Ion-Selective Ionic Polymer Metal Composite (IPMC) Actuator Based on Crown Ether Containing Sulfonated Poly(Arylene Ether Ketone)

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This study introduces the concept of ion selective actuation in polymer metal composite actuators, employing crown ether bearing aromatic polyether materials. For this purpose, sulfonated poly(arylene ether ketone) (SPAEK) and crown ether containing SPAEK with molar masses suitable for membrane preparation are synthesized. The synthesized polymers are characterized using Nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). Ionic polymer metal composite (IPMC) actuators are fabricated by electroless chemical deposition of a platinum (Pt) layer on both sides of SPAEK and crown-ether containing SPAEK membranes, resulting in electrode layers of around 120 nm thickness. Actuation experiments demonstrate cation specific responses and bending degrees of the IPMC actuators. Incorporation of crown ether units in the polymer backbone results in an improved and ion-selective bending displacement compared with SPAEK actuators. S(25)C(50)PAEK actuators show an increased bending displacement of 28% for Na\(^+\) and 20% for K\(^+\) ions.

1. Introduction

A variety of polymers have been developed to imitate natural motions. In particular, polymers that exhibit deformations in response to applied voltages,\(^[3]\) which makes them promising candidates for use in biomedical devices,\(^[2]\) biomimetic robots,\(^[3]\) artificial muscles,\(^[4]\) and biomimetic sensors\(^[5]\) have raised much interest. Specifically, conducting polymers\(^[6,7]\) and ionic polymer-metal composites (IPMCs)\(^[8]\) have been employed in the development of muscle-like actuators. IPMCs consist of a hydrated ionic polymer membrane and metal electrodes, typically

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platinum (Pt) or gold (Au), plated on both surfaces of the membrane. The ionic polymer has covalently bound negative or positive charges that are neutralized by oppositely charged mobile counter ions. Under an applied voltage, for a polyanionic membrane, the solvated mobile cations move toward the negatively charged electrode. Redistribution of the cations and water molecules results in swelling near the negative electrode, shrinkage near the positive electrode, and bending of the IPMC actuator.

In muscles, membrane proteins are ion selective and gate the flow of K⁺ and Na⁺ ions in and out of cells by adopting closed and open states. The selective transport of these ions is of central importance for muscle contraction and expansion. Up to date, Nafion and sulfonated polymers such as poly(arylene ether sulfone), poly(styrene), poly(phenyl sulfone), and a sulfonated poly(ether ether ketone)-poly(vinylidene fluoride) blend have been reported in the literature as IPMC actuator materials. However, so far ion selective actuation, as natural muscles do, has not been reported in the literature. Here, we introduce the concept of crown ether incorporation in sulfonated poly(arylene ether ketone) (SPAEK) polymers for ion selective IPMC applications. As a proof-of-concept, we prepared SPAEK and crown ether containing SPAEK IPMC actuators to elucidate the influence of crown ether moieties in the SPAEK main chain on actuation. To the best of our knowledge, no reports have appeared in the literature on the use of crown ether-bearing ionic polymers to construct ion selective IPMC actuators. In the present study, we demonstrate the successful synthesis of SPAEK possessing skeletal crown ether moieties and its use in ion selective IPMC actuation.

## 2. Results and Discussion

### 2.1. Synthesis of S(25)PAEK and S(25)C(50)PAEK

In previous work, sulfonated poly(aryl ether ketones) possessing crown ether units in the main chain were synthesized using 4,4′(5′)-di(hydroxybenzo)-18-crown-6 as a monomer, which was formed in a three-step procedure. Here, a novel crown ether moiety suitable for use in polycrystallization reactions, a benzocrown ether bearing fluoro groups, is described. This monomer, obtained in a single step (Scheme S1, Supporting Information), allows one to incorporate crown ether moieties in a variety of aromatic step growth polymers, showing a similar potential as the previously reported 4,4′(5′)-di(hydroxybenzo)-18-crown-6. The details of the polymerization, structural (1H and 13C NMR and FTIR) and thermal properties (TGA and DSC) of S(25)PAEK and S(25)C(50)PAEK polymers are given in the Supporting Information.

### 2.2. Morphology of the IPMC Actuator

IPMC actuators were fabricated by electroless chemical deposition of a Pt layer on both sides of SPAEK and crown ether containing SPAEK membranes (see the Supporting Information for the details of membrane and IPMC fabrication). Figure S6 (Supporting Information) shows the surface and cross-sectional morphology of the S(25)PAEK IPMC actuator; a densely deposited Pt layer on the S(25)PAEK membrane is clearly visible. Scanning electron microscope (SEM) analysis shows that the Pt particles are homogeneously distributed over the S(25)PAEK membrane surface with a layer thickness of around 120 nm. Surfaces and cross sections of the corresponding crown ether-containing...
polymer membranes were very similar (Supporting Information, Figure S7).

### 2.3. Bending Actuation of S(25)PAEK and S(25)C(50)PAEK IPMCs

The electromechanical bending of the membrane cantilevers was quantified by measuring the tip displacement with respect to time. Figure 1 shows the responses of the K+ saturated S(25)PAEK and S(25)C(50)PAEK actuators to a sinusoidal voltage applied at a frequency of 10 Hz. A similar bending response was also observed for the actuators in their Na+ form. This bending was repeatedly observed and is due to the migration of hydrated cations (K+ or Na+ ions) and free water molecules under the applied sinusoidal voltage. The cations and water molecules migrate through the membrane, resulting in an asymmetric swelling of the IPMC matrix.[20,21] As seen in Figure 2a, the cathode side expands due to the accumulation of hydrated cations and free water molecules, whereas the anode side contracts, producing a bending toward the anode side.[19,22]

As our focus was to develop a fast ion-selective actuator capable of mimicking natural motion, the bending displacement of the S(25)PAEK (Figure 2b) and S(25)C(50)PAEK (Figure 2c) IPMC actuators for both K+ and Na+ ions was compared at 1.5 V at frequencies of 10, 15, and 20 Hz. An improved bending displacement of S(25)C(50)PAEK compared with S(25)PAEK was observed. Figure 3c shows an increase of 127 nm in the maximum displacement for a Na+ saturated S(25)C(50)PAEK actuator at a voltage frequency of 10 Hz, compared with S(25)PAEK. For K+ saturated actuators the difference was 88 nm at 10 Hz, but this decreased significantly at higher frequencies.

Figure 3a,b shows that the maximum tip displacement of Na+ saturated and K+ saturated actuators decreases with increasing frequency from 10 to 20 Hz. This is due to the voltage polarity change becoming faster than the migration of K+ and Na+ ions and water molecules in the IPMC actuator, leading to less bending.[16] Slightly larger displacements were observed for Na+ saturated actuators compared to their K+ saturated counterparts. This could be explained by the larger hydrated radius of Na+ ions,[23] facilitating the migration of more water molecules, resulting in a larger swelling and thereby displacement of the actuator. Guzman et al. formulated a model for the bending deformation of a Nafion IPMC actuator and compared the bending performance of the actuator for five different types of cations. In agreement with our result, their computational and experimental results showed that the actuator saturated with Na+ ions displayed larger bending deformations compared with the one saturated with K+ ions.[24]

Figure 3c shows that bending displacement improvement due to crown ether incorporation diminishes in the case of the K+ saturated actuators at higher frequencies. As there is not sufficient time for the K+ ions to dissociate from the crown ether moieties (Figure 4), consequently, only K+ ions interacting with the sulfonate groups (SO3-) contribute to the bending response at a frequency of 20 Hz. Dibenzo-18-crown-6 binds selectively to K+ ions and complexes more strongly with K+ ions compared with Na+ ions.[25–27] Therefore the Na+ ions can more easily dissociate from the crown ethers under an applied potential.

The various cation–crown ether interactions, shown in Figure 4, increase the concentration of cations in the crown ether containing SPAEK membrane relative to that in the SPAEK membrane without crown ethers, as reflected in the higher ion exchange capacity (IEC) values. Moreover, also the water swelling slightly increases after incorporation of crown ether (details of membrane properties are described in the Supporting Information). These combined effects of crown ether incorporation enhanced the bending displacement by 28% for the
Na⁺ ion (20% for K⁺) containing S(25)C(50)PAEK actuator relative to the native S(25)PAEK actuator. Moreover, this proof-of-concept demonstrates that the S(25)C(50)PAEK actuator exhibits an ion selective actuation performance, which was not observed for other sulfonated materials lacking crown ethers. Therefore, incorporation of crown ether moieties into the sulfonated polymer backbone can have an important contribution to the development of ion selective biomimetic actuators.

The bending actuation of the S(25)C(50)PAEK IPMC was compared with previously reported actuators. The displacement was normalized for different-sized IPMCs and the strain was calculated according to an equation proposed in literature. The maximum strain values
for the Na⁺ and K⁺ forms of the S(25)C(50)PAEK actuator at a frequency of 10 Hz are 0.53 ± 0.03 × 10⁻⁶ and 0.47 ± 0.01 × 10⁻⁶, respectively. This is almost nine times lower than the reported value for the Li⁺ form of a sulfonated poly(ether ether ketone) (SPEEK) IPMC actuator under 1.5 V at a frequency of 7 Hz. However, it is known that Li⁺ enhances the bending performance of IPMC actuators compared with Na⁺ and K⁺. Moreover, the electrode thickness, which in the case of the Li⁺ IPMC was about 80 times thicker, has a significant influence on the maximum tip displacement. The Pt layer thickness is one of the important parameters determining bending displacement. The Pt layer eliminates large voltage drops away from the contact electrode by decreasing the surface resistance of IPMCs. A lower surface resistance enhances the conductivity through the membrane, resulting in a large bending displacement. Tang et al. prepared a SPEEK IPMC actuator with an IEC of 1.5 mol kg⁻¹ and Pt electrode thickness of 7–8 μm. In spite of their higher IEC and thicker Pt layer compared with the S(25)PAEK and S(25)C(50)PAEK actuators, the SPEEK actuator exhibited very low actuation performance under a 1.5 V applied voltage at 10 Hz with a bending strain of almost zero. This leads to the conclusion that despite our rather thin electrode layer, the current was still uniformly distributed through the IPMC, albeit at a lower bending performance compared to literature.

3. Conclusions

A newly designed, crown ether containing SPAEK IPMC actuator demonstrated ionic selective actuation with an improved bending displacement compared with SPAEK actuators lacking crown ethers incorporated in the constituent polymer main chain. Although the achieved bending displacement was low in this primary study, the performance of this actuator can potentially be tuned further by varying the degree and type of crown ether incorporation, the sulfonation degree of the polymer, and the thickness of the membrane and of the electrode layers. The promising ion selective actuation shows that this novel crown ether bearing ionic polymer actuator holds great potential to mimic natural muscle-like motion.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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