u_{j,i}^{\varepsilon}\right) \quad \text{in } \Omega^{\varepsilon}, \tag{15}$$

$$\sigma_{ij}^{\varepsilon} = C_{ijkl}^{\varepsilon} e_{kl}^{\varepsilon} \qquad \text{in } \Omega^{\varepsilon}. \tag{16}$$

The boundary conditions are given as

$$\sigma_{ij}^{\varepsilon} n_j = \bar{T}_i, \quad \text{on } \Gamma_T^{\varepsilon}, \tag{17}$$

$$u_i^{\varepsilon} = \bar{u}_i, \quad \text{on } \Gamma_u^{\varepsilon}. \tag{18}$$

Substituting equation (7) into the equilibrium equation (14) and then factorising the resulting equation with respect to ε^i, the following equations are derived by setting the coefficients of ε^i to zero due to the asymptotic principle,

$$\sigma_{ij,y_j}^{(-1)}(x, y) = 0, \tag{19}$$

$$\sigma_{ij,y_j}^{(0)}(x, y) + \sigma_{ij,x_j}^{(-1)}(x, y) = 0, \tag{20}$$

$$\sigma_{ij,y_j}^{(1)}(x, y) + \sigma_{ij,x_j}^{(0)}(x, y) + f_i = 0. \tag{21}$$

From equations (8), (11) and (19), we have

$$e_{ij}^{(-1)} = 0, \quad \sigma_{ij}^{(-1)} = 0, \quad u_i^{(0)}(x, y) = u_i^{(0)}(x). \tag{22}$$

According to the resulting equation (22), equation (12) is rewritten as

$$e_{ij}^{(0)} = e_{xij}\big(\boldsymbol{u}^{(0)}\big) + e_{yij}\big(\boldsymbol{u}^{(1)}\big), \tag{23}$$

where

$$e_{xij}\big(\boldsymbol{u}^{(0)}\big) = \frac{1}{2}\left(\frac{\partial u_i^{(0)}}{\partial x_j} + \frac{\partial u_j^{(0)}}{\partial x_i}\right), \quad e_{yij}\big(\boldsymbol{u}^{(1)}\big) = \frac{1}{2}\left(\frac{\partial u_i^{(1)}}{\partial y_j} + \frac{\partial u_j^{(1)}}{\partial y_i}\right). \tag{24}$$

From equations (20) and (23), we have

$$\frac{\partial}{\partial y_j}\big[C_{ijkl} e_{ykl}\big(\boldsymbol{u}^{(1)}\big)\big] = -\frac{\partial C_{ijkl}}{\partial y_j} e_{xkl}\big(\boldsymbol{u}^{(0)}\big). \tag{25}$$

Integrating both sides of equation (25) and using the periodical boundary conditions due to the periodical distribution of RVE, we have

$$u_i^{(1)}(\boldsymbol{x}, \boldsymbol{y}) = \chi_i^{kl}(\boldsymbol{y}) e_{xkl}\big(\boldsymbol{u}^{(0)}(\boldsymbol{x})\big), \tag{26}$$

where $\chi_i^{(kl)}(\boldsymbol{y})$ is a local-coordinate periodic function defined in the RVE. Substituting equation (26) into equation (23), we have

$$e_{ij}^{(0)} = e_{xkl}\big(\boldsymbol{u}^{(0)}\big)\big[T_{ij}^{kl} + e_{yij}\big(\boldsymbol{\chi}^{kl}\big)\big]. \tag{27}$$

Thus equation (9) may be rewritten as

$$\sigma_{ij}^{(0)} = C_{ijkl}\big[T_{mn}^{kl} + e_{ymn}\big(\boldsymbol{\chi}^{kl}\big)\big] e_{xkl}\big(\boldsymbol{u}^{(0)}\big). \tag{28}$$

The average $\sigma_{ij}^{(0)}$ in the RVE is written as

$$< \sigma_{ij}^{(0)} > = C_{ijkl}^{\mathrm{H}} e_{xkl}\big(\boldsymbol{u}^{(0)}\big), \tag{29}$$

where

$$C_{ijkl}^{\mathrm{H}} = \frac{1}{|Y|}\int_Y C_{ijmn}\left[T_{mn}^{kl} + e_{ymn}\left(\boldsymbol{\chi}^{kl}\right)\right] \mathrm{d}Y, \tag{30}$$

in which $|Y|$ denotes the REV volume. C_{ijkl}^{H} is the effective elastic stiffness tensor and is independent of $\boldsymbol{y}$. It is normally termed the homogenised equivalent elastic constant. It is observed from equation (30) that, before computing C_{ijkl}^{H}, χ_i^{kl} must be obtained by the following equation, derived from equation (25) using equations (24) and (26),

$$\frac{\partial}{\partial y_j}\left[C_{ijkl} e_{ykl}\left(\boldsymbol{\chi}^{kl}\right)\right] + \frac{\partial C_{ijkl}}{\partial y_j} = 0. \tag{31}$$

It is evident that χ_i^{kl} is a generalised displacement and $\partial(C_{ijkl})/\partial y_j$ a generalised force. Equation (31) can be written in the following equivalent form:

$$\int_Y C_{ijkl} e_{ymn}\left(\boldsymbol{\chi}^{kl}\right) e_{ij}(\phi)\, \mathrm{d}Y = -\int_Y C_{ijkl} T_{mn}^{kl} e_{ij}(\phi)\, \mathrm{d}Y. \tag{32}$$

Here, a 4-node isoparametric element is adopted, and the generalised displacement in the element is interpolated as the function of nodal displacements,

$$\boldsymbol{\chi}^{kl} = \sum_{i=1}^{4} \boldsymbol{N}_i \boldsymbol{\chi}_i^{kl}, \tag{33}$$

where $\boldsymbol{N}$ is the shape function matrix. Thus, the discretised form of equation (32) in the finite element approach follows

$$\boldsymbol{K}\boldsymbol{\chi}^{kl} = \boldsymbol{p}^{kl}, \tag{34}$$

in which

$$\boldsymbol{K} = \int_{-1}^{1}\int_{-1}^{1} \boldsymbol{B}_{8\times 3}^{\mathrm{T}} \boldsymbol{C}_{3\times 3} \boldsymbol{B}_{3\times 8} h |\boldsymbol{J}|\, \mathrm{d}\xi\, \mathrm{d}\eta, \quad \boldsymbol{p}^{kl} = -\int_{-1}^{1}\int_{-1}^{1} \boldsymbol{B}_{8\times 3}^{\mathrm{T}} \boldsymbol{C}_{3\times 3} h |\boldsymbol{J}|\, \mathrm{d}\xi\, \mathrm{d}\eta, \tag{35}$$

where h is the element thickness, $|\boldsymbol{J}|$ the determinant of the Jacobian matrix and $\boldsymbol{B}$ the strain matrix.

Numerical results for effective constitutive moduli of Nafion hydrogel membrane

In order to validate the present asymptotic homogenisation method for the computation of the effective constitutive moduli of the Nafion hydrogel membrane, several numerical investigations are carried out. Firstly the local displacement $\boldsymbol{\chi}^{kl}$ is computed by solving equation (32) or its discretised form (34). Then according to equation (24), the local strain $e_{ymn}(\chi_i^{kl})$ is obtained by the first-order derivative with respect to χ_i^{kl}. Finally, the variation of the macroscopic effective constitutive moduli C_{ijkl}^{H} with the water volume fraction are computed by equation (30), and the

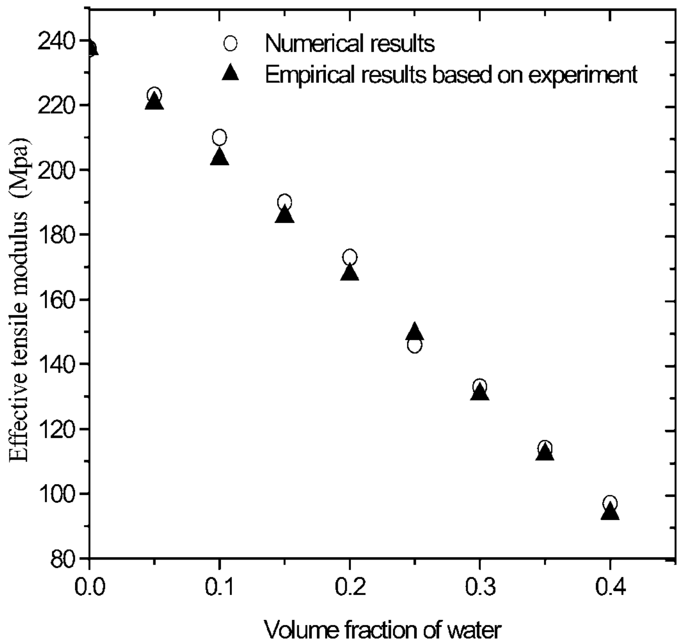


Figure 4. Effective tensile modulus *versus* the water volume fraction ($M_e = 1100$).

effective stress coefficients α_{ij} by equation (3), for the studied water-swollen Nafion hydrogel membrane.

Numerical results are shown in Figs 4–9. Figures 4 and 5 compare the computed results with the empirical data based on experimental results, for the variation of the effective tensile modulus against the water volume fraction at different equivalent weights, $M_e = 1100$ when the solid polymer tensile moduli $C^S_{1111} = C^S_{2222} = 237.4$ MPa and $M_e = 1200$ when $C^S_{1111} = C^S_{2222} = 275$ MPa. It is observed that the maximum relative difference is only 3.3%, showing that the present numerical simulations are very accurate. To investigate the variation of the effective bulk modulus with the water volume fraction of Nafion hydrogel membrane, Figures 6 and 7 are obtained with different equivalent weights, $M_e = 1100$ and 1200, for comparison of the numerical results with the analytical solutions of both Hashin-Shtrikman upper bound and the lower bound being trivially equal to zero [14]. It is clearly evident that very good agreements are achieved. Figures 8 and 9 are obtained to examine the effects of the variation of Biot effective coefficients against the water volume fraction. It is well known that the Biot effective coefficients increase with increase of water volume fraction and this is reflected in both figures. Also, it is noted from these two figures that the influence of the equivalent weight M_e on the Biot effective coefficients is very small and it can be neglected.

To summarise, we have developed a numerical methodology, based on the asymptotic homogenisation technique, for obtaining the effective constitutive moduli of Nafion hydrogel membrane. After generating the relation between the global

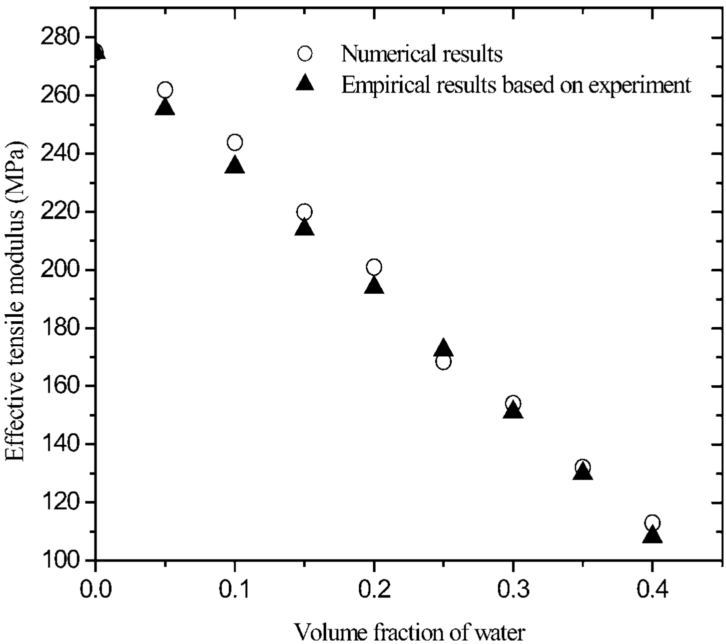


Figure 5. Effective tensile modulus *versus* the water volume fraction ($M_e = 1200$).

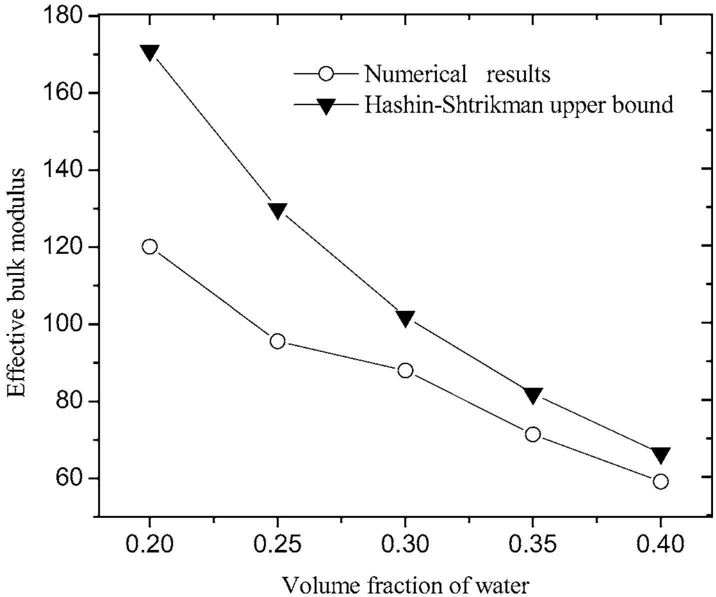


Figure 6. Effective bulk modulus *versus* the water volume fraction ($M_e = 1100$).

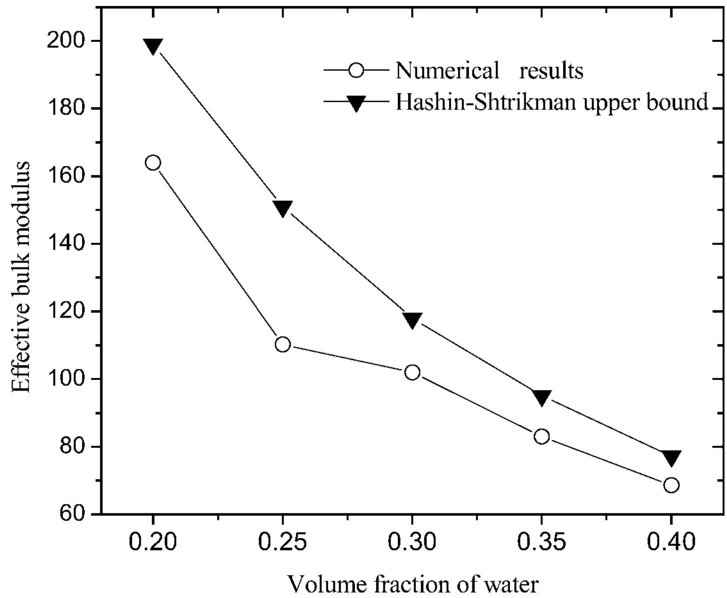


Figure 7. Effective bulk modulus *versus* the water volume fraction ($M_e = 1200$).

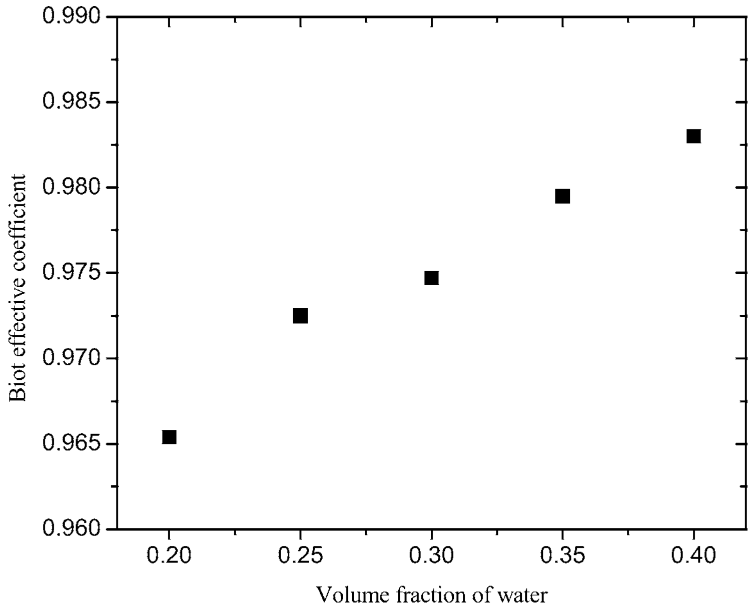


Figure 8. Biot effective coefficient *versus* the water volume fraction ($M_e = 1100$).

coordinate system for macrostructure and the local coordinate system for the RVE, the displacement, strain and stress are defined in both coordinate systems with corresponding to macro- and micro-scales. Then, by the asymptotic homogenisation

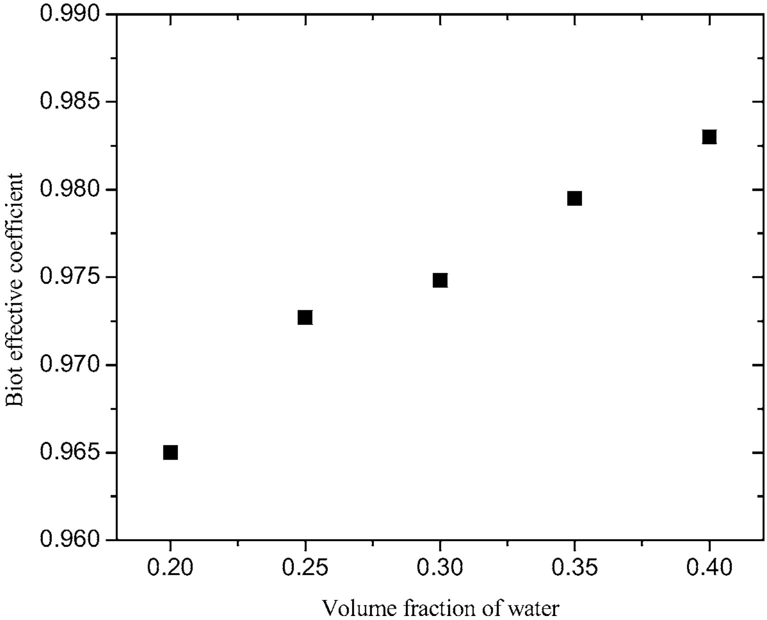


Figure 9. Biot effective coefficient *versus* the water volume fraction ($M_e = 1200$).

technique for the mechanical governing equations and boundary conditions, the constitutive moduli are obtained numerically using FEM.

TOPOLOGY OPTIMISATION OF CLUSTER SHAPE OF NAFION HYDROGEL MEMBRANE

Here we move on to further determine the cluster shape of the Nafion hydrogel membrane, where the topology optimisation technique is used to minimise the electro-elastic interaction energy between the ionic clusters and the fluorocarbon matrix. With the requirement of periodic distribution, the RVE design domain of the swollen Nafion hydrogel membrane, as shown in Fig. 10, is defined as the polymer skeleton surrounded by fluid, where the shear stress in the fluid phases is small and is neglected. An all-round fluid pressure is exerted on the solid phase. This results in a uniform strain field due to compression of the solid-phase polymer skeleton. It is noted that the scale of RVE design domain can be evaluated straightaway by the analytical method [2].

Based on the linear strain theory, the interaction energy without consideration of an externally applied voltage can be assumed as the strain energy of the solid phase subject to fluid pressure, and expressed in the following discretised finite-element form

$$U_{\text{interact}}(\rho) = \sum_{i=1}^{2} W_i \boldsymbol{U}_i^{\mathrm{T}}(\rho)\boldsymbol{P}_i = \sum_{i=1}^{2} W_i \boldsymbol{U}_i^{\mathrm{T}}(\rho)\boldsymbol{K}(\rho)\boldsymbol{U}_i(\rho), \tag{36}$$

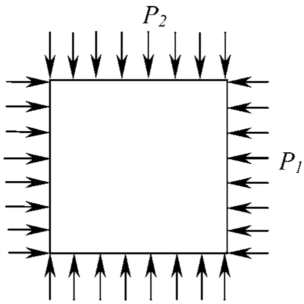


Figure 10. Design domain of microstructural RVE of Nafion hydrogel.

in which the column vector $\boldsymbol{P}_i$ is the normal fluid pressure applied on the solid-phase polymer skeleton, the column vector $\boldsymbol{U}_i$ the solid-phase displacement, and $\boldsymbol{K}$ the stiffness matrix. W_1 and W_2 are weighting coefficients, and the subscript i $(i = 1, 2)$ denotes vertical and horizontal directions respectively.

If the objective function is defined as a weighted sum of the strain energy and the imposed constraint defined as the polymer material volume, the present optimisation problem can be stated as

$$\text{Min:}\quad U_{\text{interact}}(\rho) = \sum_{i=1}^{2} W_i \boldsymbol{U}_i^{\mathrm{T}}(\rho)\boldsymbol{F}_i = \sum_{i=1}^{2} W_i \boldsymbol{U}_i^{\mathrm{T}}(\rho)\boldsymbol{K}(\rho)\boldsymbol{U}_i(\rho) \tag{37}$$

$$\text{Subject to:}\quad H(\rho) = \sum_{e=1}^{Ne} \int_{Y_e} \rho_e \,\mathrm{d}\Omega - V_0 \leqslant 0 \tag{38}$$

$$\sum_{e=1}^{Ne} \boldsymbol{K}_e(\rho_e)\boldsymbol{q}^k = \sum_{e=1}^{Ne} \boldsymbol{p}_e^k(\rho_e), \quad \rho_{\min} \leqslant \rho_e \leqslant \rho_{\max}, \quad \boldsymbol{\rho} = (\rho_1, \rho_2, \ldots, \rho_{Ne}), \tag{39}$$

where Ne is the total number of finite elements in the discretized RVE design domain. $\rho_{\min}$ and $\rho_{\max}$ are the lower and upper limits of the design variables, $\boldsymbol{\rho}$ the density vector and V_0 the specified polymer material volume. The dependence of constitutive moduli C_{ijkl} on the volume fraction is often characterized by the homogenization of sub-microstructure with a square hole [4]. In this work, however, a simple artificial relation between the element density ρ_e and the constitutive modulus is used for topology optimisation, namely the Young modulus, is assumed here to vary with the density by

$$G(\rho_e) = G_0 \rho_e^n, \tag{40}$$

where G_0 is the Young modulus of the original matrix without the hole, and n is a constant often taken as 3. Thus, if $\boldsymbol{C}_0$ represents the constitutive matrix of the solid-phase polymer skeleton, the global stiffness matrix in the equation (37) can be written as

$$\boldsymbol{K}(\rho) = \sum_{e=1}^{Ne} \boldsymbol{K}_e(\rho_e) = \sum_{e=1}^{Ne} \int_{Y_e} \boldsymbol{B}_e^{\mathrm{T}} \boldsymbol{C}(\rho_e) \boldsymbol{B}_e \, \mathrm{d}Y = \sum_{e=1}^{Ne} \int_{Y_e} \boldsymbol{B}_e^{\mathrm{T}} \boldsymbol{C}_0 \rho_e^n \boldsymbol{B}_e \, \mathrm{d}Y. \tag{41}$$

By the Optimality Criteria method [4] for topology optimisation, the design variable ρ_e is updated during each iteration,

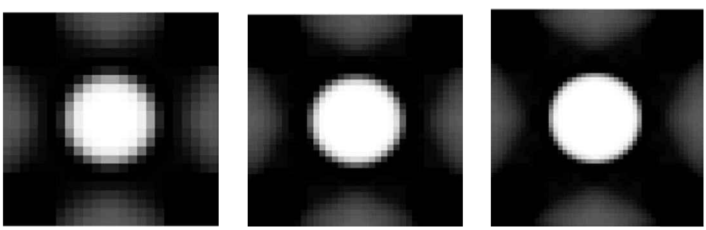
$$\rho_e^{k+1} = \begin{cases} \max\{(1-\psi)\rho_e^k, 0\} & \rho_e^k D_k^{\varsigma} \leqslant \max\{(1-\psi)\rho_e^k, 0\} \\ \rho_e^k D_k^{\varsigma} & \max\{(1-\psi)\rho_e^k, 0\} \leqslant \rho_e^k D_k^{\varsigma} \leqslant \min\{(1+\psi)\rho_e^k, 1\} \\ \min\{(1+\psi)\rho_e^k, 1\} & \min\{(1+\psi)\rho_e^k, 1\} \leqslant \rho_e^k D_k^{\varsigma}. \end{cases} \tag{42}$$

It should be noted here that a filtering technique is employed in the iteration process to prevent a checkerboard pattern. Furthermore, by the sensitivity analysis of the objective function and constraint condition, D_k is expressed as

$$D_k = \frac{n(\rho_e)^{n-1}\Delta}{\Lambda Y_e}, \tag{43}$$

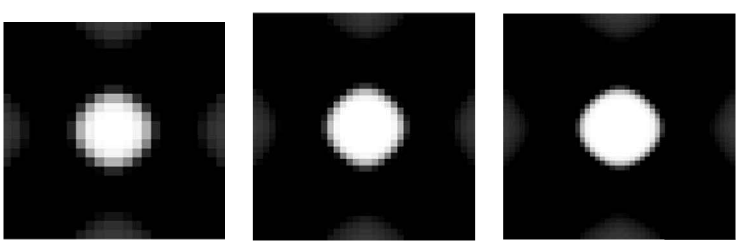
where Λ is the global Lagrangian multiplier, ζ the damping coefficient, Ψ the moving limit of each iteration, Y_e the element area, and Δ the sum of strain energy when the element density is equal to 1.

In order to validate the topology optimisation technique for the cluster shape of the Nafion hydrogel membrane, several numerical examples are carried out, in which a square RVE design domain is analysed by the FEM using two-dimensional 4-node



(a) (b) (c)

Figure 11. Optimal microstructures with $V_0 = 0.8$.



(a) (b) (c)

Figure 12. Optimal microstructures with $V_0 = 0.9$.

iso-parametric elements. The Young modulus G_0 of the original element without a hole is given by 287 MPa and the Poisson ratio by 0.48. The fluid pressure of $P_i = 1$ $(i = 1, 2)$ is taken in both vertical and horizontal directions. The values of the specified polymer material volume V_0 are set to 0.8 and 0.9, to verify that the solution is not unique or has multiple local minima of the design variables. In addition, to examine the influence of mesh characteristics, several mesh patterns, 24×24 (see Figs 11a and 12a), 36×36 (see Figs 11b and 12b) and 48×48 (see Figs 11c and 12c), are utilized. The final optimal results are obtained and shown in Fig. 11 for $V_0 = 0.8$ and Fig. 12 for $V_0 = 0.9$. It is observed that, due to the use of the filtering technique in the iteration process, the optimal results are not sensitive to the finite element mesh and volume constraint, and the two-dimensional shape of the micro-structural cluster is almost circular when no externally applied electric field is considered. The numerical optimal results agree well with both empirical evaluation [2] and experimental data [5].

CONCLUSIONS

This paper presents the development of the constitutive models for the Nafion hydrogel membrane by an asymptotic homogenisation method, and based on Biot poroelasticity theory. These presently developed constitutive models, linking the macro-mechanical constitutive moduli with the micro-mechanical characteristics, are employed to examine the influence of water volume fraction on the effective elastic moduli of the Nafion hydrogel membrane with different equivalent weights. The computed effective constitutive moduli agree well with experimental results. This accuracy can be attributed to the asymptotic homogenisation method, where the representative volume element (RVE) includes all information required to comprehensively describe the Nafion hydrogel membrane. In addition, to determine the cluster morphology in the polymer skeleton of the Nafion hydrogel membrane subject to fluid pressure, a topology optimisation model is presented to optimise the periodic microstructures of the Nafion hydrogel membrane by minimising the electro-elastic interaction energy between the polymer-based fluorocarbon matrix and the surrounding fluid. This optimisation model is validated to correctly predict the micro-structural geometric shapes of the clusters and it is also able to improve or tailor the artificial microstructures of the Nafion hydrogel membrane. The developed constitutive models and optimisation process can be easily extended to three-dimensional cases, which will be the focus of future work.

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