Computational modelling and investigation of mechanical and electrochemical response of photo-sensitive hydrogels

Chen, Xiao

2021

Chen, X. (2021). Computational modelling and investigation of mechanical and electrochemical response of photo-sensitive hydrogels. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/145822>

<https://doi.org/10.32657/10356/145822>

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**COMPUTATIONAL MODELLING AND
INVESTIGATION OF MECHANICAL AND
ELECTROCHEMICAL RESPONSE OF PHOTO-
SENSITIVE HYDROGELS**

CHEN XIAO

**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

2021

**COMPUTATIONAL MODELLING AND
INVESTIGATION OF MECHANICAL AND
ELECTROCHEMICAL RESPONSE OF PHOTO-
SENSITIVE HYDROGELS**

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A thesis submitted to the Nanyang Technological University in
partial fulfilment of the requirement for the degree of Doctor of

Philosophy

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Authorship Attribution Statement

This thesis contains material from 1 paper published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 3 is published partially as "X. Chen, H. Li, K.Y. Lam, A multiphysics model of photo-sensitive hydrogels in response to light-thermo-pH-salt coupled stimuli for biomedical applications, *Bioelectrochemistry* (2020) 107584. DOI: 10.1016/j.bioelechem.2020.107584."

The contributions of the co-authors are as follows,

- Prof Lam and Assoc Prof Li provided the initial project direction.
- I prepared the manuscript drafts, and Prof Lam and Assoc Prof Li revised the manuscript.
- I formulated the model with Prof Lam and Assoc Prof Li. I also conducted the model-based simulations using COMSOL MULTIPHYSICS package, and finished the analysis of numerical results with Prof Lam and Assoc Prof Li.

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Acknowledgements

I am sincerely grateful to my main supervisor, Prof Lam Khin Yong, for his guidance, care, support, and suggestions during my PhD study. I specially appreciate the encouragement and help from my co-supervisor, Assoc Prof Li Hua, especially his guidance to my research work in the last four years.

I am also thankful to my Thesis Advisory Committee, Assoc Prof Anutosh Chakraborty and Dr. Cui Fangsen from A*STAR, for their professional and invaluable suggestions.

My appreciation also goes for my close friends, Dr. Liu Qimin, Dr. Goh Kek Boon, Dr. Zhou Xiaoli, Assoc Prof Zhan Zhixin, Assoc Prof Li Biao, Assoc Prof Shen Fei, Assoc Prof Liu Bo, Prof Bai Lichun, Dr. Cheng Kai Xian, Mr. Zhang Xingyu, Mr. Chen Kevin, Mr. Li Weidong, Mr. Lim Chongheng, Dr. Huang Jiazhao Dr. Liu Xiaojiang, Mr. Wang Yifeng, and Dr. Hu Huanlong. I treasure every minute I was together with you guys.

Finally, I give special and sincere thanks to my beloved parents who gave life to me and support me all my life.

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Abstract

In the past years, photo-sensitive hydrogels have been extensively applied in various engineering fields, such as actuators, biosensors and electrolytes, due to their distinctive advantages, including spatial and temporal control with great ease and convenience, and wireless manipulation. However, the elementary mechanism remains unclear, regarding their mechanical and electrochemical response behaviors, especially when subjected to multiple coupled stimuli. This leads to a limitation to the exploration of their further applications. Currently, most published works were experimental-based trial-and-error, and the understanding of response mechanism might be still poor. Therefore, it is worthwhile to develop theoretical models with proper accuracy to account for the primary response mechanism of photo-sensitive hydrogels subjected to the external photo stimulus as well as other coupled stimuli. In this thesis, two academic achievements are obtained regarding the modelling of photo-sensitive hydrogels and they are briefed as follows.

The first academic achievement of the present study is the development of a multi-effect-coupling photo-stimuli (MECp) model to characterize the behavior of photo-sensitive hydrogels in response to light-thermo-pH-salt coupled stimuli. The MECp model consists of several parts: (i) the formulation of chemical

reaction kinetics, (ii) the Poisson-Nernst-Planck equation accounting for the interaction between diffusion and electrostatic fields, and (iii) the nonlinear mechanical equation for the conservation of momentum. In particular, the presented hydrogel is regarded as a reactor, where a ternary reaction system is assumed regarding photochromic groups in terms of local pH. Based on this assumption, the ordinary differential equations are then solved analytically using the Laplace transform for the quantification of each fixed chemical species. Furthermore, the ionic strength is considered in the formulation of the electrochemical potential gradient to characterize the effect of salt on the photo-stimulated response. In this study, the large mechanical deformation is expressed in the form of tensor, and the constitutive relation is derived by means of thermodynamic inequality. The validation of MECp model is performed by comparison with experimental results in the literature. The parameter studies by the MECp model are then conducted to study how photo-sensitive hydrogels respond mechanically and electrochemically to several external stimuli, including light intensity, temperature, and surrounding pH.

The second academic achievement is the modification of MECp model to characterize the metal-ion-complexation response of photo-sensitive hydrogels. In order to simplify the chemical reaction system, it is assumed that the rates of non-metal-complexation reactions remain constant, and thus the analytical

method could be employed for the analysis of coupled chemical reactions. It is confirmed by the experimental observation that the theoretical model could predict the response of photo-sensitive hydrogels subjected to metal ions. Through numerical investigation, it is then demonstrated that the metal-ion-complexation response could be tuned by multiple factors, including fixed acid groups, light intensity, buffer pH, temperature, buffer salt concentration, and polymeric material.

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Chapter 1 Introduction

This chapter presents the research background, motivation and objectives, and the outlines of the whole thesis.

1.1 Background

1.1.1 Environmentally sensitive polymers

Polymeric system is a three-dimensional (3D) structure, comprising crosslinked polymeric chains, which is achieved by means of chemical bond and/or physical interaction. The chemical bond is usually covalent while physical interaction includes hydrogen bonding, van der Waals interaction, and physical entanglement. Dynamic bonds are a special group of the above two bonds, undergoing reversible breaking and reformation [1]. In other words, dynamic bonds break up or recombine when they are subjected to a specified external stimulus. The molecular architectures of polymeric chains then change with these dynamic bonds, resulting in the macroscopic response of 3D polymeric network, by which environmentally sensitive polymers respond to external stimuli. The response behavior is usually exhibited in the form of abrupt variations in physicochemical properties of polymer [2], such as size [3-9], color [10], hydration state [11, 12], and acidity [11, 13]. In particular, researchers are very

interested in the stimulus-induced variations in mechanical and electrochemical properties of polymers, due to their great potential in applications, including but not limited to, biosensors [14-18], microfluidic devices [19-21], biomimetic actuators [22-25], on-off switches [26, 27] and soft robotics [28, 29].

For environmentally sensitive polymers with and without solution, their physiochemical properties are usually different. The polymeric network under a dry state is generally called elastomer or rubber. When immersed in a solution, the three-dimensional (3D) network swells due to the absorption of solution molecules and this swollen mixture is known as hydrogel. Therefore, a hydrogel is also defined as a polymer-solvent mixture that is able to expand and retain a high water content inside but would not dissolve in water [30]. Basically, a hydrogel is actually a binary or multi-component system, comprising a 3D polymeric network and solution molecules that fill the space between macromolecules [30]. A unique advantage of hydrogels is that they usually enjoy much larger mechanical deformation than their equivalent elastomers, which is of vital importance to the design of actuators. The volume swelling ratio (VSR) is often used to quantify the deformation of hydrogel, defined as the ratio of swollen volume to dry volume of polymer matrix. For a hydrogel, the VSR usually ranges from tens to hundreds, indicating that the mass fraction of solution is much higher than that of polymer. The reason is because lots of hydrophilic

molecular groups are bound to the polymeric network, which enables the hydrogel to absorb water molecules. Despite this, the polymeric network cannot dissolve in the solution like solutes, due to hydrophobic crosslinks between polymeric chains. Apart from the polymer itself, the surrounding solution also has a significant effect on VSR through its inherent properties, such as temperature and ionic strength [31]. The external stimulus then triggers the deformation of hydrogel by imposing an effect on polymer or surrounding solution. Based on this mechanism, stimuli-sensitive hydrogels are prepared, which could be sensitive to a wide range of stimuli, such as pH [32-35], temperature [36-41], chemical species [42-48], magnetic field [49-53], electric field [54-56] and light irradiation [57, 58].

1.1.2 Photo-sensitive hydrogels

Generally, electric-, magnetic- and light-controls are three main strategies to achieve remote-control for environmentally sensitive hydrogel system. However, the electric-sensitive polymer system needs to use electric wires to connect specimen with controlling device. Consequently, the effective control distance is limited to the length of electric wire, and worse still, the movement of specimen may be disturbed by the fixed interface with wire. Regarding the magnetic stimulus, it is difficult to modulate the magnetic field intensity accurately, despite

accessible wireless contact. Therefore, precise control over the polymer specimen is hard to achieve with magnetic field. Compared with the above remote-control methods, the light-driving strategy enables wireless activation, spatial, and temporal controls to be accessible, especially the localized manipulation that takes place of the whole-field driven. Various parameters are also exquisitely controlled in the light-mediated system, such as intensity, direction, wavelength and polarization of the incident light [59]. Therefore, the light-driving method emerges as a very promising manner for stimuli-responsive polymer system.

1.2 Motivation and objectives

Currently, photo-sensitive hydrogels are extensively used as actuators [59], fuel cells [60-62], sensors [63-66], micro-valves [67, 68], self-healing [69, 70] and drug release [71]. On the other hand, there is also a great potential application in some cutting-edge areas, such as 3D manufacture [72], photovoltaics [60, 61, 73], and wearable electronics [74-76]. These applications depend largely on the mechanical and electrochemical response of photo-sensitive hydrogels.

Nevertheless, the understanding of photo-sensitive hydrogels is quite preliminary, and most investigations are based on experimental trial-and-error, leading to a strong dependence on time-consuming efforts and restriction on the further development of smart system based on photo-sensitive polymers. The reason may

be because multiple factors like polymeric structure and surrounding solution affect the response behavior of photo-sensitive hydrogel system concurrently, which is difficult for researchers to conduct the variable-controlling approach during the experiment. As a result, it is usually not easy for experimental method to gain insight into the response mechanism since some factors may not be completely considered or controlled in the experiment.

As an alternative option, the theoretical model is an ideal technique to reveal the elementary mechanism in a mathematical fashion, which is usually cost-effective compared with experimental methods. Furthermore, the theoretical model is even able to predict some phenomena that have never been discovered, and thus, can be used to guide the experimental design, especially when subjected to a complex system like photo-sensitive hydrogel where multiple interactive processes occur at the same time. Therefore, it is necessary to develop proper theoretical models to investigate the response mechanism of a photo-sensitive polymeric system.

Therefore, the present research work aims to develop theoretical models to unveil elementary mechanism of photo-sensitive polymeric systems, subjected to multiple coupled chemical and physical fields. The specific objectives are elaborated as follows.

- Development of a multi-effect coupling photo-stimulated (MECp) model for simulation of multi-stimuli responsive behaviors of a photo-sensitive

hydrogel system, where concurrent chemical reactions, ionic diffusion, electrostatic effect, and large mechanical deformation are coupled with each other. In this model, the isomerization among photochromic groups and protonation equilibria of immobilized species are considered and formulated as functions of irradiation intensity, pH, and volumetric swelling ratio. Then analytical approach is employed to solve the kinetic of coupled reaction system, by which the distributive concentration is obtained for fixed groups. After that, Poisson-Nernst-Planck (PNP) equations are employed to characterize the transport of mobile ionic species, by which the distributive concentration of each chemical species is determined. The temperature is also considered in the theoretical model, where the temperature is integrated into the expression of the Flory-Huggins interaction parameter and reaction rate. The free energy of hydrogel system is then formulated based on all the above. Based on these efforts, the constitutive relation of large mechanical deformation is derived through laws of thermodynamics, by which the interactive relationship is built among chemical reactions, transport of mobile species, electric field, and mechanical equilibrium.

- Modification of MECp model to characterize the metal-ion-complexation behavior of photo-sensitive hydrogels. The multiple coupled chemical reactions are simplified first, including the complexation between ring-

opened isomers and metal ions, the isomerization of photochromic groups, and the protonation equilibrium among fixed species. The simplified chemical reaction system is then coupled with the governing equations characterizing mass transport, electrostatic field, and mechanical equilibrium. After that, numerical simulations are carried out to investigate the adsorption and selectivity of photo-sensitive hydrogels, subjected to metal ions in saline solution.

1.3 Outline

This thesis includes 5 chapters, as detailed below

Chapter 1 introduces the backgrounds of environmentally sensitive polymers, especially the photo-sensitive hydrogels, followed up by the motivation and objectives of the thesis.

Chapter 2 presents a literature review on both experimental and modelling works on photo-sensitive polymers that have been done before.

Chapter 3 develops the MECp model, including the formulation of governing equations, solution procedures, model validation, and numerical analysis.

Chapter 4 modifies the MECp model to capture the metal-ion-complexation behavior of photo-sensitive hydrogels.

Chapter 5 draws the conclusion on the whole thesis.

Chapter 2 Literature review

Photo-sensitive polymers are referred to those polymeric materials that could change their physicochemical properties or degrade if exposed to photo stimulus [77]. They are usually prepared by incorporating photo-sensitive groups (PSGs) into the polymeric matrix. The light irradiation activates the physical and/or chemical changes of these functional groups, such as plasmon resonance, photocleavage, photodimerization, and photoisomerization, leading to the macroscopic changes of the whole polymeric system. However, the photo-driving mechanism varies with different types of photochromic groups and polymeric matrices. Taking this into consideration, the categorization of photo-sensitive polymers is illustrated in **Figure 2.1**.

Figure 2.1. Classification of photo-sensitive polymers.

In the following sections, a literature review on photo-sensitive polymers is carried out.

2.1 Experimental investigations

2.1.1 *Photo-sensitive elastomers*

Photo-sensitive elastomers could exhibit photo-triggered macroscopic response in a solution-free environment, especially the photo-actuation. Most of them might be liquid crystal elastomers (LCEs), prepared by synthesizing crosslinked polymers with liquid crystalline molecules [78-82]. For photo-sensitive LCEs, the molecular structure was made up of stiff, ordered and rod-like photo-isomerizable functional components that are embedded in the elastomeric network [83]. These functional components underwent a reversible structural change at a molecular level upon light with a specified wavelength, resulting in the macroscopic shape-memory deformation of polymeric network. Several common molecular structures of photo-sensitive LCEs are elaborated in the following part.

Figure 2.2 illustrates a photo-sensitive LCEs developed by Lendlein [84] and Jiang [85]. At the molecular level, two photo-sensitive groups dimerized and then chemically bond together, when subjected to an irradiation with a wavelength larger than 260 nm, by which two neighbored polymeric chains were covalently crosslinked with each other. Meanwhile, this additional crosslinking broke up when the wavelength was shorter than 260 nm. Therefore, the light irradiations

with different wavelengths could be used to manipulate the photo-induced macroscopic deformation of LCEs.

Figure 2.2. Scheme of bonding and cleavage of photochromic groups [84].

Scott *et al.* developed a photo-mechanical polymer that is able to relax the stress at particular wavelengths [83, 86-88]. Within this polymeric matrix, quantities of free radical fragments were accumulated due to photo-cleavage of residual photo-initiator. As shown in **Figure 2.3**, the radical components diffused through fragmentation of the polymeric backbone, and then induced rearrangement of the polymeric structure. Though this rearrangement could not affect chemical properties and modulus of polymer, polymeric network structure was altered permanently, which had a significant effect on the photo-induced plasticity, actuation and residual stress.

Figure 2.3. Reaction mechanism for chain transfer within the polymeric backbone [83].

As one of the most common PSGs, azobenzene was extensively used for preparation of photo-sensitive LCEs [89-94]. As illustrated in **Figure 2.4**, the azobenzene molecule isomerized from *trans* to *cis* forms upon UV illumination and back to the original form through visual light or heat. The rearrangement of polymeric molecular structure was then caused by this isomerization, resulting in the macroscopic structural change of LCEs.

Figure 2.4. Trans-cis photoisomerization of azobenzene groups [95].

Apart from LCEs, the polymeric composite could also be a common fashion to fabricate photo-sensitive elastomers. For instance, Mu et al. developed a light-activated polymer laminated composite by bonding an NOA65 elastomer sheet between two light-activated polymer layers [96].

So far, the photo-sensitive LCEs have been mostly employed for photo-actuation especially the photo-modulated bending and shape-memory deformation [97-107]. These applications mainly depended on the photo-stimulated deformation of the elastomers, where photochemical reactions were usually involved. However, for most LCEs, a large volumetric swelling ratio was generally not available during the light-activated deformation, compared with the equivalent hydrogels with a large water content.

2.1.2 Photo-thermally sensitive hydrogels

Different from elastomers, photo-sensitive hydrogels were prepared by mixing with proper solvent and incorporating photochromic groups into hydrophilic polymeric chains. Several examples of common polymeric backbone materials include N-isopropylacrylamide (PNIPAAm), N-dimethylacrylamide (PDMAAm) [108-110], polyacrylamide (PAM) [111-114], and poly(sulfobetaine methacrylate) (PSBMA) [115-117]. In particular, the PNIPAAm hydrogel has been a well-known thermo-sensitive polymer that would undergo a lower critical solution temperature (LCST) phase transition from hydrophilic to hydrophobic states reversibly. Therefore, the PNIPAAm-based photo-sensitive hydrogels could be sensitive to the temperature as well. Since their LCST approaches the physiological temperature, PNIPAAm hydrogels gained much more popularity

among researchers than other hydrogels especially for the biomedical applications [118-120]. Photo-thermally sensitive hydrogels were usually prepared by combining thermo-sensitive hydrogels with PSGs that can convert light to heat, by which the photo-induced temperature rise generates the response of thermo-sensitive polymeric network.

Figure 2.5. Schematic illustration of (a) surface plasmon resonance of gold nanoparticles and (b) photo-thermal sensitive hydrogels [58].

Hauser et al. developed a photo-thermally sensitive hydrogel by taking advantage

of the surface plasmon resonance absorption of gold nanoparticles [58, 121, 122]. As shown in **Figure 2.5**, gold nanoparticles were trapped in the polymeric network and then the collective plasmon resonance absorption could be induced by the light irradiation. As such, the temperature was greatly raised by the light-generated heat deposition, resulting in the LCST volume phase transition of hydrogel. It was demonstrated by the experimental observation that the response time of photothermal deswelling was limited by the poroelastic mass transport and the shape reconfiguration could be achieved on timescales of several seconds [58].

Apart from metal nanoparticles, chlorophyllin-modified groups were also used in the preparation of photo-thermally sensitive hydrogels for the light-to-heat conversion [123-126]. Suzuki *et al.* developed a photo-thermally sensitive hydrogel by incorporating chlorophyllin moieties into the polymeric network of PNIPAAm [126]. In the experiment, the photo-induced swelling ratio could reach up to 10 times that before the irradiation for a gel disc with 1.73 mm diameter and 0.5~1 mm thickness, with a response time of only tens of seconds. At the same time, the irradiation greatly influenced the concentrations of chromophores, resulting in the discontinuous change in the transmittance ratio of the gel.

With the emerging application of two-dimensional materials, some photo-thermally sensitive hydrogels were developed based on graphene-hydrogel

composites [127-132]. For this type of gels, the graphene oxide (GO) were doped into the surface sheet of thermo-sensitive gels. The light irradiation was absorbed by these GOs and then converted to the heat deposition, leading to the temperature rise. By this way, the patterns could be fabricated on the surface of Go-based hydrogels through the light-activated deformation [127].

However, a significant drawback of photo-thermally sensitive hydrogels might be that the response was stimulated by the light-induced temperature rise, which was not reversible via light.

2.1.3 Photo-chemically sensitive hydrogels

Photo-chemically sensitive hydrogels were referred to as those photo-sensitive hydrogels, of which the response behavior was activated by photochemical reactions. Furthermore, the photo-triggered reactions vary with different types of doped photochromic groups and thus the response mechanism might be more complex than photo-thermally sensitive hydrogels.

Apart from photo-sensitive LCEs, azobenzene has also been widely used for the preparation of photo-sensitive hydrogels, but the response behavior of azobenzene-based hydrogel was usually gel-sol phase transition [92, 133-136] instead of deformation. As a result, azobenzene-based LCEs are generally used as actuators while the equivalent hydrogels were employed for drug release.

Tatsuma *et al.* developed a new class of photoredox-based hydrogels, where the photo-responsive behavior is driven through the reversible redox reaction of TiO_2 nanoparticles [137, 138]. As shown in **Figure 2.6**, two adjacent polymeric chains could be crosslinked with each through the complexation between fixed anionic chromophores and silver ions. Under the UV irradiation, this complexation broke down and the bound metal ions were released, while upon the visible illumination, the metal ions were complexed with the fixed chemical species again. As such, different light wavelengths could be used to achieve the reversible change in the crosslink density and osmotic pressure, which greatly influenced the mechanical strength of the gel. By this way, Kevin *et al.* fabricated an artificial molecular muscle using TiO_2 -based hydrogel [139]. Nevertheless, the further application of this hydrogel was limited to such a slow response that it might take several hours for the gel sample to reach an equilibrium swollen or shrinking state, which could not meet the requirement of a fast-response system.

Figure 2.6. Molecular illustration of photo-generated volumetric changes of Ag-PAA-TiO₂ gel [138].

Mamada *et al.* studied the photo-induced phase transition of PNIPAAm hydrogel incorporated with triphenyl-methane leuco (TML) derivatives [140]. As illustrated in **Figure 2.7**, anionic groups were dissociated from TML during the photochemical reaction, during which the fixed photochromic groups transformed from the nonionic to cationic form. Therefore, the electrostatic environment changed within the hydrogel as well as the ionic concentration, resulting in both mechanical and electrical properties of gels. For example, the swelling ratio of the gel was raised from 1 to around 9 after irradiation at 31 °C. However, a limitation lied in the fact that TML-based hydrogel was only sensitive to UV light, and thus a reversible volume change was not available via light with different wavelengths.

Figure 2.7. Photo-induced ionic dissociation of triphenyl-methane leuco derivatives [140].

Another important type of PSGs is spiropyran that isomerized reversibly among four different isomer states, as shown in **Figure 2.8**. The ring-closed isomer (Sp) was non-polarized and hydrophobic, while the ring-opened isomer (Mc) was highly hydrophilic when protonated as McH^+ that accounts for the largest proportion of spiropyran species within acidic solution in the dark. The reversible isomerization was driven by the irradiation with different wavelengths. In fact, McH^+ could transform into Sp quite soon together with the release of protons, once exposed to visible light. On the other hand, the counter reaction (from Sp to McH^+/Mc) resulted in an increased pH of surrounding solution under UV light. Apart from light irradiation, the ring-opening isomerization could also be achieved through heat [141] and mechanical stress [11]. Besides, pH had a significant effect on the protonation of spiropyran species. Subjected to a highly acid environment, Sp was protonated as SpH^+ , while deprotonation of McH^+ took place in a weak acidic or alkaline condition. In conclusion, spiropyran moieties together with their derivatives became one of the most widely used PSGs for preparation of photo-sensitive hydrogels, due to the reversible conversion under

a great variety of stimuli.

Figure 2.8. Reversible conversion of spiropyran among four isomer states

[142].

Regarding spiropyran-based hydrogel, the most common one was PNIPAAm hydrogel functionalized with spiropyran chromophores (pSPNIPAAm) [141, 143-149]. Though Sp itself was insoluble in water, pSPNIPAAm hydrogel could still absorb solution, due to the conjugated hydrophilic backbone material, PNIPAAm. As shown in **Figure 2.9**, the dehydration of polymeric network was generated during the photo-driven isomerization from MCH^+ to Sp, and subsequently, these changes caused the volume phase transition of gels. This mechanism was also applied to other spiropyran-based hydrogels. Since both dehydration and electrical states change remarkably during the reaction process, the spiropyran-based hydrogels could display both mechanical and electrochemical response behaviors simultaneously. However, most experimental

investigations focused on the mechanical properties of spiropyran-based hydrogels.

Figure 2.9. Deformation mechanism of pSPNIPAAm hydrogel [146].

The re-swelling rate of spiropyran-based hydrogel directly depended upon the spontaneous ring-opening rate of the spiropyrans. To address this issue, Sumaru's group prepared several kinds of spiropyran derivatives with different ring-opening rates [146]. Among those PNIPAAm gels conjugated with these derivatives, the fastest one was reported to get a fully shrinkage in less than 10 min and re-swell back to about 95% of the original volume within 10 min.

It should be noted that the subsequent protonation of Mc also affected the re-swelling behaviors of gels. Therefore, it was a must to expose this type of gel to a strongly acid media in order to generate the McH^+ species, which limited its application in microfluidic devices. To address this issue, Diamond *et al.*

developed the preparation method of spiropyran-co-NIPAM-co-acrylic acid hydrogels in which the spiropyran could be protonated in neutral solution through the dissociation of incorporated acrylic acids [72, 150-152]. They took advantage of the relative acidic coefficient of acrylic acid (AA) and Sp and Mc isomers, and designed an internal source of protons by copolymerizing acrylic acid into the gel matrix, as shown in **Figure 2.10**. Then under the illumination of visible light, the self-protonating gel could even shrink in deionized water, and re-swell to around 90% of volume size only for nearly 20 minutes [152].

Figure 2.10. Photochromism and acidochromism of spiropyran derivatives

[152].

Apart from the light, pSPNIPAAm hydrogels also responded to some other external stimuli, such as mechanical stress [11, 153, 154], pH [108], temperature [141], and heavy metal ions [155]. So far, pSPNIPAAm hydrogels have led to a great variety of applications due to their multi-stimuli responsive behaviors.

Figure 2.11. Scheme of a pSPNIPAAm hydrogel-based photo-driven actuator.

a, b, c and d are the numbers of repeat units in the chain [150].

Francis *et al.* fabricated a photo-driven actuator based on the pSPNIPAAm hydrogel incorporating acrylic acids [150]. As illustrated in **Figure 2.11**, acrylic acids were incorporated into the pSpNIPAAm hydrogels for the preparation of a bipedal hydrogel walker, and thus an internal acid microenvironment was generated. By this way the photoisomerization from McH⁺ to Sp was able to occur in a neutral aqueous solution isomerization. The gel bar was placed onto a ratcheted surface, such that the walking movement could be driven due to the reversible swelling and shrinkage of pSpNIPAAm hydrogel under different irradiation conditions. This fascinating strategy provided insight into the design of soft robotics where the autonomous movement was available.

Figure 2.12 presents a microfluidic system developed by Sugiura *et al.*, in which the pSpNIPAAm-based microvalves were used to control the fluid via light [156]. The hydrogel microvalves were fixed in the microchannels using micropillars and blocked the fluid flow in the dark when the pSpNIPAAm hydrogel was at the swollen state due to the hydrophilic McH⁺ isomers. However, if the visible light was imposed, the McH⁺ isomers converted into the hydrophobic Sp isomers and thus induced the large dehydration of hydrogel microvalves, thereby letting the fluid flow pass through the microchannels. Regarding the microfluidic system, the fast response of hydrogel should be very important to the temporal control over the fluid flow. Therefore, Sumaru et al. investigated the reaction kinetics of spiropyran and a series of experiments were performed on the swelling and reswelling rates of pSpNIPAAm hydrogels [13, 144, 146]. It was demonstrated by these experiments that the reaction rate of photoisomerization could be modulated by using different spiropyran derivatives, which then resulted in the deformation rate of a pSpNIPAAm hydrogels.

Figure 2.12. A microfluidic system based on microvalves prepared by pSpNIPAAm hydrogels [156].

Another important application of pSpNIPAAm hydrogels should be to fabricate printed patterns, as shown in **Figure 2.13**. Stumpel and Moriyama *et al.* took advantage of the photo-generated dehydration to fabricate microstructures on the surface of pSpNIPAAm hydrogel sheets using light [72, 157]. The surface of hydrogel sheet in the dark remained swollen state while it shrunk when exposed to the visible light. Therefore, the researchers could design and print all kinds of patterns on the surface of hydrogel sheet by arranging the positions of light sources. As illustrated in **Figure 2.13**, the light irradiation was imposed on the local surface of a hydrogel sheet and thus the irradiated part collapsed due to photo-induced dehydration, resulting in relevant surface topographies.

Figure 2.13. Photoswitchable ratchet surface topographies based on pSpNIPAAm hydrogels incorporating acrylic acids [72].

Apart from the photo-driven actuation, pSpNIPAAm hydrogels were also used as cell culture substrates and extracellular matrix due to their high water content and biocompatibility. It was demonstrated by Schmidt *et al.* that the cell adhesion should depend largely on many factors such as water content, hydrophobicity, and rigidity [158]. Since the hydration state of pSpNIPAAm hydrogels could change with different irradiation and temperature conditions, the light and heat might be used to modulate the cell adhesion. **Figure 2.14** presents the procedure for photo-controlled cell adhesion using the pSpNIPAAm-based culture surface, which was developed by Edahiro *et al.* [159]. The reversible isomerization between closed- and open-ring forms was achieved via the switch between visible and UV light. Consequently, the microenvironment of cells should undergo a hydration-to-dehydration transition in the photo-responsive cell culture substrate, which might be the reason for the deattachment of cells.

Figure 2.14. Scheme of cell adhesion control using the pSpNIPAAm-based culture surface [159].

Few published reports were found on the electrical response of spiropyran-based hydrogels. For instance, Sumaru et al. carried out some experiments on the photo- and temperature-induced conductivity of spiropyran-modified hydrogels [145, 147, 160]. It was observed in the experiment that the conductivity of the hydrogel could be raised via visible light twice than that in the dark [147].

2.2 Theoretical models

2.2.1 Photo-sensitive liquid crystal elastomers

Long *et al.* proposed a multiphysics model for macroscopic photo-mechanics of LCEs [161], where the photophysics, photochemistry, chemo-mechanical coupling, and mechanical deformation were integrated. The photophysics module was based on Beer-Lambert law, characterizing the propagation of light across a uniform medium without scattering or internal sources. It was based on the assumption that the absorbance of light was proportional to the length of medium and concentration of photochromic species. The photo-chemistry

module was used to predict the production and consumption of free radicals and initiators during the photon-initiator reaction. The chemo-mechanical coupling module characterized the constitutive relation between chemically-triggered structural changes of the crosslinked network and macroscopic deformation of LCEs, in which the crosslinked network was decomposed into the original and photochemically-altered networks. Finally, Cauchy stress was derived based on theory of nonlinear hyper elasticity.

Huo *et al.* developed the constitutive models to characterize the photo-mechanical response of LCEs, allowing for the nematic-isotropic phase transition affected by the photoisomerization [162-164]. In these models, the relationship was built between shear strain and photo-induced changes in shear modulus. An order tensor was then introduced into the modeling framework as an important parameter to capture the photo-induced change on molecular structure.

Bai *et al.* studied the opto-mechanics of soft dielectrics that were independent of special optical effects [165]. They considered the feature size of structure compared with the wavelength of light and combine the electro-dynamics of light and the nonlinear mechanics of elasticity.

2.2.2 Photo-sensitive hydrogels

Flory *et al.* proposed that the free energy of a swollen hydrogel should consist of

two parts, including the stretch of the polymeric network and the mixing between the polymeric chains and water molecules. This principle became the cornerstone of most current theoretical studies on the swelling of hydrogels.

The theoretical models on photo-thermally sensitive hydrogels were basically developed through the modification of those on thermo-sensitive hydrogels [36, 166]. In these modified models, a formula was usually integrated into the Flory-Huggins interaction parameter which described the temperature rise as a function of light intensity. For example, Toh *et al.* developed the theoretical model for inhomogeneous large deformation of photo-thermal responsive hydrogels with light-absorbing nanoparticles [167]. In their work, the thermal effect of light irradiation was characterized by a linear function, in which the temperature rise was proportional to the light intensity. Yan *et al.* also formulated the pH response in the model development by considering the immobilized acrylic acid groups in a simple fashion [168]. Despite this, the model was unable to characterize the complex reaction system.

Regarding the photo-chemically sensitive hydrogel, the current models mostly focused on a simple binary system describing the conversion between only two molecular species. For instance, Kuksenok and Xuan performed the modelling procedure to predict the motion of a pSpNIPAAm gel, in which only the photoisomerization between McH^+ and Sp was considered in the reaction kinetics

and the effect of ions and fixed-charged groups were neglected [169-172]. Although Dehghany and Xuan developed a coupled photo-chemo-mechanical model for TML-modified NIPAAm gels to fill this gap, they failed to present a general solution to a complex reaction kinetic system [172, 173]. Therefore, their theory might not be applied to some other photo-chemically responsive hydrogels due to the different reaction mechanisms.

Furthermore, the current models only allowed for the temperature and pH stimulus, apart from the light irradiation, whereas some other stimuli like ionic strength and heavy metal ions were not mentioned in the literature on modelling of photo-sensitive hydrogels.

2.3 Remarks

This chapter presents the review on the experimental and theoretical findings regarding photo-sensitive polymers in literature. According to the current literature review, some conclusions are given on the modeling of photo-sensitive hydrogels as follows.

- Compared with equivalent elastomers, photo-sensitive hydrogels enjoy some unique advantages, such as large deformation ratio, fast chemical reaction rate, and high conductivity, and thus gain much popularity among researchers.

- The multi-stimuli responsive behavior is usually available to photo-chemically sensitive hydrogels, especially those spiropyran-based hydrogels. This inspires some emerging applications, such as biosensor, extracellular matrix (ECM), and smart electrolyte.
- Most developed theoretical models focused on a single external stimulus, instead of multiple coupled stimuli. Furthermore, few works explored the reaction response mechanism of a photo-sensitive hydrogel system.
- So far, no model has been found to investigate the ionic-strength-responsive and metal-ion-binding behaviors of photo-sensitive hydrogels, which is a concerned issue in the biomedical application.

Therefore, it is necessary to develop a multi-effect-coupling photo-stimulus model to characterize a photo-sensitive hydrogel exposed to several external stimuli. The development of this model is thus presented in the following chapter.

Chapter 3 Development of a multi-effect-coupling photo-stimulus (MECp) model for photo-sensitive hydrogels

This chapter develops the MECp model to account for the response behavior of a photo-sensitive hydrogel subjected to several coupled stimuli. The formulation of MECp model is performed based on several assumptions to capture the mechanical and electrochemical response against coupled external stimuli, including light irradiation, temperature, pH, and ionic strength. The organization of this chapter is done as follows. An introduction is given firstly, and the formulation of MECp model is then presented in Section 3.1, including chemical reaction kinetic, conservation of mass and momentum, electrostatic field, and constitutive relation. Subsequently, Section 3.2 presents the reduced model and computational procedure, followed by the model validation in Section 3.3. Section 3.4 then exhibits the simulation findings based on the MECp model, and Section 3.5 finally draws some remarks.

3.1 Formulation of the MECp model

The following phenomena are covered in the MECp model: (i) light illumination, (ii) chemical reactions on bound species, (iii) transport of mobile species, (iv) electrostatic field generated by fixed- and mobile-charged species, and (v) large

mechanical deformation of polymeric network. In this study, the deformed and dry states of a hydrogel are referred to as the current and reference configurations, respectively. Before the formulation of MECp model, some assumptions are prescribed as detailed below

- the hydrogel and solution remain under an isothermal condition, both of which are physicochemically homogeneous and incompressible;
- the light irradiation is homogeneous and the light-generated heat is negligible, without any attenuation along the thickness of gel layer;
- the ionic diffusion is isotropic and all the chemical reactions are first-order;
- the distribution of bound species is uniform in the polymeric network; and
- the hydrogel is submerged in the unstirred solution.

In this study, the rules and symbols of algebraic operation are identical to those in Reference [174].

3.1.1 Kinetics of chemical reaction

Figure 3.1. Schematic illustration of a photo-sensitive hydrogel (pSpNIPAAm) system.

As illustrated in **Figure 3.1**, five species are included in a photo-sensitive hydrogel system, which are PSGs (Mc, McH⁺, Sp, and SpH⁺), acidic groups (AA⁻ and AAH), cations (Na⁺ and H⁺), anions (OH⁻, Cl⁻, and SO₄²⁻) and solvent molecules (H₂O). Herein, acidic groups convert between the charged and protonated forms, namely, AA⁻ and AAH, respectively. PSGs and acidic groups are bound to the polymeric network, while the other components are diffusive species that migrate across the hydrogel and solution domains. In this reaction system, the interaction occurs on multiple concurrent chemical processes, including the isomerization of PSGs and protonation equilibriums of PSGs, acidic groups and water molecules. Reactions on PSGs are given as follows,

where Ka₁ and Ka₂ are the dissociation coefficients of McH⁺ and SpH⁺, respectively, while k_c and k_o the reaction rates of closed- and open-ring isomerization, respectively. In particularly, k_c depends on the photo parameters and temperature, given by [175-177]

$$k_c = I_L F_L \varepsilon_L \phi_L \lambda_L / N_A h c_L + A_T \exp(-E_T/RT) \quad (3.2)$$

where I_L represents the intensity of irradiation, T the temperature, F_L the kinetic factor, ε_L the molar absorption coefficient, ϕ_L the quantum yield, λ_L the wavelength of light, R the gas constant, h the Planck constant, N_A the

Avogadro number, c_L the speed of light, A_T the frequency factor, and E_T the activation energy.

Here, SpH^+ and Mc are assumed to vanish when the local pH is higher and lower than a threshold, respectively [108, 178], which is determined as $(\log Ka_1 + \log Ka_2)/2$. Based on this assumption, we obtain the following processes:

if the local pH $\geq (\log Ka_1 + \log Ka_2)/2$,

while if the local pH $< (\log Ka_1 + \log Ka_2)/2$,

By **Equations** (3.3) and (3.4), the reaction process in **Equation** (3.1) is reduced to a ternary system characterized. Herein, we denote three reagents by “A”, “B”, and “C”, respectively, to study a ternary reaction system, given by

where k_1 , k_2 , k_3 , and k_4 are reaction rate constants and C is the protonated form of B. Besides, $c_A(t)$, $c_B(t)$, and $c_C(t)$ represent the concentrations of A, B, and C at a given time t , respectively, and c_A^0 , c_B^0 , and c_C^0 the corresponding initial concentrations. The kinetic of this chemical reaction system is characterized by [179]

$$\begin{cases} \dot{c}_A(t) + k_1 c_A(t) - k_2 c_B(t) = 0 \\ \dot{c}_B(t) - k_1 c_A(t) + (k_2 + k_3) c_B(t) - k_4 c_C(t) = 0 \\ \dot{c}_C(t) - k_3 c_B(t) + k_4 c_C(t) = 0 \end{cases} \quad (3.6)$$

where the dot represents derivative operator with respect to the time t . **Equation** (3.6) is a group of ordinary differential equations that could be solved numerically. However, in this study, an analytical approach is used in the solution of **Equation** (3.6), in order to improve the convergence of subsequent coupled equations for other fields and understand the reaction kinetic better.

Applying Laplace transformation to the above equations, we obtain

$$\begin{cases} s c_A(s) - c_A^0 + k_1 c_A(s) - k_2 c_B(s) = 0 \\ s c_B(s) - c_B^0 - k_1 c_A(s) + (k_2 + k_3) c_B(s) - k_4 c_C(s) = 0 \\ s c_C(s) - c_C^0 - k_3 c_B(s) + k_4 c_C(s) = 0 \end{cases} \quad (3.7)$$

where s denotes the independent variable and $c_A(s)$, $c_B(s)$, and $c_C(s)$ represent the mapping variables of $c_A(t)$, $c_B(t)$, and $c_C(t)$ in the frequency domain. The matrix form of **Equation** (3.7) is given by

$$\begin{bmatrix} s + k_1 & -k_2 & 0 \\ -k_1 & s + k_2 + k_3 & -k_4 \\ 0 & -k_3 & s + k_4 \end{bmatrix} \begin{bmatrix} c_A(s) \\ c_B(s) \\ c_C(s) \end{bmatrix} = \begin{bmatrix} c_A^0 \\ c_B^0 \\ c_C^0 \end{bmatrix} \quad (3.8)$$

Denoted by D_1 , the determinant of the coefficient matrix is equal to

$$D_1 = \begin{vmatrix} s + k_1 & -k_2 & 0 \\ -k_1 & s + k_2 + k_3 & -k_4 \\ 0 & -k_3 & s + k_4 \end{vmatrix} = s(s + \gamma_1)(s + \gamma_2) \quad (3.9)$$

where γ_1 and γ_2 are defined by

$$\begin{cases} \gamma_1 + \gamma_2 = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4 \\ \gamma_1 \gamma_2 = \mathbf{k}_1 \mathbf{k}_3 + \mathbf{k}_1 \mathbf{k}_4 + \mathbf{k}_2 \mathbf{k}_4 \end{cases} \quad (3.10)$$

Then analytical values of the mapping variables are obtained as follows:

$$\begin{aligned} c_A(s) &= \frac{1}{D_1} \begin{vmatrix} c_A^0 & -\mathbf{k}_2 & 0 \\ c_B^0 & s + \mathbf{k}_2 + \mathbf{k}_3 & -\mathbf{k}_4 \\ c_C^0 & -\mathbf{k}_3 & s + \mathbf{k}_4 \end{vmatrix} \\ &= \frac{c_A^0}{s + \gamma_2} + \frac{c_A^0 \gamma_2 - c_A^0 \mathbf{k}_1 + c_B^0 \mathbf{k}_2}{(s + \gamma_1)(s + \gamma_2)} + (c_A^0 + c_B^0 + c_C^0) \mathbf{k}_2 \mathbf{k}_4 \cdot \\ &\quad \left[\frac{1}{\gamma_2 - \gamma_1} \cdot \frac{1}{s(s + \gamma_1)} - \frac{1}{\gamma_2 - \gamma_1} \cdot \frac{1}{s(s + \gamma_2)} \right] \end{aligned} \quad (3.11)$$

$$\begin{aligned} c_B(s) &= \frac{1}{D_1} \begin{vmatrix} s + \mathbf{k}_1 & c_A^0 & 0 \\ -\mathbf{k}_1 & c_B^0 & -\mathbf{k}_4 \\ 0 & c_C^0 & s + \mathbf{k}_4 \end{vmatrix} \\ &= \frac{c_B^0}{s + \gamma_2} + \frac{(c_A^0 + c_B^0) \mathbf{k}_1 + (c_B^0 + c_C^0) \mathbf{k}_4 - c_B^0 \gamma_1}{(s + \gamma_1)(s + \gamma_2)} \\ &\quad + \frac{(c_A^0 + c_B^0 + c_C^0)}{\gamma_2 - \gamma_1} \cdot \left[\frac{1}{s(s + \gamma_1)} - \frac{1}{s(s + \gamma_2)} \right] \end{aligned} \quad (3.12)$$

$$\begin{aligned} c_C(s) &= \frac{1}{D_1} \begin{vmatrix} s + \mathbf{k}_1 & -\mathbf{k}_2 & c_A^0 \\ -\mathbf{k}_1 & s + \mathbf{k}_2 + \mathbf{k}_3 & c_B^0 \\ 0 & -\mathbf{k}_3 & c_C^0 \end{vmatrix} \\ &= \frac{c_C^0}{s + \gamma_2} + \frac{c_B^0 \mathbf{k}_3 - c_C^0 \mathbf{k}_4 + c_C^0 \gamma_2}{(s + \gamma_1)(s + \gamma_2)} \\ &\quad + \frac{(c_A^0 + c_B^0 + c_C^0) \mathbf{k}_1 \mathbf{k}_3}{\gamma_2 - \gamma_1} \cdot \left[\frac{1}{s(s + \gamma_1)} - \frac{1}{s(s + \gamma_2)} \right] \end{aligned} \quad (3.13)$$

By means of the inverse Laplace transformation, we finally obtain the following

values:

$$\begin{aligned}
c_A(t) = & \frac{c_A^0 \gamma_1 \gamma_2 + (c_B^0 k_2 - c_A^0 k_1) \gamma_1 - (c_A^0 + c_B^0 + c_C^0) k_2 k_4}{\gamma_1 (\gamma_2 - \gamma_1)} \cdot e^{-\gamma_1 t} \\
& + \frac{(c_A^0 + c_B^0 + c_C^0) k_2 k_4 - c_A^0 \gamma_1 \gamma_2 - (c_B^0 k_2 - c_A^0 k_1) \gamma_2}{\gamma_2 (\gamma_2 - \gamma_1)} \cdot e^{-\gamma_2 t} \quad (3.14) \\
& + \frac{(c_A^0 + c_B^0 + c_C^0) k_2 k_4}{\gamma_1 \gamma_2}
\end{aligned}$$

$$\begin{aligned}
c_B(t) = & \frac{(c_A^0 k_1 + c_B^0 k_1 + c_B^0 k_4 + c_C^0 k_4) \gamma_1 - c_B^0 \gamma_1^2 - (c_A^0 + c_B^0 + c_C^0) k_1 k_4}{\gamma_1 (\gamma_2 - \gamma_1)} \cdot e^{-\gamma_1 t} \\
& + \frac{c_B^0 \gamma_2^2 - (c_A^0 k_1 + c_B^0 k_1 + c_B^0 k_4 + c_C^0 k_4) \gamma_2 + (c_A^0 + c_B^0 + c_C^0) k_1 k_4}{\gamma_2 (\gamma_2 - \gamma_1)} \cdot e^{-\gamma_2 t} \\
& + \frac{(c_A^0 + c_B^0 + c_C^0) k_1 k_4}{\gamma_1 \gamma_2}
\end{aligned}$$

(3.15)

$$\begin{aligned}
c_C(t) = & \frac{c_C^0 \gamma_1 \gamma_2 + (c_B^0 k_3 - c_C^0 k_4) \gamma_1 - (c_A^0 + c_B^0 + c_C^0) k_1 k_3}{\gamma_1 (\gamma_2 - \gamma_1)} \cdot e^{-\gamma_1 t} \\
& + \frac{(c_A^0 + c_B^0 + c_C^0) k_1 k_3 - c_C^0 \gamma_1 \gamma_2 - (c_B^0 k_3 - c_C^0 k_4) \gamma_2}{\gamma_2 (\gamma_2 - \gamma_1)} \cdot e^{-\gamma_2 t} \\
& + \frac{(c_A^0 + c_B^0 + c_C^0) k_1 k_3}{\gamma_1 \gamma_2}
\end{aligned}$$

(3.16)

In particular, at the steady state, the above expressions can be reduced as follows:

$$c_A(t = \infty) = \frac{(c_A^0 + c_B^0 + c_C^0) k_2 k_4}{\gamma_1 \gamma_2} = \frac{c_A^0 + c_B^0 + c_C^0}{1 + \frac{k_1}{k_2} \left(1 + \frac{k_3}{k_4}\right)} \quad (3.17)$$

$$c_B(t = \infty) = \frac{(c_A^0 + c_B^0 + c_C^0) k_1 k_4}{\gamma_1 \gamma_2} = \frac{c_A^0 + c_B^0 + c_C^0}{1 + \frac{k_3}{k_4} + \frac{k_2}{k_1}} \quad (3.18)$$

$$c_C(t = \infty) = \frac{(c_A^0 + c_B^0 + c_C^0) k_1 k_3}{\gamma_1 \gamma_2} = \frac{c_A^0 + c_B^0 + c_C^0}{1 + \frac{k_4}{k_3} \left(1 + \frac{k_2}{k_1}\right)} \quad (3.19)$$

At the equilibrium state, the association between the concentrations and rate constants is given by

$$\frac{c_C(t = \infty)}{c_B(t = \infty)} = \frac{k_3}{k_4} \quad (3.20)$$

Meanwhile, due to the protonation equilibria between B and C, we obtain

$$K_a = \frac{c_C(t = \infty)}{c_B(t = \infty) \cdot c_{H^+}} \quad (3.21)$$

where K_a is the dissociation constant between B and C and c_{H^+} is the concentration of surrounding protons. Combined with **Equations** (3.20) and (3.21), the ratio of forward and backward rate constants is given by

$$\frac{k_3}{k_4} = K_a c_{H^+} \quad (3.22)$$

In fact, the protonation is much faster than the isomerization conversion, and thereby k_3 and k_4 are set to several orders of magnitude faster than all other rate constants in terms of **Equation** (3.22).

Based on the mathematical model of this ternary system, the molar fraction of each isomer β_j ($j=Mc, Sp, AAH, \dots, N$) at steady state is obtained as follows:

if the local $pH \geq (\log K_{a1} + \log K_{a2})/2$,

$$\beta_{Sp} = \frac{c_{Sp}}{c_p} = \frac{1}{1 + \frac{k_o}{k_c} \left(1 + \frac{K_{a1}}{c_{H^+}}\right)} \quad (3.23)$$

$$\beta_{McH^+} = \frac{c_{McH^+}}{c_p} = \frac{1}{1 + \frac{k_c}{k_o} + \frac{K_{a1}}{c_{H^+}}} \quad (3.24)$$

$$\beta_{Mc} = 1 - \beta_{Sp} - \beta_{McH^+} \quad (3.25)$$

if the local $pH < (\log K_{a1} + \log K_{a2})/2$,

$$\beta_{Sp} = \frac{c_{Sp}}{c_p} = \frac{c_p}{1 + \frac{k_o}{k_c} + \frac{c_{H^+}}{Ka_2}} \quad (3.26)$$

$$\beta_{McH^+} = \frac{c_{McH^+}}{c_p} = \frac{c_p}{1 + \frac{k_c}{k_o} \left(1 + \frac{c_{H^+}}{Ka_2}\right)} \quad (3.27)$$

$$\beta_{SpH^+} = 1 - \beta_{Sp} - \beta_{McH^+} \quad (3.28)$$

where c_p is the total molar concentration of PSGs.

Meanwhile, there also exist some other dissociation equilibriums of acidic groups and water molecules as follows,

where Ka_3 and K_w are dissociation constants acidic groups and water molecules.

The mathematical correlations are given as detailed below

$$\beta_{AA^-} = \frac{c_{AA^-}}{c_A} = \frac{Ka_3}{c_{H^+} + Ka_3} \quad (3.31)$$

$$\beta_{AAH} = \frac{c_{AAH}}{c_A} = 1 - \beta_{AA^-} \quad (3.32)$$

$$c_{H^+} \cdot c_{OH^-} = K_w \quad (3.33)$$

3.1.2 Conservation of mass

For a hydrogel system, transport of mobile ions in the solution is very important, because the movement of ions in and out of polymeric network generates the change in osmotic pressure and electrical potential difference on both sides of the

interface, resulting in the swelling or shrinking of the gel. Then Nernst-Planck equation is employed for characterizing this phenomenon, which is an extension of Fick's law of diffusion for the case where the contribution of both electrostatic forces and concentration gradient are considered during the diffusive motion of ions.

For the flux of k th mobile ions, it depends on the electric force other the ionic concentration gradient, given by [180]

$$\mathbf{j}_k = -D_k \nabla c_k + \frac{D_k z_k F}{k_B N_A T} c_k \mathbf{e} + c_k \mathbf{v} \quad (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \quad (3.34)$$

where D_k is the diffusivity of ionic species k , z_k the valence, $\mathbf{e}$ the vector of electric field, $\mathbf{v}$ the velocity vector of fluid, F the Faraday constant, and k_B the Boltzmann constant. The electric field $\mathbf{e}$ is expressed as follows [180],

$$\mathbf{e} = -\nabla \psi - \frac{\partial \mathbf{A}}{\partial t} \quad (3.35)$$

where ψ is the electrical potential and $\mathbf{A}$ the magnetic vector potential.

Equation (3.35) is also called Nernst-Planck equation and another form is written based on the Ohm's law as follows [180]:

$$\mathbf{j}_k = -\frac{D_k c_k}{N_A k_B T} \nabla \mu_k \quad (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \quad (3.36)$$

where μ_k denotes the electrochemical potential of k th mobile species. Denote by γ_k the production of chemical reaction, ν_k the stoichiometric coefficient,

and r_k the rate of chemical reaction, the diffusion equation is given by [180]

$$\dot{c}_k = -\nabla \cdot \mathbf{j}_k + \gamma_k \quad (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \quad (3.37)$$

$$\gamma_k = \nu_k r_k \quad (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \quad (3.38)$$

In this work, the solution is assumed to be in stagnation and the effect of magnetic field can be neglected. Therefore, the Nernst-Planck equation inside the hydrogel is written as follows [181, 182],

$$\dot{c}_k = \nabla \cdot \left(D_k \nabla c_k + \frac{D_k z_k F}{k_B N_A T} c_k \nabla \psi + D_k c_k \nabla \ln a_k \right) + \nu_k r_k \quad (3.39)$$

$$(k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N)$$

where a_k is the activity coefficient of ionic species k , given by [183, 184]

$$\ln a_k = \begin{cases} -B_1 z_k^2 \sqrt{I} \ln 10, & 0 \leq I < 0.02 \\ -\frac{B_1 z_k^2 \sqrt{I}}{1 + B_2 \sqrt{I}} \ln 10, & 0.02 \leq I < 0.1 \\ \left(-\frac{B_1 z_k^2 \sqrt{I}}{1 + B_2 \sqrt{I}} + B_3 I + B_4 I^2 + B_5 I^3 + B_6 I^4 \right) \ln 10, & I \geq 0.1 \end{cases}$$

$$(k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \quad (3.40)$$

where B_1 and B_2 are the constants that depends only on the nature of the solvent and temperature, B_3 , B_4 , B_5 , and B_6 the empirical coefficients, as listed in **Table 3.1**. I represents the ionic strength of surrounding solution, given by [183]

$$I = \frac{1}{2} \sum_k^N z_k^2 c_k \quad (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \quad (3.41)$$

Table 3. 1. Coefficients for calculation of ionic strength [183, 184].

Coefficient	Value
B ₁	0.509 ~ 0.524
B ₂	1.30 ~ 1.37
B ₃	-0.1300 ~ 0.02796
B ₄	0.004803 ~ 0.0260
B ₅	-0.0002736 ~ 0.0000
B ₆	0.000 ~ 0.000105

Equations (3.23)-(3.39) are derived based on the current configuration that corresponds with the deformed state of the hydrogel. To avoid a moving mesh, these equations are recast in the reference configuration referring to the non-deformed state in the following.

The Cauchy-Green tensor for macroscopic deformation reads

$$\mathbf{C} = \mathbf{F}^T \cdot \mathbf{F} \quad (3.42)$$

where $\mathbf{F}$ represents the deformation gradient. Denote $J = \det \mathbf{F}$ the *Jacobian* determinant, the correlation between the volume elements in the current and reference configurations, denoted by dv and dV , respectively, is characterized by

$$dv = J dV \quad (3.43)$$

A constraint condition is given due to the molecular incompressibility [36, 185], as follows,

$$J = 1 + \Omega C \quad (3.44)$$

where C represents the nominal concentration of solvent, defined as moles of solvent molecules per unit reference volume, and Ω the characteristic volume per mole of solvent molecules. If we neglect the clustering of water molecules, the value of Ω is estimated by the concentration of solvent molecules c as follows:

$$\Omega = \frac{1}{c} \quad (3.45)$$

Herein, the nominal concentrations are defined as detailed below

$$C_k = Jc_k \quad (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \quad (3.46)$$

$$C_f = Jc_f \quad (f = \text{Mc}, \text{Sp}, \text{AAH}\dots, N_f) \quad (3.47)$$

$$C_P = Jc_P \quad (3.48)$$

$$C_A = Jc_A \quad (3.49)$$

where c_f is the true concentration of fixed species on the polymeric network.

Similarly, the nominal production of chemical reaction is defined as follows,

$$\Gamma_k = J\gamma_k \quad (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \quad (3.50)$$

Denote by $\mathbf{J}_k$ and $\mathbf{J}$ the flux vectors for the k th mobile ions and solvent molecules in the reference configuration. The correlation between the corresponding flux vectors $\mathbf{j}$ and $\mathbf{j}_k$ in the current configuration is then given by [186]

$$\mathbf{J} = J\mathbf{F}^{-1} \cdot \mathbf{j} = -\frac{D_s C}{N_A k_B T} \mathbf{F}^{-1} \cdot \nabla_X \mu \cdot \mathbf{F}^{-1} \quad (3.51)$$

$$\begin{aligned} \mathbf{J}_k &= J\mathbf{F}^{-1} \cdot \mathbf{j}_k = -\frac{D_k C_k}{N_A k_B T} \mathbf{F}^{-1} \cdot \nabla_X \mu_k \cdot \mathbf{F}^{-1} \\ &(k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \end{aligned} \quad (3.52)$$

where the subscript “ X ” stands for the reference coordinate system, μ the

chemical potential of solvent molecules, and D_s the diffusivity of solvent. Then the law of mass conservation for the solvent and mobile ions reads

$$\dot{C} = -\nabla_X \cdot \mathbf{J} = \nabla_X \cdot \left(\frac{D_s C}{N_A k_B T} \mathbf{F}^{-1} \cdot \nabla_X \mu \cdot \mathbf{F}^{-1} \right) \quad (3.53)$$

$$\begin{aligned} \dot{C}_k &= -\nabla_X \cdot \mathbf{J}_k + \Gamma_k = \nabla_X \cdot \left(\frac{D_k C_k}{N_A k_B T} \mathbf{F}^{-1} \cdot \nabla_X \mu_k \cdot \mathbf{F}^{-1} \right) + J \nu_k r_k \\ (k &= \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \end{aligned} \quad (3.54)$$

Finally, the Nernst-Planck equation in the reference configuration is given by

$$\begin{aligned} \frac{\partial}{\partial t} \Big|_X C_k &= \nabla_X \cdot \left[D_k \mathbf{C}^{-1} \cdot \left(\nabla_X C_k + \frac{z_k F}{k_B N_A T} C_k \nabla_X \psi + C_k \nabla_X \ln a_k \right) \right] + J \nu_k r_k \\ (k &= \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \end{aligned} \quad (3.55)$$

Besides, due to the difference in the microenvironment between the hydrogel and buffer solution, the diffusion characteristic inside the hydrogel is quite different from that in buffer solution. Herein, an effective diffusivity is introduced based on the free volume theory [187], as detailed below:

$$\begin{aligned} D_k &= \bar{D}_k (1 - k_1 l_k \phi^{0.75}) \exp \left(-k_2 l_k^2 \left(\frac{\phi}{1 - \phi} \right) \right) \\ (k &= \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \end{aligned} \quad (3.56)$$

where k_1 and k_2 are undefined structural constants for a specified polymer-solvent system. $\bar{D}_k$ is the diffusivity at infinite dilution, l_k the radii of k th ionic solute, and ϕ the volume fraction of polymer in the hydrogel, given by [36, 188, 189]

$$\phi = \frac{1}{J} \quad (3.57)$$

In particular, $\bar{D}_k$ is a function of the temperature according to Stokes-Einstein equation, given as [187]

$$\bar{D}_k = \frac{k_B T}{f} \quad (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \quad (3.58)$$

where f is the frictional drag coefficient.

3.1.3 Conservation of momentum

Due to the conservation law of linear momentum [174], we obtain

$$\rho_0 \ddot{\mathbf{u}} = \nabla_x \cdot \mathbf{P} + \rho_0 \mathbf{b} \quad (3.59)$$

where ρ_0 is the mass density, $\mathbf{u}$ the displacement vector of a mass point in the domain, $\mathbf{P}$ the second-order tensor of nominal stress, $\mathbf{b}$ the body force vector at reference configuration. The correlation between stress tensors at reference and current configurations is characterized by

$$\mathbf{P} = J \mathbf{F}^{-1} \cdot \boldsymbol{\sigma} \quad (3.60)$$

where $\boldsymbol{\sigma}$ is the true stress tensor. The deformation gradient tensor $\mathbf{F}$ is obtained in by the displacement vector $\mathbf{u}$, detailed as below

$$\mathbf{F} = \mathbf{I} + \nabla_x \mathbf{u} \quad (3.61)$$

where $\mathbf{I}$ is the second-order unit tensor.

The second-order derivative of displacement and body force are generally quite small and could be neglected, and then the conservation law of linear momentum

is rewritten as follows:

$$\nabla_x \cdot \mathbf{P} = 0 \quad (3.62)$$

3.1.4 Electrostatic effect

Because of ionic species within the hydrogel and solution, a static electric field is generated locally, and then the resulted static electric force can drive the charged mobile species to move. Therefore, we need to model this effect on the distribution of concentration of species, and Poisson equation for electrostatic field is applied as follows [42, 190-194],

$$\nabla^2 \psi = - \frac{\rho_f}{\varepsilon_r \varepsilon_0} \quad (3.63)$$

where ε_r and ε_0 are the relative and vacuum dielectric constants of the ambient medium, and ρ_f represents the free charge volume density that describe charges brought from outside. Here, ρ_f is given by

$$\rho_f = F \left(\sum_k^N z_k c_k + \sum_f^{N_f} z_f c_f \right) \quad (3.64)$$

where c_f and z_f denote the concentration in the current configuration and valence of charged groups fixed at the polymer.

Combined with **Equations** (3.63) and (3.64), Poisson equation in the current configuration is expressed as follows:

$$\nabla^2 \psi = - \frac{F}{\varepsilon_r \varepsilon_0} \left(\sum_k^N z_k c_k + \sum_f^{N_f} z_f c_f \right) \quad (3.65)$$

The Poisson equation based on the reference configuration is written as follows,

$$\nabla_X \cdot (J\mathbf{C}^{-1}\nabla_X\psi) = -\frac{F}{\varepsilon_r\varepsilon_0}\left(\sum_k^N z_k C_k + \sum_f^{N_f} z_f C_f\right) \quad (3.66)$$

In this work, we introduce the ionic conductivity to capture the accumulation of mobile charges, given by [195]

$$K_s = \frac{F^2}{RT} \sum_k^N |z_k| D_k c_k^g \quad (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N) \quad (3.67)$$

where c_k^g stands for the true concentration of ionic species k within the hydrogel.

3.1.5 Constitutive relation by laws of thermodynamics

For an arbitrary domain in the hydrogel, denote the Helmholtz free energy density by W , the inequality formula is derived according to the second law of thermodynamics, detailed as below [196, 197]

$$\dot{W} - u_{\text{mech}} - u_{\text{el}} - u_{\text{dif}} - u_{\text{dis}} \leq 0 \quad (3.68)$$

where the superscript “ $\dot{\cdot}$ ” refers to the derivative with respect to the time. u_{mech} , u_{el} , u_{dif} , and u_{dis} represent the densities of powers in the reference configuration, generated by stress, static electric force, and transport of solutes and solvent, respectively.

The mechanical power is given by [186]

$$u_{\text{mech}} = J\boldsymbol{\sigma}:\mathbf{D} \quad (3.69)$$

where $\mathbf{D}$ stands for the rate of strain tensor that can be calculated by the velocity gradient $\mathbf{L}$ as follows,

$$\mathbf{D} = \frac{1}{2} (\mathbf{L} + \mathbf{L}^T) \quad (3.70)$$

$$\mathbf{L} = \dot{\mathbf{F}} \cdot \mathbf{F}^{-1} \quad (3.71)$$

The power due to electric field is given by [186]

$$u_{\text{el}} = \mathbf{E} \cdot \dot{\mathbf{H}} - F\psi \sum_k^N z_k \dot{C}_k \quad (3.72)$$

where $\mathbf{H}$ and $\mathbf{E}$ are the electric displacement and electric field vectors in the reference state, respectively. Neglecting the magnetic vector potential in an electric field, we obtain

$$\mathbf{e} = -\nabla\psi \quad (3.73)$$

$$\mathbf{E} = -\nabla_X\psi \quad (3.74)$$

$$\mathbf{H} = \varepsilon_0 \varepsilon_r J \mathbf{C}^{-1} \cdot \mathbf{E} = \varepsilon_0 \varepsilon_r J \mathbf{E} \cdot \mathbf{C}^{-1} \quad (3.75)$$

$$\mathbf{h} = \varepsilon_0 \varepsilon_r \mathbf{E} \cdot \mathbf{F}^{-1} = \varepsilon_0 \varepsilon_r \mathbf{F}^{-T} \cdot \mathbf{E} \quad (3.76)$$

$$\mathbf{H} = J \mathbf{F}^{-1} \cdot \mathbf{h} = J \mathbf{h} \cdot \mathbf{F}^{-T} \quad (3.77)$$

$$\mathbf{h} = \frac{1}{J} \mathbf{F} \cdot \mathbf{H} = \frac{1}{J} \mathbf{H} \cdot \mathbf{F}^T \quad (3.78)$$

where $\mathbf{h}$ is the electric displacement vector in the current configuration.

The rate of work produced by the transport of mobile species per volume is written by [186]

$$\begin{aligned}
u_{\text{dif}} &= -\nabla_X \cdot \left(\mu \mathbf{J} + \sum_k^N \mu_k \mathbf{J}_k \right) \\
&= -\left(\mu \nabla_X \cdot \mathbf{J} + \sum_k^N \mu_k \nabla_X \cdot \mathbf{J}_k \right) - \left(\mathbf{J} \cdot \nabla_X \mu + \sum_k^N \mathbf{J}_k \cdot \nabla_X \mu_k \right)
\end{aligned}
\tag{3.79}$$

Combined with **Equations** (3.53) and (3.54), **Equation** (3.79) is rewritten as follows:

$$u_{\text{dif}} = \mu \dot{C} + \sum_k^N \mu_k (\dot{C}_k - \Gamma_k) - \left(\mathbf{J} \cdot \nabla_X \mu + \sum_k^N \mathbf{J}_k \cdot \nabla_X \mu_k \right)
\tag{3.80}$$

Herein, we replace the molar fractions of PSGs with $\beta_i (i = 1, 2, 3)$ as follows,

$$\beta_1 = \beta_{\text{McH}^+}, \quad \beta_2 = \beta_{\text{Sp}}, \quad \beta_3 = 1 - \beta_1 - \beta_2
\tag{3.81}$$

Therefore, in a strong acidic environment, the rate of production of each mobile species is given by

$$\Gamma_{\text{H}^+} = \dot{C}_{\text{Sp}} = \dot{\beta}_2 C_{\text{P}}, \quad \Gamma_k = 0 \quad (k \neq \text{H}^+)
\tag{3.82}$$

then we obtain

$$u_{\text{dif}} = \mu \dot{C} + \sum_k^N \mu_k \dot{C}_k - \dot{\beta}_2 C_{\text{P}} - \left(\mathbf{J} \cdot \nabla_X \mu + \sum_k^N \mathbf{J}_k \cdot \nabla_X \mu_k \right)
\tag{3.83}$$

The power due to the bonding and dissociation of ion and functional group pairs is expressed as follows,

$$\begin{aligned}
u_{\text{dis}} &= -\Delta\mu_1\dot{\beta}_1C_P - \Delta\mu_3\dot{\beta}_3C_P \\
&= -\Delta\mu_1\dot{\beta}_1C_P - \Delta\mu_3(-\dot{\beta}_1 - \dot{\beta}_2)C_P \\
&= (\Delta\mu_3 - \Delta\mu_1)\dot{\beta}_1C_P + \Delta\mu_3\dot{\beta}_2C_P
\end{aligned} \tag{3.84}$$

where the constant $\Delta\mu_1$ and $\Delta\mu_3$ represent the change in chemical potentials due to the isomerization and protonation. It is noted that for the spiropyran-based hydrogel this formula applies to the strong acidic condition.

With regard to the Helmholtz free energy density W , it consists of polymer-solvent mixing energy W_{mix} , energy due to stretching the polymeric network W_{net} , the entropy of solvent-ions mixing energy W_{ion} , the fixed-group mixing energy W_{fix} , and the energy due to electrostatic field W_{el} .

The polymer-solvent mixing energy is given by [186]

$$W_{\text{mix}} = k_B N_A T C \left(\ln \frac{\Omega C}{1 + \Omega C} + \frac{\chi}{1 + \Omega C} + G_{RH}^* C_{\text{Sp}} \right) \tag{3.85}$$

where χ is the Flory-Huggins interaction parameter between the polymer and solution. The first two terms in **Equation** (3.85) refer to the polymer-solvent interaction without the chromophores, given by Flory-Huggins theory. For the spiropyran-based hydrogel, Sumaru *et al.* demonstrated that the hydrophobic groups can disrupt the hydration state of polymeric chains, and then result in a drastic phase transition of the whole network [141, 143, 148]. Therefore, the last term $G_{RH}^* C_{\text{Sp}}$ represents this photo-induced reduction in the hydration of the

polymeric network [170]. This term is proportional to the concentration of Sp form C_{Sp} , represented by the coefficient G_{RH}^* (L/mol). Differentiating

Equation (3.85) with respect to time, we obtain

$$\begin{aligned}
\dot{W}_{\text{mix}} &= k_B N_A T \dot{C} \left(\ln \frac{\Omega C}{1 + \Omega C} + \frac{\chi}{1 + \Omega C} + G_{RH}^* C_{Sp} \right) \\
&\quad + k_B N_A T \dot{C} \frac{1 + (1 - \chi) \Omega C}{(1 + \Omega C)^2} + k_B N_A T C G_{RH}^* \dot{C}_{Sp} \\
&= k_B N_A T \dot{C} \left[\ln \frac{\Omega C}{1 + \Omega C} + \frac{\chi}{1 + \Omega C} + G_{RH}^* C_P \beta_2 \right] + k_B N_A T C G_{RH}^* C_P \dot{\beta}_2
\end{aligned}
\tag{3.86}$$

The free energy density regarding elastic deformation of the polymeric network is written by [186]

$$W_{\text{net}} = \frac{1}{2} N_R k_B T [\text{tr}(\mathbf{C}) - 2 \ln J - 3] \tag{3.87}$$

where N_R is defined as the number of polymeric chains per unit reference volume.

Differentiating **Equation** (3.87) with respect to time, we obtain

$$\begin{aligned}
\dot{W}_{\text{net}} &= \frac{1}{2} N_R k_B T \frac{d}{dt} (\mathbf{I} : \mathbf{C} - 2 \ln J - 3) \\
&= \frac{1}{2} N_R k_B T \left(\mathbf{I} : \dot{\mathbf{C}} - 2 \frac{\dot{J}}{J} \right) \\
&= \frac{1}{2} N_R k_B T \left[\mathbf{I} : (2 \mathbf{F}^T \cdot \mathbf{D} \cdot \mathbf{F}) - 2 \frac{\frac{d}{dt}(1 + \Omega C)}{1 + \Omega C} \right] \\
&= N_R k_B T \left[(\mathbf{F} \cdot \mathbf{F}^T) : \mathbf{D} - \frac{\Omega \dot{C}}{1 + \Omega C} \right]
\end{aligned}
\tag{3.88}$$

The free energy density due to the entropy of solvent-ion mixing free energy is

written by [186]

$$W_{\text{ion}} = k_{\text{B}} N_{\text{A}} T \sum_k^N C_k \left(\ln \frac{C_k}{C} + \ln a_k - 1 \right) \quad (3.89)$$

Differentiating **Equation** (3.89) with respect to time, we obtain

$$\dot{W}_{\text{ion}} = k_{\text{B}} N_{\text{A}} T \sum_k^N \left[\dot{C}_k \left(\ln \frac{C_k}{C} + \ln a_k - 1 \right) + C_k \left(\frac{\dot{C}_k}{C_k} - \frac{\dot{C}}{C} + \frac{1}{a_k} \frac{\partial a_k}{\partial C_k} \dot{C}_k \right) \right] \quad (3.90)$$

The energy due to the mixing of non-charged and charged bound groups on polymeric chains is given by [186]

$$W_{\text{fix}} = k_{\text{B}} N_{\text{A}} T C_{\text{P}} [\beta_1 \ln \beta_1 + \beta_2 \ln \beta_2 + (1 - \beta_1 - \beta_2) \ln (1 - \beta_1 - \beta_2)] \quad (3.91)$$

Differentiating **Equation** (3.91) with respect to time, we obtain

$$\begin{aligned} \dot{W}_{\text{fix}} &= k_{\text{B}} N_{\text{A}} T C_{\text{P}} \left[\dot{\beta}_1 \ln \beta_1 + \dot{\beta}_1 + \dot{\beta}_2 \ln \beta_2 + \dot{\beta}_2 \right. \\ &\quad \left. - (\dot{\beta}_1 + \dot{\beta}_2) \ln (1 - \beta_1 - \beta_2) - \dot{\beta}_1 - \dot{\beta}_2 \right] \\ &= k_{\text{B}} N_{\text{A}} T C_{\text{P}} \left(\dot{\beta}_1 \ln \frac{\beta_1}{1 - \beta_1 - \beta_2} + \dot{\beta}_2 \ln \frac{\beta_2}{1 - \beta_1 - \beta_2} \right) \end{aligned} \quad (3.92)$$

The free energy density of the electrostatic field is expressed by [186]

$$W_{\text{el}} = \frac{1}{2 \epsilon_r \epsilon_0 J} \mathbf{H} \cdot \mathbf{C} \cdot \mathbf{H} \quad (3.93)$$

Differentiating **Equation** (3.93) with respect to time, we obtain

$$\begin{aligned}
\dot{W}_{\text{el}} &= \frac{J \frac{d}{dt}(\mathbf{H} \cdot \mathbf{C} \cdot \mathbf{H}) - \dot{J}(\mathbf{H} \cdot \mathbf{C} \cdot \mathbf{H})}{2\varepsilon_r \varepsilon_0 J^2} \\
&= \frac{J \frac{d}{dt}(\mathbf{H} \cdot \mathbf{C} \cdot \mathbf{H}) - (J\mathbf{I}:D)(\mathbf{H} \cdot \mathbf{C} \cdot \mathbf{H})}{2\varepsilon_r \varepsilon_0 J^2} \\
&= \frac{1}{2\varepsilon_r \varepsilon_0 J} \left[\dot{\mathbf{H}} \cdot \mathbf{C} \cdot \mathbf{H} + \mathbf{H} \cdot \dot{\mathbf{C}} \cdot \mathbf{H} + \mathbf{H} \cdot \mathbf{C} \cdot \dot{\mathbf{H}} - (\mathbf{I}:D)(\mathbf{H} \cdot \mathbf{C} \cdot \mathbf{H}) \right] \\
&= \frac{1}{2\varepsilon_r \varepsilon_0 J} \left[2\mathbf{H} \cdot \mathbf{C} \cdot \dot{\mathbf{H}} + \mathbf{H} \cdot \dot{\mathbf{C}} \cdot \mathbf{H} - (\mathbf{I}:D)(\mathbf{H} \cdot \mathbf{C} \cdot \mathbf{H}) \right] \\
&= \mathbf{E} \cdot \dot{\mathbf{H}} + \frac{1}{2\varepsilon_r \varepsilon_0 J} \left[\mathbf{H} \cdot \dot{\mathbf{C}} \cdot \mathbf{H} - (\mathbf{I}:D)(\mathbf{H} \cdot \mathbf{C} \cdot \mathbf{H}) \right] \\
&= \mathbf{E} \cdot \dot{\mathbf{H}} + \frac{1}{2\varepsilon_r \varepsilon_0 J} \left[\mathbf{H} \cdot (2\mathbf{F}^T \cdot \mathbf{D} \cdot \mathbf{F}) \cdot \mathbf{H} - (\mathbf{I}:D)(\mathbf{H} \cdot \mathbf{F}^T \cdot \mathbf{F} \cdot \mathbf{H}) \right] \\
&= \mathbf{E} \cdot \dot{\mathbf{H}} + \frac{J}{\varepsilon_r \varepsilon_0} \mathbf{h} \cdot \mathbf{D} \cdot \mathbf{h} - \frac{J}{2\varepsilon_r \varepsilon_0} (\mathbf{I}:D)(\mathbf{h} \cdot \mathbf{h}) \\
&= \mathbf{E} \cdot \dot{\mathbf{H}} + \frac{J}{\varepsilon_r \varepsilon_0} (\mathbf{h} \otimes \mathbf{h}):D - \frac{J}{2\varepsilon_r \varepsilon_0} (\mathbf{h} \cdot \mathbf{h})\mathbf{I}:D \\
&= \mathbf{E} \cdot \dot{\mathbf{H}} + \frac{J}{2\varepsilon_r \varepsilon_0} [2(\mathbf{h} \otimes \mathbf{h}) - (\mathbf{h} \cdot \mathbf{h})\mathbf{I}]:D
\end{aligned}
\tag{3.94}$$

Therefore, the sum of free energy is expressed as follows:

$$W = W_{\text{mix}} + W_{\text{net}} + W_{\text{ion}} + W_{\text{fix}} + W_{\text{el}} \tag{3.95}$$

$$\dot{W} = \dot{W}_{\text{mix}} + \dot{W}_{\text{net}} + \dot{W}_{\text{ion}} + \dot{W}_{\text{fix}} + \dot{W}_{\text{el}} \tag{3.96}$$

Then the left-hand term in **Equation** (3.68) is detailed as follows:

$$\begin{aligned}
& \dot{W} - u_{\text{mech}} - u_{\text{el}} - u_{\text{dif}} - u_{\text{dis}} \\
&= \left\{ N_{\text{R}} k_{\text{B}} T (\mathbf{F} \cdot \mathbf{F}^{\text{T}}) - J \boldsymbol{\sigma} \frac{J}{2 \varepsilon_r \varepsilon_0} [2(\mathbf{h} \otimes \mathbf{h}) - (\mathbf{h} \cdot \mathbf{h}) \mathbf{I}] \right\} : \mathbf{D} \\
&+ \left\{ k_{\text{B}} N_{\text{A}} T \left[\ln \frac{\Omega C}{1 + \Omega C} + \frac{1 + \chi + \Omega C}{(1 + \Omega C)^2} + G_{\text{RH}}^* \beta_2 C_{\text{P}} \right] \right. \\
&\quad \left. - \frac{N_{\text{R}} k_{\text{B}} T \Omega}{1 + \Omega C} - k_{\text{B}} N_{\text{A}} T \sum_k^N \frac{C_k}{C} - \mu \right\} \dot{C} \\
&+ \sum_k^N \left[N_{\text{A}} k_{\text{B}} T \left(\ln \frac{C_k}{C} + \ln a_k \right) + \frac{C_k}{a_k} \frac{\partial a_k}{\partial C_k} + F \psi z_k - \mu_k \right] \dot{C}_k \\
&+ \left(\Delta \mu_1 - \Delta \mu_3 + N_{\text{R}} k_{\text{B}} T \ln \frac{\beta_1}{1 - \beta_1 - \beta_2} \right) \dot{\beta}_1 C_{\text{P}} \\
&+ \left[N_{\text{R}} k_{\text{B}} T \left(C G_{\text{RH}}^* + \ln \frac{\beta_2}{1 - \beta_1 - \beta_2} \right) - \Delta \mu_3 \right] \dot{\beta}_2 C_{\text{P}} \\
&+ \left(\mathbf{J} \cdot \nabla_X \mu + \sum_k^N \mathbf{J}_k \cdot \nabla_X \mu_k \right)
\end{aligned} \tag{3.97}$$

The molecular incompressibility, characterized by **Equation** (3.44), is differentiated with respect to the time as follows,

$$\Omega \dot{C} - J \mathbf{I} : \mathbf{D} = 0 \tag{3.98}$$

Since the above condition must be satisfied, we multiply **Equation** (3.98) by an arbitrary function Π and rewrite **Equation** (3.68) as follows,

$$\dot{W} - u_{\text{mech}} - u_{\text{el}} - u_{\text{dif}} - u_{\text{dis}} + \Pi (\Omega \dot{C} - J \mathbf{I} : \mathbf{D}) \leq 0 \tag{3.99}$$

The final expression of imbalance of free energy is rewritten as detailed below

$$\begin{aligned}
& \left\{ N_{\text{R}} k_{\text{B}} T (\mathbf{F} \cdot \mathbf{F}^{\text{T}}) - J \boldsymbol{\sigma} \frac{J}{2 \varepsilon_r \varepsilon_0} [2(\mathbf{h} \otimes \mathbf{h}) - (\mathbf{h} \cdot \mathbf{h}) \mathbf{I}] - J \Pi \mathbf{I} \right\} : \mathbf{D} \\
& + \left\{ k_{\text{B}} N_{\text{A}} T \left[\ln \frac{\Omega C}{1 + \Omega C} + \frac{1 + \chi + \Omega C}{(1 + \Omega C)^2} + G_{\text{RH}}^* \beta_2 C_{\text{P}} \right] \right. \\
& \quad \left. - \frac{N_{\text{R}} k_{\text{B}} T \Omega}{1 + \Omega C} - k_{\text{B}} N_{\text{A}} T \sum_k^N \frac{C_k}{C} - \mu + \Pi \Omega \right\} \dot{C} \\
& + \sum_k^N \left[N_{\text{R}} k_{\text{B}} T \left(\ln \frac{C_k}{C} + \ln a_k \right) + \frac{C_k}{a_k} \frac{\partial a_k}{\partial C_k} + F \psi z_k - \mu_k \right] \dot{C}_k \\
& + \left(\Delta \mu_1 - \Delta \mu_3 + N_{\text{R}} k_{\text{B}} T \ln \frac{\beta_1}{1 - \beta_1 - \beta_2} \right) \dot{\beta}_1 C_{\text{P}} \\
& + \left[N_{\text{R}} k_{\text{B}} T \left(C G_{\text{RH}}^* + \ln \frac{\beta_2}{1 - \beta_1 - \beta_2} \right) - \Delta \mu_3 \right] \dot{\beta}_2 C_{\text{P}} \\
& + \left(\mathbf{J} \cdot \nabla_X \mu + \sum_k^N \mathbf{J}_k \cdot \nabla_X \mu_k \right)
\end{aligned}
\tag{3.100}$$

Substituting **Equations** (3.51) and (3.52) into the last term of **Equation** (3.83), it is proved to be less than zero all the time. Since $\mathbf{D}$, C , C_k , β_1 and β_2 are now arbitrary functions, it is thus conclude that to ensure the above equation to be fulfilled, the following constitutive relations must be achieved,

$$\boldsymbol{\sigma} = \frac{1}{J} N_{\text{R}} k_{\text{B}} T (\mathbf{F} \cdot \mathbf{F}^{\text{T}}) + \frac{1}{\varepsilon_r \varepsilon_0} \mathbf{h} \otimes \mathbf{h} - \frac{1}{2 \varepsilon_r \varepsilon_0} (\mathbf{h} \cdot \mathbf{h}) \mathbf{I} - \Pi \mathbf{I}
\tag{3.101}$$

$$\begin{aligned}
\mu &= k_{\text{B}} N_{\text{A}} T \left(\ln \frac{\Omega C}{1 + \Omega C} + \frac{1 + \chi + \Omega C}{(1 + \Omega C)^2} + G_{\text{RH}}^* \beta_2 C_{\text{P}} - \sum_k^N \frac{C_k}{C} \right) - \\
& \quad \frac{N_{\text{R}} k_{\text{B}} T \Omega}{1 + \Omega C} + \Pi \Omega
\end{aligned}
\tag{3.102}$$

$$\mu_k = F\psi z_k + k_B N_A T \left(\ln \frac{C_k}{C} + \ln a_k \right) + \frac{C_k}{a_k} \frac{\partial a_k}{\partial C_k} \quad (3.103)$$

$$\Delta\mu_3 - \Delta\mu_1 = k_B N_A T \ln \frac{\beta_1}{1 - \beta_1 - \beta_2} \quad (3.104)$$

$$\Delta\mu_3 = k_B N_A T \left(CG_{RH}^* + \ln \frac{\beta_1}{1 - \beta_1 - \beta_2} \right) \quad (3.105)$$

It is estimated that the characteristic value of Maxwell stress is less than 10^3 Pa, which is negligible considering that the order of characteristic elastic modulus is 10^5 Pa for a hydrogel [196]. Hence, it is reasonable to neglect the Maxwell stress to simplify the model. Then the constitutive relation is rewritten as follows:

$$\boldsymbol{\sigma} = \frac{1}{J} N_R k_B T (\mathbf{F} \cdot \mathbf{F}^T) - \Pi \mathbf{I} \quad (3.106)$$

Then the Piola stress is given by

$$\mathbf{P} = J \mathbf{F}^{-1} \cdot \boldsymbol{\sigma} = N_R k_B T \mathbf{F}^T - J \Pi \mathbf{F}^{-1} \quad (3.107)$$

At last, the equation for the mechanical equilibrium in **Equation** (3.62) is rewritten as follows:

$$\nabla_X \cdot (N_R k_B T \mathbf{F}^T - J \Pi \mathbf{F}^{-1}) = \vec{0} \quad (3.108)$$

So far, the development of MECp model has been finished. To summarize, **Equations** (3.23)-(3.28) and (3.31)-(3.33) are employed for the solution of chemical reaction system, **Equation** (3.55) for the mass conservation, **Equation** (3.62) for the momentum conservation, **Equation** (3.66) for the distributive electrical potential, and **Equation** (3.106) for the constitutive relation.

3.2 Solution procedures

In Section 3.1.5, the constitutive equations are obtained in the form of tensor based on the reference coordinate system. In this section, the algebraic form of governing equations is derived under different coordinate systems. In the practice, the block and cylinder are both common shapes among hydrogels. Therefore, we focus on the coordinate transformation between the Euler system and Lagrange system under rectangular coordinates and cylindrical coordinates. After that, we present an introduction on the computational method and software that are used in this study.

3.2.1 Governing equations in different coordinate systems

For a three-dimensional case under rectangular coordinates, we use (x_1, x_2, x_3) and (X_1, X_2, X_3) to represent the coordinates of Euler system and Lagrange system, respectively. In this work, the swelling or shrinking of a hydrogel is assumed to be linearly elastic, and its bending and rotating movements are not considered. Therefore, the mapping relationship between (x_1, x_2, x_3) and (X_1, X_2, X_3) is expressed as follows:

$$\frac{\partial x_1}{\partial X_1} = \lambda_1, \quad \frac{\partial x_2}{\partial X_2} = \lambda_2, \quad \frac{\partial x_3}{\partial X_3} = \lambda_3 \quad (3.109)$$

where λ_1 , λ_2 , and λ_3 are stretches along three directions under rectangular coordinates, respectively.

Then the deformation gradient tensor in the current state reads

$$\mathbf{F} = F_{i,j} \vec{\mathbf{e}}_i \otimes \vec{\mathbf{E}}_j, \quad (i = x_1, x_2, x_3 \text{ and } j = X_1, X_2, X_3) \quad (3.110)$$

where $\vec{\mathbf{e}}_i$ and $\vec{\mathbf{E}}_j$ stands for the unit base vector along i direction and j direction under (x_1, x_2, x_3) and (X_1, X_2, X_3) , respectively. The component $F_{i,j}$ is expressed in the form of matrix as follows:

$$F_{i,j} = \frac{\partial x_i}{\partial X_j} = \begin{bmatrix} \frac{\partial x_1}{\partial X_1} & \frac{\partial x_1}{\partial X_2} & \frac{\partial x_1}{\partial X_3} \\ \frac{\partial x_2}{\partial X_1} & \frac{\partial x_2}{\partial X_2} & \frac{\partial x_2}{\partial X_3} \\ \frac{\partial x_3}{\partial X_1} & \frac{\partial x_3}{\partial X_2} & \frac{\partial x_3}{\partial X_3} \end{bmatrix} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix} \quad (3.111)$$

Then the transpose and inverse tensors of the deformation gradient are written as follows:

$$(F^T)_{i,j} = F_{j,i} = \frac{\partial x_j}{\partial X_i} = \begin{bmatrix} \frac{\partial x_1}{\partial X_1} & \frac{\partial x_2}{\partial X_1} & \frac{\partial x_3}{\partial X_1} \\ \frac{\partial x_1}{\partial X_2} & \frac{\partial x_2}{\partial X_2} & \frac{\partial x_3}{\partial X_2} \\ \frac{\partial x_1}{\partial X_3} & \frac{\partial x_2}{\partial X_3} & \frac{\partial x_3}{\partial X_3} \end{bmatrix} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix} \quad (3.112)$$

$$(F^{-1})_{i,j} = \begin{bmatrix} 1/\lambda_1 & 0 & 0 \\ 0 & 1/\lambda_2 & 0 \\ 0 & 0 & 1/\lambda_3 \end{bmatrix} \quad (3.113)$$

The component of Cauchy-Green tensor reads

$$C_{i,j} = (F^T)_{i,k} F_{k,j} = \begin{bmatrix} \lambda_1^2 & 0 & 0 \\ 0 & \lambda_2^2 & 0 \\ 0 & 0 & \lambda_3^2 \end{bmatrix} \quad (3.114)$$

The inverse of Cauchy-Green tensor is given as

$$(C^{-1})_{i,j} = \begin{bmatrix} 1/\lambda_1^2 & 0 & 0 \\ 0 & 1/\lambda_2^2 & 0 \\ 0 & 0 & 1/\lambda_3^2 \end{bmatrix} \quad (3.115)$$

The referential divergence operator under rectangular coordinates reads

$$\nabla_X = \frac{\partial}{\partial X_k} \vec{E}_k \quad (k = 1, 2, 3) \quad (3.116)$$

The Jacobian determinant is written as follows,

$$J = \lambda_1 \lambda_2 \lambda_3 \quad (3.117)$$

Substituting **Equations** (3.111)-(3.117) into **Equations** (3.39), (3.65), and (3.108), we obtain

$$\begin{aligned} \frac{\partial c_k}{\partial t} = & D_k \left[\left(\frac{1}{\lambda_1^2} \frac{\partial^2 c_k}{\partial X_1^2} + \frac{1}{\lambda_2^2} \frac{\partial^2 c_k}{\partial X_2^2} + \frac{1}{\lambda_3^2} \frac{\partial^2 c_k}{\partial X_3^2} \right) + \right. \\ & \frac{z_k F}{k_B N_A T} \left(\frac{1}{\lambda_1^2} \frac{\partial c_k}{\partial X_1} \frac{\partial \psi}{\partial X_1} + \frac{1}{\lambda_2^2} \frac{\partial c_k}{\partial X_2} \frac{\partial \psi}{\partial X_2} + \frac{1}{\lambda_3^2} \frac{\partial c_k}{\partial X_3} \frac{\partial \psi}{\partial X_3} \right) + \\ & \frac{z_k F}{k_B N_A T} \left(\frac{1}{\lambda_1^2} \frac{\partial^2 \psi}{\partial X_1^2} + \frac{1}{\lambda_2^2} \frac{\partial^2 \psi}{\partial X_2^2} + \frac{1}{\lambda_3^2} \frac{\partial^2 \psi}{\partial X_3^2} \right) + \\ & \left(\frac{1}{\lambda_1^2} \frac{\partial c_k}{\partial X_1} \frac{\partial \ln a_k}{\partial X_1} + \frac{1}{\lambda_2^2} \frac{\partial c_k}{\partial X_2} \frac{\partial \ln a_k}{\partial X_2} + \frac{1}{\lambda_3^2} \frac{\partial c_k}{\partial X_3} \frac{\partial \ln a_k}{\partial X_3} \right) + \\ & \left. c_k \left(\frac{1}{\lambda_1^2} \frac{\partial^2 \ln a_k}{\partial X_1^2} + \frac{1}{\lambda_2^2} \frac{\partial^2 \ln a_k}{\partial X_2^2} + \frac{1}{\lambda_3^2} \frac{\partial^2 \ln a_k}{\partial X_3^2} \right) \right] + \nu_k r_k \\ & (k = H^+, Na^+, Cl^-, \dots, N) \end{aligned} \quad (3.118)$$

$$\begin{aligned} \frac{1}{\lambda_1^2} \frac{\partial^2 \psi}{\partial X_1^2} + \frac{1}{\lambda_2^2} \frac{\partial^2 \psi}{\partial X_2^2} + \frac{1}{\lambda_3^2} \frac{\partial^2 \psi}{\partial X_3^2} = & - \frac{F}{\varepsilon_r \varepsilon_0} \left(\sum_k^N z_k c_k + \sum_f^{N_f} z_f c_f \right) \\ & (k = H^+, Na^+, Cl^-, \dots, N) \end{aligned} \quad (3.119)$$

$$\begin{aligned}
& \left(N_{\text{R}} k_{\text{B}} T + \frac{\lambda_2 \lambda_3 \Pi}{\lambda_1} \right) \frac{\partial \lambda_1}{\partial X_1} \vec{E}_{X_1} + \left(N_{\text{R}} k_{\text{B}} T + \frac{\lambda_1 \lambda_3 \Pi}{\lambda_2} \right) \frac{\partial \lambda_2}{\partial X_2} \vec{E}_{X_2} \\
& + \left(N_{\text{R}} k_{\text{B}} T + \frac{\lambda_1 \lambda_2 \Pi}{\lambda_3} \right) \frac{\partial \lambda_3}{\partial X_3} \vec{E}_{X_3} = \vec{0}
\end{aligned}
\tag{3.120}$$

The above equations are the form of Poisson-Nernst-Planck equation and mechanical equilibrium equation under the rectangular coordinates based on Lagrange system.

If we use $\lambda_i = 1 + \frac{\partial u_i}{\partial X_i}$ to represent the displacement in x_i direction

u_i ($i = 1, 2, 3$), **Equation** (3.120) is rewritten as follows:

$$\begin{cases}
N_{\text{R}} k_{\text{B}} T \left(1 + \frac{\partial u_1}{\partial X_1} \right) + \Pi \left(1 + \frac{\partial u_2}{\partial X_2} \right) \left(1 + \frac{\partial u_3}{\partial X_3} \right) = 0 \\
N_{\text{R}} k_{\text{B}} T \left(1 + \frac{\partial u_2}{\partial X_2} \right) + \Pi \left(1 + \frac{\partial u_1}{\partial X_1} \right) \left(1 + \frac{\partial u_3}{\partial X_3} \right) = 0 \\
N_{\text{R}} k_{\text{B}} T \left(1 + \frac{\partial u_3}{\partial X_3} \right) + \Pi \left(1 + \frac{\partial u_1}{\partial X_1} \right) \left(1 + \frac{\partial u_2}{\partial X_2} \right) = 0
\end{cases}
\tag{3.121}$$

With respect to the cylindrical coordinates, we use (x, θ, z) and (X, Θ, Z) to denote the coordinates of Euler system and Lagrange system, respectively. The mapping relationship is demonstrated as follows:

$$x = g(X, t), \theta = \Theta, z = f(Z, t) \tag{3.122}$$

$$\lambda_z = \frac{\partial f(Z, t)}{\partial Z}, \lambda_x = \frac{\partial g(X, t)}{\partial X} \tag{3.123}$$

The referential divergence operator under cylindrical coordinates reads

$$\nabla_x = \frac{\partial}{\partial X} \vec{E}_x + \frac{1}{X} \frac{\partial}{\partial \Theta} \vec{E}_\Theta + \frac{\partial}{\partial Z} \vec{E}_z \tag{3.124}$$

where $\vec{E}_i (i = X, \Theta, Z)$ denotes the unit vector along i direction under (X, Θ, Z) coordinate. The deformation gradient tensor is written as follows:

$$\mathbf{F} = F_{ij} \vec{e}_i \otimes \vec{E}_j = \mathbf{I} + \mathbf{u} \nabla_X \quad (i = x, \theta, z \text{ and } j = X, \Theta, Z) \quad (3.125)$$

where $\mathbf{u}$ represents the displacement based on Euler system. Then the component form reads

$$F_{ij} = \begin{bmatrix} 1 + \frac{\partial u_x}{\partial X} & \frac{1}{X} \frac{\partial u_x}{\partial \Theta} - \frac{u_\theta}{X} & \frac{\partial u_x}{\partial Z} \\ \frac{\partial u_\theta}{\partial X} & 1 + \frac{1}{X} \frac{\partial u_\theta}{\partial \Theta} + \frac{u_x}{X} & \frac{\partial u_\theta}{\partial Z} \\ \frac{\partial u_z}{\partial X} & \frac{1}{X} \frac{\partial u_z}{\partial \Theta} & 1 + \frac{\partial u_z}{\partial Z} \end{bmatrix} = \begin{bmatrix} \lambda_x & 0 & 0 \\ 0 & \lambda_\theta & 0 \\ 0 & 0 & \lambda_z \end{bmatrix} \quad (3.126)$$

where $u_i (i = x, \theta, z)$ is the displacement component along i direction under (x, θ, z) coordinate, and $\lambda_\theta = \frac{x}{X}$. The Jacobian determinant is expressed as detailed below:

$$J = \lambda_x \lambda_\theta \lambda_z \quad (3.127)$$

The component matrix of inverse of Cauchy-Green tensor is written as follows,

$$(C^{-1})_{i,j} = \begin{bmatrix} 1/\lambda_x^2 & 0 & 0 \\ 0 & 1/\lambda_\theta^2 & 0 \\ 0 & 0 & 1/\lambda_z^2 \end{bmatrix} \quad (3.128)$$

Substituting **Equations** (3.124)-(3.128) into **Equations** (3.39), (3.65), and (3.108), we obtain

$$\begin{aligned}
\frac{\partial c_k}{\partial t} = & D_k \left[\left(\frac{1}{\lambda_x^2} \frac{\partial^2 c_k}{\partial X^2} + \frac{1}{\lambda_x \lambda_\theta X} \frac{\partial c_k}{\partial X} + \frac{1}{\lambda_\theta^2 X^2} \frac{\partial^2 c_k}{\partial \Theta^2} + \frac{1}{\lambda_z^2} \frac{\partial^2 c_k}{\partial Z^2} \right) + \right. \\
& \frac{z_k F}{k_B N_A T} \left(\frac{1}{\lambda_x^2} \frac{\partial c_k}{\partial X} \frac{\partial \psi}{\partial X} + \frac{1}{\lambda_\theta^2 X^2} \frac{\partial c_k}{\partial \Theta} \frac{\partial \psi}{\partial \Theta} + \frac{1}{\lambda_z^2} \frac{\partial c_k}{\partial Z} \frac{\partial \psi}{\partial Z} \right) + \\
& \frac{z_k F}{k_B N_A T} c_k \left(\frac{1}{\lambda_x^2} \frac{\partial^2 \psi}{\partial X^2} + \frac{1}{\lambda_x \lambda_\theta X} \frac{\partial \psi}{\partial X} + \frac{1}{\lambda_\theta^2 X^2} \frac{\partial^2 \psi}{\partial \Theta^2} + \frac{1}{\lambda_z^2} \frac{\partial^2 \psi}{\partial Z^2} \right) + \\
& \left(\frac{1}{\lambda_x^2} \frac{\partial c_k}{\partial X} \frac{\partial \ln a_k}{\partial X} + \frac{1}{\lambda_\theta^2 X^2} \frac{\partial c_k}{\partial \Theta} \frac{\partial \ln a_k}{\partial \Theta} + \frac{1}{\lambda_z^2} \frac{\partial c_k}{\partial Z} \frac{\partial \ln a_k}{\partial Z} \right) \\
& \left. + c_k \left(\frac{1}{\lambda_x^2} \frac{\partial^2 \ln a_k}{\partial X^2} + \frac{1}{\lambda_x \lambda_\theta X} \frac{\partial \ln a_k}{\partial X} + \frac{1}{\lambda_\theta^2 X^2} \frac{\partial^2 \ln a_k}{\partial \Theta^2} + \frac{1}{\lambda_z^2} \frac{\partial^2 \ln a_k}{\partial Z^2} \right) \right] \\
& + \nu_k r_k \\
& (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N)
\end{aligned}$$

(3.129)

$$\begin{aligned}
& \frac{1}{\lambda_x^2} \frac{\partial^2 \psi}{\partial X^2} + \frac{1}{\lambda_x \lambda_\theta X} \frac{\partial \psi}{\partial X} + \frac{1}{\lambda_\theta^2 X^2} \frac{\partial^2 \psi}{\partial \Theta^2} + \frac{1}{\lambda_z^2} \frac{\partial^2 \psi}{\partial Z^2} \\
& = - \frac{F}{\varepsilon_r \varepsilon_0} \left(\sum_k^N z_k c_k + \sum_f^{N_f} z_f c_f \right) \\
& (k = \text{H}^+, \text{Na}^+, \text{Cl}^-, \dots, N)
\end{aligned} \tag{3.130}$$

$$\begin{aligned}
& \left(\frac{\partial}{\partial X} \vec{\mathbf{E}}_X + \frac{1}{X} \frac{1}{\partial \Theta} \vec{\mathbf{E}}_\Theta + \frac{\partial}{\partial Z} \vec{\mathbf{E}}_Z \right) \cdot \left[(\lambda_x N_R k_B T - \lambda_\theta \lambda_z \Pi) \vec{\mathbf{e}}_x \vec{\mathbf{E}}_X \right. \\
& \left. + (\lambda_\theta N_R k_B T - \lambda_x \lambda_z \Pi) \vec{\mathbf{e}}_\theta \vec{\mathbf{E}}_\Theta + (\lambda_z N_R k_B T - \lambda_x \lambda_\theta \Pi) \vec{\mathbf{e}}_z \vec{\mathbf{E}}_Z \right] = \vec{0} \\
& (3.131)
\end{aligned}$$

The component form of **Equation** (3.131) is written as follows,

$$\begin{cases} \frac{\partial}{\partial X} (N_R k_B T \lambda_x - \Pi \lambda_\theta \lambda_z) + \frac{1}{X} (N_R k_B T + \Pi \lambda_z) (\lambda_x - \lambda_\theta) = 0 \\ \frac{\partial}{\partial \Theta} (N_R k_B T \lambda_\theta - \Pi \lambda_x \lambda_z) = 0 \\ \frac{\partial}{\partial Z} (N_R k_B T \lambda_z - \Pi \lambda_x \lambda_\theta) = 0 \end{cases} \tag{3.132}$$

Figure 3. 2. Scheme of one-dimensional computational model of a photo-sensitive hydrogel sphere.

As illustrated in **Figure 3. 2**, consider a free-standing spherical hydrogel at steady-state condition, the swelling stretch is viewed to be uniform, denoted by $\lambda = J^{1/3}$. Hence, the computational domain can be reduced to one-dimensional model due to the symmetry. The Neumann-type boundary conditions are imposed at the center of gel membrane, as detailed below

$$\frac{\partial C}{\partial X} = 0, \quad \frac{\partial C_k}{\partial X} = 0, \quad \frac{\partial \psi}{\partial X} = 0 \quad \text{at } X = 0 \quad (3.133)$$

while the Dirichlet boundary conditions are set on the edge of bath solution, given as follows,

$$C = \bar{C}, C_k = \bar{C}_k, \psi = 0 \text{ at } X = L_{\text{gel}} + L_{\text{sol}} \quad (3.134)$$

where the overbar refers to the parameters in the bath solution. At the equilibrium state, the electrochemical potential of solvent in a gel coincide with that in the bath, given by [198, 199]

$$\mu = \bar{\mu} = -k_B N_A T \sum_k^N \Omega \bar{C}_k \quad (3.135)$$

Substituting **Equation (3.135)** into **Equation (3.102)**, we obtain

$$\Pi = \frac{N_A k_B T}{J} + N_A k_B T \sum_k^N \left(\frac{C_k}{J-1} - \bar{C}_k \right) - \frac{k_B N_A T}{\Omega} \left(\ln \frac{J-1}{J} + \frac{\chi}{J^2} + \frac{1}{J} + G_{\text{RH}}^* \beta_2 C_P \right) \quad (3.136)$$

3.2.2 Computational implementation

In this work, we only focus on one-dimensional steady-state simulations of the theoretical model. The procedure for numerical solution of MECp model is illustrated in **Figure 3.3**, where the computation is performed using COMSOL Multiphysics, a commercial finite-element solver, which is known to solve general partial differential equations (PDEs). Among all the modules in this software, “General form” module is chosen to work as the platform, such that the model is directly written in the form of PDEs.

Figure 3.3. Scheme of numerical simulation with MECp model.

As illustrated in **Figure 3.3**, the input parameters are designated initially, and then the value of local pH is checked. If the local pH is smaller than $(\log K_{a1}K_{a2})/2$, the concentration of fixed charged species C_f is computed through **Equations** (3.26)-(3.28), (3.31) and (3.32), based on the assumption characterized by **Equation** (3.4). Otherwise, the computation is conducted in terms of **Equations** (3.23)-(3.25), (3.31) and (3.32), based on the assumption by **Equation** (3.3). After that, the computational value of C_f is used in the

solution of Poisson-Nernst-Planck equations (3.55) and (3.66) to obtain the values of ionic concentration C_k and electrical potential ψ . If the errors satisfy the tolerance requirement, the value of swelling stretch λ is updated through **Equation** (3.62). If the tolerance requirement can not be met, all the values of independent variables are returned to the initial step to conduct the next computational loop until the computational results converge.

In this way, the PDEs and coefficients are defined and input by users, respectively, and then the non-linear solver Density Matrix is employed due to its high efficiency. In order to achieve the desired accuracy, a convergence criterion with relative tolerance ε is implemented for all variables. According to the solver algorithm of COMSOL [200], the convergence criterion is given by

$$\left[\frac{1}{m} \sum_{i=1}^m |E_i|^2 \right]^{1/2} < \varepsilon \quad (3.137)$$

where E_i is the estimated error in the latest calculation result to the i^{th} component of the true solution vector, and m the degrees of freedom. Initially, the relative tolerance ε is set to be 10^{-6} . If the simulation results have no distinguishable changes when decreasing the tolerance to values lower than 10^{-6} , the numerical results are thought to converge.

3.3 Validation of the MECp model

The equilibrium swelling ratios of a pSpNIPAAm hydrogel in literature are

employed for the validation of MECp model.

3.3.1 Input parameters

During the published experiment [149], the pSpNIPAAm gel was a disc-shaped sheet with an initial thickness of 1 mm. The equilibrium swelling ratios were measured when the free-standing hydrogel was immersed in 0.5 mM HCl solution, where the light intensity was switched from 0.0 to 5.0 mW/cm² and the temperature ranged from 21 to 40 °C. Here, the normalized diameter was used to characterize the swelling degree of gel sheet, defined as the weight ratio $(m_T/m_0)^{1/3}$ and roughly equal to λ_T/λ_0 , where m_0 and m_T were the weights of the hydrogel at 21 °C in the dark and temperature T , respectively, and λ_0 and λ_T the corresponding swelling stretches [149]. The input simulation parameters are given as $L_{\text{sol}} = 2000 \mu\text{m}$, $C_P = 92 \text{ mM}$, $C_A = 0 \text{ mM}$, $T = 21 - 40$ °C, and $I_L = 0.0 - 5.0 \text{ mW/cm}^2$. Herein, N_R and F_L are estimated through the formulas and experimental results in the literature, including density of polymeric crosslinkers, swelling ratio, and total absorbance ratio of solution [108, 177, 201, 202]. A_T and E_T are determined using the Arrhenius plot to fit the published experimental data on the absorbance of each spiropyran isomer [141]. G_{RH}^* is obtained by fitting the swelling degree of pSpNIPAAm gel at $T = 25$ °C and $I_L = 5.0 \text{ mW/cm}^2$ in the open literature [141, 149, 152]. Here, the Flory-Huggins

interaction parameter is given by [188]

$$\chi = \frac{1}{2}(\chi_L + \chi_H) - \frac{1}{2}(\chi_L - \chi_H) \tanh\left(\frac{T - T_c}{\Delta T_c}\right) \quad (3.138)$$

where T_c is the transition temperature of the gel, χ_L and χ_H stand for the value of χ below and above the transition temperature, and ΔT_c denotes the width of the transition in temperatures between χ_L and χ_H . In this work, T_c and ΔT_c are obtained from the experimental observation, while χ_L and χ_H are determined in terms of the empirical formula in Reference [203]. The remaining parameters are tabulated in **Table 3.2**.

Table 3.2. Some input parameters for numerical simulation.

Parameter	Value
Gas constant, R	$8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Boltzmann constant, k_B	$1.38 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$
Avogadro number, N_A	$6.02 \times 10^{23} \text{ mol}^{-1}$
Faraday constant, F	$96,485.33 \text{ C}\cdot\text{mol}^{-1}$
Planck constant, h	$6.63 \times 10^{-34} \text{ J}\cdot\text{s}$
Light speed, c	$3.0 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
Density of polymeric chains in the dry gel, N_A [201, 202]	$1.08 \times 10^{25} \text{ m}^{-3}$
Photo-kinetic factor, F_L [108, 177]	1.94

Logarithm of frequency factor, $\log (A_T/1 \text{ s}^{-1})$ [141]	16.96
Activation energy, E_a [141]	114.41 kJ·mol ⁻¹
Interaction parameter lower than T_C , χ_L [201]	0.33
Interaction parameter higher than T_C , χ_H [201]	0.62
	$1.8 \times 10^{-3} \text{ mM}^{-1}$ at
Dehydration coefficient, G_{RH}^* [141, 149, 152]	pH<7.0 and 0 mM ⁻¹ at pH≥7.0
Diffusion coefficient, D_k [204]	$(1.33\sim 9.31) \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$
Hydrated radii, l_k [204]	2.82~3.79 Å
Polymer-solvent structural constant, k_1 and k_2	$k_1 = 0.066$ and $k_2 =$
[187]	0.263
Permittivity, $\varepsilon_r, \varepsilon_0$ (water) [205]	$7.08 \times 10^{-10} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$
Dissociation constant of McH ⁺ , K_{a_1} [108]	$10^{-6.8} \text{ M}^2$
Dissociation constant of SpH ⁺ , K_{a_2} [108]	$10^{-2.6} \text{ M}^2$
Dissociation constant of AAH, K_{a_3} [152]	$10^{-4.2} \text{ M}^2$
Equilibrium constant of water, K_w [205]	10^{-14} M^2
Transition temperature, T_C [149]	33 °C
Temperature width of phase transition, ΔT_C	4 °C
[149]	
Molar volume of solvent molecule, Ω [206]	$1.8 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$

Ring-opened reaction rate constant, k_o [151]	$2.53 \times 10^{-3} \text{ s}^{-1}$
Light wavelength, λ_L [149]	436 nm
Quantum yield, ϕ_L [207]	7%
Molar absorption coefficient, ε_L [108]	$2.3 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$

3.3.2 Comparison between experimental and numerical results

Figure 3.4. The comparison of normalized diameter for the pSpNIPAAm gel between the MECp-based simulation and published experiment [149].

Figure 3.4 is plotted for comparison in normalized diameter sizes of a pSpNIPAAm hydrogel between the experimental and simulation results [149], where the simulated normalized diameters agree well with the experiment. In

details, the global error is less than 7.0% and the maximum relative error is only 8.4%. The error above might stem from some assumptions ahead of the model development. In this work, the light irradiation is assumed to be uniform without any attenuation, leading to an underestimated value in the simulation. On the other hand, the light-induced heat is neglected here, which might cause the computational results to be overestimated. Furthermore, **Table 3. 3** tabulates the error calculated in each simulation step in terms of **Equation** (3.137), showing that the convergency of simulation is achieved. Hence, it is concluded that the simulation results are reasonable and the MECp model can predict the responsive behaviors of photo-sensitive hydrogel.

Table 3. 3. The error per iteration step of simulation for the model validation.

Iteration number	1	2	3	4	5
Error	0.66	0.068	0.0045	1.1e-05	3.2e-09

3.4 Analysis of multi-stimuli response behavior of photo-sensitive hydrogels

Photo-sensitive hydrogels have been widely studied as extracellular matrix (ECM), where cell culture depends largely on the microenvironment of biomolecules or cells, including hydration, pH, and electrical attraction [159, 208]. In Section 3.4, based on the MECp model, numerical investigations are conducted to examine the fundamental response of photo-sensitive hydrogels

against the light intensity, buffer pH, ambient temperature, and ionic strength, where we primarily focus on pSpNIPAAm hydrogels loaded with acrylic acid (AA) [151, 152]. Herein, the bath pH level is modulated by addition of NaOH or HCl. Besides, 25 °C and 37 °C are regarded as the room and physiology temperatures [158, 159], respectively. The normalized swelling stretch λ_N is defined as the ratio of current stretch λ to the initial stretch at $I_L = 0.0 \text{ mW/cm}^2$ and $T = 25 \text{ °C}$. In Section 3.4, some input parameters for the material properties are given as $L_{\text{gel}} = 50 \text{ }\mu\text{m}$ and $L_{\text{sol}} = 200 \text{ }\mu\text{m}$, while other parameters and conditions are the same with Section 3.3 if not mentioned.

3.4.1 Mechanical and chemical behaviors in response to light intensity

(a)

(b)

Figure 3.5. The responses of photo-sensitive hydrogel under different AA contents and temperatures as a function of light intensity: (a) normalized swelling stretch and (b) internal pH.

Figure 3.5 shows the normalized swelling stretch λ_N and internal pH, namely the average pH inside the hydrogel, for AA-loaded pSpNIPAAm gels in response to light intensity, where the buffer pH is set as 7.0. As seen in **Figure 3.5(a)**, an insignificant change is initially observed in λ_N with the increase of light intensity, but it collapses drastically when $I_L > 0.5 \text{ mW/cm}^2$ for $C_A = 92 \text{ mM}$ at $T = 25\text{-}31 \text{ }^\circ\text{C}$. Meanwhile, it decreases to about 0.50 if the temperature rises to $37\text{-}40 \text{ }^\circ\text{C}$ or $I_L > 0.0 \text{ mW/cm}^2$ for $C_A = 460 \text{ mM}$. This might be primarily associated with the pH changes within the hydrogel as seen in **Figure 3.5(b)**. At $25\text{-}31 \text{ }^\circ\text{C}$, the internal pH remains over 7.0 for $C_A = 92 \text{ mM}$ when $I_L < 0.5$

mW/cm², while it becomes less than 7.0 if $T = 37\text{-}40\text{ }^{\circ}\text{C}$ or $I_L > 0.5\text{ mW/cm}^2$, as well as that with $C_A = 460\text{ mM}$. It may be because the acid dissociation is promoted by the growth of AA content, while the PSG protonation is inhibited by the high temperature and enhanced irradiation. The hydrophilic-to-hydrophobic PSG isomerization then occurs due to the decrease of pH, leading to a collapse of λ_N . Meanwhile, the shear modulus was reported to increase with the volume shrinkage degree of hydrogel [201]. Furthermore, as shown in **Figure 3.5(a)** and (b), the further decrease in the swelling stretch and internal pH could hardly be observed with the increase of light intensity at $I_L > 1.0\text{ mW/cm}^2$, when more than 90% of PSGs remain the neutral closed-ring isomers. In summary, the mechanical and electrochemical properties could be modulated via the light intensity for the self-protonating photo-sensitive hydrogel, where the content of acidic groups and ambient temperature play an important role. Therefore, in an ECM made of photo-sensitive hydrogels, the light intensity could be used for the control over the cell growth and mechanical strength of cell culture substrates through the manipulation of internal pH and hydration environments.

3.4.2 Electrical behavior in response to buffer pH

The pH environment plays an important role in the biological activities. As such, **Figure 3.6** is plotted to study the pH-dependent behaviors of the photo-sensitive

hydrogels with different contents of acidic groups, including the net fixed-charge concentration c_f^{net} and average electrical potential ψ_{avg} within the polymeric network. As illustrated in **Figure 3.6**, the content of acidic groups makes a significant impact on c_f^{net} and ψ_{avg} inside the polymer during buffer pH range of 3.0-11.0. For $C_A = 460$ mM, the significant peaks are found in c_f^{net} at buffer pH=7.5-10.0, especially when $T = 37$ °C or $I_L = 1.0$ mW/cm². In details, as shown in **Figure 3.6** (a) and (b) where $T = 25$ °C, the peak value of c_f^{net} climbs up to about 250.0 mM when $I_L = 1.0$ mW/cm², which is around 40 times higher than that at $I_L = 0.0$ mW/cm², possibly because of the changes in the amount of fixed charges and volume of hydrogel. The molar number of net fixed charges is a bit small and the hydrogel volume is quite large when $I_L = 0.0$ mW/cm². Nevertheless, if the light intensity rises to 1.0 mW/cm², acidic groups are mostly dissociated into the charged form AA⁻ and protons as the pH range from 7.5 to 10.0, while the fully PSG deprotonation is almost achieved in this pH range in terms of **Equations** (3.23)-(3.28), resulting in the maximum amount of net charge fixed on the polymeric network. At the same time, the volume of hydrogel reaches the minimum value, since the photo-generated hydrophobic products dehydrate the polymeric networks, as shown in **Figure 3.5(a)**. As such, the peak of c_f^{net} is formed, and thus the influx of counter ions reaches the maximum due to the electrostatic effect. In contrast, an insignificant difference is observed in

the peak of c_f^{net} between $I_L = 0.0$ and 1.0 mW/cm^2 at $T = 37 \text{ }^\circ\text{C}$, compared with that at $T = 25 \text{ }^\circ\text{C}$ as shown in **Figure 3.6(c)** and (d), in which an increase rate of less than 25% is found. This may be because the volumetric shrinkage rate and the amount of net fixed charges approach the maximum simultaneously due to the heat-induced closed-ring isomerization at $T = 37 \text{ }^\circ\text{C}$, even if $I_L = 0.0 \text{ mW/cm}^2$, which can be confirmed by **Equations (3.23)-(3.28)** and **Figure 3.4**. Hence, the growth in the peak value of c_f^{net} at $T = 37 \text{ }^\circ\text{C}$ is not as remarkable as that at $T = 25 \text{ }^\circ\text{C}$ when I_L rises from 0.0 to 1.0 mW/cm^2 , as shown in **Figure 3.6(c)** and (d). On the other hand, for $C_A = 92 \text{ mM}$, the peak in c_f^{net} in the pH range above is not as significant as that for $C_A = 460 \text{ mM}$. It is because a considerable amount of anionic acidic groups is neutralized by the cationic photochromic groups due to their similar molar concentrations. Meanwhile, the significant variation is found in the corresponding average electrical potential ψ_{avg} during the whole buffer pH range for the AA-loaded hydrogels, as observed in **Figure 3.6(e)-(h)**, since the protonation and dissociation occur constantly to both PSGs and AA. Furthermore, the variation in ψ_{avg} depends highly on both the temperature and irradiation conditions, due to their effects on the molar fraction of each isomer with varied acidic coefficient as tabulated in **Table 3.2**. However, both c_f^{net} and ψ_{avg} almost remain zero within the hydrogel without acidic groups if the buffer $\text{pH} > 7.0$, as PSGs become

deprotonated in a base environment, leading to a zero net fixed charge. Regarding the hydrogel with $C_A = 92$ mM, the pH-dependent variation trend falls in between those with $C_A = 460$ mM and $C_A = 0$ mM, respectively. It is concluded that the photo-sensitive hydrogels could display significant electrical response against the buffer pH if incorporating acidic groups. Therefore, they might be employed as the feedback signals to detect pH changes in the bath.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 3.6. The responsive net fixed-charge concentration and electrical potential of photo-sensitive hydrogel with different AA contents against the buffer pH subject to the specified temperature and irradiation conditions: (a)-(d) refer to the net fixed-charge concentration at $T=25-37\text{ }^{\circ}\text{C}$ and $I_L=0.0-1.0\text{ mW/cm}^2$ and (e)-(f) are the corresponding average electrical potentials.

3.4.3 Distributive variations of electrical and chemical properties

Figure 3.7 is plotted for the distributive electrical potential ψ and pH across the domains of photo-sensitive hydrogel and deionized solution in the dark ($I_L=0.0\text{ mW/cm}^2$) and under light irradiation ($I_L=2.0\text{ mW/cm}^2$), where $C_A=27.6\text{ mM}$, buffer pH = 7.0, and $T=25-37\text{ }^{\circ}\text{C}$.

(a)

(b)

Figure 3.7. The local responses of photo-sensitive hydrogel and buffer solution as a function of normalized distance coordinate: (a) electrical

potential (b) pH level.

As illustrated in **Figure 3.7(a)**, the internal ψ of hydrogel runs from positive to negative potentials, if I_L rises from zero to 2.0 mW/cm² or T from 25 to 37 °C. It might be because that the amount of anionic AA overtakes that of cationic PSGs after the photo-driven or thermal isomerization of McH⁺. Meanwhile, a significant electrical potential gradient is found across the domains of hydrogel and solution, since ψ is zero in the bath according to the electroneutrality. On the other hand, the corresponding internal pH of hydrogel decreases from around 7.1 at $T = 25$ °C and $I_L = 0.0$ mW/cm² to 4.0-6.4 at $T = 37$ °C or $I_L = 2.0$ mW/cm², as shown in

Figure 3.7(b). At the same time, the buffer solution almost remains neutral, because the released protons are attracted and bond within the polymeric network by the anionic AA and neutral PSGs respectively. To our best knowledge, this is the first report on distributive electrical property and local pH environment of a photo-sensitive hydrogel immersed in deionized solution. It is suggested that the positive and negative ψ may be employed for the uptake and release of mobile charged species via light, and furthermore, the photocurrent could be generated by the gradient in ψ for the self-power bioelectronics [60]. Besides, this type of hydrogel might also be useful in the clinical areas, such as photo-controlled self-healing and drug release, because of its responsive pH characteristics in the

neutral aqueous solution.

3.4.4 Ionic-strength-responsive behavior at different temperatures

By the multiphysics model, **Figure 3.8** is plotted for the relationship between the ionic conductivity K_s and equilibrium swelling stretch λ of pSpNIPAAm hydrogels in NaCl and Na₂SO₄ solutions as a function of buffer ionic strength I , for analysis of the effect of light irradiation on the ionic strength responsive behaviors. The input parameters for the simulation are given as $I_L = 0.0\text{-}5.0$ mW/cm², $C_P = C_A = 100.0$ mM, $T = 25\text{-}37$ °C, and buffer pH = 5.0.

Figure 3.8(a) and **(b)** examine the response of pSpNIPAAm hydrogels as a function of ionic strength I at the room temperature $T = 25$ °C. As shown in **Figure 3.8(a)**, the ionic conductivity rises slightly if the light irradiation is imposed under a low ionic strength I , while the photo-induced change is hardly seen in K_s , when I increases to a high level. The increasing K_s at a low level of I results from the enlarged net fixed-charge density due to the photoisomerization according to **Equations** (3.23)-(3.28). However, as illustrated in **Figure 3.8(b)**, with the increase in I , the surrounding ionic concentration dominates the ionic conductivity in terms of **Equation** (3.67), since the effect of net fixed-charge density is gradually overwhelmed by the electrochemical potential [191], which is also confirmed by the increase in the

corresponding swelling stretch.

Figure 3.8 (c) and (d) present the ionic-strength-dependent response of a pSpNIPAAm hydrogel at $T = 31\text{ }^{\circ}\text{C}$ that is around LCST. It is clearly observed in **Figure 3.8(d)** that the equilibrium swelling stretch λ diverges sharply between NaCl and Na₂SO₄ solutions in the dark if $I > 0.10$. It may be due to the difference between NaCl and Na₂SO₄ in the ionic concentration caused by different stoichiometric coefficients, which disrupts the phase transition of polymer at $T = 31\text{ }^{\circ}\text{C}$. Under the same ionic strength, the electrochemical potential gradient is higher in NaCl solution than Na₂SO₄ solution, thereby neutralizing the dehydration effect due to LCST phase transition. As a result, **Figure 3.8(c)** shows a remarkable photo-induced decrease in K_s of hydrogel in NaCl solution under high ionic strength at $T = 31\text{ }^{\circ}\text{C}$ than that at $T = 25\text{ }^{\circ}\text{C}$. These findings indicate that the ionic species could make a significant impact on the photo-stimulated response of photo-sensitive hydrogels at a temperature around LCST.

Figure 3.8 (e) and (f) display the response behavior of a pSpNIPAAm hydrogel as a function of ionic strength at $T = 37\text{ }^{\circ}\text{C}$ when the LCST phase transition is fully achieved. The deprotonation of fixed groups is almost completed due to the thermal isomerization of McH^+ and the hydrogel remains highly dehydrated state at $T = 37\text{ }^{\circ}\text{C}$, as shown in **Figure 3.8** (f). Therefore, the light irradiation makes little impact on neither the fixed-charge density nor the volumetric change of

hydrogel. As a result, the photo-induced change in the ionic conductivity is not as significant as that at $T = 31\text{ }^{\circ}\text{C}$, which is observed in **Figure 3.8(e)**. In other words, the response of a hydrogel almost depends on the ionic strength of buffer solution at $T = 37\text{ }^{\circ}\text{C}$ regardless of light irradiation.

(b)

(c)

(d)

(e)

(f)

Figure 3.8. Response behaviors of pSpNIPAAm hydrogels as a function of ionic strength, including (a) ionic conductivity and (b) swelling stretch at $T = 25$ °C, (c) ionic conductivity and (d) swelling stretch at $T = 31$ °C, and (e) ionic conductivity and (f) swelling stretch at $T = 37$ °C.

3.5 Remarks

In this chapter, a multi-effect-coupling photo-stimulus (MECp) model has been developed to characterize the fundamental response behavior of a photo-sensitive hydrogel, subjected to light-temperature-pH-ionic-strength coupled stimuli in a computational domain covering both the hydrogel and surrounding solution. In this model, the photo-chemical reaction and protonation equilibrium are formulated by considering the light intensity, temperature, pH, and ionic strength coupled effects, in order to determine each component of immobilized groups.

Based on the law of mass conservation, the Poisson-Nernst-Planck equations are employed to capture the ionic migration and electrical potential, in which the ionic strength is integrated into the chemical potential. The nonlinear mechanical equilibrium equation is used to characterize the large mechanical deformation in the form of displacement vector, based on the law of linear momentum conservation. The formulated model is examined by comparison with the published experimental data and a good agreement is obtained. After that, a series of parameter studies are performed through the MECp model to explore the fundamental mechanism of photo-responsive extracellular matrix.

Chapter 4 Modified MECp model for photo-sensitive hydrogels in response to metal ions

Figure 4.1. Illustration of a photo-sensitive hydrogel subjected to metal ions.

For some photochromic species like spiropyran, there is an intriguing phenomenon that ring-opened isomers (Mc and McH^+) tend to form the bonds with different metal ions, which break up if exposed to visible light or heat, as illustrated in **Figure 4.1**. This fascinating feature might inspire a promising application in the removal and detection of heavy metal ions using photo-sensitive hydrogels, since the polymeric network provides a large adsorption area. Hence, a multiphysics model is proposed in this chapter to account for the metal-ion-complexation behavior of photo-sensitive hydrogels based on the modification of the MECp model, as organized as follows. Section 4.1 formulates the modified MECp model and Section 4.2 then presents the validation of the

theoretical model by comparison with the published experiment. After that, a numerical investigation is carried out on the metal-ion-complexation behavior of photo-sensitive hydrogels in Section 4.3, based on the modified MECp model. A remark is finally given on this chapter in Section 4.4.

4.1 Modification of the MECp model

In order to explore the response behaviors of spiropyran-based hydrogel, a multiphysics model is developed to characterize: (a) the complexation between metal ions and ring-opened isomers, (b) the photo-driven isomerization of PSGs, (c) the protonation equilibrium of immobilized groups, (d) the interaction between the transport of mobile ions and electrostatic effect of fixed ionic groups, and (e) the swelling and electrical behaviors of hydrogel membrane. The present multiphysics model is developed, based on the following assumptions.

(i) The rates of non-complexation reactions remain constant among isomers of photochromic groups, due to the insignificant influence of the metal ion complexation on the isomerization and protonation equilibrium of spiropyran moieties [142].

(ii) The SpH^+ and Mc isomers (including metal-ion-complexation open-ring isomers) vanish above and below a critical pH level, respectively [178]. This pH threshold is set as half the sum of acidic coefficients of SpH^+ and Mc isomers.

(iii) The light irradiation is uniform and has no intensity decay in all directions.

4.1.1 Reduction of the chemical reactions

As illustrated in **Figure 4.2**, the concurrent reactions include photo isomerization, protonation equilibrium, and reversible metal ion complexation, where M^{2+} represents the divalent metal ion ($M = Cu, Co, Ni, \dots, N$), $M-(Mc)_n^{2+}$ the deprotonated complexation in an $Mc:M^{2+}$ $n:1$ stoichiometry ($n = 1, 2$), and $M-(McH)_n^{(n+2)+}$ the protonated complexation in an $McH^+:M^{2+}$ $n:1$ stoichiometry.

Figure 4.2. Illustration of coupled chemical reactions inside a spiropyran-based hydrogel subjected to heavy metal ions.

In order to account for the coupled chemical reactions, the following ordinary differential equations (ODEs) are given, due to the kinetics of first-order chemical reactions, based on the correlation as shown in **Figure 4.2**.

$$\left\{ \begin{array}{l}
\dot{c}_{\text{SpH}^+} = k_1^b c_{\text{Sp}} - k_1^f c_{\text{SpH}^+} \\
\dot{c}_{\text{Sp}} = k_1^f c_{\text{SpH}^+} + k_c c_{\text{McH}^+} + k_c c_{\text{M-McH}^{3+}} + \\
\quad k_c c_{\text{M-(McH)}_2^{4+}} - k_1^b c_{\text{Sp}} - 3k_o c_{\text{Sp}} \\
\dot{c}_{\text{McH}^+} = k_o c_{\text{Sp}} + k_2^b c_{\text{Mc}} + k_3^f c_{\text{M-McH}^{3+}} - (k_c + k_2^b + k_3^b) c_{\text{McH}^+} \\
\dot{c}_{\text{Mc}} = k_2^f c_{\text{McH}^+} + k_5^f c_{\text{M-Mc}^{2+}} - (k_2^b + k_5^b) c_{\text{Mc}} \\
\dot{c}_{\text{M-McH}^{3+}} = k_o c_{\text{Sp}} + k_3^b c_{\text{McH}^+} + k_4^f c_{\text{M-(McH)}_2^{4+}} - \\
(k_c + k_3^f + k_4^b) c_{\text{M-McH}^{3+}} \\
\dot{c}_{\text{M-(McH)}_2^{4+}} = k_o c_{\text{Sp}} + k_4^b c_{\text{M-McH}^{3+}} - (k_4^f + k_c) c_{\text{M-(McH)}_2^{4+}} \\
\dot{c}_{\text{M-Mc}^{2+}} = k_5^b c_{\text{Mc}} + k_6^f c_{\text{M-(Mc)}_2^{4+}} - (k_5^f + k_6^b) c_{\text{M-Mc}^{2+}} \\
\dot{c}_{\text{M-(Mc)}_2^{4+}} = k_6^b c_{\text{M-Mc}^{2+}} - k_6^f c_{\text{M-(Mc)}_2^{4+}}
\end{array} \right.$$

(4.1)

where k_1^f , k_2^f , k_3^f , k_4^f , k_5^f , and k_6^f are the rates of forward reactions, and k_1^b , k_2^b , k_3^b , k_4^b , k_5^b , and k_6^b the rates of backward reactions. These reaction rates are subjected to the protonation equilibria and characterized by

$$\left\{ \begin{array}{l}
k_1^f/k_1^b = K a_2 c_{\text{H}^+} \\
k_2^f/k_2^b = K a_1 c_{\text{H}^+} \\
k_3^f/k_3^b = 1/(K_1 c_{\text{M}^{2+}}) \\
k_4^f/k_4^b = 1/(K_2 c_{\text{McH}^+}) \\
k_5^f/k_5^b = 1/(K_1 c_{\text{M}^{2+}}) \\
k_6^f/k_6^b = 1/(K_2 c_{\text{Mc}})
\end{array} \right. \quad (4.2)$$

where K_1 and K_2 are 1:1 and 1:2 binding constants for the metal ion complexation, respectively. Herein, the values of these reaction rates are set to

several magnitudes of order larger than those of k_o and k_c , since the protonation and metal ion complexation occur much faster than the isomerization of photochromic groups [209].

However, too many ODEs are coupled in **Equations** (4.1) and (4.2), which makes it very difficult to solve the equation combination. To simplify the problem, a reduction is carried out on the coupled reaction system in this study. In terms of assumption (i), deprotonated ring-opened isomers (Mc , $M-Mc^{2+}$, $M-(Mc)_2^{2+}$) could be classified as one fixed species “OR”, and those corresponding protonated groups (McH^+ , $M-McH^{3+}$, $M-(McH)_2^{4+}$) as the other species “ORH”, characterized by

$$c_{OR} = c_{Mc} + c_{M-Mc^{2+}} + 2c_{M-(Mc)_2^{2+}} \quad (4.3)$$

$$c_{ORH} = c_{McH^+} + c_{M-McH^{3+}} + 2c_{M-(McH)_2^{4+}} \quad (4.4)$$

Furthermore, ORH or OR species share the same reaction rates and dissociation constants, including k_o , k_c , Ka_1 , Ka_2 , K_1 , and K_2 . In particular, K_1 and K_2 are subjected to the following correlations,

$$c_{M-Mc^{2+}} = c_{Mc} c_{M^{2+}} K_1 \quad (4.5)$$

$$c_{M-(Mc)_2^{2+}} = c_{Mc}^2 c_{M^{2+}} K_1 K_2 \quad (4.6)$$

$$c_{M-McH^{3+}} = c_{McH^+} c_{M^{2+}} K_1 \quad (4.7)$$

$$c_{M-(McH)_2^{4+}} = c_{McH^+}^2 c_{M^{2+}} K_1 K_2 \quad (4.8)$$

Based on assumption (ii), if the local $pH > -0.5 \log(Ka_1 \cdot Ka_2)$, the concurrent

reactions are simplified as follows,

and we obtain

$$c_{\text{ORH}} = \frac{C_P/J}{1 + \frac{\text{k}_c}{\text{k}_o} + \frac{\text{Ka}_1}{c_{\text{H}^+}}}, \quad c_{\text{Sp}} = \frac{C_P/J}{1 + \frac{\text{k}_o}{\text{k}_c} \left(1 + \frac{\text{Ka}_1}{c_{\text{H}^+}}\right)}, \quad c_{\text{OR}} = \frac{C_P}{J} - c_{\text{ORH}} - c_{\text{Sp}} \quad (4.11)$$

while if the local $\text{pH} \leq -0.5 \log(\text{Ka}_1 \cdot \text{Ka}_2)$, the reactions in **Figure 4.2** are simplified as detailed below

and we then obtain

$$c_{\text{ORH}} = \frac{C_P/J}{1 + \frac{\text{k}_c}{\text{k}_o} \left(1 + \frac{c_{\text{H}^+}}{\text{Ka}_2}\right)}, \quad c_{\text{Sp}} = \frac{C_P/J}{1 + \frac{\text{k}_o}{\text{k}_c} + \frac{c_{\text{H}^+}}{\text{Ka}_2}}, \quad c_{\text{SpH}^+} = \frac{C_P}{J} - c_{\text{ORH}} - c_{\text{Sp}} \quad (4.14)$$

In addition, acrylic acid groups are often incorporated into the polymeric membrane [72, 151, 152], in which the dissociation equilibrium occurs between the neutral AAH and the anionic AA^- , as detailed below

The concentrations of AAH and AA^- species are then obtained in the same way as presented in Section 3.1.1, given by

$$c_{AAH} = \frac{c_{H^+} C_A / J}{K a_3 + c_{H^+}}, \quad c_{AA^-} = C_A / J - c_{AAH} \quad (4.16)$$

The dissociation equilibrium of water molecule is characterized by

$$K_w = c_{H^+} c_{OH^-} \quad (4.18)$$

The hydrolysis reaction on heavy metal ions is given by

where K_h is the hydrolysis constant that accounts for the following relationship,

$$K_h = \frac{c_{H^+}^2}{c_{M^{2+}}} \quad (4.20)$$

A metal-ion-complexation ratio α is defined as the concentration ratio of metal-complexed groups to the total spiropyran moieties, given by

$$\alpha = \frac{c_{M-Mc^{2+}} + 2c_{M-(Mc)_2^{2+}} + c_{M-McH^{3+}} + 2c_{M-(McH)_2^{4+}}}{C_P / J} \quad (4.21)$$

4.1.2 Governing equations derived from the MECp model

In order to characterize the interaction between ionic migration and electrostatic effect, the Poisson-Nernst-Planck equations are employed as follows,

$$\begin{cases} \dot{C}_k = -\nabla_X \cdot \mathbf{C}^{-1} \cdot \mathbf{J}_k + \Gamma_k \\ \nabla_X \cdot (J \varepsilon_r \varepsilon_0 \mathbf{C}^{-1} \cdot \nabla_X \psi) = -F \left(\sum_k^N z_k C_k + \sum_f^{N_f} z_f C_f \right) \end{cases} \quad (4.22)$$

$(k = M^{2+}, H^+, Na^+, Cl^-, \dots, N)$

where the flux vector $\mathbf{J}_k$ is given by

$$\mathbf{J}_k = -\frac{D_k C_k}{N_A k_B T} \nabla \mu_k \quad (4.23)$$

The actuation behavior of hydrogel membrane is caused by (i) elastic energy of polymeric chains, (ii) mixing energy between polymer and solution, and (iii) mixing energy between ions and solvents. Based on the derivation procedure in Section 3.2.5, the hydraulic pressure Π at the gel-solution interface and chemical potential μ_k are given by

$$\begin{cases} \Pi = \frac{N_A k_B T}{J} + N_A k_B T \sum_k^N \left(\frac{C_k}{J-1} - \bar{C}_k \right) - \\ \quad \frac{k_B N_A T}{\Omega} \left(\ln \frac{J-1}{J} + \frac{\chi}{J^2} + \frac{1}{J} + G_{RH}^* \beta_2 C_P \right) \\ \mu_k = F\psi z_k + k_B N_A T \ln \frac{C_k}{C} \end{cases} \quad (4.24)$$

At the equilibrium state, we obtain $\Gamma_k = 0$ and the equilibrium swelling stretch as follows,

$$\lambda = N_R k_B T / \Pi \quad (4.25)$$

So far, the modified MECp model has been formulated mathematically. In summary, **Equations** (4.3)-(4.8), (4.11), (4.14), (4.16), (4.18), and (4.20) are used for the kinetics of coupled reaction system, Poisson-Nernst-Planck **Equations** (4.22) for the interaction between the diffusion and electrostatic fields, **Equation** (4.24) for the constitutive relation, and **Equation** (4.25) for the equilibrium swelling stretch.

4.2 Validation of the modified MECp model

The model validation is examined via the experimental results on the photo-controlled metal-ion adsorption using a spiropyran-modified polymeric membrane [115]. **Figure 4.3** compares the concentrations of metal ions in saline solution of a photo-responsive copolymer in the dark and under visible irradiation, respectively. In the experiment, the polymeric membrane was prepared by comprising poly(sulfobetaine methacrylate) (PSBMA) and 0.1 mM spiropyran units. Four metal chlorides were examined in 1.0 wt% NaCl solution of the copolymer with an initial concentration of 3.0 $\mu\text{g/mL}$, including CuCl_2 , ZnCl_2 , NiCl_2 , and CoCl_2 . The interface area of the membrane is approximately 1.44 cm^2 and one-dimensional parameters are set as $L_{\text{sol}}^0 = 10 L_{\text{gel}}^0 = 1.0 \text{ mm}$. The wavelength of visible light is less than 420 nm with a power of around 50 W. In this study, $K_1/K_2 = 1$ is assumed, and several parameters are obtained or estimated from the literature, including binding constants $K_1 K_2 = 10^{10}$, $10^{4.82}$, $10^{4.73}$, and $10^{2.03} \text{ M}^{-2}$ for Cu^{2+} , Zn^{2+} , Ni^{2+} and Co^{2+} [210], respectively, $\chi = 0.476$ [211], and $N_R = 5.0 \times 10^{25} \text{ m}^{-3}$ [212]. The coefficient G_H^* is the only fitting parameter and set as $2.1 \times 10^{-4} \text{ mM}^{-1}$. The remaining input parameters are the same as before unless they are given. As shown in **Figure 4.3**, the simulation result agrees well with the experimental observation, which confirms the validity of theoretical model. The largest disagreement occurs to the case of Cu^{2+} under light irradiation,

possibly because the inhomogeneous light intensity and the attenuation due to the solution medium are neglected in the model. Hence, the light-induced release of metal ions is stronger in the simulation than that in the experiment, especially for the case of Cu^{2+} where the number of bound metal ions is the most among the four metal species.

Figure 4.3. Comparison between computational results and published experimental data [115].

4.3 Numerical studies of photo-sensitive hydrogels in metal-ion solution

The following studies focus on the adsorption behavior of spiropyran-modified hydrogel membrane, where the input parameters are the same as those in Sections 3.3 and 4.2 unless they are specified.

4.3.1 Effect of photo-sensitive group density

(a)

(b)

Figure 4.4. The (a) copper ion complexation ratio and (b) equilibrium swelling of PSBMA membranes loaded with different initial concentrations of spiropyran as a function of pM.

Figure 4.4 explores the variation of complexation ratio α and equilibrium swelling stretch λ of a PSBMA membrane in response to the initial buffer concentration of copper ions under different initial concentrations of spiropyran C_P , where the parameter pM is defined as $-\log(\bar{C}_{M^{2+}}^0/1 \text{ M})$. Some input parameters are given as buffer pH=7.0, $\bar{C}_{NaCl}=150 \text{ mM}$, $C_A = 0 \text{ mM}$, $T=37 \text{ }^\circ\text{C}$, and $I_L = 0.0 \text{ mW/cm}^2$. As shown in **Figure 4.4(a)**, the variation trend in metal complexation ratio is divided into three stages denoted by I, II, and III, in which pM_{up} and pM_{low} represent the upper and lower thresholds, respectively. At Stage I $pM \geq pM_{up}$, the ratio α almost remains zero due to quite few metal ions, and thus this pM range is regarded as a dead zone for the metal ion detection. At Stage II $pM_{low} \leq pM < pM_{up}$, the ratio α increases remarkably with decreasing pM, as more and more metal ions are bond with open-ring isomers. The slower growth of α is found at Stage III $pM < pM_{low}$, since less non-complexed open-ring isomers exist within the hydrogel. Similar variation trends were also observed in the experiment conducted by Shao *et al.* [213], where the metal ion complexation of spiropyran were examined in organic aqueous solution. On the other hand, the values of both pM_{up} and pM_{low} increase with C_P due to the complexation equilibrium according to **Equation (4.5)**, suggesting that the metal sensitivity is

raised. Furthermore, as C_P increases from 600 to 1600 mM, the relevant growth in threshold values is less significant than that within the range of 50-600 mM. This observation indicates that the effect of C_P on metal-binding equilibrium is overtaken by that of metal ionic concentration if $C_P = 600-1600$ mM. It is well known that the polymeric network becomes hydrated due to the ionization of fixed groups, which may be the reason for the swelling of hydrogel. However, **Figure 4.4(b)** illustrates that the swelling stretch λ hardly increases with the decrease of pM until $pM < pM_{low}$ when open-ring isomers become fixed ionic groups constantly due to metal ion complexation. The possible reason is that the effect of ionic open-ring isomers is overwhelmed by the electrochemical potential resulting from the constant concentration of salt if $pM \geq pM_{low}$. When $pM < pM_{low}$, the increasing metal ion influx disrupts the equilibrium by enlarging the electrochemical potential gradient between the hydrogel and buffer solution, thereby resulting in a jump in λ as shown in **Figure 4.4(b)**. Regarding the effect of C_P , a growth of λ is observed with an average value of 0.71 above pM_{up} , as C_P increases from 50 to 1600 mM, possibly because of the increasing fixed ionic groups.

(a)

(b)

Figure 4.5. Effect of metal ion species on (a) metal ion complexation ratio and (b) equilibrium swelling of a PSBMA membrane loaded with 100 mM spiropyran as functions of pM.

Figure 4.5 visualizes the metal complexation ratio α and equilibrium swelling

stretch λ of a PSBMA membrane as a function of pM subjected to four different metal ion species. Herein, the same input parameters are adopted as the last case study except $C_P=100$ mM. As illustrated in **Figure 4.5(a)**, only the variations of α in Stages I and II are observed in Zn^{2+} , Ni^{2+} , and Co^{2+} , compared with Cu^{2+} within the pM range of 2.0-10.0, possibly resulting from their weak binding ability. In this work, due to the much smaller binding constants than that of Cu^{2+} , quite few ring-open isomers form complexation with the above three metal ion species even when the pM value reaches 2.0, leading to the disappearance of Stage III. Accordingly, as shown in **Figure 4.5(b)**, the swelling stretch is larger in buffer solution of Cu^{2+} than those in other metal-ion solutions when $pM < pM_{low}$, because of more fixed ionic groups. It is thus suggested that the photo-responsive gel membrane has the higher sensitivity to Cu^{2+} than Zn^{2+} , Ni^{2+} , and Co^{2+} .

4.3.2 Effect of fixed-acidic-group density and light intensity

The mobile cations tend to be driven out of the polymeric network due to the metal ion complexation and protonation of photochromic species, which has a side effect on the uptake of heavy metal ions. In order to neutralize the fixed cationic groups, acrylic acids are incorporated into the polymeric network in the following studies, where the pH of buffer solution plays an important role in the

dissociation of different immobilized species.

(a)

(b)

Figure 4.6. Effect of initial fixed-acidic-group density on the (a) metal ion complexation ratio and (b) metal-ion concentration within PSBMA gel membrane as a function of buffer pH.

Figure 4.6 examines the effect of the initial fixed-acidic group concentration on the pH-dependent response of PSBMA gel membranes, where $\bar{C}_{\text{Cu}^{2+}} = 1.000 \mu\text{M}$, $\bar{C}_{\text{NaCl}} = 150 \text{ mM}$, $C_{\text{P}} = 100 \text{ mM}$, $T = 37 \text{ }^{\circ}\text{C}$, and $I_{\text{L}} = 0.0 \text{ mW/cm}^2$. It is found in **Figure 4.6** that the metal-ion-complexation response of the hydrogel without acrylic acids is divided into three stages in terms of buffer pH. When buffer pH $\geq -\log K_{\text{a}1}$, the metal-ion-complexation ratio α collapses remarkably with the decrease of the buffer pH due to the isomerization from OR to Sp in an alkaline environment as shown in **Figure 4.6(a)**, which could be confirmed by **Equation (4.11)** and the experiment conducted by Sumaru *et al.* [141]. As a result, a jump is observed in the copper ionic concentration within the hydrogel $c_{\text{Cu}^{2+}}^{\text{g}}$, as illustrated in **Figure 4.6(b)**. When $-0.5\log K_{\text{a}1}K_{\text{a}2} < \text{buffer pH} < -\log K_{\text{a}1}$, the dominated reactions among photochromic groups become the dissociation equilibrium between OR and ORH forms rather than the ring-closed isomerization, leading to a stable value of α as well as $c_{\text{Cu}^{2+}}^{\text{g}}$. When buffer pH $\leq -0.5\log K_{\text{a}1}K_{\text{a}2}$, Sp isomers are mostly protonated as SpH^+ and thus the influx of metal ions is weakened, which may be the reason for the small decline in both α and $c_{\text{Cu}^{2+}}^{\text{g}}$. Besides, if buffer pH $\geq -\log K_{\text{a}3}$, both α and $c_{\text{Cu}^{2+}}^{\text{g}}$ increase to some degree, as the initial fixed-acidic concentration C_{A} rises from 0 to 500 mM.

This may be due to the enhanced influx of metal ions that are attracted by the increasing fixed anionic groups AA^- . However, **Figure 4.6(b)** shows that the copper ionic concentration decreases significantly with the decreasing buffer pH within the hydrogels loaded with acrylic acids if buffer pH < 5.0, since AA^- becomes neutralized form AAH due to the protonation equilibrium. Furthermore, fixed acidic groups are almost fully protonated as the neutral form when buffer pH < $-\log K_{a3}$, leading to the identical variations of both α and $c_{Cu^{2+}}^g$ regardless of C_A . It is demonstrated that the fixed acidic groups might be employed to raise the uptake of metal ions. Therefore, the following studies examine the response characteristic of spiropyran-based hydrogels loaded with acrylic acids.

In order to analyze the effect of light intensity, **Figure 4.7** is plotted for the metal ion complexation ratio α and copper ionic concentration $c_{Cu^{2+}}^g$ within a PSBMA gel membrane in NaCl solution subjected to light intensities of 0-40.0 mW/cm² as functions of buffer pH, where $\bar{C}_{Cu^{2+}} = 1.000 \text{ } \mu\text{M}$, $\bar{C}_{NaCl} = 150 \text{ mM}$, $C_P = 100 \text{ mM}$, $C_A = 100 \text{ mM}$, and $T = 37 \text{ } ^\circ\text{C}$.

(a)

(b)

Figure 4.7. Photo-stimulated responses in the (a) ratio of metal complexes and (b) internal concentration of copper ions of a PSBMA gel membrane

as a function of buffer pH.

As illustrated in **Figure 4.7(a)**, a significant photo-induced decrease is observed in α , due to the isomerization from OR to Sp, which is enlarged by the increase of light intensity. Despite the visible irradiation, the α increases considerably if buffer pH > 7. In particular, α even reaches approximately 54% with a light intensity of 5.0 mW/cm², when buffer pH = 8.0, which is only around 21% smaller than that in the dark. The reason may be because an alkaline microenvironment contributes to the ring-open isomerization of spiropyran, inhibiting the photo-triggered conversion. Accordingly, $c_{Cu^{2+}}^g$ decreases slightly with the decreasing light intensity due to the weakened metal ion binding if buffer pH > 7, as shown in **Figure 4.7(b)**. In contrast, $c_{Cu^{2+}}^g$ increases with the decrease of light intensity when buffer pH < 3.0, since the electrostatic expulsion is attenuated due to less photo-generated ring-closed groups (SpH⁺).

4.3.3 Effect of polymer-solution interaction

It is demonstrated in the published findings that the metal ion adsorption of hydrogel might highly depend on the hydration of polymeric backbone materials [214]. Therefore, apart from PSBMA, another two reported spiropyran-modified copolymers are investigated in this section, in order to examine the effect of polymeric materials on the metal ion complexation response, including hydroxypropyl methacrylate (HPMA) [214] and *N*-isopropylacrylamide

(NIPAAm) [115, 215]. The hydration difference among the three polymeric materials is characterized by the interactive parameter χ and the coefficient G_H^* . HPMA is a hydrophobic polymer, where χ is given as 0.592 [216] and G_H^* is estimated as $1.3 \times 10^{-4} \text{ mM}^{-1}$ by fitting the swelling size change of a spiropyran-loaded HPMA film after visible irradiation [214]. Regarding NIPAAm, the Flory-Huggins parameter is given as a function, $\chi = (\delta h - T\delta s)/k_B T + 0.518/J$, where $\delta h = -12.46 \times 10^{-21} \text{ J}$ and $\delta s = -4.717 \times 10^{-23} \text{ J/K}$ [201, 217]. The coefficient G_{RH}^* is determined as $1.8 \times 10^{-4} \text{ mM}^{-1}$ by fitting the swelling degree of a spiropyran-based NIPAAm gel under visible irradiation at 25 °C [149].

(a)

(b)

(c)

(d)

(e)

(f)

Figure 4.8. Photo-triggered response behaviors of spiropyran-modified hydrogels based on different polymeric materials as a function of buffer NaCl concentration, including (a) metal ion complexation ratio at 25 °C, (b) internal copper ionic concentration at 25 °C, (c) equilibrium swelling stretch at 25 °C, (d) metal ion complexation ratio at 37 °C, and (e) internal copper ionic concentration at 37 °C, and (f) equilibrium swelling stretch at 37 °C.

Figure 4.8 elucidates the effect of polymeric materials on photo-stimulated changes in salt-responsive behaviours of photo-responsive membranes in saline solution containing 1.000 μM CuCl_2 , where the buffer pH = 7.0, $C_P = 100$ mM, and $C_A = 100$ mM. The numerical investigations are performed in the dark ($I_L = 0$ mW/cm²) and under visible light ($I_L = 5.0$ mW/cm²) at room and physiological temperatures, namely 25 °C and 37 °C, respectively. As illustrated

in **Figure 4.8(a)** and (d), the increase of buffer NaCl concentration $\bar{C}_{\text{NaCl}}$ promotes the metal ion adsorption in the dark as reported in the literature [115], and it also leads to a slight decline in the metal ion complexation ratio α if visible light is imposed. This observation might result from the varied quantitative relationship between the concentrations of fixed ionic groups and buffer salt ions. The electrostatic effect of fixed charge remains weakened with the enhanced buffer ionic strength, until it is completely overwhelmed by the electrochemical potential of mobile salt ions. In the dark, the polymeric network remains cationic, since metal-complexed ring-open isomers overtake the deprotonated acrylic acids, which tends to drive metal ions out of the polymeric network. Therefore, as indicated in **Figure 4.8(b)** and (e), metal ions constantly accumulate within the hydrogel as the electrostatic repulsion attenuates with the increase of $\bar{C}_{\text{NaCl}}$, resulting in the increase of α . Similarly, the visible light triggers the cationic-to-anionic transition of the polymeric network by breaking the metal ion complexation, leading to the decrease of α . Meanwhile, **Figure 4.8** also shows that spiropyran-based membranes display varied salt-responsive behaviors among different polymeric materials at 25 °C and 37 °C. In the dark, NIPAAm and PSBMA share the similar variation of α at 25 °C, while α of NIPAAm is almost identical to that of HPMA at 37 °C. The reason may be because PSBMA and HPMA remain in hydrophilic and hydrophobic states, respectively,

regardless of ambient temperature, while NIPAAm undergoes a hydrated-to-dehydrated transition when the temperature rises from 25 °C to 37 °C which makes a great change in its net fixed-charge density by volumetric response as illustrated in **Figure 4.8(c)** and (f).

4.3.4 Examination of different combinations of metal ions

Figure 4.9 compares the complexation ratio with Cu^{2+} and that with other metal ions (Zn^{2+} , Ni^{2+} , and Co^{2+}) within a PSBMA membrane immersed in 150 mM NaCl solution containing binary metal ion species, in order to examine the selectivity of different metal ions. In this binary-metal saline solution, the buffer copper ionic concentration $\bar{C}_{\text{Cu}^{2+}}$ remains 1.000 μM , and the molar concentration ratio $\bar{C}_{\text{Cu}^{2+}}:\bar{C}_{\text{M}^{2+}}$ ($M = \text{Zn}, \text{Ni}, \text{and Co}$) ranges from 1:10 to 1:10000. Two irradiation conditions are considered: (i) one is in the dark, where $I_L = 0.0 \text{ mW/cm}^2$, and (ii) another one is under visible light, where $I_L = 5.0 \text{ mW/cm}^2$. Some input parameters are given as buffer pH = 7.0, $C_P = C_A = 100 \text{ mM}$, and $T = 37 \text{ }^\circ\text{C}$. **Figure 4.9(a)** displays the comparative metal-complexation ratios between Cu^{2+} and Zn^{2+} in terms of the molar concentration ratio $\bar{C}_{\text{Cu}^{2+}}:\bar{C}_{\text{M}^{2+}}$ and irradiation condition. The complexation ratio regarding Cu^{2+} is over 60% in the dark at the molar concentration ratio of 1:10, and it still accounts for approximately 20% under visible light which is even much larger than that

regarding Zn^{2+} without irradiation. Furthermore, the copper-complexation ratio is not overtaken by Zn^{2+} until $\bar{C}_{\text{Cu}^{2+}}:\bar{C}_{\text{M}^{2+}}$ reaches 1:10000. It is indicated that Cu^{2+} could be bond with ring-open isomers much easier than Zn^{2+} in the binary solution, resulting from the larger binding constant. This variation trend is also observed in the comparison between Cu^{2+} and Ni^{2+} due to the similar binding constants of Ni^{2+} and Zn^{2+} , as illustrated in **Figure 4.9(b)**. In particular, **Figure 4.9(c)** shows that the complexation ratio with Co^{2+} is almost negligible around the whole range of molar concentration ratio, since its binding constant is quite small compared with Cu^{2+} .

(a)

(b)

(c)

Figure 4.9. Photo-stimulated response in metal-complexation ratio of a PSBMA membrane in NaCl solution containing binary heavy metal ions,

including (a) Cu^{2+} and Zn^{2+} , (b) Cu^{2+} and Ni^{2+} , and (c) Cu^{2+} and Co^{2+} .

4.4 Remarks

The MECp model is modified in this chapter to characterize the metal-ion-complexation behavior of photo-sensitive hydrogels. Apart from photo- and thermal isomerization and protonation equilibrium of fixed groups, this model also allows for the metal-ion-complexation of ring-opened isomers and hydrolysis of heavy metal ions. A reduction is conducted on multiple concurrent reactions in order to simplify the analysis of the coupled reaction system. The modified MECp model is validated by the published experiment, and a series of parameter studies are then carried out to investigate the response behavior of photo-sensitive hydrogels subjected to heavy metal ions.

Chapter 5 Conclusions and recommendations

In this chapter, the main conclusions from the current work are presented, followed by recommendations for the future research work.

5.1 Conclusions from the present work

The present research work aims to develop multiphysics models for the numerical investigation of the mechanical and electrochemical behaviors of photo-sensitive hydrogels in response to coupled external stimuli, such as light intensity, temperature, pH, ionic strength, and heavy metal ions. Multiple interactive processes are integrated into the formulation of theoretical models, including concurrent chemical reactions on fixed groups, transport of mobile species, electrostatic effect, and large mechanical deformation. In order to explore the potential applications of photo-sensitive hydrogels, parameter studies are carried out based on the present multiphysics models for the examination of their mechanical and electrochemical responses, such as swelling ratio, internal pH, and ionic conductivity. Finally, the main achievements are achieved in this thesis as follows.

The first achievement of the present study is to develop a multi-effect-coupling photo-stimulus (MECp) model for the photo-sensitive hydrogel subjected to light-thermo-pH-salt coupled stimuli.

- Multiple physical and chemical phenomena are considered in the formulation of MECp model. The kinetics of concurrent chemical reactions is formulated and solved using the Laplace transformation method, in which the variation of fixed groups is quantified under the coupled effect of photo-chemical reaction, thermal isomerization, and proton equilibrium. The Poisson-Nernst-Planck equations are employed to characterize the interaction between the movement of ions and electrostatic effect. The nonlinear mechanical equation is used for the large deformation of the hydrogel. Furthermore, the ionic strength is integrated into the formulation of the electrochemical potential.
- The comparison between the published experiment and numerical simulation is carried out on equilibrium swelling ratios of a photo-sensitive hydrogel. The simulation results agree well with the experimental observation with a global error of 8.4%, which confirms the validity of the MECp model.
- The parameters studies are performed to examine the mechanical and electrochemical behaviors of photo-sensitive hydrogels in response to light intensity, temperature, pH, and ionic strength, which are highly concerned in the biomedical engineering. It is demonstrated that the internal pH remains above 7.0 under a weak light intensity of 0.5 mW/cm^2

in a photo-sensitive hydrogel containing acrylic acids with a molar ratio of 1.0%, almost leading to a constant swelling ratio when the temperature is below 31 °C. Both the net fixed charge and volumetric shrinking ratio reach the maximum when the buffer pH ranges from 7.0 to 10.0, leading to a peak in the fixed-charge density and electrical potential in a photo-sensitive hydrogel loaded with acrylic acids. Due to the fixed ionic groups, a large jump is observed in both electrical potential and pH gradients across the hydrogel and solution, when the heat or irradiation is imposed. Furthermore, drastic changes are found in the variation trend of ionic-strength-responsive conductivities and swelling stretches of photo-sensitive hydrogels within different temperature ranges, which is affected by the salt species and light intensity.

The second achievement is the modification of MECp model for characterization of the metal-complexation behavior of photo-sensitive hydrogels.

- The chemical reaction system is simplified to reduce the complexity of reaction kinetics, which makes it easier to determine the concentration of each fixed chemical species. The metal ion complexation is assumed to have no effect on the isomerization and protonation equilibrium of photochromic groups. All the open-ring isomers are thus regarded as one species regardless of whether they are complexed with metal ions, and so

are the closed-ring isomers.

- After examination with the experimental data in the open literature, it is confirmed that the modified MECp model could predict effectively the photo-modulated metal-ion-complexation of photo-sensitive hydrogels.
- Several case studies are conducted to investigate the response behavior of photo-sensitive hydrogels subjected to metal ions. Numerical results show that the metal adsorption increases greatly if the photochromic group density rises from 50 to 600 mM, but it changes insignificantly in the range of 600-1600 mM. The metal complexation ratio is also raised by the increasing concentration of fixed acidic groups, especially when the buffer pH is between 5.0 and 6.0. On the other hand, the metal-ion-adsorption characteristic could be manipulated through the modulation of polymer-solution interaction parameters, which is achieved using different polymeric materials.

5.2 Recommendations for future work

The current work in this thesis presents the development of multiphysics models to characterize mechanical and electrochemical response behavior of photo-sensitive hydrogels. For the further understanding of response mechanism and other response behaviors, several potential works may be recommended below

on photo-sensitive hydrogels in the future.

- It would be an interesting work to study the photo-responsive behavior of a hydrogel subjected to the non-uniform irradiation condition. For many applications of light-modulated hydrogel actuators, the light intensity is usually not uniform across the irradiated surface, and furthermore it would attenuate along the propagation pathway. However, the present multiphysics models mainly focus on a uniform light field, where a constant light intensity is assumed. This assumption is reasonable when the hydrogel film is thin and the irradiation time is short, but the attenuation of light intensity along the propagation direction could not be neglected for a temporary irradiation. An imbalanced distribution of photochemical products would be generated within the photo-sensitive hydrogels due to the non-uniform irradiation, resulting in the local changes in the mechanical and electrochemical properties [146]. As such, the future work might investigate the response behavior of photo-sensitive hydrogels in a non-uniformed light field.
- The present numerical studies are mainly conducted based on the steady-state system of a photo-sensitive hydrogel. However, a transient analysis might be more helpful to the investigation of some non-equilibrium phenomena that occur in the hydrogel system. In the field of chemically

responsive hydrogels, a growing interest has recently been shown on those non-equilibrium behaviors, especially the self-sustained oscillation that is useful in the design of drug delivery and soft robotics. These response behaviors may highly depend on the transient evolution of the diffusion-reaction system within the hydrogel. Therefore, it is worth carrying out the transient simulation of a photochemically responsive hydrogel, in order to explore the potential application of its non-equilibrium response behavior.

- The future work will also focus on the development of multi-dimensional models for the photo-sensitive hydrogels, instead of one-dimensional case that is considered in the current study. This is because the multi-dimensional analysis is involved in many mechanical response behaviors of photo-sensitive hydrogels, especially the bending movement that is often used in the actuator [150]. Furthermore, one-dimensional model is unable to characterize the anisotropy of materials, and thus the present multiphysics model fails to account for some composite hydrogels comprising multiple different materials where the material microstructure is anisotropic. Therefore, it is necessary to perform two- and three-dimensional simulation of a photo-sensitive hydrogel for further exploration of its complex response behavior.

- A fascinating feature of some spiropyran-modified copolymers is their optical response to both mechanical force and photo due to the change in the mechanical properties [142]. Since the isomerization process greatly affect the overall structure of the polymer chains and thus the macroscopic properties of the polymer, the future work might be carried out on the investigation of molecular isomerization between two different rings of the switch. During this study, the multiscale simulation is expected for the study on molecular-to-microscopic-to-macroscopic structural evolution of the photo-sensitive polymers.
- Recently, the adhesion of hydrogels has attracted a growing interest among researchers, which might depend highly on the electrostatic interaction within the hydrogel. Since the internal electrostatic environment of a photo-sensitive hydrogel could be tuned via light, it would be an interesting work to study the effect of light on the adhesion change. The future work may focus on the microenvironment of a photo-sensitive hydrogel, where both molecular simulation and continuum theory should be involved.

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Publication arising from the thesis

Journal paper

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1. X. Chen, H. Li, K.Y. Lam, Modeling the responsive behaviors of photo-Sensitive hydrogels subject to several external stimuli, 10th International Conference on Materials for Advanced Technologies (ICMAT 2019), June 2019, Singapore. (Oral presentation)
2. X. Chen, H. Li, K.Y. Lam, Numerical simulation on multi-stimuli responsive behaviors of photo-sensitive hydrogel, 10th International Conference on Computational Methods (ICCM 2019), July 2019, Singapore. (Oral presentation)