

# Accepted Manuscript

The Enhancement Effect of Lithium Ions on Actuation Performance of Ionic Liquid-based IPMC Soft Actuators

Maryam Safari, Leila Najj, Richard T. Baker, Faramarz Afshar Taromi



PII: S0032-3861(15)30209-3

DOI: [10.1016/j.polymer.2015.09.004](https://doi.org/10.1016/j.polymer.2015.09.004)

Reference: JPOL 18090

To appear in: *Polymer*

Received Date: 5 June 2015

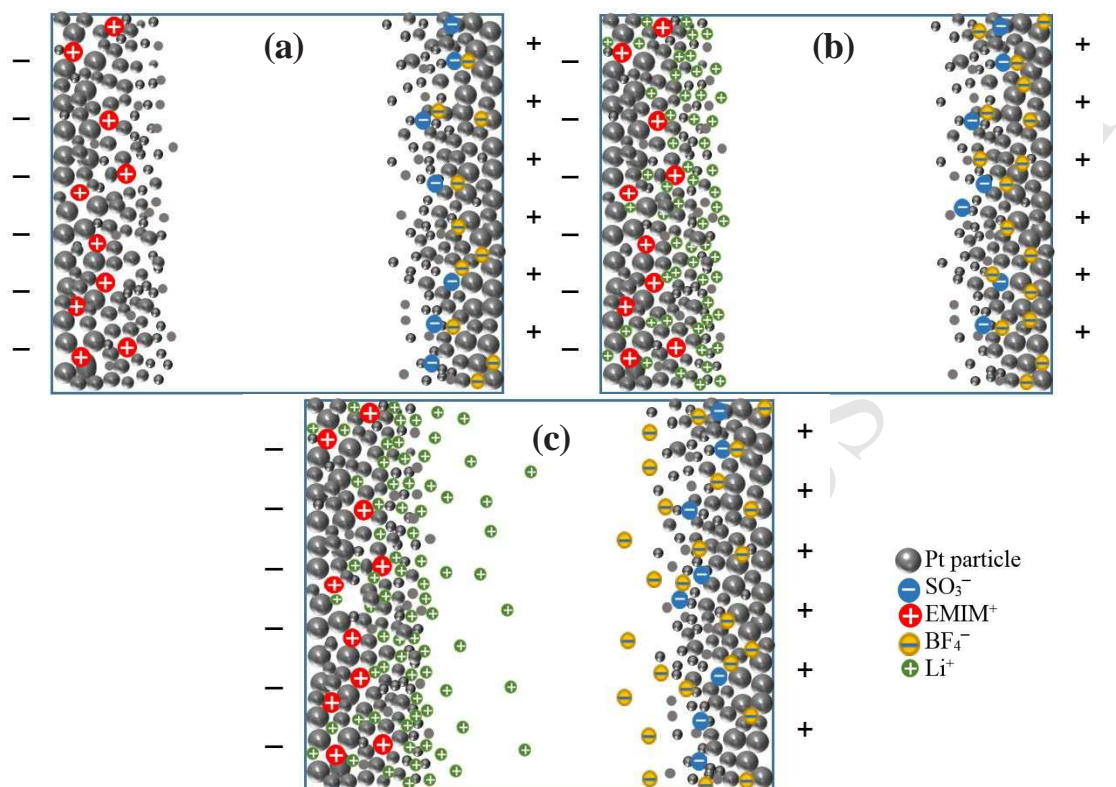
Revised Date: 29 August 2015

Accepted Date: 3 September 2015

Please cite this article as: Safari M, Najj L, Baker RT, Taromi FA, The Enhancement Effect of Lithium Ions on Actuation Performance of Ionic Liquid-based IPMC Soft Actuators, *Polymer* (2015), doi: 10.1016/j.polymer.2015.09.004.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

## Graphical Abstract



**The Enhancement Effect of Lithium Ions on Actuation Performance of Ionic Liquid-based  
IPMC Soft Actuators**

Maryam Safari,<sup>1</sup> Leila Naji,\*<sup>1</sup> Richard T. Baker,<sup>2</sup> Faramarz Afshar Taromi,<sup>3</sup>

<sup>1</sup>Department of Chemistry, AmirKabir University of Technology, 424 Hafez Avenue, Tehran  
P.O Box: 15875-4413, Iran.

<sup>2</sup> EaStChem, School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST,  
U.K.,

<sup>3</sup>Faculty of Color and Polymer Engineering, AmirKabir University of Technology, 424 Hafez  
Avenue, Tehran P.O Box: 15875-4413, Iran.

\* Corresponding author to whom all correspondence should be directed. Tel: +98 (21) 64542767;  
Fax: +98 (21) 64542762; e-mail: [leilanaji@aut.ac.ir](mailto:leilanaji@aut.ac.ir)

Keywords: Artificial muscle, IPMC actuator, Displacement measurements, Cyclic voltammetry,  
Impedance spectroscopy

---

## Abstract

Soft actuators are of great technological interest and one class of these is made from ionic polymer-metal composites (IPMCs). It has been established that replacement of water with an ionic liquid (IL) in IPMCs results in larger actuation response and considerably longer operating life. However, the rate of displacement of IL-based IPMCs is very low. In the current work, IPMC actuators were fabricated using Nafion membrane and an imidazolium-based IL. The effects of incorporating the IL with and without  $\text{Li}^+$  ions were followed using electromechanical and electrochemical measurements and were compared with the corresponding behavior of water-based  $\text{Li}^+$ -exchanged and un-exchanged IPMC actuators. The addition of  $\text{Li}^+$  ions to the IL-based system resulted in dramatic increases in the capacitance, ionic conduction, operating life and in the displacement rate of the actuator. This strategy is of considerable interest for enabling the use of IPMC-based soft actuators in medicine and robotics.

## 1. Introduction

Soft actuators are smart materials made from polymers or gels which change shape in response to an external, usually electrical, stimulus.[1] They are of great interest for application in robotics [2] – for handling fragile objects and for providing propulsion in autonomous swimming and crawling robots [3] – and in medicine [4,5] , for example, in replacement valves and artificial muscles. One class of soft actuators are made from ionic polymer-metal composites (IPMCs).[6] A typical IPMC consists of an ion-exchange polymer membrane - such as Nafion - with metal electrodes, chemically plated on opposite faces. The electrodes consist of a dendritic structure of small, interconnected metal particles, generally platinum or gold, which penetrates into the polymer membrane. [6] The protons in the Nafion are usually exchanged for cations such as  $\text{Li}^+$  and an appropriate solvent – usually water – must be taken up by the IPMC before it can be used.

Then, when an adequate potential is applied across the thickness of the IPMC, it bends dramatically and reversibly towards its positively charged surface. The magnitude and speed of the bending deformation may depend on the nature, ionic conductivity and thickness of the ion exchange polymer, the structure and capacitance of the electrodes, the solvent content of the polymer, the charge and mobility of the cations, and the specific interactions between the electrode and the cations.[7,8,9] It has been established that IPMC actuators consisting of Nafion membrane with cations of larger Van der Waals volume exhibit stronger actuation due to motion of the larger cation.[10] However, the actuation performance of conventional water-based IPMC actuators decreases over time due to the electrolysis of the water by the applied voltages and by the evaporation of water when these devices are operated in air. Replacement of water with other solvents has been investigated.[10,11,12] Ethylene glycol is polar has a viscosity of about 16 times that of water at room temperature and has a greater molecular mass. The results of a series of tests with ethylene glycol as the solvent indicated a greater uptake of solvent, greater resistance to electrolysis at high applied voltages, less stiffness, better actuation performance in air and later relaxation than with water in both Nafion- and Flemion-based IPMCs. However, the actuation of an IPMC sample with water as solvent was faster and the sample possessed higher overall electrical capacitance than with ethylene glycol.[11] Replacement of water with ionic liquids (ILs) as the solvent has also been investigated.[13,14] ILs are room temperature molten salts composed, for example, of heterocyclic organic cations and various anions.[15] The physical and electrochemical properties of ILs depend strongly on the nature and size of their cation and anion constituents. ILs are easy to handle and possess interesting properties including high thermal and chemical stability, high ionic conductivity, excellent solubility, negligible vapor pressure and non-flammability.[16] Thus, they have been considered as media in

applications where the presence of water as solvent leads to a gradual deactivation of the system over time through hydrolysis and evaporation processes.[13] Recent studies have shown that ILs can self-assemble into nanoscale aggregates, both as pristine ILs and in solution, which can result in multiple conduction phenomena.[17] These phenomena are attributed to the long-range charge motion or interfacial polarizations arising from the buildup of charge at the domain boundaries within the material.[17] In Nafion membranes, the mechanism of long-range charge transfer occurs via ion exchange processes between ionic clusters and the IL aggregates.[17] It has been established that ILs can solvate and plasticize the Nafion side groups, stimulate the organization of the fluorocarbon domains of Nafion into a microcrystalline structure reduce the degree of crystallinity of the membrane and increase its ionic conductivity.[17,18] ILs comprised of the 1-alkyl-3-methylimidazolium cation and anions including halide, nitrate, hexafluorophosphate ( $\text{PF}_6$ ) and tetrafluoroborate ( $\text{BF}_4$ ) are the most investigated ILs in applications where their ionic conductivity is exploited.[19] These imidazolium-based ILs are currently being studied as electrolytes for dye-sensitized solar cells,[20] metal plating,[21] Li ion batteries,[22] and electrochemical capacitors[23] as well as soft actuators.[24]

IPMC actuators incorporating ILs showed an extended operating time over water-based systems. However, their response times were much longer and the forces generated were decreased drastically compared to systems using water.[25,26,27,28] This limits the appropriateness of IL-based IPMC actuators as electromechanical actuators in applications where fast response and large displacement at low applied voltages is required.[29,30,31] To improve the performance of water-free IPMC actuators without significant loss in generated force output the preparation of thick IPMC actuators has been proposed.[32,33] However, it was found that the actuation displacement of the thick IPMCs was lower than that of thin IPMCs and their response time was

further increased. To the best of our knowledge, no studies have reported on methods to simultaneously increase the tip displacement and decrease response time in IL-based IPMC actuators. Researchers have shown that the electromechanical performance of IPMC actuators is influenced by the concentration of ionic liquid, and that the concentration of ionic liquid can be tuned to achieve maximum actuation performance.[12] IPMCs containing higher concentration of ionic liquid exhibited more capacitor-like behavior which led to a larger electromechanical responses.[12] The ionic conductivity and actuation speed of IL-based IPMCs also increases as the content of ionic liquid and the size of the counterions is increased.[12,13,14] Furthermore, the actuation speed of IL-based IPMCs is linearly related to the ionic conductivity of Nafion membrane.[14]

The current work reports the enhancement of the ionic conduction, capacitive characteristics, tip displacement and response time of an IL-based IPMC actuator by the addition of a small amount of  $\text{Li}^+$  ions. IPMC actuators were fabricated using Nafion membrane and an imidazolium-based IL. The effects of incorporating the IL with and without  $\text{Li}^+$  ions were followed using electromechanical measurements, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) and were compared with the corresponding behavior of water-based  $\text{Li}^+$ -exchanged and un-exchanged IPMC actuators. The addition of  $\text{Li}^+$  ions to the IL-based system resulted in dramatic increases in the operating life and in the displacement rate of the actuator over non-IL systems at ambient temperature and humidity. This strategy is therefore of considerable interest for increasing the applicability of IPMC-based soft actuators in medicine and robotics.

## 2. Experimental

### 2.1. Preparation of IPMC actuators

IPMC actuators were prepared from 0.18 mm thick sheets of Nafion-117 in its protonated form (DuPont, equivalent weight 1100) using a technique presented by Pak et al.[34] After roughening the surfaces using abrasive paper to increase the metal-polymer interface area, the membrane was washed using an established method [35,36] to remove all impurities remaining from the manufacturing process. The clean Nafion was soaked in a 4.5 M aqueous solution of tetraamineplatinum (II) chloride ( $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ , Alfa Aesar) for 24 h and a few drops of ammonium hydroxide (Aldrich) solution was added to neutralize the solution. The amount of  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  added was calculated to correspond to the number of ion exchange sites available in the Nafion membrane. After rinsing with DI water to remove the excess platinum salt solution, the membrane was placed in a small amount of DI water in a crystallization dish under stirring. An aqueous solution (100 ml) of 5 wt%  $\text{NaBH}_4$  was added gradually to the membrane. A silvery layer of Pt was formed on the surfaces of the membrane. This plating procedure was repeated twice. The membrane was rinsed with DI water and immersed in 1 M  $\text{HNO}_3$  solution for 12 h to neutralize the residual ammonium, rinsed again and stored in DI water. Four IPMC sample types were prepared, each  $5 \times 23$  mm in size. These were water-based samples with and without  $\text{Li}^+$  ion exchange and IL-based IPMCs with and without addition of  $\text{Li}^+$  ions.

$\text{Li}^+$ -exchanged water-based samples were prepared by immersing the IPMCs (in protonated form) in 0.1 M  $\text{LiBF}_4$  (Sigma Aldrich) solution for 7 d. IL-based samples were prepared by soaking the IPMCs (in protonated form) in a 50%/50% b.v. mixture (2 ml) of ethanol and 1-ethyl-3-methylimidazolium tetrafluoroborate ( $\text{EMIMBF}_4$ , from Research Institute of the Petroleum Industry) at room temperature for 7 d and then drying under vacuum at 70 °C for 4 h



to eliminate ethanol. Ethanol was applied as a supporting solvent to increase the rate of ion exchange (see Table S1 in supplementary data). Henceforth, the IPMC sample types are named to indicate the type of cations;  $H^+$  (IP-H),  $Li^+$  (IP-L) and  $EMIM^+$  (IP-E).

Three methods were applied to prepare water free IL-based IPMC actuators incorporated with  $Li^+$  ions. These methods differ in the order and the rate of the penetration of the EMIM and  $Li^+$  ions within the polymer and are described as follows; 1) water free  $EMIM^+$ -exchanged IP-E samples were immersed in 0.1M  $LiBF_4$  solution (2 ml), 2) fully dehydrated  $H^+$ -exchanged IP-H samples were immersed in a water free 50%/50% b.v. mixture (2 ml) of ethanol and  $EMIBF_4$  containing  $LiBF_4$  salt (0.1 M), and 3) fully dehydrated  $Li^+$ -exchanged IP-L samples were immersed in a 50%/50% b.v. mixture (2 ml) of ethanol and  $EMIMBF_4$ . The samples were kept in above-mentioned solutions at room temperature for 2 h and then dried under vacuum at 70 °C for 4 h to eliminate the solvents. These samples are named as IP-E/L-M1, IP-E/L-M2 and IP-E/L-M3 respectively to indicate the number of applied method.

Using method (1), IL-based IPMC actuators containing increasing amount of  $Li^+$  ions were prepared. To this end, water free IP-E samples were immersed in four  $LiBF_4$  solutions (2 ml) in concentration range of 0.05 to 0.5 M for 2 h and again dried under the above-mentioned conditions. These samples were named as IP-E/L-0.05 to IP-E/L-0.5 to indicate the concentration of applied  $LiBF_4$  solution. The concentration of  $LiBF_4$  solution was changed to alter the amount of  $Li^+$  ions absorbed within the IL-based IPMC samples and to find the best concentration in terms of obtaining IPMCs with the highest capacitive characteristic.[12] Table 1 summarises the main differences between the samples and gives their names as used in the manuscript.

## 2.2. Physical and Morphological Evaluation of IPMCs

Fully hydrated water-based IP-H and IP-L samples were vacuum dried in an oven at 80°C overnight and their dry mass,  $W_{dry}$ , measured and subtracted from their wet mass,  $W_{wet}$  and the percentage of water uptake calculated using Equation 1.

$$\% \text{ water uptake} = 100 \times (W_{dry} - W_{wet}) / W_{dry} \quad \text{Equation 1}$$

Scanning electron microscopy (SEM) was employed to study the differences in the morphology of the platinum electrode layers of IPMCs as a function of cation and solvent type using a Seron-AIS2300 SEM instrument. Cross-sections of IPMCs were obtained for SEM by freeze-fracturing in liquid N<sub>2</sub>. The topology of the sample electrodes was quantified by measuring the number of folds per unit surface area.

## 2.3. Electrochemical Evaluation of IPMCs

To compare the ionic conduction and capacitive characteristics of water- and IL-based IPMCs, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were used. Square elements of 5×5 mm were cut from the IPMCs and placed horizontally in a sample holder consisting of a pair of platinum contacts embedded within a Plexiglas clamp. These contacts had the same surface area as the sample. The measurements were performed on a potentiostat/galvanostat (Autolab) controlled by NOVA software at ambient temperature. The impedance measurements were performed with an applied a.c. voltage of 10 mV in amplitude over a frequency range of 100 kHz to 100 mHz. Z-view software was used to analyze the results. CV scans were performed in the potential range of ±1V at a scan rate of 100 mV s<sup>-1</sup>. The capacitance (C) was calculated from the CV results using Eq. 1

$$C = \frac{|I^+| + |I^-|}{2dV/dt} \quad (1)$$

where  $I^+$  and  $I^-$  are currents in A at 0 V in the two scanning directions and  $dV/dt$  is the potential scan rate ( $\text{Vs}^{-1}$ ). [37]

## 2.4. Electromechanical Measurements

Maximum tip displacement, rate of displacement and durability were measured at room temperature and in ambient air using the arrangement shown in Figure 1. The IPMC actuator was held at one end in a sample holder consisting of a pair of platinum electrical contacts fixed within an insulating clamp. The electrical contacts were connected to the two terminals of either a d.c. power supply or a function generator. All samples were subjected to d.c. voltages from 1 to 8 V. In addition, sinusoidal voltages of 4 and 5 V in amplitude, at frequencies from 0.01 to 1.00 Hz, were applied to the IL-based samples. A digital camera was used to capture video images of the bending deformation of the sample as the d.c. or a.c. voltages were applied. The maximum tip displacement was calculated using image analysis software. Displacement rate for each IPMC actuator was determined by dividing the maximum tip displacement by the time taken to reach it when they were subjected to a d.c. voltage. Actuator durability was studied by applying 4 V d.c. every 10 min and measuring the maximum tip displacement as a function of time (over 180 min). During the time intervals, the IPMC samples were kept still in the sample holder.

## 3. Results and Discussions

### 3.1. Morphology of IPMCs

In the cross-sectional SEM image of the freeze-fractured IP-H sample shown in Figure 2(a) two parallel, bright layers along the surfaces of the Nafion membrane are observed. These layers are assigned as the platinum electrodes. The similarity in thickness of the platinum electrodes at both

surfaces indicates that the plating process gave a uniform coverage. The high concentration of platinum at the outer surface is seen as a layer of dense appearance and relatively uniform thickness along the surface of the membrane.

In Figures 2(b)-(e), top-down SEM images of the platinum electrode in each sample type are compared. The electrode appears to be highly folded in water-soaked IP-H (Figure 2(b)) and IP-L (Figure 2(c)) samples compared to the IL-soaked IP-E and IP-E/L-0.1 samples (shown in Figure 2(d) and 2(e), respectively). This might be attributed to the formation of larger ionic clusters in the water-soaked samples and a stronger ionic interaction between the small cations of  $H^+$  and  $Li^+$  with the fixed sulfonate groups.[14] Nafion is not cross-linked and the ionic clusters size and the resulting ionic conductivity may vary according to the type of applied solvent and electrolyte. [38,39] The addition of more polar solvents such as water which interact preferentially with the ionic clusters (hydrophilic regions), which are minor domain in the Nafion structure, cause microscopic swelling. However, IL can solvate and plasticize the Nafion side groups [17,18] and reduce the cross-linking dipolar interactions inside the polar domains and increase the mobility of the main fluorocarbon backbone chains (hydrophobic regions), which are major domain, and cause macroscopic swelling. Furthermore, it is expected that smaller ionic clusters to be formed within the IL-based samples due to weaker electrostatic interactions between large organic  $EMIM^+$  cations with the fixed ion exchange sites.[7] Therefore, the observed smoother platinum electrode surface in IL-based IP-E actuators (shown in Figure 2(d)) can be attributed to the higher degree of the macroscopic swelling of the polymer and the formation of smaller ionic clusters within these samples. It must be mentioned that the level of absorbed atmospheric moisture for the IL-based actuators is expected to be negligible as

compared with water-based actuators because the hydrophilic domains are filled with the ILs. [17]

Comparison of the SEM images of the water-based IPMC samples also shows that the electrode surface is more folded in IP-L samples compared to IP-H. Determination of water content of IP-H and IP-L samples revealed that Li<sup>+</sup>-exchanged IP-L samples had higher water content – approximately 2.5 times – than the H<sup>+</sup>-exchanged IP-H samples. Therefore, larger ionic clusters could be formed within the IP-L samples. The formation of larger ionic clusters within the water-based actuators, especially in the case of IP-L samples, was confirmed by data obtained from SAXS study of the samples (see Figure S1 in Supplementary Data). The presence of Li<sup>+</sup> ions in the IP-E/L-0.1 sample also led to the formation of folds in the electrode (see Figure 2(e)). This similarly can be attributed to the formation of larger ionic clusters [40] within this sample compared to water free IP-E actuators as shown in Figure S1.

### 3.2. Electrochemical evaluation of IPMCs

Figure 3 shows the voltamograms of the IP-H, IP-L, IP-E samples. All three appear similar in shape but differ in the magnitude of the current. The symmetric shape of the CV curves can be assigned to excellent charge distribution in the electrode region of the IPMCs. This indicates that the platinum plating process has given rise to two equivalent electrodes with similar thicknesses, as was observed by SEM. In previous work, it was found that the platinum particles penetrate the polymer to a depth of ~10 μm and provide a porous electrode structure at both surfaces of the IPMC.[41] The CV curves of the IPMCs are close to rectangular, indicating a capacitive behavior and a low contact resistance. Generally, the shape of the loop in the CV response of an ideal capacitor should be rectangular; however, greater resistance changes the loop, causing an

oblique angle and narrower loop. [42] Nafion-based IPMC actuators can be considered as polyelectrolyte-based capacitors [43] since they consist of a pair of conductive platinum electrodes sandwiching the cation exchange Nafion membrane. Nafion is a perfluorinated copolymer that can be considered to have a poly(tetrafluoroethylene) backbone from which are suspended perfluorinated ether side chains terminating in anionic sulfonate groups. In the samples used in this work, these are paired with counter cations such as  $H^+$ ,  $Li^+$  and  $EMIM^+$ . Since the sulfonate groups are covalently tethered by the side chains to the perfluorinated molecular backbone they cannot move away whereas their counter cations can be detached by an electric field.[44] When a voltage is applied to a water-based IPMC actuator, redistribution of ions takes place in the Nafion membrane.[35,36] Cations would migrate towards the negatively charged platinum electrode region and form an electric double layer at the interface, while the double layer at the other interface is formed from the immobile sulfonate groups located in the vicinity of the positively charged electrodes. Therefore, regardless to the type of counter cation within the Nafion membrane it is expected that a thicker double layer is formed near the negatively charged electrode.

As can be seen in Figure 3, the CV loop of water-based IP-H and IP-L actuators were narrower than for IL-based IP-E actuators, indicating that capacitance increases in the order: IP-E>IP-L>IP-H. This indicates that replacing water with IL generally led to a higher current response - and therefore higher characteristic capacitance. Since Nafion consists of non-polar tetrafluoroethylene segments and the polar perfluorosulfonic vinyl ether segments four polarization mechanisms can occur within this polymer; electronic polarization, ionic polarization, orientational polarization and interfacial polarization. The more easily the various polarization mechanisms can act, the larger the dielectric permittivity and the capacitance will

be. [45] All polarization mechanisms can be described as a number of resistance and complex capacitance elements connected in series and parallel.[17] The ionic conductivity relates to the exchange of ions between different domains within the bulk of the Nafion membrane, while the overall capacitance describes the accumulation of ions at the polymer/platinum electrode region. A local accumulation of ions is produced in the bulk of the Nafion membrane (interfacial polarization) due to the presence of hydrophobic and hydrophilic domains with different permittivity. An interfacial conductivity is associated with charge exchange at the interfaces between domains with different permittivity. [17] As discussed previously, the incorporation of large hydrophobic organic cation of EMIM<sup>+</sup> and also use of ethanol as the supporting solvent cause the polymer to swell macroscopically [38,39] to a higher extent compared to water-soaked samples.[7] Therefore, it is expected that the mentioned polarization mechanisms happen easier in IL-based IP-E actuators. In Figure 3, it can also be seen that Li<sup>+</sup>-exchanged water-based IP-L actuators showed a higher current compared to the H<sup>+</sup>-exchanged water based IP-H actuators. This difference can be explained by the presence of larger ionic clusters with higher water content within the IP-L samples. This leads to a higher microscopic [38,39] swelling in these samples and facilitate the polarization mechanism.

It has been established that IPMC actuators with more capacitor-like behavior show larger electromechanical responses.[12] Figure 4 compares the calculated capacitance of IP-E actuators with that of IP-E/L-M1, IP-E/L-M2 and IP-E/L-M3 actuators (IL-based actuators incorporating Li<sup>+</sup> ions) to evaluate the effect of the sample preparation technique on the capacitance of these samples. As can be seen, IL-based IPMC actuators incorporating Li<sup>+</sup> ions show higher capacitance than that considered for IP-E actuators with no Li<sup>+</sup> addition. Moreover, the capacitance of IP-E/L-M2 and IP-E/L-M3 actuators was considerably lower than that of IP-E/L-

M1 actuators, while it was still higher compared to IP-E actuators. This indicates that the microscopic structure of Nafion membrane changes as the order and the rate of the penetration of the ions within the polymer are altered. It seems under influence of the applied electric field the transport and migration of ions towards the oppositely charged electrodes occurs easier in the case of IP-E/L-M1 actuators and thicker double layers are formed. These actuators were first impregnated with EMIM<sup>+</sup> cations, using a mixture of IL and ethanol, and then with Li<sup>+</sup> ions. Since they showed to have the highest capacitive characteristic all IP-E/L actuators (IL-based actuators incorporated with Li<sup>+</sup> ions) used in this work were prepared using the preparation method described as method (1) in Section 2.2.

In Figure 5 – part (a) the CV voltamograms of IL-based IP-E samples with no Li<sup>+</sup> ion addition is compared with that of IP-E/L-0.05, IP-E/L-0.1, IP-E/L-0.25 and IP-E/L-0.5 samples with increasing amounts of Li<sup>+</sup> ions. It can be seen that adding Li<sup>+</sup> ions into the IL-based IPMCs led to a higher current response and therefore higher characteristic capacitance in IP-E/L-0.05, IP-E/L-0.1 and IP-E/L-0.25 actuators compared to that for IP-E actuators, the highest of the three being for IP-E/L-0.1. However, water-free IP-E/L-0.5 actuators with the highest Li<sup>+</sup> ion content showed a current response lower than IP-E actuators. The variation in the capacitance of the IL-based actuators as a function of Li<sup>+</sup> ion content can be followed more clearly in Figure 5(b). The calculation of the capacitance from the CV plots revealed that the charge storage capacity of IP-E/L-0.1 is, about two and four times higher than that of IP-E and IP-E/L-0.5 actuators, respectively. The capacitance of IL-based IP-E/L-0.1 actuators was also about four and twenty three times higher than that of the water-based IP-L and IP-H actuators, respectively. This indicated that there exists an optimum concentration of Li<sup>+</sup> ions at which the current response and so the capacitive characteristic is maximized, and the optimum concentration is not the



highest  $\text{Li}^+$  ion concentration. The observed drop in capacitive characteristic beyond the optimum concentration of  $\text{Li}^+$  ions is attributed to accumulation of ions toward the center of the IPMC actuator. When a small electric field is applied across the thickness of IP-E/L actuators  $\text{Li}^+$  ions can move easier and faster towards the negatively charged platinum electrode than large  $\text{EMIM}^+$  cations. Thus, they can contribute in the formation of a thicker double layer at the interface of polymer/platinum electrode in these samples and improve the capacitance characteristic of the sample. This was observed as higher current response and higher characteristic capacitance in CV response of IP-E/L-0.05 and IP-E/L-0.1 actuators compared to that considered for IL-based IP-E actuators with no  $\text{Li}^+$  addition (see Figure 5). However, the improving effect of  $\text{Li}^+$  ions on the capacitance of the IL-based IPMC actuators reached a percolation threshold for IP-E/L-0.1 actuators; the capacitance of IL-based actuators containing higher amount of  $\text{Li}^+$  ions decreased. As the concentration of  $\text{Li}^+$  ions within the IL-based IPMC actuators is increased the number of the free ions (unbounded ions) within the bulk of the polymer increases since the excess ions cannot contribute in the formation of the electric double layer. This can enhance the ionic conductivity of the bulk of the polymer and reduce the capacitive characteristic of the actuators. These results were confirmed with the data obtained from EIS studies on the IPMC actuators which will be discussed later. Figure 6 – parts (a) and (b) illustrates a schematic depiction of the re-distribution of ions under influence of applied electric field and formation of electric double layer at the interface of polymer/platinum electrode in an IL-based IP-E actuator containing (a) no  $\text{Li}^+$  ions, (b) an optima concentration (0.1 M) and (c) a higher concentration of  $\text{Li}^+$  ions ( $>0.1$  M), respectively.

The response of an electrochemical system to a small applied a.c. voltage in impedance spectroscopy is usually displayed as a Nyquist plot of the imaginary component of impedance

against the real part. Nyquist plot appears as a vertical line for ideal capacitors and a point on x-axis for resistors. Also in these plots a semicircle is fitted as a resistor and capacitor in parallel. In highly conductive systems, the semicircle in Nyquist plot is not observable; however, for less conductive systems the semicircle is present in a distorted form. Moreover, the vertical line indicating electrode capacitance is tilted because the electrode surfaces are not ideally smooth. Here, the electrochemical system is an IPMC sample sandwiched between two platinum electrodes, so the alternating current flows through the Nafion membrane. The impedance of the IPMCs is a function of three variables; the mobility of ions in the Nafion membrane, the polarization of the Nafion structure and the double-layer capacitance at the platinum electrodes/polymer. The degree of mobility of ions determines the conductivity of the Nafion membrane. Small ions migrate faster and provide higher conductivity. Figure 7 –parts (a) and (b) shows the Nyquist plots obtained by EIS for IP-H, IP-L, IP-E and IP-E/L-0.1 actuators. As can be seen, both plots shown for the IP-E and IP-E/L-0.1 actuators are nearly linear in the low frequency region and have a semicircle in the high frequency region. This indicates that at low frequencies these IL-based actuators behave like capacitors while at high frequencies they behave like resistors. For IP-E/L-0.1 the semicircle appeared in a higher frequency range compared to the IP-E actuator. This shift is related to the added  $\text{Li}^+$  ions causing a decrease in the ionic resistance of the IL-based IPMC actuator. Contrary to the IL-based IPMCs, for water-based IP-H and IP-L actuators only large semicircles were observed which extended over a wide frequency range. Moreover, amongst the four IPMC samples, the largest semicircle region was observed for the water-based IP-H actuator, indicating the highest impedance (charge transfer resistance) in this IPMC. Replacing  $\text{H}^+$  with  $\text{Li}^+$  caused a significant decrease in the impedance of the water-based IP-L compared to that of the IP-H, due to increase in ionic conduction of the

sample. The high frequency intercepts on the real axis were used to calculate the ionic resistance of IPMC actuators. The IP-L and IP-E actuators had the highest and lowest ionic conduction, respectively. The description of ionic conductivity of Nafion-based IPMC actuators is complicated due to the presence of multiple interfacial polarizations, as discussed earlier. These polarizations are the result of the presence of several different percolation pathways along the interfaces between the hydrophobic and hydrophilic domains in the Nafion membrane. [46] The ionic transport in Nafion membrane is closely related to the size and number of ionic clusters formed within the swollen Nafion membrane and it is described by Grotthuss (hopping) and vehicle (diffusion) mechanisms.[47] According to the Grotthuss mechanism, an ion can hop from a sulfonate site to a nearby acceptor solvent molecule. In contrast, in the vehicle mechanism, an ion transfers by the diffusion of carrier species in the electrolyte in the form of a solvated ion. Both of the two mechanisms can occur easier in the case of the water-based IP-L actuators since they contain larger ionic clusters with higher ionic and water content. This leads to a higher ionic conduction for this sample compared to water-free IP-E actuators which contain smaller ionic clusters. (see Figure S1 in Supplementary Data). Adding  $\text{Li}^+$  ions to an IL-based IPMC led to a decrease in ionic resistance of this actuator in which the IP-E/L-0.1 actuator appeared to have ionic conduction of about the average of the values of the IP-L and IP-E actuators. This indicates that the ionic transport mechanism have been facilitated in the IP-E/L-0.1 samples, probably due to the formation of larger ionic clusters. EIS data are commonly analyzed by fitting them to an equivalent electrical circuit model. The Randles model is one of the simplest and most common models. This model includes a solution resistance,  $R_s$ , a double layer capacitor,  $C_{dl}$  and a charge transfer resistance,  $R_{ct}$ . Figure 7 – part (c) and (d) illustrates the obtained equivalent circuit for water-based and IL-based IPMCs, respectively. As can be seen, IL-based IPMCs have an

additional Warburg element in their equivalent circuit, indicating diffusion processes are important in these actuators.

### 3.3. Actuation performance of IPMCs

The tip displacements of the IP-H, IP-L, IP-E and IP-E/L-0.1 actuators in response to d.c. voltages of 1 to 8 V are shown in Figure 8(a). The four actuators exhibited qualitatively similar dependences on the amplitude of the applied voltage in that tip displacement increased as a function of input voltage in a roughly linear relationship. Tip displacements were much larger for IP-E than IP-H, indicating a significant increase in the actuation response on replacing water with the IL as the solvent and much larger for IP-L than IP-H, demonstrating the improvement due to addition of Li ions. Furthermore, water-based IP-L actuators showed smaller tip displacements than IP-E at the low applied voltages (1 to 4 V). Results show that the IL-based actuators with the highest capacitive characteristic show larger tip displacement over water-based actuators. The observed difference in the magnitude of the actuation response can be attributed to the difference in the Van der Waals volume of the  $H^+$ ,  $Li^+$  and  $EMIM^+$  as counterions. [10] The actuation performance of IPMC actuators is solely the result of motion of ions through the Nafion membrane. As mentioned earlier, upon application of an electric field, cations and anions are mobilized and migrate toward electrodes of opposite charge. The accumulation of ions near the electrodes results in an imbalance in volume within the samples and thus a bending deformation. Since  $EMIM^+$  ions have the highest Van der Waals volume, their accumulation at the cathode results in the largest bending deformation for the IP-E actuator. Adding Li ions to the IL-based IPMCs also gave rise to a considerable increase in tip displacement in IP-E/L-0.1 over IP-E. Amongst the four actuators, IL-based actuators containing

$\text{Li}^+$  ions (IP-E/L-0.1) showed the highest tip displacement over the applied voltage range. This indicates that, in addition to enhancing ionic conduction, addition of Li ions induces a larger volume imbalance in IP-E/L-0.1 than in IP-E, which in turn causes a larger bending deformation. Figure 8-parts (b1) to (b4) present the overlaid digital images captured at the starting point and end point for each IPMC actuator in response to the d.c. voltage of 7 V in amplitude to show the influence of the preparation variables on their actuation performance.

The measured tip displacements of the actuators IP-E and IP-E/L-0.1 in response to the sinusoidal voltages of 4 and 5 V in amplitude and over a frequency range of 0.01 to 1 Hz are shown in Figure 9. It can be seen that these actuators exhibited qualitatively similar dependencies on the amplitude and frequency of the applied sinusoidal voltages. Over the whole frequency range, a small increase in the tip displacement of both the actuators occurred when the amplitude of the sinusoidal input voltage was increased. For both samples at both voltages, there is a strong, approximately inverse relationship between tip displacement and frequency. At low frequencies, the polarity of the electrodes changes slowly, and so a greater number of ions have time to concentrate near the oppositely charged electrodes leading to stronger actuation.[41] The largest differences between the tip displacement of the IP-E and IP-E/L-0.1 actuators occurred at low frequencies. The tip displacement of the IP-E/L-0.1 actuator was generally larger (about 5 times larger at 5 V and 0.01 Hz) than for IP-E, indicating again the contribution of the  $\text{Li}^+$  ions to increasing the degree of bending deformation.

In Figure 10 the calculated displacement rate (in  $\text{mms}^{-1}$ ) of the IP-H, IP-L, IP-E and IP-E/L-0.1 actuators, in response to a 4 V d.c. input, are presented. IP-L and IP-E are respectively the fastest and the slowest responding actuators under these conditions. Even though IP-E showed larger tip displacements (see Figure 8) than IP-H and IP-L, its rate of displacement was about 29 and 10

times lower than for IP-L and IP-H, respectively. It is reasonable to consider the differences in size of the mobile  $H^+$ ,  $Li^+$  and  $EMIM^+$  ions present within these actuators for comparing their displacement rate. On application of the same voltage,  $Li^+$  and  $H^+$  ions would diffuse faster towards the oppositely charged electrode because of their smaller size and more spherical shape than  $EMIM^+$ . [41] It was also found that the displacement rate of IP-E/L-0.1 was approximately twenty six times greater than for the IP-E, although it was still slightly lower than for IP-L. This means that addition of  $Li^+$  ions had the combined positive effect of significantly increasing tip displacement and greatly decreasing the response time of the IL-based IPMC actuator. This can be attributed to the faster motion of  $Li^+$  ions towards the oppositely charged electrode under the influence of the applied electric field and its promoting effect on the formation of an electric double layer being greater in IP-E/L-0.1 than in IP-E.

In Figure 11 the performance over time of the IP-L, IP-E and IP-E/L-0.1 actuators is presented in terms of the variation in tip displacement on application of 4 V d.c. every 10 min. The tip displacement of the IP-E actuator, which was the lowest amongst the three, underwent no significant change over time. This suggests that approximately no evaporation or decomposition of imbibed IL occurred during the experiment. For IP-L the tip displacement increased to a maximum value after 10 min. but decayed gradually over time to close to zero after 180 min. This can be attributed to evaporation of water from the sample and possibly also to loss of water by electrolysis. Finally, for IP-E/L-0.1, there was a similar increase in tip displacement after 10 min. However, it later reached a stable minimum after approximately 60 min. which was about 100 and 2 times higher than the minima observed for IP-L and IP-E, respectively. Consequently, it is reasonable to consider the IL-based IPMC containing a small percentage of  $Li^+$  ions (IPEL) to be an IPMC with improved tip displacement, durability and displacement rate.

#### 4. Conclusions

IL- and water-based IPMC actuators were prepared using commercially available Nafion-117 membrane and were compared using SEM, CV, IS and in electromechanical measurements. Water-based IPMC actuators were prepared in  $\text{Li}^+$ -exchanged and (un-exchanged) protonated form. IL-based IPMC actuators were prepared with and without incorporation of a small percentage of  $\text{Li}^+$  ions.

SEM analysis showed that platinum electrode structures had good surface coverage and penetrated into the polymer and that the surface morphology of the platinum regions was dependent on the type of solvent and the identity of the cation. The IL gave rise to smoother and denser platinum-impregnated regions in pure IL-based actuators. The roughest platinum-impregnated regions were observed in actuators with  $\text{Li}^+$ -exchanged Nafion. A slight roughness was introduced into the platinum electrode of IL-based actuators by addition of  $\text{Li}^+$  ions to their structure.

In electrochemical tests the electrode capacitance and the frequency response of IPMC actuators were compared for both set of actuators, using CV and EIS methods. The effect of the solvent and cation type was examined. A greater contact resistance was observed in the water-based actuators, especially in the actuator with Nafion in protonated form. The IL-based actuator incorporating  $\text{Li}^+$  ions showed the closest behavior to that of an ideal capacitor and appeared to have the highest charge storage capacity of any actuator. It was found that IL-based actuators possessed an additional Warburg element in their equivalent circuit.

In electromechanical tests the maximum tip displacement, durability and displacement rate were recorded for actuators. The effect of amplitude and frequency of the applied voltage on displacement was examined. The IL-based actuator incorporating  $\text{Li}^+$  ions generated much larger

tip displacements. For all actuators, displacement increased with increasing applied voltage but decreased with increasing frequency. The small displacement rate of IL-based actuator was enhanced by twenty six times by adding  $\text{Li}^+$  ions and it also showed the lowest actuation decay over time. Water-based  $\text{Li}^+$ -exchanged IPMC actuators had the highest ionic conduction and showed the highest rate of displacement. However, their tip displacement was considerably lower than IL-based IPMC actuators incorporated with  $\text{Li}^+$  ions, which also possessed the highest electrode capacitance. Results revealed that there was a direct linear relationship between response time and the ionic conduction process in the IPMC actuators while the magnitude of tip displacement was largely dependent on the electrode structure and capacitance.



Table 1. Naming system of IPMC samples

Sample	Preparation process	Elimination of solvent	Cation type
IP-H	IPMC immersed in 1M HNO <sub>3</sub> (aqueous)	-	H <sup>+</sup>
IP-L	Dehydrated IP-H immersed in 0.1M LiBF <sub>4</sub> (aqueous)	-	Li <sup>+</sup>
IP-E	Dehydrated IP-H immersed in EMIMBF <sub>4</sub> /Ethanol	✓	EMIM <sup>+</sup>
IP-E/L-M1	Dehydrated IP-E immersed in 0.1M LiBF <sub>4</sub> (aqueous)	✓	EMIM <sup>+</sup> /Li <sup>+</sup>
IP-E/L-M2	Dehydrated IP-H immersed in 0.1M LiBF <sub>4</sub> (EMIMBF <sub>4</sub> /Ethanol)	✓	EMIM <sup>+</sup> /Li <sup>+</sup>
IP-E/L-M3	Dehydrated IP-L immersed in EMEBF <sub>4</sub> /Ethanol	✓	EMIM <sup>+</sup> /Li <sup>+</sup>
IP-E/L-0.05	Dehydrated IP-E immersed in 0.05 M LiBF <sub>4</sub> (aqueous)	✓	EMIM <sup>+</sup> /Li <sup>+</sup>
IP-E/L-0.10	Dehydrated IP-E immersed in 0.1 M LiBF <sub>4</sub> (aqueous)	✓	EMIM <sup>+</sup> /Li <sup>+</sup>
IP-E/L-0.25	Dehydrated IP-E immersed in 0.25 M LiBF <sub>4</sub> (aqueous)	✓	EMIM <sup>+</sup> /Li <sup>+</sup>
IP-E/L-0.50	Dehydrated IP-E immersed in 0.5 M LiBF <sub>4</sub> (aqueous)	✓	EMIM <sup>+</sup> /Li <sup>+</sup>

**Figure captions:**

Figure 1. Schematic diagram and photographic view of experimental set-up for measurement of tip displacement on IPMC actuators

Figure 2. (a) Cross sectional SEM image of IP-H actuator and longitudinal SEM images of IPMC samples showing the platinum electrode surface structures in (b) IP-H, (c) IP-L, (d) IP-E and (e) IP-E/L

Figure 3. Comparison of the CV response of the fabricated water-based IP-H, IP-L actuators with IL-based IP-E actuator with no  $\text{Li}^+$  ion addition

Figure 4. Comparison of the calculated capacitance of IL-based IP-E actuators with IL-based IPMC actuators incorporated with  $\text{Li}^+$  ions; IP-E/L-M1, IP-E/L-M2 and IP-E/L-M3 prepared using method (1) to (3), respectively.

Figure 5. (a) Comparison of the CV voltamograms of IL-based IP-E samples with no  $\text{Li}^+$  addition with that of IL-based samples with increasing amount of  $\text{Li}^+$  ions. (b) Variation in the capacitance of the IL-based actuators as a function of  $\text{Li}^+$  ion content

Figure 6. Schematic depiction of the double layer structure in IL-based IP-E actuators containing (a) no  $\text{Li}^+$  ions, (b) an optima concentration (0.1 M) and (c) a higher concentration of  $\text{Li}^+$  ions ( $>0.1$  M)

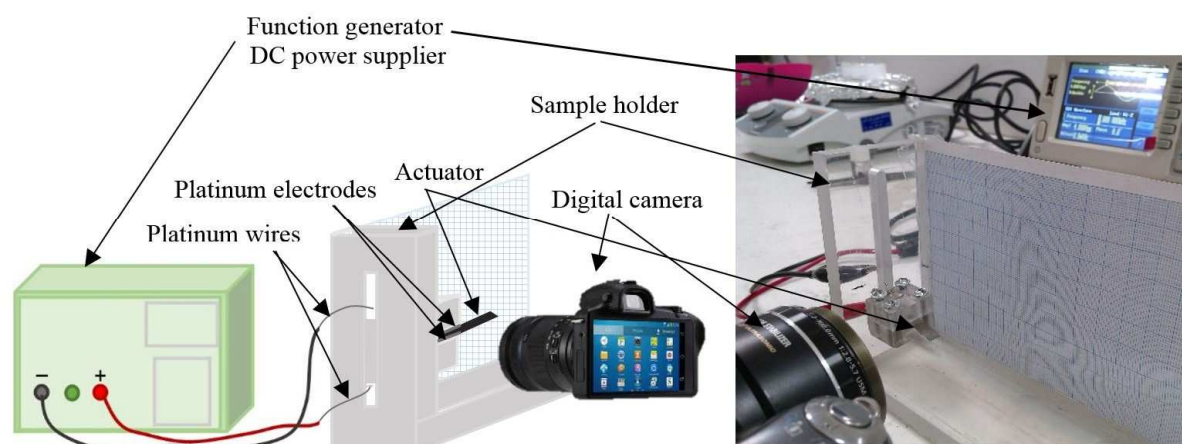
Figure 7. Comparing Nyquist plots of all IPMC actuators (a) in full view and (b) in the selected region shown in part (a) and obtained equivalent circuit for (c) IP-H and IP-L actuators and (d) IP-E and IP-E/L-0.1 actuators

Figure 8. (a) Comparison of the dependence of tip displacement on amplitude of the input d.c. voltage for fabricated IPMC actuators and (b<sub>1</sub>), (b<sub>2</sub>), (b<sub>3</sub>) and (b<sub>4</sub>) are the corresponding overlaid digital images captured at the starting point and end point for IP-H, IP-L, IP-E IP-E/L-0.1 actuators, respectively, in response to the d.c. voltage of 7 V in amplitude.

Figure 9. Comparison of the tip displacement against frequency of applied voltage signal for IL-based IPMC actuators. Data are presented for actuators subjected to voltages of 4 and 5 V in amplitude.

Figure 10. Comparison of the calculated displacement rate (in mmS<sup>-1</sup>) of the IPMC actuators; IP-H, IP-L, IP-E and IP-E/L-0.1, in response to the same d.c. voltage of 4 V in amplitude

Figure 11. Comparison of the operating life of the IPMC actuators; IP-L, IP-E and IP-E/L-0.1 actuators as they subjected to 4 V d.c. potential with time interval of 10 min.

**Figure 1**

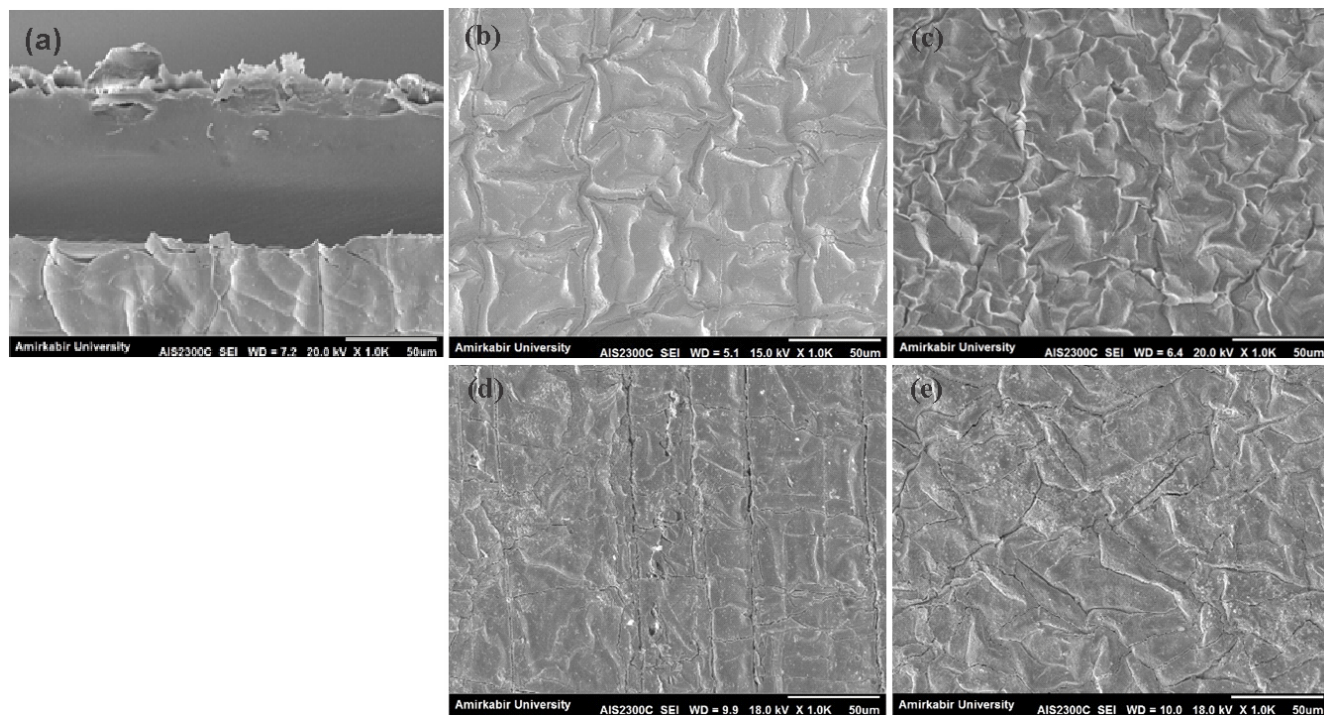


Figure 2

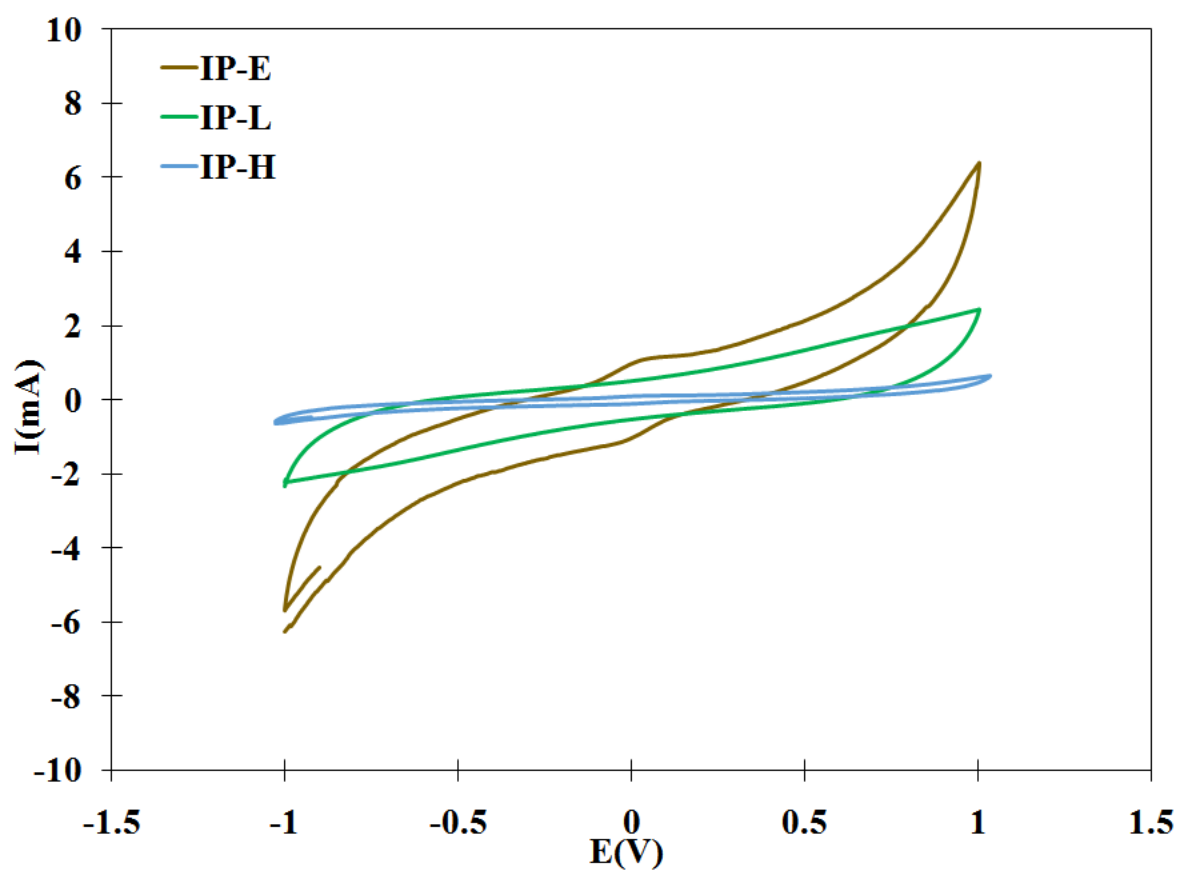


Figure 3

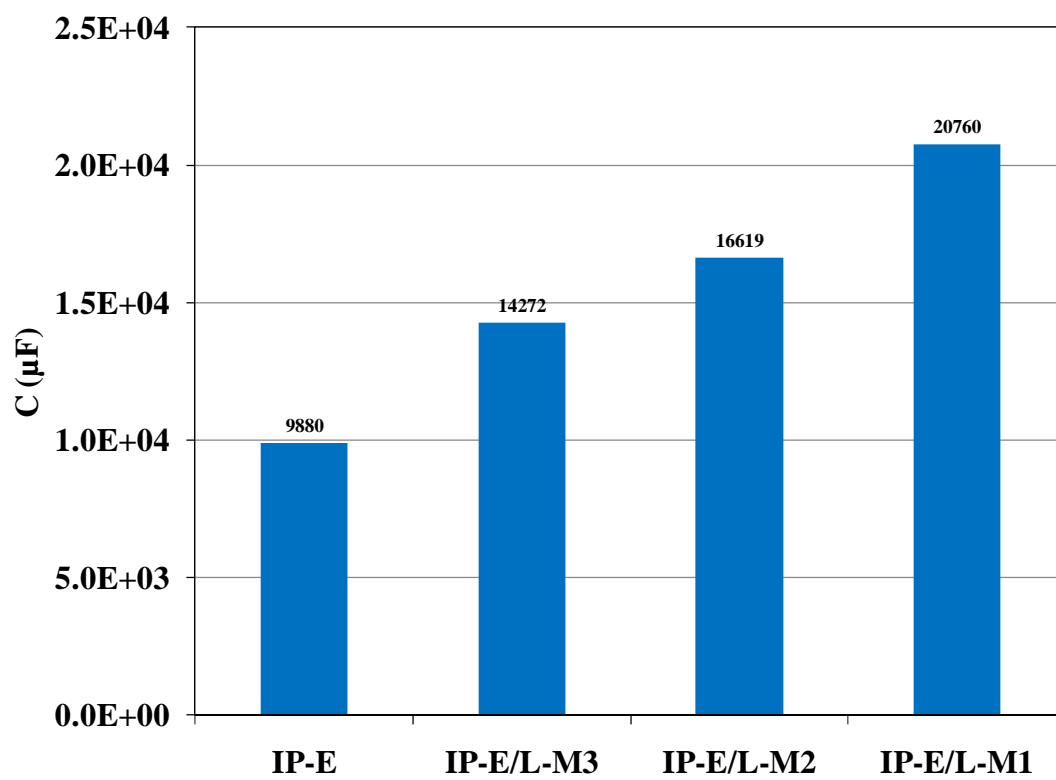


Figure 4

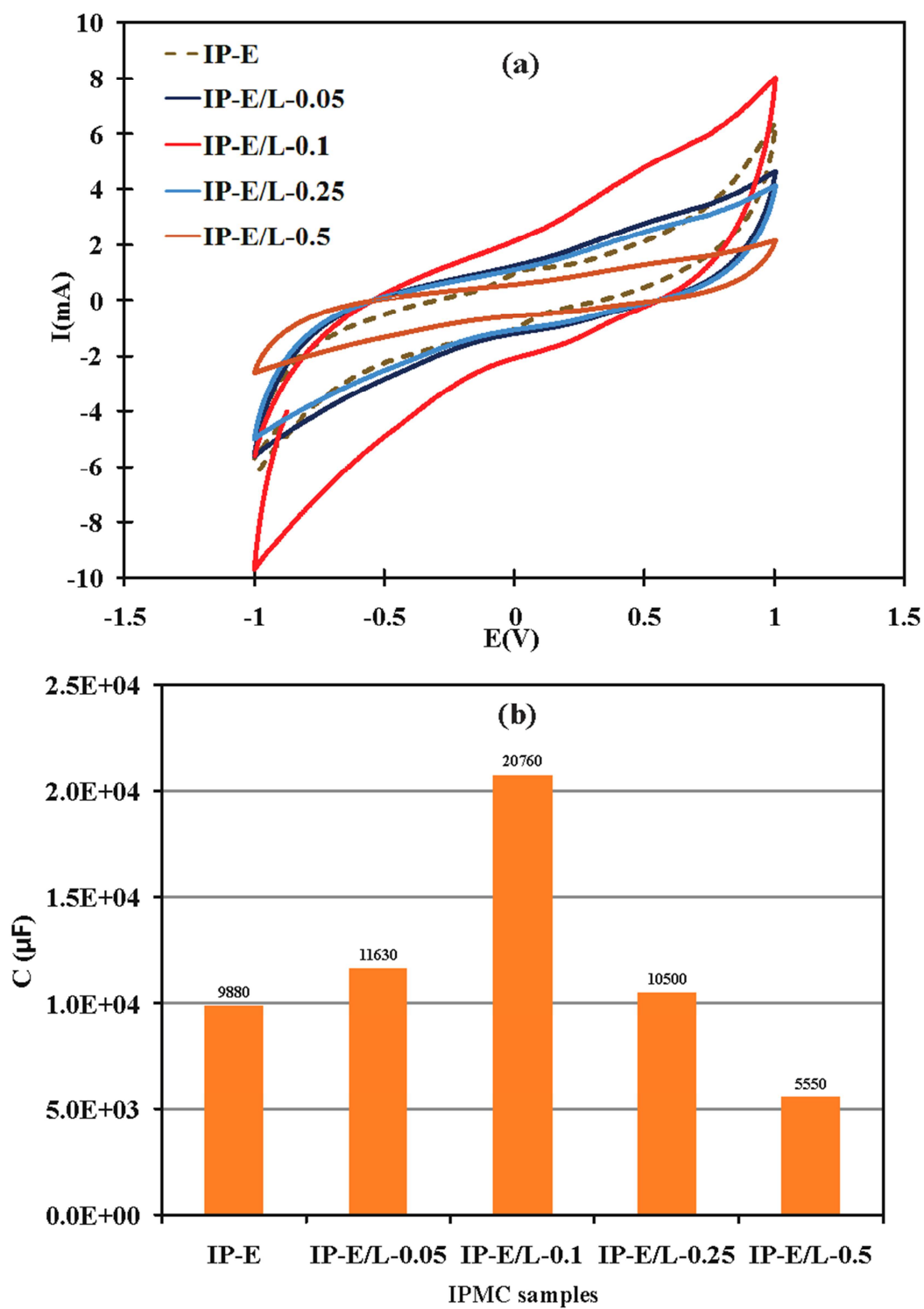


Figure 5



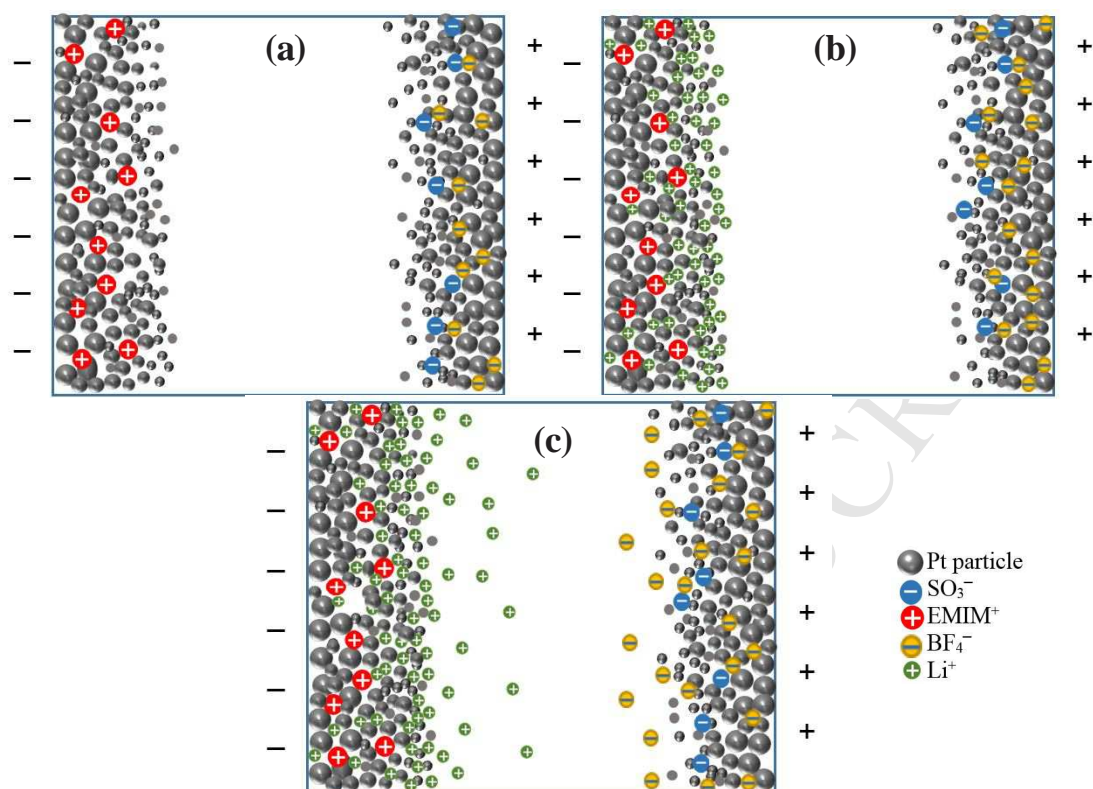


Figure 6

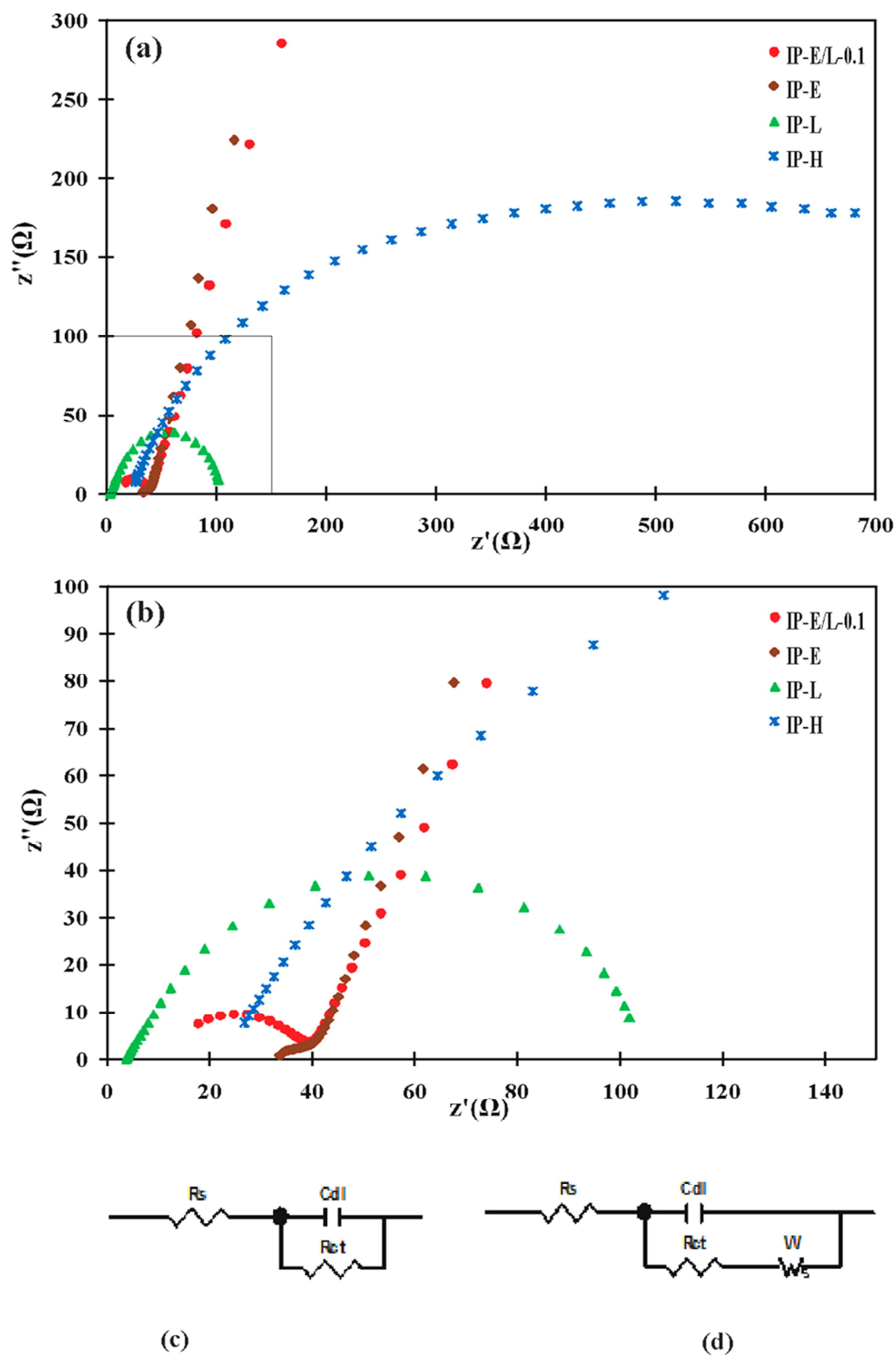


Figure 7

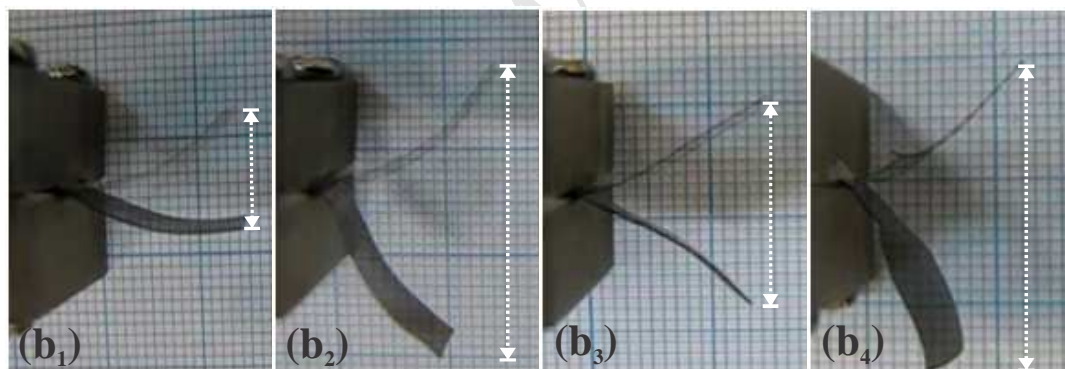
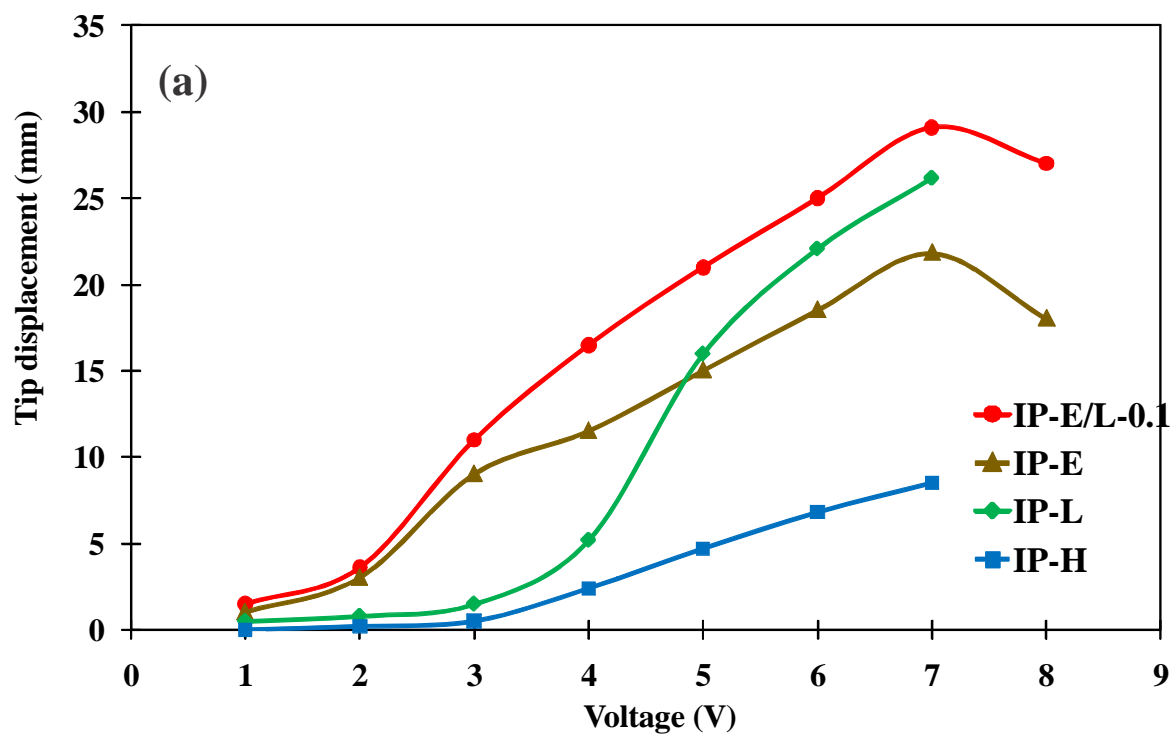


Figure 8

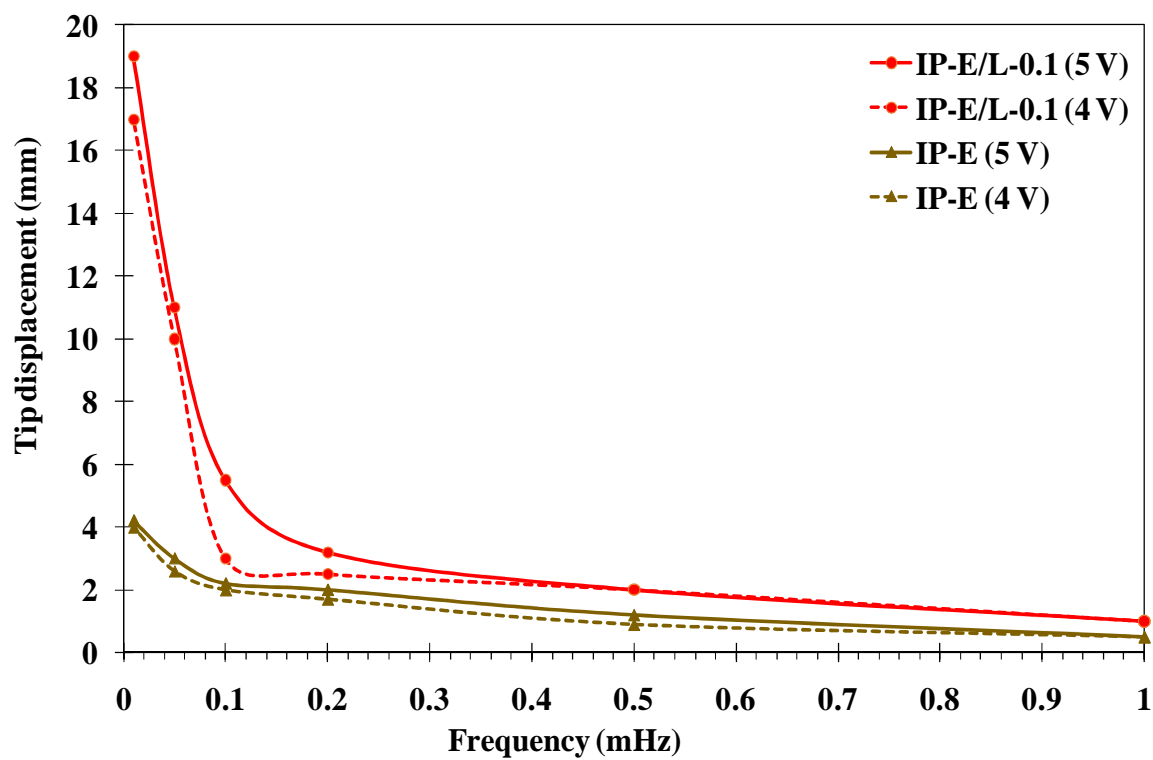


Figure 9

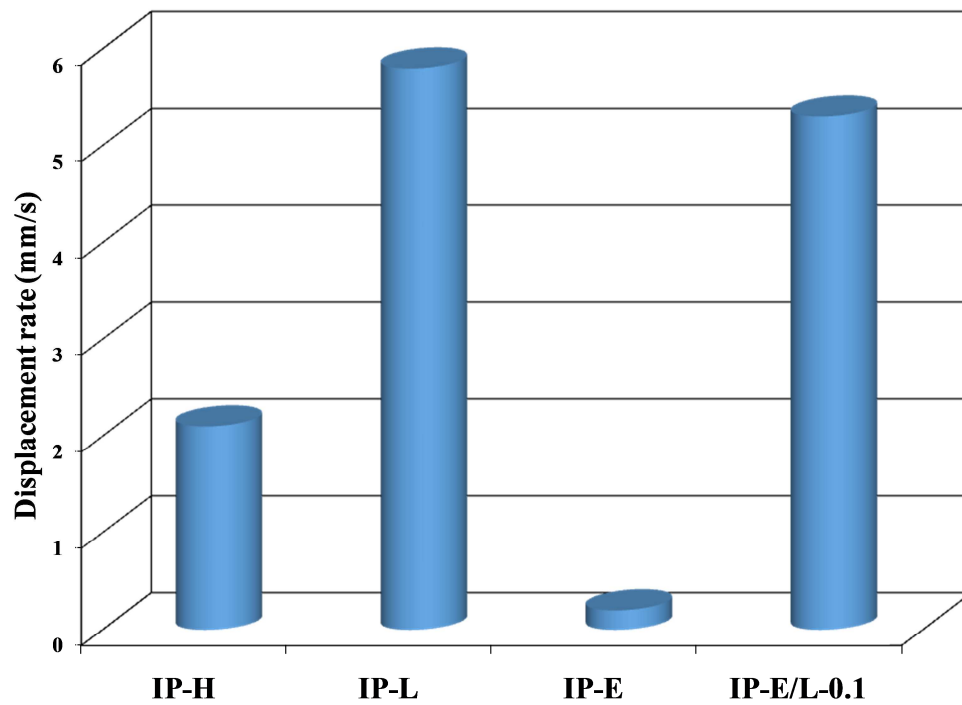


Figure 10

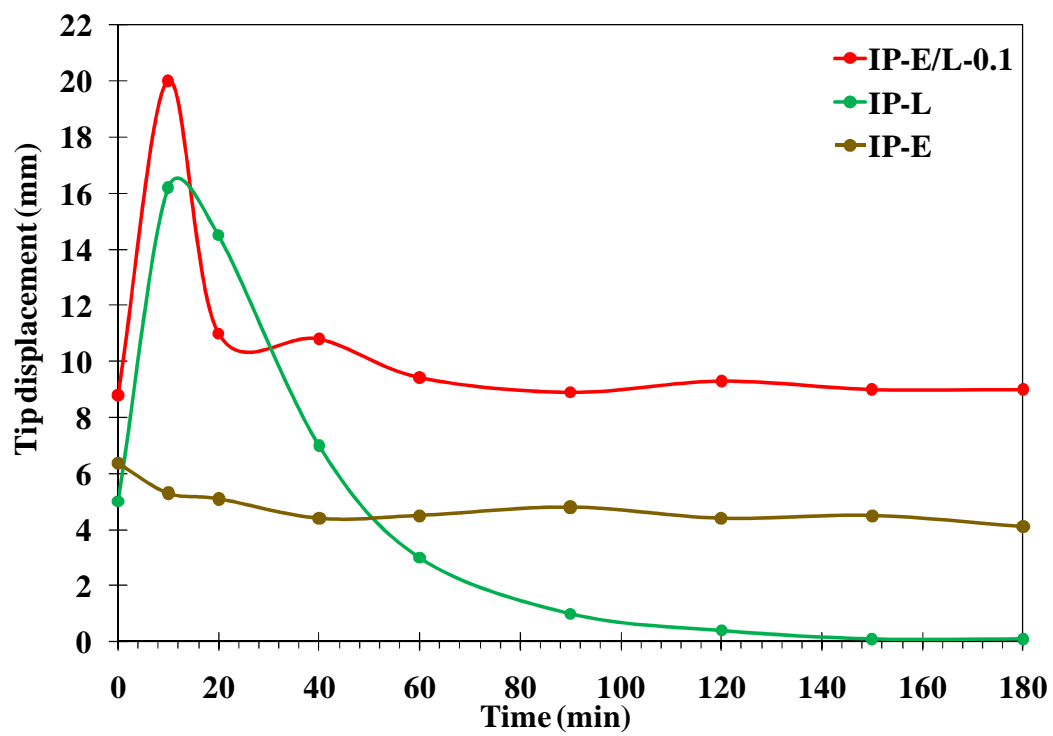


Figure 11

## References

- [1]. Y. Bar-Cohen, *Adv. Mater.*, 2006, 38, 3.
- [2]. S.-W. Yeom, & I.-K. Oh, *Smart Mater. Struct.* 2009, 18, 085002
- [3]. V. Palmre *et al.* . *Smart Mater. Struct.* 2013, 22, 014003.
- [4]. M. Shahinpoor, K. J. Kim, *Smart Mater. Struct.*, 2005, 14, 197.
- [5]. Y. Bar-Cohen, C. Mavroidis, M. Bouzit, B. Dolgin, L. Deborah, *8th Ann. Inter. Symp. on Smart Structures & Materials, Smart Structures & Materials, Proc. SPIE*, 2001, Paper No. 4329-47.
- [6]. C. Jo, D. Pugal, I.-K. Oh, K. J. Kim, K. Asaka, *Prog. Polym. Sci.*, 2013, 38, 1037.
- [7]. Y. Bar-Cohen, “Electroactive Polymer (EAP) Actuators as Artificial Muscles – Reality, Potential & Challenges”, *SPIE Press*, Bellingham WA, 2001.
- [8]. Z. Zhu, L. Chang, K. Takagi, Y. Wang, H. Chen, and D. Li, *Applied Physics Letters*, 2014, 105, 054103.
- [9]. T. Sugino, K. Kiyohara, I. Takeuchi, K. Mukai, K. Asaka, *Sensors and Actuators B*, 2009, 141, 179.
- [10] J. W. Hong, C. Meis, J. R. Heflin, R. Montazami, *Sensors and Actuators B*, 2014, 205, 371.
- [11]. S. Nemat-Nasser, S. Zamani, *Smart Structures & Materials*, 2003, 5051, 233.
- [12] J. W. Hong, A. Almomani, R. Montazami, *Organic Electronics*, 2014, 15, 2982.
- [13] J. M. D. Bennett, D. J. Leo, *Sensors and Actuators A*, 2004, 115, 79.
- [14] J. M. D. Bennett, D. J. Leo, G. L. Wikes, F. L. Beyer, T. W. Pechar, *Polymer*, 2006, 47, 6782.
- [15]. A. Dharaskar Swapnil , *J. Chemical Sciences*, 2012, 2, 8, 80.
- [16]. S. Sowmiah, V. Srinivasadesikan, M. Tseng and Y. Chu, *Molecules*, 2009, 14, 3780.
- [17] J. V. D. Noto, M. Piga, G. A. Giffin, S. Lavina, E. S. Smotkin, J. – Y. Sanchez and C. Iojoiu, *J. Phys. Chem. C*, 2012, 116, 1370.
- [18] J. V. D. Noto, E. Negro, J. – Y. Sanchez and C. Iojoiu, *J. Am. Chem. Soc.*, 2010, 132, 2183.
- [19]. G. Raabe and J. Köhler, *J. Chem. Phys.*, 2008, 128, 15, 154509.
- [20]. J. D. Decoppet, T. Moehl, S. Salem Babkair, R. A. Alzubaydi, A. A. Ansari, S. Habib, H. W. Schmidt, Sh. M. Zakeeruddin and M. Grätzel, *J. Mater. Chem. A*, 2014, DOI:10.1039/C4TA01995D.
- [21]. Ch. J. Rao, K. A. Venkatesan, K. Nagarajan, T. G. Srinivasan and P. R. V. Rao, *J. Nuclear Materials*, 2011, 408, 25.

- [22]. Y. Lu, K. Korf, Y. Kambe, Z. TuandProf. L. A. Archer, *Angewandte Chemie*, 2014, 126, 2, 498.
- [23]. L. Wei, M. Sevilla, A. B. Fuertes, R. Mokaya, and G. Yushin, *Advanced Functional Materials*, 2012, 22, 4, 827.
- [24]. J. Sakthi Swarrup, R. Ganguli, and G. Madras, *Advanced Science: Engineering and Medicine*, 2014, 6, 7, 741.
- [25]. K. Oguro, K. Asaka, and H. Takenaka, *US Patent Specification*, 1993, 5, 268, 082.
- [26]. S. Liu, W. Liu, Y. Liu, J. H. Lin, X. Zhou, M. J. Janik, R. H. Colby, and Q. Zhanga, *PolymInt*, 2010, 59, 321.
- [27]. J. Wang, Ch. Xu, M. Taya and Y. Kuga, *Smart Mater. Struct.*, 2007, 16, 214.
- [28]. N. Terasawaa, I. Takeuchia, H. Matsumotob, *Sensors and Actuators B*, 2009, 139, 624.
- [29]. F. Carpi, E. Smela (Eds.), "Biomedical Applications of Electroactive Polymer Actuators" ,Wiley and Sons, Ltd, Chichester, 2009.
- [30]. V. Palmre, E. Lust, A. Jänes, M. Koel, A.L. Peikolainen, J. Torop, U. Johanson, A. Aabloo, *J. Mater. Chem.*, 2011, 21, 2577.
- [31]. J. Toropa, T. Sugino, K. Asakab, A. Jänesc, E. Lustc, A. Aablooa, *Sensors and Actuators B*, 2012, 161, 629.
- [32]. B. K. Kim, B. M. Kim, J. W. Ryu, I. H. Oh, S. K. Lee, S. E. Cha, and J. H. Park, *Smart Structures and Materials*, 2003, 5051, 486.
- [33]. L. A. Zook and J. Leddy, *Analytical Chemistry*, 1996, 68, 21, 3793.
- [34]. J. J. Pak, S. E. Cha, H. J. Ahn, S. K. Lee, *Proc. of the 32nd Intl. Symp. on Robotics (ISR)*, 2002, 51, 9, 455.
- [35]. L. Naji, J. A. Chudek and R. T. Baker, *Soft Matter*, 2008, 4, 1879.
- [36]. L. Naji, J. A. Chudek and R. T. Baker, *J. Phys. Chem. B*, 2008, 112, 568.
- [37]. J. Torop, V. Palmre, M. Arulepp, T. Sugino, K. Asaka, A. Aabloo, *CARBON*, 2011, 49, 9, 3113.
- [38]. A.M. Affoune, A. Yamad, M. Umed, *J. Power Sources*, 2005, 148,9.
- [39]. A. Elliott, S. Hanna, A.M.S. Elliott, G.E. Cooley, *Polymer*, 2001, 42, 2251.
- [40]. Y. Kawano, Y. Wang, R. A. Palmer, S. R. Aubuchon, *Polímeros: Ciência e Tecnologia*, 2002, 12, 2, 96.
- [41]. L. Naji, J. A. Chudek, E. W. Abel, R. T. Baker, *J. Mater. Chem. B*, 2013,1, 2502.
- [42]. T. Sugino, K. Kiyohara, I. Takeuchi, K. Mukai, K. Asaka, *Sensors and Actuators B*, 2009, 141, 179.



- 
- [43]. X. Bao, Y. Bar-Cohen, S. S. Lih, *Smart Structures & Materials, Proc. of SPIE*, 2002, 4695, 220.
- [44]. X. Gong, A. Bandis, A. Tao, G. Meresi, Y. Wang, P. T. Inglefield, A. A. Jones, W. Y. Wen, *Polymer*, 2001, 42, 6485.
- [45]. A. Nussbaum, *Electronic and Magnetic Behavior of Materials*, Prentice-Hall, 1967.
- [46]. G. A. Giffin, G. M. Haugen, S. J. Hamrock and V. D. Noto, *J. Am. Chem. Soc.*, 2013, 135, 822.
- [47]. P. Choi, N. H. Jalani, and R. Datta, *Journal of The Electrochemical Society*, 2005, 152, 3, 123.

### Highlights

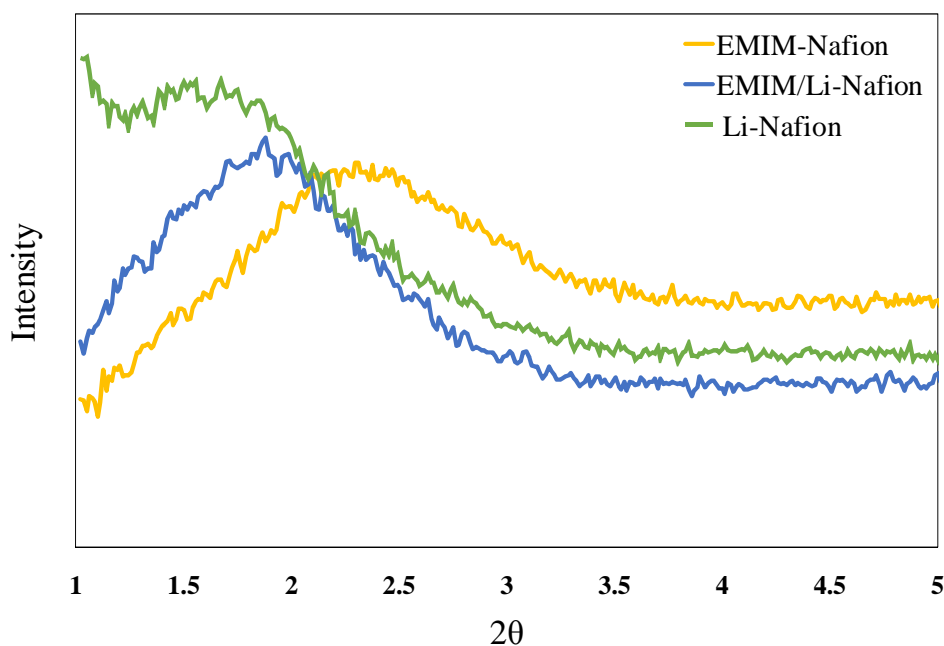
- Preparation of Li incorporated IL-swollen IPMC actuators
- Enhancing effect of Li ions on ionic conduction and capacitance of IL-swollen IPMCs
- Li ions increased rate of displacement and operating life of IL-swollen IPMCs

## Electronic Supplementary Information (ESI)

**Table S1.** Effect of the type of supporting solvent on IL uptake

Sample	Ion exchange membrane	Ionic liquid	Supporting solvent	Initial dry mass (g)	Swollen, dry mass (g)	Ionic liquid Absorbed ( $\times 10^{-5}$ mol/g)
IPMC1	Nafion-117	EMIBF <sub>4</sub>	-	0.037	0.039	1.41
IPMC2	Nafion-117	EMIBF <sub>4</sub>	DI Water	0.037	0.042	2.53
IPMC3	Nafion-117	EMIBF <sub>4</sub>	Methanol	0.038	0.047	4.73
IPMC4	Nafion-117	EMIBF <sub>4</sub>	Ethanol	0.038	0.049	5.36

The difference in mass between the dried EMIM<sup>+</sup>- exchanged IPMCs and the original dried IPMC in protonated form was assigned to be the mass of EMIBF<sub>4</sub> absorbed. The data presented in Table S1 show that the amount of absorbed ionic liquid increased strongly in the order IPMC1 < IPMC2 < IPMC3 < IPMC4. This trend implies that ethanol is a more effective supporting solvent than methanol, which in turn is better than water, because it facilitates the penetration of more of the large organic cations of the ionic liquid into the membrane. Thus, ethanol was chosen as the supporting solvent for subsequent studies of ionic liquid-soaked IPMC.



**Figure S1.** Comparison of SAXS patterns obtained for water-soaked  $\text{Li}^+$ -exchanged and ionic liquid soaked  $\text{EMIM}^+$  and  $\text{EMIM}^+/\text{Li}^+$  - exchanged Nafion membranes.

In Figure S1, it can be seen that the cluster reflection – the main peak - moved to lower scattering angles on moving from  $\text{EMIM}^+$ - to  $\text{EMIM}^+/\text{Li}^+$  - and to  $\text{Li}^+$ - exchanged Nafion membranes. The corresponding intercluster spacings were 37.7, 48.1 and 54.4 Å, respectively. These results clearly indicates that the intercluster spacing increases as the large  $\text{EMIM}^+$  cation is partly and then completely replaced by  $\text{Li}^+$  ions with lower ionic radius, due to the formation of larger ionic clusters..