

Novel High Energy Density Supercapacitors

Steven Risser, Bing Tan, Homero Castaneda, Kevin Spahr, Mark Stasik, Vincent McGinniss
Battelle Memorial Institute, Columbus, OH, USA, rissers@battelle.org

ABSTRACT

Cost-effective electrical storage is a critical need for markets as varied as portable electronics, transportation, and renewable energy. In all these markets, improvements in energy density and power density are desired, as is longer cycling lifetime. One technology Battelle has been actively investigating is hybrid supercapacitors which consist of a high surface area electrode with an aqueous or non-aqueous electrolyte.

Control of both the electrode composition and electrolyte allows the performance to be tuned to meet specific application targets. One target has been high energy density with extended cycling lifetime, for use with photovoltaic energy sources. We demonstrate energy density of 50 Wh/kg with stable performance over hundreds of charge/discharge cycles. Another target has been increased power and energy densities with charge/discharge time on the order of one second. We demonstrate energy density during discharge of 10 Wh/kg at power density of 10 kW/kg.

Keywords: hybrid supercapacitor, metal oxide, energy density, power density

1 INTRODUCTION

There is a growing need for efficient and cost-effective ways to store and deliver electrical power. Most commonly, electrical power has usually been stored in batteries, although batteries are not well-suited to many possible storage applications. A second class of device for storing power is a capacitor, and more recently the so-called supercapacitor. These commercially available devices are commonly composed of two high surface area carbon electrodes with a liquid electrolyte. The capacitance arises from a double layer mechanism, where the ions in the electrolyte move adjacent to the electrode surface. In this case, the capacitance increases as a result of the increase in the surface area of the electrode due to the surface area available, and the decrease in the charge separation distance.

Recent advances in the synthesis of high surface area materials have also led to initial development of the "hybrid" supercapacitor. In these devices, both double-layer and the faradaic mechanism are present, to provide the operational advantages of each mechanism. The faradaic mechanism uses reversible reactions at the electrode-electrolyte interface to exchange charges into the structure of the high surface area material (commonly an oxide or nitride) [1]. This combination of mechanisms

allows creation of an energy storage system which has both high energy and high power density, while maintaining a long cycle life.

Achieving high energy and power densities requires development of materials which not only possess high capacity for charge, but also are able to facilitate the transport of charge into and out of the system. Battelle has been actively engaged in developing hybrid supercapacitors by combining various metal oxide nanomaterials with high surface area conductive supports such as foamed metals, carbon nanotubes, and carbon blacks. The nano-sized electrode materials are obtained through the controlled synthesis and formulation of super high surface area and high conductivity metal oxides with conductive supports.

The ability to control both the electrode composition and its architecture allows the performance of the hybrid supercapacitor to be tuned to meet specific performance and cost targets. Initial targets have been selected to demonstrate the ability of this technology to satisfy unmet energy storage needs on both slow and fast discharge applications: low cost supercapacitors that provide high energy density at low power levels with a cycling lifetime of several thousand charge/discharge cycles, and supercapacitors with enhanced power density and energy density with charge/discharge time of one second. The remainder of this paper will outline the synthesis and characterization of the metal oxide nanomaterials, the electrochemical testing methods, results for both low power and high power conditions, and finally conclusions to be drawn from this work.

2 EXPERIMENTAL

2.1 Metal Oxide Synthesis and Characterization

The metal oxide nanoparticles were synthesized using a sol-gel process adapted from literature [2,3]. After formation, the gel was aged, solvent-exchanged, and then dried to produce the final metal oxide/hydroxide.

The metal oxide/hydroxide was characterized by several methods, including XRD, EDS, SEM/TEM, and BET. Figure 1 shows a representative SEM image of the materials synthesized and tested. Samples for BET analysis were degassed at 50 °C under vacuum for 8 hours or longer. The BET analysis of a typical sample gave surface area of 319 m²/g.

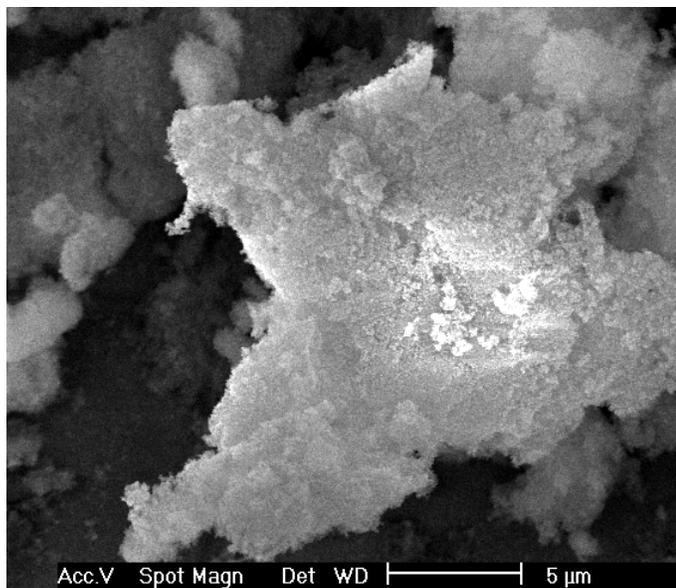


Figure 1. SEM image of metal oxide.

2.2 Electrochemical Methods

Electrodes for testing were formed by grinding the metal oxide powder, adding carbon, binder, and solvent. The mixture was again ground to form a paste, which was then applied to the current collector and dried. A Nylon filter disc was placed over the dried metal oxide electrode. The electrode/filter disc assembly was placed in the electrochemical apparatus for measurement.

The fabricated electrodes were characterized to determine their capacitance, voltage window, open circuit potential, and impedance. Figure 2 shows the half-cell configuration used to measure specific capacitance. The metal oxide electrode was used as the working electrode covering a stainless steel current collector with a platinum mesh counter electrode. Additional capacitance measurements in a full-cell configuration were conducted. Testing using a full-cell configuration was performed to measure energy and power density. Each half of the full-cell testing configuration is similar to the half-cell depicted in Figure 2.

The set of electrochemical experiments used to fully characterize the electrodes includes:

- Open circuit potential with time
- Electrochemical Impedance Spectroscopy (10 mV amplitude) 10KHz to 0.01Hz
- Cyclic voltammetry, and
- Galvanic voltammetry.

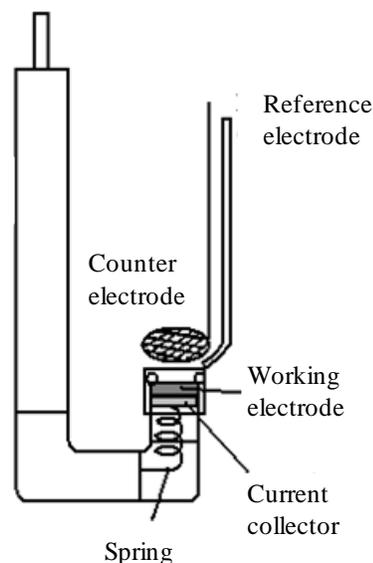


Figure 2. Half-cell test configuration.

3 RESULTS

This section reports the experimental results for the supercapacitor materials described above. Testing was performed using a variety of electrolytes, under a wide range of experimental conditions. The specific capacitance values reported here were calculated by dividing the measured capacitance by the total mass of the working electrode, including carbon support and binder. Energy and power densities reported were calculated by dividing the measured energy and power by the total mass of both electrodes and the minimum electrolyte mass needed to provide the charge stored at the electrode interface.

3.1 Low-Power Slow Discharge Results

The first performance target for this hybrid supercapacitor technology is high energy density at low power levels with a cycling lifetime of several thousand charge/discharge cycles. This performance target is useful for providing energy storage for renewable energy sources, such as photovoltaic applications. In this case, a lifetime of thousands of cycles would match the lifetime of the energy storage device to that of the photovoltaics, eliminating the need to replace storage batteries every few years.

The specific capacitance was measured using cyclic voltammetry at several voltage scan rates. The capacitance showed sharp decrease with increasing voltage scan rate. To best represent envisioned operation conditions, the data reported was measured at a scan rate of 0.1 mV/s, using a standard organic electrolyte. The specific capacitance measured was 530 F/g, with a 2.2 V voltage window. The limitation on cell voltage was attributed to trace amounts of water in the non-aqueous solvent due to

absorption from the atmosphere. Testing performed under more rigorous water-free conditions showed cell voltage could be extended to 2.7 V or higher.

The energy density for this system was calculated from symmetric full-cell measurements of the stored energy, using the mass of the pair of electrodes and the mass of electrolyte required to achieve cell voltage of 2.2 V. These calculations show that the system achieved energy density of 50 Wh/l. Increasing the cell voltage to 3.0 V or higher, which can be readily achieved under moisture-free conditions, shows energy density should exceed 70 Wh/l.

Another performance target for this slow-charge application is stability under cycling. The cycling performance in non-aqueous electrolytes is best illustrated in Figure 3, which plots the measured specific capacitance as a function of cyclic voltammetry (CV) cycle number. This initial interface stability testing in non-aqueous solvents showed the capacitance to be stable for 50 cycles after some initial fluctuation due to interface stabilization. Analysis of CV curves indicated that the primary capacitance mechanism appears to be double layer in non-aqueous electrolytes.

After the preliminary testing, the electrode went through additional repeated rounds of testing and characterization, including measurements of capacitance and impedance, with no significant change in measured properties after more than 100 voltage cycles (greater than 1200 hours under testing).

3.2 High-Power Fast-Discharge Results

The second target application for this hybrid supercapacitor technology is high energy and power densities with charge or discharge times on the order of one second. This application is useful for providing very large power bursts, or absorbing large power surges.

The devices were fabricated as described previously using two different metal oxides to form the pair of electrodes. The energy density for this system was determined with galvanic voltammetry measurements on a non-symmetric full-cell using an aqueous electrolyte and maximum cell voltage of 1.5V. The energy was determined from the time-dependent cell voltage. The average power was determined by dividing the total energy stored or discharged by the charge or discharge time. Testing was performed at current densities of up to 40 A/g, at which point the measurements became unstable due to equipment limitations. At 20 A/g, the energy density during discharge was determined to be 11.3 Wh/kg, with a power density of 10 kW/kg. This corresponds to a 5 second charge or discharge period.

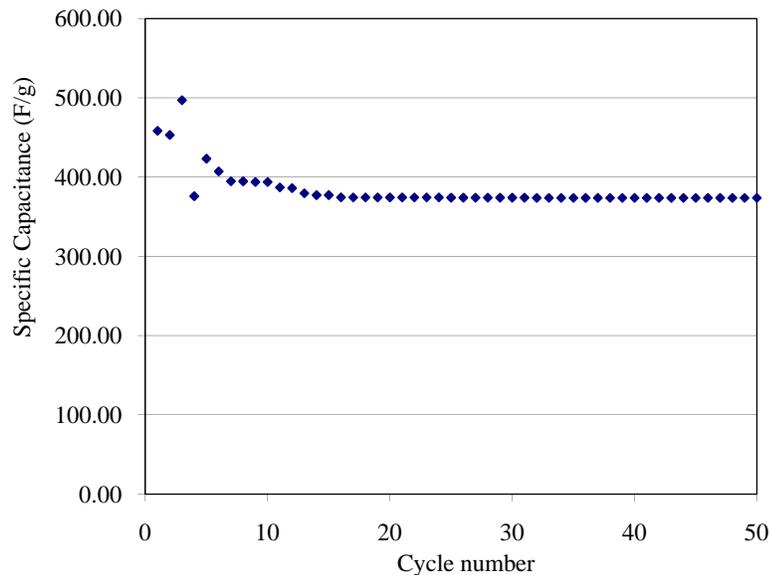


Figure 3. Capacitance as a function of cycle number.

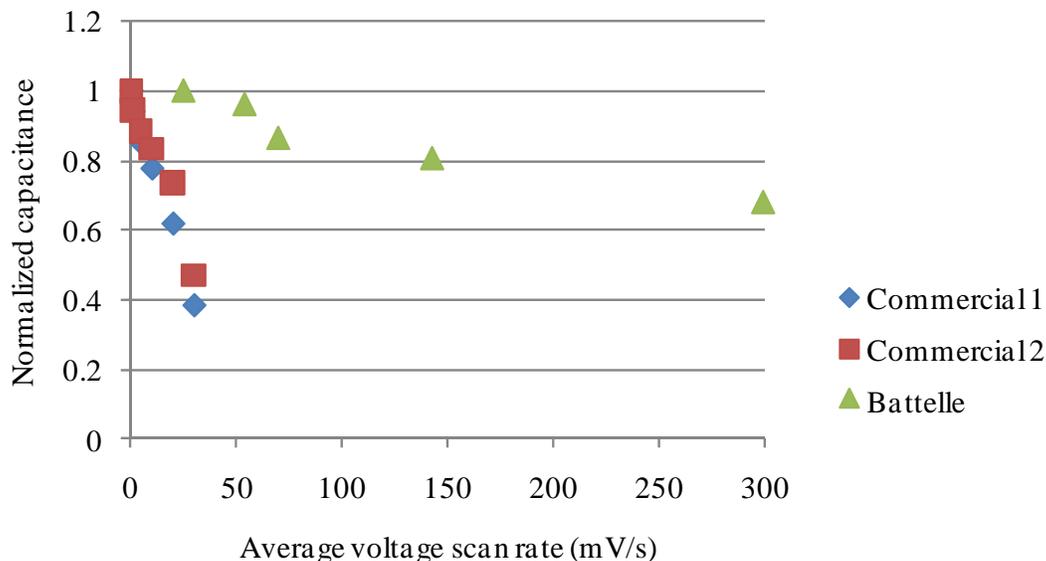


Figure 4. Dependence of capacitance on charge rate.

The capacitance of the non-symmetric full-cell device as a function of the charge-discharge rate is shown in Figure 4. The data is normalized to the capacitance measured at the slowest charge rate. The figure shows the capacitance at the highest charge rate is still 70% of that measured at the lowest charge rate. Based on these results, we expect these devices would exhibit good performance at even higher charge rates. For comparison, the charge rate dependence of two commercial carbon supercapacitors was also measured and is shown in the Figure 4. Comparison of this work to the commercial supercapacitors shows the vast improvement in high charge/discharge performance that has been achieved here.

4 CONCLUSIONS

Hybrid supercapacitors based on a composite of metal oxides and carbon were developed. The composition of these supercapacitors can be modified to allow performance of the supercapacitor to be tuned to specific application requirements. For devices requiring high energy density with a cycling lifetime of several thousand charge/discharge cycles, we have demonstrated energy density of 50 Wh/liter, which can be easily extended to more than 70 Wh/l through control of moisture in the electrolyte. These devices have also been shown to be extremely stable for more than 1200 hours of testing. For devices with increased power and energy densities that have a charge/discharge time on the order of one second, we have shown energy density during discharge of more than 11

Wh/kg with power of 10 kW/kg, corresponding to a discharge time of 5 seconds. The small change in capacitance as charge rate increases leads us to believe these devices can perform well at even higher charge or discharge rates.

REFERENCES

- [1] For example, see Piao et al. *J. Electrochem Soc.* 146, 2794-2798 (1999).
- [2] Walker et al. *J. Solid State Chemistry* 180, 2290-2297, 2007.
- [3] Cui et al., *J. Non-Cryst Solids* 351, 2102-2106, 2005.