

NEW CAPACITIVE STORAGE DEVICE

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Abstract: Ionic polymer metal composites (IPMCs) are one of the most new and promising materials being studied for their electromechanical properties. They are robust, light-weight, fabricated easily and into nearly any size or shape, and can produce large macro bending deformations while under low driving voltages or conversely produce measurable electric signals (sensing) when deformed [1]. Our recent discovery of capacitive behaviour in dry prepared IPMCs has led to development of high energy density devices. Here we report the use simple microfabrication of electrodes to produce ionomer composites sandwiched between two thin metal films. These composites exhibit capacitance per unit planar area of $\sim 1.0 \text{ mF cm}^{-2}$ (40 mF/g) for the $\sim 127 \text{ }\mu\text{m}$ -thick substrate. We further report on the scalability of these devices. These composites could open the door to high energy density flexible and scalable thin films needed to meet energy storage solutions of tomorrow.

Keywords: Capacitor, Polymer, Thin Film, Ionomer, Power Storage

INTRODUCTION

Fabricating an ionic polymer metal composite begins with an ionomer with ion exchanging capabilities that is sandwiched between two conductive metal electrodes usually through a chemical reduction process [2]. Ion exchange polymers are designed to selectively exchange cations or anions of a single charge with their own incipient ions.

The research surrounding ionic polymer metal composites (IPMCs) has mostly been limited to hydrated perfluorosulfonic acid polymers used for novel actuators or to a lesser degree that of sensors. It is well documented [2] that ionic polymer metal composites can exhibit large dynamic deformation if hydrated with suitable solvent (typically water), electroplated and placed in a time-varying electric field. Conversely they can generate a small amount of electric charge if mechanically deformed. Nafion and other perfluorinated ionic polymers have been previously used for their ion exchange properties in fuel cell technology [3] and as a component in electrolyte formulation for electrochemical supercapacitors to improve mechanical properties and stability during charge discharge cycles [4]. However, very little has been published on the properties of non-hydrated (dry) IPMC specimens, and none on the capacitive behaviour of dry ionic polymers. In hydrated IPMCs under an electric potential the mobile cations migrate creating a higher density of water molecules on one side of the membrane converting the electrical potential into mechanical work via strains for actuation [2]. This behaviour is similar to supercapacitors [5], however the electric potential is dissipated in the form of

mechanical work. When an IPMC sample is hydrated and Pt is impregnated into the hydrated membrane the IPMC will mechanically deform due to water molecules binding to the mobile cations thus causing one side of the IPMC to swell. If the IPMC is prepared dry the actuation ability is eliminated as there are too few water molecules to cause swelling. We hypothesized that in dry samples the cations would still be able to migrate towards an opposing charge while the density offset could be negated and therefore the stored electric potential could be maintained for long periods of time.

EXPERIMENTAL

Design and Fabrication of Capacitors

As a consequence of the need to hydrate specimens and impregnate Pt electrodes for actuation, a complex and time consuming fabrication process [6] has been required and the variability in fabrication of IPMCs is a likely cause for poor agreement between published results [7]. Our composites were fabricated from 30cmx30cm sheets of Nafion® N-115 membrane cut to various sizes with a knife edge. The Nafion® N-115 membranes have a mean nominal thickness of 127 μm . 5nm of Cr and 100nm of Au were RF sputtered onto both sides N-115 sheets respectively, using a Corona RF Sputtering machine. The Cr is sputter first to guarantee good adhesion of the polymer and gold interface. The only preparation done was slight surface roughening of N-115 membrane with emery clothe, no other acid baths, solvents etc were used as has been the case with past IPMC devices [2, 6].

Figure 1 shows SEM micrographs of the

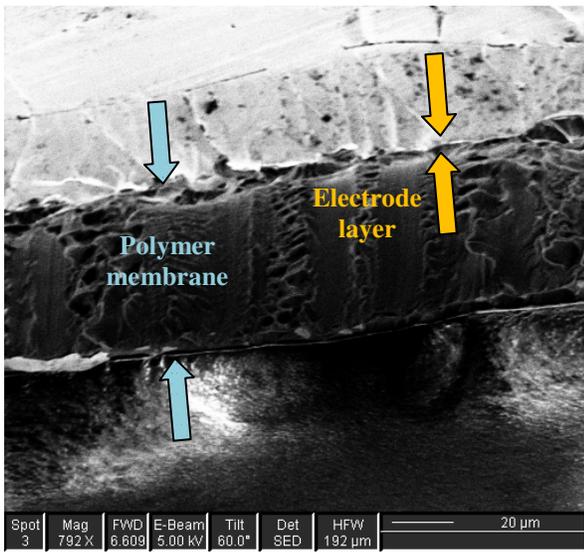
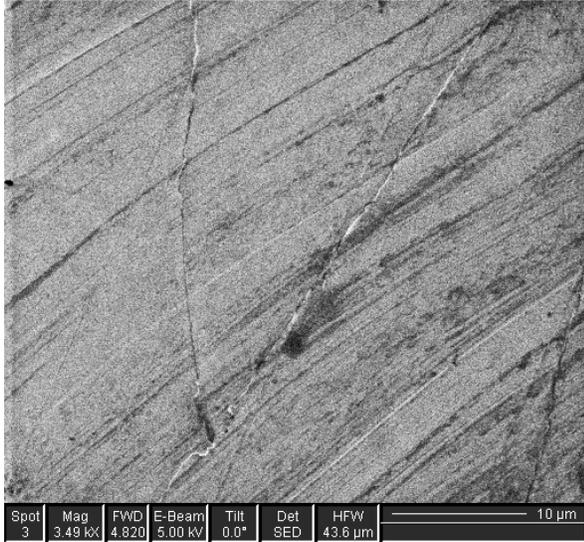


Fig. 1. SEM micrographs of top layer Au-Cr electrode, a few micro-cracks are visible which are due to the dry nature of the Nafion membrane. A cross-sectional view taken at a 60° tilt showing Au and Nafion layers.

Figure 1 shows SEM images of the surface and cross-sections of an IPMC sample fabricated using RF sputtering. It is known that Nafion exhibits charge storage but due to its high resistivity charge does not accumulate quickly in the material itself [8]. We found that the single step RF sputtering yielded similar surface morphology to that of typical five to seven step [6] initial composting with surface electroplating process [2] even though the Nafion membrane was not hydrated. These composites were found to exhibit excellent properties with rapid charging closer to that of a purely capacitive device.

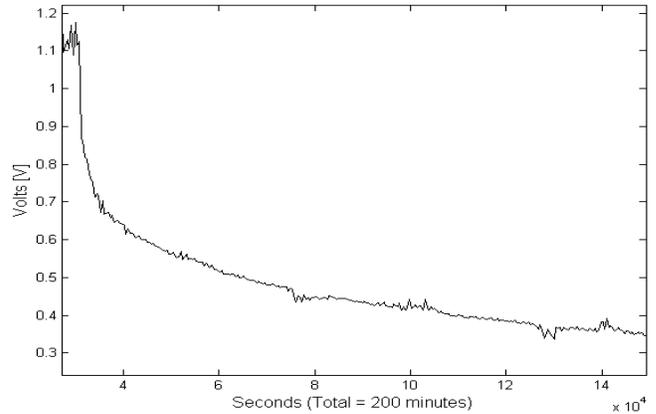


Fig. 2. Capacitor Discharge Cycle for 0.5mA input.

Specific Capacitance Tests

The composites were tested initially for capacitance using a Fluke 8846A DMM multimeter. A National Instruments c-DAQ 9127 USB data acquisition system using an NI 9205 module interfaced through a custom LabView virtual instrument model, was used to measure the charge/discharge characteristics of the composites. Each of the composite samples with charged for 60 seconds with an input of 0.5mA and then allowed to discharge for up to 200 minutes, where the test was then ended as shown in Figure 2.

RESULTS AND DISCUSSION

Experimental tests showed the IPMC samples exhibited levels of capacitance of 1mF cm^{-2} or 40mF/g (defined as the weight of active materials Nafion and Au). Under an input of 0.5mA each sample charge quickly within seconds to 1.2V followed by initial rapid discharge to 0.5V before leveling off and maintaining this potential for the period of the test (Figure 2). Furthermore several of the IPMC samples were cut with a knife edge and these smaller samples were tested for scalability. A 20% reduction in size (area and volume) yielded almost exactly a 20% reduction in capacitance. From a manufacturing perspective this is extremely impressive as very large sheets of these IPMC based capacitors can be fabricated and then simply cut into any size or shapes as necessary for a given application. These tests were repeated several times for each sample to ensure reproducibility. This puts the composites in the range of larger sized (by volume) commercial electrolytic capacitors. Table 1 gives a comparative analysis of the current work alongside commercially available electrolytic capacitors as well as other reported capacitance measures of IPMCs. Due to the variability in specific capacitance reporting, all the

Table 1 | Comparison of selected solid state capacitors. Our current work demonstrates specific capacitance higher than other non-supercapacitive devices.

Reference device	Device Class	Electrode type	Fabrication [no. of steps]	C per planar area mF cm ⁻²	C per unit mass mF/g
Current work	Dry	Au-Cr (100nm)	Au-Cr RF sputtering [1]	1	40
Shahinpoor et al. 2003 IPMC	Hydrated	Pt overlaid with Au (20 μm)	Initial composting with electroplating [7]	0.025	0.1*
Kim 2007 IPMC	Hydrated	Au Pt (20 μm)	Electro-less plating Au with Pt impregnation	1.5	8
Akle et al. 2008 Super-capacitive transducer	Hydrated electro-chemical super-capacitor	SWNT (10%) RuO ₂ (35%) (30 μm)	Direct Assembly Process with RuO ₂ electrode "painting"	50	133 ¹
Equivalent rated electrolytic	Commercially available	Conductive polymer Aluminum			<1
	Nichicon LF series Al-polymer 1000 μF	Tantalum conductive polymer SMD			<1
	Kemet T520 series conductive polymer 1000 μF				

specific capacitances for the devices listed in Table 1 were calculated for the whole device (electrodes, membranes, dielectrics etc.).

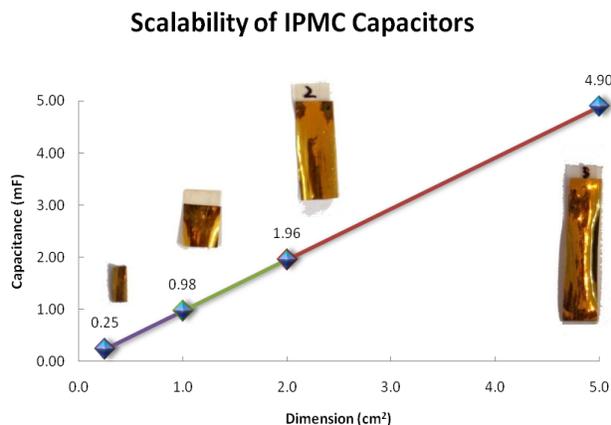


Fig. 3: Plot with images of actual samples tested illustrating the linear scalability of capacitance as a function of geometry.

The polymer material had been kept at ambient temperature and humidity for several months before it was cut and electrodes fabricated. This shows good robustness of this material. The experimental charge-discharge cycles of a 1cm² capacitor is shown in Figure 2 for 0.5mA and 1mA inputs. It was also

discovered that scaling up or down the size of these capacitors yield a very linear relationship between capacitance and area. Figure 3 illustrates various sample sizes and their respective measured capacitances. A clear linear relationship can be seen as the capacitors are scaled up some 0.5cm² to 5cm².

Conventional capacitors are restricted by size, shape, in the case of electrolytic capacitors direction of charge, and typically must be wired directly to the circuit board. Such restrictions take up valuable space inside the electronic device packaging. One great advantage of IPMCs is how they can be fabricated into nearly any size, shape and dimension to fit the requirements of the designer and device at hand [5]. For example, an IPMC capacitor could be fitted around the device and electronics, molded as a lining for the inside of the packaging, or possibly incorporated as part of the packaging container.

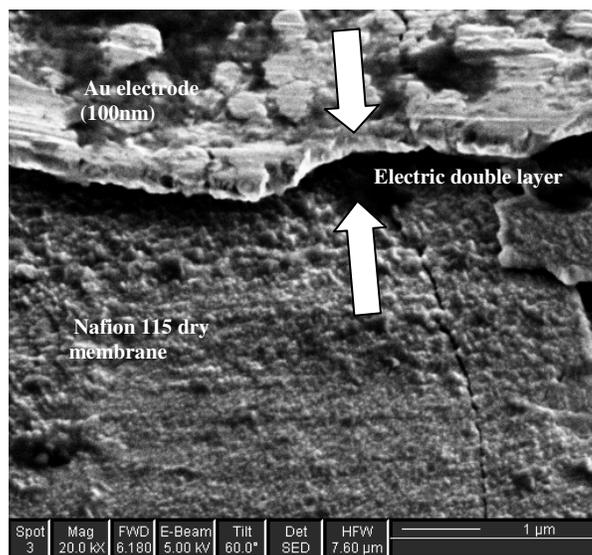


Fig. 4: SEM image showing electric double layer formed between Au electrodes and polymer membrane.

This would lend well towards maximizing the surface area and thus capacitance of the capacitor while minimizing the space taken up inside the device.

It has been proposed that the capacitive nature of ionomers such as Nafion composited with conductive electrodes is due to an electric double layering formed at the interface of the electrodes diffused through the ionomer electrolyte. An electric double layer is defined as a region at the boundary of two substances, with dimensions at a molecular scale, containing charges particle (e.g. ions) across which an electrical field exists due to the separation of electrical charges [9]. The electrostatic attraction between the two separated charges causes an electric field to be established across the interface. There has been some

recent work to model and build on this by introducing pseudocapacitive properties via RuO₂ [10] based electrodes to generate redox charge-storing Faradic reactions [11]. In contrast to those works, the composites presented in the current work have electrodes which are not diffused into the polymer membrane and do not have pseudocapacitive properties enabling an electrochemical doublelayer to create a supercapacitive cell. Despite this disadvantage the current work devices exhibit capacitances per unit weight close to that of those utilizing electrochemical doublelayers (Table 1). We have shown here high energy densities without the use of supercapacitive rare metal composites such as RuO₂. One possible explanation for this high level of performance may lie within the close inspection of the electrode interface of the composites presented in the current work a very small separation (<10nm) can be seen in Figure 5. Such a separation would allow for charge to accumulate at the interface between the surface of the conductor and the ionomer membrane hence forming a double layer [12]. This separation occurs due to the micro-fractured nature and surface roughness of the dry Nafion samples.

CONCLUSION

We have shown fabrication using a single step RF sputtering process to produce high-density capacitors with 40mF/g capacitance. Such capacitors in this range fill the gap between ultra electrochemical capacitors and commercial electrolytic capacitors, while being much smaller, more flexible in design and easy to manufacture. Design models of the capacitance properties of these composites are currently being developed to further optimize these devices. Future research will concentrate on investigation of the leakage observed during the charge and discharge cycles.

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