This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Reaction-Induced Swelling of Ionic Gels

ShaoBao Liu \(^1,2\), PengFei Wang \(^2,3\), GuoYou Huang \(^2,4\), Lin Wang \(^2,4\), JinXiong Zhou \(^1,2\), Tian Jian Lu \(^1,2\), Feng Xu \(^2,4\), Min Lin \(^2,4\)*

\(^1\) State Key Laboratory for Strength and Vibration of Mechanical Structures, School of Aerospace, Xi’an Jiaotong University, Xi’an 710049, P.R. China

\(^2\) Bioinspired Engineering and Biomechanics Center (BEBC), Xi’an Jiaotong University, Xi’an 710049, P.R. China

\(^3\) Qian Xuesen Laboratory of Space Technology, China Academy of Space Technology, Beijing 100094, P.R. China

\(^4\) MOE Key Laboratory of Biomedical Information Engineering, School of Life Science and Technology, Xi’an Jiaotong University, Xi’an 710049, P.R. China

*Corresponding author: minlin@mail.xjtu.edu.cn

† Co-first authors: They contributed equally to this work.

A chemomechanical theory is proposed to describe the dynamic behavior and response time of ionic gels, which exhibit a large deformation accompanying with the migration of mobile ions driven by a common non-equilibrium chemical reaction. Besides the positive validation of the theoretical model with existing experimental data, further investigation demonstrated that the dynamic deformation and response time of an ionic gel depend on the concentration of reactive and nonreactive ions, period of external stimuli, initial state and density of ionizable groups on polymer chains.
I. INTRODUCTION

Gels consisting of ionic polymers and solution (i.e., ionic gels) exhibit large deformation in response to force \(^1,^2\), temperature \(^3^{-5}\), pH \(^6\), light \(^7^{-9}\), electric \(^10,^{11}\) and magnetic \(^12\) fields. Natural ionic gels in the cellular periphery of plants and animals play important roles in water regulation and stability of cell shapes \(^13,^{14}\). In engineering, synthetic ionic gels have been widely used as environmental sensors \(^15\), biomimetic actuators \(^16\), autonomous flow control \(^6\), and drug delivery system \(^12,^{17}\), etc. In these applications, the dynamic characteristics of ionic gels play an important role in the performance of the devices. Recently, the improvement in the response time of the ionic gels based device has become a critical parameter for proper design \(^4,^6\). For example, to shorten the response time of a microfluidic valve, David et al. \(^6\) use an array of the hydrogel-coated cylinder owing to the short diffusion instead of a hydrogel-coated cylinder with large diameter in the channel. The ionic gel, possessing great potential in the field of sensors and smart valves, also requires a short response time to ensure its higher accuracy. However, ionic gels usually undergo a dynamic large deformation accompanying with the migration of ions in and out of the gel resulting from a non-equilibrium ionic chemical reaction \(^6\). Development of theoretical models is therefore an urgent need for the design and optimization of ionic gels based devices. Among these models, the exploration of the dynamic behavior of ionic gels in response to the chemical stimuli is of particularly interesting.

Various theories have been proposed for stimuli-sensitively ionic gels. Based on a simplified model coupling the geometrical changes and the reaction-diffusion regimes \(^18\), Yashin and Balazs \(^19,^{20}\) proposed a chemomechanical theory on self-oscillating gels driven by the Belousov-Zhabotinsky reaction. Suo et al. \(^21\) proposed another model to describe the large deformation and electrochemical behavior of polyelectrolyte gels. Their theories describe the chemomechanical behavior without any non-equilibrium kinetics of chemical reaction. Specifically, Marcombe, Tanaka and Doi et al. \(^22^{-24}\) developed theoretical models to describe the response of reactively ionic gels to pH and electric fields by coupling the Donnan theories and the equilibrium theory of
chemical reaction. Doi et al. mainly studied the response of ionic gels to electric fields (chemical reaction with the assumption of fast equilibrium, non-equilibrium kinetics of diffusion in relatively large gels) \(^{23}\), dynamics of volume transition (no chemical reaction, equilibrium kinetics of diffusion) \(^{25}\), swelling dynamics of polymer gels under mechanical constraint, constrained thin-plate gels, cylindrical gels (no chemical reaction, equilibrium kinetics of diffusion)) \(^{26-28}\). Therefore, the theories proposed by Doi et al. are free of non-equilibrium kinetics of chemical reaction. Tanaka et al. mainly focused on the light scattered spectrum of viscoelastic gels \(^{29}\), collapse of polyacrylamide gels \(^5\), theory of the kinetics of swelling of gels (no chemical reaction, non-equilibrium kinetics of diffusion) \(^{30}\), phase transition of nonionic gels \(^{31}\), swelling of ionic gel (chemical reaction with the assumption of fast equilibrium) \(^{24}\), critical kinetics of gels (no chemical reaction, non-equilibrium kinetics of diffusion) \(^{32}\), pattern formation in three-dimensional gels \(^{33}\), phase synchronization in self-oscillating gels (experimental study) \(^{34}\), thermosensitive gels using in a controlled drug-release microchip (experimental study) \(^{35}\). Therefore, the theories proposed by Tanaka et al. are also free of any non-equilibrium kinetics of chemical reaction too. In addition, Osada \(\text{et al.}\) mainly focuses on the electrokinetic modeling of polyelectrolyte gels \(^{36}\), electrically activated mechanochemical devices of ionic gels \(^{37}\), reversible volume change of microparticles in an electric field \(^{38}\) and a worm-like motion of ionic gel driven by electric field \(^{39}\). They do not refer to the theories of ionic gels about the non-equilibrium kinetics of chemical reaction. In summary, their works do not involve the non-equilibrium kinetics of chemical reaction in the gels, but mainly focus on the non-equilibrium kinetics of diffusion. There is still lack of a non-equilibrium theory to describe the dynamic response of reactive ionic gels.

In this paper, we consider the system of a block ionic gel immersed into a dilute solution with reactive and nonreactive ions. The gel performs dynamic behavior (swelling or shrinking) due to a non-equilibrium chemical reaction within the gel. By coupling the theories of large deformation, Donnan effect and non-equilibrium kinetics of chemical reaction, a chemomechanical theory was developed to describe
the dynamic behavior of the gel. We validated the predictions from the proposed theory by comparing with the existing experimental and theoretical results. As illustrations, we presented the oscillation deformation of an actuator changing with the period of external chemical stimuli and the response time of a sensor affected by initial state, density of ionizable group and measuring concentration.

II. KINETICS OF IONIC GELS

1. A chemomechanical system

Immersed in a solution containing several reactive ions, a polymer network with fixed ionizable groups begins swelling or shrinking due to the ionic reaction between fixed and mobile species, resulting in a non-equilibrium ionic gel. We focused on a specific system but without loss of generality, i.e., a non-equilibrium process of the dissociation and association of an ionizable groups, \[ AB \xleftarrow{k_1} A^- + B^+ \] (Fig. 1(a)-(b)), where \( k_1 \) and \( k_2 \) represent the rate constants of forward and reverse processes, respectively. The ionizable groups \( AB \), chemically bonded on the polymer chains, dissociate into mobile ions \( B^+ \) in the solvent and conjugate bases \( A^- \) fixed on the polymers chains when the network imbibes a number of solvent molecules. During the reversible reaction, the network of the polymer chains is charging and discharging. For example, the increasing conjugate bases \( A^- \) give rise to the fixed electric charges of the polymer chains and consequently induce the deformation of the reactive ionic gels (forward reaction). It performs the opposite process during backward reaction. Besides of the mobile ions \( B^+ \) and water molecules, the solution also consists of nonreactive counter ions (+) and co-ions (−). It is noteworthy that this reaction-deformation system represents the basic working mechanism of broad categories of applications, such as hydrogel-based testing devices \(^{15}\), and drug carriers \(^{12, 17}\). To illustrate the essentials of the method, we neglected the ions of \( H^+ \) and \( OH^- \) from water dissociation assuming that their concentrations are much lower than ions of interest. Besides the polymer chains, there are six fixed and mobile species in the system of the ionic gel, i.e., water molecules, counter ions, co-ions, \( B^+ \), \( AB \),
Accordingly, the nominal concentration of those ions are \([ C^0, C^{\delta}, C^\psi, C^{\phi}, C^\tau ]\), or, \([ C^0, C^1, C^2, C^3, C^4 ]\). The true concentrations are expressed as \([ C^0, C^{\delta}, C^\psi, C^{\phi}, C^\tau ]\) or, \([ C^0, C^1, C^2, C^3, C^4 ]\) respectively, which are related to the nominal concentration by \( c^\alpha = C^\alpha / \det F \), where \( F \) is defined as the deformation gradient of the gel. We use the Lagrange coordinate system in the reference configuration (Fig. 1(c)) and the Euler coordinate system in the current configuration (Fig. 1(d)). In the current state, the gel bears a stress tensor \( \sigma \) with the components \( s_{ik} \) and swells by a tensor of deformation gradient \( F \) with the components \( F_{ik} \). The function \( x(\mathbf{X},t) \) describes the deformation field of the gel network: a material mark with the coordinate \( \mathbf{X} \) in the reference state moves to another place with the coordinate \( \mathbf{x} \) in the current state at time \( t \). Consequently, \( F_{ik} \) equals to \( \partial x(X,t) / \partial X_k \).

2. Reaction kinetics

In the gel, the change of the fixed species \( A^- \) only depends on the chemical reaction progress. Therefore, the increased number of \( A^- \) per volume in the current state, produced by the forward reaction during a period \( dt \), is \( k_1 c^{AB} dt \). Meanwhile, the one consumed by the reverse reaction is \( k_2 c^{-} c^B dt \). So the integrated change of \( A^- \) (i.e., \( dC^A^- \)) for the total gel volume (i.e., \( \det F \)) equals to \( k_1 c^{AB} dt - k_2 c^e c^{B'} dt \) \( \det F \).

Recalling the relationship between true concentration and nominal concentration, the kinetics of the chemical reaction in the gel is given by

\[
\frac{dC^A^-}{d\tau} = C^{AB} - \frac{k_2}{k_1} \frac{C^A^- C^{B'}}{\det F}
\]

where \( \tau = t / k_1^{-1} \) is the dimensionless time when adopting a time scale of chemical reaction, \( \tau_k = k_1^{-1} \).
3. Thermodynamics

For the sake of reasonable simplicity, thermodynamic analysis involves a block gel with relatively small size. Since that the time scale of diffusion ($\tau_D$) depends on the size of the gel (i.e., $\tau_D \sim L^2 / D$, where $L$ is the size of the gel, and $D$ is the diffusion coefficient) \(^1\), the time scale of diffusion could be much smaller than that of reaction in a sufficiently small gel (i.e., $\tau_D / \tau_R \ll 1$), namely, the diffusion of mobile species reaches equilibrium instantaneously during the chemical reaction. The dynamical behavior of the reactively ionic gels should be reaction-controlled. Meanwhile, we assume that the mechanical equilibrium of the system always exists by neglecting the viscosity. The gels with small size may be invisible, but have found applications in the field of microchip and microfluidic valves \(^6,35\).

Upon one constant temperature, the ionic gel, reservoir and the mechanical force constitute a closed thermodynamic system. The gel exchanges mobile species with the external solution in the reservoir. $\mu^\alpha$ is the electrochemical potential of mobile species $\alpha$ in the reservoir—that is the increase of the free energy of the reservoir when the reservoir gains one molecule of species $\alpha$. $\delta \bar{C}^\alpha$ represents the change of the number of mobile species in the reservoir during ions exchange between the gel and reservoir. Thermodynamics dictates that the free energy of the system should never increase, namely

$$\delta W + \sum_{\alpha=0}^3 \mu^\alpha \delta \bar{C}^\alpha - s_{ik} \delta F_{ik} \leq 0 \quad (2)$$

The inequality and equality hold when the system is not or is in thermodynamic equilibrium, respectively. In the left-hand side, the free energy change of the system is the sum of the free energy change of the gel, the free energy change in the external solution, and the potential energy change of the mechanical forces. $\delta$ represents the change of a variable during a short time.

4. Governing equations
In both the gel and the external solution, water molecules, counter ions and co-ions do not participate in chemical reactions. The changes of these species in the gel are entirely induced by the related molecules left from the reservoir, namely $\delta C^{0} = -\delta \overline{C}^{0}$, $\delta C^{(\pm)} = -\delta \overline{C}^{(\pm)}$ and $\delta C^{(\mp)} = -\delta \overline{C}^{(\mp)}$. Differently, both chemical reaction and migration contribute to the change of $B^r$ in the gel, namely, $\delta C^{B^r} = \delta \xi - \delta \overline{C}^{B^r}$, where $\delta \xi$ is the nominal extent of the chemical reaction. The fixed species $AB$ and $A^-$ mutually transform from each other and cannot be produced by other mobile species, so $\delta C^{AB} = -\delta \xi$ and $\delta C^{A^-} = \delta \xi$. The total number of the fixed species should be constant, namely, $C^{\alpha} + C^{\overline{\alpha}} = f / \Omega$, where $f$ is the total number of fixed reactive species on a monomer and $\Omega$ is the approximate volume per monomer or water molecule, i.e., the densities of the ionizable group. We assumed that electroneutrality prevails both in the gel $(C^{(\pm)} + C^{\overline{\pm}} = C^{(\pm)} + C^{(\overline{\pm})})$ and in the external solution $(\overline{C}^{(\pm)} + \overline{C}^{\overline{\pm}} = \overline{C}^{(\pm)})$, where $\overline{C}^{\alpha}$ is the true concentration of specie $\alpha$ in the external solution. For a large swelling gel in a dilute solution, the individual polymers and solvent molecules are considered to be incompressible and the total volume of ions in the gel is negligible. Consequently, when the dry gel network with a unit volume imbibes $C^{0}$ number of solvent molecules and becomes to a swelling gel with the deformation gradient $F$, the condition of volume incompressibility satisfies the condition $1 + \Omega C^{0} = \det F$. Considering the above conditions of species conservation, ions electroneutrality and volume incompressibility, the thermodynamic inequality (2) gives the mechanical equilibrium (Supplementary Materials-Part 1)

$$s_{ik} = \frac{\partial W}{\partial F_{ik}} - \Pi_{i} H_{ik} \det F$$

(3)

where $\Pi_i$ is the osmotic pressure and $H_{ik}$ is defined as the transpose of the inverse of the deformation gradient, namely, $H_{ik} H_{il} = \delta_{kl}$ and $H_{ik} H_{jk} = \delta_{ij}$.

Meanwhile, the electrochemical potential of mobile species in the reservoir are also
given by

\[
\begin{align*}
\mu^\alpha &= \left( \frac{\partial W}{\partial C^\alpha} + \Pi_1 \Omega \right) \quad \alpha = 0 \\
\frac{\partial W}{\partial C^\alpha} + (\Pi_2 - \Pi_1) z^\alpha \quad \alpha = 1, 2, 3
\end{align*}
\] (4)

where \( \Pi_2 - \Pi_3 \) is the Donnan potential resulting from the difference of the electrochemical potentials between the gel and the external solution. The dimensionless parameter \( z^\alpha \) represents the valence of an ion \( \alpha \).

The thermodynamics derives the requirement for the non-equilibrium chemical reaction as

\[
\sum_{\alpha=1}^{S} \frac{\partial W}{\partial C^\alpha} \nu^\alpha \delta x^\alpha \leq 0
\] (5)

where \( \nu^\alpha \) is the coefficient of reactant \( \alpha \) in the chemical reaction. According to our previous study \(^{40}\), the kinetics of the chemical reaction in a reactive gel, Eq.(1), agrees well with the condition (5) of thermodynamics.

It is considered that there are few forces acting between the mobile species in a dilute solution: no Van-der-Waals nor any coulomb forces (i.e., ideal solution). In the external solution including several species, the chemical potential of solvent is

\[
\mu^0 = -k_B T \sum_{\alpha=1}^{S} \Omega e^\alpha \].

Based on the Flory-Huggins theory \(^{40, 41}\), the free energy of the gel is taken to be a function of the deformation gradient and the concentration of all species: \( W = W \left( F, C^0, C^{(+)}, C^{(-)}, C^{(+\beta)}, C^{(-\beta)}, C^{(\alpha)}, C^{(-\alpha)} \right) \). Using the specific forms of free energy \( W \) based on the Flory-Huggins theory (Supplementary Materials-Part 2), Eq.(3) becomes

\[
s_{ik} = N k_B T \left( F_{ik} - H_{ik} \right) - \Pi_i H_{ik} \det F
\] (6)

where the osmotic pressure \( \Pi_i \) is specifically written as
The first item on the right-hand results from the imbalance of the number of ions in and out of the gel; the second item comes from the entropy of mixing the polymers-solvent and the enthalpy of mixing measured by a dimensionless parameter \( \chi \). The hydrating effect of the fix species (\( AB \) and \( A^- \)) on the enthalpy of the mixing of polymer-solvent is also considered by the dimensionless coupling parameter \( \chi_{AB} \) and \( \chi_{A^-} \), which characterizes the change of the hydrophobicity of polymer chains affected by the group \( AB \) and \( A^- \).

Considering the chemical potential of species \( \alpha \) in the external solution with \( \mu^\alpha = k_B T \ln \left( \frac{\bar{\tau}^\alpha}{c_{\text{ref}}^\alpha} \right) \), Eq.(4) gives

\[
\frac{c^\alpha}{\bar{\tau}^\alpha} = \exp \left[ - \left( \Pi_2 - \Pi_1 \right) \frac{\tau^\alpha}{k_B T} \right], \quad \alpha = 1, 2, 3
\]

The general equations above are well known as the Donnan equilibrium.

For a freely ionic gel with an isotropic stretch \( \lambda \) without considering the hydrating effect, namely, \( s_{ik} = 0 \), \( \chi_{AB} = \chi_{A^-} = 0 \), combining with Eqs.(1) and (6)~(8), the kinetics of this reaction-deformation system is obtained (Supplementary Materials-Part 3):

\[
\frac{d\lambda}{d\tau} = \psi \frac{d\kappa}{d\tau}
\]

(9)

\[
\frac{d\kappa}{d\tau} = \frac{\zeta}{\left( 1 + \frac{1}{\kappa^2} \right) + 3\psi \left( \kappa - 1/\kappa \right) / \lambda}
\]

(10)

where \( \kappa = \left( \frac{c^\alpha}{\bar{\tau}^\alpha} \right)^{\frac{1}{\psi}} \) represents the dimensionless concentration of mobile ions in the gel, while \( \psi \) and \( \zeta \) could be expressed as:

\[
\psi = \frac{\Omega \left( 1 - \frac{1}{\kappa^2} \right) \left( \bar{\tau}^{\psi^+} + \bar{\tau}^{\psi^-} \right)}{N \chi^3 \lambda^2 - \left( \bar{\tau}^{\psi^+} + \bar{\tau}^{\psi^-} \right) + 3 \left[ \bar{\tau}^2 \left( 1 - 1/\lambda^2 \right) - 2 \bar{\tau}^2 - 2\lambda^2 \right] \},
\]

and \( \zeta = \left[ \frac{f / \Omega}{\left( \bar{\tau}^{\psi^+} + \bar{\tau}^{\psi^-} \right) \lambda^2 - \left( \kappa - 1/\kappa \right) } \right] \frac{k_\lambda}{k_1} \left( \kappa - 1/\kappa \right) \bar{\tau}^\psi \).

The governing equations (9) and (10) describe the deformation of the gel and the change of ions concentration in the gel during the non-equilibrium chemical reaction.
III. NUMERICAL RESULTS AND DISCUSSIONS

To study the dynamic response of ionic gels, we obtained the solutions of the coupling equations by employing a numerical method in MATLAB. In the numerical calculations below, a representative value of the volume per molecule is \( \Omega=10^{-29}\text{m}^3 \), the number of polymer chains per unit volume of the dry network gives \( N=10^{22}\text{m}^{-3} \). In order to focus on the reactive kinetics in the ionic gels, we consider the changes of the ionisable group involved in the target chemical reaction, by ignoring the disturbance of neighboring acid groups on the \( \text{pH} \) changes, i.e., the value of the dissociation constant \( k_i/N_{\text{red}}k_2 \) keeps constant. The initial state is considered that the gel instantaneously reaches mechanical equilibrium by absorbing sufficient solvent molecules while the fixed group \( AB \) rarely dissociates during this short period, i.e., all of the fixed groups at the initial time are at the associated state \( AB \). The initial state assumes that the gel absorbs enough water while the acid groups do not start dissociation. The calculation of the initial stretch is \( \lambda_0=3.39 \), which is calculated by equations of a non-ionic gel \((\kappa=1)\) for the mechanical equilibrium state, namely, \( d\lambda/d\tau=d\kappa/d\tau=0 \). We firstly validated the theoretical model by comparing the steady solutions of a pH-sensitive gel (a familiar ionic gel: \( A^- \) is the carboxylic acids groups, \( B^- \) is the \( H^+ \)) reported by Marcombe et al. \(^{22}\) with the long time-limited solutions of our model (approximate to a steady state). The solutions of our theoretical model at a longer dimensionless time agreed well with the steady solutions from Marcombe et al. \(^{22}\), as shown in (Fig.2(a) and (b)). Then we compare the swelling ratio of our theoretical predictions at longer dimensionless time \((\tau=100)\) and experimental results at steady state from Eichenbaum et al. \(^{42}\) with different concentration of \( B^- \) \((\bar{c}_{B^-}/N_A)\). Here \( A^- \) is the methacrylicacid-co-acrylic acid groups, \( B^- \) is the \( H^+ \). The solutions of our theoretical model at a longer dimensionless time also agreed well with the experimental results from Eichenbaum et al. \(^{42}\), as shown in (Fig.2(c)). In the next investigation, we only focus on the
continuous deformation of ionic gels instead of discontinuous transition. Without loss of generality, the free swelling of an ionic gel is demonstrated in Fig. 3. When this gel is immersed into a solution with constant concentration of $B^+$ and salt ($i.e.$, $\bar{\varepsilon}^+/N_A = 10^{-3} \text{M}$, $\bar{\varepsilon}^{-+}/N_A = 10^{-3} \text{M}$), the stretch of the gel $\lambda$ varies over time due to the dissociation of the fixed groups (Fig. 3(a)), which is obviously affected by the dissociation constants $k_1/N_Ak_2$. For different dissociation constants, the swelling of the gel presents different tendencies and reaches various equilibriums after a sufficient period. These results indicate that the chemical reaction induces redistribution of ionic species and solvent molecules to reach another mechanical and electrochemical equilibrium. With increasing dissociation constant, the final stretch of the gel is larger while the response time, defined as the period of reaching equilibrium state from the initial state, becomes longer. The reason is that a larger dissociation constant $k_1/N_Ak_2$ means more dissociated ions at the equilibrium state of the chemical reaction, $i.e.$, the network bears more fixed charges $A^-$. Because the fixed charges must be neutralized by the counter ions, the mobile ions are more concentrated in the gel than in the external solution. The imbalance of ions concentration in and out of the gel considerably affects the osmotic pressure so that more solvent molecules tend to enter the gel resulting in a larger swelling of the gel.

Due to the longer process between the initial state and the equilibrium state with increasing dissociation constant, it takes more time to reach the electrochemical and mechanical equilibrium. Fig. 3(b) shows a series of stretches $\lambda$ of an ionic gel at different times as a function of the salt concentration in the external solution ($\bar{\varepsilon}/N_A$), at fixed concentration of $B^+$ and the dissociation constant. With increasing dimensionless time, the stretch of the gel increases and tends to reach a steady state at a longer dimensionless time. Interestingly, the dynamic behavior of the gel significantly varies depending on the salt concentration. For instance, the gel rarely deforms when the salt concentration is high enough ($i.e.$, $\bar{\varepsilon}^{-+}/N_A = 10^{-1} \text{M}$). This may be attributed to the fact that the number of counter ions in the gel is almost as much as
that out of the gel no matter how much extent the chemical reaction progresses. Thereby, the osmotic pressure contributed by the counter ions is negligible and the gel does not swell. At lower salt concentrations, the stretch of the gel increases significantly with increasing salt concentration. That is because the Donnan equilibrium, $c^{(+)}/c^{(-)} = c^{B+}/c^{B-}$, requires two kinds of ions in and out of the gel be distributed proportionally. When the salt concentration is much lower ($c^{(+)}/N_A = 10^{-6}\text{M}$), there will be $c^{(+)}/c^{B+}$ in the external solution and $c^{B+} > c^{(+)}/N_A$ in the gel. The ionizable groups $AB$ tend to a fully-associate limit causing a nearly neutral gel with a smaller stretch. As the $c^{(+)}/N_A$ increases, more counter ions move into the gel resulting in the increase of gel stretch.

An ionic gel may transform the chemical energy to mechanical energy through the periodic volume deformation when experiencing continuous changes of the chemical environment in the external solution. For example, the gel exhibits oscillating deformation with responsive curves assemble separately as rectangular wave and sawtooth wave. Those two characteristic responsive curves are in different amplitudes when the concentration of $B^+$ in the external solution changes rhythmically with two different periods (i.e., $T=5, 25$), Fig. 4(a)-(b). We further assessed the influence of the period of the external stimuli on the amplitude of oscillating deformation (Fig. 4(c)), which decreases quickly with increasing frequency of external stimuli in certain range (i.e., $2^3 < 1/T < 2^3$), but keeps almost unchanged when the frequency is sufficiently high or low. The reason for this phenomenon is that there is enough time for the reaction in the gel to reach the equilibrium state when the frequency of external stimuli is very low (i.e., the period is sufficiently long) and the amplitude of response keeps constant as long as the swelling of the gel reaches equilibrium. On the contrary, there is little time for the evolvement of the chemical reaction in the gel if the frequency of stimuli is high enough, i.e., the gel always keeps in the state closed to the initial condition and rarely deforms.
As previously mentioned, the response time plays an important role in the accuracy of the ionic-gel-based devices. To directly characterize the response behavior, an assumption is proposed that a gel is initially stored in a solution with a concentration of $B^r$ ($\overline{c}_0^{B^r}/N_A$) and keeps in a steady state. When a measurement process is carried out, the gel is transferred into a target solution with another concentration of $B^r$ ($\overline{c}^{B^r}/N_A$) and performs dynamic reaction and deformation. Here we consider the reactively ionic gels with a designable densities of ionizable group $f$. The response time $\tau_{eq}$ is defined as the period that a gel undergoes a process to achieve 99.99% of the equilibrium deformation in response to the external changes. Fig. 5 shows the response time of a gel as a function of target concentration ($\overline{c}^{B^r}/N_A$) with different densities of ionizable group (i.e., $f = 0.01, 0.02$) and different initial concentrations of $B^r$ (i.e., $\overline{c}_0^{B^r}/N_A = 10^{-7}, 10^{-4}$ M). For the three situations, the response time will become longer when the target concentration becomes lower. That is because the slower reactions in a solution with lower concentration result in longer response time.

For each situation of them, blue line ($\overline{c}_0^{B^r}/N_A = 10^{-7}$ M) shows a shorter response time around the initial concentrations of $B^r$ ($\overline{c}^{B^r}/N_A = 10^{-7}$ M). That is because the chemical reaction close to the equilibrium ($\tau_{eq} \approx 0$) around the initial concentrations of $B^r$. For the same reasons, the red and green line ($\overline{c}_0^{B^r}/N_A = 10^{-4}$ M) also show shorter response times around the initial concentrations of $B^r$ ($\overline{c}^{B^r}/N_A = 10^{-4}$ M). In comparison with blue line ($f = 0.02$), red line and green line ($f = 0.01$) represent shorter response time. The decreased response time with a smaller density of ionizable group $f$ is associated with the fact that there are a smaller number of ionizable groups for reaction. These response characters of ionic gels may contribute to the design of devices for specific applications.
IV. CONCLUSION

In summary, a chemomechanical theory has been proposed to describe the dynamic behavior of ionic gels under non-equilibrium process. We found that (i) the dynamic behavior of an ionic gel depends not only on the dissociation constant of ionizable groups on the polymer chains but also on the concentration of reactive and nonreactive ions in the external solution; (ii) when the ionic gel bears alternating stimulus of reactive ions in the external solution, the corresponding behaviors are significantly affected by the frequency of the stimulus; (iii) the response time of an ionic gel for different measuring concentrations of reactive ions is correlated to the initial state and density of ionizable groups on polymer chains.
ACKNOWLEDGEMENTS

This work was financially supported by the Major International Joint Research Program of China (11120101002), the National Natural Science Foundation of China (11372243, 10872157, 11072185, 11402192), South Wisdom Valley Innovative Research Team Program of China, the National 111 Project of China (B06024), Key Program for International S&T Cooperation Projects of Shaanxi (2013KW33-01). Feng Xu was also partially supported by the China Young 1000-Talent Program and the Program for New Century Excellent Talents in University.
References

An ionic polymer network, immersed in a solution including several species, swells due to a reversible chemical reaction $AB \xleftarrow{\frac{1}{k_1}} A^+ + B^-$ and a set of mechanical forces (e.g., hydrostatic pressure). Assuming that ionizable groups $AB$ (●) and $A^-$ (●) are fixed on the polymer network, the species $B^+$ (●) freely migrate into and out of the gel; Counterions (▲) and Co-ions (▲) arise from the ionization of salt. (a) A deswelling network of polymers with fully associated ionic groups; (b) a swelling network of polymers with partly dissociated ionic groups; (c) the reference state is a unit cube of stress-free dry polymer and a mark has the initial coordinates $X$; (d) the current state at time $t$, the gel bears a stress tensor $\mathbf{s}$ and swells by a tensor deformation gradient $\mathbf{F}$. The mark $X$ moves to another place with current coordinates $x(X, t)$ due to the deformation of the gel.
FIG. 2 (color online). Swelling ratio of a pH-sensitive gel changes (a) as a function of the concentration of $B^+$ ($\tilde{c}^{(1)}/N_s$) and (b) as a function of salt concentration ($\tilde{c}^{(1)}/N_s$) at different dimensionless time points. The red dots are the steady solution from Marcombe et al. The mole fraction of ionizable group $f = 0.05$, the dissociation constant $k_i/N_s k_z = 10^{+3}$. (c) Comparison between the swelling ratio of our theoretical predictions at longer dimensionless time ($\tau = 100$) and experimental results at steady state with different concentration of $B^+$ ($\tilde{c}^{(1)}/N_s$). The scattered dots are experimental data from Eichenbaum et al. and the solid lines are the simulated results from our theoretical model. Material parameters are given in ref.:

$\tilde{c}^{(1)}/N_s = 0.03 \text{M}$, $\chi = 0.45 + 0.489/\lambda^3$, $k_i/N_s k_z = 10^{+3}$, $f = 0.35$. 

$B^+ B A C N^+ ( )$
FIG. 3 (color online). Free swelling of a non-equilibrium ionic gel. The stretch $\lambda$ of the ionic gel changes (a) as a function of dimensionless time with different dissociation constants ($k_i/N_k$) and (b) as a function of salt concentration ($\bar{c}^{\text{eq}}/N_j$) at different dimensionless time points.
FIG. 4 (color online). Oscillating deformation of an ionic gel in response to the periodic changes of the concentration of $B^+$ in the external solution. (a) The period of changes is $T = 25$; (b) The period of changes is $T = 5$; (c) The amplitude of swelling stretch, $(\lambda_{\text{max}} - \lambda_{\text{min}})/2$, changes with the frequency of stimulation.
FIG. 5 (color online). Response time $\tau_{eq}$ as a function of the measuring concentration of $B^+$, $\bar{c}_i^{R+}/N_A$ with different initial concentrations of $B^+$, $\bar{c}_o^{R+}/N_A$ and different density of the ionizable groups, $f$. 

\[
\tau_{eq} = B^+ + (A^+ C N + B^+ + 0) B^+ C N + f \]