Self healing properties of Cu-Pt coated ionic polymer actuators

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INTRODUCTION

Composite actuators consisting of sheets of the solid polymer electrolyte with Cu^{2+} counter-ions inserted and coated with platinum and copper metal layers (so-called Ionomeric Polymer-Metal Composites; IPMCs) have been synthesised and their electromechanical performance upon actuation has been monitored. Resistance 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 IPMCs.

EXPERIMENTAL

Ready-made Pt-coated Na-ions containing MuscleSheet™ IPMCs were purchased from BioMimetics Inc. These IPMCs are 0.2-0.4 mm thick, and contain ionic polymer which is similar to Nafion® 1110. 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 deionised 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 colour. The blue colour 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, according to the procedure described by Uchida et al [1].

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 µm. 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.

The experimental setup used for the resistance measurements and its benefits in the context of IPMCs have been described in detail elsewhere [2]. A schematic picture of the experimental setup is shown in Figure 1A.

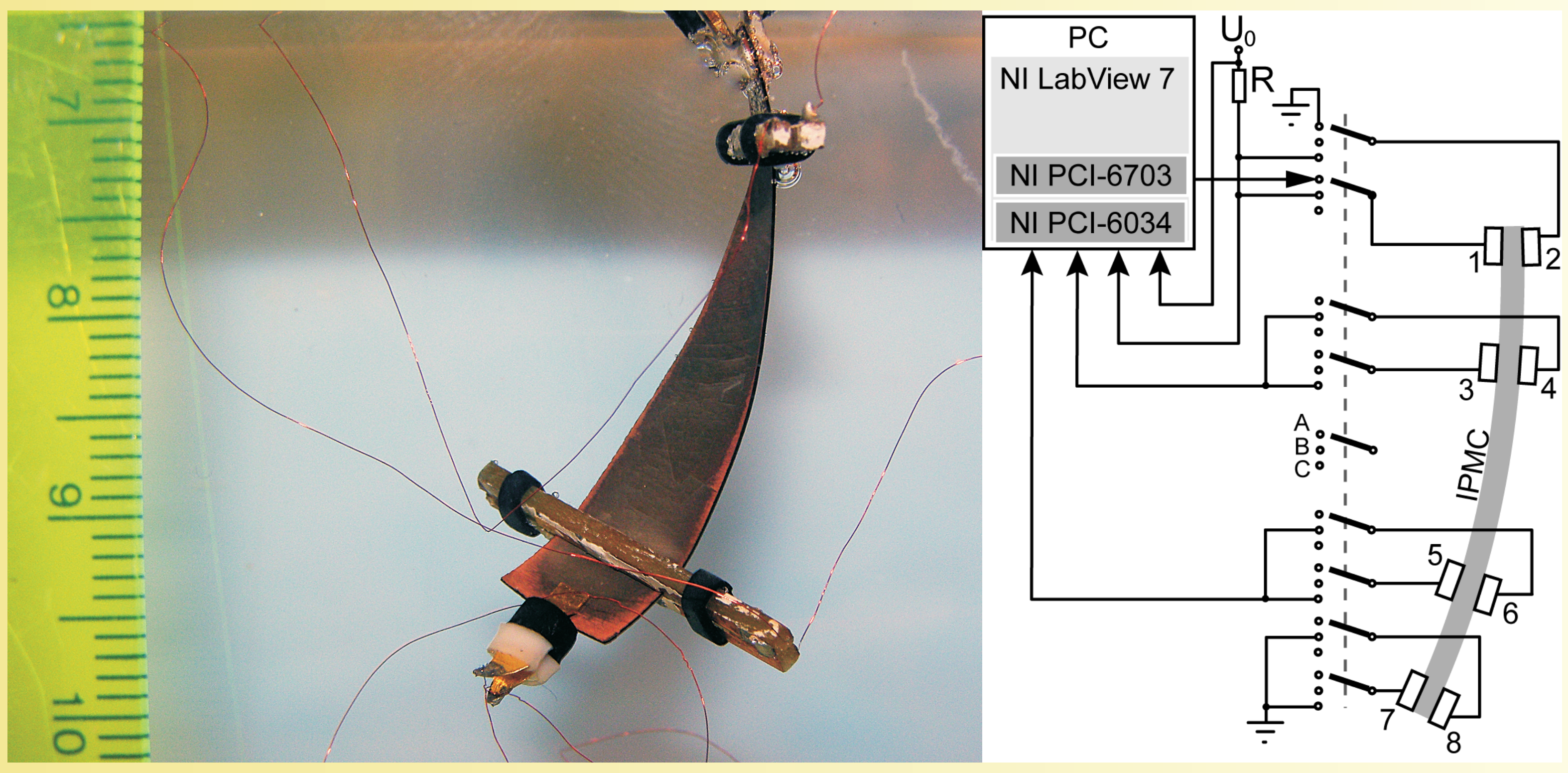

Figure 1. A) A Cu-coated IPMC sample with contact,
B) The experimental setup for measuring resistance on the surface layer of an IPMC.

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 (Figure 1B). 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.

The measurements of the surface resistance were conducted using a four-probe system. The actual values of the reference voltage U_0 and the resistor R in Figure 1 B 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 Figure 1 B, 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.

The measurements were conducted in the following order:

1. The switch was in position A, and the samples were fed with asymmetrical driving pulses: 2 seconds with one polarity, followed 1 second with the opposite polarity. The samples were treated for 100 cycles before the surface resistance was measured.
2. By swiftly switch to positions B and C, the surface resistances of both sides of the samples were measured.

The experiment was repeated by applying reversely asymmetrical driving pulses; the pulse for one cycle is shown in Figure 2 A.

RESULTS

Pt-coated actuators

- Figure 2 B shows how the surface resistance changes upon mechanical bending. Very typical situation for such type of IPMC-s shows that the strips are somewhat bended in their relaxed states.
- The strips behave as expected: when bended to the left, the metal surface layer on the right side of the electrode cracks, which results in a severe increase in resistance per unit length.
- At the same time, the resistance on the left side of the material decreases, due to that the metal particles are being pressed together.
- This process is reversible, so that when the material is bent in the other direction, to the right, the resistance drops on the right side, while it increases on the left.

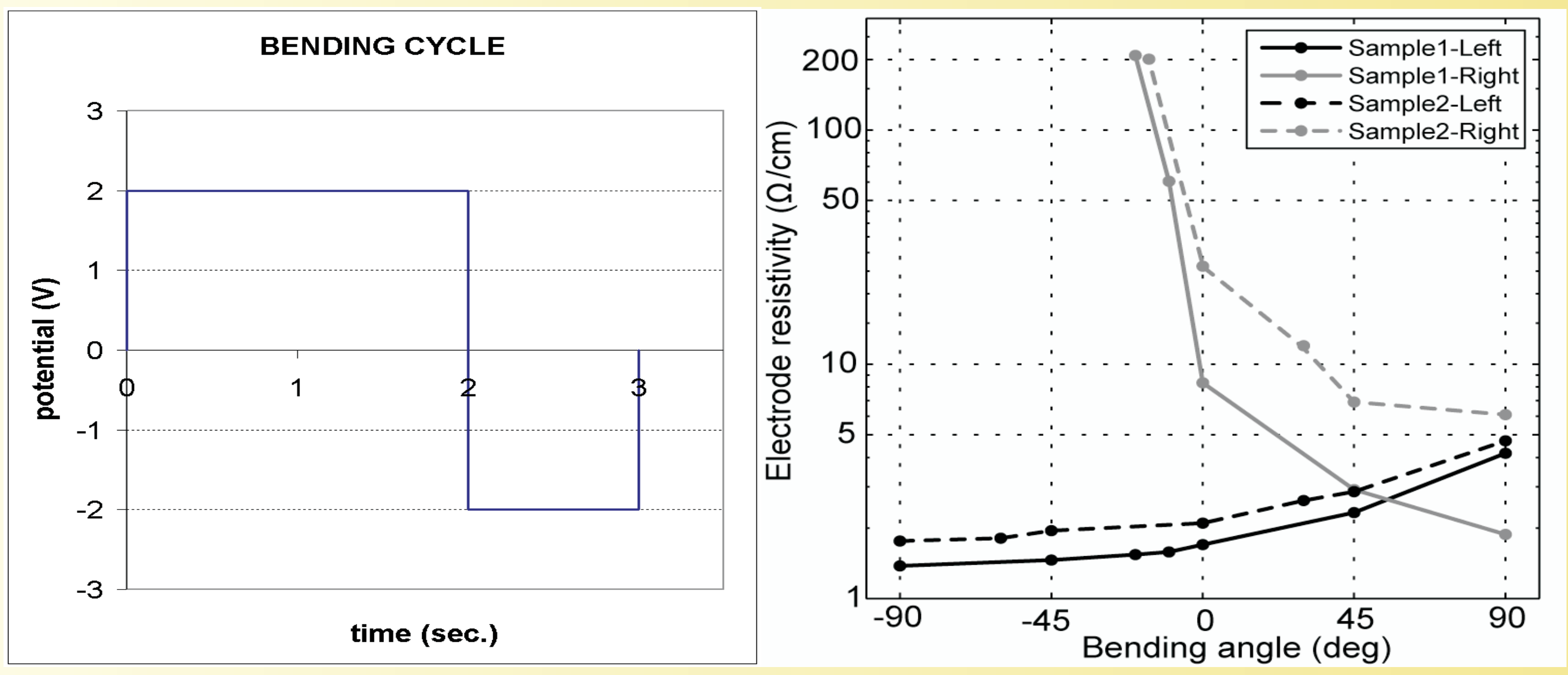

Figure 2. A) Driving pulses during one cycle in a resistance measurement.
B) Electrode resistance per unit length at the left and right electrode for Pt-IPMC-s upon mechanical bending. Bending to negative angles corresponds to bending towards the left.

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

Table 1. Resistance measurements of the three samples after they have been coated with an additional copper layer.

- The behaviour of copper plated IPMC electrode resistance per unit length is ecactly oposite to the to the behaviour of IPMC without copper layer. Resistance decreases at the cathode side.
- This process is reversible, so that when the material is bent in the other direction, the resistance drops on the new catode side.
- Typically during the experiments conductivity values of electrodes are improving.

CONCLUSIONS

- We have here presented a quantitative study of the variations in electrode resistance per unit length for Cu-coated Nafion®-based IPMCs 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 IPMCs.
- This represents an excellent possibility to overcome the problem of resistivity increase due to the electrode cracking on the cathode side upon actuation.

ACKNOWLEDGEMENTS

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