



Increased working voltage of hexamine-coated porous carbon for supercapacitors

Stephanie L. Candelaria · Guozhong Cao

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Abstract Highly porous carbon, both unmodified and hexamine-coated on the pore surfaces, is tested at high working voltages in organic electrolyte for supercapacitors in order to enhance the energy density and power density. Sol-gel processing allows for excellent control of the porous structure and chemical composition of carbon, resulting in a material with high surface area and a low level of impurities. This porous carbon can be modified using a simple solution-based method to enhance capacitance. Increasing the working voltage from 2.0 to 3.0 V significantly improves performance for both unmodified and hexamine-coated carbon. The energy density and power density increase at higher working voltage, and under certain conditions, the capacitance increases as well. Cyclic stability is also investigated, with hexamine-coated carbon retaining more of its initial capacitance than unmodified carbon at all working voltages.

Keywords Supercapacitor · High voltage · Porous carbon · Hexamine · Surface modification · Nitrogen

1 Introduction

Carbon-based supercapacitors, also known as ultracapacitors or electrochemical capacitors, are emerging as a viable solution to the energy storage challenges that society is

beginning to encounter. Aside from already finding applications in electric vehicles and industrial equipment, such as forklifts and cranes, supercapacitors may find widespread use as a means to collect and store energy generated by wind, solar, and other renewable resources [1–6].

There are several advantages that supercapacitors have over other energy storage devices. They can charge and discharge quickly and have cyclic stability that can exceed millions of cycles [7, 8]. Supercapacitors are also environmentally friendly, are safe, and can operate in a wide range of temperatures [2–4]. They have high power density that can reach over 10 kW/kg, which is about 10 times larger than secondary batteries [9, 10]. However, supercapacitors are limited by their energy density, which is often <10 Wh/kg, while batteries can reach 1,000 Wh/kg [1]. Increasing the energy density of supercapacitors represents an important challenge in order to make these devices more competitive with batteries and to decrease costs [11].

Energy density can be increased through increasing the capacitance or working voltage of the device according to Eq. (1),

$$E = \frac{1}{2} CV^2, \quad (1)$$

where E is the energy density, C is the capacitance, and V is the applied voltage. Since voltage is squared, increasing it will have a much greater effect on the energy density than only increasing the capacitance. A higher voltage will also have an effect on the power density P according to Eq. (2),

$$P = \frac{V^2}{4R_s m}, \quad (2)$$

where R_s is the equivalent series resistance (ESR), and m is the mass of the electrodes. Like energy density, the power

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S. L. Candelaria · G. Cao (✉)
Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195-2120, USA
e-mail: gzcao@u.washington.edu

density depends on the square of voltage, so a higher working voltage will significantly increase this value.

The most significant limitation to increase the working voltage of a device is the stability of the electrolyte. While the capacitance is high for devices using aqueous electrolytes (100–300 F/g), the voltage window is limited. The thermodynamic stability of water is 1.23 V, but the working voltage is usually restricted to 0.8 V due to concerns of uncontrolled potential at each electrode and capacitance mismatch [8, 12]. In contrast, organic electrolytes have a more modest capacitance (40–150 F/g), but the voltage window is typically 2.0–2.3 V [12]. Devices are rarely tested at higher working voltages because as the voltage approaches 3 V, organic electrolytes can break down due to reactions with oxygen and other unwanted impurities in the porous carbon electrodes [13, 14]. Higher working voltages are also known to decrease device lifetime and durability. This is due to the higher voltage amplifying the effects of electrolyte degradation due to impurities and mechanical breakdown from the electrode swelling during charge and discharge [13].

Synthesis of a highly pure carbon can prevent reactions between impurities and the electrolyte from occurring, and therefore, the working voltage can be pushed higher. In a study by Izadi-Najafabadi et al. [13], high-purity carbon nanotubes (CNTs) were used as electrodes for supercapacitors subjected to high working voltage. Vertically aligned single-wall CNTs were synthesized through water-assisted chemical vapor deposition and then pressed into binderless electrodes. Devices were tested in organic electrolyte up to 4.0 V and achieved a power density as high as 210 kW/kg. Despite this promising result, CNTs often suffer from low specific surface areas and remain expensive to manufacture, severely limiting their practical application.

Highly porous carbon prepared through sol–gel processing is an inexpensive alternative to CNTs. These porous carbons have high specific surface areas and a tunable three-dimensional hierarchical morphology. Sol–gel-derived carbon also has low mass densities, has continuous porosities, and can be easily fabricated in large quantities. Through careful manipulation of processing conditions, sol–gel processing allows for precise control over the specific surface area, pore volume, pore size, and pore size distribution of porous carbon [15–17]. Additionally, depending on precursor and catalyst selection, the level of unwanted impurities in porous carbon synthesized through sol–gel processing can be limited to <2 wt% [17].

Recently, we have shown that selected dopant atoms, such as boron [18], nitrogen [19, 20], and sulfur [21–23], can induce pseudocapacitive reactions in porous carbons used for electrochemical capacitors. Unlike decorating carbon structures with transition metal oxides, which can

result in materials with very high capacitance but low rate capacity and limited cycle life due to material instability, these dopant atoms can enhance the capacitance of carbon with minimal detrimental effects. Nitrogen-modified materials are already highly researched in literature [24], showing excellent performance in both aqueous and organic electrolytes. Nitrogen doping can be achieved through many different processes, including the use of nitrogen-containing carbon precursors [25–29], heat treatment in ammonia [30–33], sublimation [19, 34], and coating with conductive polymers [35–38].

Our previous studies have demonstrated that porous carbon modified with hexamine, a small nitrogen-containing molecule, shows particular promise for supercapacitors with enhanced performance [19, 20]. As such, it is believed that these materials may have excellent properties at higher working voltages as well, especially in regard to energy density and power density. In this work, high-purity unmodified carbon and hexamine-coated carbon are tested as electrode materials in supercapacitors up to a working voltage of 3 V. The objective is to determine under what conditions (nitrogen content and working voltage) the performance of supercapacitor devices are maximized, paying particular attention to energy density and power density. The effect on cyclic stability will also be investigated.

2 Experimental

2.1 Synthesis

Highly porous carbon cryogels are prepared from precursors resorcinol and furfuraldehyde using hexamethylenetetramine (hexamine or HTMA) as the catalyst. The procedure for synthesizing highly porous carbon is similar to that reported elsewhere [16, 17]. The furfuraldehyde-to-resorcinol molar ratio is set to 2.5, and the resorcinol-to-hexamine molar ratio is 75. The resorcinol and furfuraldehyde are mixed together first, followed by the addition of the solvent *tert*-butanol, and finally hexamine to catalyze the reaction. The mixture is sealed and cured in an oven at 80° for 7 d to allow for gelation and aging to strengthen the newly formed three-dimensional gel network. The wet organic gel is dried under vacuum at –50° in a Labconco FreeZone 1 L freeze dryer. After drying for several days, the organic gel is pyrolyzed at 900° for 3 h under nitrogen flow with a ramp rate of 5°/min. Activation takes place under dry air flow at 420° for 4 h with a ramp rate of 5°/min, followed by heating again 900° for 3 h under nitrogen flow to remove new functional groups that may have formed during activation.

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