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Evidence of counterion migration in ionic polymer actuators via investigation of electromechanical performance

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ABSTRACT

Functional ionomeric polymer membranes are the backbone of a wide range of ionic devices; the mobility of ions through the ionomeric membrane is the principle of operation of these devices. Drift and diffusion of ions through ionomeric membranes strongly depend on the ionic properties of host membrane, as well as the physical and chemical properties of the ions. It is well-established that cations and anions provided via a dopant (e.g. electrolyte or ionic liquid) are mobilized under stimulation. However, in this study, we report that in addition to ions sourced by the dopant, counterions of the ionomeric membrane are also mobilized when stimulated. In particular, we have investigated the electromechanical response of ionic electroactive polymer actuators consisting of Nafion ionomeric membranes with different counterions and have demonstrated that those with cation counterions of larger Van der Waals volume exhibit stronger actuation due to motion of the larger cation counterions compared to actuators consisting of Nafion with counterion of smaller Van der Waals volumes.

1. Introduction

Ionic properties and ion permeability of ionomeric membranes, especially those of Nafion, have been the subject of extensive and continuous studies in the past several years [1–4]. The significance of such studies is mainly due to the increasing importance and application of ionomeric membranes in ionic/electronic devices for energy generation and storage applications. The functionality of ionic devices relies on mobility of ions through the ionomeric membrane. Ion diffusion and/or drift through ion permeable polymer membranes is the most essential requirement for operation of ionic devices; such as lithium-ion polymer batteries, fuel cells, super capacitors and ionic electroactive polymer sensors and actuators, to name a few examples [5–12]. For instance, diffusion of protons through a proton-exchange membrane is the principle of operation of hydrogen fuel cells [13], and charging of secondary cell metal-ion polymer batteries (used in most smartphones and tablets) is solely based on the ion drift through a polymer electrolyte membrane when an external electric field is applied [14]. Better understanding of ion mobility through ionomeric membranes will provide means for development of electric/ionic devices with higher performance and efficiency.

Although ion mobility, both diffusion and drift, is well utilized in commercial devices, we still lack a complete understanding of this phenomenon. It is not yet clear to the scientific community the detailed process of how ions move through the ionomeric membranes and how this process can be manipulated. The general understanding is that Nafion is a proton-exchange membrane; thus, H^+ can easily diffuse through it. Diffusion of H^+ through Nafion is well studied and applied in many conceptual applications such as fuel cells [15]. There is no doubt about H^+ permeability of Nafion; however, when subjected to an electrical field Nafion is also permeable to drift of other ions [16–21]. Our prior work on ionic electroactive polymer (IEAP) actuators confirmed that, when doped with ionic liquid, Nafion is permeable to both cations and anions of the ionic liquid; and, the electromechanical response of IEAP actuators is directly proportional to concentration of the ions from dopant [22,23]. The functionality of IEAP actuators is solely the result of motion of ions through the ionomeric membrane. The common understanding is that cations and anions provided by the doping of the ionomeric membrane with electrolyte are responsible for the electromechanical response of IEAP actuators. Upon application of an electric field, cations and anions are mobilized

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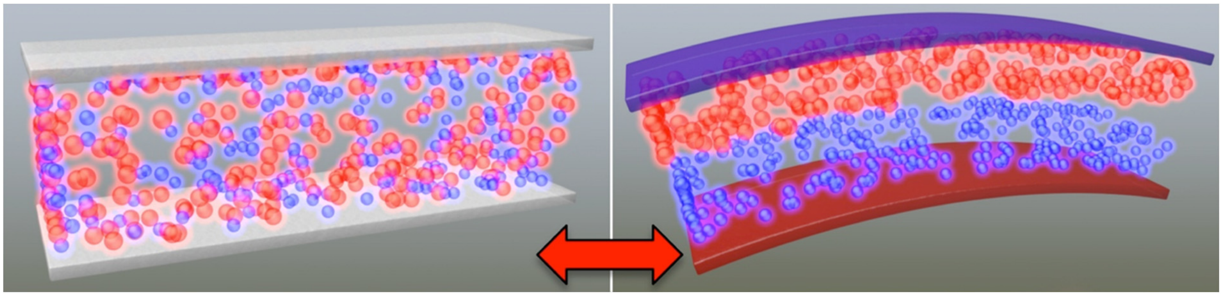

Fig. 1. Schematics of uncharged and charged doped 3-layer ionic electroactive polymer actuator. Red and blue spheres illustrate cations and anions, respectively. (*Not to scale*). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

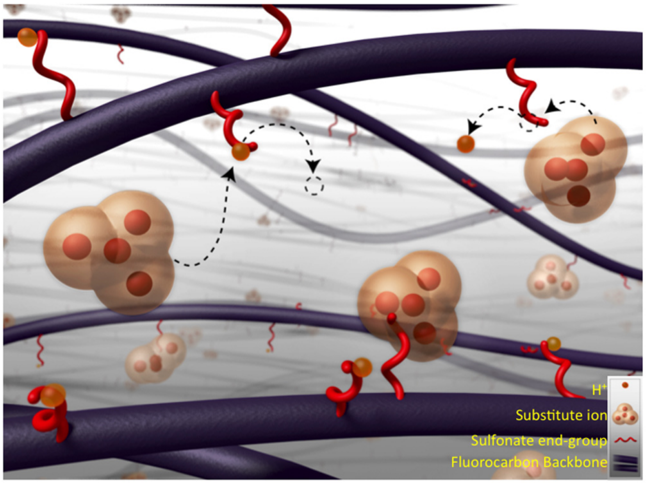

Fig. 2. Schematic presentation of ion-exchange process in Nafion. Proton counter-ions are substitute by other cations.

and move toward electrodes of opposite charge. Since cations and anions have different Van der Waals volumes, their accumulation at the cathode and anode results in a volume imbalance in the system; and thus, a mechanical deformation [24]; this phenomena is schematically presented in Fig. 1.

In this study we have altered the functionality of ionomeric membranes by exchanging the proton counterion of Nafion with larger cations; and have utilized the electromechanical response of IEAP actuators, consisting of Nafion with different counterions and dopants, as a means to study the mobility of ions through Nafion ionomeric membranes and, more specifically, investigate mobility of counterions of Nafion. Ion-exchange process is schematically demonstrated in Fig. 2. This work contributes to the knowledge of electric and ionic properties of ionic functional materials and their applications in electric and ionic devices such as sensors, actuators, fuel cells and metal-ion polymer batteries.

2. Experimental

2.1. Materials

Commercially-available Nafion membrane of 90 μm thickness (Ion Power, Inc.) was used as the base ionomeric membrane. 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-Tf, molecular formula: $C_7H_{11}F_3N_2O_3S$), triethylsulfonium bis(trifluoromethylsulfonyl)imide (TES-TFSI, molecular formula: $C_8H_{15}F_6NO_4S_3$) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI, molecular formula: $C_{11}H_{20}F_6N_2O_4S_2$) ionic liquids, and 1-ethyl-3-methylimidazolium chloride (EMI-Cl), zinc chloride and sodium chloride salts were purchased from Sigma Aldrich and used without further modification. Transferable 24 K gold leafs of 50 nm thickness were purchased from L.A. Gold Leaf and cut to desired size before using.

2.2. Methods

2.2.1. Ion-exchange

Salt solutions were prepared at 0.5 M concentration by dissolving the proper amount of the desired salt in deionized water. The solution was then stirred overnight. Ionic membranes of the desired size ($2.5 \times 12\,\text{cm}^2$) were cut out of a sheet of 90 μm thick Nafion and boiled in diluted (1 M) sulfuric acid solution at 100 °C for 120 min. Water was added frequently to keep the volume of the mixture constant and to compensate for the evaporated water. The samples were then boiled in deionized water at 100 °C for 120 min, then dried using a wipe and cut into smaller pieces ($2.5 \times 6\,\text{cm}^2$). Cut samples were then placed in ample amount of saturated salt solution in container with tightened caps, and heated to 80 °C for two days. The temperature was then reduced to 60 °C for another eight days to assure ion-exchange between the Nafion and salt solution. Considering high sensitivity of Nafion-ionic liquid systems to humidity [25,26], samples were then placed under vacuum (∼−100 kPa) and heated to 115 °C for three days to dehydrate and were kept in desiccator or used immediately.

2.2.2. Doping and assembly

Samples were then cut into smaller pieces ($2.5 \times 2.5\,\text{cm}^2$), weighed and soaked in the desired ionic liquid to uptake ∼40 wt% of their dry weight. Eq. (1) was used to calculate the electrolyte uptake, where $W_e(\%)$ is the weight-percent of the electrolyte; and, W_d and W_f are the weights of dry and doped samples, respectively.

$$W_e(\%) = \frac{W_f - W_d}{W_d} \times 100 \tag{1}$$

Gold leaves were hot-pressed at 95 °C, under 4500 N for 25 s on both sides of the ionic liquid-doped samples to fabricate ionic electroactive actuators.

2.2.3. Electromechanical characterization

Actuators were cut into approximately $1.5 \times 15\,\text{mm}^2$ pieces and tested under application of a 4 V applied potential. Electromechanical response of the actuators was monitored and recorded using a charge-coupled device (CCD) video camera, mounted to an in-house fabricated micro-probe station, at 30 frames per second. Individual frames were then analyzed to measure the radius of curvature (r) as a function of time and to calculate curvature (Q) from Eq. (2).

$$Q(t) = \frac{1}{r(t)} \tag{2}$$

For actuators with small tip displacement, strain can be calculated from free length, thickness and tip displacement of the