

## Multifunctional Electrode Nanoarchitectures for Electrochemical Capacitors

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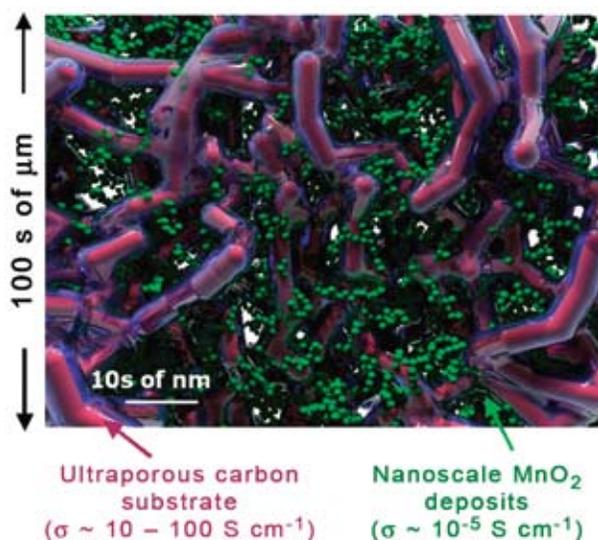
**Introduction:** The term electrochemical capacitor (EC) describes a diverse class of energy-storage devices that bridges the critical performance gap on the power vs energy density plane between the high power densities offered by conventional capacitors and the high energy densities of batteries.<sup>1</sup> Although from both practical and fundamental perspectives, ECs are closely related to batteries, electrochemical capacitors can be differentiated by charge-discharge response times that are on the order of seconds and by their exceptional cycle life (typically many tens to hundreds of thousands of cycles). The most visible technologies that will be impacted by ECs are hybrid-electric power systems, where significant increases in energy efficiency can be achieved through the recovery of energy normally wasted during braking of repetitive motion, thanks to the rapid charge-discharge response of ECs. Hybrid-electric power systems will become increasingly beneficial not only for transportation applications but also for large industrial equipment, including cranes and elevators.

Improvements in the high-power performance of electrochemical capacitors and batteries for applications ranging from mission-critical electronics and sensors to hybrid-electric power systems require a fundamental re-design of the underlying electrode architectures on the nanoscale. We recently demonstrated one such example of a multifunctional electrode nanoarchitecture in which electroactive nanoscale manganese oxide deposits cover the walls of the tortuous aperiodic structure of ultraporous carbon nanofoams

and related porous carbons.<sup>2</sup> In such a configuration (see Fig. 1), the nanostructured carbon substrate serves as a high-surface-area, massively parallel 3D current collector for the poorly conducting  $\text{MnO}_2$  coatings, and defines the internal pore structure of the electrode, which facilitates the infiltration and rapid transport of electrolyte (i.e., solvent and ions) to the nanoscopic  $\text{MnO}_2$  phase. The interest in manganese oxides for ECs has grown rapidly in recent years, primarily due to the low cost and low toxicity of  $\text{MnO}_2$  compared to other metal oxides.<sup>3</sup> By redesigning the structures of  $\text{MnO}_2$ -containing electrodes as multifunctional nanoarchitectures, significant improvements in charge-discharge response will be achieved, while retaining the inherent advantages of  $\text{MnO}_2$ .

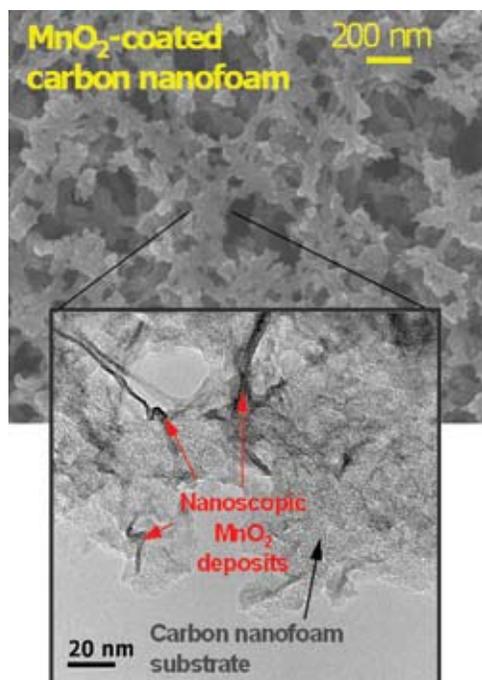
**New Results:** To achieve the multifunctional  $\text{MnO}_2$ -carbon nanoarchitecture illustrated in Fig. 1, we developed a simple, scalable electroless deposition process, based on the redox reaction of aqueous permanganate with pre-formed carbon nanofoam substrates. We discovered that by maintaining the permanganate precursor solution between neutral and basic pH conditions,  $\text{MnO}_2$  deposits directly on the surface of the nanofoam in a self-limiting fashion as 10–20 nm thick coatings of  $\text{MnO}_2$  nanofilaments (see transmission electron micrograph in Fig. 2), and these  $\text{MnO}_2$  deposits permeate the macroscopic thickness (180  $\mu\text{m}$ ) of the carbon nanofoam. Nitrogen-sorption measurements and scanning electron microscopy confirm that the through-connected pore network of the nanofoam is retained in the  $\text{MnO}_2$ -carbon nanoarchitecture, which is critical for realizing rapid charge-discharge of the resulting electrode.

In an electrochemical capacitor, the  $\text{MnO}_2$  coating serves as a “bank” for charge storage via redox reactions involving cations from the contacting aqueous electro-



**FIGURE 1**

Schematic of the interior of a multifunctional nanoarchitecture comprising a carbon nanofoam or related ultraporous carbon coated with nanoscale deposits of nanoscale  $\text{MnO}_2$ . The approximate electrical conductivities ( $\sigma$ ) of both components are noted.

**FIGURE 2**

Scanning electron micrograph (top) and transmission electron micrograph (bottom) of a MnO<sub>2</sub>-carbon nanofoam hybrid nanoarchitecture.

lyte and electrons from the external circuit, resulting in significant enhancements in capacitance for MnO<sub>2</sub>-carbon nanoarchitectures with respect to what can be achieved solely by the innate double-layer capacitance ( $20\text{--}40\ \mu\text{F cm}^{-2}$ ) at the unmodified carbon nanofoam surface. For example, the mass-normalized capacitance of carbon nanofoam structures can be increased by a factor of four, even at MnO<sub>2</sub> weight loadings of <40%. Enhancements in charge-storage capacity are even more dramatic when normalized to either the volume or the geometric area (i.e., the “footprint” of the electrode on the current collector) of the electrode structure, which are unaltered by MnO<sub>2</sub> deposition. For the same conditions described above, both the volumetric and the footprint-normalized capacitance are increased by a factor of ten after MnO<sub>2</sub> deposition, and in terms of absolute performance, the footprint-normalized capacitances of the MnO<sub>2</sub>-carbon nanofoams routinely exceed  $3\ \text{F cm}^{-2}$ . The ability to realize high capacitance per unit area, enabled in this case by the 3D multifunctional electrode design, is a critical advantage when powering microelectronics devices that have a limited areal footprint for the power source. Although these initial results are very promising, we anticipate further performance improvements by tuning such parameters as the mass loading and crystal structure of the MnO<sub>2</sub> mass loading, and the pore structure of the supporting carbon nanofoam.

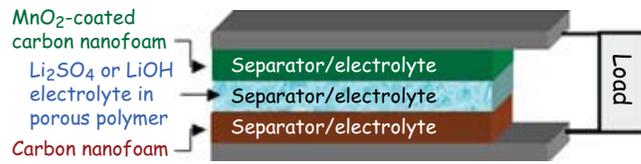
**Impact:** Ultimately, the materials developed in this program will be deployed in 2-V aqueous asymmetric capacitors, in which high-rate performance will be

significantly enhanced through the use of well-designed MnO<sub>2</sub>-carbon nanoarchitecture cathodes. Prototype EC cells assembled and tested at NRL are already demonstrating such promise (see Fig. 3). With further fine-tuning of MnO<sub>2</sub>-carbon cathodes and application of the nanoarchitecture design approach to the carbon anode, asymmetric ECs that deliver energy densities  $>40\ \text{Wh kg}^{-1}$  and exhibit charge-discharge response times of  $<10\ \text{s}$  can be realized, which would represent a significant advancement over current state-of-the-art ECs, which have energy densities of  $<5\ \text{Wh kg}^{-1}$ . Combining such performance metrics in an EC design that utilizes aqueous electrolytes will yield a class of safe, low-cost energy-storage devices with superior combinations of energy and power density that will enable emerging civilian and military applications. The transition of technology resulting from this program is already under way, with a patent application and corresponding licensing agreement to develop and commercialize ECs based on NRL-developed materials.

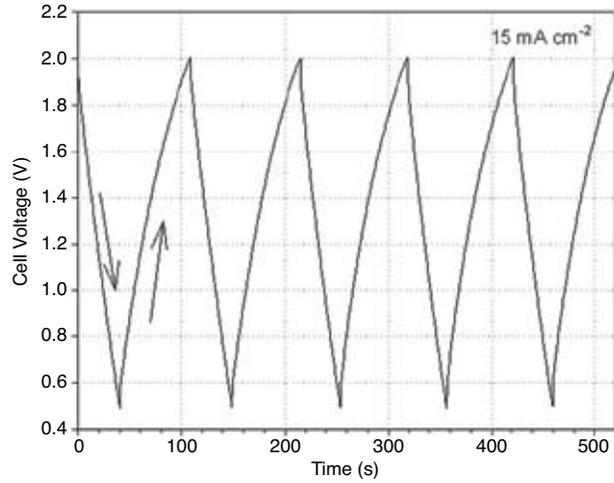
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#### References

- <sup>1</sup> B.E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications* (Kluwer Academic/Plenum Publishers, New York, 1999).
- <sup>2</sup> A.E. Fischer, K.A. Pettigrew, D.R. Rolison, R.M. Stroud, and J.W. Long, “Incorporation of Homogeneous, Nanoscale MnO<sub>2</sub> within Ultraporous Carbon Structures via Self-limiting Electroless Deposition: Implications for Electrochemical Capacitors,” *Nano Lett.* **7**, 281-286 (2007).
- <sup>3</sup> D. Bélanger, T. Brousse, and J.W. Long, “Manganese Oxides: Battery Materials Make the Leap to Electrochemical Capacitors,” *Interface* **17**, in press. ★



\*both electrodes are 180- $\mu$ m thick



**FIGURE 3**

Schematic of asymmetric EC cell with NRL-developed electrodes (top); photo of prototype cell (bottom left); and electrochemical cycling of an aqueous-electrolyte EC pouch cell between 0.5 and 2 V, showing full cell charge-discharge in tens of seconds.