Electrode reactions in Cu-Pt coated Nafion® actuators

U. Johanson[1, a], U. Mäeorg[2, b], D. Brandell[1, c],

A. Punning[1, d], J. Torop[1, e], M. Kruusmaa[1, f] and A. Aabloo[1, g]

[1]IMS Lab,Institute of Technology,Tartu University, Nooruse 1, 50411 Tartu, Estonia

[2]Institute of Chemistry, Tartu University, Jakobi 2, 51014 Tartu, Estonia

[a]urmas.johanson@ut.ee, [b]uno.maeorg@ut.ee, [c]brandell@vt.edu, [d]andres.punning@ut.ee, [d]janno.torop@ut.ee, [f]maarja.kruusmaa@ut.ee, [g]alvo.aabloo@ut.ee,

Abstract. Composite actuators consisting of sheets of the solid polymer electrolyte (similar to Nafion®) with Cu^{2+} counter-ions inserted and coated with platinum and copper metal layers (so called Ionomeric Polymer-Metal Composites; IPMC-s) have been synthesized and their electromechanical performance upon actuation has been monitored. Resistivity measurements on the electrodes show that the electrical conductivity of the membranes metal surface increases on the cathode side during the actuation process, contradictory to the situation when Cu is absent from the metal coating. This phenomenon is explained by the subsequent reduction of Cu^{2+} ions on the cathode upon actuation; Cu layer growth in this side prevents it from cracking and decreases its electrode resistance. The phenomenon opens up for longer life-times for Cu-based IPMC-s. However, additional problems with Cu layer oxidation and Cu dendrite growth on the electrodes should be considered.
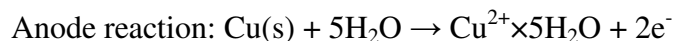
Introduction

Electroactive polymers (EAP-s) are polymer materials that change their shape or size in response to electrical stimuli. The feature makes this class of materials to a good candidate for using in the field of biomimetic devices, since it mimics the behavior of biological muscles. EAP-s inhibit similar properties to biological materials in terms of force, strain and speed. They are attractive for creating artificial muscles used in biologically inspired robots [1], biomedical devices and security applications [2].

Ion-conducting polymers have been used widely as EAP materials. They have the advantage of operating at low electric voltages. Among the most commonly used ionic EAP systems are the ionomeric polymer-metal composites (IPMC-s), consisting of a 200 to 400 micron thick ionomer membrane (most commonly Nafion® [3]) plated with metal (typically with Pt or Au) and with metal ions coordinating to the ionic groups in the polymer. The material exhibits a bending motion when a potential of 1-5 V is applied over the metal surfaces [4]. The applied electrical field causes the mobile cations in the swollen polymer film to move towards the cathode, which leads to an expansion at this side of the membrane and therefore causes the membrane to bend towards the anode in an actuating motion [5].

One of the problems facing these materials, and their future use as actuator, is that the bending motion gives rise to cracks in the surface metal layers that constitutes the electrodes. The cracks lead to leakage of solvent from the ionomer, and thus to lower ion conductivity and a lower degree of bending. The phenomenon also gives rise to a higher electronic resistance in the surface electrode layers, and thus to slower response time and a smaller actuating motion. Therefore, an increase of active lifecycles could be achieved by improving the mechanical and electrical properties of the surface electrode layers [6].

In our study presented here, we report on our efforts to overcome the problem with the metal cracking by using Cu as a composite material together with Pt as electrode, and Cu^{2+} as counter ion to the Nafion® sulphonate groups. Similar type of IPMC materials are reported first by Uchida and Taya [7,8,9]. They showed that when a voltage is applied over the membrane, the following electrochemical reactions occur in the material:

Anode reaction: $Cu(s) + 5H_2O \rightarrow Cu^{2+} \times 5H_2O + 2e^-$
Cathode reaction: $Cu^{2+} \times 5H_2O + 2e^- \rightarrow Cu(s) + 5H_2O$

They also observed that when a series of electrical impulses with the same voltage polarity were applied for a long time, copper on the surface of the anode vanished. At the same time a new copper layer was formed on the cathode side. In the meantime, Cu^{2+} ions in the polymer transported water molecules from the anode to the cathode side. The process is reversible, so that when the polarity of applied impulses to the electrodes change, the water and Cu-ions transport goes in the opposite direction through the membrane.

Since the expansion of the cracks in the Pt-layer occur on the same side of the membrane as the Cu-layer growth (i.e. the cathode side), this growth may compensate for some of the cracking, leading to increased electrical conductivity and higher mechanical and chemical stability in the cathode surface layer. We have monitored this by measuring the resistance per unit length in the two surface layers using the non-symmetrical actuation process.

Experimental

IPMC synthesis. Ready-made Pt-coated Na-ions containing MuscleSheet™ IPMC-s were purchased from BioMimetics Inc. These IPMC-s are 200-400 microns thick, and contain ionic polymer which is similar to Nafion® 1110 but not fully fluorinated. Three 3 cm long and 1 cm wide strips were cut out, and their actuator response was tested prior to further synthesis.

Subsequently, the strips were boiled for 20 minutes in 1 M HCl (aq) to substitute all Na^+-ions with H^+-ions, after which the samples were cleaned from residue of hydrochloric acid by boiling in demonized water. Thereafter, the sheets were put in 2 M $CuSO_4$ (aq) for 12 hours; afterwards the presence of Cu^{2+}-Nafion® was verified by optical microscopy: the cross-section of the membranes had a clear blue color. The blue color also indicates that each Cu^{2+}-ion is complexed by 5 molecules of water. Finally, the IPMC sheets were coated with Cu-layer by electrochemical plating from $CuSO_4$ solution. All chemicals used were analytical grade, and were used without further purification.

The quantity of copper deposited during the electrochemical plating was controlled by the amount of charges passing through the system during the copper layer preparation. Calculated from the passed current, the average thickness of the copper layers was 2 microns. The formed copper layers were however uneven, which is a familiar effect of the electrical field being stronger at the rim, therefore resulting in a faster metal layer formation there.

For detection of Cu^+ compound formation, some samples were left overnight in 2 M $CuSO_4$ (aq) while other samples were left in demonized water prior to X-ray microanalysis.

Surface resistance measurements and X-ray microanalysis. The experimental setup used for the resistance measurements and its benefits in the context of IPMC-s have been described in detail elsewhere [10]. A schematic picture of the experimental setup is shown in Fig. 1.

We clamped the IPMC strips in vertical cantilever positions in a container filled with de-ionized water. Four pairs of contacts (gold) were attached to each sample. These contacts were made as lightweight as possible, but strong enough to ensure good contact. The measurements were conducted using National Instruments LabView7 control software. The driving voltage was

generated by NI PCI-6703 DAQ board and amplified with NS LM675 power op-amp. Voltages on all contacts with respect to the ground were measured with National Instruments PCI-6034 DAQ board.
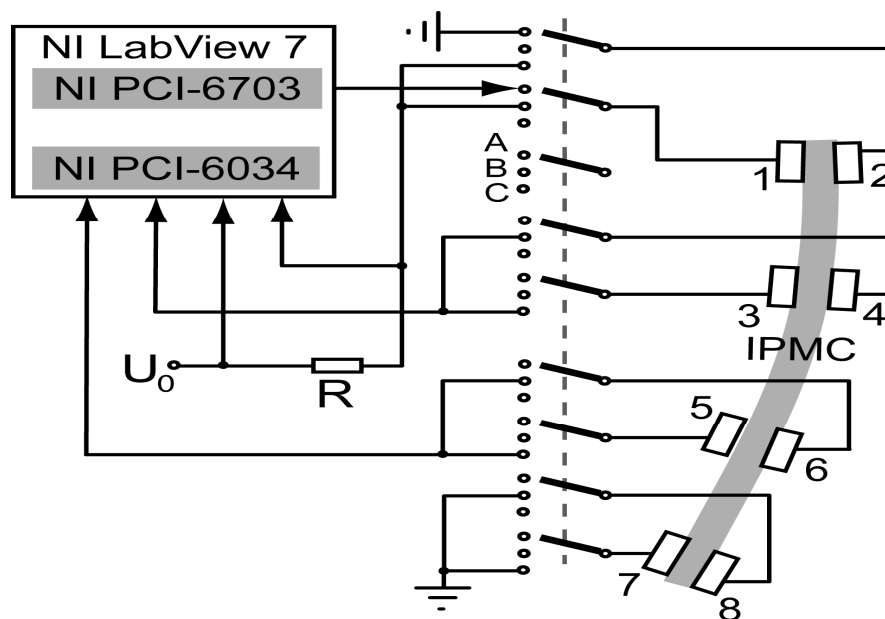

Figure 1. The experimental setup for measuring resistance on the surface layer of an IPMC.

The measurements of the surface resistance were conducted using a four-probe system. This method has been shown to eliminate inexactnesses caused by the inconsistent current density and resistance from the contacts [11]. The actual values of the reference voltage U_0 and the resistor R in Fig. 1 were selected according to the range of the DAQ performing the measurements, but were all far below the voltage limit for electrolysis. The actual electric current during the measurement of membrane surface metal layer (electrode) resistance was in the range of 1-6 mA.

In order to ensure galvanic insulation of the contacts on the opposite sides of the sample during the measurements, a 8-channel 3-position switch was used. In position A in Fig. 1, the driving voltage from the switch is fed to contacts 1-2 on the sample. In position B, the surface resistance on one side of the sample is measured between contacts 3-5, using the contacts 1-3-5-7. In position C, the surface resistance on the other side of the sample is measured between the contacts 4-6.

To study the growth of Cu dendrites, the muscle sheet actuation was driven at a too high voltage for this kind of material – 4.5 V – which made the system short-circuit after 300 cycles. Samples prepared this way were used for X-ray microanalysis measurements and for taking scanning electron microscope images.

The composition of the IPMC actuators was determined by X-ray microanalysis using JXA-840 (JEOL, Japan) equipment supplied with an energy dispersive spectrometer (Voyager, Noran, USA). The K_α lines were used as analytical X-ray lines for the determination of the content of Cu, Cl, S. The L_α lines were used as analytical X-ray lines for the determination of the content of Pt.

Results and discussion

Cu-Pt coated IPMCs. Table 1 summons the resistance measurements of the three samples after they have been coated with an additional copper layer. Similar to untreated membranes, there is a large difference in electrode resistance per unit length between the left and right side of the

membranes, and between the individual membranes, probably due to cracks and other imperfections in the coating metal layers. All samples were then first bended to the right direction for 100 cycles, where the motion during one cycle was actuated by a 2V pulse of 2 seconds, followed by a opposite potential step from a -2V pulse during 1 second. It could be observed that the bending angle decreases continuously over the cycles, with the initial bending being at around 45º.

Table 1. Electrode resistance measurements results.

Total No. of bending cycles	Bending direction during next 100 cycles	Left electrode resistance [Ω/cm]	Right electrode resistance [Ω/cm]	Left electrode resistance [Ω/cm]	Right electrode resistance [Ω/cm]	Left electrode resistance [Ω/cm]	Right electrode resistance [Ω/cm]
		Sample 1		*Sample 2*		*Sample 3*	
0		9.5	57	4.1	26	2.0	13
100	Right	2.4	> 400	1.5	> 400	1.2	200
200	Left	5.7	0.95	2.1	3.2	2.0	0.65
300	Right	0.62	1.7	0.58	21	0.60	100

Electrode resistance per unit length at the left and right electrode for Cu-Pt-coated IPMC-s after bending with cycles containing asymmetrical steps in one direction (first, +2V for 2 s and −2V for 1 s after that) or in another direction (first, −2V for 2 s and +2V for 1 s).

Due the ionic conductivity of the membrane, it is impossible to measure the electrode resistance directly at the same time as when the voltage is applied to the sheet and therefore the corresponding measurements were done quickly after switching off the voltage. However, after switching off the outside voltage a very fast relaxation process of the sheet occurs. It relaxes back from its bent state due to water leakage through the electrode cracks and water diffusion towards the anode. This relaxation goes faster for the Cu/Cu^{2+}-based IPMC-s than for the conventional forms, based on Li^+- or Na^+-Nafion®. The reason for this is that the water molecules transported to the electrode surface are uncomplexed to any cation after the reduction of Cu^{2+} to Cu, and therefore are freely mobile. All measurements of the electrode resistance were thus done in non-bent state. After these measurements, the polarity of the driving pulses was switched, and the samples were bent another 100 cycles to the left direction. Finally, they were bent yet another 100 cycles to the right direction.

It is clear from the data presented in Table 1 that the Cu-coated membranes display an opposite phenomenon compared with those only coated by Pt. The resistance per unit length increases at the side to which the material is bended (the anode side) and it decreases at the other (cathode) side. Therefore we assume that a new layer of Cu is formed between Pt-particles in the electrode layer and also in the Nafion® matrix close to the Pt-electrode on the cathode side. At the same time, Cu is depleted from the anode side during the creation of Cu^{2+} ions. Both these electrode reactions occur while the Cu^{2+} ions migrate toward the cathode in the polymer matrix, and thus the process assists to pump water in that direction, causing the actuating motion. This continuous production of Cu^{2+} also represents an elimination of another limitation to the use of IPMC-s, since back-diffusion of cations towards the anode will be much less of a problem. Yet another positive factor to take into account is that the number of possible mobile cations increases with several orders of magnitude compared to IPMC-s without electrochemical electrode reaction. In IPMC-s the number of mobile ions is usually limited by cations initially paired to the polymer $-SO_3^-$ groups, while here new Cu^{2+} ions are created at the anode during the actuation process. Therefore the water quantity which can be
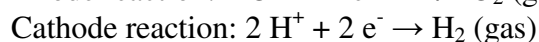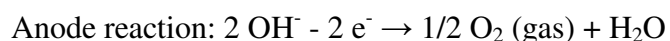
transported in this system should be significantly higher. This, however, increases the importance of solvent leakage protection at the electrodes.

Although the variations in resistance per unit length is large, and fluctuates severely upon switching the polarity for 100 cycles, it is also clear from the data presented in Table 1 that the final resistance values of the electrodes are lower than the initial values prior to cycling. The only exception to this rule is the right side electrode of sample 3, which however displayed highly fluctuating values in resistance, possibly due to an imperfect Pt coating. In fact, the data in Table 1 suggests that the electrode conductivity is continuously improving upon cycling. These results indicate that the Cu layers in the samples are displaced over the cycling process, getting more evenly distributed over the surface and in better contact with the Pt particles.

The results in Table 1 are promising in the context of developing IPMC-s, since they show that the problems of cracking here have been overcome, which opens up for longer lifetimes. The problem with this type of IPMC-s rather seems to be the Cu depletion on the anode side, which possibly is the reason for the decreasing bending angle upon cycling. This problem should however be possible to solve by improving methods of preparation of copper on the electrodes, or any other electronically conductive additive to the membrane surfaces. The artificial muscle fibers also actuate at a low voltage, which avoids the problems of electrolysis – common for other IPMC-s – and generates bending as far as 90º already at 2V.

Unwanted side-reactions. Although the resistance data for the Cu-coated IPMC-s look promising, we observed unwanted side-reactions during our measurements. These side-reactions in turn cause new problems for the IPMC-s. First, if the sheet actuation was driven at too high voltage for such type of material – 4.5 V – the system clearly short-circuit after 300 cycles. This indicates the growth of Cu dendrites, which is known to occur in many other systems for example lithium batteries [12], and was confirmed by optical microscopy and SEM. SEM data shows that the actuator contains a lot of holes in polymer matrix.

The only obvious explanation for these holes is that they are results of micro-explosions of detonating gas (a 2:1 mixture of hydrogen and oxygen), which melts the surrounding polymer. Both gases are produced on the copper dendrites (which in turn are connected with electrodes) during the alternating polarity:

Anode reaction: $2\ OH^- - 2\ e^- \rightarrow 1/2\ O_2\ (gas) + H_2O$
Cathode reaction: $2\ H^+ + 2\ e^- \rightarrow H_2\ (gas)$

For the gas explosion to occur, however, a catalyst (platinum) is needed at the room temperature. Nevertheless, an actuator with platinum electrodes, and which is prepared using impregnation-reduction methodology, always contains small amount of platinum inside of the polymer matrix.

Another observation is the appearance of non-conductive insoluble Cu^+ compounds on the electrodes. Cu^+ ions are created through the spontaneous redox reaction between Cu atoms in the metal electrode layer and Cu^{2+} ions in the membrane:

$Cu(s) + Cu^{2+} \rightarrow 2\ Cu^+$
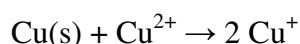
Cu^+ compounds are quite stable in these conditions (often insoluble in water), which means that the salt formation depletes the Cu(s) layers, and thus raises the resistance again on the electrode surfaces; the salts are also electronically isolating. The formation of Cu^+ salts severely decreases the lifetime of the IPMC-s, and it was therefore necessary to conduct our resistance measurements directly after the Cu-coating. If the samples were left overnight in 2 M solution of $CuSO_4$, the Cu-layer had transformed almost completely into a Cu^+ salt. In addition, initially blue colored ionic

polymer layers turned colorless after long time (several days) due to the reduction of blue colored water complex of Cu^{2+} to colorless Cu^+ compounds.

Using X-ray microprobe elemental analysis, we found that this salt only contains the elements copper and chlorine. It gives us reason to suppose that it is CuCl, since there exists no other insoluble compound containing only these two elements. When putting fresh copper plated IPMC samples in deionized water, i.e. without boiling it in hydrochloric acid first, no essential changes could be observed. We therefore reached the conclusion that small remains of Cl^- ions after the cleaning in hydrochloric acid caused the CuCl (s) formation.

Summary

We have here presented a quantitative study of the variations in electrode resistance per unit length for Cu-coated Nafion®-based IPMC-s upon actuation cycling. We showed that the depletion of Cu(s) at the anode side, and the formation of a new Cu(s) layer at the cathode side, give raise to an opposite resistance per unit length profile than for ordinary Pt-coated IPMC-s. This, in turn, represents an excellent possibility to overcome the problem of resistivity increase due to the electrode cracking on the cathode side upon actuation. However, formation of Cu dendrites and insoluble Cu^+ compounds cause severe limitations for these IPMC-s, and these problems must be treated further. It is also necessary to overcome the water leakage through the electrode cracks.

Acknowledgements

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