

**AQUEOUS ASYMMETRIC ELECTROCHEMICAL
CAPACITORS: FUNDAMENTAL DESIGN AND
PRACTICAL CONSIDERATIONS EN ROUTE TO SAFE,
HIGH-PERFORMANCE PULSE POWER**

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Electrochemical capacitors (ECs) are a well-established class of energy-storage devices that span the critical performance divide between conventional capacitors (high specific power) and batteries (high specific energy), and are thus well poised to address the challenging energy and power requirements of advanced devices. Commercially available ECs are still largely based on the original symmetric device configuration in which charge is stored in the electrochemical double-layer formed at the interface between the high-surface-area carbon-based powder-composite electrode and the nonaqueous electrolyte. The reliance on charge storage in the electrochemical double-layer ultimately limits the specific energy (3–6 W h kg⁻¹) of the symmetric carbon-carbon EC, restricting their application space. Advances in nanoscale science and high-voltage electrolytes offer the promise of enhanced specific energy of these symmetric carbon-carbon ECs, but even with these improvements, symmetric carbon-carbon ECs will still fail to meet the requirements of applications demanding higher specific energy (10–25 W h kg⁻¹).

The next evolution in ECs aims to address the energy/power performance gap that exists between symmetric carbon-carbon ECs (high power/moderate energy) and batteries (low power/high energy).¹ The specific energy of ECs can be increased through the incorporation of materials, such as metal oxides, that store charge via rapid and reversible faradaic reactions (pseudocapacitance), thus augmenting the double-layer capacitance.² The availability of pseudocapacitance makes aqueous electrolytes viable for ECs, particularly when distinct electrodes are paired in an asymmetric configuration to extend the operating voltage beyond the thermodynamic limit of water (~1.2 V).¹ In order to fully utilize the enhancements in specific energy offered by aqueous asymmetric ECs, while maintaining specific power comparable to symmetric carbon-carbon ECs, the electrode constructions containing pseudocapacitive materials should be redesigned from an architectural perspective.

Carbon nanofoams are attractive electrode architectures due to high specific surface area (300–600 m² g⁻¹), electrical conductivity (20–80 S cm⁻¹), and size-tunable, through-connected pore structures (tens of nanometers to micrometers), all of which support high-rate operation in electrochemical energy-storage devices.³ To incorporate pseudocapacitance functionality in carbon nanofoams, we use self-limiting electroless deposition methods to apply conformal, nanoscale metal oxide (MnOx or FeOx) coatings at the carbon walls throughout the macroscopic thickness (70–300 μm) of the nanofoam.²

The pseudocapacitance of the incorporated metal oxide increases the charge-storage capacity of the nanofoam by factors of 2–10, while the conformal, nanoscale nature of the metal oxide ensures that the fast charge-discharge capabilities of the underlying carbon nanofoam are retained.^{4,5,6} Prototype aqueous asymmetric electrochemical capacitors composed of a MnOx-carbon nanofoam positive electrode and an FeOx-carbon nanofoam negative electrode provide operating voltages approaching 2 V.² The increased operating voltage and the nanoarchitectural electrode design result in cell-level specific capacitance >30 F g⁻¹ and a specific energy of 14 W h kg⁻¹ available within a 10-s charge-discharge timeframe.

In order to further improve electrode design, particularly for high-rate operation, we are systematically investigating the interplay of electrode architecture (pore size and distribution, macroscale thickness) and fundamental charge-transfer kinetics (associated with the pseudocapacitance reactions of the metal oxide). In addition, we are also exploring more practical issues related to aqueous asymmetric ECs, including the down-selection of current collectors, separators, and aqueous electrolytes that promote high power, long cycle life, and effective low-temperature operation. Such practical optimizations will be critical to the commercialization of aqueous asymmetric ECs.

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