FIRST Center Research Perspective:

Title: Micro-supercapacitors

Yury Gogotsi, Majid Beidaghi, Vadym Mochalin,
John K. McDonough
Drexel University

Research Summary: We developed miniaturized on-chip supercapacitors, also called micro-supercapacitors, with high power density, rate handling ability and frequency response. We showed that by a rational design of the device architecture and electrode materials, micro-supercapacitors could approach the power density of conventional electrolytic capacitors, while delivering much higher energy density. We also demonstrated that the energy density of micro-supercapacitors could be further increased by using ionic liquids as the electrolyte. Furthermore, we showed that by using a eutectic mixture of ionic liquids as the electrolyte, micro-supercapacitors can be made functional over a wide range of temperatures from − 50 °C to 80 °C. Microscale supercapacitor electrodes also enable *in situ* studies of fundamental charge-discharge mechanisms of electrochemical capacitors.

Technical Details:

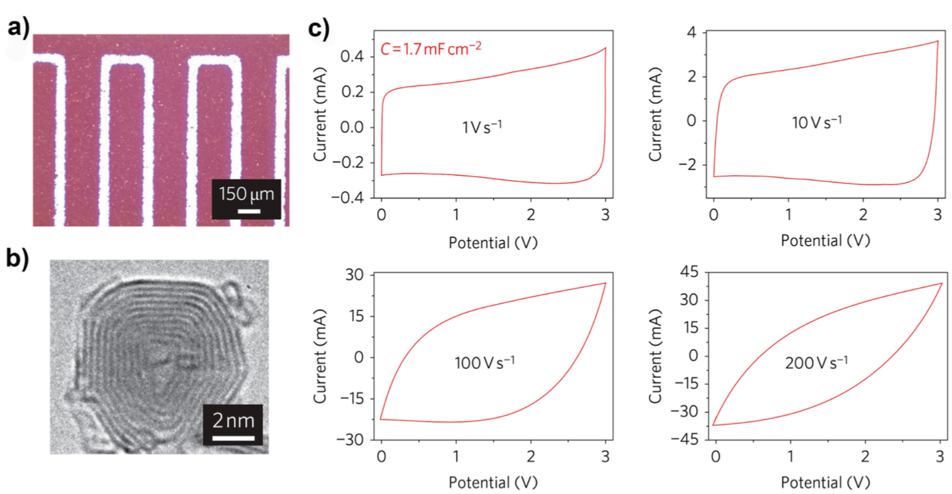

Figure 1. (a) Optical image of interdigital electrodes of OLC. (b) Transmission electron microscopy image of a carbon onion. (c) cyclic voltammograms at different scan rates for a micro-supercapacitor with 16 interdigital electrodes [Pech, 2010]

Building on extensive fundamental studies of onion-like carbon (OLCs)-electrolyte interfaces conducted by FIRST researchers (McDonough, 2011; McDonough, 2013; Anjos, 2013) we developed OLC-based devices. A micro-supercapacitor fabricated by electrophoretic deposition of OLC on the interdigital gold electrodes patterned on a Si wafer is shown in **Figure 1a**. The OLC-based micro-supercapacitors were tested in a typical organic electrolyte (1 M NEt4BF4 solution in propylene carbonate) and offered an ultra-high power handling capability and could be cycled at very high scan rates (**Figure 1c**), showing capacitive performance at cyclic voltammetry (CV) scan rates as high as 100 Vs^{-1}. Also, Electrochemical Impedance Spectroscopy (EIS) studies showed a resistive-capacitive (RC) time constant of only 26 ms for these micro-supercapacitors. The observed performance is related to properties of electrode materials, binder-free fabrication method and also interdigitated electrode architecture of these microdevices. OLC has an exohedral structure (**Figure 1b**) with no interparticle porosity, which offers a lower specific surface area compared to porous activated and carbide-derived carbon materials. However, the surface of OLC is highly accessible for electrolyte ions resulting in a high rate capability and high power density of OLC based supercapacitor electrodes. Also, the fabrication of the electrodes by electrophoretic deposition eliminates the need to use polymeric binder in the electrodes, which results in their higher conductivity. We showed that the architecture of a micro-supercapacitor also has immense impact on its performance. The small distance between the microelectrode fingers results in the reduction of mean ionic diffusion path between the electrodes. The effect of the size and spacing of the interdigital electrodes on the performance of the device was studied by changing the number of electrode fingers for a constant geometrical surface area of the electrode. For a higher number of the electrode fingers, (i.e. smaller width of the electrodes and smaller spacing between them) a higher specific capacitance and a better rate capability was achieved. The OLC-based micro-supercapacitor showed a maximum power density of 1 $kWcm^{-3}$, approaching the power density of electrolytic capacitors, and offering orders of magnitude higher energy density at the same time.

We also used a eutectic mixture of ionic liquids (IL) as electrolyte for OLC based micro-supercapacitors and demonstrated a larger working potential and also working temperature range for these microdevices (Huang, 2013). This device was electrochemically characterized by cyclic voltammetry and electrochemical impedance spectroscopy in [$Pip_{13}FSI:Pyr_{14}FSI$] 1:1 ionic liquid electrolyte mixture at different scan rates and different temperatures. At 20 °C, a micro-supercapacitor operating in a voltage window of 3.7 V and tested at a CV scan rate of 200 mVs^{-1} showed a capacitance of 1.1 $mF{\cdot}cm^{-2}$ per footprint area of the device. The microdevice maintained 76% of its capacitance when tested at -50 °C at the same voltage range and with a scan rate of 10 mVs^{-1}. Therefore, we showed that by using the IL mixture, OLC based micro-supercapacitors can be potentially used in portable electronic devices that are required to work under temperature extremes.

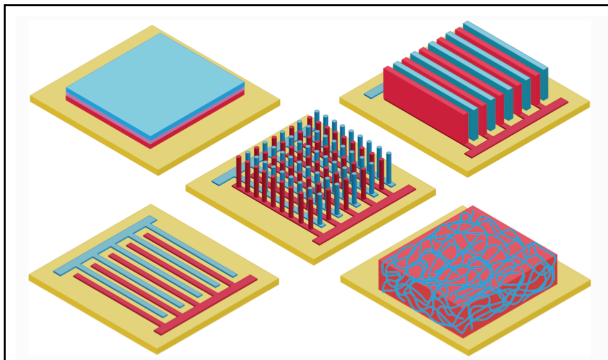

Figure 2. Schematic illustration of five possible device architectures for micro-supercapacitors.

Micro-supercapacitors are relatively new devices with a great potential for applications in microelectronics and self-powered micro-/nanosystems. In a recent review paper (Beidaghi, 2013), we have summarized the current state of research and development of micro-supercapacitor technology and identified the key scientific and technological challenges in developing micro-supercapacitors with improved power and energy densities. The performance of micro-supercapacitors is highly dependent on the architecture of the device. Among the possible device architectures for on-chip micro-supercapacitors (as shown in **Figure 2**), a three-dimensional design could potentially lead to a much higher energy density.

Significant Impacts on Science and Technology: Our work on design and fabrication of micro-supercapacitors, showed that by designing the device architecture and using appropriate electrode materials and electrolyte, supercapacitors with extremely high power density and frequency response can be developed. Our study shows the promise of supercapacitors for replacing electrolytic capacitors for line-filtering application or powering devices working at extreme temperatures.

Publications and Manuscripts:

1. Beidaghi, M.; Gogotsi, Y. Capacitive Energy Storage In Micro-Scale Devices: Recent Advances In Design And Fabrication Of Micro-Supercapacitors, *Energy & Environmental Science* **2013** [DOI: 10.1039/c3ee43526a] (invited review article).

2. Huang, P.; Pech, D.; Lin, R.; McDonough, J.K.; Brunet, M.; Taberna, P.L.; Gogotsi, Y.; Simon P. On-Chip Micro-Supercapacitors for Operation in a Wide Temperature Range, *Electrochem. Commun.***2013,** *36,* 53-56, [DOI: 10.1016/j.elecom.2013.09.003].

3. Pech, D.; Brunet, M.; Durou, H.; Huang, P.; Mochalin, V.; Gogotsi, Y.; Taberna, P. L.; Simon, P. Ultrahigh- Power Micrometre-Sized Supercapacitors Based on Onion-Like Carbon, *Nature Nanotech.* **2010**, *5* (9), 641-654, [DOI: 10.1038/NNANO.2010.162]. (More than 300 citations)

4.McDonough, J.; Frolov, A. I.; Presser, V.; Niu, J.; Miller, C. H.; Ubieto, T.; Fedorov, M. V.; Gogotsi, Y. Influence of the Structure of Carbon Onions on Their Electrochemical Performance in Supercapacitor Electrodes, *Carbon* **2011**, *50*, 3298-3309, [10.1016/j.carbon.2011.12.022].

5. McDonough, J. K.; Gogotsi, Y. Carbon Onions: Synthesis and Electrochemical Applications, *Interface* **2013**, *12,* 61-66.

6. Anjos, D.M.; McDonough, J.K.; Perre, E.; Brown, G.M.; Overbury, S.H.; Gogotsi, Y.; Presser, V. Pseudocapacitance and Performance Stability of Quinone-Coated Carbon Onions, *Nano Energy* **2013**, *2*,702-712, [10.1016/j.nanoen.2013.08.003].