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# Development of sulfonated poly(vinyl alcohol)/aluminium oxide/graphene based ionic polymer-metal composite (IPMC) actuator

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ABSTRACT

A novel ionic polymer-metal composite (IPMC) actuator based on the ionomeric composite film composed of sulfonated poly(vinyl alcohol)/aluminium oxide/graphene/platinum (SPVA-Al-GR-Pt) was successfully developed. The SPVA-Al-GR films were prepared by solution casting strategy followed by electroding with platinum using electroless plating or chemical reduction method. The SPVA-Al-GR films showed good ion-exchange capacity (1.8 meq $g^{-1}$ of the dry film) and water uptake (125% at 45 °C for 10 h of drenching time). Moderate solvent (water) loss, good proton conductivity, stability at higher temperatures and electromechanical properties of proposed IPMC actuator places itself as a promising alternative to conventional polymer based IPMC actuators. By building up a small scale holding framework, it was demonstrated that this IPMC actuator can be utilized as a part of miniaturized scale mechanical devices.

## 1. Introduction

Ionic polymer-metal composites (IMPCs) based soft actuators are considered to be one of the most delicate actuation materials, because of their large and fast bending deformation in response to low external electrical stimulus (1–6 V) [1,2]. Recently, IPMCs have attracted increasing interest from researchers and industry engineers because of their quick response, lightweight, adaptable nature, simple control system etc. [3–8]. IPMCs can be utilized as a part of assorted miniaturized devices, for example, biomedical gadgets, smaller than usual or artificial muscles, bio-mimetic robotics, automobiles, and microsensors and switches [2,9–19] attributable to their qualities including large, quick, and delicate bending actuation. A normal IPMC film comprises an ionomeric layer sandwiched between a couple of electrodes mostly Pt or Au. Usually, an ionomeric layer contains mobile ions (e.g. metal cations) and a polar solvent to facilitate ionic mobility. Under-connected electric potential, asymmetric diffusion of cations toward the negatively charged electrode is responsible for the twisting actuation towards positively charged electrode [3,20]. More often, the commercial perfluorinated polymers, for example, Nafion, Flemion, Aciplex and so on are utilized as a result of their high level of proton conductivity and powerful thermo-chemical stabilities arising from their novel perfluorinated structure [1,21]. These industrial ionomers, *i.e.* polymer electrolytes, have a two-stage blend of a steady Teflon spine interweaved with the ionic bunches. The spine structure holds mechanical quality while bunches with ionic groups give the exchange channels to solvated (hydrated) cations. Be that as it may, these conventional actuators have a few downsides as well including very high cost, environmentally unsafe and require steady humidification to counteract the drying of these films [1,22,23]. Thus, a number of non-perfluorinated polymers as a substite of these perfluorinated polymers have been developed [24–29]. Among non-perfluorinated polymers, block copolymers are perceived as promising cutting edge materials for IPMC actuator applications because of their lower cost, mechanical strength, and dimensional stability from solvation to actuation, and magnificent ionic conductivity owing to the efficient microphase-isolated structures. A few of the relevant non-perfluorinated polymers, which can act as

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substitute to the perfluorinated one include sulfonated polystyrene [25], sulfonated styrene/ethylene/butylene based triblock copolymer [26], sulfonated styrene/methylbutylene diblock copolymer, tert-butyl-styrene/ethylene/propylene/styrene/styrene sulfonate penta square copolymer [27,28], Kraton pentablock copolymer [29,30], sulfonated poly(vinyl alcohol)/polpyrrole [31], polyacrylonitrile–Kraton–graphene [32], Kraton/GO/Ag/Pani [33] and thorium(IV) phosphate-polyaniline [34]. The majority of these ionomers bear cation leading polymer layers since cations diffuse speedier than anions with a comparative effective radius.

In the present study, a novel non-perfluorinated sulfonated poly(vinyl alcohol), aluminium oxide ($Al_2O_3$), graphene and platinum (SPVA-Al-GR-Pt) based IPMC film actuator was developed by solution casting strategy with chemical reduction of Pt on the film surfaces as electrodes. The composite of two or more materials has advantageous and desirable properties which could not possible to be present in the individual material. The configuration of our interest was to develop such polymeric composite material based IPMC film, which can alternate highly expensive, environment non-friendly perfluorinated polymer, beside this having desirable properties and good actuation performance for robotic applications. Herein, a cost-effective non-perfluorinated polymer-sulfonated poly(vinyl alcohol) was used as base ionomeric material because of its certain advantageous properties such as admirable film forming capacity, easy modification of chemical properties, high ion exchange and water retention capacity and high proton conductivity. Recently, graphene (GR) became a very interesting filler for the composite materials because of its electronic transport properties, excellent electrical conductivity, exceptional thermal and high mechanical strength. Therefore, the incorporation of this two-dimensional carbon nanostructure has been predicted an immense pledge for many potential applications such as nanoelectronics, actuators and sensors, supercapacitors and nanocomposites [35–39]. Thus, the addition of GR to the SPVA can enhance the performance of IPMC [40,41]. The most familiar approach to produce a suitable dielectric material is the addition of inorganic particles to ionomeric composite. Incorporation of inorganic particles such as $Al_2O_3$ in composite results in improved dielectric properties, resistance, thermal stability and conductivity [42]. Thus, the combined chemical and electromechanical properties of composite SPVA, GR, $Al_2O_3$ may improve the mechanical stability, tip displacement and repeatability in the fabricated SPVA-Al-GR-Pt IPMC film. Therefore, SPVA-Al-GR-Pt IPMC can afford an easy and worthy way out for realization of the novel actuator, which can show good potential in miniaturized scale robotic system and related applications.

## 2. Experimental

### 2.1. Material

Poly(vinyl alcohol) (PVA) and hydrochloric acid (HCl-35%); (Central Drug House Pvt. Ltd., India), ammonium hydroxide ($NH_4OH$-25%); (Merck Specialties Pvt Ltd., India), graphene, aluminium oxide ($Al_2O_3$), 4-sulfophthalic acid ($HO_3SC_6H_3$-1,2-$(CO_2H)_2$-50 wt% aqueous solution); (Sigma-Aldrich Pvt. Ltd., USA), tetraamine platinum(II) chloride monohydrate [$Pt(NH_3)_4Cl_2 \cdot H_2O$ (Crystalline)]; (Alfa Aesar, USA) and sodium borohydride ($NaBH_4$); (Thomas Baker Pvt. Ltd., India), were utilized.

### 2.2. Preparation of the reagent solutions

Aqueous solutions of tetraamine platinum(II) chloride monohydrate (0.04 M), $NaBH_4$ (5.0%) and $NH_4OH$ (5.0%) were prepared utilizing demineralised water (DMW). Graphene dispersion was made by blending 50 mg of graphene in 20 ml of tetrahydrofuran (THF) with steady mixing up to 6 h at room temperature (25 ± 3 °C).

### 2.3. Fabrication of films

The ionomeric films were fabricated by dissolving almost 3 g of PVA in 75 ml of DMW followed by stirring at 60 °C for 6 h. For sulfonation of prepared homogeneous PVA solution, 3 ml of 4-sulfophthalic acid was added with constant stirring for 15 h at 60 °C. To this sulfonated poly(vinyl alcohol) (SPVA) solution, 0.5 g of $Al_2O_3$ powder was added trailed by adding 10 ml suspension of GR with consistent blending for 3 h at 45 °C. From that point onward, the homogeneous composite solution of SPVA, $Al_2O_3$ and GR (SPVA-Al-GR) was spread in 4 Petri dishes (100 × 15 mm (S line)) secured with Whatman filter paper (1) for the moderate vanishing of the solvents at 45 °C in an indoor thermostat oven. The film was crosslinked by setting in an indoor thermostat oven at 150 °C for 1 h. Thus, using 3 g of PVA four films of Petri dish sizes were fabricated. Therefore, the exact amount of PVA in one ionomeric polymer film was 0.75 g.

### 2.4. Water uptake

To decide the water uptake (WU) limit of SPVA-Al-GR polymer composite film, the pre-measured film was absorbed by DMW for 6 h. Subsequently, it was grabbed from the DMW and surface was wiped with filter paper, the film was weighed utilizing an advanced digital balance to calculate the weight of water absorbed by the polymer film. The WU of the proposed polymer layer was figured at room temperature (25 ± 3 °C) and 45 °C for the various interim of times e.g. 2, 4, 6, 8, 10 and 20 h. The WU of the polymer layer was calculated using the following formula:

$$WU = \frac{\left(W_{wet} - W_{dry}\right)}{W_{dry}} \times 100 \qquad (1)$$

Where $W_{wet}$ is the weight of water absorbed film and $W_{dry}$ is the weight of the dry film.

### 2.5. Ion-exchange capacity

The ion-exchange capacity (IEC (meq $g^{-1}$)), in general, a measure of the $H^+$ ions released by neutral salts to move through the polymer film was obtained by standard column process. The dried SPVA-Al-GR polymer film (0.25 g) was cut into little pieces and drenched in 1 M $HNO_3$ for 24 h to change into $H^+$ form, trailed by neutralization with refined water, and was dried at 45 °C. The dried SPVA-Al-GR polymer film in the protoned form was stuffed into a glass column. A 1 M $NaNO_3$ as eluent was utilized to elute the protons totally from the column, keeping up a moderate flow rate of 0.5 ml $min^{-1}$. A standard (0.1 M) NaOH solution was utilized to titrate the effluent using phenolphthalein as indicator, and the IEC (meq $g^{-1}$) was calculated using following equation:

$$Ion \quad exchange \quad capacity = \frac{Volume \quad of \quad \mathrm{NaOH} \quad consumed \times Molarity \quad of \quad \mathrm{NaOH}}{Weight \quad of \quad dry \quad film} \qquad (2)$$

### 2.6. Electroless plating

The SPVA-Al-GR-Pt film based IPMC was created by an electroless plating strategy [30,31]. The entire procedure of plating platinum comprised of the reduction utilizing a strong reductant ($NaBH_4$). The SPVA-Al-GR polymer film was at first roughened by gentle sand paper so as to expand the surface regions, trailed by washing with DMW, absorbing in an aqueous solution of 2 M HCl