



Kraton based ionic polymer metal composite (IPMC) actuator



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ABSTRACT

In this study, the tip displacement, proton conductivity, current density, water uptake and ion exchange capacity of kraton non-perfluorinated IPMCs are examined and the results are compared with nafion based IPMCs membranes. The water holding capacity of kraton membrane and nafion film was found to be 308.69% and 16.20%, at 65 °C and 45 °C within 10 h of immersion time, respectively. The kraton membrane and nafion film have the ion exchange capacity of 1.9 and 0.75 meq g⁻¹ of dry membrane, respectively. SEM studies revealed that the morphology of nafion membrane was negligibly affected after performing the action experiment while in kraton membrane ruptures and notable spaces at joint were observed. The electrical properties revealed better actuation performance of kraton membrane. The tip displacement for nafion and kraton membrane was also carried out at 3 V DC electrical voltages. Kraton film showed larger displacement and therefore actuation as compared to that of nafion film.

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1. Introduction

Ionic polymer metal composites (IPMCs) have been considered as a promising candidate for electric stimuli sensitive materials in actuators, bioinspired artificial muscles and sensors because of their advantageous properties like operation at low electric voltage (1–5 V), large dynamic deformation, lighter weight, flexibility and precise sensing ability [1–9]. Typically, an IPMC comprises of a neutralized semi permeable ion exchange polymer membrane coated with metal Pt or Au as electrode at both sides and water as inner medium for the dissociation for metal cation. When an electric field is applied the metal cations move towards the negative electrode along with water molecules. Therefore, the polymer membrane swells near the cathode which causes a strain near the cation rich region in IPMC membrane, resulting in bending motion in the film towards the anode [10]. Under dry conditions the cross-linked cations are not free to move. However, in wet condition (on hydration) cations are surrounded by water molecules to make the whole film mobile. Thus, transduction in the IPMCs film is because of the movement of cations with the water molecules [11]. Typically, perfluorinated IPMC membranes with the trade name of nafion are being used as actuators and dynamic sensors because of its useful

properties like high proton exchange capacity, thermal, mechanical and chemical stabilities [12–23]. However, its high cost as well as high evaporation of water molecules under applied voltage limits its further application. Therefore, researchers are working towards developing low cost non-perfluorinated membranes having high water holding capacity even at high temperatures, to replace the commercial nafion membranes [24–27,19]. In this study, non-perfluorinated kraton polymer based ionic polymer metal composite membranes were prepared and characterized for bending actuation. The results are compared with that of nafion membrane.

2. Experimental

2.1. Material

A nafion membrane (0.05 mm thick, NRE-212) (Sigma Aldrich), tetraamineplatinum(II) chloride monohydrate [Pt(NH₃)₄Cl₂·H₂O (Crystalline)] (Alfa Aesar, USA) and a non-perfluorinated kraton [pentablock copolymer poly((*t*-butyl-styrene)-*b*-(ethylene-*r*-propylene)-*b*-(styrene-*r*-styrene sulfonate)-*b*-(ethylene-*r*-propylene)-*b*-(*t*-butyl-styrene) (tBS-EP-SS-EP-tBS)](MD9200) (Nexar Polymer, USA), sodium borohydride and hydrochloric acid (35%) (Thomas Baker Pvt. Ltd., India) and ammonium hydroxide (25%) (Merk Specialties Pvt. Ltd., India) were used as received without any purification.

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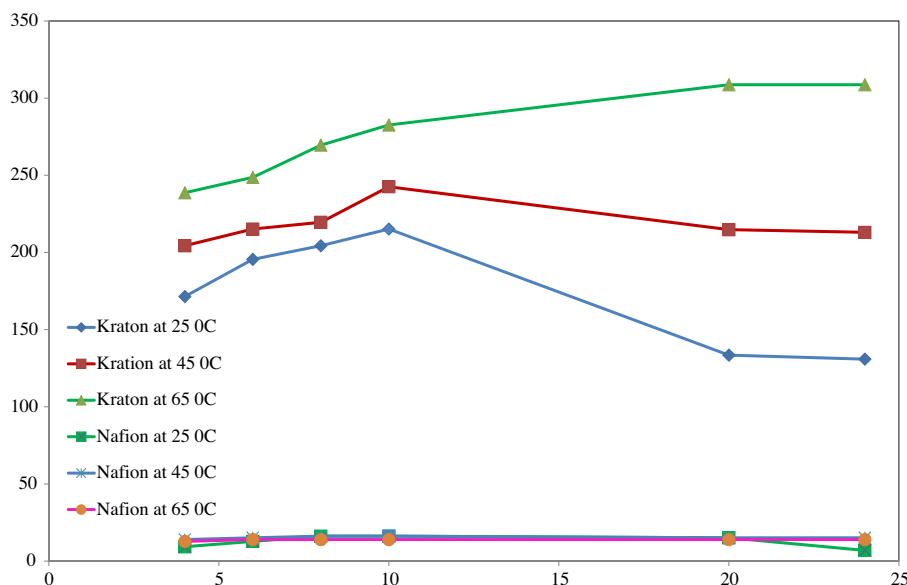


Fig. 1. Water uptake of kraton and nafion based IPMCs films at room temperature ($25 \pm 3^\circ\text{C}$), 45°C and 65°C for a time period of 4 h, 6 h, 8 h, 10 h, 20 h and 24 h.

2.2. Membrane preparation

An ionic polymer metal composite (IPMC) film of kraton polymer was prepared by casting 5 ml of kraton in a petri dish ($50\text{ mm} \times 17\text{ mm}$) with the help of a pipette. After casting the polymer solution, the petri dish was covered with Whatman filter paper (No. 1) for slow evaporation of the solvents at room temperature ($25 \pm 3^\circ\text{C}$) for 5 h. However, evaporating the solvent in a thermostated oven at and above 30°C solidifies kraton film with visible surface cracks. After drying, the film was removed from the petri dish with the help of a foreship and spatula. The film was stored in a desiccator to carry out further studies.

2.3. Water uptake

To find out the water uptake capacity of nafion and kraton polymer films were kept in demineralized water. A series of experiments for water uptake at different time duration and temperatures were performed. The experiments were performed at room temperature ($25 \pm 3^\circ\text{C}$), 45°C and 65°C , for different times 4 h, 6 h, 8 h, 20 h and 24 h as shown in Fig. 1.

2.4. Ion exchange capacity

The films were converted into H^+ ion form by placing in 1.0 M HNO_3 for 24 h followed by neutralization with demineralized water and dried at 45°C . A 0.25 g of polymer film was cut into small pieces and packed into a glass column. The acidic form of the film was converted into Na^+ form by passing 1 M NaNO_3 through the column to elute the H^+ ions keeping a slow flow rate ($\sim 0.5\text{ ml min}^{-1}$). The effluent was titrated against 0.1 M NaOH solution using phenolphthalein indicator. The ion exchange capacity of polymer film in meq g^{-1} of dry film was obtained using following formula (1) and given in Table 1.

Ion exchange capacity

$$= \frac{\text{Volume of NaOH consumed} \times \text{Molarity of NaOH}}{\text{Weight of the dry membrane}} \quad (1)$$

2.5. Electroless plating

The fabrication of ionic polymer metal composite (IPMC) membranes was started with surface roughening of membranes on both sides which was carried out by using mild sandpaper and followed by cleaning ultrasonically for 30 min, i.e., electroless plating method described in the literature [28,29].

After cleaning, the membranes were treated with an aqueous solution of 2.0 N HCl in hot air oven at 45°C followed by washing with demineralized water for 1 h. The membranes were treated with 4.5 ml of aqueous solution of 0.04 M tetraammineplatinum(II) chloride monohydrate and 0.1 ml of 5.0% aqueous solution of NH_4OH , with constant stirring up to 5 h at room temperature. After the exchange of protons of membranes with platinum ions, the membranes were stirred in distilled water for 15 min to remove excess platinum absorbed at the surface of the membranes and then transferred to another flask. A 0.5 ml of 5% aqueous solution of NaBH_4 was added after every 30 min for reduction of platinum ions into Pt metals. Further, 5 ml of NaBH_4 solution was added followed by stirring for 1 h at room temperature. The membranes were washed with distilled water for termination of reduction reaction. Finally, membranes were converted into acidic form by placing membranes in 0.1 M HCl solutions at room temperature up to 1.5 h.

2.6. Proton conductivity

The proton exchange capacity of the ionic polymer metal composite (IPMC) membrane is one of the most important features to achieve bending which occurs because of forming hydronium ions by the existing protons at the IPMC membrane in hydrated state. The bending movement of IPMC membrane is because of movement of hydrated cation towards the cathode as shown in Scheme 1. The proton conductivity of hydrated IPMC film ($1\text{ cm} \times 3\text{ cm}$) was

Table 1
Ion exchange capacity and proton conductivity of kraton and nafion based IPMCs films.

Material	Ion exchange capacity (meq g^{-1} of dry membrane)	Proton conductivity (σ) (S cm^{-1})
Nafion membrane	0.75	4.026
Kraton membrane	1.9	17.15

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