

A Self-Oscillating Ionic Polymer-Metal Composite Bending Actuator

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This paper presents an electro-mechanical model of an ionic polymer-metal composite (IPMC) material. The technique of the modelling is Finite Element method (FEM). An applied electric field causes the drift of counter-ions (e.g. Na⁺) which in turn drags water molecules along. The mass and charge imbalance inside the polymer is the main cause of the bending motion of the IPMC. All foregoing physical effects have been considered as time dependent and modelled with FEM. The model takes into account the mechanical properties of Nafion polymer as well as thin coating of the platinum electrodes and platinum diffusion layer. The modelling of the electrochemical reactions in connection with self-oscillating behavior of an IPMC is also considered. Reactions occurring on the surface of the platinum electrode, which is immersed into formaldehyde (HCHO) solution, are described by partial differential equations and also modeled using FEM. By coupling the equations to the rest of the model, we are able to simulate self-oscillatory behavior of an IPMC sheet.

I. INTRODUCTION

Electroactive polymer (EAP) based materials are valuable for many applications from micro robotics to military and space applications. Some of the advantages of EAP materials are light weight, noiseless actuation, simple mechanics and large displacement. In addition some EAPs, such as IPMCs Shahinpoor and Kim [1], are able to function in aqueous environments. Those qualities make the materials possible to use as artificial muscles. In this paper we consider simulations of IPMC type materials with the Finite Element method.

IPMC materials are highly porous polymer materials such as NafionTM, filled with a ionic conductive liquid. There are water based IPMCs which operate in aquatic environment and current is caused by ions such as Na⁺, K⁺ dissociated in water. Other kind of IPMCs - ionic liquid based, do not need wet environment for operating. A sheet of an ionic polymer is coated with a thin metal layer, usually platinum or gold. All freely mobile cations inside the polymer migrate towards an electrode due to an applied electric field, causing expansion of the material at the one end of the sheet and contraction at the other end, which results in bending of the sheet.

For simulating actuation of an IPMC sheet we need to solve coupled problems due to the complex nature of bending of an IPMC. It includes simulations in different domains such as mechanical, electrostatic and mass transfer, and even electrochemical for more advanced models. Some authors Wallmersperger et al. [2], Nemat-Nasser and Zamani [3] have already simulated mass transfer and electrostatic effects. We have used similar approaches in our model. Toi Toi and Kang [4] has shown a Finite Element Model including viscosity terms in transportation processes explicitly. However, the basis of the described model is a rectangular beam with 2 pairs of electrodes. Our approach for simulating mechanical bending is taking advantage of the numerical nature of FEM problems - we use continuum mechanics equations instead of analytical Euler beam theory which is more commonly used by authors Lee et al. [5], Wallmersperger et al. [6]. By coupling equations from different domains, we get a model for an IPMC muscle sheet, which allows us to use it as a starting point for solving more complex problems, thus we have introduced a simulation of electrochemical reactions on the platinum electrode of an IPMC sheet, which leads to self-oscillating

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actuation. Spontaneous oscillations are common phenomena in nature, including electrochemical systems such as oxidation of organic materials and metals Miller and Chen [7]. Under certain conditions such system can generate oscillations Krischer [8]. We have conducted a series of tests, where an IPMC sheet have been immersed into acidic formaldehyde (HCHO) solution and exposed to a constant potential. The measurements, however show current oscillations, which in turn result in oscillating bending of the IPMC sheet Kim et al. [9]. Hence we have introduced a FEM model in this paper to describe time dependent bending of a self-oscillating IPMC.

II. BENDING SIMULATION DETAILS

An IPMC sheet consists of a polymer host and a metal coating. In our experiments, we have used NafionTM 117, coated with a thin layer of platinum. Mass transfer and electrostatic simulations are done in three mechanical domains - pure backbone polymer, pure platinum coating, and mixture of polymer and platinum - some platinum diffuses into the polymer during coating process Nemat-Nasser and Wu [10]. Physical properties and dimensions of pure, 2 μm thick platinum coating are considered only when calculating bending. That gives us five mechanical domains as shown in Fig. 1. Most simulations are carried out for an IPMC strip, 2 – 4 cm long, 200 μm thick polymer, including 10 μm thick Pt diffusion region on each side, coated with 2 μm thick platinum, in a cantilever configuration - one end of the strip is fixed.

The Nernst-Planck equation describes diffusion, convection and in presence of electric field and charges, migration of the particles. The general form of the equation is

$$\frac{\partial C}{\partial t} + \nabla \cdot (-D\nabla C - z\mu FC\nabla\phi) = -\vec{u} \cdot \nabla C, \quad (1)$$

where C is concentration, D diffusion constant, F Faraday constant, \vec{u} velocity, z charge number, ϕ electric potential, and μ mobility of species, which is found by using known relation $\mu = D/(RT)$. There T is absolute temperature and R universal gas constant. Mobile counter ions are described by Eq. (1). As anions are fixed, they maintain constant charge density throughout the polymer. After a voltage is applied to the electrodes of an IPMC, all free cations will start migrating towards cathode, causing current in the outer electric circuit. Because of the fact that ions cannot move beyond the boundary of the polymer, charges start to accumulate, resulting in increase of the electric field, which cancels out the applied one. The process could be described by Gauss' Law:

$$\nabla \cdot \vec{E} = -\Delta\phi = \frac{F \cdot \rho_c}{\varepsilon}, \quad (2)$$

where ρ_c is charge density, ε is absolute dielectric constant and E is the strength of the electric field. The charge density variable is related to charge concentration:

$$\rho_c = zC + z_{anion}C_{anion}. \quad (3)$$

The second term in Eq. (3) is constant at every point of the polymer. The coupling between equations (1) and (2) is strong, i.e. no weak constraints have been used. Absolute dielectric constant ε could be explicitly written as $\varepsilon = \varepsilon_0\varepsilon_r$, where ε_0 is dielectric constant in vacuum and equals $8.85 \times 10^{-12} \text{ F/m}$. The measured value of absolute dielectric constant ε is shown in Table II. A steady state of the cations forms when electric field created by distribution of cations cancels out the applied electric field, i.e. the strength of the electric field inside the polymer is approximately zero, as also shown in Fig. 2. The steady state cation concentration, with average value of 1200 mol/m^3 is also shown in the same figure. It is interesting to notice that there are fluctuations in charge distribution only in really thin boundary layers, leading to the conclusion that there is no charge imbalance inside the polymer. General understanding is that locally generated charge imbalance nearby platinum electrodes is directly connected, and mainly responsible, to the bending of an IPMC Nemat-Nasser and Li [11]. Therefore we define longitudinal force per unit area at each point in the polymer of an IPMC as follows Wallmersperger et al. [6]:

$$\vec{F} = (A \rho_c + B \rho_c^2) \hat{x}, \quad (4)$$

where ρ_c is charge density and A and B are constants which are found by fitting simulations according to experimental results using system identification. Values of the constants are brought out in Table II and it is interesting to notice that the ratio A/B is close to the value suggested by Wallmersperger Wallmersperger et al. [6]. Equations (1)-(4) are described only for pure NafionTM and Pt diffusion domain (see Fig. 1). There is no ion diffusion nor migration in thin Pt coating domain.

Table I: Material parameters used in continuum mechanics equations.

Parameter	Value	Unit	Domain where applied
E_N	200	MPa	Nafion TM
ν_N	0.49	-	Nafion TM
E_{Pt}	168	GPa	Pt
ν_{Pt}	0.38	-	Pt
E_{diff}	84	GPa	Pt diffusion layer (estimated)
ν_{diff}	0.42	-	Pt diffusion layer (estimated)

Table II: Parameter values used in bending simulations.

Parameter	Value	Unit
D	1×10^{-6}	cm^2/s
R	8.31	$J/(K mol)$
T	293	K
z	1	-
F	96.5×10^6	mC/mol
ε	25	mF/m
A	110	$N m/mol$
B	10	$N m^4/mol^2$
$\alpha_{polymer}$	0	s^{-1}
$\beta_{polymer}$	1.5	s

To relate the force in Eq. 4 to the physical bending of an IPMC sheet, we introduce a set of continuum mechanics equations, which are effective in all domains (Fig. 1). These equations are described in the Comsol Multiphysics structural mechanics software package. Normal and shear strain are defined as

$$\varepsilon_i = \frac{\partial u_i}{\partial x_i}, \quad \varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right), \quad (5)$$

where u is the displacement vector, x denotes a coordinate and indices i and j are from 1 to 3 and denote components correspondingly to x, y, or z direction. The stress-strain relationship is

$$\sigma = D\varepsilon, \quad (6)$$

where D is 6×6 elasticity matrix, consisting of components of Young's modulus and Poisson's ratio. The system is in equilibrium, if the relation

$$-\nabla \cdot \sigma = \vec{F}, \quad (7)$$

is satisfied. This is Navier's equation for displacement. The values of Young's modulus and Poisson's ratios, which are used in the simulations, are shown in Table I. The values for platinum diffusion region are not measured, but estimated as an average of values of the pure NafionTM and Pt regions.

As our simulations are dynamic rather than static, we have to introduce an equation to describe the motion of an IPMC sheet. To do that, we use Newton's Second law

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} - \nabla \cdot c \nabla \vec{u} = \vec{F}, \quad (8)$$

where the second term is the static Navier's equation and c is Navier constant for static Navier's equation. The first term in Eq. (8) introduces the dynamic part. Several authors have reached to the conclusion that IPMC materials exhibit viscoelastic behavior Newbury and Leo [12], Yagasaki and Tamagawa [13], which is especially noticeable for high frequency movements Newbury and Leo [14]. However, we include the viscoelastic term in our equations by means of using Rayleigh damping Lord [15] model, which is described for a system of one degree of freedom as follows:

$$m \frac{d^2 u}{dt^2} + \xi \frac{du}{dt} + ku = f(t), \quad (9)$$

where the damping parameter ξ is expressed as $\xi = \alpha m + \beta k$. The parameter m is mass, k is stiffness and α and β are correspondingly damping coefficients. The equation for the multiple degrees of freedom is

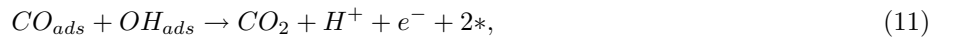
$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} - \nabla \cdot \left[c \nabla \vec{u} + c \beta \nabla \frac{\partial \vec{u}}{\partial t} \right] + \alpha \rho \frac{\partial \vec{u}}{\partial t} = \vec{F}. \quad (10)$$

By coupling Eq. (10) to the previously described equations, a good basic model for IPMC actuation has been obtained. The damping equation turned out to be very necessary to describe correct movement of an IPMC strip. Though the values of the parameters α and β are empirical (see Table II), they have an important role of improving the dynamical behavior of the model for non-constant applied voltages.

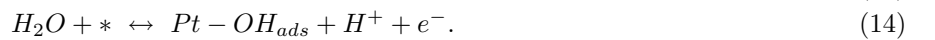
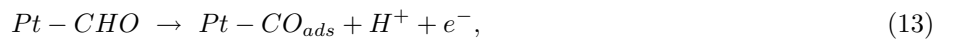
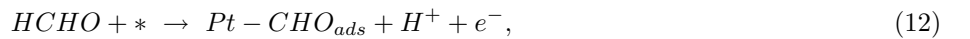
All values, which are used in the simulations, have been brought out in Table II. Fig. 3 shows a comparison between the simulation and an experiment Punning et al. [16]. More comparative figures are introduced in the next section of the paper.

III. MODELING SELF-OSCILLATIONS

We have conducted a series of tests with IPMCs in a constant electric field in formaldehyde (HCHO) solution. Measurements show that current oscillations begin from applied potential of ca. 0.75 V. More information about experiments and conclusions is described in the previous paper Kim et al. [9]. Studies show that there are sequential electrochemical reactions, which take place on the platinum cathode. The initial burst of the current is caused by the reaction



where subscript *ads* denotes species adsorbed to the platinum and * denotes an active platinum site. The result of the reaction (11) is clearing up 2 platinum sites, which causes CO to adsorb again. Chronopotentiometry scans show that before reaction (11), the following reactions occur:



HCHO is dissociated on the electrode surface at lower anodic potentials. Higher anodic potentials cause dehydrogenation of water which results in water oxidation with intermediate Pt-OH formation. We believe that these reactions lead to oscillating potentials, which in turn lead to self-oscillating motion of the IPMC sheet.

Series of chronopotentiometry scans were conducted to characterize oscillations for different HCHO concentrations and current densities. As was brought out in our previous paper Kim et al. [9], the oscillations start at approximately 7 mA/cm². The experiments were conducted up to current density values of 40 mA/cm². Tests with HCHO concentrations of 1 M, 2 M, and 3 M show that oscillations frequencies remain constant up to the current density of 14 mA/cm², but after further increasing the current, in 1 M HCHO, the frequency decreases, in 2 M HCHO, the frequency remains constant, and in 3 M HCHO solution, the frequency starts to increase, as also shown in Fig. 4. Our goal is to develop a model for describing the frequency behavior depending on HCHO concentration and the current density. The basic model and concepts are introduced by D. Kim Kim [17] and work of P. Strasser Strasser et al. [18]. To describe the oscillations, four dynamic parameters, therefore four differential equations, must be observed: concentration of adsorbed OH, CO, the change of the double layer potential due to electrochemical reactions, and the change of the concentration of HCHO near the surface of platinum. First two variables are expressed for a certain current density and HCHO concentration as Kim [17]:

$$\dot{\theta}_{CO} = k_2 M - k_4 \theta_{CO} \theta_{OH}, \quad (15)$$

$$\dot{\theta}_{OH} = k_3 \theta_{CO} M - k_{-3} \theta_{OH} - k_4 \theta_{CO} \theta_{OH}, \quad (16)$$

where θ_{CO} and θ_{OH} are normed adsorption coverages of CO and OH. Variables k_i and M are described by equations

$$k_i(\phi) = \exp[s_i(\phi - \phi_i)], \quad (17)$$

$$M = (1 - \theta_{CO} - \theta_{OH}), \quad (18)$$

where s_i are modeling coefficients and ϕ_i are potentials of the reactions Kim [17]. As our model is highly dynamic, the double layer with thickness δ near the platinum electrode is introduced. At the far end of the layer, the concentration

Table III: Variables and values used in the simulation of electrochemical oscillations.

Parameter	Value	Unit
S_{tot}	0.5×10^{-6}	mol/cm^2
C_{dl}	1	mF/cm^2
A	1.2	$cm^7 / (mA^2 \times mol)$
k	100	-
δ^a	3×10^{-2}	cm
D_{FA}^a	2.5×10^{-5}	cm^2/s
$\phi_{1,2,3,-3,4}^b$	[0.2, 0.3, 0.01, 0.512, 0.77]	V
$s_{1,2,3,-3,4}^b$	[10, -11, 9, -9, 20]	V^{-1}

^aRef. Strasser et al. [18]

^bRef. Kim [17]

of the formic acid is considered constant, and due to the adsorption of $HCHO$ on Pt, the concentration of the solution is changing in time near the electrode. There are two components responsible of decrease of the concentration. The first one is direct oxidation of the formic acid to CO_2 and $2H^+$, the second one is adsorption of CO on the platinum surface due to electrochemical reactions Strasser et al. [18]. The mechanism, which restores the $HCHO$ concentration near the surface is diffusion. So the amount of the formic acid is decreasing significantly while the adsorption rate is high and increasing due to the diffusion during the low adsorption period. The equation describing the diffusion process is

$$\frac{\partial c_{FA}}{\partial t} = \nabla \cdot (D_{FA} \nabla c_{FA}) \quad (19)$$

with constant concentration at the far end of the double layer and flux

$$f = k_2 M (1 + k c_r) S_{tot}, \quad (20)$$

as boundary condition on the electrode. Here S_{tot} denotes the total number of platinum sites per surface area, c_r is normed concentration near boundary layer and equals $c_r = c_{FA}/c_0$, where c_0 is an initial concentration. Variable k is a simulation constant. The second term of Eq. (20) represents simplified version of the direct oxidation path Strasser et al. [18]. Considering those equations and interesting nature of frequency characteristic for different amounts of HCHO (Fig. 4), we can now describe empirical, gray box Shahinpoor and Kim [19] equation for the last dynamic variable - the double layer potential:

$$\dot{\phi} = \frac{1}{C_{dl}} [j_{th} - j_d + A B j^2 (j - j_{th}) c_r - S_{tot} F (k_1 M + k_4 \theta_{CO} \theta_{OH})], \quad (21)$$

where j is applied current density, j_{th} is threshold current density with approximate value of $10 mA/cm^2$, j_d is direct current density and is proportional to the second term of Eq. (20). The variable B is explicitly written as $B = c_0 - c_{neutral}$, where $c_{neutral}$ corresponds to concentration of $2 M$. This is denoted as ‘‘natural’’ concentration, because as it is shown in Figure 4, the oscillation frequency for the case $c_0 = c_{neutral} = 2 M$ does not depend on the applied current density. The numeric data can be found in Table III. The third term in Eq. (21) is empirical and reflects the interesting behavior of the oscillations frequency for different formic acid concentrations. Other terms are similar to the ones described by Strasser et al. [18]. However, some values are adjusted to get realistic simulation results. Measured voltage oscillation comparison to simulation data could be seen in Fig. 5. The simulation does not require any change in boundary or initial conditions for the basic model, which is described in the previous section. However, equations (15), (16), (17), and (21) are simulated using the weak form differential equation on the anode boundary.

By using the obtained voltage output in the base Finite Element Model, which is described in the previous section, we can simulate oscillating deflection of an IPMC muscle. Two sample results for different HCHO concentrations and current densities are shown in Figures 6 and 7. As it could be seen, the amplitude, frequency and for the most part, shape of the deflection show reasonable agreement between modeling and experimental data. However, there is some disharmony at the areas of maximum deflection, where the experiments show distinctly sharp deflections in comparison to rather smooth simulation results.

Figure 1: Illustration of domains and dimensions used in simulations. The length of 3 cm was used also in number of experiments. Notice that there are three different mechanical domains - pure NafionTM polymer, pure Pt coating and diffusion layer, where Pt has diffused into the polymer.

Figure 2: The concentration of counter ions and electric field strength inside the polymer according to simulations.

IV. SUMMARY AND CONCLUSIONS

We have developed a Finite Element model for simulating actuation of an IPMC. The model is largely based on physical quantities and well known or measurable variables. The migration and diffusion of the counter ions inside the NafionTM polymer is described along the electric field change due to the charge imbalance. This in turn is tied into continuum mechanics and dynamics equations, forming a complete system of equations to describe the bending of an IPMC sheet.

The comparison of experimental and simulated tip displacement in time shows reasonable agreement, especially for smaller deflections. The future work is to perform simulations more precise for large displacements, possibly including equations, which describe voltage distribution on the surface of the electrodes depending on the curvature of the IPMC. Taking into account the surrounding environment of the IPMC could also improve the results.

The second part of the work describes the extended model for self-oscillating IPMCs. The oscillations occur when a platinum coated IPMC is immersed into formic acid solution and subjected to a constant potential or current. The extended model takes into account formic acid concentration changes near the electrode and poisoning level of the platinum sites. This in turn results in the oscillating double layer potential, which is used in the base model for calculating time dependent tip displacement of the IPMC muscle. For the most part, the model follows simulation data closely. However, the experimental deflection shows distinctly sharp movements at certain regions, but the simulation gives rather smooth displacement profiles. The future work includes studying further this interesting behavior and possibly improving the model.

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Figure 3: Experimental and simulation results of tip displacement. The simulation is done for potential of 2 volts. Although there is a slight difference of graphs in large displacement region, the model gives precise estimation for smaller displacement.

Figure 4: Experimental Kim et al. [9] and simulated frequency dependence on concentration of HCHO and applied current density. Simulations for 1 M HCHO concentration does not go past 30 mA/cm^2 , because given equation system did not give reasonable results beyond that current density.

Figure 6: Oscillating tip displacement. Experimental Kim [17] data and simulation data for 1 M HCHO solution, applied current density of 20 mA/cm^2 .

Figure 7: Oscillating tip displacement. Experimental Kim [17] data and simulation data for 3 M HCHO solution, applied current density of 10 mA/cm^2 .

Figure 5: Potential oscillations. Measured data Kim [17] and simulated data for 3 M HCHO solution. The potential oscillations were measured between the cathode and anode of the IPMC strip during the experiment. The applied current was maintained at constant value of 20 mA/cm^2 .