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Time-dependent chemo-electro-mechanical behavior of hydrogel-based structures

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ABSTRACT

Charged hydrogels are ionic polymer gels and belong to the class of smart materials. These gels are multiphasic materials which consist of a solid phase, a fluid phase and an ionic phase. Due to the presence of bound charges these materials are stimuli-responsive to electrical or chemical loads. The application of electrical or chemical stimuli as well as mechanical loads lead to a viscoelastic response. On the macroscopic scale, the response is governed by a local reversible release or absorption of water which, in turn, leads to a local decrease or increase of mass and a respective volume change.

Furthermore, the chemo-electro-mechanical equilibrium of a hydrogel depends on the chemical composition of the gel and the surrounding solution bath. Due to the presence of bound charges in the hydrogel, this system can be understood as an osmotic cell where differences in the concentration of mobile ions in the gel and solution domain lead to an osmotic pressure difference.

In the present work, a continuum-based numerical model is presented in order to describe the time-dependent swelling behavior of hydrogels. The numerical model is based on the Theory of Porous Media and captures the fluid-solid, fluid-ion and ion-ion interactions. As a direct consequence of the chemo-electro-mechanical equilibrium, the corresponding boundary conditions are defined following the equilibrium conditions. For the interaction of the hydrogel with surrounding mechanical structures, also respective jump conditions are formulated. Finally, numerical results of the time-dependent behavior of a hydrogel-based chemo-sensor will be presented.

Keywords: Polyelectrolyte Gel, Hydrogel, Porous Media, Numerical Simulation, FEM, Transport, Osmosis

1. INTRODUCTION

Polyelectrolyte gels are a class of chemically synthesized materials. They comprise a solid phase, i.e. a polymer network with fixed charges and a fluid phase which is an electrolyte, i.e. an aqueous solution with mobile ions. Hydrogels are immersed in a solution bath and show a response to variations of the external conditions. Changing the concentration of the surrounding solution will lead to a reversible swelling or deswelling of the hydrogel. By applying an external electric field a bending behavior¹ can be observed.

Its chemo-electro-mechanical properties make hydrogels a promising material for new applications such as sensor systems, e.g. pH sensors developed by Gerlach et al.,² or micro-fluidic processors as presented by Richter et al.³ An approach for the generalization of the hydrogel swelling is presented in Ehrenhofer et al.⁴ Numerical analyses play an important role in the further development of these approaches. To make hydrogels accessible to numerical investigations a continuum based model is developed and presented in the present study.

There exist different modeling approaches to describe the swelling behavior of hydrogels. By treating the constituents of electroactive polymers separately, their interactions can be considered based on the material properties of the constituents itself. Based on this modeling approach which is called Theory of Mixtures – first described by Bowen⁵ – and the concept of volume fractions, the Theory of Porous Media can be derived. Essential enhancements have been done by Bowen⁶ and Mow et al.⁷ in which theoretical and experimental results can be found, and by de Boer,⁸ Frijns et al.,⁹ Sun et al.¹⁰ and van Loon et al.¹¹ presented a triphasic and quadriphasic mixture theory for the simulation of hydrated tissues. For ionic gels, a modeling approach was

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presented by Ehlers et al.¹² and by Acartürk.¹³ A thermodynamically consistent model for polyelectrolyte polymeric gels, which also respects electrical quantities, is given by Leichsenring et al.¹⁴ A more general approach for a multiple-component, multiple-phase, polarizable, swelling porous medium with charged particles is given by Bennethum and Cushman.^{15,16} An examination of the electric potential inside charged, soft, hydrated tissues was given by Lai et al.¹⁷

2. NUMERICAL MODEL

The macroscopic behavior of hydrogels is driven by processes on the microstructure of the material. The structural composition of the hydrogel microstructure is highly irregular. The microstructure is composed of polymer chains which form a solid matrix with an interconnected void. The void is filled with a solution consisting of a solvent and mobile charges. For ionic hydrogels, fixed charges are bonded to the polymer chains. A schematic representation of the hydrogel structure is shown in Fig. 1. To obtain a continuum based numerical model, a homogenization process has to be performed for the microstructure. To avoid evaluating interfacial effects with respect to the geometry and structure of the moving components, the Theory of Porous Media is applied, while a definition of relevant quantities is given in subsection 2.1. The kinematical relations of the continuum are summarized in subsection 2.2 which is followed by a brief introduction of the balance laws in subsection 2.3.

Figure 1: Homogenization of the hydrogel microstructure based on the Theory of Porous Media

2.1 Theory of Porous Media

The homogenization procedure is performed in two steps. First, by applying the theory of mixtures, a single material point consists of every constituent of the material. Therefore, the whole body is governed by

$$\mathcal{B} = \bigcup_{\alpha \in \mathcal{V}} \mathcal{B}^{\alpha} \quad \text{with} \quad \alpha \in \mathcal{V} = \{1, \dots, \mathcal{N}\}, \quad (1)$$

where $\mathcal{B}^{\alpha}$ denotes the domain of a specific constituent $\mathcal{V}^{\alpha}$ of the set of constituents $\mathcal{V}$. It is worth mentioning, that the material element is defined by a unique coordinate $\vec{x}$ and no distinction is made for the individual $\mathcal{V}^{\alpha}$. Instead of that, the differential volume of the material element is defined by the superposition

$$dv = \sum_{\alpha \in \mathcal{V}} dv^{\alpha}, \quad (2)$$

where dv^{α} denotes the incorporated differential volume of constituent $\mathcal{V}^{\alpha}$. Consequently, the volume of the whole mixture $\mathcal{V}$ can be obtained by

$$v = \int_{\mathcal{B}} dv = \int_{\mathcal{B}} \sum_{\alpha \in \mathcal{V}} dv^{\alpha} = \sum_{\alpha \in \mathcal{V}} \int_{\mathcal{B}^{\alpha}} dv^{\alpha} = \sum_{\alpha \in \mathcal{V}} v^{\alpha}. \quad (3)$$

The second step of the homogenization procedure is a quantification of the mixture defined in Eq. (3). Therefore, the concept of volume fractions is introduced in order to describe the composition of the mixture $\mathcal{V}$ by the volume fraction

$$\varphi^{\alpha} = \frac{dv^{\alpha}}{dv} \quad (4)$$

In order to obtain a continuum based model for hydrogels and referring to the composition of hydrogels as shown in Fig. 1, a solid phase consisting of the polymer matrix $\mathcal{V}^p$ and fixed charges $\mathcal{V}^{fc}$ as well as a fluid phase

$\mathcal{V}^F$ is respected. The fluid phase $\mathcal{V}^F$ consists of ionic constituents $\mathcal{V}^I$, these are mobile anions $\mathcal{V}^-$ and mobile cations $\mathcal{V}^+$, and the liquid $\mathcal{V}^L$. A definition of the subsets is given as follows:

$$\text{Mixture} \quad \mathcal{V} = \mathcal{V}^S \bigcup \mathcal{V}^F = \bigcup_{\alpha \in \mathcal{V}} \mathcal{V}^\alpha, \quad \alpha \in \mathcal{V} = \{S, F\} = \{P, fc, L, +, -\}, \quad (5a)$$

$$\text{Fluid phase} \quad \mathcal{V}^F = \mathcal{V}^I \bigcup \mathcal{V}^L = \bigcup_{\beta \in \mathcal{V}^F} \mathcal{V}^\beta, \quad \beta \in \mathcal{V}^F = \{L, +, -\}, \quad (5b)$$

$$\text{Mobile ions} \quad \mathcal{V}^I = \mathcal{V}^- \bigcup \mathcal{V}^+ = \bigcup_{\gamma \in \mathcal{V}^I} \mathcal{V}^\gamma, \quad \gamma \in \mathcal{V}^I = \{+, -\}. \quad (5c)$$

In the present model formulation, the transport phenomena inside hydrogels are described by respective mass density fields. By following the definition of the respective volume fractions in Eq. (2), the mass of a constituent $\mathcal{V}^\alpha$ can be referred to the bulk volume fraction dv or to the volume fraction dv^α of the constituent itself. Therefore, two distinct density measures

$$\varrho^\alpha = \frac{dm^\alpha}{dv} \quad \text{and} \quad (6a)$$

$$\varrho^{\alpha R} = \frac{dm^\alpha}{dv^\alpha} \quad (6b)$$

exist, where ϱ^α is the partial density and $\varrho^{\alpha R}$ is the material density of $\mathcal{V}^\alpha$. They are coupled by Eq. (4) and

$$\varrho^\alpha = \varphi^\alpha \varrho^{\alpha R} \quad (7)$$

follows. Furthermore, if one considers the presence of a fluid phase, a density measure with respect to the volume of the fluid phase can be defined in the same manner, such that

$$\varrho^{\beta F} = \frac{dm^\beta}{dv^F}. \quad (8)$$

This relation is proven to be convenient in order to obtain a formulation for the ionic constituents depending on their molar concentration c_m^α . With a given molar mass M_m^α and the amount of substance n_m^α , the density can then be obtained by

$$\varrho^{\beta F} = M_m^\beta c_m^\beta \quad \text{with} \quad c_m^\beta = \frac{dn_m^\beta}{dv^F}. \quad (9)$$

2.2 Kinematics of the mixture

The definition of independent constituents as well as the quantities for the whole mixture will be pursued by defining the kinematical relations of the continuum based numerical framework. As shown in Fig. 2, the motion of the constituents $\mathcal{V}^\alpha$ are defined by independent motion functions as

$$\vec{x} = \vec{\chi}^\alpha(\vec{X}^\alpha, t), \quad (10)$$

where $\vec{x}$ is the location of the observed material point in the current configuration of $\mathcal{B}$ and $\vec{X}^\alpha$ is the corresponding location of the constituents $\mathcal{V}^\alpha$ in the reference frame $\mathcal{B}^0 = \mathcal{B}(t=0)$. The corresponding displacement field $\vec{u}^\alpha$, as well as the velocity field $\vec{v}^\alpha$, is then defined as

$$\vec{u}^\alpha = \vec{x} - \vec{X}^\alpha \quad \text{and} \quad (11a)$$

$$\vec{v}^\alpha = \frac{\partial \vec{x}(\vec{X}^\alpha, t)}{\partial t}. \quad (11b)$$

For the derivation of the constitutive laws, the formulation of the velocities with respect to the solid phase $\mathcal{V}^S$ is convenient. Considering the definition of the constituents of the mixture in Eq. (5), the velocity of the

Figure 2: Reference configuration and current configuration of a mixture with two constituents

constituents of $\mathcal{V}^F$ with respect to the solid phase is defined as $\vec{w}^\beta$. Furthermore, a weighted velocity measure for the fluid phase $\mathcal{V}^F$ is denoted as $\vec{w}^F$, such that

$$\vec{w}^\beta = \vec{v}^\beta - \vec{v}^S \quad \text{and} \quad (12a)$$

$$\vec{w}^F = \vec{v}^F - \vec{v}^S \quad \text{with} \quad \vec{v}^F = \frac{1}{\varrho_{FR}} \sum_{\beta \in \mathcal{V}^F} \varrho^{\beta F} \vec{v}^\beta. \quad (12b)$$

2.3 Balance laws

Proceeding from the relations for the kinematic behavior and the definition of the composition of the mixture, balance equations and additional constitutive laws will be derived. Furthermore, the imposed restrictions of the mixture will be discussed. First, the balance of mass is stated in subsection 2.3.1 and corresponding assumptions for the mixture are discussed. Second, the balance of linear momentum is stated in subsection 2.3.2.

2.3.1 Balance of mass

The balance of mass for a constituent $\mathcal{V}^\alpha$ is stated in the local form as

$$\dot{\varrho}^\alpha = -\varrho^\alpha \vec{\nabla} \cdot \vec{v}^\alpha + \hat{\varrho}^\alpha, \quad (13)$$

where $\hat{\varrho}^\alpha$ is the mass production density of the constituent $\mathcal{V}^\alpha$ and $\vec{\nabla} = (\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \frac{\partial}{\partial x_3})$ is the nabla operator.

The material time derivative of the density ϱ^α is denoted by the $(\dot{\cdot})$ operator, which is, for e.g. an arbitrary scalar quantity a^α , defined as

$$\dot{a}^\alpha = \frac{da^\alpha(\vec{x}(\vec{X}^\alpha, t), t)}{dt} = \frac{\partial a^\alpha(\vec{x}, t)}{\partial t} + \frac{\partial a^\alpha(\vec{x}, t)}{\partial \vec{x}} \cdot \frac{d\vec{x}(\vec{X}^\alpha, t)}{dt} = \frac{\partial a^\alpha}{\partial t} + \vec{\nabla} a^\alpha \cdot \vec{v}^\alpha. \quad (14)$$

The presented balance law for the conservation of mass in Eq. (13) is similar to the well known balance law for a one-phasic material extended by a production density term. Following the superposition principle of the mixture theory, the physical quantity of the mixture can be calculated by a superposition of the respective quantities of the constituents $\mathcal{V}^\alpha$. Therefore, for an arbitrary scalar quantity and its time derivative,

$$a = \sum_{\alpha \in \mathcal{V}} a^\alpha \quad \text{and} \quad \sum_{\alpha \in \mathcal{V}} \dot{a}^\alpha = \dot{a} - \sum_{\alpha \in \mathcal{V}} (\vec{\nabla} a^\alpha \cdot (\vec{v} - \vec{v}^\alpha)) \quad (15)$$

holds. Furthermore, for a one-phasic material, the production density needs to vanish. As a consequence, the restriction

$$\sum_{\alpha \in \mathcal{V}} \hat{\varrho}^\alpha = 0 \quad (16)$$

has to hold for the mixture. By applying the relations obtained in Eq. (15) and Eq. (16), Eq. (13) reads for the whole mixture

$$\dot{\varrho} = -\vec{\nabla} \varrho^\alpha \cdot \vec{v}. \quad (17)$$

In this paper, the mass product density is neglected for each constituent and therefore $\hat{\varrho}^\alpha = 0$. Furthermore, the partial density of each constituent is assumed to be constant, i. e. $\varrho^{\alpha R} = \text{const.}$ From these two restrictions, the balance law Eq. (13) can be transformed into

$$\dot{\varphi}^\alpha + \varphi^\alpha \vec{\nabla} \cdot \vec{v}^\alpha = 0. \quad (18)$$

The mixture is assumed to be fully saturated. Therefore,

$$\sum_{\alpha \in \mathcal{V}} \varphi^\alpha = \varphi^S + \varphi^F = 1 \quad (19)$$

has to hold. For the derivation of the field equations, an evaluation of the balance of mass for the fluid phase $\mathcal{V}^F$ as well as for the ionic constituents $\mathcal{V}^\gamma$ are performed. By incorporating Eqs. (9), (12a) and (19), the balance of mass can be stated as

$$\varphi^F (c_m^\gamma)^{\prime S} + c_m^\gamma \vec{\nabla} \cdot \vec{u}^S = -\vec{\nabla} \cdot (\varphi^F c_m^\gamma \vec{w}^\gamma), \quad (20)$$

where the superscript $(\cdot)^{\prime S}$ denotes a time derivative $\frac{d^S(\cdot)}{dt}$ with respect to the motion of the solid phase, cf. Eq. (14). The mass balance for the fluid phase $\mathcal{V}^F$ reads as

$$\vec{\nabla} \cdot \vec{u}^S = -\vec{\nabla} \cdot (\varphi^F \vec{w}^F). \quad (21)$$

2.3.2 Balance of linear momentum

The balance of linear momentum is given as

$$\varrho^\alpha \vec{a}^\alpha = \vec{\nabla} \cdot \mathbf{T}^\alpha + \varrho^\alpha \vec{f}^\alpha - \hat{\varrho}^\alpha \vec{v}^\alpha + \hat{s}^\alpha, \quad (22)$$

where $\vec{a}^\alpha = \dot{\vec{v}}^\alpha$ is the acceleration of constituent $\mathcal{V}^\alpha$, the CAUCHY stress tensor is denoted by $\mathbf{T}^\alpha$ and $\vec{f}^\alpha$ is a body force density. The linear momentum production density of constituent $\mathcal{V}^\alpha$ is denoted by $\hat{s}^\alpha$. In the present paper, inertial forces and body forces are neglected. Considering also the absence of the mass production density $\hat{\varrho}^\alpha$ described in subsection 2.3.1, the balance of linear momentum can be stated in a simplified form. As shown in Eq. (15), the balance law for the whole mixture can be found by a superposition. Therefore

$$\text{for the constituents } \mathcal{V}^\alpha : \quad \vec{0} = \vec{\nabla} \cdot \mathbf{T}^\alpha + \hat{s}^\alpha \quad \text{and} \quad (23a)$$

$$\text{for the mixture } \mathcal{V} : \quad \vec{0} = \vec{\nabla} \cdot \mathbf{T} \quad (23b)$$

holds.

2.3.3 Balance relations of electrodynamics

The balance relations of electrodynamics for the overall mixture will be introduced axiomatically. Due to the diffusion dominated processes and thus a slowly varying electric field no electro-dynamical effects are taken into account. In the absence of an external magnetic field the electro-static balance equations can be derived from the MAXWELL-equations as shown e. g. in.¹⁸ They can be stated in its macroscopic form as

$$\vec{\nabla} \cdot \vec{d}_e = \varrho_e \quad \text{and} \quad (24a)$$

$$\vec{\nabla} \times \vec{e}_e = \vec{0}, \quad (24b)$$

where the primary variable is denoted by the electric field $\vec{e}_e$, and the electric displacement field $\vec{d}_e$ can be expressed as

$$\vec{d}_e = \varepsilon_0 \vec{e}_e + \vec{p}_e. \quad (25)$$

To solve for the electric field, constitutive laws for the electric polarization $\vec{p}_e$ and the electric charge density ϱ_e have to be defined. Furthermore, in electrostatics, the electric field can be related to an electric potential ψ_e . Following this, from Eq. (24b) and a substitution of Eq. (25) in Eq. (24a)

$$\varepsilon_0 \vec{\nabla}^2 \psi_e = -\varrho_e + \vec{\nabla} \cdot \vec{p}_e \quad (26)$$

can be derived.

2.3.4 Closing the system of equations

The derived balance equations consist of unknown quantities which need to be quantified to obtain a closed system of equations. In the framework of continuum mechanics, this is performed by defining respective constitutive laws. For convenience, the derivation of the constitutive laws is not shown in detail. Instead, the unknown quantities in the balance of the ionic constituents (20), in the balance of the fluid phase (21), in the linear momentum balance (23) and in the balance relation for electrostatics Eq. (26) are given with respect to the primary variables of the model.

The derivation of the constitutive laws is performed considering thermodynamic consistency. The evaluation is then performed by applying the concept of effective stresses.¹⁹ Additionally, the saturation condition leads to a hydraulic pressure π^{hyd} , cf.⁶ It is derived by extending the entropy inequality by a LAGRANGE multiplier and an evaluation following.²⁰ As shown in,⁵ an additional pressure contribution is obtained from the evaluation of the chemical potential of the constituents of the fluid phase $\mathcal{V}^F$. This pressure contribution can be identified as osmotic pressure $\pi^{\beta, \text{osm}}$ and is obtained by

$$\text{for the constituents } \mathcal{V}^\beta : \quad \pi^{\beta, \text{osm}} = R_s^\beta \theta \varrho^{\beta F} \quad \text{and} \quad (27a)$$

$$\text{for the mixture } \mathcal{V} : \quad \pi^{\text{osm}} = \sum_{\beta \in \mathcal{V}^F} \pi^{\beta, \text{osm}}, \quad (27b)$$

where $R_s^\beta = \frac{R}{M_m^\beta}$ denotes the specific gas constant and θ is the absolute temperature. The unknown stress tensors of the constituents can then be obtained following¹³ as

$$\text{for the constituents } \mathcal{V}^\beta : \quad \mathbf{T}^\beta = (-\varphi^F \pi^{\beta, \text{osm}} - \varphi^\beta \pi^{\text{hyd}} - \psi_e \varrho_e^\beta) \mathbf{I}, \quad (28a)$$

$$\text{for the solid phase } \mathcal{V}^S : \quad \mathbf{T}^S = \mathbf{T}^{S, \text{mech}} - (\varphi^S \pi^{\text{osm}} + \varphi^S \pi^{\text{hyd}} + \psi_e \varrho_e^{\text{fc}}) \mathbf{I}. \quad (28b)$$

For the momentum production densities, the evaluation of the entropy inequality leads to

$$\text{for the ionic constituents } \mathcal{V}^\gamma : \quad \hat{s}^\gamma = \pi^{\gamma, \text{osm}} \vec{\nabla} \varphi^F + \pi^{\text{hyd}} \vec{\nabla} \varphi^\gamma + \psi_e \vec{\nabla} \varrho_e^\gamma - \mathbf{C}^{\gamma F} \cdot \vec{d}^\gamma, \quad (29a)$$

$$\text{for the fluid phase } \mathcal{V}^F : \quad \hat{s}^F = \pi^{\text{osm}} \vec{\nabla} \varphi^F + \pi^{\text{hyd}} \vec{\nabla} \varphi^F + \psi_e \vec{\nabla} \varrho_e^I - \mathbf{C}^{FS} \cdot \vec{w}^F. \quad (29b)$$

The quantities $\mathbf{C}^{\gamma F}$ and $\mathbf{C}^{FS}$ in Eq. (29) are second-order friction tensors to account for the momentum production due to a relative motion of the ionic constituents and of the fluid phase, cf. Eq. (29a); and for the momentum production due to a relative motion of the fluid phase and of the solid phase, cf. Eq. (29b). They are defined by following,²¹ such that

$$\mathbf{C}^{\gamma F} = (\varphi^F)^2 \frac{\varrho^\gamma R_s^\gamma \theta}{D^\gamma} \mathbf{I} \quad \text{and} \quad (30a)$$

$$\mathbf{C}^{SF} = (\varphi^F)^2 \frac{\gamma^{\text{FR}}}{k^F} \mathbf{I} \quad (30b)$$

holds. In Eqs. (30), D^γ denotes the diffusivity of the constituent $\mathcal{V}^\gamma$ in the fluid, γ^{FR} and k^F are the effective fluid weight and the DARCY coefficient, respectively.

For the ionic constituents $\mathcal{V}^\gamma$, the evaluation of the balance of linear momentum (23a) and a substitution of Eq. (28a) and Eq. (29a) leads to

$$\varphi^F \varrho^\gamma \vec{w}^\gamma = -\frac{D^\gamma}{R_s^\gamma \theta} \left(\vec{\nabla} \pi^{\gamma, \text{osm}} + \varrho_e^{\gamma F} \vec{\nabla} \psi_e \right) + \varphi^F \varrho^\gamma \vec{w}^F, \quad (31)$$

where the simplification of a vanishing volume fraction of the ionic constituents $\frac{\varphi^\gamma}{\varphi^F} \rightarrow 0$ is made.

For the fluid phase $\mathcal{V}^F$, the evaluation of the balance of linear momentum (23a) for $\mathbf{T}^F = \sum_{\beta \in \mathcal{V}^F} \mathbf{T}^\beta$ and a substitution by Eq. (28a) and by Eq. (29b) leads to

$$\varphi^F \vec{w}^F = -\frac{k^F}{\gamma^{\text{FR}}} \left(\vec{\nabla} \pi^{\text{osm}} + \vec{\nabla} \pi^{\text{hyd}} + \varrho_e^{\text{IF}} \right), \quad (32)$$

where the friction tensor (30b) has been used. A comparison with Eq. (21) shows that Eq. (32) is an expression for the flux definition of the right hand side of the balance of mass for the fluid phase $\mathcal{V}^F$.

For the whole mixture $\mathcal{V}$, the evaluation of the balance of linear momentum (23b) for $\mathbf{T} = \sum_{\alpha \in \mathcal{V}} \mathbf{T}^\alpha$ and a substitution by Eq. (28a) and by Eq. (28b) leads to

$$\vec{0} = \vec{\nabla} \cdot (\mathbf{T}^{\text{S,mech}} - (\pi^{\text{osm}} + \pi^{\text{hyd}}) \mathbf{I}) , \quad (33)$$

where the electric charge density for the whole mixture $\varrho_e = \sum_{\alpha \in \mathcal{V}} \varrho_e^\alpha \approx 0$ is assumed to vanish.

To finally close the system of equations, a constitutive law has to be defined for the electric polarization and the electric charge density. Following the classical procedure in electrodynamics, a linear relation of the electric polarization and the electric field is defined

$$\vec{p}_e = \varepsilon_0 \chi_e \vec{e}_e , \quad (34)$$

where χ_e is the electric susceptibility of the material. The electric charge density is calculated by the number of electric charges per volume. Hence, ϱ_e can be calculated by

$$\varrho_e = \varrho_e^{\text{fc}} + \sum_{\gamma \in \mathcal{V}^I} \varrho_e^\gamma = F z^{\text{fc}} \frac{dn_m^{\text{fc}}}{dv} + \sum_{\gamma \in \mathcal{V}^I} F z^\gamma \frac{dn_m^\gamma}{dv} = F z^{\text{fc}} \varphi^F c_m^{\text{fc}} + \sum_{\gamma \in \mathcal{V}^I} F z^\gamma \varphi^F c_m^\gamma , \quad (35)$$

where F is the FARADAY constant and z^γ denotes the valence of the constituent $\mathcal{V}^\gamma$. A substitution of Eq. (34) and Eq. (35) into Eq. (26) leads to

$$\vec{\nabla}^2 \psi_e = - \frac{F \varphi^F}{\varepsilon_0 \varepsilon_r} \left(z^{\text{fc}} c_m^{\text{fc}} + \sum_{\gamma \in \mathcal{V}^I} z^\gamma c_m^\gamma \right) . \quad (36)$$

The derived field equations form a closed system of partial differential equations consisting of Eqs. (20), (21), (31), (32), (33) and Eq. (36).

3. NUMERICAL ANALYSIS

Since the analysis associated with the current study are based on the assumption of infinitesimal displacement gradients, the distinction between the current configuration and the reference configuration for the whole domain is neglected, i. e.

$$\mathcal{B} \approx \mathcal{B}^0 . \quad (37)$$

Table 1: System of partial differential equations of the field equations and of the constitutive laws of the fully coupled chemo-electro-mechanical model

Solid phase	Field equation	$\vec{\nabla} \cdot (\mathbf{T}^{\text{S,mech}} - \pi \mathbf{I}) = \vec{0}$
	Constitutive law	$\mathbf{T}^{\text{S,mech}} = {}^4 \vec{E} : \boldsymbol{\varepsilon}^{\text{S}}$
Fluid phase	Field equation	$\vec{\nabla} \cdot \vec{u}^{\text{S}} = -\vec{\nabla} \cdot (\varphi^F \vec{w}^F)$
	Constitutive law	$\varphi^F \vec{w}^F = - \frac{k^F}{\gamma^{\text{FR}}} \left(\vec{\nabla} \pi + F \sum_{\gamma \in \mathcal{V}^I} z^\gamma c_m^\gamma \vec{\nabla} \psi_e \right)$
Ionic phase	Field equation	$\varphi^F (c_m^\gamma)^{\text{S}} + c_m^\gamma \vec{\nabla} \cdot \vec{u}^{\text{S}} = -\vec{\nabla} \cdot (\varphi^F c_m^\gamma \vec{w}^\gamma)$
	Constitutive law	$\varphi^F c_m^\gamma \vec{w}^\gamma = -D^\gamma \left(\vec{\nabla} c_m^\gamma + \frac{F z^\gamma c_m^\gamma}{R\theta} \vec{\nabla} \psi_e \right) + \varphi^F c_m^\gamma \vec{w}^F$
Electric field	Field equation	$\vec{\nabla}^2 \psi_e = - \frac{F \varphi^F}{\varepsilon_0 \varepsilon_r} \left(\sum_{\gamma \in \mathcal{V}^I} z^\gamma c_m^\gamma + z^{\text{fc}} c_m^{\text{fc}} \right)$

(a) Simplified geometry

(b) Nine node shell element. The nodes are discretized such that the primary variables are $u_x^S, u_y^S, \pi, c^+, c^-$ and ψ_e .

Figure 3: Two-dimensional modelling approach

As a consequence, the infinitesimal strain tensor

$$\epsilon^S = \frac{1}{2} \left((\vec{\nabla} \vec{u}^S)^T + \vec{\nabla} \vec{u}^S \right) \quad (38)$$

can be defined for the solid phase $\mathcal{V}^S$. The infinitesimal strain assumption further leads to the definition of the linearized JACOBIAN. Considering the definition of the motion function in Eq. (10), the linearization leads to

$$\frac{dv^S}{dv^{S,0}} = J^S \approx 1 + \text{tr}(\epsilon^S) \quad \text{and} \quad (39a)$$

$$\frac{dv^{S,0}}{dv^S} = (J^S)^{-1} \approx 1 - \text{tr}(\epsilon^S). \quad (39b)$$

As a consequence of the assumption of infinitesimal strains, the material behavior for the solid phase is assumed to be linear elastic. Therefore, the linearized stress tensor of the solid phase $\mathcal{V}^S$ is defined as

$$\mathbf{T}^{S,\text{mech}} = {}^4\vec{E} : \epsilon^S, \quad (40)$$

where ${}^4\vec{E}$ denotes the fourth-order tensor of elasticity.

The numerical analysis of the derived field equations of the coupled chemo-electro-mechanical problem is performed in the framework of the Finite Element Method. Therefore, the set of field equations, which are summarized in Tbl. 1, are solved in the weak form. For the time integration, the implicit EULER discretization scheme is used. The numerical implementation is then performed in order to obtain a nine node shell element

Table 2: Material parameters for the fully coupled two-dimensional simulation

Description	Variable	Value	Unit
YOUNG'S modulus	E	70	kPa
POISSON'S ratio	ν	0	—
Diffusion constant of the cationic constituents	D^+	$1.33 \cdot 10^{-9}$	m^2/s
Valence of the cationic constituents	z^+	+1	—
Diffusion constant of the anionic constituents	D^-	$1.33 \cdot 10^{-9}$	m^2/s
Valence of the anionic constituents	z^-	-1	—
Initial concentration of the fixed charges $\mathcal{V}^{\text{fc}}$	c^{fc}	50	mol/m^3
Valence of the fixed charges $\mathcal{V}^{\text{fc}}$	z^{fc}	-1	—
Relative electric permittivity	ϵ_r	80	—
Temperature	θ	293	K
Specific hydraulic permeability	$\frac{k^{\text{F}}}{\gamma^{\text{FR}}}$	$9.6 \cdot 10^{-15}$	$\text{m}^4/(\text{N s})$
Initial volume fraction of the solid phase	φ^S	0.25	—

(a) Schematic illustration of the two-dimensional geometry and its boundaries

(b) Ionic concentration drop at the boundary of the domain B

Figure 4: Illustration of the geometry (left) and boundary condition of the ionic constituents (right)

as shown in Fig. 3b. The numerical analysis is then performed in a cross sectional area of sample body shown in Fig. 3a with a length in z -direction much larger compared to the dimensions $\ell_x = \ell_y = 100 \mu\text{m}$. The mechanical behavior of the polymer matrix is assumed to be isotropic and hence the YOUNG's modulus E and the POISSON's ratio ν are chosen in order to define the tensor of elasticity ${}^4\vec{E}$. All material properties are summarized in Tbl. 2.

In the present work, the hydrogel free swelling is investigated for a domain $\mathcal{B}$ with a rectangular shaped cross-section and permeable boundaries. For the numerical analysis of the one-dimensional hydrogel swelling behavior, the reader is referred to Refs. 22 and 23. A schematic illustration of the numerical geometry is shown in Fig. 4a. Please note, that the numerical analysis has been performed with 15×15 elements considering the symmetry of the model. To trigger the swelling of the hydrogel, a drop in the ionic concentration $\bar{c}_m^{\gamma,0} \rightarrow \bar{c}_m^{\gamma,1}$ of the mobile charges is prescribed at the boundary of the hydrogel domain, see Fig. 4b. From equilibrium conditions, cf. Ref. 13 and Ref. 24, respective boundary conditions for the primary variables can be derived.

Table 3: Summary of the physical instants of time chosen for the evaluation of the numerical results

	t_0	t_1	t_2	t_3	t_4	t_∞
t (ms)	0	1.3	3.3	6.0	26.7	∞

An evaluation of the results shows, that the swelling process is governed by a water uptake over the boundary of the hydrogel domain. As shown in Fig. 5, the magnitude of the fluid flux is the highest in the middle of the hydrogel boundary and zero at the edges of domain the $\mathcal{B}$. From the time-dependent results, a exponential decay of the fluid flux can be identified. A summary of the instants of time for the evaluation of the results is given in Tbl. 3. Please note, that the fluid flux in Fig. 5 is defined as $\vec{j}^F = \varphi^F \vec{w}^F$. As there is no application of an external pressure, the fluid flux $\vec{j}^F$ is zero in the stationary case at $t = t_0$ and $t = t_\infty$.

Figure 5: Magnitude of the fluid flux $\|\vec{j}^F\|$ for six instants of time on the deformed configuration

Figure 6: Mechanical stress $T_{xy}^{S,mech}$ for six instants of time on the deformed configuration

The fluid flux leads to an initial stretch of the edges of the domain $\mathcal{B}$. This swelling process is then followed by local stretch of the bulk domain. Consequently, the mechanical normal stress is initially the highest at the boundary of the gel domain which propagates towards a homogeneous stress distribution for $t \rightarrow t_\infty$. Due to the distributed water uptake over the domain boundary, a time-dependent shape change of the domain can be observed. As a consequence, mechanical shear stresses in the material occur which are shown in Fig. 6. The time-dependent behavior exploits a shear stress which, due to the symmetry of the loading and geometry, only shows a symmetric shear stress if the absolute value is plotted. In the stationary equilibrium at $t = t_0$ and $t = t_\infty$ the mechanical shear stress T_{xy}^S has vanished due to the homogeneous strain field.

4. CONCLUSION

In the present paper, a coupled chemo-electro-mechanical formulation based on the Theory of Porous Media has been applied to hydrogels. Therefore, a continuum-based model formulation has been pursued, while the thermodynamic consistency has been respected in order to define the constitutive laws.

The field equations have been solved in the framework of the Finite Element Method. Subsequently, the hydrogel free swelling behavior is analysed as a response to a chemical stimulus. The numerical results have been obtained by making use of a nine-node shell element. From the numerical results, the time-dependent behavior of hydrogels has been analyzed. The uptake of water has been shown to vary over the edge of the hydrogel domain. As a consequence, hydrogels exhibit a non-uniform time-dependent swelling behavior which leads to a time-dependent mechanical shear stress.

The formulation based on the Porous Media Theory allows to capture the time-dependent effects in the hydrogel under a chemical stimulus. Concluding, the applied model (i) is capable of describing the chemo-electro-mechanical behavior of gels and (ii) can be applied to enhance the design of hydrogel based structures.

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