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Modeling and simulation of transport phenomena in ionic gels

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ABSTRACT

Ionic hydrogels belong to the class of polyelectrolyte gels or ionic gels. Their ability to swell or shrink under different environmental conditions such as change of pH, ion concentration or temperature make them promising materials, e.g. for microsensoric or microactuatoric devices. The hydrogel swelling exhibits nonlinear effects due to the occurrence of different interacting transport phenomena.

Numerical simulations are an essential part in the ongoing development of microsensors and microactuators. In order to determine transport effects due to diffusion, migration and convection a multiphase mesoscale model based on the Theory of Porous Media is applied. The governing field equations are solved in the transient regime by applying the Finite Element Method.

By means of the derived numerical framework a detailed investigation of the different transport phenomena is carried out. Numerical experiments are performed to characterize the dominating transfer phenomena for ionic gels under chemical stimulation.

Keywords: Ionic Gel, Hydrogel Swelling, Finite Element Method, Numerical Simulation, Porous Media

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 liquid phase which is an electrolyte, i.e. an aqueous solution with mobile ions. The structure of a hydrogel is shown in Fig. 1. Hydrogels are immersed in a solution bath and show a response

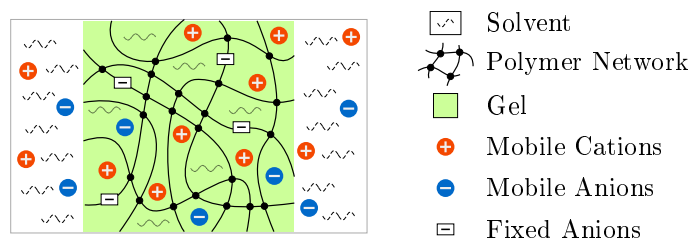


Figure 1: Composition and structure of a hydrogel in a solution bath

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 behavior can be observed.

Its chemo-electro-mechanical properties make hydrogels a promising material for new applications such as sensor systems, e.g. developed by Gerlach et al.,¹ or micro-fluidic processors as presented by Richter et al.² Numerical analysis plays an important role in further development of these approaches. To make hydrogels accessible to numerical investigations a continuum based model is developed and presented in the present study.

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2. LITERATURE REVIEW

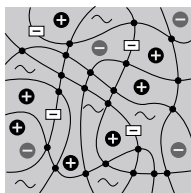
There exist different modeling approaches to describe the swelling behavior of gels. A first fundamental approach was given by Flory and Rehner³ in the 1950s. It is based on a thermodynamic formulation with statistically identified material parameters. Based on the equation of motion, Tanaka and Filmore⁴ described the swelling kinetics. This theoretical framework is adopted and extended in several continuum based models. Recent work can be found in literature, e.g. in Refs.^{5,6} the transient swelling behavior under a chemical stimulus is investigated.

For a more precise understanding of the swelling behavior of polyelectrolyte gels models incorporating the material properties on the micro-scale are developed. In Gurtin et al.⁷ the volume phase transition is assumed to be triggered by the motion of evolving interfaces of the incorporated constituents. A formulation to consider the interaction of an electroactive polymer in a solution bath is based on accounting for several superimposing fields. For considering chemical and electrical fields research work has been done by Doi et al.,⁸ incorporating chemical, electrical and mechanical fields recent work can be found e.g. in Wallmersperger and Ballhause⁹ and Attaran et al.¹⁰

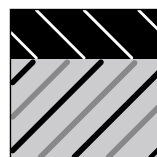
By treating the constituents of electroactive polymers separately, their interactions can be considered based on their properties. Based on the Theory of Mixtures which was first described by Bowen¹¹ and the concept of volume fractions, the Theory of Porous Media can be derived. Essential enhancements have been done by Bowen,¹² by Mow et al.¹³ in which theoretical and experimental results can be found, and by de Boer.¹⁴ For ionic gels, a modeling approach was presented by Ehlers et al.¹⁵ and by Acartürk.¹⁶ A more general approach for a multiple-component, multiple-phase, polarizable, swelling porous medium with charged particles is given by Bennethum and Cushman.^{17,18} An examination of the electric potential inside charged, soft, hydrated tissues was given by Lai et al.¹⁹

3. NUMERICAL MODEL

The hydrogel swelling is driven by transport phenomena due to convection, diffusion and migration. Hence, interactions of the moving constituents have to be investigated. Observing the hydrogel on the micro-structure level, a solid matrix formed by polymer chains with an interconnected void can be found. The void is filled with a solution consisting of a solvent with mobile charges. For ionic hydrogels, fixed charges are bonded to the polymer chains. A schematic representation of the hydrogel structure is shown in Fig. 2a.



(a) Microscopic structure of the hydrogel with the incorporated constituents



(b) Homogenized structure of the hydrogel on the mesoscale

Figure 2: Hydrogel structure on the micro- and mesoscale

In the present work the hydrogel is considered as a porous medium. The fundamentals of the porous media theory are given in Sec. 3.1. In Sec. 3.2 the governing balance equations are shown followed by the specific constitutive assumptions which are presented in Sec. 3.3. The numerical implementation as well as the application of the respective boundary conditions are discussed in Sec. 3.4.

3.1 Porous media theory

To account for the complex interactions of the moving constituents, assumptions have to be made on the microscale to describe the material behavior with a continuum mechanical approach. To avoid evaluating interfacial effects with respect to the geometry and structure of the moving components, the fluid-structure interaction

within the hydrogel is captured by a somehow homogenization of a representative elementary volume. By applying the theory of mixtures a statistical homogenization is performed by a superposition

$$\Theta = \sum_{\alpha} \Theta^{\alpha} \quad \text{with} \quad \alpha = 1 \dots N \quad (1)$$

of a physical quantity Θ^{α} of the constituent α . The number of the incorporated constituents is denoted by N . To quantify the so obtained mixture as illustrated in Fig. 2b the concept of volume fractions is applied. In the deformed configuration the substantial differential volume of the mixture dv is defined by the sum of the partial volumes of each constituent dv^{α} by

$$dv = \sum_{\alpha} dv^{\alpha} . \quad (2)$$

The local volume fraction φ^{α} can then be found by

$$\varphi^{\alpha} = \frac{dv^{\alpha}}{dv} . \quad (3)$$

As the constituents are treated individually the current configuration is defined by constituents originating from differing positions exhibiting independent motions as can be seen in Fig. 3. Hence

$$x_i = \chi_i^{\alpha}(X_i^{\alpha}, t) \quad (4)$$

holds where χ^{α} is the motion of the constituent α , \mathbf{X}^{α} is the position of the observed constituent in the reference configuration and \mathbf{x} is the position in the current configuration. For the velocity \mathbf{v}^{α} of the constituent α , denoted

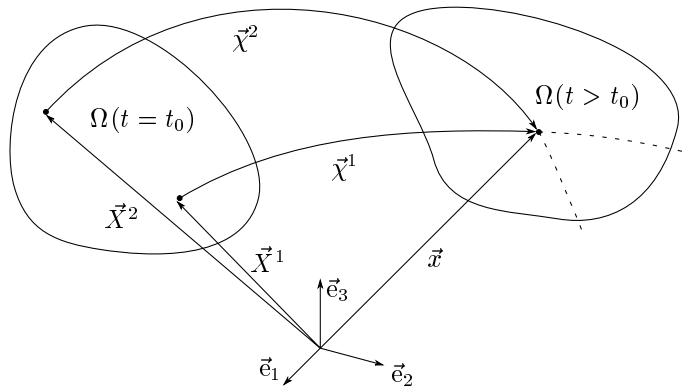


Figure 3: Kinematics of a multiphasic continuum

in Lagrangean form, one can find

$$v_k^{\alpha} = \frac{\partial}{\partial t} \chi_k^{\alpha}(X_k^{\alpha}, t) . \quad (5)$$

An analogous expression applies for the acceleration \mathbf{a}^{α} . Following the consideration of individual motion vector fields the material time derivative of an arbitrary vector field function has to be defined with respect to the velocity of a constituent and is defined as

$$\left(\dot{\Theta}_k \right)^{\alpha} = \frac{\partial}{\partial t} \Theta_k + \Theta_{k,l} v_l^{\alpha} . \quad (6)$$

Based on the fundamentals of the mixture theory and the concept of volume fractions the continuum mechanical approach for describing the hydrogel swelling behavior based on the Theory of Porous Media can be obtained.

3.2 Balance equations

The balance equations are formulated following the principles of classical one-phasic thermo-mechanics of continua. They are extended by production terms to capture the fluid-structure interaction of the multi-phasic material. Summarized, the balance equations are given as follows:

$$\begin{aligned}
 &\text{Conservation of mass} && (\dot{\varrho}^\alpha)^\alpha + \varrho^\alpha v_{k,k}^\alpha = \hat{\varrho}^\alpha && (7a) \\
 &\text{Balance of momentum} && \sigma_{kl,k}^\alpha + \varrho^\alpha (b_l^\alpha - a_l^\alpha) = -\hat{p}_l^\alpha && (7b) \\
 &\text{Balance of angular momentum} && \varepsilon_{klm} \sigma_{lm}^\alpha = \hat{m}_k^\alpha && (7c) \\
 &\text{First law of thermodynamics} && \varrho^\alpha (\dot{u}^\alpha)^\alpha - \sigma_{kl}^\alpha v_{l,k}^\alpha + q_{k,k}^\alpha - \varrho^\alpha r^\alpha = \hat{\varepsilon}^\alpha && (7d) \\
 &\text{Entropy balance equation} && \varrho^\alpha (\dot{\eta}^\alpha)^\alpha - \phi_{k,k}^\alpha - \zeta^\alpha = \hat{\xi}^\alpha && (7e)
 \end{aligned}$$

The density ϱ^α of the constituent is defined by its mass m^α divided by the differential volume of the mixture $\varrho^\alpha = \frac{dm^\alpha}{dv}$. The Cauchy-stress tensor is denoted by σ^α , \mathbf{b}^α is the body force density and ε_{klm} denotes the permutation tensor. The internal energy density is denoted by u^α , the heat flux by \mathbf{q}^α and r^α is the internal heat source. Balancing the entropy density η^α , the entropy flux density ϕ^α and the entropy production density ζ^α the second law of thermodynamics can be obtained. The direct production densities for the mass, momentum, angular momentum, energy and entropy production are denoted by $\hat{\varrho}^\alpha$, \hat{p}^α , \hat{m}^α , $\hat{\varepsilon}^\alpha$ and $\hat{\xi}^\alpha$, respectively.

The mixture theory allows to split the total production densities into a direct and an indirect part. Following the principles for one-phasic continuum mechanics, the sum of the total production densities has to vanish for the whole mixture. Furthermore using the second law of thermodynamics and the entropy balance equation, the Clausius-Duhem inequality can be obtained. From these conditions restrictions for the constitutive behavior can be found. For a detailed derivation the interested reader is referred to Greve²⁰ and Ehlers and Bluhm.¹⁵

Next, the electrical behavior of the charged porous medium is investigated. 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 Eringen and Maugin²¹

$$\varepsilon_0 \varepsilon_r E_{k,k} = \rho_e \quad \text{and} \quad (8a)$$

$$\varepsilon_{klm} E_{m,l} = 0 \quad (8b)$$

where ρ_e denotes the charge density, \mathbf{E} is the electric field, ε_0 and ε_r are the vacuum and relative permittivities. Please note that the constitutive relation for the electric field and the electric displacement field is assumed to be linear and homogeneous for the whole mixture.

3.3 Further assumptions and constitutive model

The homogenized model for the hydrogel consists of a solid phase {S} and a fluid phase {F}. Fixed charges (fc) are assumed to be attached to the solid skeleton and hence follow the motion of the solid skeleton. The fluid phase consists of the liquid constituent {w} and a freely movable ionic phase { γ } with anions {-} and cations {+}. As a summary the following definition can be given:

$$\alpha = \{S, F\} \quad \text{with } F = \{w, \gamma\} \quad \text{and } \gamma = \{+, -\}. \quad (9)$$

The constitutive laws result from assumptions for the material behavior considering the evaluation of the second law of thermodynamics. For the solid skeleton, a linear elastic material behavior is assumed. In Lagrangian notation the stress strain relation for the solid phase is therefore given by

$$\sigma_{kl}^S = C_{klmn} \varepsilon_{mn}^S = \frac{1}{2} C_{klmn} (u_{m,n}^S + u_{n,m}^S) \quad (10)$$

with the assumption of linearized kinematics. The elasticity tensor is denoted by C_{klmn} , the displacement of the solid phase is given by u_k^S and ε_{kl}^S is the linearized elastic strain of the solid phase. The constitutive behavior of the ions can be derived from a formulation for the Helmholtz free energy following Acartürk.¹⁶ It is defined

as a purely chemical potential without considering electro-mechanical influences. Furthermore, the Helmholtz free energy of the ions depend only on the configuration of the observed constituent itself and therefore it is independent of the surrounding constituents:

$$\psi^\gamma = \mu_0^\gamma + \frac{RT}{M^\gamma} \left(\ln \frac{\varrho^\gamma}{\varphi^F} - 1 \right). \quad (11)$$

For the liquid constituent the same Helmholtz free energy applies. As the density of the liquid with respect to the local fluid density undergoes only marginal changes, the Helmholtz free energy of the liquid constituent is assumed to be constant.

Further considerations to obtain the field equations shall be mentioned in the following. Isothermal conditions are assumed and therefore the heat flux \mathbf{q}^α and the heat source r^α vanish. The investigated constituents are assumed to be non-polar and hence $\mathbf{m}^\alpha = 0$ applies. This yields to the symmetry of the stress tensor $\sigma_{kl}^\alpha = \sigma_{lk}^\alpha$. Furthermore, body forces are not taken into account. As the swelling kinetics are diffusion dominated, forces of inertia are neglected. Hence $\mathbf{b}^\alpha = 0$ and $\mathbf{a}^\alpha = 0$ applies. Mass transfer, e.g. as a result of chemical reactions, from one constituent to another is excluded and $\hat{\rho}^\alpha = 0$ in equation (7a) holds for each constituent.

The Clausius-Duhem inequality is evaluated following the scheme of Coleman-Noll. To achieve the coupling of the electrical field with the thermo-mechanical balance equations, the Clausius-Duhem inequality is extended by further restrictions, i.e. the electroneutrality condition and the saturation condition which are defined as

$$\text{Saturation condition} \quad f_{\text{sat}} = \sum_{\alpha} \varphi^\alpha = 1 \quad (12a)$$

$$\text{Electroneutrality condition} \quad f_{\text{en}} = \sum_{\alpha} \rho_e^\alpha = 0. \quad (12b)$$

Please note that for the electroneutrality condition also the fixed charges have to be incorporated. The restrictions (12) in weak form are incorporated following Liu²² with respective Lagrange multipliers. The extended Clausius-Duhem inequality is then given as

$$\hat{\eta} + \lambda_{\text{sat}} \left(\dot{f}_{\text{sat}} \right)^S + \lambda_{\text{en}} \left(\dot{f}_{\text{en}} \right)^S \geq 0 \quad (13)$$

with the Lagrangian multipliers λ_{sat} and λ_{en} .

By an evaluation of Eq. (13) the Lagrange multipliers as well as constitutive restrictions can be obtained. For λ_{sat} one can identify this factor as the effective hydraulic pressure π_{hyd} acting on the overall mixture. It is found as

$$\lambda_{\text{sat}} = \pi_{\text{hyd}} = \frac{(\varrho^F)^2}{\varphi^F} \sum_{\gamma} \frac{\partial \psi^\gamma}{\partial \varrho^\gamma}. \quad (14)$$

The Lagrangian multiplier λ_{en} is interpreted as the electrostatic force acting on an electric charge and hence

$$\lambda_{\text{en}} = \Psi \quad \text{with} \quad \Psi_{,k} = -E_k \quad (15)$$

applies. A quantity π_{osm} – which is defined as the osmotic pressure – is obtained by

$$\pi_{\text{osm}} = \sum_{\gamma} \pi_{\text{osm}}^\gamma = \frac{1}{\varphi^F} \sum_{\gamma} (\varrho^\gamma)^2 \frac{\partial \psi^\gamma}{\partial \varrho^\gamma}. \quad (16)$$

The coupling of the interfering constituents is achieved with respective production densities, i.e. in the case of isothermal hydrogel swelling in terms of moment production densities. By evaluating restrictions occurring from Eq. (13) the interaction of the fluidic constituents with the solid phase is then defined as the contribution of four quantities

$$\hat{p}_k^F = -\hat{p}_k^S = \underbrace{\varphi_{,k}^F \pi_{\text{hyd}}}_{\text{Hydraulic contribution}} + \underbrace{\varphi_{,k}^F \pi_{\text{osm}}}_{\text{Osmotic contribution}} + \underbrace{\Psi \sum_{\gamma} \rho_{e,k}^\gamma}_{\text{Electrostatic contribution}} - \underbrace{(\varphi^F)^2 \frac{k^F}{\gamma^F} (v_k^F - v_k^S)}_{\text{Mechanical contribution}} \quad (17)$$

where in the last term the Darcy's law for porous multiphasic materials is used. The material parameters are denoted by k^F for the hydraulic conductivity and γ^F for the effective fluid weight. A detailed discussion can be found in Refs.²³⁻²⁵

3.4 Boundary conditions and primary variables

For a general porous medium the primary variables \mathcal{X} are given by Ehlers and Bluhm.¹⁵ With respect to the constitutive assumptions and following the concept of Acartürk¹⁶ they are defined as

$$\mathcal{X} = \{u_k, p, c^\gamma, \Psi\} \quad (18)$$

where u_k is the displacement of the solid phase, p is the sum of the hydraulic pressure π_{hyd} and the osmotic pressure of the mixture π_{osm} . The concentration of an ionic species c^γ can be derived by

$$c^\gamma = \frac{1}{\varphi^F} \frac{\varrho^\gamma}{M^\gamma} \quad (19)$$

where M^γ is the molar mass of the constituent and ϱ^γ its density.

The final set of field equations can then be defined as

$$\text{Momentum balance of the solid skeleton} \quad 0 = (\sigma_{kl}^S - p\delta_{kl})_{,k} \quad (20a)$$

$$\text{Conservation of mass of the fluid phase} \quad 0 = (\dot{u}_k^S)_{,k} + (\varphi^F (v_k^F - v_k^S))_{,k} \quad (20b)$$

$$\text{Conservation of mass of the ionic species} \quad 0 = \varphi^F (\dot{c}^\gamma)^S + c^\gamma (\dot{u}_k^S)_{,k} + (\varphi^F c^\gamma (v_k^\gamma - v_k^S))_{,k} \quad (20c)$$

$$\text{Poissons equation for electrostatics} \quad 0 = \Psi_{,kk} + \frac{F}{\epsilon_0 \epsilon_r} \varphi^F \left(\sum_\gamma z^\gamma c^\gamma + z^{fc} c^{fc} \right) \quad (20d)$$

$$\text{Darcy's law} \quad \varphi^F (v_k^F - v_k^S) = -\frac{\kappa^F}{\gamma^F} \left(p_{,k} - \sum_\gamma \rho_e^\gamma \Psi_{,k} \right) \quad (20e)$$

$$\text{Modified Nernst-Planck equation} \quad \varphi^F c^\gamma (v_k^\gamma - v_k^S) = c^\gamma \varphi^F (v_k^F - v_k^S) - D^\gamma \left(c_{,k}^\gamma + \frac{F}{RT} z^\gamma c^\gamma \Psi_{,k} \right) \quad (20f)$$

The obtained numerical model is capable of representing the transport phenomena within the gel domain. In this formulation boundary effects are neglected and therefore the transition zone from the gel domain to the surrounding solution cannot be resolved. To formulate appropriate boundary conditions of the charged porous medium, the Donnan equilibrium is claimed and hence the chemical potential $\mu^\gamma = \varphi^F \frac{\partial(\varrho^\gamma \psi^\gamma)}{\partial \varrho^\gamma}$

$$\mu^{\text{sol}} = \mu^{\text{gel}} \quad (21)$$

in gel and solution has to be identical. The electroneutrality condition

$$\rho_e^{\text{gel}} = \rho_e^{\text{sol}} = 0 \quad (22)$$

has to be fulfilled in both, the gel and the solution domain. The sum of the electric charge of the mobile ions in the gel depends on the charge density of the ionic species fixed to the solid matrix. Therefore the boundary conditions are strain-dependent which is typical for problems considering the interaction of a fluid with an elastic structure.

The numerical implementation of the derived field equations is performed in the framework of the Finite Element Method. For the time discretization the implicit Euler method is used. The spatial discretization is performed in one dimension with linear shape functions for the primary variables except for the solid displacement where quadratic shape functions are used. With the Newton method the transient solution can be obtained by solving an algebraic system of coupled linear equations.

4. NUMERICAL ANALYSES

In the present research the swelling behavior of ionic gels under a chemical stimulus is investigated. A schematic representation of the hydrogel swelling behavior is shown in Fig. 4. For this, the gel is initially assumed to be in an equilibrium state. It can be derived from the Donnan potential that ionic gels always have a concentration difference to the ambient solution. The resulting osmotic pressure leads to an initial pre-stress or pre-stretch of the material. Hence, the equilibrium state is defined as a pre-stretched configuration by subtracting the initial osmotic pressure from the elastic mechanical stress tensor σ_{kl}^S .

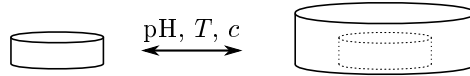


Figure 4: Schematic representation of the hydrogel swelling behavior under

The simulations are all performed on the same geometry with a hydrogel length of 1 mm.

The mechanical behavior of the polymer matrix is assumed to be isotropic and hence the Young's modulus E^S and the Poisson ratio ν^S are defined for the solid skeleton. All material properties are given in Tab. 1. As the numerical model is one-dimensional for all vectorial quantities the subscripts are no longer used.

Table 1: List of material properties

Description	Variable	Value
hydraulic conductivity	k^F	$0.1 \cdot 10^{-9} \text{ m/s}$
effective fluid weight	γ^F	$10 \cdot 10^3 \text{ N/m}^3$
relative permeability	ε_r	80
Young's modulus	E^S	$300 \cdot 10^3 \text{ Pa}$
Poisson ratio	ν^S	0.5
anionic valence	z^-	-1
cationic valence	z^+	+1
valence of the fixed charge	z^{fc}	-1
initial concentration of the fixed charges	c_0^{fc}	300 mol/m^3
initial volume fraction of the solid skeleton	φ_0^S	0.1

In the following, first only the field equations for the chemical and electrical field are numerically investigated (Sec. 4.1), i.e. the hydrogel is considered rigid. In Sec. 4.2, the fully coupled chemo-electro-mechanical simulation is performed, i.e. the hydrogel is treated elastically.

4.1 Chemo-electrical simulation

Starting from an equilibrium state the hydrogel is chemically stimulated. At $t = 0$ the concentration in the solution is reduced from $c_{\text{sol}}^+ = c_{\text{sol}}^- = 1000 \text{ mol/m}^3$ to $c_{\text{sol}}^+ = c_{\text{sol}}^- = 800 \text{ mol/m}^3$. The equilibrium states at $t < 0$ and the converged result are shown schematically in Fig. 5. The field equations are solved for the gel domain for

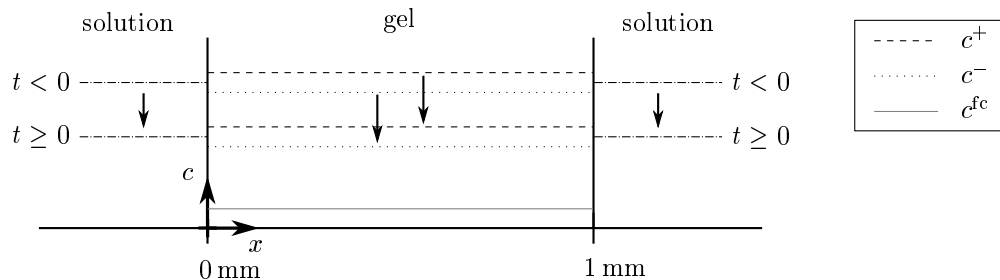


Figure 5: Schematic representation of the equilibrium states of the one-dimensional model

both, the chemical and electrical field, with the simplification of a rigid solid skeleton. The obtained results can be used to analyze the ion transport due to diffusion and migration, e.g. through thin membranes or in biological tissues. To demonstrate the influence of varying diffusion constants two different test cases are investigated. In test case 1 the ionic constituents have an equal diffusion constant of $D^+ = D^- = 0.5 \cdot 10^{-3} \text{ mm}^2/\text{s}$. In test case 2 the ionic constituents have an equal diffusion constant of $D^+ = D^- = 0.8 \cdot 10^{-3} \text{ mm}^2/\text{s}$. A summary of the additional material parameters of the test cases is shown in Tab. 2. All simulations start from the same

Table 2: Varying diffusion constants for test case 1 and test case 2

case name	D^+	D^-
test case 1	$0.5 \cdot 10^{-3} \text{ mm}^2/\text{s}$	$0.5 \cdot 10^{-3} \text{ mm}^2/\text{s}$
test case 2	$0.8 \cdot 10^{-3} \text{ mm}^2/\text{s}$	$0.8 \cdot 10^{-3} \text{ mm}^2/\text{s}$

equilibrium conditions ($t < 0$) which are summarized in Tab. 3. The boundary conditions are formulated with

Table 3: Equilibrium conditions of the chemo-electrical simulation for $t < 0$

domain	field variable	value
gel	c_{gel}^+	$1161.2 \text{ mol}/\text{m}^3$
	c_{gel}^-	$861.2 \text{ mol}/\text{m}^3$
	p_{gel}	$55.4 \cdot 10^3 \text{ Pa}$
	Ψ_{gel}	$-3.838 \cdot 10^{-3} \text{ V}$
solution	c_{sol}^+	$1000 \text{ mol}/\text{m}^3$
	c_{sol}^-	$1000 \text{ mol}/\text{m}^3$
	p_{sol}	0 Pa
	Ψ_{sol}	0 V

respect to a concentration drop in the surrounding solution. With the equilibrium conditions from Eqs. (21) and (22) the respective boundary conditions can be calculated for both gel boundaries, c.f. Tbl. 4. The symmetrical

Table 4: Initial boundary conditions of the chemo-electrical simulation for $t = 0$

domain	field variable	value
gel	c_{gel}^+	$963.9 \text{ mol}/\text{m}^3$
	c_{gel}^-	$663.9 \text{ mol}/\text{m}^3$
	p_{gel}	$69.1 \cdot 10^3 \text{ Pa}$
	Ψ_{gel}	$-4.787 \cdot 10^{-3} \text{ V}$
solution	c_{sol}^+	$800 \text{ mol}/\text{m}^3$
	c_{sol}^-	$800 \text{ mol}/\text{m}^3$
	p_{sol}	0 Pa
	Ψ_{sol}	0 V

problem is solved in space and time. The ion concentrations tend towards the new equilibrium state. The results for the cationic concentration in space and time as well as the cationic flux over the boundary of the gel domain versus time are presented in Fig. 6. One can clearly see that with an increasing diffusion coefficient the equilibrium state is reached faster. This result can be expected as the hydrogel swelling behavior is diffusion driven.

A further proof for the diffusion driven transport is the exponential decay of the ionic flux through the boundary surface of the gel domain. Please note that the migrative part of the ionic flux leads to a decrease of the total ionic flux in order to maintain the electroneutrality condition. To investigate frictional effects the fully coupled field equations have to be considered as presented in the Sec. 4.2.

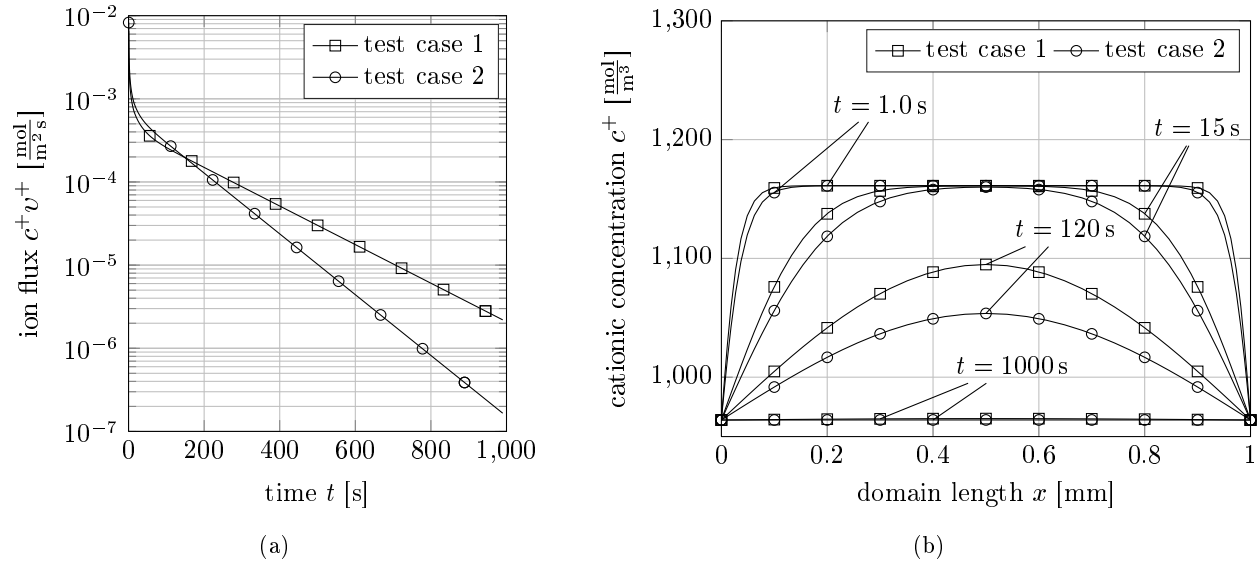


Figure 6: Chemo-electrical simulation: (a) Cationic flux at the boundary of the gel domain versus time, the velocity of the cations is denoted by v^+ ; (b) Cationic concentration in the gel domain for selected instants in time

4.2 Chemo-electro-mechanical simulation

Starting from the same equilibrium state as described in Sec. 4.1 the unconstrained hydrogel swelling behavior is investigated. The fully coupled field equations are solved without introducing any further simplifications. Considering a statically determinate system the hydrogel is geometrically constrained at the outer left node. As presented in Sec. 4.1 a chemical stimulation of the hydrogel is performed. The material will swell which leads to converging concentrations of the mobile ions. This process is followed by a decrease of the osmotic pressure in the gel compared to the inelastic case. The steady state elongation can be calculated from the equilibrium of the osmotic pressure with the mechanical stress in the material. The simulation is carried out for test case 1

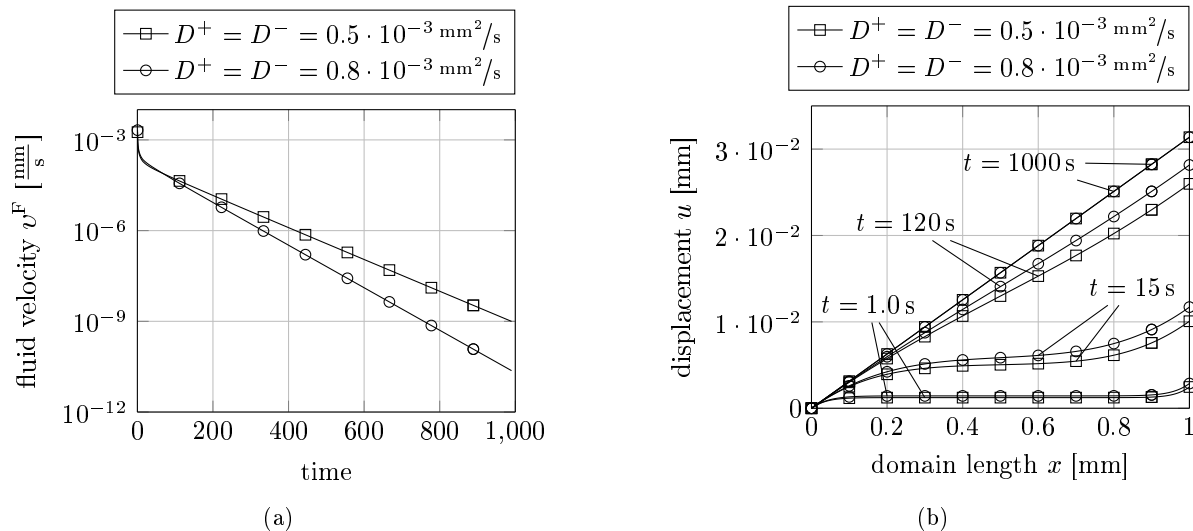


Figure 7: Fully coupled simulation for a hydrogel under a chemical stimulus: (a) fluid velocity over the boundary of the gel; (b) displacement field for the free hydrogel swelling

and test case 2 as presented in Sec. 4.1. Due to the diffusion driven swelling behavior the equilibrium swelling is reached faster for increasing diffusion constants. A comparison of the displacement field within the gel domain

is shown for four instants of time, c.f. Fig. 7b. Furthermore the fluid velocity over the boundary of the hydrogel is shown for both test cases in Fig. 7a. Due to the diffusion driven swelling behavior one can see that for larger diffusion constants the fluid velocity decreases faster in time.

4.3 Comparison

In Fig. 8, a comparison of the cationic flux over the boundary for both, the chemo-electrical and the chemo-electro-mechanical simulation is given. One can clearly see that the cationic flux is influenced by the transient swelling behavior and therefore the interaction of convective, diffusive and migrative transport phenomena are resolved. Consequently the results obtained by the elastic (c.f. Sec. 4.2) and rigid case (c.f. Sec. 4.1) converge for the equilibrium swelling.

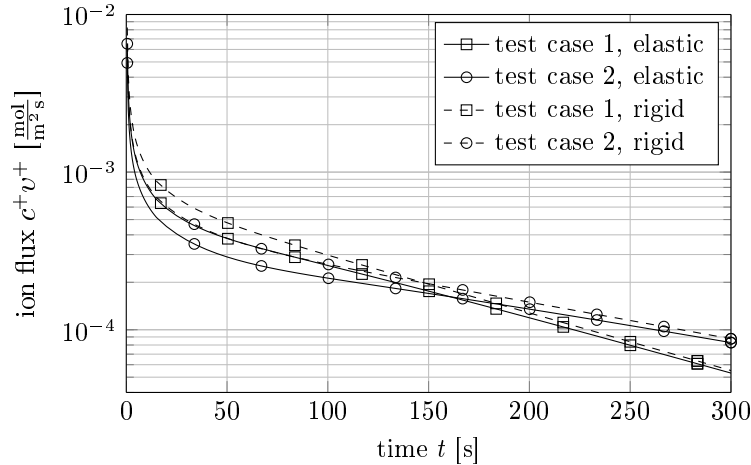


Figure 8: Comparison of the cationic flux over the boundary of the gel domain for the assumption of a rigid solid skeleton and the solution considering the fully coupled chemo-electro-mechanic material behavior

Looking at the plot for the electric potential versus the gel domain in Fig. 9, in steady-state one can depict a difference between the results of the elastic and inelastic simulation. It is shown that due to the elongation of the gel in the elastic test case the concentrations and the osmotic pressure are reduced leading to a smaller electric potential difference between gel and solution domain.

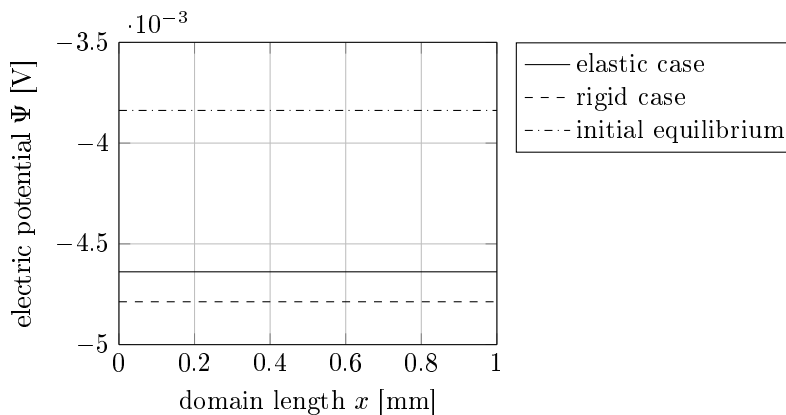


Figure 9: Comparison of the steady-state electric potential for the inelastic and elastic simulation

5. CONCLUSION

In the present paper a coupled chemo-electro-mechanical formulation based on porous media has been applied to electroactive polymers. For different one-dimensional test cases, the response of polyelectrolyte gels to a chemical stimulus has been investigated for both, a rigid and an elastic polymer matrix. It has been shown that on the one hand the chemo-electric behavior has a fundamental influence on the mechanical behavior (swelling) of these gels. On the other hand, the mechanical deformation also influences both, the concentration of the mobile ions and the different fluxes.

By the formulation based on the porous media theory the transient effects in the hydrogel under a chemical stimulus can be captured. 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 microsensoric and microactuatoric devices containing polyelectrolyte gels.

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