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Structural modeling of actuation of IPMC in dry environment: effect of water content and activity

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Abstract. Structural modeling of unencapsulated ionic polymer metal composite (u-IPMC) actuators that are used for flapping the insect scale-flapping wing of micro air vehicles (FMAV) in dry environmental conditions is carried out. Structural modeling for optimization of design parameters for retention of water, maximize actuation performance and to study the influence of water activity on the actuation characteristics of u-IPMC is explored for use in FMAV. The influence of equivalent weight of Nafion polymer, cations, concentration of cations, pre-treatment procedures on retention of water of u-IPMCs and on actuation parameters, flapping angle, flexural stiffness and actuation displacement are investigated. IPMC designed with Nafion having equivalent weight 900-1100, pre-heated at 30^0C and with sodium as the cations is promising for optimum retention of water and actuation performance. The actuation parameters while in operation in dry and humid environment with varying water activity can be tuned to desirable frequency, deflection, flap angle and flexural stiffness by changing the water activity and operational temperature of the environment.

Keywords: ionic polymer metal composite (IPMC) actuators; structural modeling; retention of water; water activity and actuation performance

1. Introduction

Soft actuation ionic polymer metal composite (IPMC) devices possess favorable characteristics viz. electro mechanical coupling, large bending displacement, low driving voltage, potential biocompatibility and ability to operate without moving parts (Gong *et al.* 2009, Akle *et al.* 2006). These attractive features make IPMC a potential material in biomimetic design (Paquette *et al.* 2005). IPMCs are proposed as actuators in biomimetic robotics, medical devices, micromanipulators and flapping-wing micro air vehicle (FMAV). FMAV have broad applications such as hazardous environment exploration, reconnaissance, and search and rescue. In contrast to the applications of IPMC in wet environment such as artificial muscles and biomedical devices, IPMC as flapping micro air vehicles have to operate mostly in dry environment. FMAV often encounter hazardous and dry environment. As the inner water in the IPMC dries in air, the actuation performance of the IPMC continuously varies. Moreover, once the inner water has completely dried out, the IPMC cannot actuate.

IPMCs consist of ionomer film, usually Nafion [poly (perfluoro-3,6-dioxa-4-methyl-7-octene sulfonic acid – co - tetrafluoroethene)] sandwiched between two metal electrodes (Bhandari *et al.* 2012) such as gold or platinum. Nafion ionomer consists of polytetrafluoroethylene (PTFE) backbone with perflorinated side-chains ended by sulfonic groups arranged at intervals along the backbone (Shahinpoor and Kim 2001, Kawano *et al.* 2002).

Nafion undergoes phase separation into discrete hydrophobic and hydrophilic domains. The hydrophobic domain is formed on the surface with the fluorocarbon backbone, and the hydrophilic domain is formed in the core as ionic cluster with the perfouroether side chains terminated with sulfonic acid groups. Interestingly, Nafion possesses high ionic conductivity mechanical, thermal and chemical stability (Kawano *et al.* 2002). With Nafion ionomer, the covalently fixed sulfonic acid anions can be neutralized with counter ions such as Na^+, Li^+, K^+, H^+ etc (Lughmani *et al.* 2009). Therefore, under an electric field, water-swollen Nafion membrane based IPMCs have a tendency to deform (Lin *et al.* 2014) due to the movement of water associated with conduction of cations between the electrodes (Chen *et al.* 2011a, Duan *et al.* 2013, Doyle *et al.* 2003). The hydration of Nafion decreases the cation - anion interaction and increases the ionic conductivity. This facilitates the bending motion of the actuators (Jung *et al.* 2003). Under a DC electric field, while the cathode boundary layer expands due to the migration of hydrated positive ions, the anode boundary layer shrinks.

While the water uptake and swelling of the ionic clusters in Nafion and extent of migration of ions influence the properties of the actuator such as response time, electrical capacitance, stress, strain, and work density (Mirfakhrai *et al.* 2007, Jalani and Datta 2005a, Morris and Sun 1993), the retention of water in dry environment also influence the properties of the actuator. The water sorption changes with dimension (Morris and Sun 1993, Beattie *et al.* 2001) and mechanical, thermal and chemical properties of Nafion

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(Kawano *et al.* 2002). Therefore, the actuation of IPMC device and its lifetime performance is mainly dependent upon the content of water retained in the hydrophilic domain of Nafion-IPMC. If the retention of water is less, it results in low deflection, low flap angle and high stiffness and results in material imperfections during actuation. On the other hand, more retention of water causes swelling of the Nafion membrane. Though the electrode region does not expand with the water, the Nafion swelling exerts pressure on the electrode region (Lee *et al.* 2005) and causes cracks (Punning *et al.* 2007) in the electrode resulting in water leakage and decreased conductivity of the electrode region. IPMC based actuators may undergo failures due to the cracks formed on the surface of the electrode by repeated contraction and relaxation and decrease of surface conductivity (Lee *et al.* 2006), dehydration and loss in performance when operated in air (Kim *et al.* 2006).

The gradual evaporation of water contained in Nafion during the actuation in air reduces the performance of the IPMC. The water loss can be prevented using different strategies such as change of solvent, use of thicker Nafion membranes and application of polymer coating on IPMC etc. Heavy water (D_2O) and dimethyl sulfoxide (DMSO) were tried instead of water to prevent solvent loss; however D_2O led to reduced actuation response. On the other hand, the IPMC swelled too much in DMSO and could not generate actuation force (Lee *et al.* 2006). Water loss was prevented using thicker Nafion membrane; however, with the increased stiffness of the beam, the actuator displacement is significantly reduced (Chen *et al.* 2011b). To eliminate evaporation of water from the Nafion-IPMC, waterproof materials such as parylene, silicone rubber and other polymers were used to encapsulate the IPMC. Though the water loss was prevented to some extent by encapsulation with parylene coating, the parylene coating underwent delamination from the surface of the electrode during actuation (Kim *et al.* 2006). Beyond the electrolysis limit of aqueous solvent, splitting of water into hydrogen and oxygen gases usually takes place which can creates blisters under the barrier coating and delamination from the polymer transducer (Bennett and Leo 2004). Substituting the solvent with ionic liquid was attempted to prevent the water loss; but ionic liquid increases the time of response of IPMC and swelling of Nafion which results in a swollen and soft actuator (Palmre *et al.* 2009).

The water diffusivity, interfacial mass transport and volume available for transport of water in Nafionis influenced by the retention of water and water activity. Though encapsulation of IPMC can aid the retention of water to a large extent, such encapsulation can lead to increasing mechanical stiffness, which could affect the actuation characteristics adversely. Therefore, the encapsulation of IPMC for use as FMAV is not preferred. The performance indicators of IPMC actuator for FMAV in dry air such as displacement, force and the lifetime is influenced by water activity in Nafion-IPMC. Therefore, research on the influence of water activity on the actuation characteristics of unencapsulated Nafion-IPMC (u-IPMC) for operation in dry air is highly relevant.

To the best of author's knowledge, the research efforts so far made on unencapsulated Nafion-IPMC as a smart actuator for FMAV remain inconclusive. Structural modeling of IPMCs is of great engineering importance. If a particular design of an IPMC enhances actuation force and actuation lifetime, the same design reduces the actuation displacement and force (Saher *et al.* 2004). Structural modeling of IPMCs for the following criteria was carried out. First, modeling of the different fabrication parameters which can retain water without any loss and achieve maximum actuation performance is investigated. Second, the effect of water activity during use in dry environment is carried out. Therefore, the present paper deals with structural modeling of unencapsulated Nafion-IPMC for optimization of design parameters for the retention of water and to maintain the actuation capability. The paper also deals with the studies on the influence of water activity on the actuation characteristics of unencapsulated Nafion-IPMC for use in FMAV.

2. Methodology

2.1 Structural modeling for the actuation of IPMC due to variation in water uptake

Structural modeling is considered for predicting the actuation performance of IPMCs. Mukherjee and Ganguli (2010) have modeled IPMC actuators for use as flapping wing of bio inspired dragonfly-like flapping MAV. In the present research, structural modeling of IPMC for actuation under varying water holding capacity and water activity for the compensation of water loss and for operation in dry environment is carried out. The water holding capacity is defined as the ratio of moles of absorbed solvent per mole of sulfonic acid groups within Nafion. The hydration volume is represented as the ratio of volume of absorbed water to the dry volume of the polymer (Nasser *et al.* 2006). The water holding capacity as a function of different parameters was modeled using the Buechler and Leo model (Buechler and Leo 2007). Energy method using variational principle was adapted to solve the IPMC cantilever actuator structure. Hamilton's principle was used to derive the equations of motion

$$\int_{t_1}^{t_2}\left(\delta\mathcal{T}-\delta\mathcal{V}+\delta\mathcal{W}^{ext}\right)dt=0 \quad \delta\Big|_{t_1}^{t_2}=0 \tag{1}$$

$\delta\mathcal{T}$ = Variation in kinetic energy,

$\delta\mathcal{V}$ = Variation in potential energy,

$\delta\mathcal{W}^{ext}$ = Variation in work done by the external force.

The variation in kinetic energy, potential energy (Strain energy, coupling potential energy and dielectric potential energy) and external work done is expressed as Eq. (2) to (6).

$$\delta\mathcal{T}=\delta\underline{A}'\left(\int_{V_{ol}}-\rho\underline{\Phi}_u\underline{\Phi}_u{}'dV_{ol}\right)\ddot{\underline{A}} \tag{2}$$

$$\delta V_{se} = \delta \underline{A}' \left[\int_{V_{ol}} \left(L_u \underline{\Phi}_u' \right)' \mathrm{c}^{\mathrm{D}} \left(j\omega \right) \left(L_u \underline{\Phi}_u' \right) dV_{ol} \right] \underline{A} \tag{3}$$

$$\begin{aligned} \delta \mathcal{V}_{couple} = & -\delta \underline{A}' \left[\int_{V_{ol}} \left(L_u \underline{\Phi}_u' \right)' \mathrm{h} \left(j\omega \right) \Phi_D' dV_{ol} \right] \underline{q} \\ & -\delta \underline{q}' \left[\int_{V_{ol}} \underline{\Phi}_D \mathrm{h}' \left(j\omega \right) \left(L_u \underline{\Phi}_u' \right) dV_{ol} \right] \underline{A} \end{aligned} \tag{4}$$

$$\delta \mathcal{V}_{dielectric} = \delta \underline{q}' \left[\int_{V_{ol}} \underline{\Phi}_D \varepsilon^{\mathrm{T}^{-1}} \left(j\omega \right) \underline{\Phi}_D' dV_{ol} \right] \underline{q} \tag{5}$$

$$\delta \mathcal{W}^{ext} = \delta \underline{A}' \underline{\Phi}_u' \underline{f}' + \delta \underline{q}' \delta \underline{V}' \tag{6}$$

Some of the assumptions adopted in the modeling of IPMC actuators are: 1. IPMC are rectangular beams with base Nafion membrane and electrodes on both sides 2. The beam is assumed slender and the displacement is only in X_3 direction 3. The Euler-Bernoulli assumption is satisfied with only one electrode on both sides of the beam 4. Constant electrical displacement is considered 5. The mode shapes of the uncoupled beam are found by approximating them as shape functions. A second order differential equation that solves the IPMNC actuation was developed in matrix form (Buechler and Leo 2007)

$$\begin{Bmatrix} \underline{A}(j\omega) \\ \underline{q}(j\omega) \end{Bmatrix} = \begin{bmatrix} -\mathbf{M}_s\omega^2 + \mathbf{K}_s(j\omega) & \underline{\Psi}(j\omega) \\ \underline{\Psi}'(j\omega) & \mathbf{C}^{-1}(j\omega) \end{bmatrix}^{-1} \begin{Bmatrix} \Phi_u \underline{f}'(j\omega) \\ \underline{v}'(j\omega) \end{Bmatrix} \tag{7}$$

The capacitance, mass, stiffness matrices and the coupling vector matrices are obtained from the variation of dielectric potential, kinetic energy, strain energy and coupling potential energy, respectively. The dry Young's modulus was taken as 300 MPa (Nasser and Thomas 2004) and dry density as 2.225 g/cm^3. The initial dimension used for the modeling of the IPMC were: length 35 mm: width 3.5 mm. The platinum electrode layer has Young's modulus (Y_M) 75 GPa and density (ρ_M) 20 g/cm^3 (both the platinum and gold layer)(Nasser and Thomas 2004). Also, ρ_B and ρ_M are the density of the wet Nafion and metal, respectively. The modeling parameters used for the optimization of design parameters of Nafion and IPMC for optimum water uptake are given in Table 1. The change in retention of water (water uptake) with variation in dimension of the IPMC is calculated as reported elsewhere (Wu *et al.* 2011).

The change material properties such as Young's modulus, density and dielectric permittivity due to different water uptake conditions are calculated. The average Young's modulus is obtained using the equations given below (Nasser and Thomas 2004).

$$\bar{Y}_{IPMC} = \frac{Y_M Y_B}{BA_B Y_M + (1 - BA_B) Y_B} \tag{8}$$

$$B = \frac{(1+\bar{w})(1-f_M)}{(1+\bar{w}(1-f_M))}, \quad w = \bar{w}(1-f_M)$$

where A_B = concentration factor (0.55),

Y_B = Young's modulus of Nafion at solvation of IPMC ($\bar{w}$),

w and $\bar{w}$ = water uptake of Nafion membrane and IPMC respectively.

f_M and scaling factor (SF) = volume fraction of the metal plating in a dry sample and the weight fraction of dry polymer in the IPMC (Nasser and Thomas 2004).

$$f_M = \frac{(1+SF)\rho_B}{(1+SF)\rho_B + SF\rho_M} \tag{9}$$

$$\rho^* = \frac{(\rho_d + w\rho_w)}{(1+w)} \tag{10}$$

$$1 = \left(\frac{\bar{\kappa} RT}{C^- F^2} \right)^{1/2} \tag{11}$$

where ρ^* = effective density of hydrated Nafion membrane, ρ_d and ρ_w = density at dry and wet condition, respectively.

$\bar{\kappa}$ = overall electric permittivity of the hydrated IPMC membrane;

l = length of the boundary layer,

C^- = mole concentration of the anions (value depends on the water intake of the Nafion region),

F = Faraday's constant; R, universal gas constant = 8.314 J/mol/K

T = cluster temperature (Nasser 2008).

The Young's modulus, density and dielectric permittivity of Nafion membranes and IPMC were calculated from Eqs. (8) to (11) for different water uptake levels.

The optimization of design and fabrication parameters [changes in concentration of cations (concentration of NaCl 0 to 4 mol/L), type of cations (Li, Na, K and Cs), equivalent weight of Nafion polymer (800 to 1400), sorption and desorption of water, pre-treatment procedure (heat treatment)] for the retention of water and its effect on the actuation parameters (tip deflection, resonant frequency, flapping angle and flexural stiffness of the actuator) are modeled. The modeling parameters used for the optimization of design parameters of Nafion and IPMC for optimum retention of water is given in Table 1. The change in dimensions for a dry and wet IPMC sample is derived based on the literature (Li and Zhao 2013). The modeling parameters used for the research on the effect of water activity (a_i) and actuation of IPMC under dry environmental and operational conditions (influence of temperature and variation of water activity) is given in Table 2.

In our previous work, the validation of the present model is done by modeling the cantilever beam with the dimensions proposed by Buechler and Leo (Buechler and Leo 2007) and a correct match of the present model with the Buechler and Leo model was presented (Swarrup *et al.* 2014) (Fig. 1).

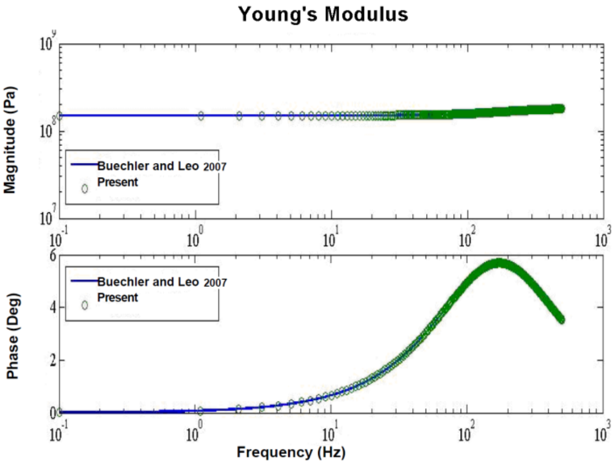


Fig. 1 Change of Young's Modulus with frequency and comparison of the present model with the Buechler and Leo model (Swarrup *et al.* 2014)

3. Results and discussion

3.1 Effect of water retention and its activity on Nafion

The extent of solvation and expansion of Nafion membrane is accomplished by the overall influence of osmotic pressures, electrostatic forces, and elastically induced interfacial stresses within the Nafion membrane (Nasser and Thomas 2004). The elastic resistance of the PTFE backbone is dependent on the nature of the cation used for neutralization (Nasser and Thomas 2004). The solvent-induced swelling strains in Nafion-IPMC are smaller than in the virgin Nafion polymer due to the sandwiching of Nafion between two metal electrodes.

In dry state, the hydrophobic matrix of Nafion is responsible for ~90 vol% and the hydrophilic sulfonic acid groups account for ~10 vol% (Zhao *et al.* 2011). The first event with the exposure of water to dry Nafion having surrounding water activity 0.01 is the hydration of sulfonic acids and formation of hydronium ions. The initial event of solvation of hydrophilic shell results in chemically bound water with reduced diffusivity of water. The effective diffusivity is also diminished by the tortuous network of hydrophilic domains (Zhao *et al.* 2011). However, with the increase of water content, the water in hydrophilic clusters converts to free bulk water and diffuses more easily. The degree of water sorption is controlled by net effect of the energy of hydration of the hydrophilic cluster moieties and the energy to swell the hydrophobic matrix.

In dry and operational conditions, the retention of water and actuation largely depend on the nature of water present in the ionic cluster of hydrophilic shell. Normally, the water bound with sulfonic groups in the cluster remains as structured water and the water which is not bound remains freely. Free water present in Nafion membrane has a dielectric constant of 78 at room temperature which enables it to reorient to oppose applied electric fields (Nasser and Thomas 2004). The structured bound water exhibits a reduced effective dielectric constant, ~ 6 at room temperature (Bockris *et al.* 1998). Under these conditions, the response of the IPMC actuator largely depends on the retained water and extent of migration of cation ions along with the water.

Different empirical models such as finite multilayer Brunauer-Emmett Teller (BET) (Thampan *et al.* 2000), modified BET (Tsonos *et al.* 2000) and Flory-Huggins explain the behavior of water uptake in Nafion (Futerko *et al.* 1999). Variation in water uptake in Nafion membrane influences the material properties significantly. Freger developed a model that relates the shear modulus to the swelling pressure of the polymer due to water sorption (Freger *et al.* 2002). Choi and his co-workers reported an empirical formula using OEH technique to obtain Young's modulus for different volume fractions of water in Nafion (Choi *et al.* 2005). They calculated Young's modulus for samples with different water sorption as one third of shear modulus by assuming Poisson ratio of 0.5 for Nafion (Choi *et al.* 2005). While higher water uptake of Nafion results in a decrease of Young's modulus, very high level of water uptake may swell the membrane causing destruction (Choi *et al.* 2005). The change in linear strain with dimensional changes due to water absorption was reported by Majsztrik *et al.* (2008).

The present structural modeling of IPMC reveals interesting influence on actuation parameters (actuation displacement, frequency, flapping angle and flexural stiffness) due to variation in retention of water and water activity. The retention of water is influenced by the (i) fabrication parameters (change in equivalent weight of Nafion, concentration of cations, type of cations and pre-treatment procedures). The variation in water activity under operational conditions influences the actuation of u-IPMC.

3.2 Optimization of design parameters of u-IPMC for optimum water retention

3.2.1 Water retention and actuation of u-IPMC due to dimensional variation

The swelling of hydrophilic phase due to water sorption of Nafion, increases the volume available for water transport (Zhao *et al.* 2011). The linear expansion of the hydrophilic domains is much larger than the linear expansion of the whole Nafion membrane. Zhao and his co-workers reported that 40% expansion of Nafion due to water absorption originates from 600% volume expansion of the hydrophilic domain (Zhao *et al.* 2011). The water uptake in IPMC swells the Nafion membrane and induces dimensional change. The dimensions of the dry IPMC are L x W x T = 29 mm x 4.49 mm x 283 µm (Li and Zhao 2013). The dimensions of the wet IPMC are L x W x T = 33 mm x 4.95 mm x 323 µm (Li and Zhao 2013). The higher water absorption increases the mass of the actuator and decreases the Young's modulus thereby having an effect on the displacement, flap angle and frequency (Fig. 2). It is observed that the deflection and flap angle are higher in case of wet sample compared to the dry samples.

Table 1 Optimization of design parameters of u-IPMC for optimum water retention

Studies		Actuator Details
1.1 Effect of water retention and actuation of u-IPMC due to dimensional variation		Dry Sample- L x W x T 29 mm x 4.49 mm x 283 µm(Li and Zhao 2013) Wet Sample- L x W x T 33 mm x 4.95 mm x 323 µm (Li and Zhao 2013) Young's modulus Nafion, dry and wet -300 MPa, 70 MPa (Nasser and Thomas 2004) Density dry, wet (Li and Zhao 2013) Dielectric permittivity, dry and wet- 0.65 and 0.593 (Li and Zhao 2013)
1.2 Effect of cation, water retention and actuation of IPMC	1.2.1 Effect of cation concentration	Concentration of NaCl vs water uptake values (Nasser and Wu 2006) Sample- L x W x T 35 mm x 3.5 mm x 274 µm (Nafion 1110) Young's modulus dry-300 MPa, after water uptake calculated using Eq. (8), Dry density-2.225g/cm^3, Density and dimension change with water uptake obtained from literature (Morris and Sun 1993, Wu *et al.* 2011); Effective density calculated using Eq. (10)
	1.2.2 Effect of type of cations	The modelling parameters, Young's Modulus, density and water uptake for differe nt type of cations are obtained from literature (Nasser and Wu 2006) Sample- L x W x T 35 mm x 3.5 mm x 197.8 µm (Nafion 117). Dimension change with water uptake obtained from literature (Wu *et al.* 2011); Effective density calculated using Eq. (10)
1.3 Effect of equivalent weight of Nafion, water retention and actuation of IPMC		Nafion (H^+ ions) Equivalent weight vs. water uptake (Doyle *et al.* 2003). Sample- L x W x T 35 mm x 3.5 mm x 197.8 µm (Nafion 117). Young's modulus dry-300 MPa, after water uptake calculated using Eq. (8), Dry density-2.225 g/cm^3, Density and dimension change with water uptake obtained from literature (Morris and Sun 1993, Wu *et al.* 2011); Effective density calculated using Eq. (10)

Table 2 Actuation of IPMC under operational conditions-Efect of water activity and physical state of absorbing water

Studies		Actuator Details
2.1 Effect of water activity and physical state of absorbing water	2.1.2 Effect of sorption and desorption of water on the actuation of IPMC-influence of activity of water in vapour phase	Variation in water uptake vs. activity of water in vapour phase (a_i) for sorption and desorption (Jalani *et al.* 2005b). Sample- L x W x T 35 mm x 3.5 mm x 197.8 µm (Nafion 117). Young's modulus dry-300 MPa, after water uptake calculated using Eq. (8), Dry density- 2.225 g/cm^3, Density and dimension change with water uptake obtained from literature (Morris and Sun 1993, Wu *et al.* 2011); Effective density calculated using Eq. (10)
	2.1.2 Effect of temperature on the activity of water in vapour phase	Effect of water uptake at vapor phase and at temperatures 30 and 90 ^{0}C (Jalani *et al.* 2005b). Sample- L x W x T 35 mm x 3.5 mm x 197.8 µm (Nafion 117). Young's modulus dry-300 MPa, after water uptake calculated using Eq. (8), Dry density- 2.225 g/cm^3, Density and dimension change with water uptake obtained from literature (Morris and Sun 1993, Wu *et al.* 2011); Effective density calculated using Eq. (10)
	2.1.3 Effect of the activity of water in vapour phase for operation at high temperature	Young's modulus values for different temperatures for fixed a_i values are obtained from the report of Majsztrik (2008). Sample- L x W x T 35 mm x 3.5 mm x 274 µm (Nafion 1110). Density and dimension change with water uptake obtained from literature (Morris and Sun 1993, Wu *et al.* 2011); Effective density calculated using Eq. (10)

The frequency is higher in case of the dry sample than the wet sample. The deflection increased from 0.2 mm to 1.4 mm whereas the frequency dropped from 37.5 Hz to 16.6 Hz. In spite of the favorable influence of retention of water on the actuation, the excessive number of water molecules that are uncombined with cations resist the mobility of hydrated cations.

3.2.2 Effect of cation, water retention and actuation of IPMC

Type of cations

The number of water molecules in the hydration shell around sulfonic acid in Nafion membrane depends on the type of cations associated with the sulfonic acid (Choi *et al.* 2005). For K^+-exchanged Nafion membrane two water molecules are bound per SO_3^- side chain. With Na^+ and Li^+ exchanged Nafion membrane, 3-5 molecules are bound. Overall, the number of water molecules per sulfonic acid in Nafion is around 4-6 in the fully hydrated state (Choi 2004). Therefore, the diameter of ionic cluster with Li and Na cations with hydrophilic site is relatively higher than that of K, Rb and Cs cations.

For a particular input voltage, water in tandem with the cations present in the membrane move toward the cathode. The movement of waterfrom one region to other happens either through primary solvation shell migration of water or other solvent molecules, or through secondary electroosmotic migration of water (Nasser and Thomas

2004). The change in water uptake of Nafion membrane with variation in cationic forms was analyzed by Jalani and Datta (2005a). The material properties for different cations and water uptake are obtained from Nasser and Wu (2006). As the atomic radius of cations increases, the water content in Nafion decreases (Xie *et al.* 1998). As the acid dissociation constant increases, the water uptake increases up to a certain level and then plateaus. Similarly, the density of acid groups influence the water absorption of polymer (Jalani and Datta 2005a). The rate of migration of alkali metal ions through Nafion membrane at high concentration, is in the order Li+ < Cs+ < Rb+ < Na+ < K+. Small cations move faster than the large cations. It has been reported that Lithium based Nafion-IPMC exhibit fast actuation followed by some small reverse relaxation under constant voltage (DC) across its faces, while extensive back relaxation is observed for sodium, potassium, rubidium, cesium, thallium ion based Nafion-IPMCs (Nasser and Zamani 2003). The relaxation is due to the migration of water from the high-pressure cathode boundary layer towards anode boundary layer; the relaxation continues until the water equilibrium is established.

As the size of cation increases, Young's modulus also increases with reduced water uptake (Xie *et al.* 1998, Nasser and Zamani 2006, Nasser 2008). The present modeling reveals that Li ions with the minimum size favors holding of more water and migration of water along with cation with reduced tortuousity. The effect of cations on the electrostatic and osmotic forces within the ionic clusters influence the flow of water into or out of the ionic clusters. Therefore, Li based IPMC favors higher deflection of 5 mm and flap angle of 9 deg compared to the other cations Na, K and Cs with Cs. The least deflection of 1.9 mm is observed with Cs based IPMC (Fig. 3). The Cs ion containing IPMC has a higher resonant frequency of 18.7 Hz whereas Li based IPMC has a resonant frequency of 10.8 Hz. Therefore, to have a reasonable frequency and deflection value, Na ion is highly preferable. The deflection for Na ion based actuator is 2.87 mm with frequency of 14.4 Hz. Comparing the flexural stiffness values, Na ion IPMC has 0.6 $\times 10^{-6}$ N/m^2 whereas Li ion IPMC has 0.39 $\times 10^{-6}$ N/m^2 and Cs ion IPMC has 1.11 $\times 10^{-6}$ N/m^2

Cation concentration

The present research with Na^+ exchanged Nafion-IPMC reveal interesting variation of actuation properties with concentration of Na^+. With Na^+ exchanged Nafion, 3-5 molecules are structurally bound (Choi 2004). The water uptake for different cation concentration reported by Nasser *et al*. (2006) was adopted. It is known that the cations counter the charges of anions and promote ionic conduction in tandem with migration of water. Therefore, higher the concentration of cations, higher is the conductivity. However, in the present study, as the concentration of cation increases, the level of water retention decreases. With increase of cation concentration, interaction forces between the cations and the fixed anions within the clusters become greater and display pseudo-crosslinking resulting in higher stiffness of IPMC (Nasser and Thomas 2004). Therefore, removal of all the cations from the clusters results in a decrease in the corresponding stiffness and frequency. Therefore, it is observed that as the concentration of NaCl increased from 0 to 4 mol/L, the deflection decreases from 0.64 mm to 0.6 mm and the frequency increases from 25.7 Hz to 27.8 Hz (Fig. 4). Therefore, the concentration of NaCl up to 4 mol/L does not affect the actuation parameters substantially.

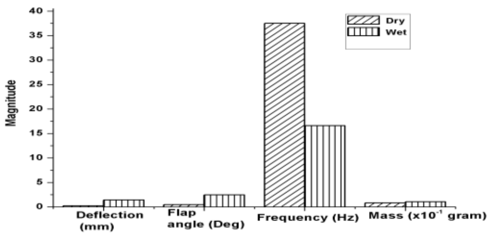


Fig. 2 Variation of actuation characteristics of of wet and dry IPMC

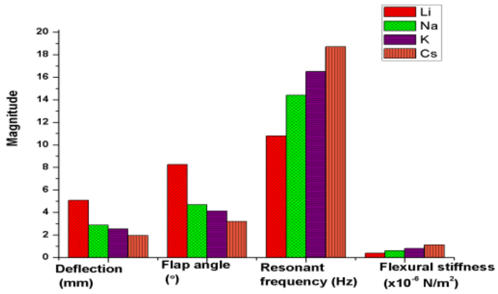


Fig. 3 Effect of type of cations on the actuation parameters of IPMC

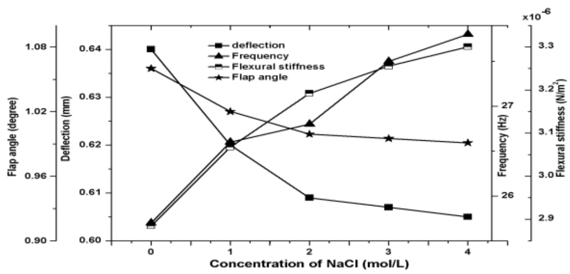


Fig. 4 Variation of concentration of cations on the actuation parameters of IPMC

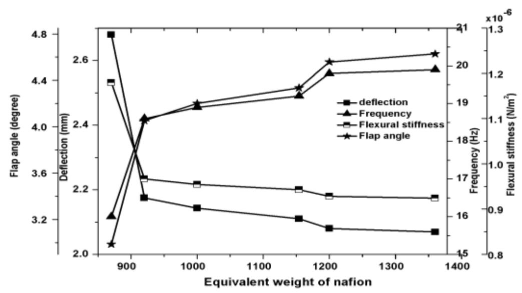


Fig. 5 Effect of the equivalent weight of Nafion on the actuation parameters of IPMC

3.2.3 Effect of equivalent weight of Nafion, water retention and actuation of IPMC

With Nafion membrane, the degree of ionic cluster formation depends on the equivalent weight of Nafion polymer. Lower the equivalent weight of Nafion polymer, higher is the degree of ionic cluster formation and water holding capacity. The equivalent weight of Nafion polymer affects the crystallinity, elasticity, swelling and transport properties (Choi *et al.* 2005). It is observed that, at vapor phase, the water absorption remains constant irrespective of any equivalent weight of Nafion polymer, whereas in the liquid phase, the water absorption changes with change in equivalent weight (Choi *et al.* 2005). Nafion with very low equivalent weight undergoes gelling due to higher degree of ionic clusters and water absorption (Choi *et al.* 2005). Therefore, optimizing equivalent weight for achieving the required water content good actuation performance is important.

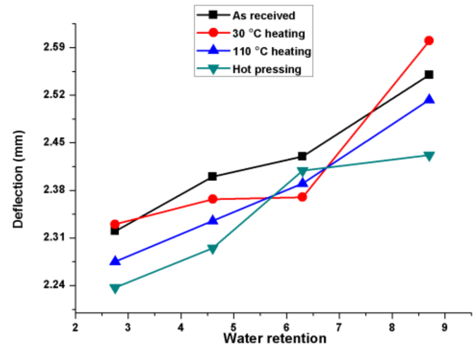
The effect of Nafion with H^+ ions for different equivalent weight and water uptake is reported by Doyle *et al*. (2003). In the present studies, the retention of water of Nafion is higher for Nafion having lesser equivalent weight. For an equivalent weight of 870, the retention of water is nearly 0.5 and for equivalent weight of 1360, the retention of water is 0.17. Considering the actuation parameters with the variation of equivalent weight from 800 to 1360, the deflection decreased from 2.68 mm to 2 mm while frequency increased from 16 Hz to 19.9 Hz (Fig. 5). The low equivalent weight of Nafion results in increased swelling and dimension of u-IPMC. The stiffness increases from 0.8 $x10^{-6}$ N/m^2 to 1.24 $x10^{-6}$ N/m^2. In this case, to have a trade off between frequency and deflection, an equivalent weight of 920 to 1100 is preferable to obtain deflection of around 2.1 mm and frequency around 19 Hz.

3.2.4 Pre-treatment procedures on the water retention and actuation of IPMC

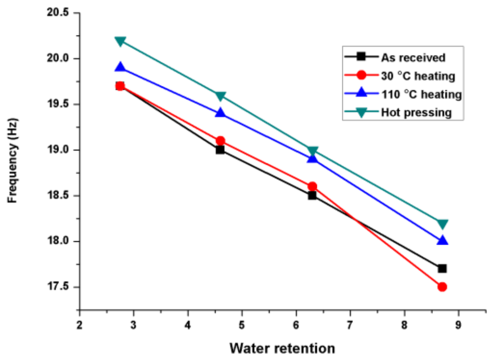
Pre-treatments of Nafion membrane carried out during the preparation of Nafion membrane and purifications can lead to micro structural changes in the membrane, which can also affect its sorption and water holding capacity. As far as the preparation of Nafion membrane is concerned, the preparation can be either (i) dried Nafion membrane is hydrated at 25℃ or, (ii) the nondried hydrated H+sample is ion exchanged at 25℃, or (iii) the dry ion-exchanged Nafion is hydrated at 100℃ (Yeager *et al.* 1982). The Nafion membrane prepared as per step (iii) can retain its swollen nature for more than several weeks (McGee 2002) due to the change in hydration state introduced near the glass transition temperature of Nafion (104℃). This treatment should provide for the optimized water-swollen state for the H+form of the IPMC.

The present pre-treatment procedures such as heating the Nafion at 30^oC and 100^oC and hot pressing at 170^0C has strong influence on the retention of water in Nafion as reported elsewhere (Jalani *et al.* 2005b). The variation of water uptake versus water activity in vapor phase under different pre-treatments was adopted from the report of Jalani *et al.* (2005b). In the present investigation, it is observed that the untreated- Nafion retains more water compared with treated-Nafion. As the retention of water of both untreated and treated Nafion increases, the deflection increases and frequency decreases. However, it is also observed that at retention of water 2.75, the deflections are 2.32, 2.33, 2.27 and 2.23 mm for the untreated Nafion, heated at 30^0C, 110^0C and hot pressed at 170^0C, respectively (Fig. 6). At retention of water 2.75, the frequency increases to 19.7, 19.7, 19.9 and 20.2 Hz for the above pre-treatment conditions.

The hot-pressed Nafion shows a decrease in deflection compared to other pre-treatment cases except at retention of water 6.3. The 110^0C heated - Nafion shows a steady increase in deflection for increased water content. When comparing untreated Nafion with the treated Nafions for the retention of water between 4.6 to 6.3, it is observed that, the deflection is always higher in the former. At retention of water 4.6, the untreated Nafion exhibits higher deflection of 2.4 mm compared to other pre-treatment cases. The lowest deflection was observed at retention of water 4.6, for the hot pressed Nafion with 2.27 mm at 19.6 Hz. Interestingly, for higher deflection at high and low water retention, Nafion membranes pre-treated at 30^0C have the highest deflection. This clearly reveals that at lower retention of water, the pre-treatment procedures at high temperature have almost no impact on the actuation parameters. Considering the frequency graph, the hot pressed Nafion has the highest frequency values. To optimize between frequency and deflection values, the 30^0C heated Nafion is the best option.



(a) Variation of deflection



(b) Variation of frequency

Fig. 6 Effect of pre treatment procedures on the actuation of IPMC

3.3 Actuation of IPMC under operational conditions-Effect of water activity and physical state of absorbing water

A humid environment elicits the best performance from Nafion-IPMC actuators. However, by using a solid electrolyte instead of a liquid electrolyte or by suitable encapsulation introduced during the fabrication, some IPMCs can be operated in a dry environment (Kim *et al.* 2006). However, these changes result in increased stiffness that could be detrimental for the actuation performance especially for flapping micro air vehicles. Lantada *et al.* (2012) have reported the mechanical response of u-IPMC outside an ionic liquid medium; the maximum amplitude of the deformations obtained by the unencapsulated Nafion-IPMC actuator exhibits an exponential decline which leads to a 50% reduction in their actuation capability during the first 10 min of their being out of water. Therefore, the performance of u-IPMCs as actuators in dry environments with varying water activity has to be assessed to predict the lifetime of the device.

Though the performance of Nafion-IPMC depends on the extent of the water retention by Nafion membrane which is influenced by the ion-exchange capacity, cationic forms of the membrane and pre-treatment of membrane; the physical state of absorbing water (whether the adsorption is from water in liquid or vapor phase) also determines the water retention and actuation of IPMC. The rate of water absorption in Nafion is higher in liquid phase compared to that in vapor phase. With liquid phase, Nafion absorbs 22 water molecules per acid site, whereas it is around 14 molecules per acid site in vapor phase resulting in higher adsorption rate in the former compared to the latter (Jalani and Datta 2005a).

3.3.1 Effect of sorption and desorption of water on the actuation of IPMC-influence of activity of water in vapour phase

When the dry Nafion-IPMC neutralized with a cation is immersed in water, osmotic pressure is developed which reduces the anion-cation interaction within the clusters leading to hydration and expansion of ionic clusters. The expansion of ionic cluster continues until the pressure induced by the elasticity of the hydrophobic matrix material equals to the osmotic pressure (Nasser and Thomas 2004). During water sorption, primary hydration cluster of the sulfonic acid groups occurs at low water activity (< 0.5) with water uptake ～4 water molecules and at high water activity (> 0.8), a second and additional hydration cluster forms (Zhao *et al.* 2011). James *et al.* (2000) have reported small clusters (3–5 nm diameter) gathering into super-clusters up to 30 nm diameter. Upon hydration, the total number of clusters decreases while the size of each cluster increases by consolidation of clusters. The liquid/Nafion interface and vapor/Nafion interface influence the entry of water molecules into the hydrophilic domains. At high water activity, the length of the diffusion path through the hydrophilic domains is reduced to a straight-line distance across the membrane resulting in low tortuosity and higher water uptake (Zhao *et al.* 2011).

Rivin *et al.* (2001) have reported that the sorption rate decreases dramatically in Nafion 117 with increasing water vapor activity. The sorption rates are lower than desorption rates over a fixed interval of water vapor activity. The water retention also increases with increase of water activity. The behavior of sorption and desorption of water in Nafion with the activity of water in vapor phase (relative humidity) was reported by Jalani *et al*. (2005b). With the sorption and desorption of water in Nafion, hysteresis in the actuation parameters is observed in the present studies. For the activity of water in vapor phase, from 0.2 to 0.8, the deflection, flap angle and frequency do not change abnormally with the sorption and desorption cycles, though hysteresis is observed (Fig. 7). The hysteresis between water sorption and desorption of water (‘skin effect’) is attributed to the viscoelastic nature of Nafion (Jalani *et al.* 2005b). As the water activity increases from 0.4, the effect of hysteresis is realized largely between the sorption and desorption schedules. At 0.2 water activity, the deflection and frequency for sorption and desorption are 2.10 mm, 20.8 Hz and 2.14 mm, 20.6 Hz, respectively. From 0.4 water activity, the difference in deflection increases from 2.12 mm to 2.32 mm for sorption and desorption with reduction of 1 Hz frequency. Therefore, for water vapor activity 0.2, the deviation in actuation parameters is very less for sorption and desorption of water in Nafion membrane.

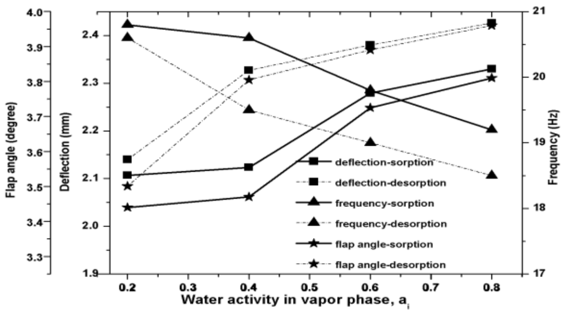


Fig. 7 Variation of actuation of IPMC with activity of water in vapour phase under sorption and desorption

Effect of influence of temperature on the activity of water in vapour phase

It is known that the viscoelasticity of a polymer changes under heat (Jalani *et al.* 2005b). Therefore, the water sorption under liquid or vapor phase also affects the material properties of Nafion polymer. The effect of water uptake at vapor phase and at temperatures 30 and 90 ^{0}C on the actuation were analyzed with the data obtained from Jalani *et al.* (2005b). As the water activity increases, the deflection and flap angle of IPMC increases, while the flexural stiffness and frequency decreases. At water activity 0.2, and temperature 30^{0}C, the deflection and frequency are 2.11 mm and 20.7 Hz, respectively (Fig. 8). For the same water activity at 90^{0}C, the deflection increases to 4.9 mm with resonant frequency of 12.5 Hz. At higher water activity 0.8 at 30^{0}C, the deflection increases from 2.11 mm to 2.46 mm and frequency decreases from 20.7 Hz to 18 Hz. But, the increase in water activity combined with the higher temperature has a great impact on the actuation parameters. At 0.8 water activity, the deflection value increases from 2.46 mm at 30^{0}C to 5.69 mm at 90^{0}C; the resonant frequency drops from 18 Hz at 30^{0}C to 11.5 Hz at 90^{0}C. The stiffness at 30^{0}C is higher than that at 90^{0}C. Nafion heat-treated at 30^{0}C with water activity 0.8, can result in good resonant frequency and stiffness of 1.01x10^{-6}N/m^2.

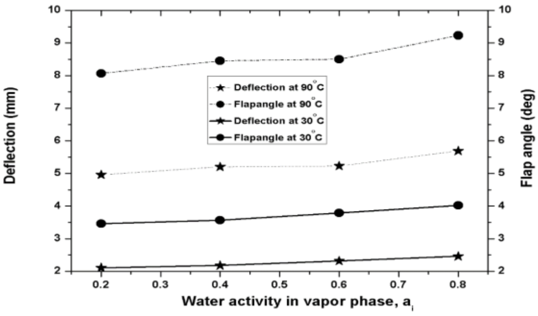
To have higher deflection (5.2 mm) with reduced stiffness of 4.58x10^{-7}N/m^2 and frequency 12.2 Hz, Nafion with water activity of 0.4 can be treated at temperature 90^{0}C.

Effect of activity of water in vapor phase for operation at high temperature

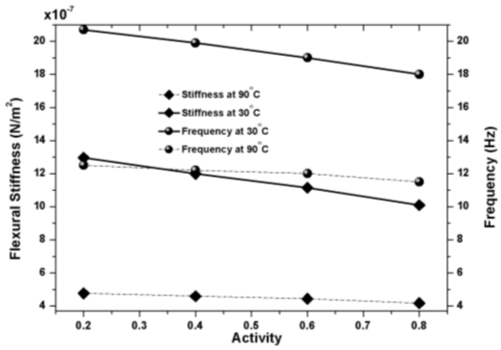
Nafion surface is hydrophobic when contacting water vapor, but becomes hydrophilic when contacting liquid water. In dry Nafion, interaction between ionic groups through electrostatic attraction of S-H groups imparts pseudo-crosslinking (Majsztrik 2008). However, at temperature 50-80°C the strength of this bond is deactivated leading to increase of creep strain. In wet Nafion, hydrogen bonds formed between sulfonate groups are stronger than the bonding occurring in dry Nafion; the strong hydrogen bonds produce mechanical response, which varies with wide range of temperature. Therefore, increased creep strain for hydrated Nafion at room temperature is attributed to increased free volume and freedom for side chain movement (Majsztrik 2008). When Nafion is exposed to an increasingly hot environment, a gradual decrease in Young's modulus is expected (Kawano *et al.* 2002).

The actuation of IPMC having a definite water activity is analyzed at different temperatures. Nafion with water activity ranging from 0 to 1.0 is considered in the investigation. For the present modeling, Young's modulus values for different temperatures for a definite water activity are obtained from the report of Majsztrik (2008). The deflection and flap angle of IPMC increase with the increase of temperature from 23^{0}C to 70^{0}C in all Nafion having water activity from 0 to 1.0; but the frequency and flexural stiffness decreases. At low temperature, 23 ^{0}C, the deflection of IPMC increased from 0.29 mm to 0.64 mm with all Nafion having water activity 0 to 1.0, while frequency and flexural stiffness decreased from 42.5 Hz to 24.9 Hz and from 6.66 x10^{-6}N/m^2 to 2.53 x10^{-6}N/m^2, respectively (Figs. 9 and 10). Therefore, it is clear that the change of frequency is more pronounced than that of the deflection with the increase in water activity. Interestingly, at high temperature, 70^{0}C, the deflection at water activity 0 is 2.91 mm whereas at higher water activity 0.95 the deflection is reduced to 1.07 mm.

The rise in water activity and temperature should have a positive influence on the deflection and flap angle. But, in the present study the deflection of IPMC with high water activity, (0.95), is lesser at higher temperature than that observed at the same temperature with IPMC having water activity 0.

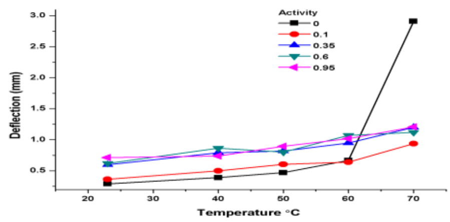


(a) Variation of deflection and flapping angle

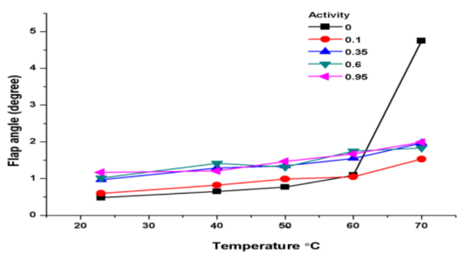


(b) Variation of flexural stiffness and frequency

Fig. 8 Effect of temperature on the activity of water in vapor phase and actuation of IPMC

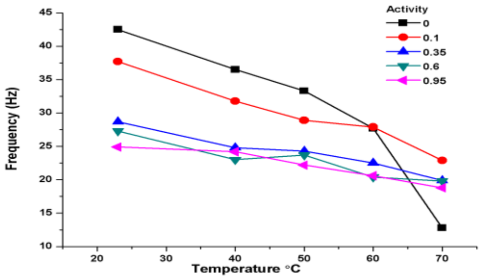


(a) Variation of deflection

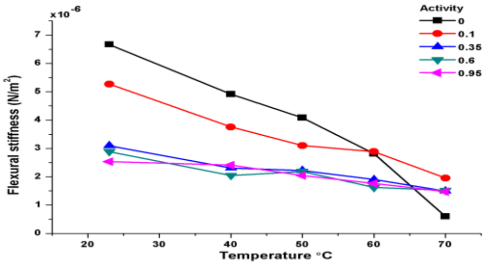


(b) Variation of and flapping angle

Fig. 9 Effect of temperature on water activity and actuation of IPMC



(a) Variation of frequency



(b) Variation of flexural stiffness

Fig. 10 Effect of temperature on water activity and actuation of IPMC

This is attributed to the reduced plasticization of Nafion membrane at higher water activity and temperature resulting in lesser deflection and increased resonant frequency. The effect of reduced plasticization is more pronounced from 60^0C. The effect of plasticization of Nafion can be exploited to change the deflection and frequency when IPMC is used as an actuator for flapping.

Generally, any change in voltage of IPMC can vary the deflection under constant resonant frequency. In the present studies, the change in temperature can alter all u-IPMC actuation parameters.

For a u-IPMC actuator to deflect around 0.6 mm and 28 Hz, the following parameters can be adapted. (i) at water activity, 0 or 0.1 and temperature 60^0C (ii) at water activity 0.35 and temperature 23^0C and (iii) at water activity 0.6 and temperature 23^0C. But at water activity 0.95, the deflection of 0.6 mm can be achieved at 23^0C at a reduced frequency of 25 Hz. As the plasticization effect is less pronounced at the higher water activity and higher temperature, the following strategy may be followed to achieve 20 Hz frequency, (i) the actuator with water activity 0.95 can be actuated at 60^0C with 0.91 mm deflection, (ii) the actuator with water activity 0.6 can be actuated at 60^0C with 1.07 mm deflection (iii) the actuator with water activity 0.35 can be actuated at 70^0C with 1.2 mm deflection. Therefore, it is clear that 20 Hz frequency is obtained around 60 to 70^0C; but with lesser water activity, higher deflection is obtained.

4. Conclusions

Structural modeling of unencapsulated ionic polymer metal composite (u-IPMC) actuators intended for use under dry environmental conditions is carried out. Optimization of design parameters of u-IPMC for the retention of water andinfluence of water activity on the actuation characteristics of unencapsulated Nafion-IPMC for use in FMAV are studied. The equivalent weight of Nafion polymer, cations, concentration of cations, pre-treatment procedures have significant effect on retention of water of u-IPMCs and on actuation parameters, flapping angle, flexural stiffness and actuation displacement. The variation of concentration of cation has a small effect on the actuation. Na^+ ions as cation and equivalent weight of Nafion between 920 and 1100 are favorable to achieve reasonable deflection and frequency. Comparing with different pre-treatment procedures, 30^0C pre-treated Nafion offers a good combination of deflection, frequency and stiffness.

The research on the effect of water activity and physical state of absorbing water on the actuation reveal interesting results. It is observed that at 0.2 water activity, the hysteresis for sorption and desorption of water is lower, leading to minimal deviation of actuation parameters compared to higher water activity. The effect of increase in temperature has a higher impact in altering the material properties and performance of actuators compared to that of water activity at vapor phase. Reduced plasticization of Nafion is seen at higher water activity and temperature.

This results in stiffening the IPMC resulting in less deflection and more frequency. Therefore, Nafion with equivalent weight between 900 and 1100, pre-heated at 30 ^{0}C, with sodium as the cations offers a superior actuation performance. The studies also reveal that the actuation parameters while in operation can be tuned to desirable frequency, deflection, flap angle and flexural stiffness by changing the water activity and operational temperature of the environment.

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CC

Appendix: Nomenclature

$\mathbf{C}^{-1}$:	Inverse of capacitance
$\underline{f}$:	Force vector
J:	Square root of -1
$\mathbf{K_s}$:	Diagonal stiffness matrix
$\mathbf{M_s}$:	Diagonal mass matrix
s:	Laplace variables
T:	Kinetic energy
V:	Potential energy
$\mathcal{V}_{se}$:	Strain energy
$\mathcal{V}_{couple}$:	Coupling potential energy
$V_{dielectric}$:	Dielectric potential energy
W^{ext}:	Work done by external force
X_i:	Cartesian axes (i=1,2,3)
δ:	Variation
ρ:	Density of IPMCs
Φ_u:	Mechanical shape functions
Φ_D:	Electrical shape functions
Ψ:	Coupling vector
ω:	Frequency
$\underline{A}$:	Generalized coordinate of mechanical displacements
$\underline{q}$:	Generalized coordinate of electrical displacements
$\mathbf{H}$:	Electromechanical coupling matrix
$\mathbf{c}^{\mathbf{D}}$:	Stiffness matrix as constant electric displacement
v:	Electric potential applied on each electrode
$\boldsymbol{\varepsilon}^{\mathbf{T}}$:	Dielectric permittivity matrix at constant stress