

ALL SOLID-STATE MICRO-SUPERCAPACITORS USING IONOGEL ELECTROLYTE

B. Hsia¹, S. Wang^{1,2}, M.-S. Kim¹, C. Carraro¹, and R. Maboudian^{1}*

¹Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA, USA

²Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun, CHINA

ABSTRACT

All solid-state micro-supercapacitors are an attractive solution for integrated, on-chip energy storage. Photoresist-derived porous carbon, which has a high specific capacitance and good conductivity, is used as an electrode material in conjunction with an ionogel electrolyte to fabricate a high energy density supercapacitor. Fabricated devices yield extremely high volumetric capacitance of 9.8 F/cm³ and a wide electrochemical voltage window of 3 V.

KEYWORDS

Supercapacitor, ionogel, photoresist, porous carbon, on-chip power sources

INTRODUCTION

Due to their high power density and robust cycling performance relative to batteries, supercapacitors have drawn increasing research and industrial interest [1]. On-chip microscale supercapacitors, in particular, could be integrated with MEMS sensors and actuators as an energy storage medium for applications that require high power or frequent cycling such as data transmission in autonomous wireless sensor networks [2]. While current commercial macroscale supercapacitors primarily utilize a liquid phase aqueous or organic electrolyte, microdevice packaging and fabrication requirements would be significantly simplified with the development of an all solid-state energy storage device. With this motivation, we have fabricated a supercapacitor using photoresist-derived porous carbon electrodes in conjunction with an ionic liquid based gel (or “ionogel”) electrolyte. With this combination, we have achieved an order of magnitude higher energy density than reported previously for the same electrode material in aqueous electrolyte [3].

Supercapacitor electrode materials must meet two primary requirements: they must have a high specific surface area for double-layer formation at the electrode/electrolyte interface and they must be sufficiently conductive to allow for rapid charging and discharging. For these reasons, activated carbon materials are commonly found in commercial supercapacitors. However, due to the difficulties in fabricating planar activated carbon devices, many other high surface area carbon materials [4-12] have been explored for micro-supercapacitor electrodes, including carbon nanotubes (CNT) [4], laser-scribed reduced graphene oxide [5], onion-like carbon [6], carbide-derived carbon [7, 8], graphene-CNT carpets [9]. Photoresist-derived carbon (PRDC) is another natural material choice for microscale energy storage due to its simple microfabrication techniques and good electrochemical performance [3, 10]. It has sufficient conductivity to serve as both an active

electrochemical surface and a current collector, and has shown high volumetric capacitance in excess of 10 F/cm³ in aqueous electrolyte [3]. Photoresist is also easily patternable, simplifying on-chip integration with existing microdevices. Additionally, pyrolysis of photoresist is highly tunable, with properties like porosity, conductivity, thickness, electrolyte wettability, and electrochemical activity all highly dependent on processing conditions [3, 11-13].

For the solid electrolyte, ionogels, which consist of an ionic liquid supported by a porous silica matrix, have been shown to exhibit good ionic conduction and electrolyte function in macroscale supercapacitors with glassy carbon electrodes [14]. Ionogels maintain the excellent electrochemical properties of ionic liquids while also eliminating concerns such as leakage. Recent studies have demonstrated good electrochemical performance of ionogel electrolytes on planar flexible micro-supercapacitors fabricated via laser scribing of reduced graphene oxide [5]. In addition to the fabrication and stability advantages of solid relative to liquid electrolytes, ionic liquids have a higher potential stability window than water-based electrolytes. Aqueous electrolytes limit device operation to about 1 V or less due to the electrochemical breakdown of water at higher voltages. Ionic liquids, on the other hand, have a larger operational voltage window, and ionogel-based micro-supercapacitors have been demonstrated at up to 2.5 V [5]. This larger window has a significant effect on the energy density of the device, as the energy stored is proportional to the square of the voltage window. Fabricated ionogel-based supercapacitors show energy densities which are competitive with Li-ion thin film batteries [5].

EXPERIMENTAL

The fabrication procedure for the PRDC/ionogel supercapacitor is as follows. SPR-220-7.0 photoresist is spin coated onto a Si wafer which is then diced into chips. The photoresist is heated in a low-pressure tube furnace (~1 mTorr base pressure) to 300 °C for 30 min in Ar, heated to 900 °C in Ar, and then annealed in an H₂/Ar atmosphere at 900 °C for one hour. This multi-step procedure is designed to maximize porosity and electrolyte wettability [3]. After pyrolysis, two chips (to serve as the two electrodes) are immersed into a mixture of tetramethoxysilane (TMOS), formic acid, and ionic liquid ([EMI][TFSI]) [14]. See Fig. 1 for the molecular structures of the ionogel components, with the formic acid being used to catalyze the formation of the TMOS-based silica gel. The mixture is allowed to gel for over 12 hours before testing. Electrical connection to the two chips is made by a silver epoxy connected to Cu wire.

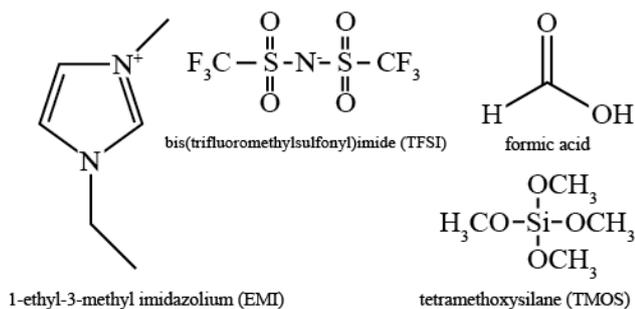


Figure 1: Molecular structures of ionogel components used in the present studies.

RESULTS & DISCUSSION

The specific ionogel formulation has a significant effect on the gel quality. For the present study, a 1:6:6 molar ratio mixture of TMOS), formic acid, and [EMI][TFSI] was used for its high ionic liquid content and good mechanical properties [14]. A higher formic acid or TMOS content leads to brittle gels with poor electrochemical and mechanical properties. For a micro-supercapacitor application, the volume changes during gelation could cause a reduction in electrode/electrolyte contact area, thus the minimal volumetric change expected for the 1:6:6 formulation is an important factor for successful supercapacitor fabrication [14]. Also, an extremely low Young's modulus, about 5 kPa, is measured for this ionogel formulation, indicating good mechanical compliance [14], another important consideration for device applications.

Cyclic voltammograms (CV) of the PRDC electrodes in 1:6:6 ionogel formulation are shown in Fig. 2 for a variety of voltage scan rates. The scans are fairly rectangular, even at scan rates as high as 10 V/s, with the current scaling linearly with scan rate. The apparent

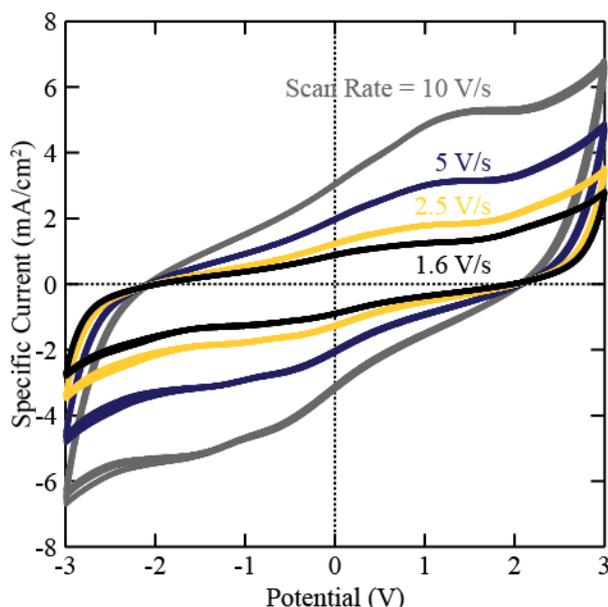


Figure 2: Cyclic voltammograms performed on photoresist-derived carbon electrodes in ionogel electrolyte at a variety of scan rates. Specific current is calculated by dividing by the projected area of one electrode.

peaks at voltages of ± 1 V can be attributed to electrochemical reactions of the residual water in the ionogel. Efforts to remove residual water such as vacuum drying and fabrication in a controlled environmental chamber are under investigation. The specific capacitance of one electrode can be calculated from the CV scans via Eq. 1:

$$C = \frac{2I_{avg}}{sA} \quad (1)$$

where C is the specific areal capacitance, I_{avg} is the current averaged over both the positive and negative sweeps, s is the scan rate in V/s, and A is the projected area of one electrode. The factor of 2 is inserted to obtain the specific capacitance for one electrode, as the whole device is comprised to two capacitors in series. The areal capacitance is found to be $980 \mu\text{F}/\text{cm}^2$ for a scan rate of 1.6 V/s. Dividing by the thickness ($\sim 1 \mu\text{m}$) of the PRDC electrode yields an extremely high volumetric capacitance of $9.8 \text{ F}/\text{cm}^3$. While the measured capacitance value is less than the value obtained for the same pyrolyzed photoresist films in aqueous electrolytes at a similar scan rate ($1.7 \text{ mF}/\text{cm}^2$ for a scan rate of 1 V/s) [3], the 1 V accessible voltage window of the aqueous electrolyte severely limits the overall energy density. For an ionogel, we have achieved a voltage window of up to ± 3 V without significant electrolyte degradation.

Figure 3 shows the variation in CV shape for 3 different potential windows, 1 V, 3 V, and 6 V. The large current increase at about ± 5 V corresponds to electrolyte breakdown, indicating that a potential window greater than 3 V and less than 5 V may also be feasible. However, complete removal of residual water will be necessary to further probe the potential limits of the ionogel electrolyte, as discussed previously.

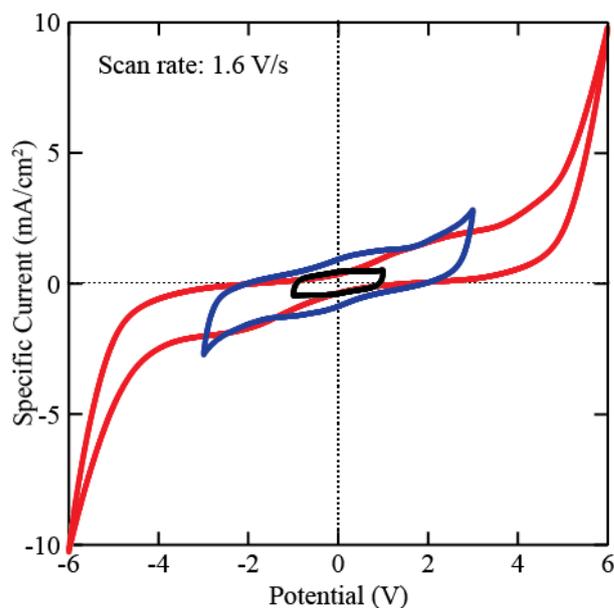


Figure 3: Cyclic voltammograms performed on photoresist-derived carbon electrodes in ionogel electrolyte at a variety of scan rates. Specific current is calculated by dividing by the projected area of one electrode.

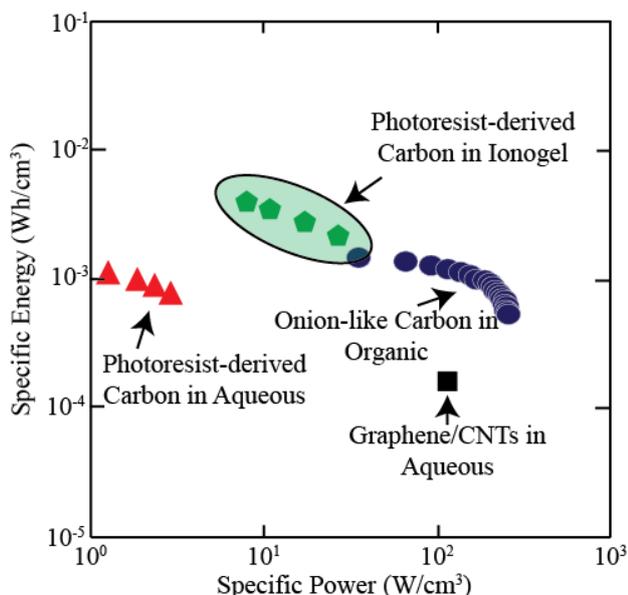


Figure 4: Ragone plot comparing volumetric energy and power density achieved in ionogel electrolyte vs. in aqueous electrolyte. Photoresist-derived carbon data from Ref. [3]. Onion-like carbon (OLC) data from [6]. Graphene/CNTs (G-CNT) data from [9].

The specific areal capacitance achieved for the fabricated supercapacitor device is significantly higher than that of previously studied pyrolyzed photoresist electrodes in aqueous electrolytes, which give $< 50 \mu\text{F}/\text{cm}^2$ [10, 12] and require electrochemical activation or complex 3D microstructures to achieve practical energy densities. These referenced films were pyrolyzed at a higher temperature of $1000 \text{ }^\circ\text{C}$ (vs. $900 \text{ }^\circ\text{C}$ in this case) and used only one gas ambient throughout (H_2/N_2) in contrast to multi-step procedure described above. The higher temperature results in a less porous film [11], while the use of only one gas results in reduced wettability toward aqueous electrolytes [3]. Using the pyrolysis procedure detailed here and in Ref. [3], a much higher capacitance is achieved. The resulting energy and

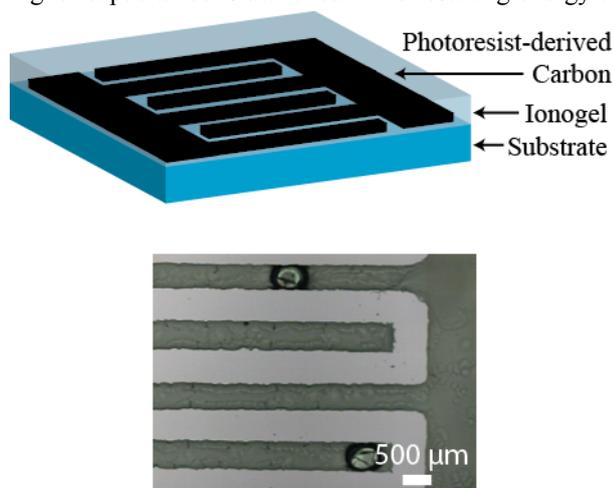


Figure 5: All solid-state microsupercapacitor schematic (top). Optical microscopy image of pyrolyzed photoresist electrode patterned by photolithography (bottom).

power densities can be calculated via Eqs. 2 and 3.

$$E = \frac{1}{2} \left(\frac{C}{2} \right) V^2 \quad (2)$$

$$P = \frac{E}{\Delta t} \quad (3)$$

where E and P are the areal energy and power densities, respectively, C is the specific areal capacitance of one electrode and is divided by 2 to give the capacitance for a symmetrical device, V is the voltage window, 3 V in this case, and Δt is the CV discharge time. The calculated energy and power densities of the device can be plotted on a Ragone plot (Fig. 4). The volumetric energy and power densities have been estimated by dividing the corresponding areal densities by the thickness of the carbon film, $\sim 1 \mu\text{m}$ and further dividing by a factor of 3 to estimate the fill factor of one interdigitated electrode. As can be seen, the energy and power densities of the ionogel electrolyte device exceed those of the aqueous counterpart and compare favorably with state of the art micro-supercapacitor technologies.

Patterned micro-supercapacitors were also fabricated by lithographic patterning of the photoresist prior to pyrolysis. Fig. 5 shows a device schematic as well as optical microscopy images of the patterned photoresist before and after pyrolysis, showing good fidelity. Drop casting of the ionogel mixture onto the patterned electrodes resulted in microdevices with low specific capacitance ($< 10 \mu\text{F}/\text{cm}^2$) which we attribute to the difficulties in achieving a uniform gelation in porous media. Current efforts to increase capacitance of these devices include fundamental studies of film wetting by electrolyte as well as optimization of pyrolysis parameters to maximize electrode/electrolyte interfacial area.

CONCLUSION

In summary, all solid-state high performance supercapacitors are fabricated using carbon electrodes derived from pyrolyzed photoresist in conjunction with an ionogel electrolyte. These devices show higher energy and power density than similar devices fabricated using aqueous electrolytes. Furthermore, the use of a solid electrolyte should simplify packaging requirements and result in easier integration into device applications. Ongoing work includes incorporation of ionogel onto planar interdigitated electrodes for an all solid-state microdevice.

ACKNOWLEDGEMENTS

We gratefully acknowledge the National Science Foundation grant EEC-0832819 (through the Center of Integrated Nanomechanical Systems) and a Graduate Research Fellowship (BH), and DARPA Science & Technology Center, CIEMS.

REFERENCES

- [1] P. Simon and Y. Gogotsi, "Materials for Electrochemical Capacitors," *Nat Mater*, vol. 7, pp. 845-854, 2008.
- [2] F. Simjee and P. H. Chou, "Everlast: long-life, supercapacitor-operated wireless sensor node," in

Low Power Electronics and Design, 2006.
ISLPED'06. Proceedings of the 2006 International Symposium on, 2006.

- [3] B. Hsia, M. S. Kim, M. Vincent, C. Carraro and R. Maboudian, "Photoresist-derived porous carbon for on-chip micro-supercapacitors," *Carbon*, vol. 57, pp. 395-400, June 2013.
- [4] E. Frackowiak, K. Metenier, V. Bertagna and F. Beguin, "Supercapacitor electrodes from multiwalled carbon nanotubes," *Appl Phys Lett*, vol. 77, pp. 2421-2423, 2000.
- [5] M. F. El-Kady and R. B. Kaner, "Scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage," *Nat. Commun.*, vol. 4, p. 1475, February 2013.
- [6] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna and P. Simon, "Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon," *Nat Nanotechnol*, vol. 5, pp. 651-654, 2010.
- [7] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon and Y. Gogotsi, "Monolithic Carbide-Derived Carbon Films for Micro-Supercapacitors," *Science*, vol. 328, no. 5977, pp. 480-483, 2010.
- [8] F. Liu, A. Gutes, I. Laboriante, C. Carraro and R. Maboudian, "Graphitization of n-type polycrystalline silicon carbide for on-chip supercapacitor application," *Appl Phys Lett*, vol. 99, no. 11, p. 112104, 2011.
- [9] J. Lin, C. Zhang, Z. Yan, Y. Zhu, Z. Peng, R. H. Hauge, D. Natelson and J. M. Tour, "3-Dimensional graphene carbon nanotube carpet-based microsupercapacitors with high electrochemical performance," *Nano Lett*, vol. 13, pp. 72-78, 2013.
- [10] M. Beidaghi, W. Chen and C. Wang, "Electrochemically activated carbon micro-electrode arrays for electrochemical micro-supercapacitors," *J Power Sources*, vol. 196, pp. 2403-2409, 2011.
- [11] G. M. Jenkins and K. Kawamura, *Polymeric carbons - carbon fibre, glass and char*, London: Cambridge University Press, 1976.
- [12] S. Ranganathan, R. McCreery, S. M. Majji and M. Madou, "Photoresist-Derived Carbon for Microelectromechanical Systems and Electrochemical Applications," *J Electrochem Soc*, vol. 147, no. 1, pp. 277-282, 2000.
- [13] J. Kim, X. Song, K. Kinoshita, M. Madou and R. White, "Electrochemical Studies of Carbon Films from Pyrolyzed Photoresist," *J Electrochem Soc*, vol. 145, no. 7, pp. 2314-2319, 1998.
- [14] A. I. Horowitz and M. J. Panzer, "High-performance, mechanically compliant silica-based ionogels for electrical energy storage applications," *J Mater Chem*, vol. 22, pp. 16534-16539, 2012.
- [15] E. Frackowiak, "Carbon materials for supercapacitor application," *Phys Chem Chem Phys*, vol. 9, pp. 1774-1785, 2007.
- [16] A. G. Pandolfo and A. F. Hollenkamp, "Carbon properties and their role in supercapacitors," *J Power Sources*, vol. 157, pp. 11-27, 2006.
- [17] Y. Zhai, Y. Dou, D. Zhao, P. F. Fulvio, R. T. Mayes and S. Dai, "Carbon Materials for Chemical Capacitive Energy Storage," *Adv Mater*, vol. 23, pp. 4828-4850, 2011.

CONTACT

*R. Maboudian, tel: +1-510-6433489;
maboudia@berkeley.edu