

Electrochemical Behavior and Electromechanical Actuation of Polyaniline in Non-aqueous Electrolytes

Wen Lu and Benjamin R. Mattes

Santa Fe Science and Technology

3216 Richards Lane, Santa Fe, NM 87505, USA

Due to their properties of being lightweight and low operational voltages, use of conducting polymers in the development of electrochemical actuators has been an attractive topic in recent years. This type of actuator relies upon the application of an electrochemical stimuli to change the oxidation level of the polymer, which results in the ingress and egress of counterions to satisfy the neutrality and thereby its volume. The majority of research into conducting polymer actuators to date has been carried out in aqueous electrolytes. However, several disadvantages associated with aqueous electrolytes (e.g. narrow electrochemical window and fast electrolyte evaporation) and conducting polymers in aqueous media (e.g. degradation at high potentials) have been confirmed to be the main factors limiting the lifetime of conducting polymer based electromechanical actuators. Therefore, use of non-aqueous electrolytes with a high boiling point, a low vapor pressure, a high dielectric constant and a wide electrochemical window would be advantageous for the fabrication of stable and durable conducting polymer actuators. In this work, we investigated the effect of dopant anion on the electroactivity and electro-mechanical bending actuation of gilded polyaniline bilayers in propylene carbonate, and then fabricated a solid-state polyaniline bending actuator.

Freestanding polyaniline films used to fabricate the actuators were prepared from emeraldine base dissolved in N-methyl-2-pyrrolidinone (NMP). After acid doping, these films generally have conductivities between 1-10 S/cm and consequently the applied voltage would decrease along the length of the polymer film. Therefore, the EB films were gilded using commercially available gold leaf (thickness approx. 5 μ m) by applying a 2 wt % EB/NMP solution to one side of the polyaniline film and then carefully applying one layer of the gold leaf. With the attachment of a thin gold layer on the back, a uniform potential distribution in the polyaniline films could be achieved. The gilded EB films were doped in 1 M acidic aqueous solutions for 24 hours and then dried under dynamic vacuum for 24 hours to remove any water.

The electroactivity of conducting polymers in the electrolytes used plays an important role in determining their actuation properties. Electrochemical behavior of gilded doped polyaniline films in 1 M lithium perchlorate/propylene carbonate from -0.4 to +0.8 V vs Ag/Ag⁺ was performed using an EcoChemie pgstat30 potentiostat with a three-electrode system. It was found that the electroactivity of doped polyaniline films in propylene carbonate was strongly determined by the solubility of doping acid anion in the electrolyte. We investigated a range of acids for the doping of the polyaniline films, and according we could classified the acids into two groups based on the solubility of the dopant anion in propylene carbonate. The polyaniline films doped with group 1 acids (i.e. HClO₄, HBF₄, CF₃COOH, HPF₆ and CH₃SO₃H) showed well-defined electroactivity due to the fact that the dopant anion was soluble in the propylene carbonate electrolyte. On the other hand, for acids whose corresponding anions were insoluble in the electrolyte, labeled group 2 acids (i.e. HCl, HNO₃, H₂SO₄,

CF₃SO₃H, C₆H₅SO₃H), showed little or no electroactivity in the electrolyte. This was confirmed to be due to the difficult expulsion of dopant anion into the electrolyte.

In bending actuation measurements, a gilded polyaniline film was partially immersed into the propylene carbonate electrolyte. The sample was connected to the potentiostat using a gold-plated alligator clamp without teeth. The polyaniline film was imaged using a video camera, and a transparent protractor was placed over the image on the TV screen so that bending angles could be measured (to an accuracy of less than 1 degree). The bending angle was recorded manually during potentiodynamic stimulation from -0.4 V to 0.8 V vs Ag/Ag⁺ at a scan rate of 5 mV/s. As expected, the action performance of the doped polyaniline films is related to the electroactivity of the film in the propylene carbonate electrolyte. For the polyaniline films doped with group 1 acids, good actuation of the gilded film was observed. The highest bending angle (99⁰) was obtained for the CF₃SO₃H doped polyaniline film. However, for films doped with group 2 acids, no bending actuation was observed due to the difficult expulsion of the dopant anion.

Electrochemical AC impedance measurements were used to investigate the relationship between polyaniline actuation and its faradic and capacitive behavior for the gilded polyaniline films doped with group 1 acids. This measurement was performed in 1 M LiClO₄/propylene carbonate electrolyte at different potentials between 0.05 Hz and 100 kHz using an amplitude of 10 mV for the sine wave. It was found that the capacitive behavior of the polymer was the major contributor to bending actuation of polyaniline in non-aqueous electrolytes.

Finally, a solid-state polyaniline bending actuator was fabricated from two identical gilded CF₃SO₃H doped polyaniline films, as this material displayed the highest bending angle. A PMMA/PC/EC/LiClO₄ gel electrolyte was sandwiched between these two gilded polyaniline bilayers. The applied voltage needed to operate our prototype actuator was around 0.8 V, which was much lower than that of ~5 V that was used for the previously reported by Kaneto et al¹⁻². Bending was achieved as soon as the voltage was applied (about 25⁰ for the first cycle) and then increased slightly for the following cycles for our prototype. The bending degree of our actuator (~40⁰) was about the same as that of the previously reported actuator and the bending time of our prototype was only 12 to 15 seconds even with an applied voltage of 0.8 V. From the best result obtained for the previously reported actuator (V_{app} = 5 V, bending degree = 40⁰, bending time = 2 minutes), the actuation speed can be estimated as 0.3⁰/sec, while that of our actuator was 2.5⁰/sec (i.e. 8 times faster).

References

1. K. Kaneto, Y. Min and A.G. MacDiarmid, *US Patent* #5,556,700 (1996).
2. Y. Min, A.G. MacDiarmid, K. Kaneto, *Polymer Mater. Sci. Eng.*, (1994) **71**, 713-714.