**Electroactive polymer actuators with carbon aerogel electrodes**

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**Abstract**

Electroactive polymers (EAPs) are soft materials whose shape is changed in response to the voltage stimulus. They can be used as actuators or sensors. Several researchers have introduced different materials and methods for assembling EAPs. Now it is generally accepted that the porous structure of electrodes with possibly high specific area can greatly improve the actuation performance. In this paper, a carbon aerogel is introduced as a new material for fabrication of nanoporous electrodes for EAP actuators. Using the direct assembly process (DAP), carbon ionic-liquid EAPs with either activated or non-activated carbon aerogel electrodes are synthesized. Their electrochemical and electromechanical characteristics are presented and compared to our recently reported actuators based on carbide-derived carbon and activated carbon electrodes. The results show that our newly developed actuators with non-activated carbon aerogel electrodes and activated carbon aerogel electrodes have maximum strains of 1.3% and 1.1%, respectively, which are comparable to our previously reported actuators and also any other low-voltage driven EAP actuators.

*Keywords*: Actuator; Electroactive polymer; EAP; Ionic Polymer Metal Composite; Nafion; Carbon Aerogel; Carbon Electrode; Carbide Derived Carbon.

**1. Introduction**

Electroactive polymers (EAP) are soft, flexible materials that can convert electrical energy into mechanical energy or vice versa. The ability to respond quickly with large bending deformations makes them attractive for a wide range of applications including biomimetics, robotics, micro-electromechanical systems, and medical devices. EAPs can be manufactured using variety of different materials. Based on the actuation mechanism, they are generally divided into two principal classes: electronic EAPs, *e.g.* dielectric elastomers, in which the actuation is initiated by electric field or Coloumb forces, and ionic EAPs, in which the actuation is produced by displacement of ions inside the polymer [[[2]](#endnote-1)].

One of the most widely studied ionic EAPs are ionic polymer-metal composites (IPMCs), which typically consist of thin ionic polymer membrane (*e.g.* NafionTM) plated on both faces with noble metal (Pt or Au) electrodes. When the voltage is applied to the electrodes, the IPMC undergoes a large bending deflection [[[3]](#endnote-2)]. However, IPMCs in their conventional configuration suffer from several issues like time-consuming and expensive manufacturing process (i. e. electroless plating of noble metals) [[[4]](#endnote-3)], platinum layer cracks under continuous actuation [[[5]](#endnote-4)], processing of gold is relatively complex and gives results with low reproducibility, water as a solvent inside the polymer decomposes when operated at higher voltage, which in turn degrades the actuation properties and thermodynamic efficiency [[[6]](#endnote-5)].

Due to these limitations, a lot of attention has been focused on developing manufacturing techniques using inexpensive electrode materials and more stable solvents, *e.g.* ionic liquids [[[7]](#endnote-6)]. Lately Akle *et. al.* proposed a new manufacturing technique – Direct Assembly Process (DAP) – in which the electrode is spray painted on the ionic-liquid swollen NafionTM membrane and hot-pressed [[[8]](#endnote-7)]. Other than conventional IPMC fabrication techniques that base on chemical reactions, the DAP is fast and flexible process allowing to use variety of different solvents and electrode materials. Furthermore, the whole process can be directly controlled, which also provides good reproducibility.

Now it is generally understood that the large interfacial surface area of electrodes gives rise to better actuation performance, therefore designing EAPs with high specific surface area electrodes is of interest. Using the DAP, Akle and their co-workers synthesized ionic liquid (Emi-Tf) based IPMCs with porous RuO2 electrodes, which showed great actuation performance and reliability for long-time operation in air [[[9]](#endnote-8)]. Recently, Fukushima and Asaka *et. al.* came up with unique fabrication technique for assembling bucky gel actuators [[[10]](#endnote-9)]. In this process the dry actuator can be fabricated simply through layer-by-layer casting of “bucky gel” – gelatinous room-temperature ionic liquid that contains single walled carbon nanotubes (SWNTs).

In our previous paper, we reported high-strain IPMC actuators using for the first time highly porous carbide-derived carbon (CDC) and coconut shell-based activated carbon as an electrode material [[[11]](#endnote-10)]. Actuators with CDC electrodes produced more than twice as much strain as previously reported RuO2-based actuators. In this paper, we introduce carbon aerogels as new alternative for assembling EAP actuators with nanoporous electrodes. We synthesize carbon-ionic-liquid electroactive polymers (CIL-EAPs) with either activated carbon aerogel or non-activated carbon aerogel electrodes. The carbon electrodes are applied onto ionic liquid-swollen Nafion membranes using the direct assembly process. The assembled CIL-EAPs are characterized in terms of actuation performance and compared to our recently reported actuators based on carbide-derived carbon and activated carbon electrodes.

Carbon aerogel is highly porous carbon material obtained by the pyrolysis of organic aerogel. It has large specific surface area and extremely low density. Due to these properties they can be used as adsorbents, materials for chromatographic separation, membranes and carriers for metal catalysts. Furthermore, having a controllable porous structure and electrically conductive network, they may be used as electrodes for capacitors or fuel cells [[[12]](#endnote-11)]. Carbon aerogels used in this study are derived from 5-methylresorcinol-formaldehyde gel [[[13]](#endnote-12)]. After drying in the supercritical carbon dioxide the gel forms an aerogel, which is then pyrolysed in an inert (N2) atmosphere to obtain a carbon aerogel. Activation is carried out at 1,173 K in continuous flow of CO2 for 1 – 4 hours.

**2. Experimental**

*2.1 Chemicals and materials*

Carbon aerogels (activated and non-activated) were prepared as described by Koel *et al* [12]. Nafion™ 117 membrane (product of DuPont) was purchased from FuelCellStore.com™. Gold foil from Gold-Hammer (24-carat, 80x80 mm2) was used as contact material on electrode surface.

All reagents were of analytical grade and used without further purification: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-TF, Fluka); lithium perchlorate (LiClO4, Fluka); 2-Propanol ((CH3)2CHOH, 99.9%, Sigma Aldrich); ethanol (CH3CH2OH, 96%, Sigma Aldrich); hydrochloric acid (HCl, 36%, Stanchem). All solutions were prepared using deionised water (18 MΩ ∙ cm)

The physical properties(nimekiri) of electrode materials used are listed in Table 1.

*2.2 Preparation of the CIL-EAP-s*

Bare Nafion™ 117 membrane was pretreated by roughening both sides with emery paper(paberi number) in order to remove the outer polymer surface layer, which due to its relatively high hydrophobicity interacts weakly with the solutions used further on. Roughening also enlarges the polymer-electrode interface area, thereby providing better adhesion. Both sides of the membranes were roughed until the surface appeared to be non-transparent, after which the membranes were washed by boiling in 1 M hydrochloric acid for 30 minutes, followed by boiling in de-ionized water for 1 h to remove acid residuals.

In order to prevent degradation of the ionomer during the relatively long drying procedure at elevated temperature [[[14]](#endnote-13)], the membranes were ion-exchanged by boiling for 2 h in a 1 M LiClO4 solution. The membranes were then dried in vacuum at 150o C for 12 h. Thereafter, the membranes were instantly immersed in neat ionic liquid (Emi-Tf) and heated for 5 h at 150o C. Afterwards, the uptake of Emi-Tf is expected be near 60% of the dry weight of the membrane [8].

The electrodes were applied to the membrane using DAP [7]; *i.e.,* a conductive powder with high specific area was mixed with an ionomer solution and painted directly on the diluent-swollen membrane and sandwiched between two gold foils followed by hot-pressing. A 5 wt% Nafion 1110 dispersion was prepared by heating the ionomer in an autoclave for 3 h at 210o C under continuous stirring in the presence of a 50% ethanol/water solution. Thereafter, the ionomer dispersion was mixed with conductive powder. For RuO2 electrodes, the mixture was prepared containing of 6 wt% ruthenium (IV) oxide powder, 47 wt% of Nafion solution (5%) and 47 wt% of isopropanol. The mixture for carbon electrodes was adjusted to contain 1.7 wt% of carbon powder, 48.3 wt% of Nafion solution and 50 wt% of isopropanol. All mixtures were then sonicated for 1 to 3 h to disperse the conductive powder particles.

The conductor/ionomer mixtures were applied to the membrane using an SB-1107 Sumake airbrush operated by compressed-air. Volatile solvents were removed under an infrared lamp (150 W, Philips) after application of each layer. Typically 8 to 15 layers of the conductor/ionomer mixture were sprayed on each membrane to achieve uniform thicknesses. After painting on the electrodes, a layer of 5% Nafion solution was applied onto the sprayed electrode to provide better surface adhesiveness to the gold foil. Thereafter, the membranes were placed under IR light for an additional 15 minutes. Finally, the membranes were sandwiched between two gold foils (270 nm thick) and fused together by hot-pressing at 150o C under 3.5 MPa for 5-10 s. This decreases the surface resistance of painted layers to less than 1 Ω/cm, according to measurements.

By this process, two sets of samples with three membranes in each set were prepared. All samples were 40 mm in length × 8 mm in width.

*2.3 Electromechanical Characterization*

For electromechanical characterization, the experimental setup described in [26] was used. A National Instruments PCI-6034 DAQ with an SCC-RTD01 module was used to measure the resistances of the surfaces using a four-probe system. This method eliminates inexactnesses caused by the inconsistent current density and the resistances of the contacts. The SCC-RTD01 is a dual-channel resistance-temperature detector (RTD) module that accepts 2, 3, or 4-wire RTDs. Each channel of the SCC-RTD01 has an amplifier with a gain of 25 and a 30 Hz lowpass filter. In addition, the module has a 1 mA excitation source for powering the RTDs. The range of the module allows reliable measurement of resistances from 0 to 200 Ω. In order to connect the four probes simultaneously to the IPMC strip, a special flexible contact strip was made by fixing four contacts made of gold foil onto the surface of a thin ribbon of PTFE. The distance between the test-contacts was kept at 21 mm.

A schematic of the experimental setup for the characterization of the actuator strain and speed is shown in Figure 1. The actuators were clamped in vertical cantilever position and measurements were done in the dry state in air. Rectangular or sinusoidal driving pulses were applied via a fixed contact U and a ground contact made of gold. The measurements were conducted with National Instruments LabView7 control software. The driving voltage was generated by a NI PCI-6703 DAQ board and amplified by electric current from a NS LM675 power op-amp. The voltages with respect to the ground were measured with a NI PCI-6034 DAQ board. One input contact of the IPMC sample was also connected to the ground. The electric input current of the sample was measured as a voltage drop over the resistor R. The value of the resistor should be chosen as low as possible, but still sufficiently high with respect to the value of the current and the sensitivity of the measuring equipment. In the course of the experiments described here, the value of the resistor R was 0.5-1 Ω. Electric current was calculated according to Ohm’s law.

The bending motions of the actuator were recorded with a firewire camera, Dragonfly Express from Point Grey Research Inc., recording images at 30 frames per second. The direction of the camera was set transverse to the actuator and the experiment was illuminated from the background through a frosted glass and a graph paper. In this camera position, the recorded image of the actuator consists of a single curved contrast line.

The resistances (conductivities) of both electrodes were measured using a four-probe system. The values of the shunt conductivity parameters were determined using impedance spectroscopy with variable-voltage step pulses as described in [27]. Blocking force was measured at zero displacement using the Panlab MLT0202 load cell. Sample stiffness was determined by a 3-point bending test [28].

*2.4 Scanning electron microscopy*

Scanning electron micrographs were obtained on all samples using a Hitachi Tabletop Microscope TM-1000 in standard backscattered electron (BSE) image mode with 15 keV primary electron energy.

**3. Results and discussion**

Prepared CIL-EAP actuators were characterized in terms of maximum strain, strain rate, capacitance, electrode surface resistance, blocking force and stiffness (Young modulus). Table 2 represents a summary of performed measurements. The results were obtained by measuring three samples for each electrode material (non-activated and activated carbon aerogel). In case of all experiments, the standard deviation percentages (error %) were below 15%.

First, the electrode surface resistance was measured in order to make sure there are no significant cracks or disjunctions in the electrode layer, which may occur during the hot-pressing procedure. As observed in Table 2, the electrode resistances range from 0.3 to 0.4 ohms/cm. These measurements confirm that the gold foil on the surface is in great condition, providing good conductivity along the sample length. Exceptionally similar values in electrode resistances also assure that the samples can be adequately compared in terms of other characteristics. It should also be mentioned that these results are in good agreement with our previously reported actuators based on carbide-derived carbon (CDC) and activated carbon electrodes (see Table 3), which show that the used manufacturing process (direct assembly process) provides good reproducibility.

Table 2. Summary of the results (measured at ±2 V rectangular actuation signal).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Electrode material** | **Maximum peak-to-peak strain (%)** | **Maximum strain rate (%/s)** | **Capacitance (mF/cm2)** | **Electrode surface resistance (Ω/cm)** | **Blocking force (mN)** | **Stiffness (MPa)** |
| Non-activated carbon aerogel | 1.28 | 0.15 | 8 | 0.4 | 1.7 | 99 |
| Activated carbon aerogel | 1.15 | 0.13 | 14 | 0.3 | 1 | 100 |

Table 3. Properties of our previously reported actuators (measured at ±2 V rectangular signal) .

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Electrode material** | **Maximum peak-to-peak stain (%)** | **Maximum strain rate (%/s)** | **Capacitance (mF/cm2)** | **Electrode surface resistance (Ω/cm)** | **Blocking force (mN)** | **Stiffness (MPa)** |
| Carbide derived carbon (CDC) | 2.04 | 0.23 | 16 | 0.7 | 3.6 | 97 |
| Activated carbon | 1.03 | 0.16 | 51 | 0.6 | 3.1 | 103 |

Another property that can greatly affect the electromechanical properties (blocking force and strain) is the sample’s stiffness i.e. Young modulus. The stiffness was determined by the 3-point bending test, described in [[[15]](#endnote-14)]. As can be seen from the data in Table 2, respective values of Young modulus for both samples are around 100 MPa. Since there is almost no variation in Young modulus, the sample’s stiffness will not affect the comparison of other electromechanical parameters. The data also compares well to our previous work (see Table 3), in which the Young modulus for actuators based on CDC and activated carbon electrodes were 97 MPa and 103 MPa, respectively. The results indicate that the sample’s stiffness is mainly determined by the fabrication process, not by specific porous electrode material or binding polymer framework, which is similar in the samples. All samples were prepared as similar as possible, which explains very minor variations in stiffness.

The maximum strain was calculated according to the equation described in [7]: ,

where *t* is the thickness of the sample and *R* is the curvature radius at maximum deflection. The measurements show that the actuators with non-activated and activated carbon aerogel electrodes are capable for generating strains up to 1.28% and 1.15%, respectively, at ±2 V actuation signal. These peak-to-peak strains are comparable to our previously reported actuators (Table 3) and best to our knowledge to any other low-voltage driven EAP actuators. It is interesting to note that although activated carbon aerogel has significantly higher specific surface area than non-activated carbon aerogel, they perform relatively similar in terms of strain. As can be seen on the plots of pore size distributions in figure 2, the activated carbon aerogel, while having almost the same pore distribution in micropore range (> 1 nm), exhibits considerably higher amount of nanopores in range of 0.5 – 0.6 nm. Nanopores in this size, however, are too small to be easily accessible for electrolyte (EMI-TF) ions (the diameter of EMI+ is 7.6 nm). Therefore, the actuation is mainly generated in micro- and mesopores, which are freely passable for electrolyte ions (under the applied electric field, the repulsive interactions between the ions in formed double layer induce the actuation). As observed in figure 2, both carbons have almost identical pore distribution in micropore range (> 1 nm), which explains similar performance in strain output. When compared to the previous results, the newly developed actuators outperform the activated carbon while lagging behind the CDC electrodes. This is probably related to the structural differences between these materials. As discussed in [10], CDC has very uniform and well-structured framework, being easily stretched out upon the ionic interactions, which gives rise to better actuation performance. Activated carbon with relatively non-uniform structure is too rigid to be deformed by electrostatic interactions. Carbon aerogel, also having relatively rigid structure, shows enormously high pore volume (…..), which facilitates the ion migration (displacement) in electrodes, thereby showing better performance compared to the activated carbon.

Figure 2. Incremental pore size distribution of activated and non-activated carbon aerogel. Graafiku x-telg pole veel nii nagu vaja

The maximum strain rate was calculated from recorded video clip, indicating the highest speed the sample experiences while actuating from one maximally deflected position to another. As the measurements show, the maximum strain rates for non-activated and activated carbon aerogel electrodes are 0.15 mε/s and 0.13 mε/s. Appears that the differences in results are relatively minor. The actuator’s speed is closely related to the porous structure of electrode, since it directly affects the electrolyte migration. As discussed earlier, both carbons have almost the same microporous structure, which also explains rather small variation in strain rates.

As mentioned before, the interfacial area between the electrodes and electrolyte greatly affects the actuation performance (strain output). In this regard, the capacitance measurements were performed, in order see how the specific area of electrodes correlates with actuation. Typically, higher capacitance indicates larger interfacial area and more electrolyte involved in double layer formation, which in turn refers to a greater strain due to the stronger repulsive interactions in double layer. However, in the context of the data presented here, the capacitances are not in correlation with respective strain values of the samples. Non-activated carbon aerogel, showing slightly higher strain, has considerably lower capacitance (8 mF/cm2) compared to the activated carbon aerogel (14 mF/cm2). This is actually not unexpected, since different electrode materials with different structures are compared. As discussed earlier, activated carbon aerogel has significantly higher amount of nanopores (< 1 nm) compared to the non-activated carbon aerogel. The nanopores are too small to be freely passable for electrolyte ions, but they may still contain electrolyte ions that are immobile and constrained in the pores. These immobile ions are not contributing to the actuation, but still give rise to the capacitance, which explains high capacitance for activated carbon aerogel electrodes, while having slightly lower bending performance…………..

**4. Conclusions**

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