

Finite Element Model of a Self-Oscillating IPMC

Deivid Pugal

*Active Materials and Processing Laboratory, Mechanical Engineering Department, University of Nevada, Reno, U.S.A and
IMS Lab, Institute of Technology, Tartu University, Estonia*

Kwang J. Kim*

Active Materials and Processing Laboratory, Mechanical Engineering Department, University of Nevada, Reno, U.S.A

Heiki Kasemägi and Alvo Aabloo

IMS Lab, Institute of Technology, Tartu University, Estonia

This paper presents a 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. (Furthermore, the water drift and the counter ion drift inside the polymer backbone is considered separately.) As self-oscillating behavior of an IPMC was described in our previous paper, the modelling of the electrochemical reactions 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, 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, Teflon, filled with some kind of 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 movable cations inside the polymer migrate towards an electrode due to 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 like Wallmersperger and

Nemat-Nasser have already simulated mass transfer and electrostatic effects. We have used similar approach in our model. Toi[toi2005fea] has shown a Finite Element model including viscosity terms in transportation processes. However, the described model is good for 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 as used by many authors[.]. 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 actuation. Spontaneous oscillations are common phenomena in nature and have been studied in many experiments, including electrochemical systems such as oxidation of organic materials and metals[miller2006oid]. Under certain conditions such system can generate oscillations[krischer2001sfs]. We have conducted series of tests, where 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[.]. 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 backbone polymer and a metal coating. We have used NafionTM 117, coated with

*Electronic address: kwangkim@unr.edu

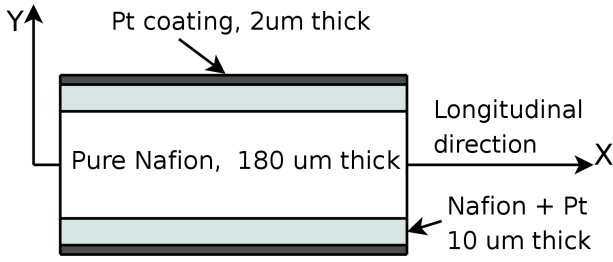


Figure 1: Illustration of domains and dimensions used in modeling

thin layer of platinum in our experiments. Mass transfer and electrostatic simulations are done in three mechanical domains - pure backbone polymer and mixture of polymer and platinum - it comes from the fact that some platinum is diffused into the polymer during coating process [1]. Physical properties and dimensions of pure, $2\mu\text{m}$ thick platinum coating are considered only when calculating bending. That gives us five mechanical domains as shown in Figure 1. Most simulations are carried out for an IPMC strip, 2 - 4 cm long, $200\mu\text{m}$ thick polymer, including $2\mu\text{m}$ thick Pt diffusion region on each side, coated with $2\mu\text{m}$ thick platinum, in a cantilever configuration - one end of the strip is fixed. Gravitational forces are not considered in any of the simulations.

Nernst-Planck equation describes diffusion, convection and in presence of electric field and charges, migration of 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, μ mobility of species, D diffusion constant, T absolute temperature, R gas constant, F Faraday constant, \vec{u} velocity, z charge number and ϕ electric potential. This equation is described for movable cations. As anions are fixed, they maintain constant charge density throughout the polymer. As voltage is applied to the electrodes of an IPMC, all free cations start migrating towards cathode, causing current in the outer electric circuit. As ions cannot move beyond the boundary of the polymer, charges start to accumulate, resulting in increase of electric field, which cancels out the applied one. It could be described by Gauss' Law:

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

where ρ is charge density, ε is absolute dielectric constant and E is the strength of the electric field. A steady state of the cations forms when electric field created by distribution of cations cancels out applied electric field, i.e. the strength of electric field inside the polymer is approximately zero as shown in Figure 2. The steady state cation concentration of $1200\frac{\text{mol}}{\text{m}^3}$ is also brought out in the same figure. It is interesting to notice that there are fluctuations in charge distribution only in really thin boundary layers. There is no charge imbalance

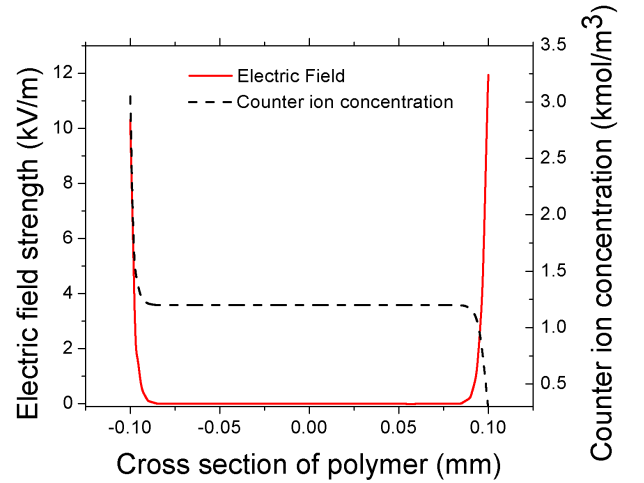


Figure 2: The concentration of counter ions and electric field strength inside the polymer according to simulations.

inside the polymer. General conclusion by many authors is that locally generated charge imbalance nearby platinum electrodes is directly connected to the bending of an IPMC[nematnasser2000eri]. As it worked out very well for our model, we followed the example of Leo[leo:cmi] and defined longitudinal force per unit area in each point in the polymer of an IPMC as follows:

$$\vec{F} = (A \cdot \rho + \text{sgn}(\rho) \cdot B \cdot \rho^2) \cdot \hat{x}, \quad (3)$$

where ρ is charge density and A and B are constants which could be found from different experiments. $\text{sgn}(\rho)$ is to preserve correct sign of the excess charge. The shape of the force inside the polymer is also shown in Figure . To relate the force to the physical bending of an IPMC sheet, we use continuum mechanics equations, described in Comsol Multiphysics structural mechanics software package. Normal and shear strain are defined as:

$$\varepsilon_i = \frac{\partial u_i}{\partial x_i}, \quad \varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right), \quad (4)$$

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

$$\sigma = D\varepsilon, \quad (5)$$

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 following relation is satisfied:

$$-\nabla \cdot \sigma = \vec{F}, \quad (6)$$

which is basically Navier's equation for displacement. The stress generated in the polymer is shown in Figure .

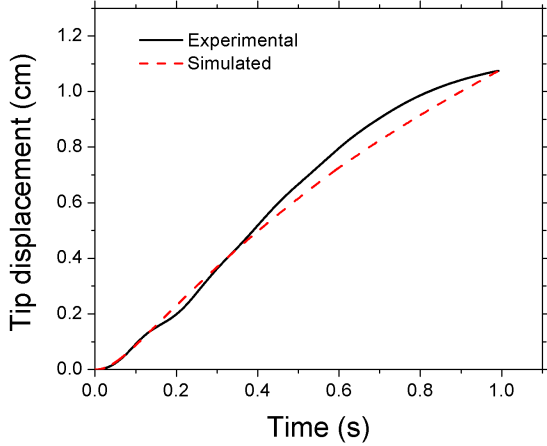


Figure 3: Experimental and simulation results of tip displacement.

As our simulations are rather dynamic 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

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} - \nabla \cdot c \nabla \vec{u} = \vec{F}, \quad (7)$$

where the second term is the static Navier's equation. Dynamic part is introduced by the first term of the equation. To describe damping of the system, we use Rayleigh damping model, which is for a system of one degree of freedom as follows:

$$m \frac{d^2 u}{dt^2} + \xi \frac{du}{dt} + ku = f(t), \quad (8)$$

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

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} - \nabla \cdot \left[c \nabla \vec{u} + c \beta \nabla \frac{\partial \vec{u}}{\partial t} \right] + \alpha \rho \frac{\partial \vec{u}}{\partial t} = \vec{F}. \quad (9)$$

By coupling Eq. (9) to the previously described model, good basic model for IPMC actuation has been got. Figure 3 shows simulation result in comparison to an experiment. All values used in the simulations have been brought out in Table I.

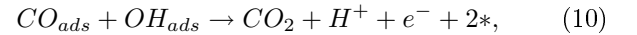
III. SELF-OSCILLATIONS

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. 0.75V. More about experiments

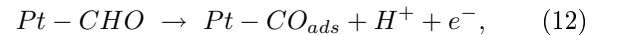
Table I: Parameter values used in bending simulations.

Parameter	Value	Unit
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and conclusions could be read from our previous letter . However, studies show that there are sequential electrochemical reaction taking 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 (10) is freeing up 2 platinum sites, which causes CO adsorb again. Chronopotentiometry scans show that before reaction (10), the following reactions occur:



HCHO is dissociated on the electrode surface at lower anodic potential. Higher anodic potential causes dehydrogenation of water which results in water oxidation with intermediate Pt-OH formation. We believe that these reaction 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 concentration and current densities. As was brought out in our previous paper [], the oscillations start at approximately 7 mA/cm^2 . The experiments were conducted up to current density values of 40 mA/cm^2 . Tests with HCHO concentrations of 1 M, 2 M, and 3 M show that oscillations frequency remains constant up to current density of 14 mA/cm^2 , but after further increasing 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 . Our goal is to develop a model of the frequency behavior depending on HCHO concentration and current density. The basic model and concepts are taken from PhD thesis of D. Kim [] and work of P. Strasser []. To describe oscillations, the four dynamic parameters, therefore 4 differential equations, must be observed: concentration of adsorbed OH, CO, change of double layer potential due to electrochemical reactions, and change of concentration of HCHO near the surface of platinum. First two variables could be expressed for a certain current density and

$HCHO$ concentration as []:

$$\dot{\theta}_{CO} = k_2M - k_4\theta_{CO}\theta_{OH}, \quad (14)$$

$$\dot{\theta}_{OH} = k_3\theta_{CO}M - k_{-3}\theta_{OH} - k_4\theta_{CO}\theta_{OH}, \quad (15)$$

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

$$k_i(\phi) = \exp[s_i(\phi - \phi_i)], \quad (16)$$

$$M = (1 - \theta_{CO} - \theta_{OH}), \quad (17)$$

where s_i is a modeling coefficient and ϕ_i are potentials of reactions. 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 of formic acid is considered constant, and due to 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 formic acid to CO_2 and $2H^+$, the second one is adsorption of CO on platinum surface due to electrochemical reaction.[] The mechanism restoring the $HCHO$ concentration near the surface is diffusion. So the amount of 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

$$\frac{\partial c_{FA}}{\partial t} = \nabla \cdot (D_{FA}\nabla c_{FA}) \quad (18)$$

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

$$f = k_2M(1 + kc_r) \cdot S_{tot}, \quad (19)$$

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 initial concentration. Variable k is a simulation constant. The second term of EQ (19) represents simplified version of the direct oxidation path, shown by Strasser. Considering those equations and interesting nature of frequency characteristic for different amounts of HCHO (Figure []), we can now describe somewhat empirical equation for the last dynamic variable - double layer potential:

$$\dot{\phi} = \frac{1}{C_{dl}} [j_{th} - j_d + A \times B \times j^2 \times (j - j_{th}) \times c_r - S_{tot}F(k_1M + k_4\theta_{CO}\theta_{OH})], \quad (20)$$

where j is applied current density, j_{th} is threshold current density with approximate value of $10mA/cm^2$, j_d is direct current density and is proportional to the second term of EQ. (19). Variable B could be explicitly written as $B = c_0 - c_{neutral}$, where $c_{neutral}$ corresponds to

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

Parameter	Value	Unit
S_{tot}	0.5×10^{-6}	mol/cm^2
F	96×10^6	mC/mol
C_{dl}	1	mF/cm^2
A	1.2	$cm^7 / (mA^2 \times mol)$
k	0.5×10^2	-
$\phi_{1,2,3,-3,4}^a$	[0.2, 0.3, 0.01, 0.512, 0.77]	\bar{V}
$s_{1,2,3,-3,4}^a$	[10, -11, 9, -9, 20]	V^{-1}

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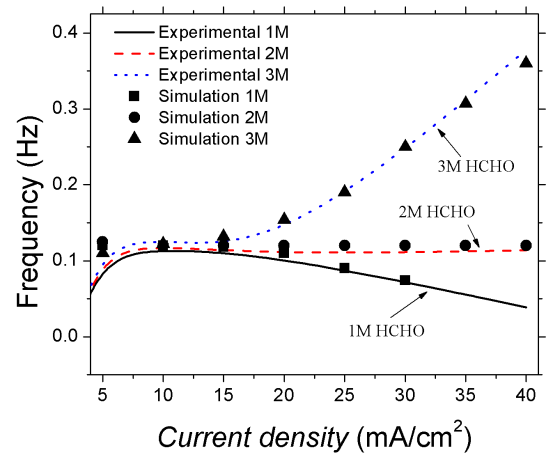


Figure 4: Experimental and simulated frequency dependence on concentration of HCHO and applied current density. Simulations for 1 M HCHO concentration does not go past $30 mA/cm^2$, because given equation system did not give reasonable results beyond that current density.

concentration of 2 M. This is denoted as “neutral” concentration, because as could be seen in Figure , the oscillation frequency for the case $c_0 = c_{neutral} = 2M$ does not depend on the applied current density. F is Faraday constant. The numeric data could be found in Table III. The third term in EQ. (20) 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[]. However, some values are adjusted to get realistic simulation results. Measured voltage oscillation comparison to simulation data could be seen in Figure 5.

By coupling described equations to the base Finite Element Model, described in previous section, we can simulate oscillation deflection of an IPMC muscle. Two sample results for different HCHO concentrations and current densities are shown in Figures 6 and 7.

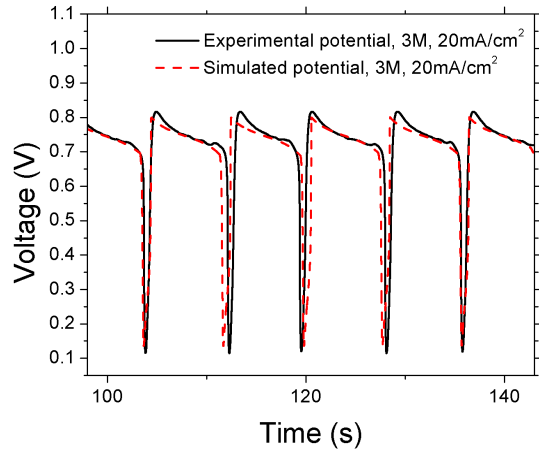


Figure 5: Potential oscillations. Measured data and simulated data for 3M HCHO solution, with applied current density of 20 mA/cm^2 .

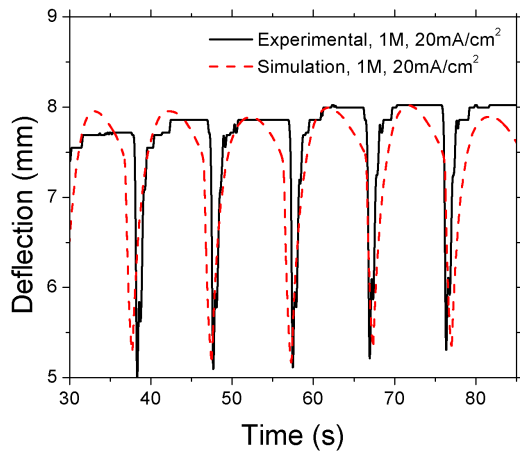


Figure 6: Oscillating tip displacement. Experimental data and simulation data for 1M solution, applied current density of 20 mA/cm^2 .

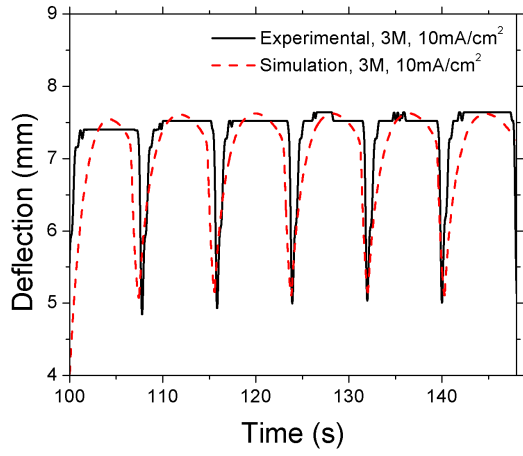


Figure 7: Oscillating tip displacement. Experimental data and simulation data for 3M solution, applied current density of 10 mA/cm^2 .