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Electrochemical performance of ionic polymer metal composite under tensile loading

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Abstract

Cracks in polymer composites can lead to premature failure, which can be disastrous for polymer-based energy storage devices. Detecting these cracks is essential to guarantee the reliability and safety of such devices. However, detecting cracks in composite polymers such as ionic polymer metal composites (IPMCs) is a challenging task, which makes it difficult to ensure their performance and safety. The overall goal of this study is to investigate the effect of cracks or damage caused by tensile loading on the mechanical properties and electrochemical characteristics of IPMC based capacitors. During tensile testing, the deformation of the IPMC strips causes changes in the ion distribution and concentration in the polymer matrix, influencing the performance of the material. The measurements were conducted utilizing electrochemical impedance spectroscopy at a room temperature (21 °C) and frequency range of 10 KHz to 1 Hz. The method utilized in this study proved to be easy and quick with consistent results. The IPMC capacitor was found to increase its capacitance after major cracking in the Pt electrodes from high tensile mechanical loads. Furthermore, at lower frequency range (<100 Hz), the real (ϵ') and imaginary (ϵ'') part of permittivity increase with the addition of loads. This displays that the dielectric property of the material is affected due to the increasing of the loads. It is concluded that, at frequencies above 100 Hz, the permittivity is weakly load dependent.

Keywords: ionic polymer metal composites (IPMCs), cracks, tensile loadings, dielectric material, capacitance, mechanical properties, electrochemical characteristics

(Some figures may appear in colour only in the online journal)

1. Introduction

Ionic polymer-metal composite (IPMC) is an electroactive polymer (EAP) that consists of an ion exchange polymer film and two conducting electrodes [1]. A standard IPMC

comprises of a thin polymer membrane ($\sim 180 \mu\text{m}$) with metal electrodes ($5\text{--}10 \mu\text{m}$ thick) such as platinum, gold, silver, carbon composites, and so on plated on both sides of the membrane. Platinum and gold are often used due to their low electric resistivity as well as chemical stability. The polymer membrane has two main characteristics: permeability and ion selectivity [2]. These characteristics are met using ionomers such as NafionTM, comprising of organic ionic groups connected by covalent bonds to the polymer backbone.

There are several studies that show IPMC materials as actuation elements in electromechanical systems [3, 4]. The working principle of IPMC as an actuator can be associated

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with electromechanical transduction. Electromechanical transduction or actuation takes place when a voltage ($\sim 1.2\text{--}1.5\text{ V}$) is applied across the electrodes, the hydrated cations move towards the cathode, creating a large bending motion [4–7]. The typical cations utilized in IPMC are lithium ion, hydrogen ion, or sodium ion. The volume near the anode decreases and the IPMC bends toward the cathode. This causes the IPMC to swell up on the cathode side [1]. Furthermore, when under stress; for instance, under tension, IPMC creates a voltage difference making it a suitable candidate to be used as a sensor and/or capacitor.

A study was conducted in order to evaluate the functionality of IPMC as capacitors [8, 9] as well as the dependency of IPMC capacitance on temperature. In the study, IPMCs were utilized to conduct the measurements. The Nafion™-115 was plated on both sides with gold utilizing radio frequency sputtering machine. The IPMC was charged for a fixed time using a fixed electric charging current and then allowed the IPMC to discharge, examining the material property itself. The result displayed that the capacitance measurements stayed constant with the increase of temperature. Furthermore, the used IPMC samples were cut into smaller sizes to examine their storage capacitance scalability. It was shown that a reduction of 20% of the surface area resulted in a 20% of its storage capacitance, displaying a linear relationship.

When a material stores energy when voltage is applied, it is identified as dielectric. When a dielectric material is sandwiched between parallel metallic plates and assigned to a voltage, the capacitance measurement depends on the dielectric material and its geometry. Dielectric materials have permittivity which indicates that they can store a large amount of electric charges in an electric field. This is caused by the polarization of the material being generated by the electric field, resulting in the parting of the charges. The separation of the positive and negative charges creates a dipole moment, which adds to the materials capability to store charges. This paper goes over the influence of dielectric properties on the mechanical and electrochemical properties of IPMC.

1.1. Principles of dielectric properties

The material's ability to store energy or electric charge is measured using the real (ϵ') and imaginary (ϵ'') part of permittivity. The real part of permittivity relates to the ability of the material to store and release electrical energy in response to an applied electric field. The imaginary part of permittivity relates to the loss of electrical energy within the material. There is a certain amount of energy that is lost as heat due to the resistance of the material. A lower value represents lower energy losses.

The permittivity of a material is affected by various factors, including the materials' composition, temperature, and frequency. The permittivity (ϵ) values of the dielectric were calculated utilizing the following equations:

$$\epsilon = \frac{C_p L}{\epsilon_0 A}, \quad (1)$$

$$\epsilon' = \epsilon^* \sin(\theta), \epsilon'' = \epsilon^* \cos(\theta) = \epsilon' \tan(\delta).$$

where C_p is the capacitance and L is the thickness of the sample, A is the surface area of the electrodes, $\epsilon_0 = 8.85 \times 10^{-12} \frac{\text{F}}{\text{m}}$ is the dielectric constant of free space, θ is the phase angle in degree, and δ is $90 - \theta$ in degree. The loss factor, $\tan(\delta)$, is obtained directly from the permittivity measurements (figure 1).

The conductivity measurements are determined using the following relationship and they are used to determine the dielectric relaxation, which examines the phenomenon of relaxation in dielectric materials

$$\sigma_{ac} = \epsilon_0 \omega \epsilon'' \quad (2)$$

where $\omega = 2\pi f$ is the angular velocity.

$$M' = -\omega C_0 Z'', \quad M'' = \omega C_0 Z' \quad (3)$$

where C_0 is the geometrical capacitance.

1.2. Surface morphology of IPMC

The electrodes are deposited utilizing the impregnation reduction technique which can cause the IPMC sample to have different textures since the user has minimum control over how much platinum is deposited into the membrane. Furthermore, despite platinum having high electrochemical stability and excellent conductivity, after long cyclic deformation, it tends to develop cracks which leads to a higher surface resistance that affects the performance of the IPMC [10, 11]. Although gold is more elastic and provides a better mechanical durability [12], its low stability in aqueous environments make the fabrication process difficult. Moreover, it is essential to notice that the surface geometry of the electrodes relates to their performance [13]. The platinum electrodes penetrated the Nafion™ membrane results in a very large interfacial surface area between the polymer and the electrodes which leads to larger capacitance measurements. It is understood that the larger the specific surface of the electrodes, the higher the electromechanical output [14]. This is due to the accumulation of charges close to the electrodes. The quality of the electrode layer and performance of the IPMC directly depends on the fabrication process.

In this work, we study how mechanical stress-induced cracks impact the mechanical and electrochemical properties of IPMC. It is also important to note that the layer of the metals embedded into the Nafion™ membrane functions as a barrier for water evaporation. It slows down the evaporation process when working under dry conditions. In general, some efforts and improvements must be made with the fabrication process of IPMC in order to attain a higher surface conductivity, longer water retention when working under dry conditions, and mechanical properties.

1.3. Essential of this study

The need for lightweight designs of electronics has grown in the past decades. Therefore, to meet this need, novel methods

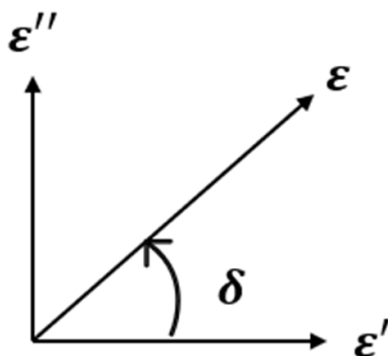


Figure 1. Loss tangent vector.

in material and product development are useful. As technology continues to grow, we are seeing more and more electronics that are being designed to be smaller and more compact. This movement towards miniaturization has led to a need for energy storage devices that are able to fit into these smaller devices. Batteries and capacitors have been used in the development of these devices; however, most batteries and capacitors have limitations. The capacitors and batteries studied in the past lack flexibility, are heavy, and occupy large spaces. Furthermore, some capacitors must be soldered directly to the integrated circuit.

IPMC display capacitive properties once they are placed in an ionic solution. Currently, the ability of IPMC materials to be utilized as planar and flexible capacitive elements for storing electrical energy has begun to be explored [7]. One big improvement of IPMCs from conventional capacitors is how they can be manufactured to any planar shapes and sizes in order to meet the needs of specific applications [8]. Mechanical loading (stress application) can cause deformation or damage to the capacitor; therefore, examining is important for effective longer use. However, very little work has been reported on the influence of stress on the capacitive behavior of IPMC. This work is conducted to determine the influence of cracks caused by tensile loading on the mechanical and electrochemical performance of IPMC.

The research of crack propagation caused by tensile loadings in IPMC energy storage devices is crucial. Studying how cracks form and propagate under tensile loading can help researchers improve the design of energy storage devices to reduce the risk of failure. For instance, by altering the shape or size of the IPMC, researchers can minimize the amount of stress that the material is exposed to, which can increase its durability and reliability. In addition, the presence of cracks in IPMCs can negatively affect their mechanical and electrochemical properties, which can lead to a decline in performance [15–17]. By studying crack propagation, researchers can examine how these cracks affect the energy storage capacity and overall performance of IPMC devices. This knowledge can be utilized to develop mitigation strategies that aim to decrease crack propagation and improve the durability and reliability of IPMCs.

Overall, this work advances the energy field by exhibiting understandings into how IPMCs can be optimized for use in

energy storage devices. By understanding how cracks form and propagate in IPMCs, researchers can build strategies to prevent this type of damage. Additionally, this knowledge can be utilized to develop new materials that are better suited for use in energy storage applications.

For instance, researchers can utilize the knowledge gained from studying crack propagation to enhance the performance of existing technologies that use IPMCs and other EAP based energy devices. This can direct us to the expansion of more efficient and reliable energy storage systems that can be used in different fields, including renewable energy, medical devices, and consumer electronics.

2. Experimental setup

2.1. IPMC fabrication process

The IPMC sample is fabricated utilizing the chemical reduction process (impregnation-reduction or chemical deposition) due to the low cost and good surface strength achieved utilizing this technique [9]. The method consists of four basic steps: surface treatment or roughening, ion exchange, primary plating, and secondary plating. Prior to plating, the Nafion membrane is roughened by # 800 sandpaper to improve the surface area. Then, the membrane was boiled for 45 min in a H_2SO_4 solution and deionized water respectively, after which the sample was immersed in a Platinum (Pt) salt solution ($[Pt(NH_3)_4]Cl_2$ or $[Pt(NH_3)_6]Cl_4$) for 4 h. Next, $NaBH_4$ is utilized as a reducing agent to metalize the polymer. Subsequently, the IPMC sample is boiled in 0.5 M of H_2SO_4 solution and soaked in a LiCl for cation exchange. Typically, platinum and gold are used as electrode materials due to their high electrochemical stability and excellent electrical conductivity [13]. Kim and Shahinpoor showed a thorough description of different IPMC fabrication methods with performance comparison [18]. A more detailed electroless IPMC fabrication process can also be found in Pak *et al* [19]. It is important to note that a big sheet of IPMC based capacitor was fabricated and cut into smaller pieces for testing. This means that the fabrication process is consistent for all samples.

2.2. Scanning electron microscope (SEM)

Scanning electron micrographs of IPMC were acquired utilizing the Hitachi TM 3030 microscope with a 15 KV accelerating voltage (figure 2). The typical morphology of IPMC samples displayed unevenness in the surface of the electrode. For this study, the images were captured at various displacement measurements to examine the effect of electrode morphology cracks induced inside the SEM.

2.3. Dynamic mechanical analyzer (DMA)

A DMA was utilized to obtain the stress–strain relationship for fabricated IPMC sample in the tension loading application. The Young's modulus measurements were determined from the stress–strain measurement utilizing the Perkins Elmer Pyris Diamond DMA Analyzer that provides force up to 9.8 N.

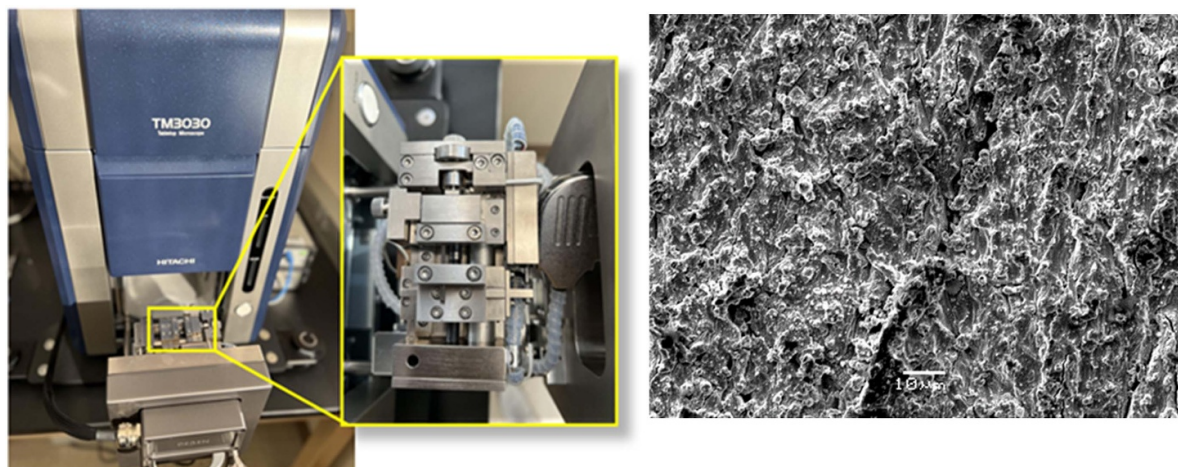


Figure 2. SEM (Hitachi TM3030, Japan) showing an adapter for tensile setup (left) and SEM image of the platinum surface of an IPMC fabricated using the electroless deposition technique (right).

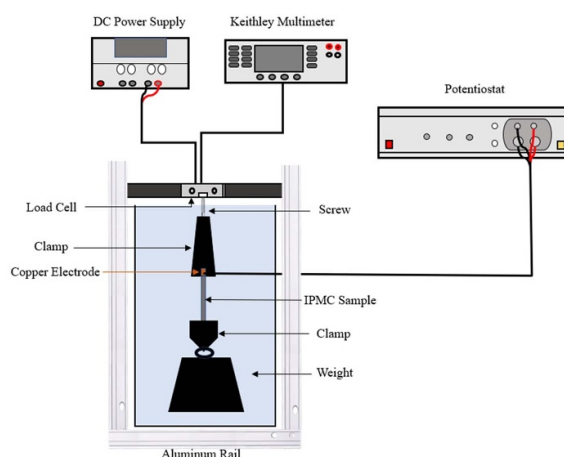


Figure 3. Experimental setup used for electromechanical and electrochemical characterization and corresponding schematic diagram. The measurements were conducted in wet conditions (in deionized water) at a room temperature (21 °C); therefore, the effect of water loss may be neglected. The electrochemical impedance spectroscopy (EIS) measurements were conducted in a two-electrode configuration. Furthermore, the electrochemical measurement plots were obtained from EIS measurements at a frequency range of 10 KHz–1 Hz utilizing an AC perturbation of 10 mV.

The force is increased at the rate 0.5 N min^{-1} . The specimen is a rectangular strip with a size of 14 mm in length, 2 mm in width, and 0.20 mm in thickness. The tests were conducted in air condition at room temperature (21 °C) and normal humidity ($\sim 30\%$). Although IPMCs are known to work better in water due to ion mobility [20], a few assumptions were considered when investigating the measurements taken in real-time work environments. When working in dry conditions, we are considering there may still be some level of moisture present in the surrounding environment or within the IPMC material itself. The presence of residual water, humidity, or moisture adsorbed onto the IPMC surface could contribute to a certain level of ion mobility and produce precise measurements [21].

2.4. Mechanical and electrochemical characterization

The electromechanical and electrochemical responses of the prepared IPMCs were measured utilizing a DC power supply

(HY3005F-3), load cell (GSO-1K, Transducer techniques), PGZ-402 Potentiostat (Radiometer Analytical), and Keithley (DMM6500) Multimeter. An IPMC sample with a size of $4 \text{ mm} \times 18 \text{ mm}$ and thickness of 0.20 mm was clamped from both ends and the input voltage is applied at the clamp contacts as shown in figure 3. To calculate the forces, Newton's second law of motion was used ($F = ma$), while considering the buoyant force. The weights were increased in 100 g increments, beginning at 62 g. The experiments were repeated with three samples for each loading and the average was taken as reasonable measurements.

3. Results and discussion

3.1. Stress–strain measurements

The tensile testing results in terms of normal stress and normal strain on an IPMC are displayed in figure 4. IPMCs have an increase in the mechanical properties, such as stiffness and

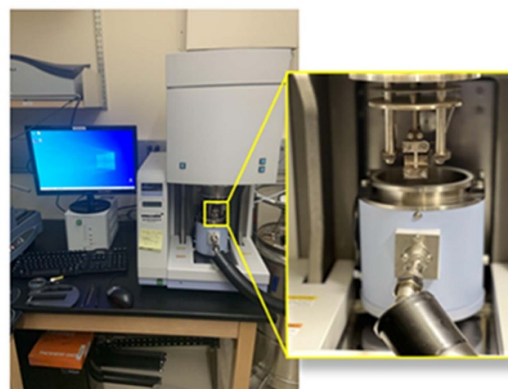
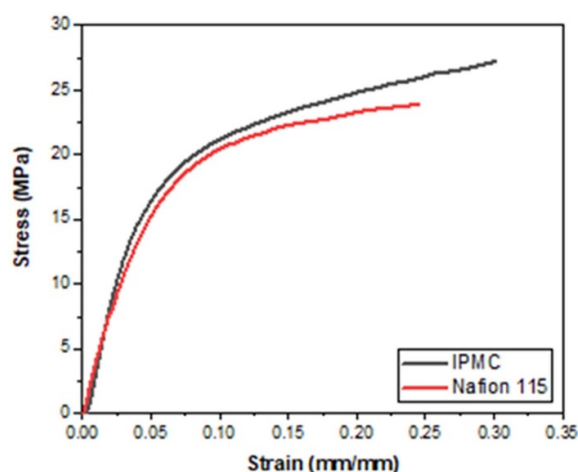


Figure 4. Stress–strain relationship of an IPMC sample (left) measured in a dynamic mechanical analyzer (DMA) (right).

the modulus of elasticity, compared to a Nafion membrane. However, the stress–strain behavior is similar, illustrating that the mechanical performance is led by the polymer membrane itself rather than the platinum electrodes [22]. However, this will not be the case when working in a bending mode. The intrinsic mechanical properties of the polymer membrane and electrodes impact each other. This work is not covered in this study.

3.2. Crack propagation

The Pt IPMCs were examined using SEM to study crack propagation and the influence of these cracks on the capacitance, permittivity, and other electrochemical properties. The platinum layer on the top of the composite works as a highly conductive current collector. As stated above, it is very important to examine the surface conditions of the electrodes, as the surface geometry relates to the electric resistance of the electrodes, permittivity, and capacitance. Figure 5 displays images of the IPMC sample under the SEM. The sample was clamped on both ends horizontally and it was extended by an increment of 1 mm. The results showed significant crack formations and propagation. It looked like crack propagation begins at 2 mm. A 31 μm crack was observed when the sample was extended to 7 mm. Furthermore, a small separation at the interface between the electrodes and the polymer was noticed; the separation allows for charges to accumulate at the interface forming double layer. It should be noted that two additional samples were tested under SEM to confirm that they all exhibited similar crack propagation under various strains. Moreover, it is important to note that the IPMC samples were subjected to a tensile load under the DMA until they reached the maximum force limit of the equipment, which was approximately 10 N, while the SEM measurements were taken throughout the testing process, up until the sample failed.

Although this paper examines the influence of cracks on the mechanical and electrochemical properties of IPMC, it does not investigate the types of cracks formulated.

It is crucial to establish a relationship between crack formation and strain based on the SEM images. As expected, the application of stress resulted in an increase in crack formation with the corresponding strain (figure 6). Crack propagation is influenced not only by the application of stress, but also by environmental conditions such as temperature, humidity, and corrosion [15].

3.3. Permittivity

One of the most essential properties of IPMCs is their permittivity, which displays the material's ability to store electrical energy in an electric field (figure 7). The permittivity of the material is affected by the mechanical deformation caused by tension loading. This type of deformation changes the distance between the metallic electrodes of the IPMC, resulting in changes in permittivity. It is noted that both the real and imaginary part of the permittivity decrease with increasing of the applied frequency. The decrease in permittivity can be attributed to various reasons, including the relaxation processes that arise within the material at higher frequencies. At lower frequency, the dipoles play a significant role in the total polarization of the polymer, and they align themselves with the applied electric field. At higher frequencies, however, the role of the dipoles to the total polarization becomes small; therefore, dipoles are unable to keep up with the fast changes in the applied electric field resulting in low values. In other words, the dipoles are not able to rotate with the same frequencies; therefore, when the applied frequency increases, the real and imaginary part of permittivity values decline. Furthermore, the ionic polarization caused by the application of the electric field on the materials, causes a displacement of the cations relative to the anions, allowing the permittivity values to decrease with increase in frequency.

Figure 7 displays that the dielectric property of the material is affected due to the increasing of the loads at lower frequency (<100 Hz). It is also noted that at frequencies above 100 Hz, the permittivity is weakly load dependent. At the lower frequency range, the ϵ' and ϵ'' values seem to increase

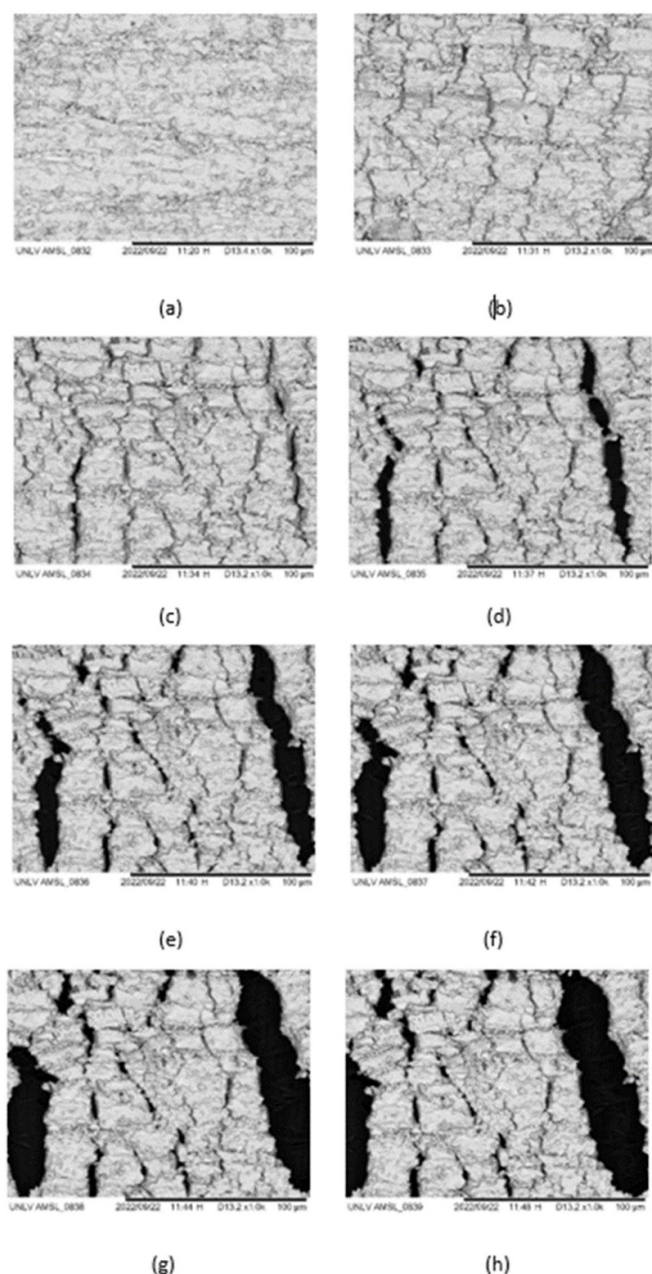


Figure 5. SEM images of Pt-IPMC sample under no strain (a), 1 mm (b), 2 mm (c), 3 mm (d), 4 mm (e), 5 mm (f), 6 mm (g), 7 mm (h) extension.

with the addition of loads or stress (figure 8). The addition of the loads at higher frequency, make the IPMC exhibit small to no change in permittivity. This could be due to an increase in stiffness and lowered flexibility of ions within the polymer matrix. When a tensile force is applied on the IPMC, the Nafion matrix becomes elongated, resulting in a reduction in the density charged species within the matrix. This decrease in charged species leads to small to no changes in the permittivity of the IPMC.

3.4. Dielectric loss ($\tan \delta$)

Dielectric loss determines the energy loss due to the dissipation of the electric field in the material. The dielectric

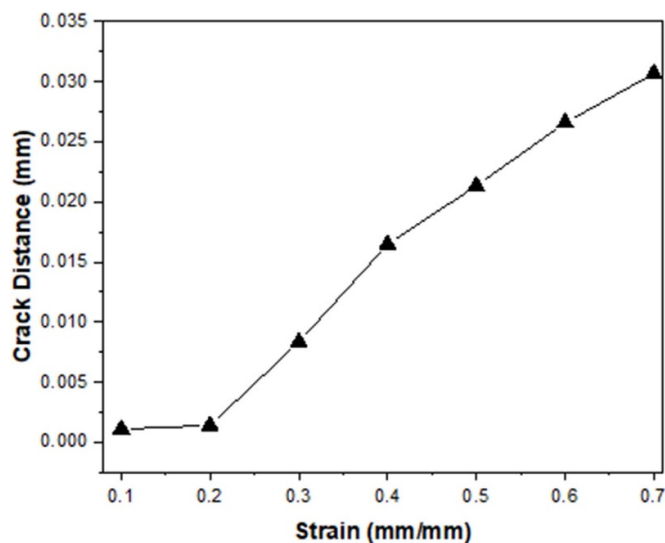


Figure 6. Crack propagation with the addition of loads.

loss, $\tan \delta$ as a function of frequency at different loads is obtained from equation (1) and displayed in figure 9. The dielectric loss of an IPMC varies with frequency and the addition of the loads. At low frequencies, the dielectric loss of the IPMC increases with the increase in stress. This might be due to the applied stress causing some type of adjustment in the orientation of the polymer chains influencing the dielectric properties of the material. At low frequencies, the dielectric loss behavior is governed by electrode polarization as well as ionic conduction. The dielectric loss that is credited to ionic conduction implies the migration of ions over large distances. As the ions move, they lose some of their energy to the lattice as heat. This explains the dissipation of electrical energy as heat.

Furthermore, as it was shown in the SEM images, the applied stress causes the formation of microcracks or voids in the polymer matrix. This will increase the dielectric loss due to the existence of trapped charges. As frequency increases, the dipole relaxation becomes more significant and causes the dielectric loss. Moreover, at high frequencies, the space charge influences also play significant role in determining the dielectric behavior. The tension loading induces mechanical stress on the metallic electrodes. This affects their electrical properties and influences the overall dielectric loss.

3.5. Dielectric modulus

One of the important characteristics of IPMCs is their dielectric modulus, which displays the relationship between the electric field and strain under various loading settings. The dielectric modulus is obtained from equation (3) and is displayed in figure 10. Due to the presence of interfaces, most polymeric materials display interfacial polarization. This effect is due to the accumulation of charges at the interface between the metallic electrodes and the polymer membrane. In addition, the electrical conductivity of the polymeric material has been studied by the modulus technique.

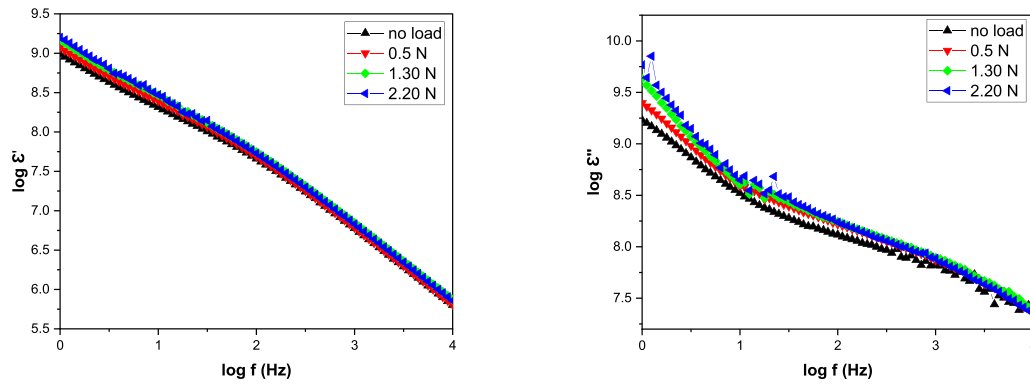


Figure 7. The real part (left) and the imaginary part (right) of permittivity versus the applied frequency with the addition of loads.

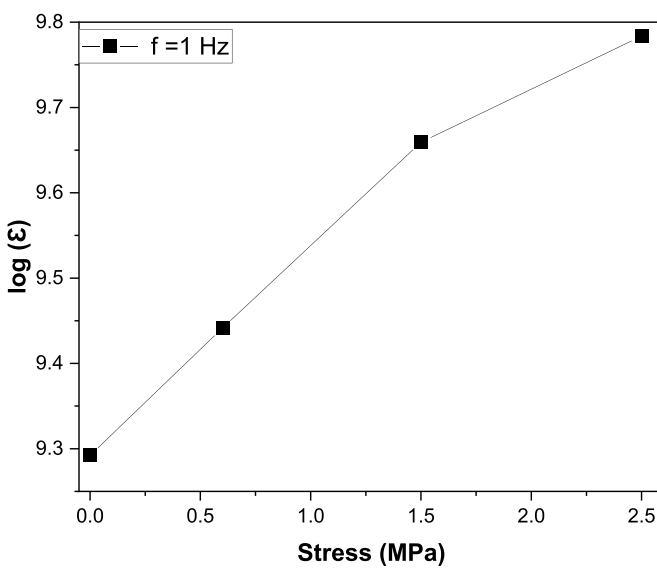


Figure 8. The change in permittivity with stress at 1 Hz.

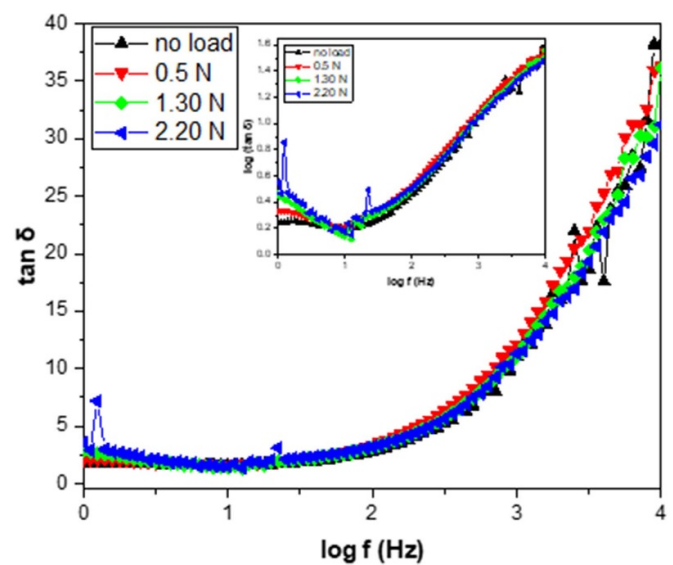


Figure 9. The tangent loss $\tan \delta$ vs frequency for various loadings; the log–log scale plot is also shown for better interpretation.

In the higher frequency range, both the M' and M'' part increase sharply and linearly with the applied frequency. The increasing of the elastic modulus reaches maximum values at high frequencies due to β -relaxation process. The β transition appears when only one side group of the component inside the polymer membrane moves instead of the larger segment of it moving as seen in α -transition. Furthermore, the results displayed that the dielectric modulus values have opposite frequency performances compared with dielectric constant or permittivity measurements. It is noticeable from the permittivity figures that permittivity decreases with frequency, while dielectric modulus is increasing.

Under tension loading setting the M' part of the dielectric modulus displays the stiffness of the IPMC material. As shown in figure 10, the M' part of the dielectric modulus increases with increasing frequency. This displays that the IPMC becomes stiffer at higher frequencies. This characteristic is caused by the mobility of the ions in the material becoming more constrained at higher frequencies. The M'' component of the dielectric modulus is a key sign of

the damping performance of IPMC. Specifically, when the material is under tension loading, an increase in frequency causes the M'' part to increase as well. This shows that IPMC is able to provide stronger damping at higher frequencies. This behavior is caused by the inability of the ions mobility at higher frequencies, resulting in more damped response.

3.6. AC conductivity

The frequency dependence of the AC conductivity (σ_{AC}) under various tension loadings is obtained by equation (2) and shown in figure 11. As seen in the figure, under tension loadings, the σ_{AC} increases with the increase in the frequency of the applied electric field. At low frequencies, the conductivity is governed by the movements of the ions in the polymer membrane's matrix. The motion of the ions is slowed by the polymer chain. As the frequency increases, polymer membrane starts to relax and the mobility of the ions is improved, resulting in increased conductivity.

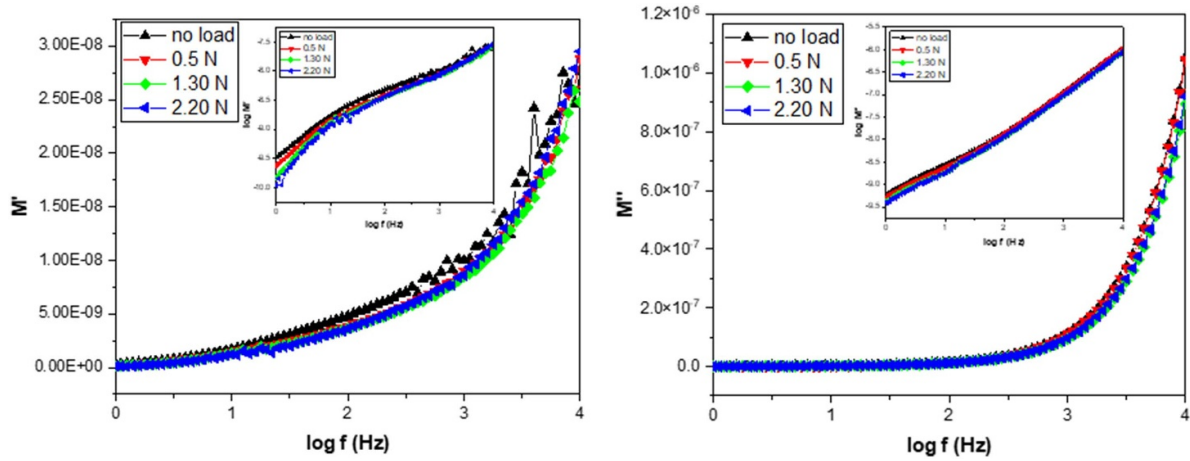


Figure 10. The dependency of the real (M') part (left) and imaginary (M'') part (right) of the dielectric modulus on frequency under various loadings.

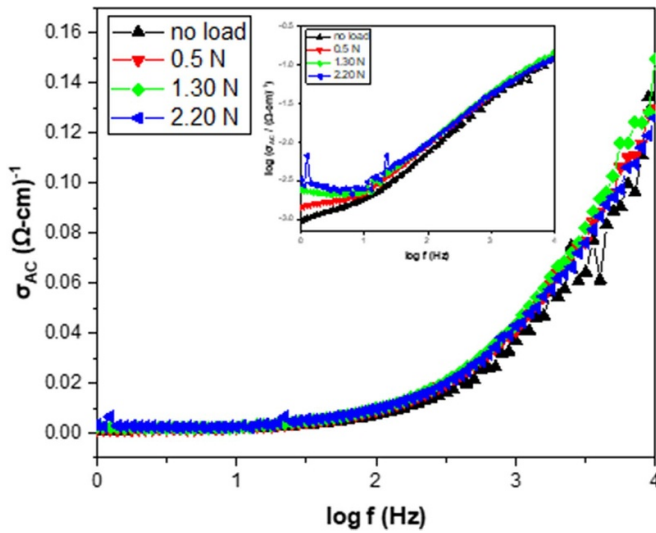


Figure 11. The dependency of AC conductivity on frequency under various loadings; log–log scale plot is shown for better interpretation.

In the lower frequency range, the conductivity increases with the addition of the weights. At the higher frequencies (>100 Hz); however, the effect of the loads seems to no longer affect the conductivity measurements. Although the conductivity of IPMC significantly improved by increasing the applied frequency, the addition of the loads has no effect on the conductivity at higher frequencies. The increase in the conductivity due to the application of the loads could be explained by the dependency of the conductivity on the direction of the applied stress with respect to the polymer chain orientation. Stretching the IPMC sample along the polymer membrane's chain direction will improve the connectivity of the ion-conducting channels. However, stretching the IPMC sample perpendicular to the polymer's chain direction will interrupt the channel and decrease or have no change in the conductivity.

3.7. Impedance spectra

The Impedance measurements seen in figure 12, represent the phase change between the current that flows through and the electric potential that is applied to the IPMC sample. The phase change is due to the dielectric properties of the material. Figure 12 displays the dependency of both the real and imaginary part of the IPMC on frequency at various tension loadings. At low frequencies (<100 Hz), both Z' and Z'' impedance measurements decrease with increase of the loads. A sharp decrease is noticed in both the real and imaginary impedance measurements at high frequencies. The sharp decrease in impedance is due to the bending and stretching modes of the IPMC. Furthermore, the decrease in impedance measurements with the increase of frequency as well as the applied loads suggests an increase in the AC conductivity of the sample [23, 24]. For all the applied loads at high frequencies, both Z' and Z'' impedance values become independent of frequency. This may be the result of the release of space charge causing the decrease in barrier properties of the IPMC sample. It is noted that for the load 1.30 N and 2.20 N, there is increase in the Z'' values reaching the maximum ($Z_{\max}''$) at low frequencies. The Z'' values then start to decrease. This phenomenon is seen in figure 13 as well. In addition, the $Z_{\max}''$ shifts to higher frequency with the addition of the loads (from 130 N to 2.20 N). This is an indication of the dependency of the load or mechanical stress with the relaxation time in polymer chain. The relaxation behavior of the IPMC changes due to the variations of its mechanical properties.

3.8. Capacitance

The specific capacitance of a material under tension loading as shown in figure 14, depends on different factors, including the frequency of the applied electric potential. At low frequencies, the ionic motion inside the membrane's matrix is slow; therefore, the capacitance is higher. Nevertheless, at high frequencies, there is not enough time for the ions to move and align themselves with the applied electric potential inside the

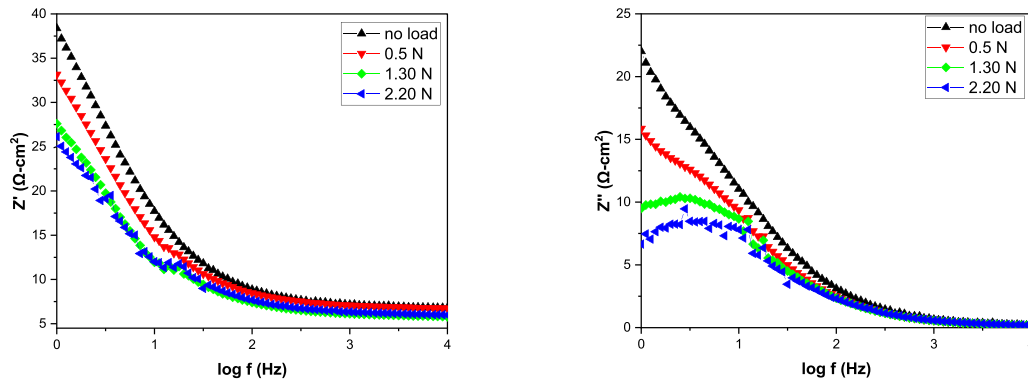


Figure 12. The real (Z') part (left) and the imaginary (Z'') part (right) of impedance vs frequency under various loadings.

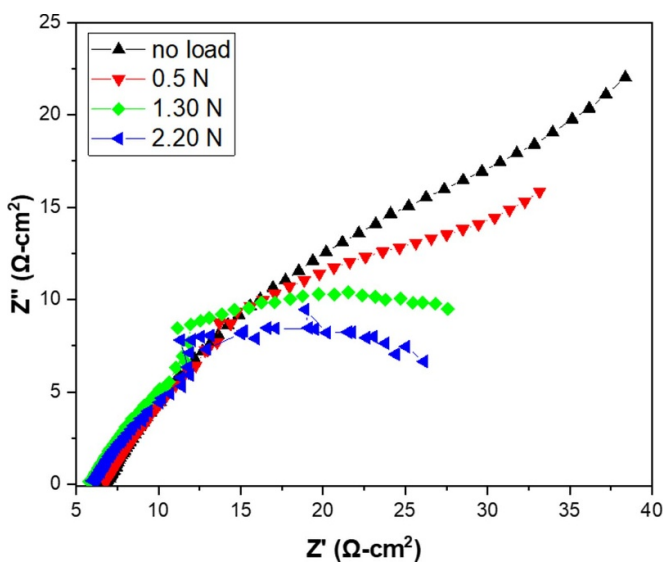


Figure 13. The real (Z') part and the imaginary (Z'') part of impedance under various loadings.

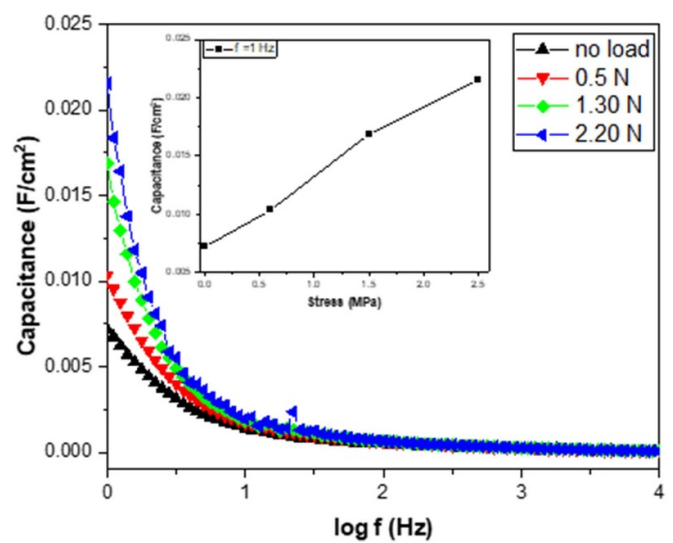


Figure 14. The capacitance measurements with frequency at various tension loadings.

NafionTM matrix. Due to that, the capacitance measurements drop. In addition, at higher frequencies, the dielectric properties of IPMC begin to weaken, which causes a decrease in the capacitance measurements.

At low frequencies, the measured capacitance increases irreversibly with increasing stress as seen in figure 15. The increase in capacitance during loading is attributed to the formation of cracks resulting from the separation of the metallic electrodes and polymer under mechanical stress. This separation allows for charges to accumulate at the interface between the electrodes and the dielectric material forming double layer, resulting in increased capacitance measurements. Stretching the IPMC sample also increases the surface area of the electrodes, increasing the sample's capacitance. Furthermore, under tension loading, the IPMC sample experiences a change in the dimensions, this change influences the distance between the parallel electrodes. The reduction of the distance between the electrodes increases capacitance.

There is irreversibility in the capacitance upon unloading in the lower frequency. The irreversibility is described by the capacitance being smaller during unloading than during the

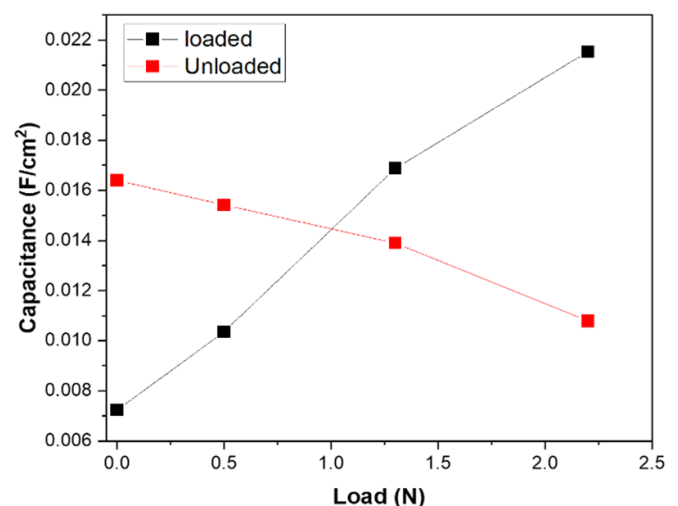


Figure 15. The effect of stress on the measured capacitance during loading and unloading.

prior loading setting. The change in the capacitance measurements between loading and unloading shows the increase in polarization during loading and its decrease during unloading.

The types of cracks formed during this study could also be a factor for the increase and decrease in the capacitance values. However, the types of cracks formed are not investigated in this work.

4. Concluding remarks

Electrochemical Impedance Spectroscopy measurements were conducted in order to investigate the influence of stress on the mechanical and electrochemical performances of IPMC. It has been shown in the past that the sensing and actuation properties of IPMCs are strongly dependent on the mechanical and electrical properties. The IPMC samples display unique dielectric properties under tensile loadings. Also, the result displayed that the permittivity and capacitance decrease with increase in the applied frequency. When the IPMC is stretched, its capacitance changes due to the change in the distance between the electrodes. The reduction of the distance between the electrodes increases capacitance. Moreover, when the IPMC sample is stretched, cracks or small separation occur between the electrode and the polymer. This separation allows for charges to accumulate at the interface between the electrodes and the dielectric material forming double layer, resulting in increased capacitance measurements.

The dependence of the dielectric properties of IPMC is shown by considering two elements: dielectric relaxation and electrode polarization. At low frequencies, dielectric relaxation occurs when the dipoles inside the polymer react to applied electric potential by reorienting themselves. In addition, at low frequencies, the ionic mobility inside the polymer matrix is slow; therefore, the capacitance is high, and the loss tangent is low. At high frequencies, however, the dipoles inside the polymer matrix are not able to reorient themselves quickly enough to respond to the electric potential. Therefore, the capacitance decreases while the loss tangent increases due to increased ion mobility and electrode polarization. Furthermore, electrode polarization occurs when charges accumulate at the interface between the electrode and the polymer membrane due to differences in permittivity.

Overall, understanding the electrochemical performance of IPMC under tension loading is an essential area of research, in order to utilize this material in practical applications. By examining the electrochemical behavior under various loading conditions, researchers can expand insights into how to enhance the design and performance of this material for various applications including robotics.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

- [1] Yuan Ong Yon 2016 (Malaysia: Universiti Tunku Abdula Rahman) Muscle-like actuator based on ionic polymer metal composite (IPMC) (<http://eprints.utar.edu.my/2758/1/MH-1203202-1.pdf>)
- [2] Mondal M, Datta A and Kanti Bhattacharyya T 2022 IPMC based flexible platform: a boon to the alternative energy solution *Management and Applications of Energy Storage Devices* (IntechOpen) (<https://doi.org/10.5772/intechopen.99434>)
- [3] Akhtar S N, Cherusseri J, Ramkumar J and Kar K K 2016 Ionic polymer metal composites *Compos. Mater. Process. Appl. Charact.* **223**–49
- [4] Kim B, Kim B M, Ryu J, Oh I-H, Lee S-K, Cha S-E and Pak J 2003 Analysis of mechanical characteristics of the ionic polymer metal composite (IPMC) actuator using cast ion-exchange film *Proc. SPIE* **5051** 486
- [5] Lee S G, Park H C, Pandita S D and Yoo Y 2006 Performance improvement of IPMC (ionic polymer metal composites) for a flapping actuator *Int. J. Control Autom. Syst.* **4** 748–55
- [6] Nemat-Nasser S and Thomas C 2010 Ionomeric polymer-metal composites *Electroactive Polymer (EAP) Actuators as Artificial Muscles: Reality, Potential, and Challenges, Second Edition* pp 171–230
- [7] Landrock C K and Kaminska B 2011 Ionomer composite thin film capacitors *IEEE Trans. Compon. Packag. Manuf. Technol.* **1** 1305–10
- [8] Landrock C K and Kaminska B 2009 New capacitive storage device pp 1–4
- [9] Khmelnsky I K, Vereschagina L O, Kalyonov V E, Lagosh A V and Broyko A P 2017 Improvement of manufacture technology and investigation of IPMC actuator electrodes *Proc. 2017 IEEE Russia Section Young Researchers in Electrical and Electronic Engineering Conf., ElConRus 2017* pp 892–5
- [10] Punning A, Kruusmaa M and Aabloo A 2007 Surface resistance experiments with IPMC sensors and actuators *Sens. Actuators A* **133** 200–9
- [11] Hiemstra D L and Sottos N R 1993 Thermally induced interfacial microcracking in polymer matrix composites *J. Compos. Mater.* **27** 1030–51
- [12] Fujiwara N, Asaka K, Nishimura Y, Oguro K and Torikai E 2000 Preparation of gold-solid polymer electrolyte composites as electric stimuli-responsive materials *Chem. Mater.* **12** 1750–4
- [13] Palmre V, Kim S J, Pugal D and Kim K 2014 Improving electromechanical output of IPMC by high surface area Pd-Pt electrodes and tailored ionomer membrane thickness *Int. J. Smart Nano Mater.* **5** 99–113

- [14] Akle B, Nawshin S and Leo D 2007 Reliability of high strain ionomeric polymer transducers fabricated using the direct assembly process *Smart Mater. Struct.* **16** S256–61
- [15] Naebe M, Abolhasani M M, Khayyam H, Amini A and Fox B 2016 Crack damage in polymers and composites: a review *Polym. Rev.* **56** 31–69
- [16] Xi X and Chung D D L 2019 Piezoelectricity, piezoresistivity and dielectricity discovered in solder *J. Mater. Sci., Mater. Electron.* **30** 4462–72
- [17] Buggisch C, Gagani A and Fiedler B 2021 Capacitance measurements on integrated conductors for detection of matrix cracks in GFRP *Funct. Compos. Mater.* **2** 2
- [18] Kwang J K and Shahinpoor M 2003 Ionic polymer-metal composites: II. Manufacturing techniques *Smart Mater. Struct.* **12** 65–79
- [19] Pak J J, Cha S, Ahn H and Lee S 2001 Fabrication of ionic polymer metal composites by electroless plating of Platinum *Proceedings of the 32nd International Symposium on Robotics ISR2001* 19–21
- [20] Bahramzadeh Y and Shahinpoor M 2014 A review of ionic polymeric soft actuators and sensors *Soft Robot.* **1** 38–52
- [21] Swarrup J S, Ranjan G and Giridhar M 2017 Structural modeling of actuation of IPMC in dry environment: effect of water content and activity *Smart Struct. Syst.* **19** 553–65
- [22] Bhandari B, Lee G Y and Ahn S H 2012 A review on IPMC material as actuators and sensors: fabrications, characteristics and applications *Int. J. Precis. Eng. Manuf.* **13** 141–63
- [23] Chérif S F, Chérif A, Dridi W and Zid M F 2020 Ac conductivity, electric modulus analysis, dielectric behavior and bond valence sum analysis of $\text{Na}_3\text{Nb}_4\text{As}_3\text{O}_{19}$ compound *Arab. J. Chem.* **13** 5627–38
- [24] Bouaamlat H, Hadi N, Belghiti N, Sadki H, Naciri Bennani M, Abdi F, Lamcharfi T-D, Bouachrine M and Abarkan M 2020 Dielectric properties, AC conductivity, and electric modulus analysis of bulk ethylcarbazole-terphenyl *Adv. Mater. Sci. Eng.* **2020** 1–8