

# **Influence of Electrolytes of Li salts, EMIMBF<sub>4</sub> and Mixed Phases on Electrochemical and Physical Properties of Nafion Membrane**

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*

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## Abstract

Electrolyte-soaked Nafion is commonly used as an ionic polymer in soft actuators. Here, a multi-technique investigation was applied to correlate the electrochemical behavior of Nafion membranes with their microstructures and nanostructures as a function of electrolyte type. The influence of electrolytes of Li salts with different counteranions on the Nafion membranes was investigated in terms of hydration level, structure (using x-ray diffraction and small angle x-ray scattering), stress-strain characteristics and electrochemical behavior (by cyclic voltammetry and electrochemical impedance spectroscopy). The effects of using ionic liquid, as the electrolyte, addition of different supporting solvent and the addition of  $\text{Li}^+$  ions to water-free ionic liquid (IL)-soaked membranes on the structural and electrochemical properties of Nafion were examined. The nano- and microstructure of the Nafion changed considerably as a function of the identity of the electrolyte solution. The electrochemical behavior of the IL-soaked samples was compared with that of the water-soaked  $\text{Li}^+$ -exchanged Nafion. It was seen that the ionic conductivity of the Nafion membranes was reduced significantly when water was replaced by pure IL. Using the supporting solvents increased the conductivity of IL-soaked Nafion membranes dramatically. The presence of a small amount of  $\text{Li}^+$  ions together with the IL ions caused a significant decrease in charge transfer resistance and increases in double layer capacitance and in ionic conductivity over that of the water-free sample and also over water-soaked  $\text{Li}^+$ -exchanged Nafion. These findings can be useful to improve the knowledge on Nafion's microstructure and also to improve the electromechanical behavior of Nafion-based IPMC actuators.

## 1. Introduction

Significant advances have been made in the area of so-called artificial muscles - or soft actuators - aimed at practical applications in bio-medical devices, [1] bio-mimetic robots and micro-manipulators. [2] Ionic Polymer-Metal Composites (IPMCs) have attracted considerable attention as the basis for soft actuators because of their ease of processing, low power requirement, large displacements, flexibility, bio-mimetic activation and bio-compatibility. [2] A typical IPMC consists of a thin, ionic polymer membrane with metal electrodes deposited chemically at both faces. [3] When soaked with a suitable electrolyte, IPMCs will bend under the influence of a small potential applied between the metal electrodes. A great deal of research has been performed on IPMCs based on the cation-exchanged perfluorinated sulphonic acid membrane, Nafion, manufactured by Du Pont. Nafion has high ionic conductivity, [4,5] significant mechanical strength, [6] good chemical and thermal stability [7,8] and high selectivity to the desired ionic species. [9,10] These properties are a result of the hydrophobic perfluorinated molecular backbone and hydrophilic ionic clusters in this polymer. [11] Cluster diameters are about 4–10 nm depending on the water content of the membrane. Nafion is able to absorb large amounts of water and other protic liquids into these hydrophilic regions. It has been reported that the ionic clusters may contain up to 100 sulfonate groups, with up to 20 water molecules around each cluster. [12] The actuation performance of IPMC actuators is influenced by the type of charge balancing cations at the sulfonate groups, the material and the structure of the electrodes, the solvent, the level of solvation and the thickness and other dimensions of the membrane. [13] Several investigations indicate the strong influence of the cation type on the actuation performance of IPMCs. [14,15] It is reported that the  $\text{Li}^+$ -exchanged IPMCs produce the greatest tip displacement and smallest back-relaxation and are superior to those containing other alkali

metals. [16] This is attributed to the strong solvation of the small  $\text{Li}^+$  cation and to high  $\text{Li}^+$  ion mobility. A typical chemical structure of  $\text{Li}^+$ -exchanged Nafion is depicted in Figure 1(a).

The bending deformation of IPMC actuators depends on the migration of cation species within the Nafion membrane [16] for which the solvent (often water) provides the medium. Therefore, an IPMC requires optimum solvent uptake in order to show its best actuation performance. However, IPMC actuators containing water should not be operated at voltages higher than 1.22 V due to loss of water through electrolysis. To overcome this problem, solvents including ethylene glycol [17] and ionic liquid (IL) [18] have been used. Applying ethylene glycol and glycerol as inner solvent for IPMCs showed to have a reducing effect on the response rate of IPMCs compared to water-based IPMCs, due to the large size and high viscosity of these solvents. [17] ILs show superior electrical and thermal stability, compared to water. Since ILs consist of ions, they can be considered to act both as solvent and electrolyte. However, the actuation response of the IPMC is very slow in these cases. [18] Researchers have also investigated the effect of the polarity of the solvent, [19,20] on the electrochemical properties of Nafion membranes using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrical conductivity of Nafion containing different mixtures of methanol and water was higher at low water content than that of the individual constituents while the reverse was true at high water content. [16] The secondary structure of Nafion has been studied using techniques including small angle x-ray scattering (SAXS), neutron scattering, [21] magnetic resonance imaging (MRI), [22,23] transmission electron microscopy (TEM) analysis, [24] MAS,  $^{19}\text{F}$ , and  $^{129}\text{Xe}$  NMR. [25] To study the relationship between the microstructure and actuation mechanism of IPMCs, the electrically induced diffusion of water in a commercial membrane [26] and in an operating IPMC soft actuator device [22] (both based on  $\text{Li}^+$ -

exchanged Nafion) have been investigated *in situ* by the authors by deploying a functioning electrochemical cell inside a magnetic resonance imaging (MRI) instrument. [13] In another study, diffusion-weighted imaging (DWI) was employed in MRI-based experiments to map directly the spatial variation of the diffusion coefficients of water molecules in a cast, Li<sup>+</sup>-exchanged Nafion membrane and also in an operating IPMC sample.[23] The results of these studies were explained in terms of the electro-induced diffusion of [Li(H<sub>2</sub>O)<sub>x</sub>]<sup>+</sup> species through the Nafion material in which highly ionic regions exist within a highly hydrophobic major domain but where these ionic regions are interconnected by regions of intermediate hydrophilicity. [13]

In this contribution, a comparative study of structural and electrochemical characteristics of water- and IL- soaked Nafion membranes was performed. Dry Nafion samples were soaked in an appropriate solution of LiOH, LiClO<sub>4</sub> or LiBF<sub>4</sub> electrolytes and the influence of the counteranion on water uptake and transport, polymer structure, stress-strain characteristics and electrochemical behavior was determined. Similar experiments were carried out on Nafion membranes incorporating the IL, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF<sub>4</sub>), shown in Figure 1(b). The effect of the supporting solvents on IL permeation within the Nafion membrane was also evaluated. Furthermore, a small percentage of Li<sup>+</sup> ions were incorporated into IL-soaked Nafion membranes to determine the joint effect of both. The results indicated that electrochemical and mechanical properties of Nafion membrane are changed considerably as a function of the identity of the electrolyte solution, due to the microscopic and macroscopic structural changes. It was seen that the ionic conductivity of the Nafion membranes was reduced significantly when water was replaced by pure IL. Using the supporting solvents increased the conductivity and capacitance characteristic of IL-soaked Nafion membranes dramatically. IL-

soaked Nafion membranes incorporated with  $\text{Li}^+$  ions showed the highest ionic conduction and double layer capacitance. This implies a higher energy storage ability of these membranes that usually leads to a larger bending deformation of Nafion-based IPMCs under influence of an electric field. These findings can be useful to improve the knowledge on Nafion's microstructure and also to improve the electromechanical behavior of Nafion-based IPMC actuators.

## 2. Experimental

### 2.1. Materials

DuPont Nafion-117 sheet with a thickness of 0.2 mm in acid form with an equivalent weight of 1100 (Aldrich) was cut into 8×8 mm squares and cleaned to remove all impurities introduced during the manufacturing process.[22] This involved heating in 2 M  $\text{HNO}_3$  at 80°C for 2 h to exchange all cations on the sulfonate groups for protons and removal of organic impurities and small polymer fragments by ultrasonication in 50/50 b.v. ethanol-DI water for 2 h. The membranes were boiled in fresh DI water for 1 h after each of these steps. The samples were dehydrated in an oven at 70°C. These samples were soaked in aqueous 1M  $\text{LiOH}$ ,  $\text{LiClO}_4$  or  $\text{LiBF}_4$  (all from Sigma-Aldrich) solution or pure  $\text{EMIMBF}_4$  (Research Institute of Petroleum Industry) at ambient temperature, for 7 days to allow population of all the ion exchange sites (the  $-\text{SO}_3^-$  groups) with the appropriate cation. The amount of cation added was calculated to correspond to the number of ion exchange sites available in the dry mass of the Nafion membrane, which was estimated according to the definition of equivalent weight,  $EW$ , for each sample. [16] To study the effect of supporting solvents on the absorption of the IL by the Nafion, the  $\text{EMIMBF}_4$  was dissolved in DI water, methanol or ethanol in a 1:1 mole ratio and dry Nafion

samples were immersed in these solutions. The membranes were then dried under vacuum at 70°C for 12 h to remove the solvents. Henceforth, the samples are named to indicate what had been added to them: aqueous LiOH ('NH'), LiClO<sub>4</sub> ('NC') or LiBF<sub>4</sub> ('NB'), pure IL ('NPI'), or a mixture of IL and DI water ('NWI'), methanol ('NMI') or ethanol ('NEI'), where N stands for Nafion. Pure Nafion membranes in acid form are named 'PN' throughout this text.

To study the combined effects of IL as non-aqueous media and Li<sup>+</sup> ions on their physical, structural and electrochemical characteristics, water-free IL-soaked Nafion samples incorporating 1.5% Li<sup>+</sup> ions were also prepared. Dry NEI samples were soaked in the 0.1M LiBF<sub>4</sub> solution (2 ml) at ambient temperature for 2 h. The mass ratio of LiBF<sub>4</sub>/EMIMBF<sub>4</sub> was chosen to be 1.5%. The samples were then placed under vacuum in an oven at 70°C for 12 h to remove the water. EMIMBF<sub>4</sub> is chemically inert toward water; however, it slowly absorbs water when exposed to air. Therefore, the IL-soaked samples were placed in a dry box to avoid exposure to the humid air. Hereafter, these samples are referred to as NEIL. Of the IL-containing Nafion samples, NEI was chosen since it was found to have the highest IL content. This will be discussed later in the text.

## 2.2. Physical Characterization

Aqueous Li<sup>+</sup>- and EMIM<sup>+</sup>- exchanged Nafion membranes were vacuum dried in an oven at 80°C overnight and their dry mass,  $M_{dry}$ , measured and subtracted from their wet mass,  $M_{wet}$  and the percentage of solvent uptake calculated using Equation 1.

$$\text{Solvent Uptake\%} = (M_{wet} - M_{dry})/M_{dry} \quad (1)$$

Pre-cleaned Nafion membranes in protonated form were vacuum dried in an oven at 80°C until constant weights were obtained. The membranes were then soaked in aqueous 1M LiOH, LiClO<sub>4</sub>

or LiBF<sub>4</sub> (all from Sigma-Aldrich) solution or EMIMBF<sub>4</sub> at ambient temperature, for 7 days to exchange H<sup>+</sup> with the appropriate cation. Both the pH and the conductivity were measured before and after electrolyte incorporation to determine the concentration of ions inside the membranes. The incorporation degree (mol/m<sup>3</sup>) was determined using Equation 2, where  $k_0$  and  $k_{equil}$  represent the conductivity of the initial electrolyte solution and equilibrium solution, respectively, while  $\lambda_{H^+}$  is the proton conductivity.

$$\text{Incorporation degree} = (k_{equil} - k_0) / \lambda_{H^+} \quad (2)$$

The quantity of absorbed ions (mol/membrane mass) was determined by taking into account the solution volume and the mass of the Nafion membrane. [27] The ion exchange capacity of Nafion (0.90 meq / g) indicates the number of sulfonate groups within a fixed volume of the polymer, and is defined as the milliequivalents of H<sup>+</sup> per weight of the dry membrane. The mole ratio of the absorbed ions to the ion exchange sites present within the Nafion samples were also calculated.

The stress-strain measurements were conducted on an Instron 5566 with a 1 KN load cell using samples of about 20 × 5 mm at 25°C. The preload force was 0.006 N, the force ramp rate, 0.165 N.mm<sup>-2</sup> and the cross-head speed, 5 mm/min. These experiments were carried out in accordance with the ASTM D882-91 standard test protocol for thin film tensile tests.

XRD was applied to identify the changes in the degree of crystallinity of dry Nafion samples on absorption of the electrolytes described above. An EQUINOX3000 Intel instrument with Cu K $\alpha$  source operating at a voltage of 40 KV and a current of 40 mA was used. The samples were scanned at 10°/min for 2 $\theta$  = 2–120°. The regular arrangement of atoms or molecules in perfectly crystalline materials gives sharp diffraction peaks whereas x-rays scattered from material with

less long-range order produce broad diffraction peaks which are called amorphous halos. In Nafion, which is a semi-crystalline polymer, a superposition of both sharp and broad features occurs and the XRD pattern is the sum of crystalline and amorphous peaks. The XRD patterns of the samples were deconvoluted into their constituent peaks using the software Origin. The crystalline and amorphous peaks were identified and the percentage of crystallinity was calculated using Equation 3. [28]

$$\%Crystallinity = \frac{\text{Area under crystalline peaks}}{\text{Total Area under all peaks}} \times 100\% \quad (3)$$

SAXS was also applied to study the nanostructure and swelling behavior of the water- and IL-soaked Nafion samples. The SAXS patterns were recorded on an X'Pert Pro MPD PANalytical instrument, equipped with a theta-theta goniometer and a Cu/K $\alpha$  source operated at 40 kV and 40 mA. The samples were scanned at 0.5°/min between 2 $\theta$  values of 0.8° and 5°. Intercluster spacing,  $d$ , were calculated from SAXS peaks using X'Pert software as  $d = 2\pi/q$  where  $q = 4\pi \sin\theta/\lambda$ , and where  $\lambda$  and  $\theta$  are the wavelength of the X-ray radiation and the measured diffraction angle, respectively. [29]

### 2.3. Electrochemical Characterization

Electrical properties of Nafion membranes were studied using CV and EIS experiments. These measurements were performed using a potentiostat/galvanostat (Auto Lab), controlled by NOVA software. The samples were placed in a sample holder consisting of a pair of platinum contacts within an insulating clamp. [13] CV scans were performed in the potential range from +1 to -1 V at a scan rate of 100 mV s<sup>-1</sup>. Impedance spectra were obtained by applying an AC potential of amplitude 10 mV and varying the frequency from 10 KHz to 100 mHz. The ionic conductivity

( $\sigma$ ) was obtained from the ohmic resistance found by extrapolating the Nyquist curve at high frequencies to the real axis. Uncompensated (ohmic) resistance,  $R_{\Omega}$ , charge transfer resistance,  $R_{ct}$ , and double layer capacitance,  $C_{dl}$ , were also obtained from the Nyquist plots using Fara software.

### 3. Results and Discussion

#### 3.1. Physical Characterization

The results presented in Table 1 reveal that the NH, NC and NB samples had higher water content – approximately 2.5 times – than the PN samples. This suggests that  $\text{Li}^+$  ions generally facilitate the penetration of water molecules into the Nafion membranes. The observed higher water content of the NH, NC and NB samples can be explained by the higher concentration of  $\text{Li}^+$  ions in the Li electrolytes used (1 M) compared to the hydronium ion concentration ( $1 \times 10^{-7}$  M) in distilled deionized water. That is, the more concentrated ionic solutions experience greater uptake into the ionic environments of the Nafion than does pure water. Regardless of the type of Li electrolyte used, Nafion generally absorbed more  $\text{Li}^+$  ions (~10 times) than the number of ion exchange sites available. This suggests that in addition to the  $\text{Li}^+$  ions that replace the protons on the sulfonate groups, more ions were either dissolved in the hydrophilic regions with their counteranions or in water-filled voids present within the hydrophobic regions of the polymer. This can be attributed to the lack of formal cross-links in the Nafion membrane and its flexible structure which can imbibe solvated ions in different levels depending on the electrolyte nature. [30] In other words, the excess absorbed ions might have penetrated within the Nafion membrane over non-exchange mechanism. [31,32] The choice of electrolyte counteranion also

dramatically influences the  $\text{Li}^+$ -content of the samples. NH and NB samples have higher  $\text{Li}^+$  content - approximately 3.5 times - than the NC samples. This can be attributed to the variations in the solvation of  $\text{Li}^+$  ions and the ionic association interactions resulting from the difference in anion structure and coordination strength. [33] The  $\text{BF}_4^-$  and  $\text{ClO}_4^-$  anions are both tetrahedral, approximately of the same size and they are larger than the  $\text{OH}^-$  ions. Thus, hydroxyl ions, with the highest charge density, are expected to be solvated with a greater number of water molecules and to have the lowest tendency to form coordination bonds to the  $\text{Li}^+$  ions since they possess only one donor atom in their structure. This leads to a higher concentration of highly solvated solute ions in the  $\text{LiOH}$  electrolyte than in the  $\text{LiBF}_4$  and  $\text{LiClO}_4$  electrolytes, assisting the penetration of more  $\text{Li}^+$  ions into the polymer (See Table 1). Similarly, the higher content of  $\text{Li}^+$  in the NB sample than in the NC sample can be explained by a greater tendency of  $\text{BF}_4^-$  anions to be solvated with water molecules through hydrogen bonding interactions since they contain F atoms with higher electronegativity.

The data presented in Table 2 show that, the number of absorbed IL cations in the IL-soaked Nafion samples shows a strong increase in the order  $\text{NPI} < \text{NWI} < \text{NMI} < \text{NEI}$  (the NMI and NEI having an IL-exchange site ratio well over unity). This trend shows that the physical properties of Nafion change considerably with the presence, and with the identity, of the supporting solvent. [34] Ethanol is a more effective supporting solvent than methanol or water as it facilitates the penetration of a higher percentage of the large organic cations of the IL into the membrane. Thus, ethanol was chosen as the supporting solvent for subsequent studies of IL-soaked Nafion. The mole ratio of absorbed ions to ion exchange sites in the NEI sample was however lower than that observed for water-soaked Nafion samples, probably due to the larger size of  $\text{EMIM}^+$  ions and their lower mobility.

SEM images showed Nafion surface becomes rougher in water-based Li<sup>+</sup>-exchanged NH, NB and NC samples ((Figure 2 – parts (b) to (d)) compared to the H<sup>+</sup>-exchange PN sample (Figure 2(a)). This might be attributed to the formation of larger ionic clusters in the Li<sup>+</sup>-exchanged samples and their higher water content. NH sample appeared to have the roughest surface among all samples. The formation of larger ionic clusters within the water-based Li<sup>+</sup>-exchanged Nafion membranes, especially in the case of NH samples, was confirmed by data obtained from SAXS study of the samples, which would be discussed later. Water interacts preferentially with the hydrophilic regions (minor domain) of the Nafion membrane and causes microscopic swelling. However, EMIMBF<sub>4</sub> can reduce the cross-linking dipolar interactions inside the polar domains and increase the mobility of the main fluorocarbon backbone chains in hydrophobic regions (major domain) and cause macroscopic swelling. Thus, it is expected that smaller ionic clusters to be formed within the IL based samples due to weaker electrostatic interactions between large organic EMIM<sup>+</sup> cations with the fixed ion exchange sites. Therefore, the observed blisters at the surface of the NEI sample (shown in Figure 2(e)) can be attributed to the higher degree of the macroscopic swelling of the polymer. The presence of Li<sup>+</sup> ions in the NEIL sample (Figure 2(f)) also made the membrane surface rougher. This similarly can be attributed to the formation of larger ionic clusters within the NEIL compared to NEI sample. (See Figure 2(e))

The degree of crystallinity of the samples as a function of electrolyte type was studied by XRD. XRD patterns of PN, NB and NEI samples which present protonated, Li<sup>+</sup>- and EMIM<sup>+</sup>-exchanged Nafion samples, respectively, are compared in Figure 3. Since Nafion is semicrystalline, a superposition of both sharp and broad features occurs. Thus all peaks include contributions from crystalline and from amorphous regions. The XRD pattern of the PN sample showed a peak at 2θ~39.1°, which is assigned to scattering from the interfaces between the

hydrophilic ionic clusters and the hydrophobic perfluorinated molecular backbone. The peak at  $2\theta \approx 28.0^\circ$  is attributed to diffraction from the crystalline domains and the peak at  $2\theta \approx 16.4^\circ$  corresponds to scattering from polymeric segments which form clusters in the membrane. [35,36,37] Comparing all three patterns in Figure 3, the highest peak intensity was observed for PN while the broadest peaks with the lowest intensity were observed for NEI. This indicates that Nafion in the protonated form generally possesses the highest degree of crystallinity.  $\text{Li}^+$ -exchanged (NB) and  $\text{EMIM}^+$ -exchanged (NEI) Nafion membranes showed to possess the peak maximum at the similar  $2\theta$ , but these maximums were slightly shifted to the lower  $2\theta$  for NB and to the higher  $2\theta$  for NEI. This means that the largest ionic clusters have formed in NB while the smallest formed in NEI. [29,38] As mentioned earlier, the XRD pattern of Nafion, which is a semi-crystalline polymer, is the sum of crystalline and amorphous peaks. Thus, the crystalline and amorphous peaks were identified by deconvoluting the XRD pattern of each sample into their constituent peaks. Figure 4 shows the results of a peak profile fitting analysis in the range  $2\theta = 11\text{--}23^\circ$ . For each sample, the raw data and the fitted line “a” is shown by the dashed line, the de-convoluted components “b” and “c” corresponding to amorphous and crystalline peaks are shown by red and green lines, respectively. The crystallinity of the PN samples was calculated to be about 31% while it decreased to 28% and 18% for  $\text{Li}^+$ -exchanged (NB) and  $\text{EMIM}^+$ -exchanged (NEI) samples, respectively. This implies that the ionic interaction between protons and sulfonate groups is strongest and it decreases slightly in the  $\text{Li}^+$ -exchanged membrane, because of the small differences in size and charge density between these two cations. However, the weakest ionic interactions occur for the large organic cations in the  $\text{EMIM}^+$ -exchanged sample. The difference in the crystallinity observed between the PN and NB samples can also be partly attributed to the presence of a higher percentage of ions and water in NB, which increases

the size of the ionic clusters within the membranes. [29] As is seen in Table 2, the NEI sample absorbed more EMIM<sup>+</sup> cations than the number of ion exchange sites calculated to be present in this sample. Therefore, it is expected that a part of the relatively hydrophobic IL could be distributed in the per-fluorinated molecular backbone (major domain) of the polymer. Therefore, it seems that the incorporation of large organic cations in the ionic clusters (minor domain), and also use of ethanol as the supporting solvent - which predominately affects the major domain of the polymer - leads to a significant decrease in the crystallinity of the polymer. These results are consistent with the SAXS results for these samples.

The secondary structure of Nafion focuses on the cluster-network model proposed by Gierke [39] who described the membrane as a series of clusters or inverted micelles, interconnected by narrow pores. In this model, the term clusters refers to the tightly packed regions formed by aggregation of ionic groups ( $-\text{SO}_3\text{Li}^+$ , in Figure 1) in Nafion, as a result of electrostatic interactions. The cluster reflection appears in SAXS patterns of Nafion and it is considered to be caused essentially by scattering resulting from the density contrast between microscopically phase-separated domains of fluorocarbon matrix and absorbed electrolyte solution in the ionic clusters. [40] In order to interpret the SAXS results, it was assumed that Nafion polymer consist of two regions, the hydrophobic backbone phase and the hydrophilic ionic phase. Figure 5 shows the SAXS curves for the swollen NB, NEI and NEIL samples. It can be seen that the cluster reflection – the main peak - moved to lower scattering angles on moving from NEI to NEIL to NB. The corresponding intercluster spacings for these samples were 37.7 Å for NEI and 54.4 Å for NB. The value for NEIL was intermediate between the latter two at 48.1 Å. This is logical since this sample contains both IL, like NEI, and LiBF<sub>4</sub>, like NB. The results clearly indicates that the intercluster spacing increases as large EMI<sup>+</sup> cation is replaced with Li<sup>+</sup> ions with lower

ionic radius, due to the formation of larger ionic clusters in NB. Additionally, the value of intercluster spacings for NEIL (IL-soaked membrane incorporated with  $\text{Li}^+$  ions) shows that larger ionic clusters are formed in these samples compared to NEI. The difference in intercluster spacing of the samples can be followed in the schematic images depicted in Figure 6. It was also found that the intercluster spacings depends on the choice of electrolyte counteranion. The SAXS curves of NH, NC and NB are compared in Figure 7 to evaluate the effect of the type of Li electrolyte on the microstructure of the Nafion. The low peak intensity for the NH sample indicates a dissimilar microscopic swelling behavior to that of the NC and NB samples. The intercluster spacings corresponding to the main SAXS peaks were 40.8, 45.1 and 54.4 Å for NH, NC and NB, respectively. The lowest intercluster spacing for NH indicates the formation of the smallest ionic clusters in this sample. Since there is no significant difference between the water contents (see Table 1) of these samples this feature might be attributed to the effects of penetration of counteranions into the Nafion membranes during the cation exchange stage or to differences in their effect on the polymer structure. [34] Of these three Li electrolytes, Nafion absorbed a higher number of  $\text{Li}^+$  ions from LiOH. It is expected that this leads to the formation of larger ionic clusters in NH samples. However, the peak position and its low intensity in the SAXS pattern of NH indicate that this did not happen. The results suggest that the number density of the clusters over the whole membrane has increased for NH while for NB the size of clusters increased [29] possibly due to a higher plasticizing effect of the  $\text{BF}_4^-$  ions on the per-fluorinated molecular backbone of the polymer.

Polymer chain orientation, crystallinity, size and shape of crystal and ionic interactions can have strong effects on the stress-strain curve of Nafion. [41]. The curve gives information about the Young modulus (slope at the origin), yield point, break point and elongation at break. As

discussed earlier, the ions and water molecules absorbed by the Nafion membrane are incorporated into the ionic clusters and channels. These clusters swell according to the water content or the nature of solvents, changing the mechanical and chemical properties of membrane. [42] It has been established that Young's module of Nafion membrane decreases by increasing the water content of the membrane and increases by incorporating larger cations within the membrane. [43] Figure 8 shows the stress-strain curves of the PN, NB, NEI and NEIL samples. The initial slope – giving Young's modulus - of the curve decreased in the following order: NEIL>PN>NEI>NB, reflecting a decrease in the stiffness of the membranes as a function of the type of electrolyte they contained. The higher ion and water content of water-soaked Li<sup>+</sup>-exchanged Nafion samples (NB) leads to a lower Young's modulus, delayed yield point and greater elongation than for water-soaked H<sup>+</sup>-exchanged Nafion samples (PN). [42] Nafion samples containing IL show a higher Young's modulus and greater elongation than membranes containing only aqueous electrolytes. IL-soaked NEI sample presented the highest degree of elongation and a higher Young's modulus compared to the NB sample. The ionic clusters in Nafion act as physical cross-linkers. Thus, the formation of smaller ionic clusters in the NEI sample seems to lead to an increase in the polymer chain mobility and the polymer has become softer. This was observed as the lower crystallinity of the NEI sample in the XRD results shown in Figure 3. However, the presence of a small amount of Li<sup>+</sup> ions in IL-soaked NEIL sample caused an increase in stiffness and a decrease in elongation than for NEI (without Li<sup>+</sup>) due to an increase in the ionic interactions. IPMC actuators prepared based on Nafion membranes with greater Young's modulus and elongation characteristics can show enhanced electromechanical performances. [16]

### 3.2. Electrochemical Characterization

The variation in characteristic capacitance of Nafion membranes as a function of the electrolyte and solvent type was followed by CV measurements, the traces of which are presented in Figure 9. For CV the samples were sandwiched between two equally sized platinum electrodes and fixed in a sample holder, this assembly being similar to a parallel plate capacitor. The current,  $I$ , through an ideal capacitor subjected to a varying applied potential,  $V$ , can be expressed in terms of accumulated charge,  $Q$ , Capacitance,  $C$ ,  $V$  and time,  $t$ , as in Equation 4.

$$I = \frac{dQ}{dt} = C \frac{dV}{dt} \quad (4)$$

Since for all CV measurements  $dV/dt$  was constant, large differences in  $I$  implied significant differences in sample capacitance,  $C$ . For each Nafion sample (assuming ideal behavior),  $C$  can be considered to be constant and can be expressed in terms of the surface area,  $A$ , of the platinum contacts, the dielectric constant of the Nafion membrane,  $\epsilon$ , and the distance,  $d$ , between the electrodes (the thickness of the polymer), as given in Equation 5.

$$C \approx \frac{\epsilon A}{d}, A \gg d^2 \quad (5)$$

The values of  $d$  and  $A$  for all the Nafion samples were approximately the same. Therefore, variations in  $C$  can be attributed (to a first approximation) to variations in  $\epsilon$ .

Figure 9(a) shows the voltamograms of NH, NC and NB. The three voltamograms are similar in shape but the size of the current varies, indicating different values of characteristic capacitance of the Nafion, depending on the identity of the counteranion in the electrolyte solution. Since there was no significant difference in thickness between these samples, dielectric permittivity

(see Equation 5) increased in the order:  $NH < NC < NB$ . The high value for NB can be attributed to its having the greatest plasticizing effect because of the interaction of the  $BF_4^-$  anions with the per-fluorinated molecular backbone of Nafion, as indicated in the SAXS study described above. In Figure 9(b) the CV response of the IL-soaked samples, NEI and NEIL, are compared with that of NB. It can be seen that replacing water with IL generally led to a higher current response - and therefore higher characteristic capacitance and higher dielectric permittivity - the higher of the two being for NEIL, which contains two dissimilar cations,  $EMIM^+$  and  $Li^+$ . Three polarization mechanisms can occur within materials; electronic polarization, ionic polarization and orientational polarization. In non-conducting materials only electronic polarization occurs while the ionic and orientational polarization mechanisms are available to materials possessing ions and permanent dipoles respectively. [44] Nafion consists of non-polar tetrafluoroethylene segments and the polar perfluorosulfonic vinyl ether segments. Thus, all three mentioned polarization mechanism can occur within this polymer. The more easily the various polarization mechanisms can act, the larger the dielectric permittivity will be. Ionic and orientational polarization happens easier in more plasticized Nafion samples (i.e. with a lower degree of crystallinity) because the intermolecular forces that must be overcome to polarize are smaller. Therefore, the highest degree of ionic and orientational polarization would be expected in NEIL, which did indeed show the highest current (Figure 9(b)). These results are consistent with the results obtained from EIS experiments of the samples.

Impedance is the response of an electrochemical system to an applied alternating voltage. The frequency dependence of impedance can reveal the underlying processes in electrochemical systems. The complex response of the electrochemical system is usually displayed in Nyquist form, the plot of the real part of impedance against the imaginary part. 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, sometimes in a distorted form. The frequency reaches its high and low limit, respectively, at the leftmost end and rightmost end of the semicircle. The impedance of the Nafion samples 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 Pt electrode/polymer interfaces. The degree of mobility of ions determines the conductivity of the Nafion membrane. Typical Nyquist plots of imaginary impedance,  $Z''$ , versus real impedance,  $Z'$ , for the NH, NC and NB samples are illustrated in Figure 10(a). Of these, NB showed the lowest impedance which corresponds to the highest ionic conductivity. Comparison of impedance values obtained from the spectra in Figure 10 parts (a) and (b) shows that the ionic conductivity of the Nafion membranes was reduced significantly when water was replaced by pure IL (in NPI). Also, using the supporting solvents increased the conductivity of IL-soaked Nafion membranes dramatically. It seems that the supporting solvent acts as a plasticizer and facilitates the free rotation of the molecular backbone causing an increase in backbone segment mobility. [34,45,46] Components which increase the number density or the size of ionic clusters or the free volume available to polymer chain segments are expected to increase the conductivity of the Nafion membrane. [16] Amongst the IL-soaked samples, the ionic conductivity is highest for NEI. This implies that ethanol has the most plasticizing effect on the Nafion membrane and provides the highest percentage of free volume within the polymer since it can interact preferably with the polymer molecular backbone. The presence of a small amount of  $\text{Li}^+$  ions together with the  $\text{EMIM}^+$  ions in NEIL caused a significant increase in conductivity over that of the water-free sample (NEI). In fact, the spectra of NEIL and NB are very similar as shown in Figure 11. EIS data are commonly analyzed

by fitting them to an equivalent electrical circuit model. The Randles model (shown in Figure 11) is one of the simplest and most common models. This model includes an ohmic resistance (also called solution resistance),  $R_s$ , a double layer capacitor,  $C_{dl}$  and a charge transfer resistance,  $R_{ct}$ . The high frequency intercept on the real axis is used to calculate  $R_s$ . The low frequency intercept on the real axis is used to calculate  $R_{ct}$  of the system. The frequency corresponding to the top of the semicircle is used to calculate  $C_{dl}$  according to Equation 6, where  $\omega$  is frequency in radians per second and  $f$  is frequency in Hertz.

$$\omega_{\max} = 1/C_{dl} R_{ct}, \omega = 2\pi f \quad (6)$$

The ionic conductivity ( $\sigma$ ) was obtained from the  $R_{ct}$  according to Equation 7, where  $L$  and  $A$  are the sample thickness (in cm) and surface area (in  $\text{cm}^2$ ), respectively.

$$\sigma = L/AR_{ct} \quad (7)$$

The calculated values of  $R_s$ ,  $R_{ct}$ ,  $C_{dl}$ , and ionic conductivity,  $\sigma$ , are summarized in Table 3. The electrical double layer is formed on the interface between electrode and Nafion membrane by ions interacting with the electrode surface. Values of  $C_{dl}$  depend on factors including ionic concentration and type of ions. The variation in dielectric permittivity of Nafion on changing the identity of electrolyte solution can be followed more clearly as changes occurring in the double layer capacitance of the samples. Of the water-soaked Nafion membranes, NB showed the lowest  $R_{ct}$  and the highest  $\sigma$  and  $C_{dl}$ . This corresponds to the highest ionic conductivity and diffusion of ions towards and away from metal electrodes and the highest concentration of  $\text{Li}^+$  ions on the interface between electrode and Nafion membrane, respectively. [47] As discussed before, this can be attributed to the lowest degree of crystallinity of this sample. Comparison of  $R_{ct}$ ,  $C_{dl}$  and  $\sigma$  values obtained for IL-soaked NPI sample with NB shows that ionic conductivity and diffusion

of EMIM<sup>+</sup> ions are more restricted which can be attributed to the hydrophobic nature of EMIM<sup>+</sup> ions and their lower charge density. However, using the supporting solvents increased the ionic conductivity and diffusion of ions in IL-soaked Nafion membranes dramatically. Amongst the IL-soaked samples, the  $R_{ct}$  is lowest for NEI while the  $C_{dl}$  and  $\sigma$  are highest. This implies that ethanol addition facilitates the diffusion of large cations of EMIM<sup>+</sup> within the polymer more than water addition. The presence of a small amount of Li<sup>+</sup> ions together with the EMIM<sup>+</sup> ions in NEIL caused a significant decrease in  $R_{ct}$  and increases in  $C_{dl}$  and  $\sigma$  over that of the water-free sample (NEI) and also over water-soaked NB. Consequently, it is reasonable to consider that incorporation of Li<sup>+</sup> into IL-soaked Nafion improved the electrochemical and electromechanical properties of these Nafion – based IPMC actuators and sensors. Such an approach might also be applied in other applications such as electrolytes for Li<sup>+</sup> ion batteries where high dielectric permittivity, capacitance and ionic conduction are required.

#### **4. Conclusion**

Solvent uptake, ionic content, ionic conduction, double layer capacitance and mechanical properties are important parameters to consider and control to improve the electromechanical performance of Nafion-based IPMC actuators. This study demonstrated how the above mentioned properties can be varied as a function of electrolyte type. To this end, Nafion membranes were immersed in aqueous solutions of LiOH, LiClO<sub>4</sub> or LiBF<sub>4</sub> and these samples were compared in terms of water uptake, structure, stress-strain behavior and electrochemical properties. The structural and electrochemical changes occurring in Nafion membranes soaked in

an imidazolium-based IL as the electrolyte, on addition of a supporting solvent and on addition of  $\text{Li}^+$  ions were also followed.

It was shown that, the nano- and microstructure of the Nafion changed considerably as a function of the identity of the electrolyte solution. For water-soaked Nafion, both the type of cation (Li or imidazolium) and also the counteranions in the Li electrolytes showed a significant impact on the physical and structural properties of the Nafion. Of the four electrolytes, the smallest ionic clusters were formed in IL-soaked Nafion and the largest formed in water-soaked  $\text{Li}^+$ -exchanged Nafion prepared using  $\text{LiBF}_4$ . Amongst water-soaked  $\text{Li}^+$ -exchanged Nafion samples, the maximum characteristic capacitance and ionic conductivity were observed for the membrane immersed in  $\text{LiBF}_4$  solution.

The ionic conductivity of the Nafion membranes was reduced significantly for the membrane immersed in pure IL. Using the supporting solvents increased the ionic conductivity of IL-soaked Nafion membranes dramatically. Of the IL-soaked Nafion samples, the maximum ionic conductivity was observed for the membrane immersed in IL/EtOH solution. However, the ionic conductivity of this sample was still about five times smaller than what was considered for water-soaked  $\text{Li}^+$ -exchanged Nafion prepared using  $\text{LiBF}_4$ . Nafion samples containing IL showed a higher Young's modulus and greater elongation than membranes containing only aqueous electrolytes. Furthermore, these samples showed a higher characteristic capacitance compared to water-soaked  $\text{Li}^+$ -exchanged samples while they possessed lower ionic content. This was attributed to the lower crystallinity of these samples which can facilitate polarization processes.

It was found that  $\text{Li}^+$  ions can contribute to the formation of larger ionic clusters in water free IL-soaked Nafion membranes. The presence of a small amount of  $\text{Li}^+$  ions together with the  $\text{EMIM}^+$  ions in these samples caused an increase in stiffness and a slight decrease in elongation. A significant increase ( $\sim 10$  times) in ionic conductivity and capacitance characteristic over that of the water-free IL-soaked samples were observed. IL-soaked membranes incorporated with  $\text{Li}^+$  ions also showed to have higher ionic conductivity ( $\sim 1.5$  times) and double layer capacitance ( $\sim 18$  times) over water-soaked  $\text{Li}^+$ -exchanged Nafion (immersed in  $\text{LiBF}_4$ ). IPMC actuators prepared based on Nafion membranes with improved ionic conductivity, double layer capacitance and mechanical properties can show enhanced electromechanical performances. Thus, water-free Nafion membrane incorporated with  $\text{Li}^+$  and  $\text{EMIM}^+$  ions can be considered as a good choice for this application.

Table 1: Effect of the type of Li electrolyte on water uptake and ion exchange capacity of Nafion membranes

<b>Samples</b>	<b>Dried weight (g)</b>	<b>Swollen weight (g)</b>	<b>Water uptake (%)</b>	<b>Ion exchange sites (<math>\times 10^{-5}</math> mol/g)</b>	<b>Absorbed Li<sup>+</sup> ions (<math>\times 10^{-4}</math> mol/g)</b>	<b>Mole ratio of ions to ion exchange sites</b>
<b>PN</b>	0.036	0.042	14.0	2.99	-	
<b>NC</b>	0.036	0.049	35.8	3.24	1.37	4.60
<b>NB</b>	0.030	0.042	34.6	2.72	4.70	15.8
<b>NH</b>	0.033	0.045	35.6	2.97	5.00	16.8

Table 2: Effect of the type of supporting solvent on IL uptake and ion exchange capacity of Nafion membranes

<b>Samples</b>	<b>Supporting solvent</b>	<b>Dried weight (g)</b>	<b>Swollen weight (g)</b>	<b>Ion exchange sites (<math>\times 10^{-5}</math>mol/g)</b>	<b>Absorbed IL (<math>\times 10^{-5}</math>mol/g)</b>	<b>Mole ratio of IL to ion exchange sites</b>
<b>NPI</b>	-	0.037	0.039	3.41	1.41	0.410
<b>NWI</b>	DI water	0.037	0.042	3.41	2.53	0.740
<b>NMI</b>	Methanol	0.038	0.047	3.46	4.73	1.38
<b>NEI</b>	Ethanol	0.038	0.049	3.46	5.36	1.57

Table 3. The calculated values of ohmic resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ), double layer capacitance, ( $C_{dl}$ ) and ionic conductivity ( $\sigma$ ) for all samples.

<b>Sample Names</b>	<b><math>R_s(\Omega)</math></b>	<b><math>R_{ct}(\Omega)</math></b>	<b><math>C_{dl}(\mu F)</math></b>	<b><math>\sigma(\mu s/cm)</math></b>
<b>NH</b>	1.80	10420	3.40	6.90
<b>NC</b>	7.11	8786	5.10	8.19
<b>NB</b>	8.94	5100	6.03	14.1
<b>NPI</b>	6450	78950	4.10	0.910
<b>NWI</b>	2270	36110	6.78	1.99
<b>NEI</b>	1520	25509	11.4	2.82
<b>NEIL</b>	82.64	3521	108.0	20.2

## Figure captions

Figure 1. Chemical Structure of (a)  $\text{Li}^+$ -exchanged Nafion and (b) 1-ethyl-3-methylimidazolium tetrafluoroborate ( $\text{EMIMBF}_4$ ).

Figure 2. Longitudinal SEM images of Nafion membranes (a) PN, (b) NH, (c) NB, (d) NC, (e) NEI and (f) NEIL.

Figure 3. XRD patterns of Nafion membrane in protonated (PN),  $\text{Li}^+$ -exchanged (NB) and  $\text{EMIM}^+$ -exchanged (NEI) forms.

Figure 4. XRD patterns of water-soaked PN and NB samples and IL-soaked NEI samples. Curves fitted to experimental data “a” were de-convoluted into amorphous “b” and crystalline “c” peaks.

Figure 5. Comparison of SAXS patterns obtained for water-soaked NB sample and IL-soaked NEI and NEIL samples.

Figure 6. Schematic representation of intercluster spacing in Nafion membranes (a) NEI, (b) NEIL, (c) NB

Figure 7. SAXS patterns obtained for Nafion membranes with different  $\text{Li}^+$  electrolytes.

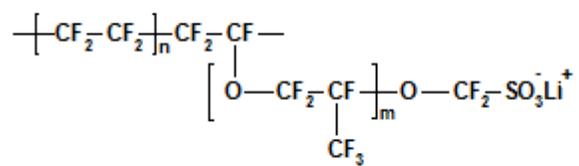
Figure 8. Variation in stress-strain curves of Nafion membrane samples as a function of cation and solvent type.

Figure 9. Dependence of cyclic voltammetry behavior of Nafion membranes on (a) the type of  $\text{Li}^+$  electrolyte and (b) solvent type.

Figure 10. Impedance spectra of Nafion membranes with (a) different Li electrolytes for water-soaked samples and (b) different supporting solvents for IL-soaked samples.

Figure 11. Comparison of Nyquist plots for water-soaked NB sample and IL-soaked NEI and NEIL samples. Inset is the diagram of a simplified Randles model describing the electrochemical interface between an electrode and electrolyte.

(a)



(b)

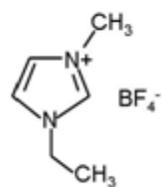
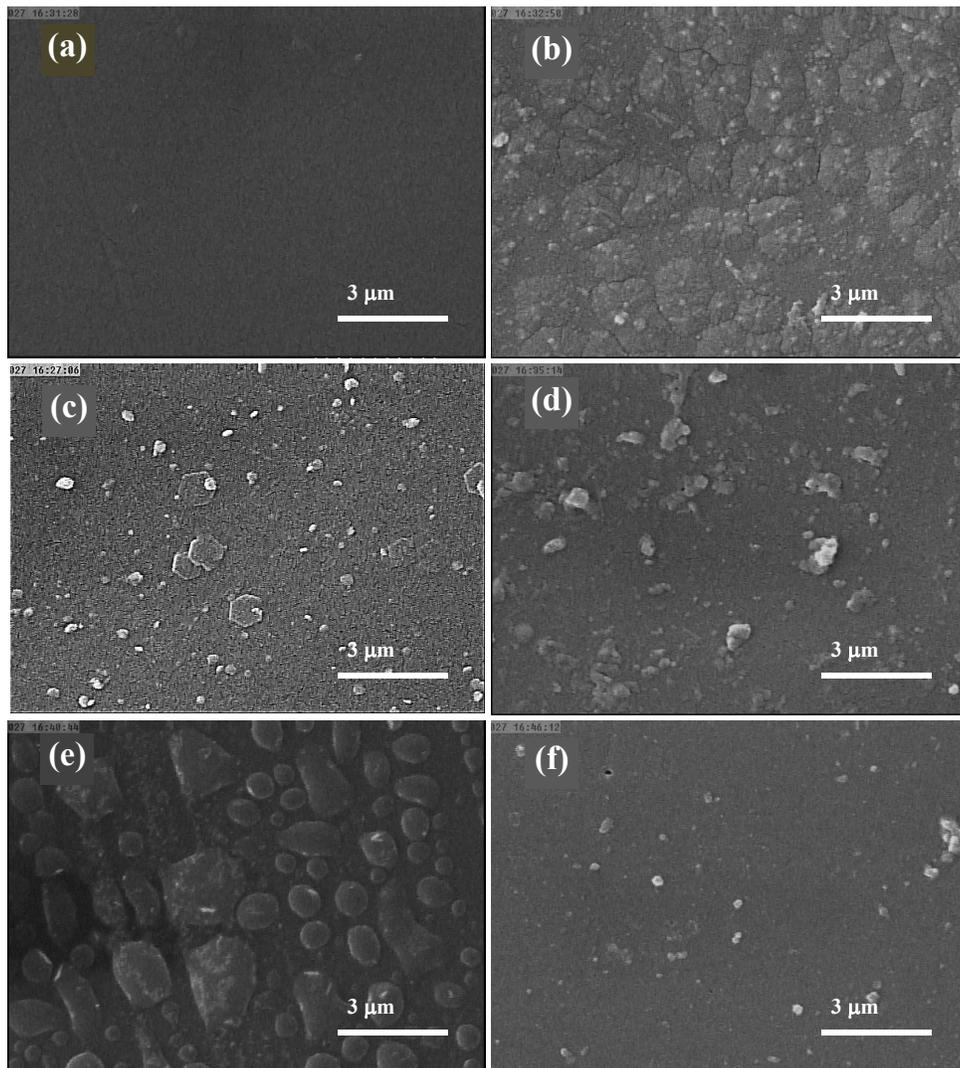


Figure 1



**Figure 2**

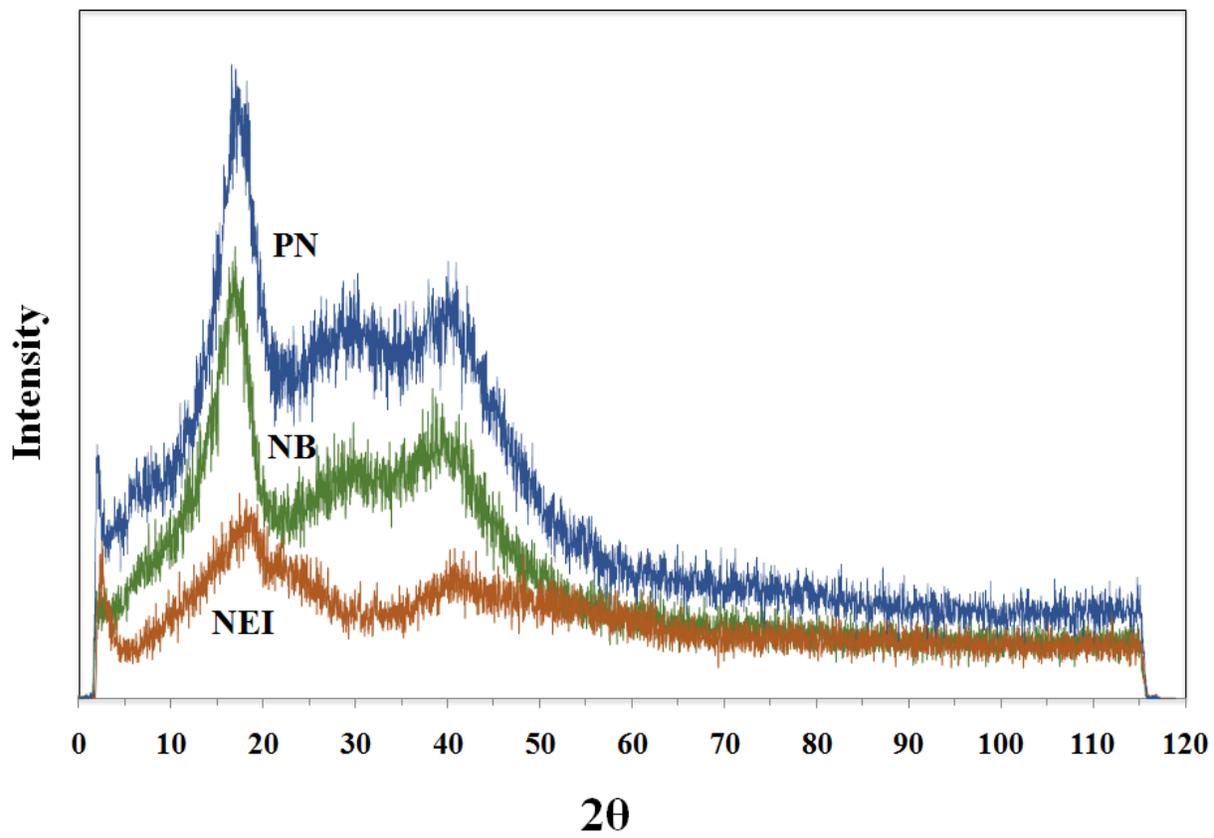


Figure 3

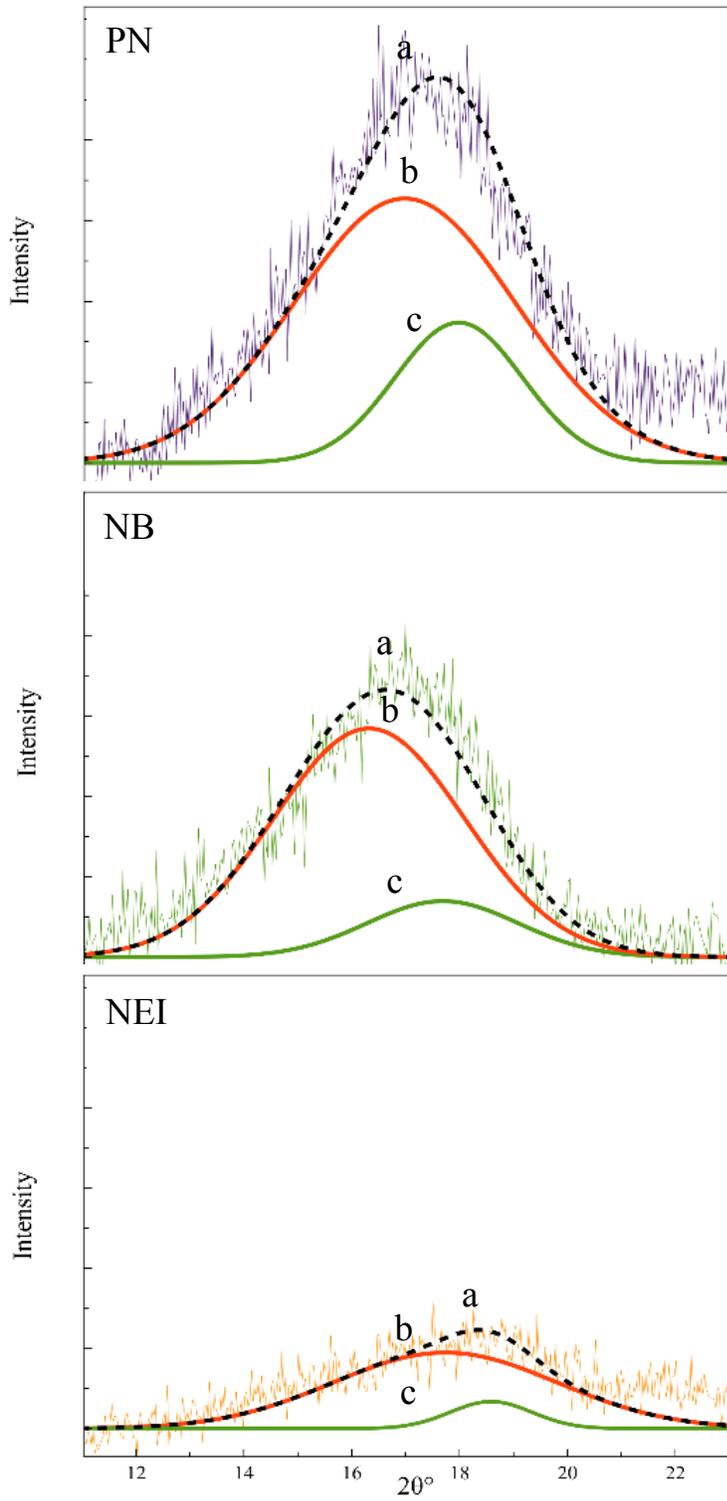


Figure 4

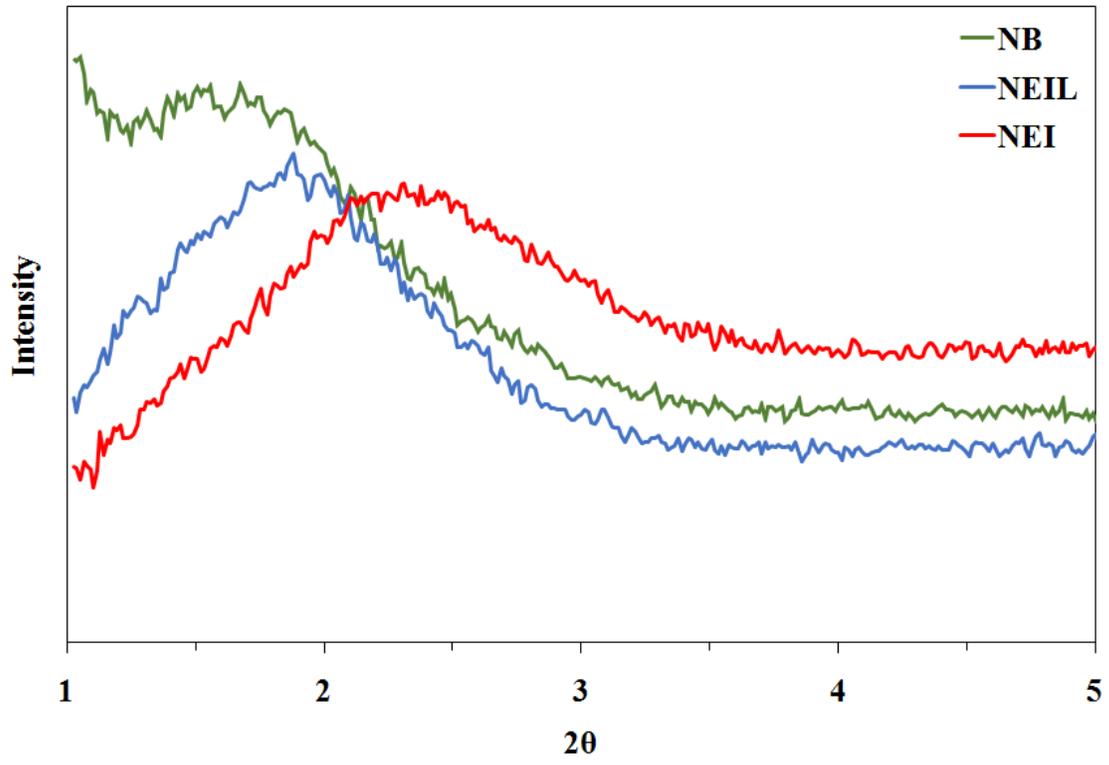


Figure 5

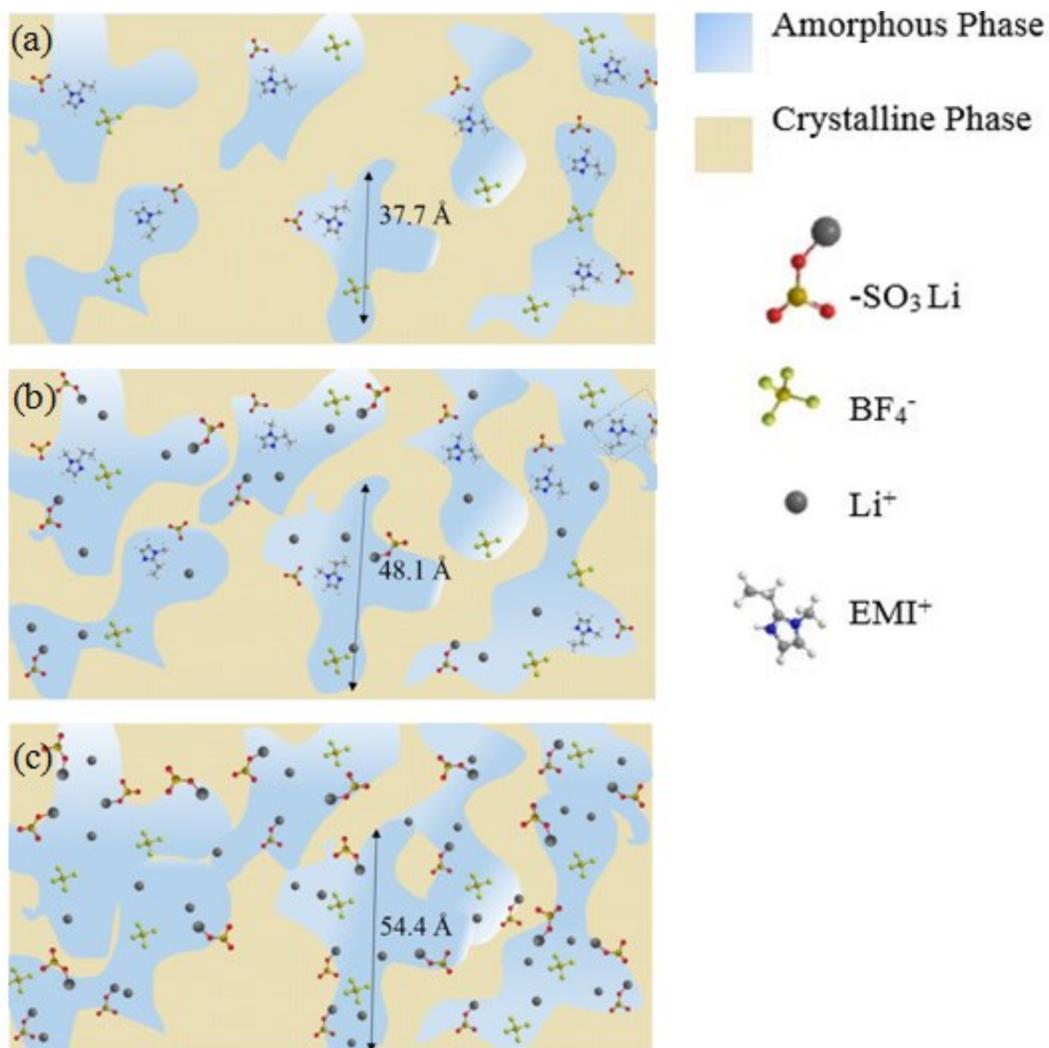


Figure 6

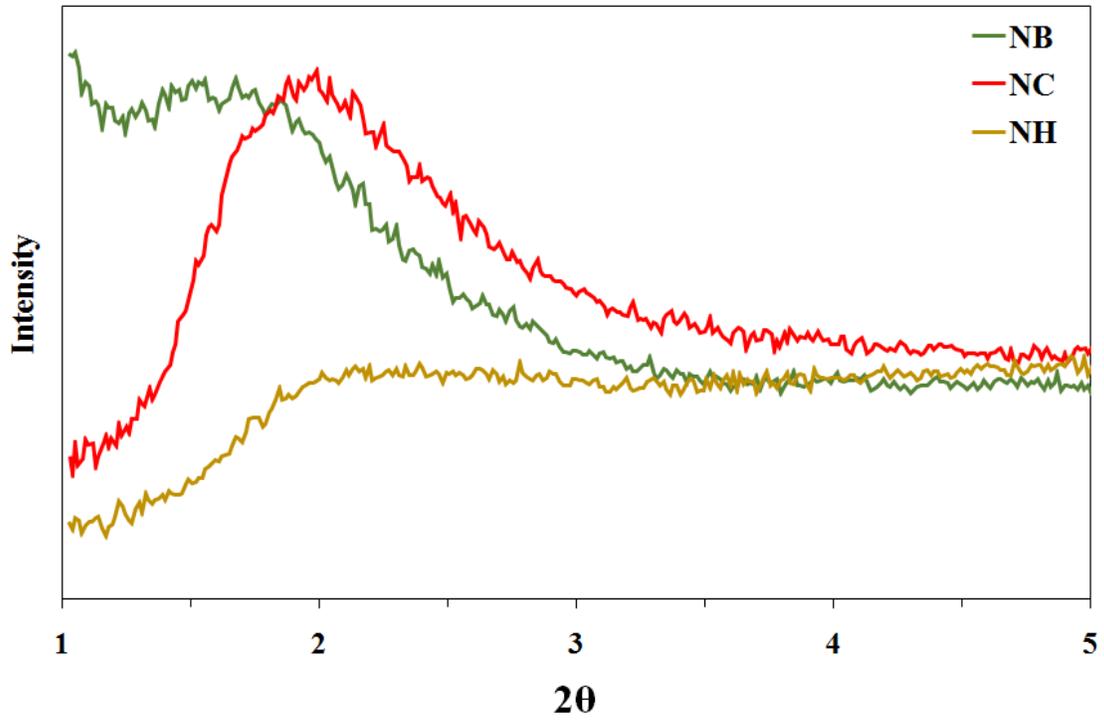


Figure 7

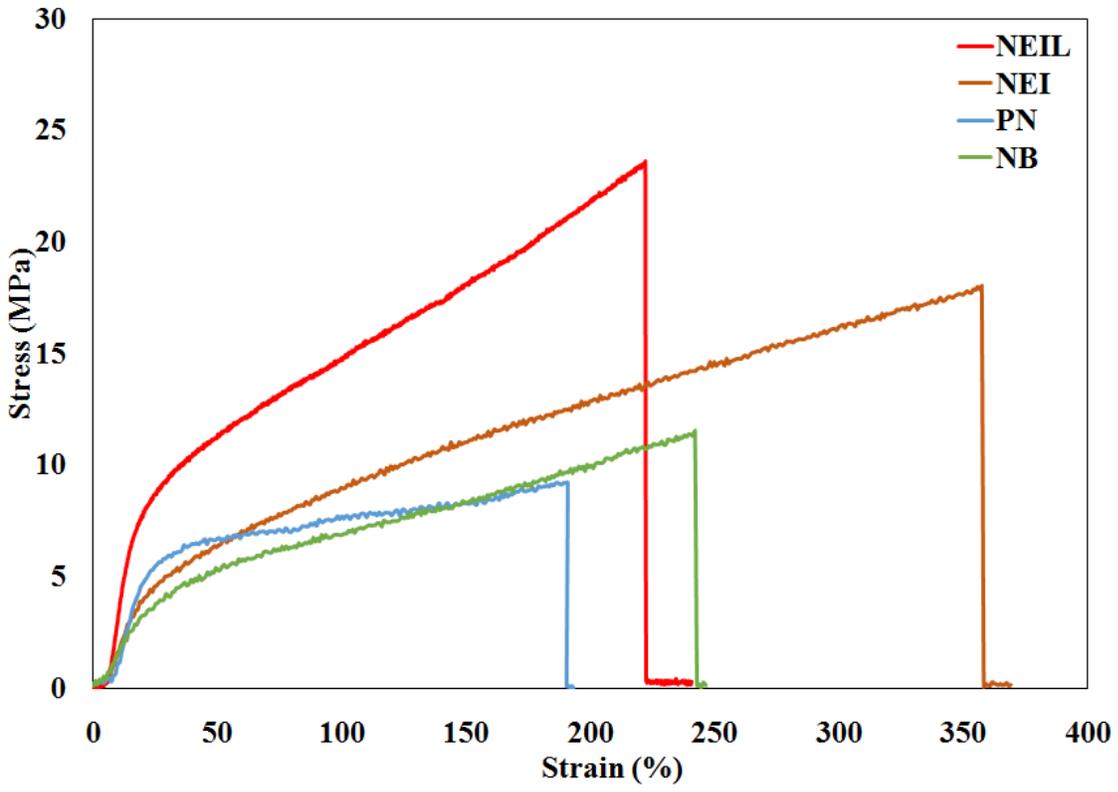


Figure 8

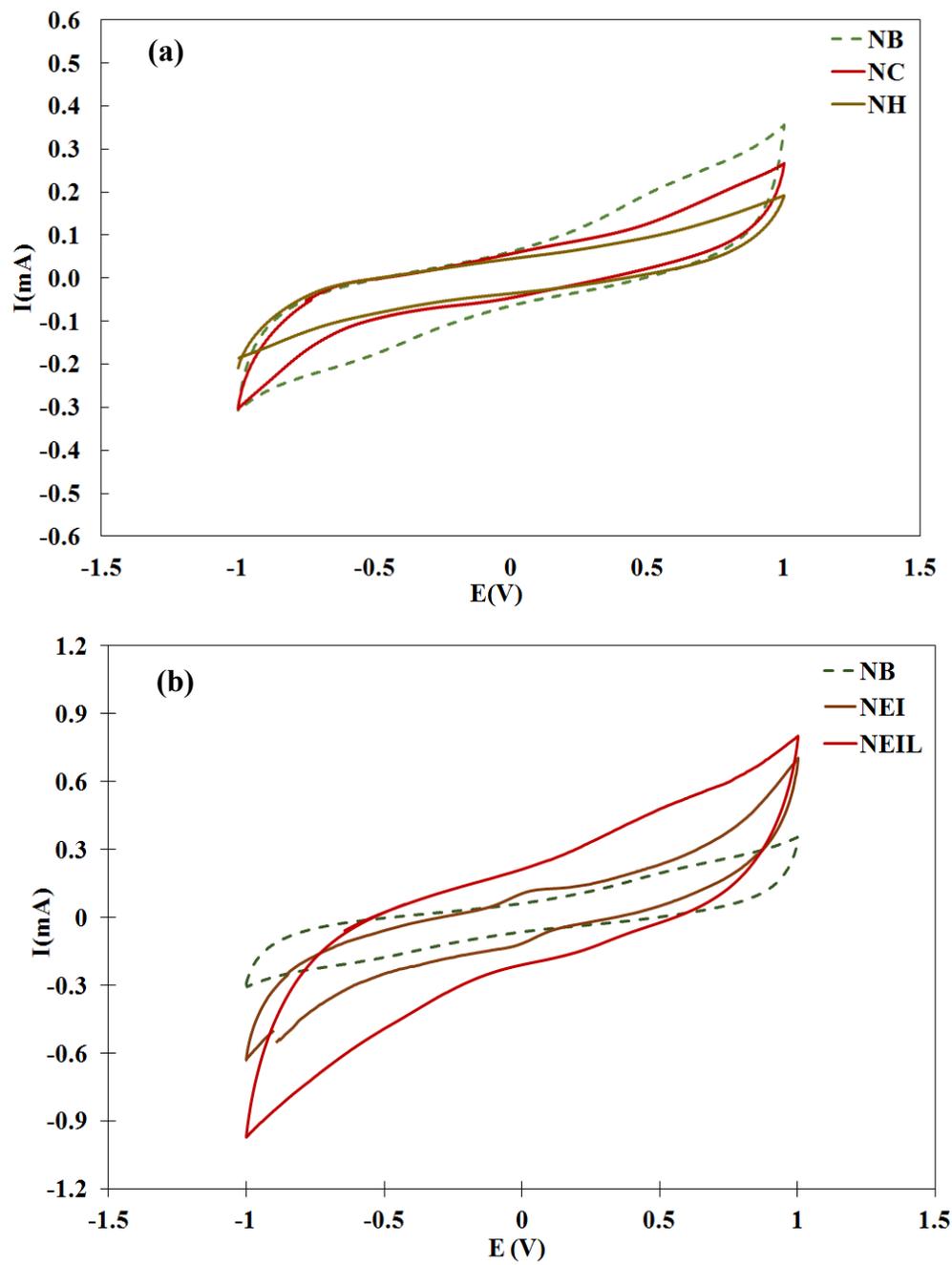


Figure 9

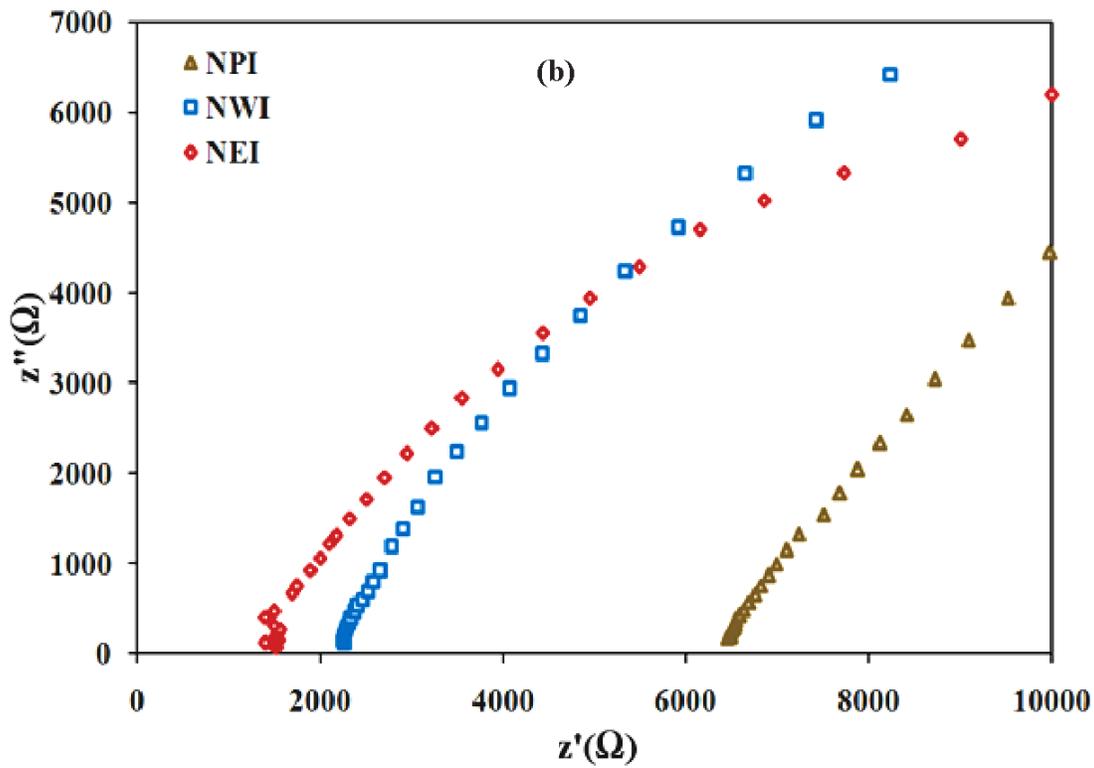
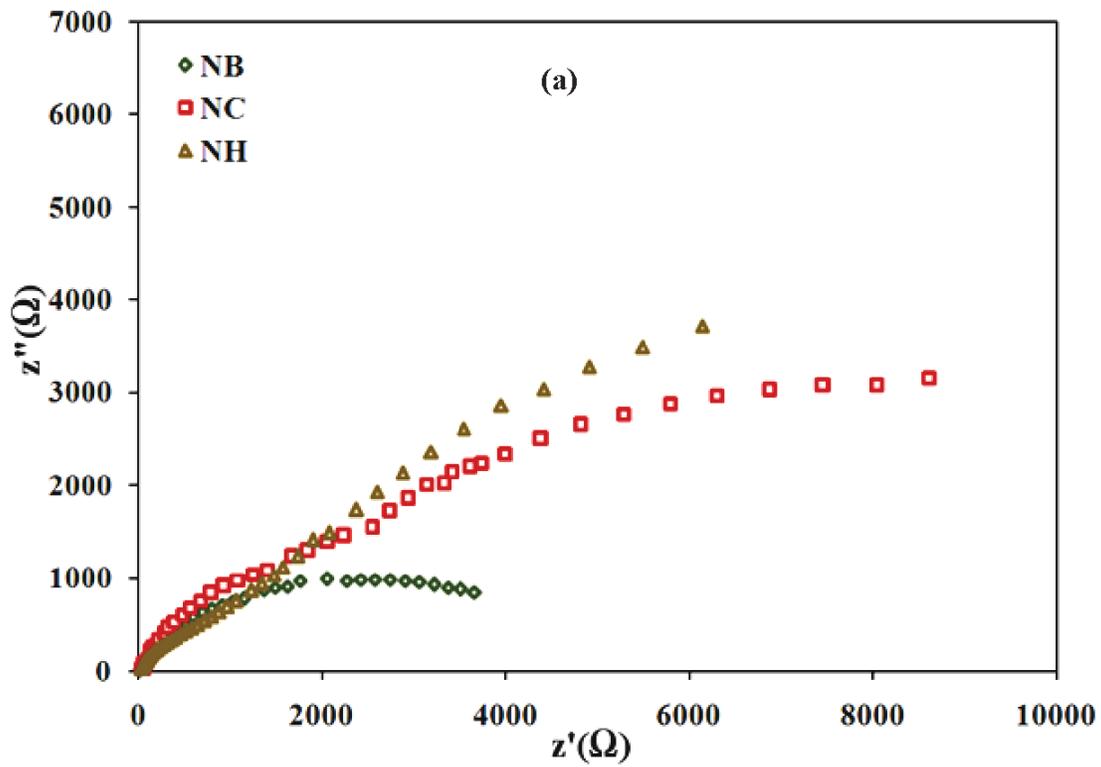


Figure 10

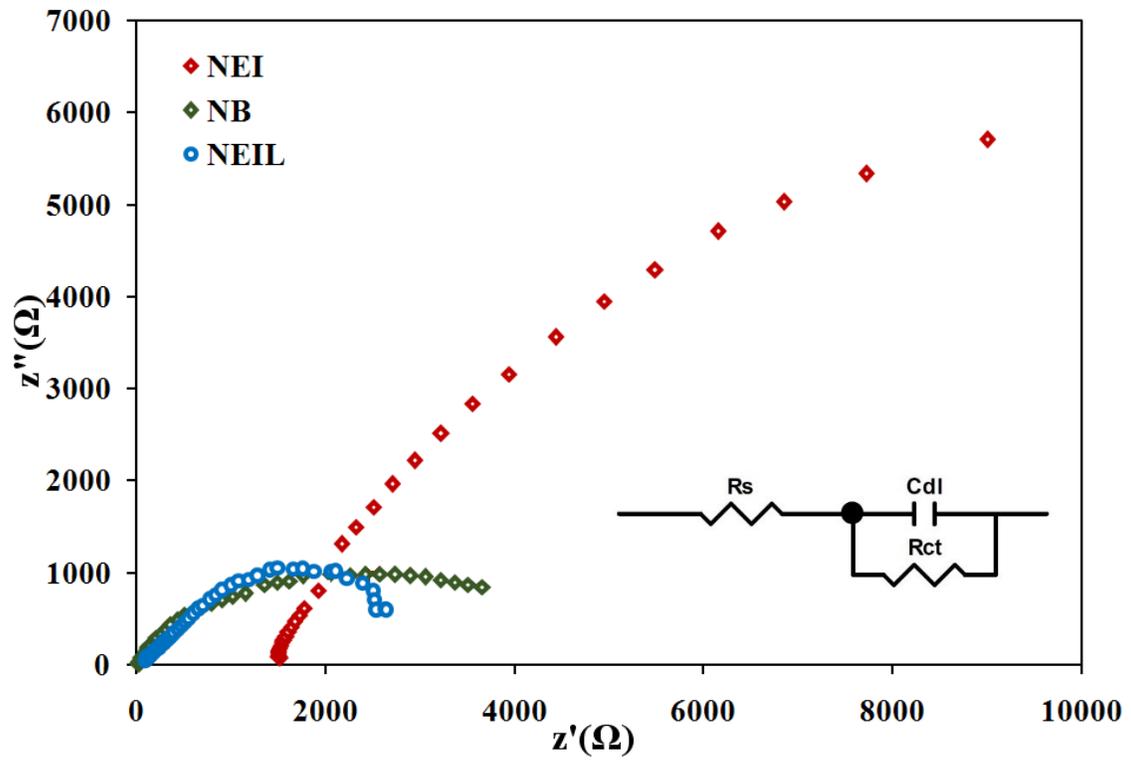


Figure 11

## References

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- [1]. Shahinpoor M, Kim KJ, (2005) Ionic polymer–metal composites: IV. Industrial and medical applications. *Smart Mater Struct* 14:197-214.
- [2]. Shahinpoor M, Kim KJ and Mojarrad M, (2007) *Artificial Muscles: Applications of advanced polymeric nanocomposites*. CRC Press, Taylor & Francis Group.
- [3]. Shahinpoor M, Mojarrad M, (2000) Soft actuators and artificial muscles. US Patent 6109852.
- [4]. Abed Affoune M, Yamada A, Umeda M, (2005) Conductivity and surface morphology of Nafion membrane in water and alcohol environments. *J. Power Sources* 148:9-17.
- [5]. Fontanella JJ, Wintersgrill MC, Chen RS, Wu Y, Greenbaum SG, (1995) Charge transport and water molecular motion in variable molecular weight Nafion membranes: High pressure electrical conductivity and NMR. *Electrochimica Acta* 40(13-14):2321-2326.
- [6]. Nemat-Nasser S, Zamani S, (2003) *Smart Smart Structures & Materials Proc.* SPIE 5051.
- [7]. Yeager HL, Steck A, (1979) Ion-exchange selectivity and metal ion separations with a perfluorinated cation-exchange polymer. *Anal Chem* 51:862-865.
- [8]. Eisenberg A, King M, Stein RS, (1977) *Polymer Physics*. Academic Press, New York, Chap 4.
- [9]. Yeager HL, O'Dell B, Twardowski Z., (1982) Transport Properties of Nafion® Membranes in Concentrated Solution Environments. *J. Electrochem Soc* 129(1):85-89.
- [10]. Grownowski AA, Yeager HL, (1991) Factors Which Affect the Permselectivity of Nafion® Membranes in Chlor-Alkali Electrolysis, I. *J. Electrochem Soc* 138(9):2690-2697.
- [11]. Lin HL, Yu TL, Han FH (2006) A Method for Improving Ionic Conductivity of Nafion Membranes and its Application to PEMFC. *J of Polym Res* 13:379–385.
- [12]. Hsu WY and Gierke TD, (1983) Ion transport and clustering in nafion perfluorinated membranes. *J. Membr. Sci.* 13:307-326.
- [13]. Naji L, Chudek JA, Abel EW, Baker RT, (2013) Electromechanical behaviour of Nafion-based soft actuators. *J. Mater. Chem. B* 1: 2502-2514.
- [14]. Abe Y, Mochizuki A, Kawashima T, Yamashita S, Asaka K, Oguro K, (1998) Effect on bending behavior of counter cation species in perfluorinated sulfonate membrane–platinum composite. *Polym Adv Technol* 9(8):520-526.
- [15]. Kim KJ, Shahinpoor M, (2003) Ionic polymer–metal composites: II. Manufacturing techniques. *Smart Mater Struct* 12:65-79.
- [16]. Bar-Cohen Y, (2001) *Electroactive Polymer (EAP) Actuators as Artificial Muscles – Reality, Potential & Challenges*. SPIE Press, Bellingham WA.

- 
- [17]. Nasser SN, (2003) Experimental study of Nafion- and Flemion-based ionic polymer–metal composites (IPMCs) with ethylene glycol as a solvent, in: Proceedings of the SPIE Smart Structures and Materials Symposium, EAPAD Conference, San Diego, CA, USA.
- [18]. Chen IWP, Cottinet PJ, Tsai SY, Foster B, Liang R, Wang B, Zhang C, (2012) Improved performance of carbon nanotube buckypaper and ionic-liquid-in-Nafion actuators for rapid response and high durability in the open air. *Sensors and Actuators B* 171– 172:515-521.
- [19]. Elliot JA, Hanna S, Elliot AMS, Cooley GE, (2001) The swelling behavior of perfluorinated ionomer membranes in ethanol/water mixtures. *Polymer* 42:2251-2253.
- [20]. Affoune AM, Yamada A, Umeda M, (2005) Conductivity and surface morphology of Nafion membrane in water and alcohol environments. *J. Power Sources* 148:9-17.
- [21]. Yeager HJ, Eisenberg A, (1982) Perfluorinated Ionomer Membranes. *American Chem Soc* 180(1):41-63.
- [22]. Naji L, Chudek JA, Baker RT, (2008) Magnetic resonance imaging study of a soft actuator element during operation. *Soft Matter* 4:1879-1886.
- [23]. Naji L, Chudek JA, Baker RT, (2008) Time-resolved mapping of water diffusion coefficients in a working soft actuator device. *J PhysChem B* 112:9761-9768.
- [24]. Xue T, Trent S, Osseo-Asare K, (1989) Characterization of nafion® membranes by transmission electron microscopy. *J MembrSci* 45(3):261-271.
- [25]. Meresi G, Wang Y, Bandis A, Inglefield PT, Jones AA, Wen WY, (2001) Self-diffusion of water, ethanol and decafluoropentane in perfluorosulfonate ionomer by pulse field gradient NMR. *Polymer* 42:6153-6160.
- [26]. Baker RT, Naji L, Lochhead K, Chudek JA, (2003) In situ magnetic resonance imaging of electrically-induced diffusion in a Nafion film. *Chem. Commun.* DOI: 10.1039/B301039B, 962-963.
- [27]. V. Romero, M. V. Martínez de Yuso, A. Arango, E. Rodríguez-Castellón, and J. Benavente, (2012) Modification of Nafion membranes by II-cation exchange: chemical surface, electrical and interfacial study, *International Journal of Electrochemistry*, Volume 2012, Article ID 349435.
- [28]. Alexander LE, (1969) *X-ray Diffraction Methods in Polymer Science*. Wiley, Interscience, New York.
- [29]. James PJ, Elliott JA, McMaster TJ, Wills HH, Newton JM, Elliott AMS, Hanna S, Miles MJ, (2000) Hydration of Nafion studied by AFM and X-ray scattering. *Journal of Material Science* 35(20):5111-5119.
- [30]. Willson AD and Prosser HJ, “Developments in ionic polymers-2”, Elsevier Applied Science Publisher, London, 1986.
- [31]. Belchinskaya L, Novikova L, Khokhlov V, Tkhi JL, (2013) Contribution of Ion-Exchange and Non-Ion-Exchange Reactions to Sorption of Ammonium Ions by Natural and Activated Aluminosilicate Sorbent. *Journal of Applied Chemistry* 2013, article ID 789410.

- 
- [32]. Subramaniam Iyer ES, Datta A., (2012) Influence of external electrolyte on ion exchange in Nafion membranes. *RSC Advances*, 2:8050–8054
- [33]. Jow TR, Xu K, Borodin O, Ue M., (2014) *Electrolytes for Lithium and Lithium Ion Batteries*. Chapter 1, Springer.
- [34]. Sears JK, NW Touchette, (1982) Plasticizers, *Encyclopedia of Chemical Technology*, 3<sup>rd</sup> Edition. John Wiley and Sons, 18:111-183.
- [35]. Gebel G, Moore RB, (2000) Small-angle scattering study of short pendant chain perfluorosulfonatedionomer membranes. *Macromolecules* 33:4850-4855.
- [36]. Schmidt-Rohr K, Chen Q, (2008) Parallel cylindrical water nanochannels in Nafion fuel-cell membranes. *Nature Materials* 7:75-83.
- [37]. Rubatat L, Gebel G, Diat O, (2004) Fibrillar structure of Nafion: Matching Fourier and real space studies of corresponding films and solutions. *Macromolecules* 37:7772.
- [38]. Lee GW, Yoo YT, (2009) Anion effects in imidazolium ionic liquids on the performance of IPMCs. *Sensors and Actuators B* 137:539-546.
- [39]. Gierke TD, (1997) Ionic clustering in Nafion perfluorosulfonic acid membranes and its relationship to hydroxyl rejection and chlor-alkali current efficiency. *The electrochemical Society Extended Abstracts*, 77(2), 438, 1139.
- [40]. Elliott JA, Hanna S, Elliott AMS, Cooley GE, Interpretation of the small-angle X-ray scattering from swollen and oriented perfluorinatedionomer membranes. *Macromolecules* 33:4161-4171.
- [41]. Freeman W J, (1990) *Polymers: Polymer Characterization and Analysis*. John Wiley, New York.
- [42]. Kawano Y, Wang Y, Palmer RA, Aubuchon SR., (2002) Stress-Strain Curves of Nafion Membranes in Acid and Salt Forms. *Polímeros: Ciência e Tecnologia*, 12( 2):96-101.
- [43]. Barclay Satterfield M, Benziger JB., (2009) Viscoelastic Properties of Nafion at Elevated Temperature and Humidity. *Journal of Polymer Science: Part B: Polymer Physics*, 47:11–24.
- [44]. [http://www.doitpoms.ac.uk/tlplib/dielectrics/polarisation\\_mechanisms.php](http://www.doitpoms.ac.uk/tlplib/dielectrics/polarisation_mechanisms.php).
- [45]. Das S, Suresh BR, Jayaraman N, Bhattacharyya AJ, (2012) Ionic conductivity of bis(2-cyanoethyl) ether-lithium salt and poly(propylether imine)-lithium salt liquid electrolytes. *J Polym Res* 19:9924-9927J. *Polym Res*. 19, 9924.
- [46]. Chong WG, Osman Z, (2014) The effect of carbonate-phthalate plasticizers on structural, morphological and electrical properties of polyacrylonitrile-based solid polymer electrolytes. *J Polym Res* 21:381-38.
- [47]. Yuan XZ, Song C, Wang H, Zhang J, (2010) *Electrochemical Impedance Spectroscopy in PEM Fuel cells*. Springer.

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