

Design Considerations and Characterization of Origami Electrochemical Capacitors

by

Gabriel G. Blanton

Submitted to the Department of Mechanical Engineering in
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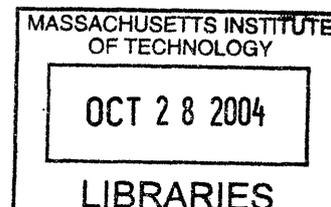
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To my family because you always have been
and to my friends because I know you always will be.

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Abstract

Electrochemical capacitors, also known as supercapacitors, ultracapacitors, and electric double-layer capacitors, have recently received attention as electrical energy storage devices. The devices are both high power and high energy, making them ideally suited for load balancing applications in such demanding applications as electric vehicles, transmission devices, and other systems with intermittent peaks in power. Recent trends in miniaturization have created applications where size and weight constraints are critical. Micropower devices such as microelectromechanical systems (MEMS) and miniature remote sensors with consumption in the range of milliWatts to Watts are increasingly common. To help meet the power demands of these miniature devices, micron-scale electrochemical capacitors are being developed that utilize traditional two dimensional fabrication techniques combined with folding methods to form the third dimension. Devices produced in this manner allow for close packing of multiple layers, resulting in high power and energy densities. This work examines the scientific fundamentals governing electrochemical capacitors and the design, fabrication, and testing of devices produced at the Massachusetts Institute of Technology utilizing the OrigamiTM technique.

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1 Introduction

Electrochemical capacitors, devices which store electrical energy in the double-layer of charge separation at the interface of an electrolyte and solid electrodes, are known variously as supercapacitors, ultracapacitors, and electric double-layer capacitors (EDLC). The terms supercapacitor and ultracapacitor are the tradenames of devices developed by Nippon Electric Company (NEC) and Pinnacle Research Institute (PRI), respectively, for commercial and military applications [1]. The term electric double-layer capacitor describes the mode of storage but is lengthy. The term used throughout this text is then electrochemical capacitor, preferred for its brevity and inclusiveness of all types of electrochemical capacitors, both those that are dominated by charge storage in the electric double-layer and those that exhibit Faradaic pseudocapacitance at the electrode surfaces.

The simplest electrochemical capacitors operate on electrostatic charging of the electric double-layer formed between each electrode and the electrolyte. More complex ones additionally exhibit pseudocapacitance due to Faradaic transfers of charge between the surface of the electrodes and the electrolyte. These transfers allow far more charge, and therefore energy, to be stored than in the double-layer alone and greatly increase the devices' capacitances. Because the charge is transferred only to the surface of the electrode and there is little reaction within the material itself, these reactions are highly reversible. The high reversibility of the storage mechanisms results in both high efficiencies and long life.

The behavior of electrochemical capacitors is intermediate that of existing battery technologies and traditional capacitors. The large specific capacitances of electrochemical capacitors allow them to store significantly greater energy than traditional capacitors, nearly as much some types of batteries. The current delivery of electrochemical capacitors is not as limited by the oxidation-reduction reaction rates that limit batteries, giving them greater power capabilities, although larger series resistances prevents them from delivering the high power of traditional capacitors. Ragone plots, such as the one presented in Figure 1, graphically demonstrate the typical specific energy and specific power of energy storage devices and display the intermediary characteristics of electrochemical capacitors.

Due to their unique characteristics, electrochemical capacitors have been the subject of increased interest and study. In electrical systems that demand intermittent pulses of high power, electrochemical capacitors can be utilized to balance the load on the main power source. In such load balancing applications the combination of low impedance, high power capacitors with high impedance, high energy batteries results in a low impedance, high power, and high energy source of significantly reduced volume and weight. Electrochemical capacitors are seen as essential components for the realization of electric vehicles and similar high power electromechanical systems.

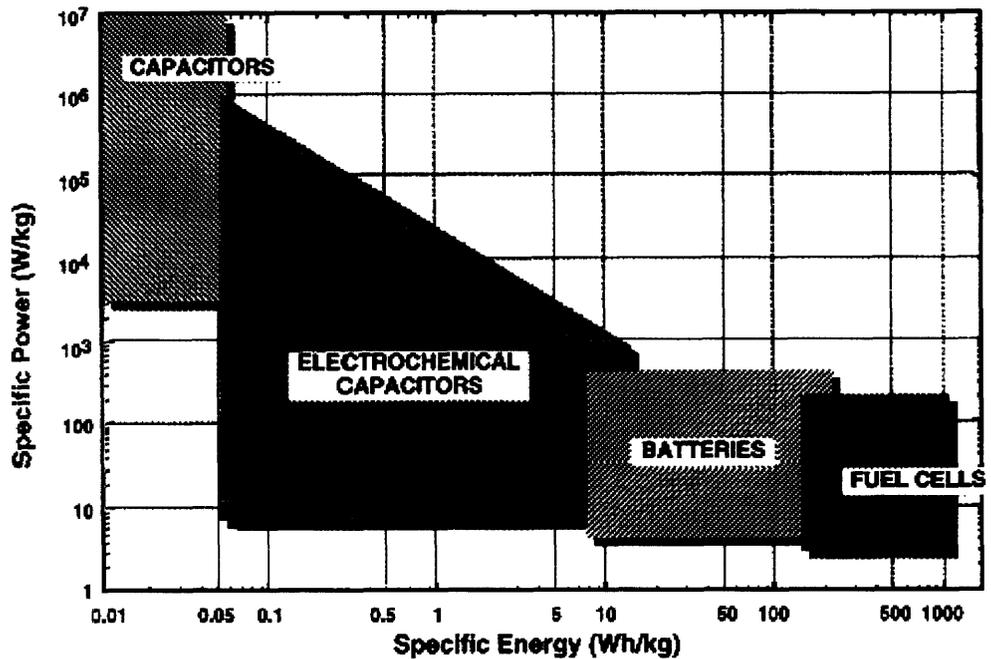


Figure 1 Ragone plot of the specific power and specific energy capabilities of various electrical devices, including electrochemical capacitors [2].

Recent trends in miniaturization have led to many applications which require micropower in the range of milliWatts to Watts. Microelectromechanical systems (MEMS), microsensors and transmitters, as well as consumer electronics such as cellular phones, PDAs, and laptop computers are all examples of applications where intermittent pulses of power are necessary and where volume and weight are critical. Electrochemical capacitors are ideally suited to help provide the power requirements of such devices due to their very high specific power, resulting in much smaller and lighter devices at a given capacitance than could be achieved with traditional capacitor technologies. The utilization of these capacitors can significantly reduce the overall size and weight of the power sources in these critical applications.

Electrochemical capacitor research has focused largely on the selection and engineering of materials suitable for use as electrodes and electrolyte. In addition to summarizing the basic principles which govern electrochemical capacitors, this work evaluates the design of electrochemical capacitors under development in the 3D Optical Systems Group at the Massachusetts Institute of Technology. The design and fabrication of these devices are discussed, as well as appropriate test methods and preliminary results.

2 Principles of Electrochemical Capacitors

The basic laws governing the storage of energy are the same for electrochemical capacitors as for traditional electrostatic capacitors.

2.1 Scientific fundamentals

The simplest capacitor, illustrated in Figure 2, consists of two parallel plates of area A separated by a distance d . When a potential difference V is applied across the plates of such a capacitor current flows and charge accumulates on the two plates until the capacitor's potential matches that of the source or the source is removed.

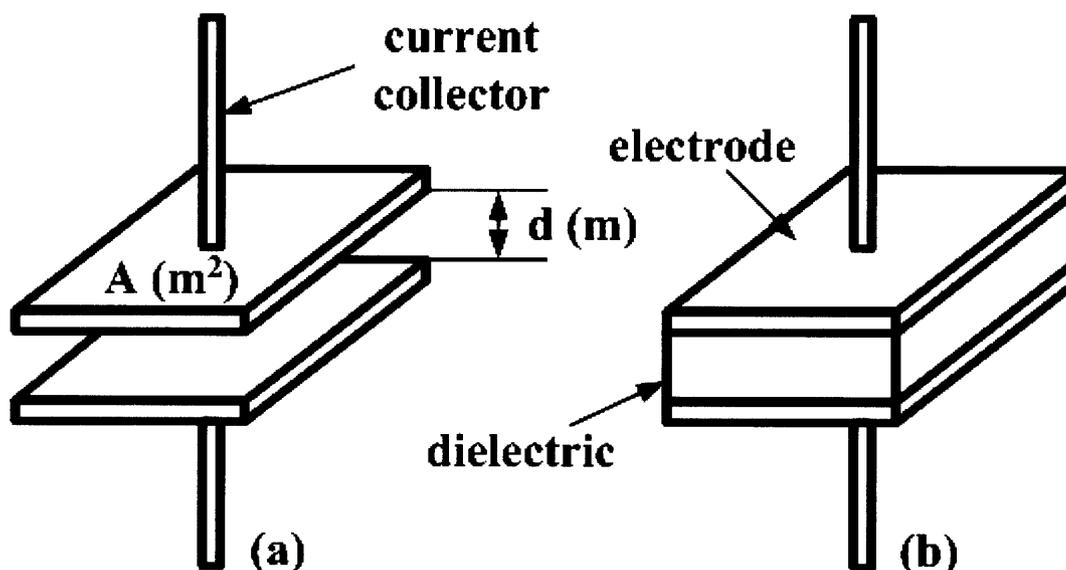


Figure 2. The basic components of a capacitor: (a) without a dielectric and (b) with one.

Capacitance is defined as the ratio of the magnitude of this change in charge dQ to the change in potential difference dV established between the two conductors:

$$C = \frac{dQ}{dV}. \quad 1$$

Because the system is linearly proportional, this is equivalent to:

$$C = \frac{Q}{V}. \quad 2$$

The unit of capacitance is the Farad (F) and is equal to one coulomb per volt (1 F= 1 C/V).

For a uniform electric field of magnitude E that passes through a Gaussian surface of area A , Gauss's law reduces to:

$$Q = \epsilon_0 EA, \quad 3$$

where the permittivity constant $\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$.

The charge Q is thus related to the area. The potential difference V across the two conductors is equal to the line integral of the electric field along any path s between the two and can be expressed as:

$$V = \int^+ E ds = E \int^d ds = Ed. \quad 4$$

The capacitance can then be rewritten by the substitution of Equation 3 and Equation 4 into Equation 2:

$$C = \frac{\epsilon_0 A}{d}, \quad 5$$

which illustrates that the capacitance depends only upon the geometry of the capacitor.

The work done in establishing the separation of charge in a capacitor is responsible for the storage of energy with the capacitor. At a given charge Q the capacitor's plates will have a potential difference V equal to:

$$V = \frac{Q}{C}. \quad 6$$

The transfer of an additional increment charge dQ will require an increment of work dW given by:

$$dW = VdQ. \quad 7$$

The stored energy U is equal to the total work W necessary to charge a capacitor to a value Q :

$$U = W = \int dW = \frac{1}{C} \int_0^Q QdQ = \frac{Q^2}{2C}. \quad 8$$

Utilizing Equation 2, the stored energy can be rewritten as:

$$U = \frac{1}{2} CV^2. \quad 9$$

The addition of a dielectric between the plates of the capacitor has the effect of scaling the capacitance by a constant factor κ known as the dielectric constant:

$$C = \frac{\kappa \epsilon_0 A}{d}. \quad 10$$

This is equivalent to:

$$C = \frac{\epsilon A}{d}, \quad 11$$

where the permittivity ϵ of the dielectric has been defined as:

$$\epsilon = \kappa \epsilon_0. \quad 12$$

3 Current Capacitor Technologies

All but the simplest electronic circuits require capacitive elements. Capacitors are essential elements in radios, cellular phones and other communication devices, most power supplies, digital computers, portable defibrillators, and countless other devices. A variety of capacitor technologies have been developed to fulfill the requirements of the wide range of applications where the use of capacitors is necessary or beneficial.

3.1 Traditional capacitors

Electrochemical capacitors have only recently been introduced as viable commercial products. A range of conventional capacitor technologies have been developed to meet the various demands of specific applications.

The simplest capacitor consists of two parallel conducting plates separated by a distance. As shown in Section 2, the capacitance and energy storage of such a device is directly proportional to the surface area of the plates and inversely proportional to distance between them.

The addition of a polarizable insulator, called a dielectric, between the plates of a capacitor increases its characteristics in three ways. First, because dielectrics breakdown and allow charge to flow at higher potentials than air or vacuum, higher potentials may be applied to the capacitor. This results in greater energy storage within the capacitor. Second, since dielectrics are insulating, they allow the plates to be brought very close together without making contact, thereby increasing capacitance by reducing plate separation. Third, dielectrics reduce the electric field between the plates by a constant factor, which reduces the work required to move a charge from one plate to the other. This results in the capacitance being increased by the same constant factor, as is the amount of energy that may be stored within the device.

The development of traditional capacitors has focused on improving one or more of the three factors in Equation 11, to suit the needs of particular applications.

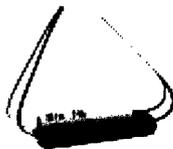
Initial efforts focused on controlling the geometric relationships of the capacitor, increasing the surface area by rolling thin plates together while minimizing the distance between them. Parallel plate capacitors, typified in column (a) of Table 1, can withstand high voltages when utilizing ceramic dielectrics, but are limited to energies of a few microWatt-seconds due to their overall small (picoFarad) capacitance values. Rolled capacitors, column (b), achieve higher (nanoFarad) capacitance values by closely rolling together thin sheets of conductors separated by thin dielectric films and energies of milliWatt-seconds. The selection of the dielectric affects not only the capacitance value but also the potential range, resulting in a two-fold impact on energy storage and has been the focus of many research efforts.

Diverging from such solid-state capacitors, electrolytic capacitors, columns (c) and (d), replace one electrode with a conducting electrolyte solution. The surface area is increased by the atomic level of interaction between the electrolyte and the remaining metallic electrode. A thin oxide layer forms on the metallic electrode, serving as an insulator that separates the two electrodes by distances on the order of hundreds of nanometers. High (micro- to milliFarad) capacitances may be achieved with such small separation, but potential is limited to tens of Volts by the breakdown voltage of most

applicable electrolytes. Typical energies of electrolytic capacitors are in the range of several milli- to Watt-seconds.

Table 1 summarizes typical values of capacitance and energy storage associated with the various types of commercial capacitor technologies. The final column, column (e), introduces electrochemical capacitors, which are typified by much greater capacitance values than any conventional capacitor technology.

Table 1. Characteristic examples of the various existing capacitor technologies, comparing typical capacitances, energy storage, and applications [3].

	(a)	(b)	(c)	(d)	(e)
Typical Capacitance (F)	1×10^{-12}	1×10^{-9}	1×10^{-6}	1×10^{-3}	1000
Example	 Plate capacitors with 50 pF. Left: an element from an old vacuum-tube radio in the form of two plates rolled to a cylinder, max. 450 V. Right: modern ceramic element, max. 100 V	 Rolled capacitor with 51 nF, max. 63 V	 Electrolytic capacitor with 10 mF, max. 35 V (bent wire is positive electrode)	 Electrolytic capacitor with 1000 mF, max. 25 V (positive electrode left)	 Electrochemical capacitor with 1500 F, max. 2.5 V (positive electrode left)
Energy Storage	10^{-6} Ws (μ Ws)	10^{-3} Ws (mWs)	10^{-3} Ws (mWs)	several Ws (Ws)	Watt hours (Wh)
Applications	High frequency technology: e.g. radio, TV, PC	Low frequency technology: general electronics, e.g. audio amplifiers	Low frequency technology: general electronics, e.g. audio amplifiers	Power supply units	Novel applications in power electronics: e.g. in electric cars, and replacing batteries

3.2 Electrochemical capacitors

Electrochemical capacitors are based upon the electric double-layer, Figure 3, that forms at the interface of an electrolyte and conducting electrodes. At each electrode a double-layer of charge separation is formed as negative electrolytic ions migrate towards the cathode and positive electrolytic ions toward the anode. The separation of charge in such a system is on the order of 0.1 to 100 nanometers. The reduction of this distance to atomic distances is nevertheless only partially responsible for the high capacitances (Farad to kiloFarad) achievable with electrochemical capacitors.

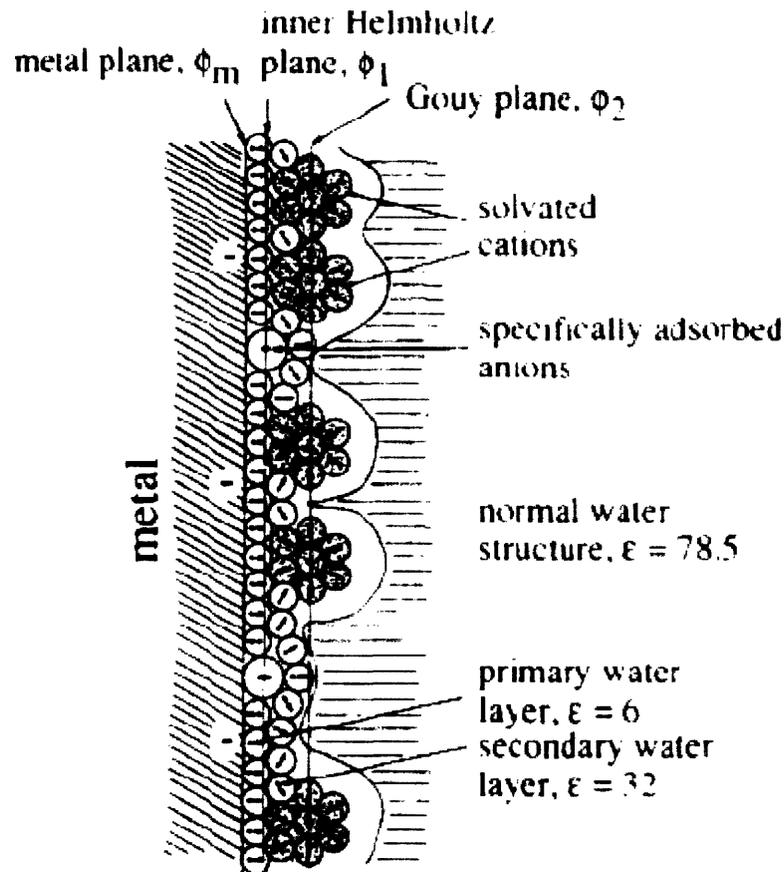


Figure 3. The current model of the electric double layer. The close proximity of the electrolyte ions to the large surface are results in the large specific capacitance of electrochemical capacitors [4].

The second mechanism, however, is enabled by the proximity of the charge layers. Since the electrolyte is typically a solution, it can penetrate the boundary of the electrode's surface, making use of the extensive internal surface area of such materials as activated carbons and porous metal-oxides. Carbons have been developed with surface areas in excess of 1000 square meters per gram, making feasible electrochemical capacitors with very high specific capacitances. Although these high capacitances are limited to relatively low voltages due to aqueous and organic electrolyte breakdown voltages of about 1.2 Volt and 2.5-3.5 Volt, respectively, high energies are nevertheless obtainable. Power output is, however, limited by the relatively high series resistance of the electrolyte and carbon electrodes.

In electrochemical capacitors consisting of metal-oxides, such as ruthenium-dioxide and manganese-oxide, an additional charge storing mechanism arises. Two or three successive oxidation-reduction steps, each dependent upon electrode potential, give rise to a pseudocapacitance that is measured as a real capacitance but is more rate-limited than the simple double-layer capacitance. Typically, metal-oxide electrochemical capacitors effectively exhibit both pseudocapacitance and double-layer capacitance, resulting in high energy storage and, due to low resistances, high power capabilities. However, because ruthenium-dioxide in particular is high cost, most research efforts have centered on carbon-based electrodes.

Table 2. A summary of current commercial electrochemical capacitor manufacturers and the parameters of their products [1].

Company	Device Name	Capacitance (F)	Potential (V)	Web Address
AVX	BestCap	0.060-0.700	3.5-8.0	http://www.avxcorp.com
Cap-XX	Supercapacitor	0.090-2.80	2.25-4.5	http://www.cap-xx.com
Cooper	PowerStor	0.47-50	2.3-5	http://www.powerstor.com
ELNA	Dynacap	0.33-100	2.5-6.3	http://www.elna-america.com
ESMA	Capacitor Mod.	100-8000	12-52	http://www.esma-cap.com
Epcos	Ultracapacitor	5-5000	2.3-2.5	http://www.epcos.com
Evans	Capattery	0.033-1.5	5.5-25	http://www.evanscap.com
Kold Ban	KAPower	1000	6.5-13	http://www.koldban.com
Maxwell	Boostcap	1.8-2600	2.5	http://www.maxwell.com
NEC	Supercapacitor	0.01-6.5	3.5-12	http://www.nec-tokin.net
Ness	EDLC	10-3500	3	http://www.nesscap.com
Panasonic	Gold Capacitor	0.1-2000	2.3-5.5	http://www.maco.panasonic.co.jp
Tavrma	Supercapacitor	0.13-160	14-300	http://www.tavrma.com

4 Origami Electrochemical Capacitor Design

The Nanostructured Origami™ 3D Fabrication and Assembly Process being pioneered by the 3D Optical Systems Group at the Massachusetts Institute of Technology has been applied to the design of a novel electrochemical capacitor.

4.1 Motivation

Perhaps the most commonly cited application for electrochemical capacitors is as a part of the power supply in electric vehicles. By supplying the intermittent pulses of power necessary for periods of quick acceleration, electrochemical capacitors can reduce the overall size and weight requirements of the battery or fuel cell, greatly enhancing the overall performance and feasibility of electric vehicles.

Within such a design, as with proposed uses as backup power for consumer electronics, large scale capacitors with power capabilities of kilowatts and mass on the order of kilograms are acceptable. Yet, many applications involving much lower power requirements and more stringent size and weight requirements exist. Micropower applications include implantable medical devices, microsensors and microtransmitters, smart cards and labels, and MEMS. In each of these applications the reduction of size and weight is highly desirable and may be achieved by improving battery and capacitor technologies to better suit the devices' energy and power needs.

With such applications in mind, the 3D Optical Systems Group at the Massachusetts Institute of Technology has developed a concept for electrochemical capacitors that are based on a technique inspired by the Japanese paper-folding art "origami".

4.2 Technique

The Nanostructured Origami™ 3D Fabrication and Assembly Process utilizes established two-dimensional silicon lithography in a novel manner to achieve high accuracy in three dimensions. The lithography process consists of using a series of masks and photo-resists. Portions that are masked are then either protected from or exposed to (depending on the type of photo-resist, either positive or negative) etching and or depositional stages. Lithography technology is currently capable of patterning lines below 50 nanometer dimensions. This allows for the creation of very complex structures at the nano- to microscale, but the process is inherently two-dimensional.

After the initial stage of patterning, etching, and depositing materials with traditional lithography methods, the Origami™ technique creates a third dimension by folding the two-dimensional structures. The lithography patterns are created with the final configuration of the structure in mind and are constructed such that necessary interconnections between layers are formed when the structure is folded.

The task of folding structures on this miniature scale is a novel one that allows for novel solutions. The most straightforward method, manual manipulation, is a possibility only for the simplest structures and must be performed with a steady hand under high magnification. Due to the delicate nature of the devices, the manual folding task is both time consuming and low yield as many structures are damaged. While it is possible to

perform under the proper conditions, manual folding is an option best left to prototype devices.

For production level quantities, Origami™ devices must be able to be folded with a minimum of external manipulation. It has been demonstrated that by depositing layers of pre-stressed material on microscale thin films, they may indeed fold themselves when released from their substrate [5]. By controlling the deposition of the material, the stresses may be controlled to produce either tension or compression to accurately control the direction of the folds and create complex geometries [6].

Folding may also be accomplished in a process known as plastic deformation magnetic assembly (PDMA) [7]. In this process a controlled magnetic force is applied externally generate the desired fold. Since most materials used in the construction microdevices are nonferrous a layer of magnetic alloy is typically applied to interact with the external field and produce the fold. Alternatively, the device may be designed to be folded using Lorentz forces generated by passing an electrical current through the device and exposing in to an external magnetic field.

Since the dimensions of devices produced with the Origami™ technique are generated from precise two-dimensional lithography their third dimensional accuracy is also high. The Origami™ technique allows for the creation of complex three-dimensional structures on the nano- and microscale. The addition of this third dimension can greatly increase both the functionality and compactness of devices produced in this manner.

5 Test of Concept

In order to evaluate the effectiveness of the Origami™ electrochemical capacitors a porous carbon electrode, aqueous electrolyte prototype was produced and evaluated. A range of tests were performed in the Electrochemical Energy Lab to evaluate the capacitor's performance and recommend directions of further development.

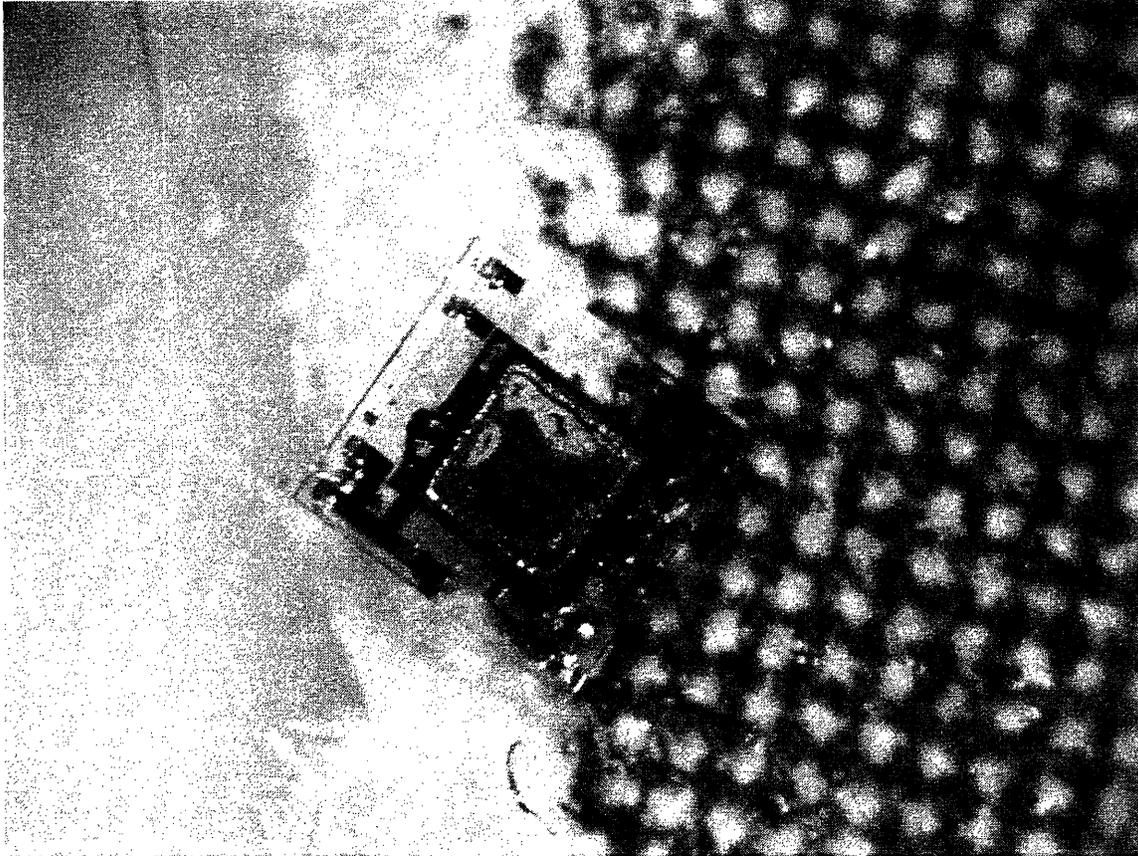


Figure 4. An digital image of a prototype Origami™ electrochemical capacitor developed by MIT's 3D Optical Systems Group and under evaluation by the Electrochemical Energy Lab. The device is 750 microns on a side and the dark electrode region is a 450 micro square.

5.1 Fabrication

The Origami™ electrochemical capacitors were fabricated in the facilities provided by the Microsystems Technology Laboratories at the Massachusetts Institute of Technology. The process is illustrated in Figure 5 and Figure 6. In the first step (a), a thin silicon wafer is masked and etched to produce a grid of recessed pyramids across what would become the current collector surface. In this prototype, these pyramids have a square base of 3 microns (1 micron = $1\ \mu\text{m} = 10^{-9}\ \text{m}$) with a wall angle of 54.74 degrees. 784 of these pyramids were evenly distributed across the 450 by 450 micron square current collector area. A layer of gold 1.5 microns thick was then deposited (b) to form current collectors and the traces that function as the capacitors' leads. This gold fills the previously removed pyramids. Next (c), a 20 microns thick layer of the photo-resist SU-8, a polymer commonly used as a structural material for MEMS, was deposited to form the 750 by 750 micron square structure of the device. Finally (d), the silicon substrate was chemically etched from beneath the device, freeing it.

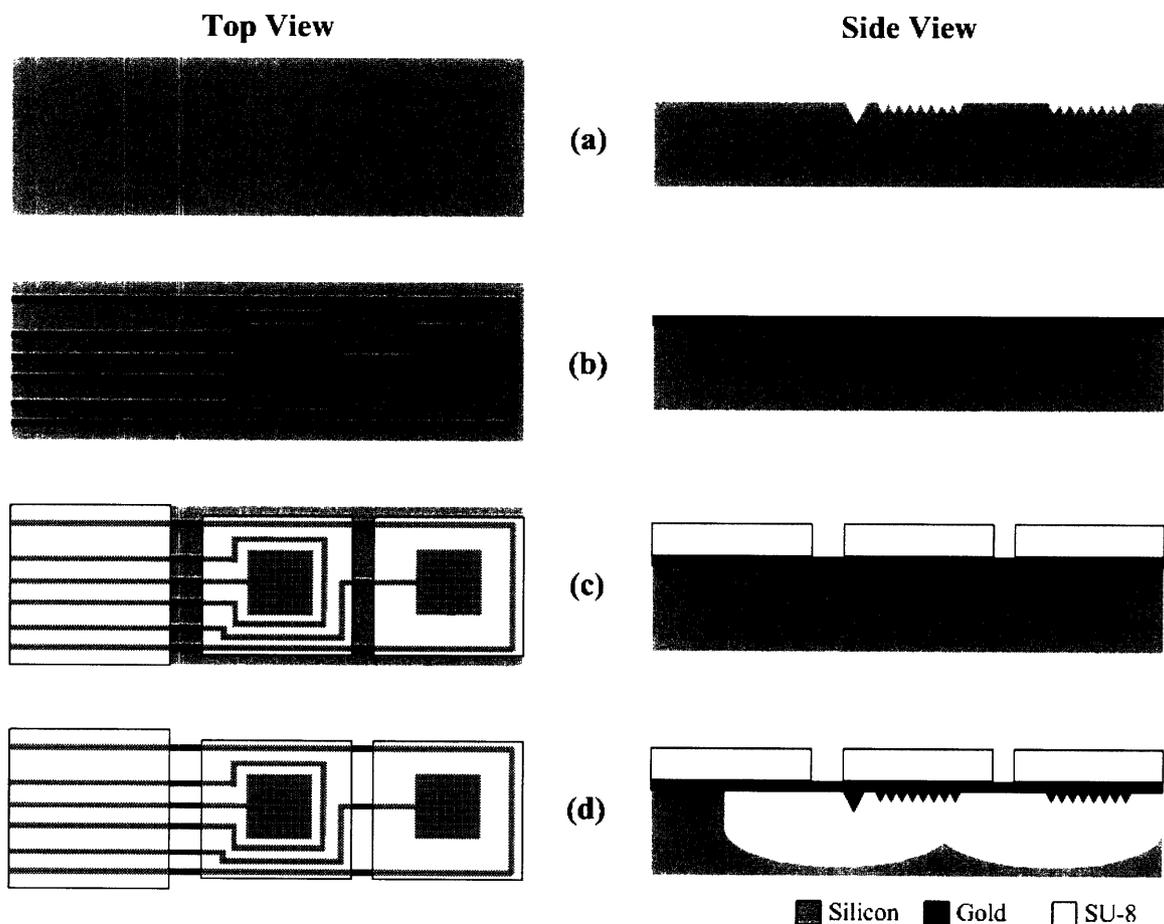


Figure 5. The fabrication of the Origami™ electrochemical capacitor consists of: (a) etching pyramids into a silicon substrate, (b) depositing gold leads and collectors, (c) depositing SU-8 structural material, and (d) releasing the device from its substrate.

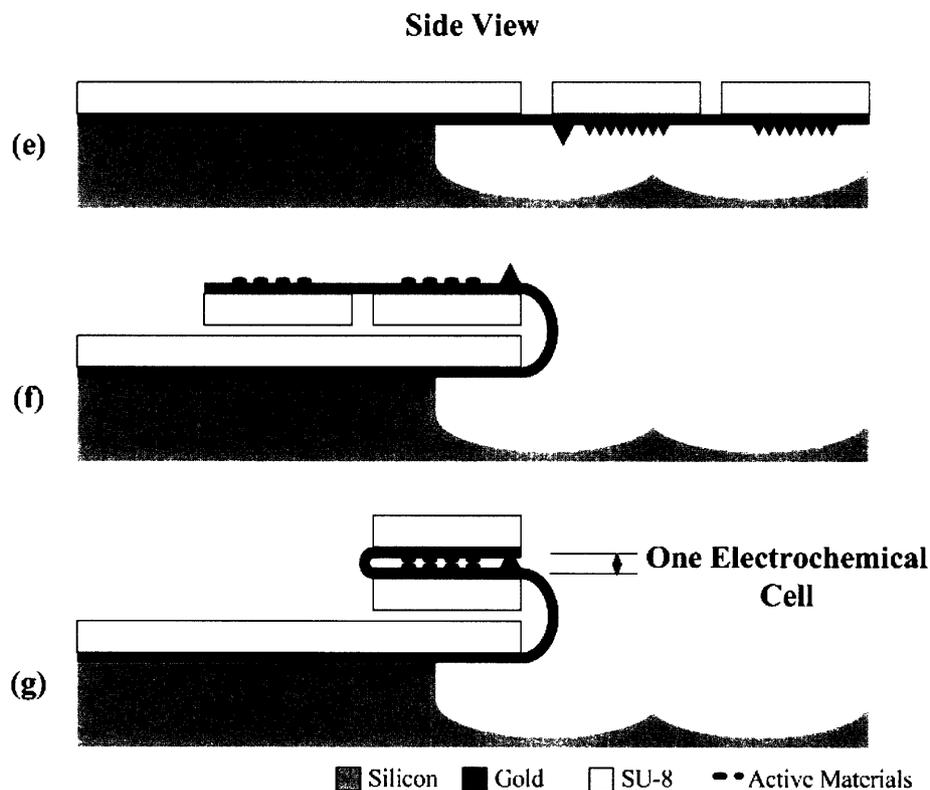


Figure 6. After being released, the device current collectors are coated with active materials (carbon in this prototype) to form the electrodes and the device is folded.

After being released from the silicon substrate the device's electrodes are formed by coating with active materials. For the prototype, carbon paint was produced from ninety weight percent Super P Black (MMM Carbon, Brussels, Belgium) and ten weight percent polyvinylidene fluoride binder. The two were ground together until there was no visible variation in the mixture. Approximately 20 milliliters of 1-methyl-2-pyrrolidone solvent was added to the 2 gram mixture to obtain a thick paint and was stirred for approximately ten minutes with a magnetic stirrer. This paint was then applied to the gold pyramids that form the current collector and the device manually folded using the probes of microprobe station. A completed device was shown above in Figure 4.

5.2 Materials

The materials of the Origami™ electrochemical capacitor were selected for a combination of their mechanical, electrical, and electrochemical properties. It was additionally necessary to limit the choice of materials to those suited for lithography.

The silicon substrate is essential to the lithography process as atomically smooth platform on which to build. Gold is an excellent conductor and is mechanically easy to deform, making it an ideal choice for the leads which double as hinges. The SU-8 polymer photo-resist has been a structural material commonly used in MEMS due to its suitability for the lithography process [8]. Additionally, it has a relatively high yield stress (34 MPa) and can be built to high thicknesses and maintain a high aspect ratio of

height to surface area. These essentially structural elements are also not chemically reactive, suiting them well for use in the electrochemical capacitor.

The most important consideration was for the materials of the electrodes and electrolyte. High surface area carbons are ideally suited for use in electrochemical capacitors. Their high specific surface areas range from 30 to over 1000 square meters per gram and are responsible for their high specific capacitances of 50 to 100 F g⁻¹ [9, 10]. Super P carbon has an apparent density of 0.2 g mL⁻¹ and a real surface area of nominally 38-45 m² g⁻¹, according to the product literature.

The selection of the electrolyte was restricted to aqueous solutions for the initial prototype. Within that constraint, the most desirable electrolytes are those that dissociate strongly and have small ionic size. Smaller ions migrate more quickly than large ones in and are better able to penetrate the pores of the electrode area. Typically, the higher the concentration, the lower the resistance and higher the capacitance of the electrochemical capacitor, with a limit occurring as the available surface area of the electrode is saturated with ions [11]. With these considerations in mind, the hydrochloric (HCl) and sulfuric (H₂SO₄), both strong acids, were selected for experimentation. They were prepared in 0.1, 0.5, 1, and 2.5 normal solutions. Strong bases potassium hydroxide and sodium hydroxide were originally considered but abandoned due to damage they caused to the silicon substrate, which in the prototype is still necessary for forming electrical and mechanical connection.

5.3 Results

AC impedance spectroscopy, galvanostatic charge and discharge cycling, and potentiostatic charge and discharge (cyclic voltammetry) tests were performed on several of the capacitors produced in the manner described above (see Appendix A for description of these test methods) [12]. A Solartron 1260 Impedance/Gain-Phase Analyzer (SN: 40015Q) was used to obtain AC impedance measurements, and a EG&G Princeton Applied Research Potentiostat/Galvanostat Model 263A (SN: 12110) was utilized for potentiostatic and galvanostatic tests. Of the devices tested, several were obvious short-circuits and were discarded. Of the two remaining devices, only one ever exhibited considerable pure capacitive behavior, and that was during its initial assessment bathed in 0.1N HCl aqueous solution. The Bode plots of five separate frequency sweeps, all at 10mV AC, are presented in Figure 7. One of the trials has been fitted and the capacitance of the device is estimated to be approximately 1.65 picoFarads.

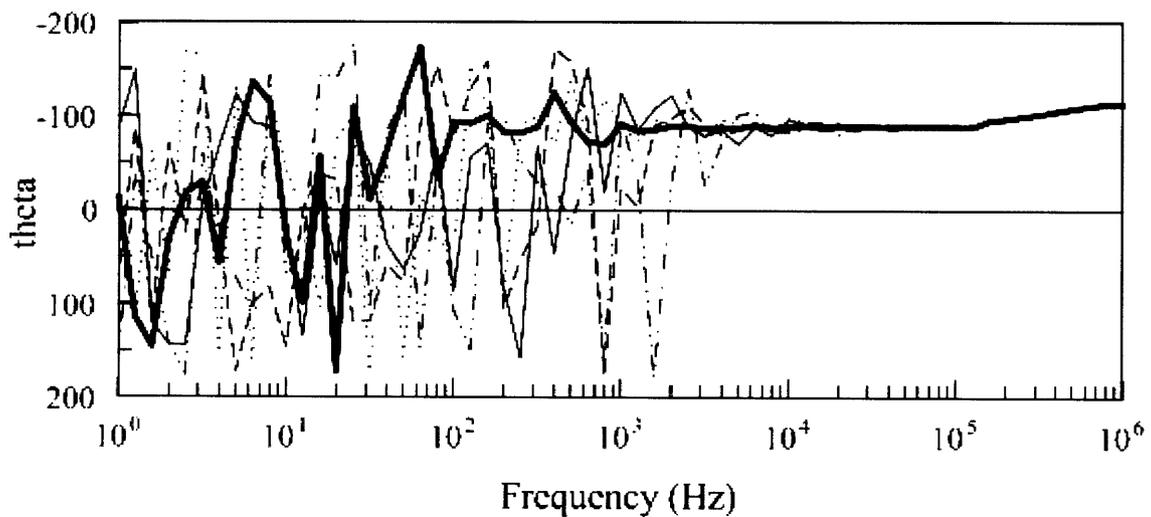
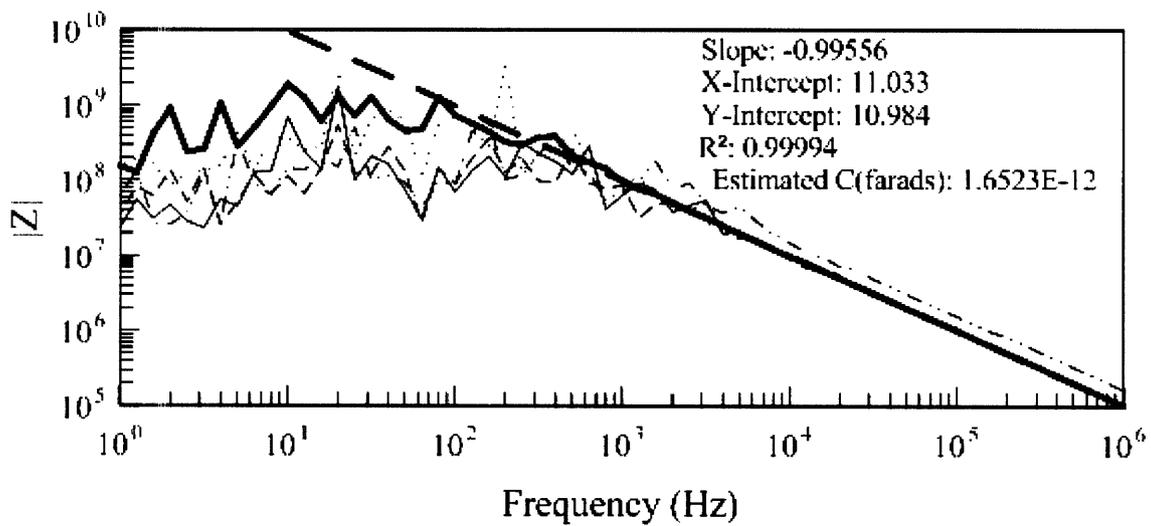


Figure 7. AC impedance spectroscopy results for an Origami™ electrochemical capacitor with carbon electrodes and 0.1N HCl electrolyte. The AC amplitude was 10 mV for all five sweeps.

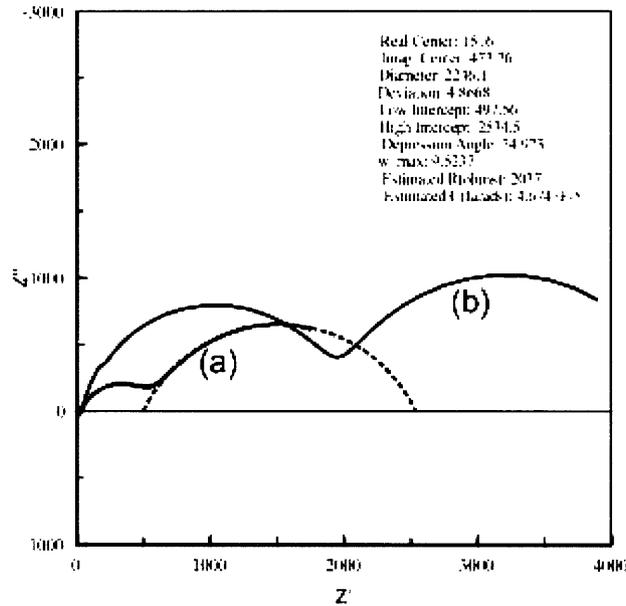


Figure 8. Nyquist plot of two functional devices in 0.5N HCl solution: (a) with a measured capacitance of 46.7 microFarads, and (b) with 23.8 microFarads.

Additional tests of the device, in 0.5N HCl solution, yielded increased capacitance of 46.7 microFarad according to AC impedance measurements and a parallel resistance of 2037 ohms. Galvanostatic testing indicated a capacitance of 271 microfarads for the same device. A separate cell was also examined in 0.5N HCl solution, and was measured at 23.8 microFarads and 2793 ohms under AC impedance measurement and 173 microfarads according to galvanostatic charging. Figure 8 presents the complex-plane plots of these tests.

6 Discussion

Electrochemical capacitors have the ability to reduce the size and weight of stored electrical energy power source when they are correctly sized for the application's requirements. The Origami™ electrochemical capacitors examined here are intended at least initially to be utilized as integrated power components for MEMS devices and other micropower applications.

Electrochemical analysis of the capacitor cells via AC impedance spectroscopy, galvanostatic cycling, and potentiostatic cycling indicated that most of the cells were damaged. This was apparent in most cases through low digital multi-meter readings of low resistance, when an un-shortened capacitor should have near-infinite DC resistance.

The measured value of 1.65 picoFarads is rather low, even in comparison to calculations that don't account for the high surface area of the carbon—if the double layer were two gold plates separated 100 angstroms, the cell would be expected to exhibit a capacitance of roughly 90 picoFarads. The measured capacitance relates to a specific capacitance of $3.7 \times 10^{-8} \text{ F g}^{-1}$ total mass or $2 \times 10^{-3} \text{ F g}^{-1}$ of active material (carbon). In activated carbons are expected to have specific capacitances of approximately 50 F g^{-1} , which is far greater than observed here.

The relatively low capacitance may be due to several factors. The choice of Super P carbon seems to be a poor one, as much higher surface area carbons are available and are essential to most electrochemical capacitor designs. Additionally, this value was obtained at only 0.1N HCl solution, which is far below typical electrolyte concentrations, which range up to several normal.

The 0.5N HCl solution indeed yielded higher capacitances, in the range of tens to hundreds of microFarads, which corresponds to a specific capacitance of approximately 5 F g^{-1} total mass, and 100 F g^{-1} carbon. These values are far more typical of porous carbon electrode electrochemical capacitors and indicate that the concept is a viable one.

In the near term it is recommended that the devices be painted in a controlled manner to prevent shorts upon folding or damage during handling. It seems worthwhile to pursue deposition of the carbon layer. The Lorentz force folding technique may also reduce physical damage.

In the long run it may be worthwhile to pursue metal-oxide (RuO, MnO) electrodes and or non-aqueous electrolytes. When considering metal-oxides, the application should be kept in mind as the Faradaic pseudocapacitance will be more rate limited than the simple double layer capacitance exhibited by carbon electrodes.

References

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Appendix

A Test Methods

There are several laboratory tests that can be used to evaluate the performance of electrochemical devices including electrochemical capacitors. The tests presented in this appendix have been chosen for their ability to quickly and easily reveal important characteristics of the device. Additional methods can be found in the “Electric Vehicle Capacitor Test Procedures Manual” authored by J.R. Miller and A.F. Burke for the United States Department of Energy (DOE/ID-10491 1994).

Galvanostatic

During galvanostatic testing a constant current I is applied to the capacitor under examination. Charge accumulates on the capacitor in response to this current at the rate:

$$\frac{dQ}{dt} = I. \quad \text{A1}$$

The charge on the capacitor is then given by:

$$Q = \int I dt. \quad \text{A2}$$

Capacitance is defined in Equation 1 as the change in charge on the capacitor plates divided by the change in voltage between them:

$$C = \frac{dQ}{dV}. \quad \text{A3}$$

Plotting the charge on a capacitor (the applied current integrated over time) against its measured voltage, a linear region is observed during most of charging. The slope of this region ($\frac{dQ}{dV}$) is the device's capacitance.

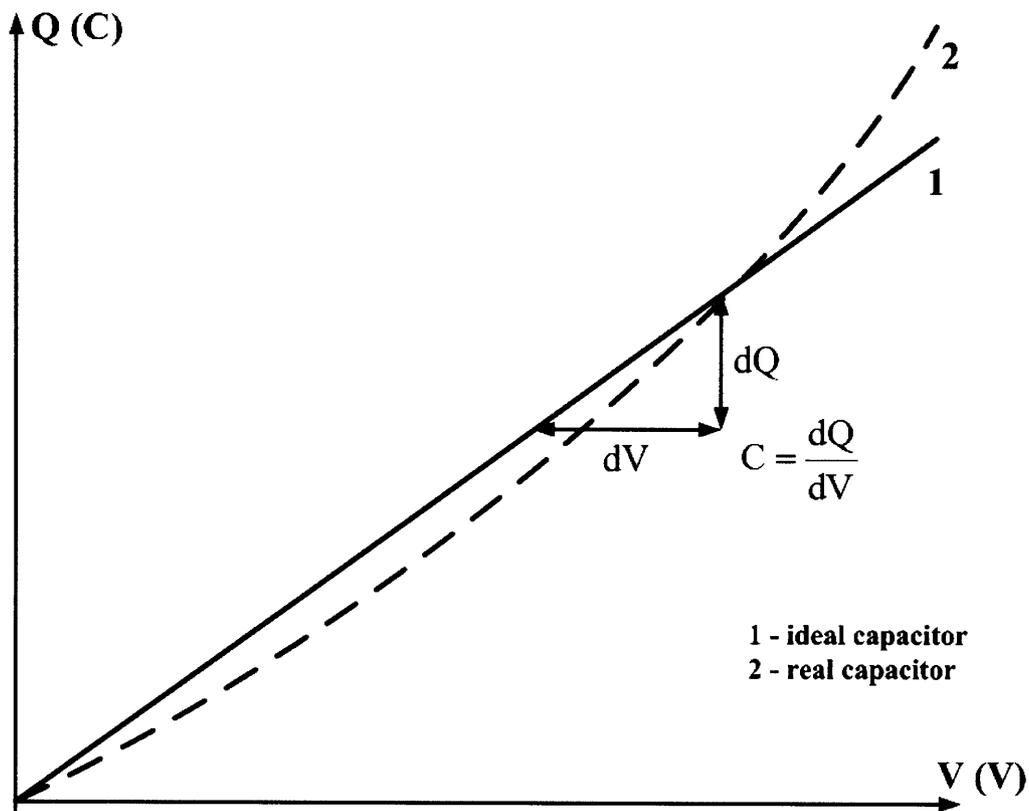


Figure 9. A method for determining capacitance by plotting charge Q (C) against potential V (V) during galvanostatic (constant current) charging.

When there is no straightforward method of plotting the charge on the capacitor, an alternative method is available. Rearranging Equation 2, the charge on a capacitor is:

$$Q = VC. \quad \text{A4}$$

Combining Equation A1 and Equation A4 gives:

$$I = \frac{dQ}{dt} = C \frac{dV}{dt}. \quad \text{A5}$$

Rearranging Equation A5 expresses the capacitance of the device as:

$$C = \frac{I}{(dV/dt)} \quad \text{A6}$$

Hence, the capacitance of the device can be determined by using even the simplest oscilloscope to record the potential difference over time, and calculating the capacitance as the current divided by the slope of the linear region.

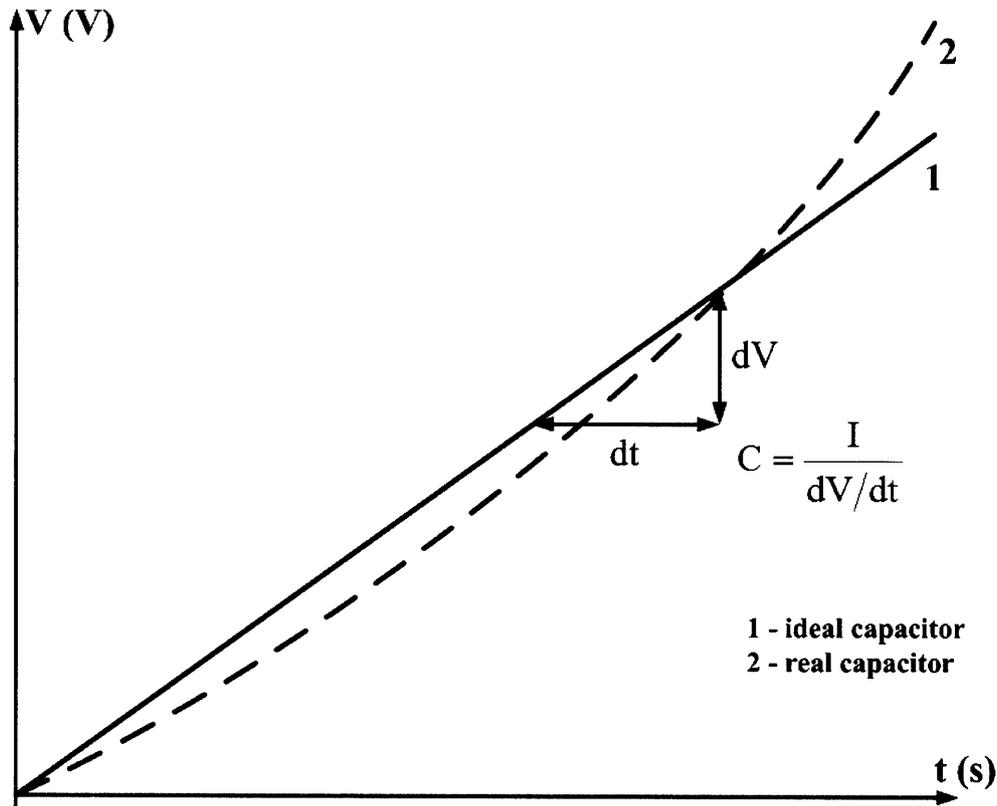


Figure 10. A method for determining capacitance value from change in voltage over time during galvanostatic charging.

Potentiostatic

Cyclic voltammetry is a potentiostatic test during which the potential is scanned at a constant rate and the current response recorded. The test is typically set to cycle for specific time in each direction or between two set potentials. The scan rate s is given as:

$$s = \frac{dV}{dt}. \quad \text{A7}$$

Equation A5 relates this scan rate to the current flowing into the device by:

$$I = C \frac{dV}{dt} = Cs. \quad \text{A8}$$

If current is plotted against potential, as is typically the case in cyclic voltammetry, response of an ideal capacitor will be a rectangular plot, with a constant current during charging and discharging which switches direction instantly at the endpoints, as illustrated in Figure 11.

The capacitance may be calculated directly from this constant charging current I_c :

$$C = \frac{I_c}{s}. \quad \text{A9}$$

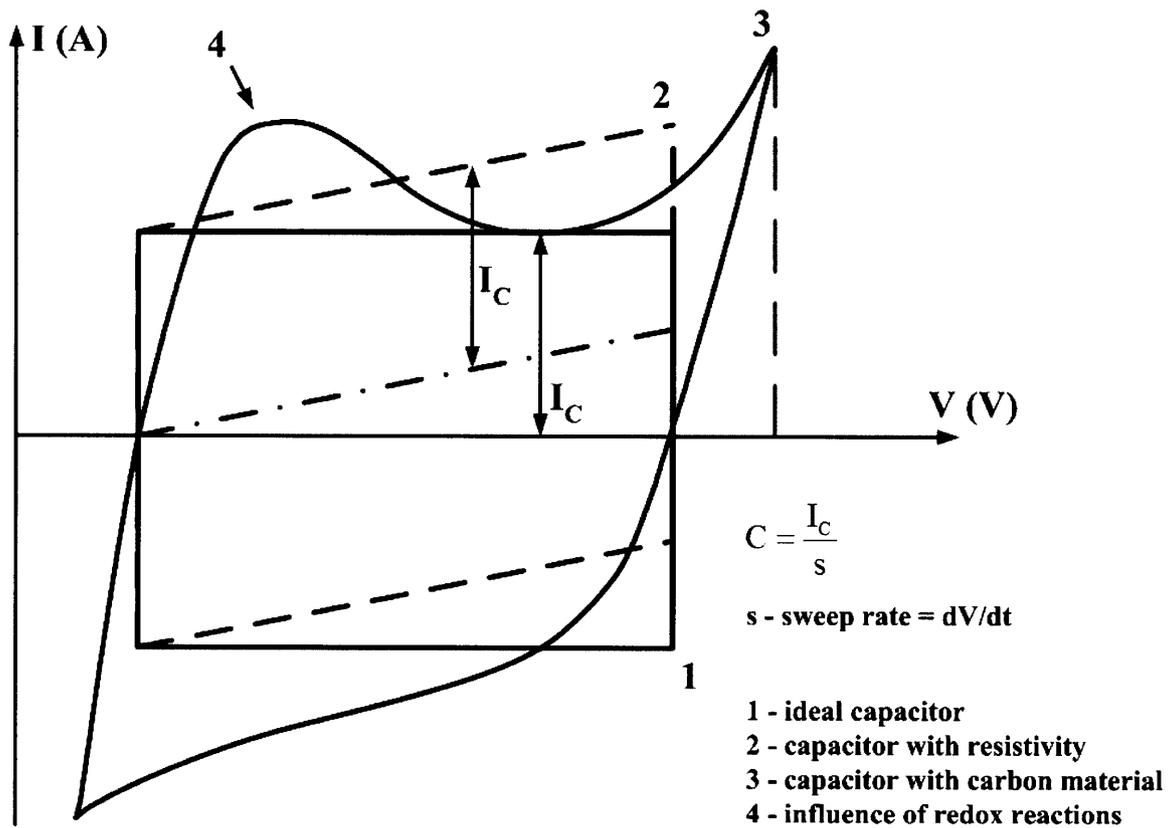


Figure 11. The key features a cyclic voltammogram for various characteristic capacitors.

Alternatively, a range of sweep rates may be evaluated and the charging current of each plotted against the sweep rate. This results in performing the same operation as Equation A6 by simply measuring the slope of the fitted line through these points.

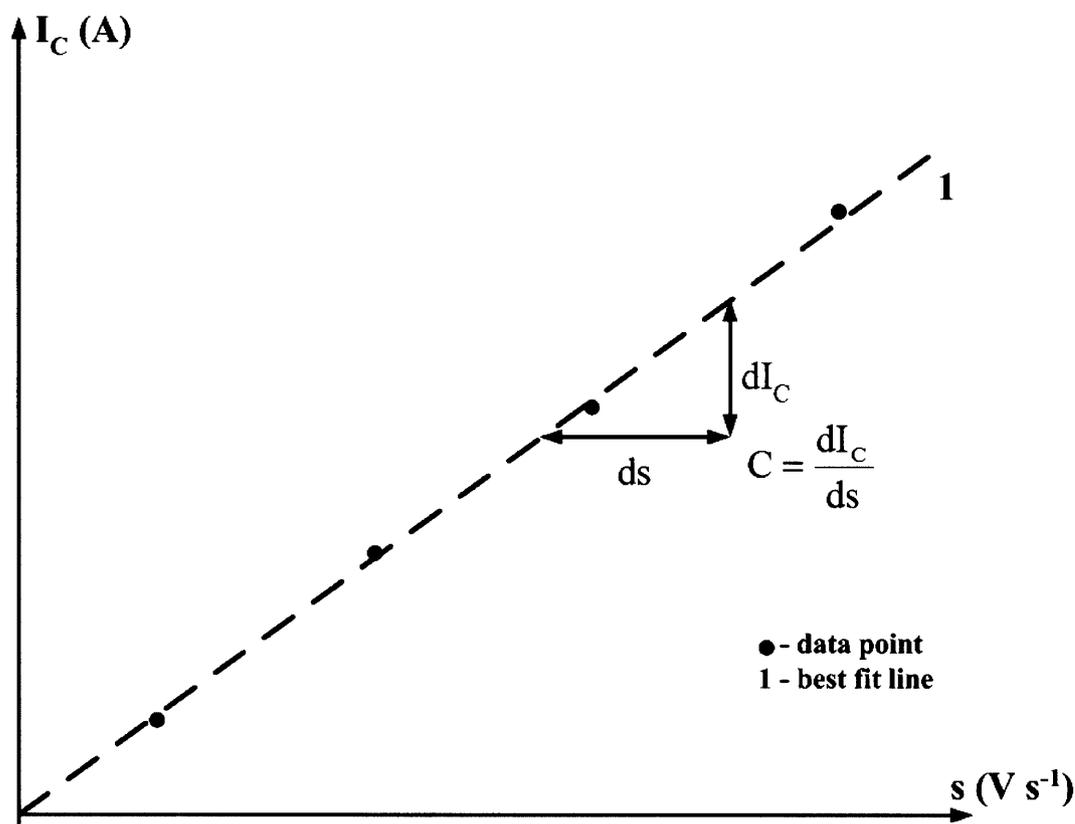


Figure 12. A method for determining capacitance through repeated cyclic voltammetry measurements.

In addition to these capacitance measurements, cyclic voltammetry can offer insight into electrochemical behavior of the capacitor. Figure 11 includes the typical response of electric-double layer capacitance and the influence that characterizes oxidation-reduction reactions. When cycled numerous times or at varying rates the stability of the capacitor can be observed.

AC Impedance

AC impedance spectroscopy is a powerful measurement technique that scans through the frequency spectrum and records the magnitude and phase of the capacitor's response. The resulting Nyquist and Bode diagrams indicate the magnitude of DC resistance and AC impedance, giving an indication of the reactions within the cell and their configuration.

A sinusoidal potential given by:

$$V(t) = V_0 \sin(\omega t) \quad \text{A10}$$

where V_0 is the amplitude of the signal and

$$\omega = 2\pi f \quad \text{A11}$$

where f is the frequency in Hertz. Ohm's law gives that:

$$I = \frac{V(t)}{R} = \frac{V_0}{R} \sin(\omega t). \quad \text{A12}$$

Utilizing Equation A4 and Equation A5, this becomes:

$$I = \omega C V_0 \cos(\omega t). \quad \text{A13}$$

Given an AC sine input function, the response current is a cosine function, thus the current is -90 degrees out of phase with the potential.

The impedance of a capacitor is then:

$$\frac{V}{I} = \frac{V_0}{\omega C V_0} = \frac{-j}{\omega C}, \quad \text{A14}$$

where the $-j$ has been added to compensate for the phase shift between current and potential.

The impedance characteristics of the basic electronic components are as follows:

1. an ohmic resistance, R , component's impedance is independent of the frequency, $Z' = R$ and the phase angle is zero throughout
2. a pure capacitor with capacitance C has a frequency-dependent imaginary impedance $Z'' = -j/(\omega C)$ and a phase angle equal to -90° across the spectrum
3. a pure inductor with inductance L has a frequency-dependent imaginary impedance $Z'' = j\omega L$ and a phase angle equal to 90° across the spectrum.

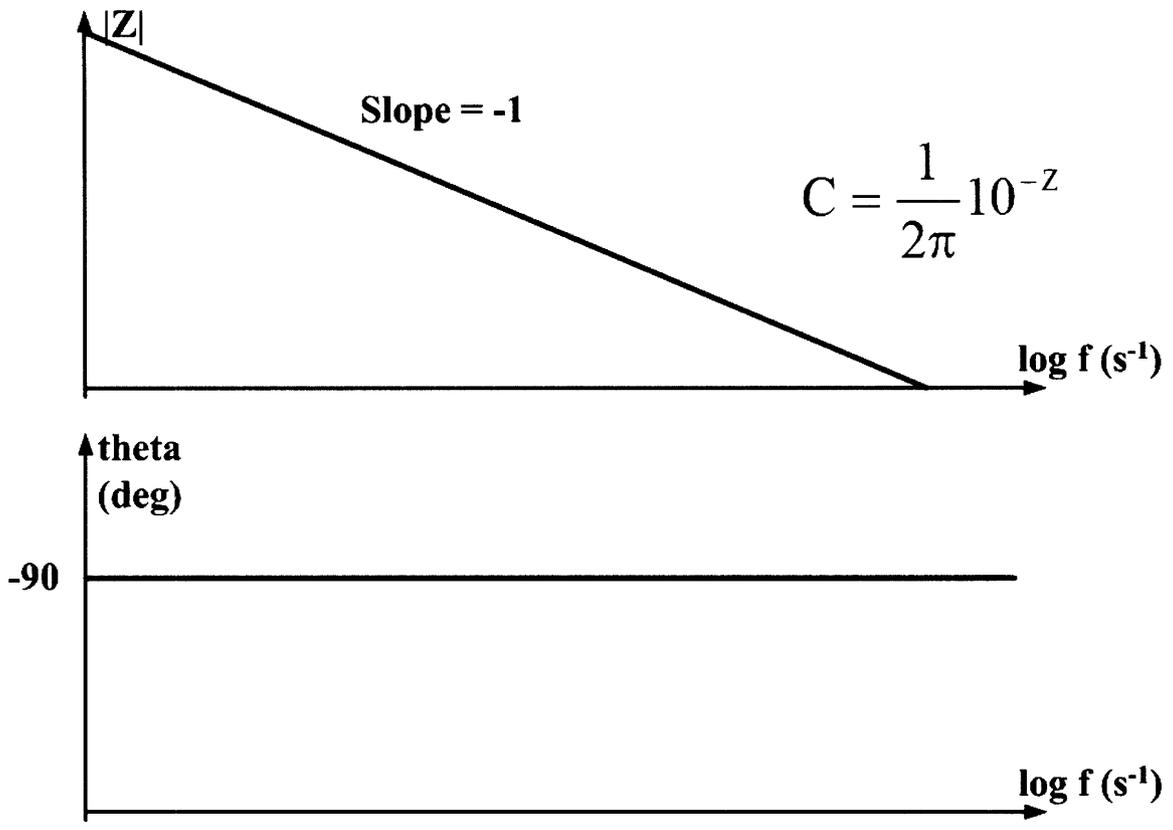


Figure 13. Bode plots of AC impedance response of an ideal capacitor.

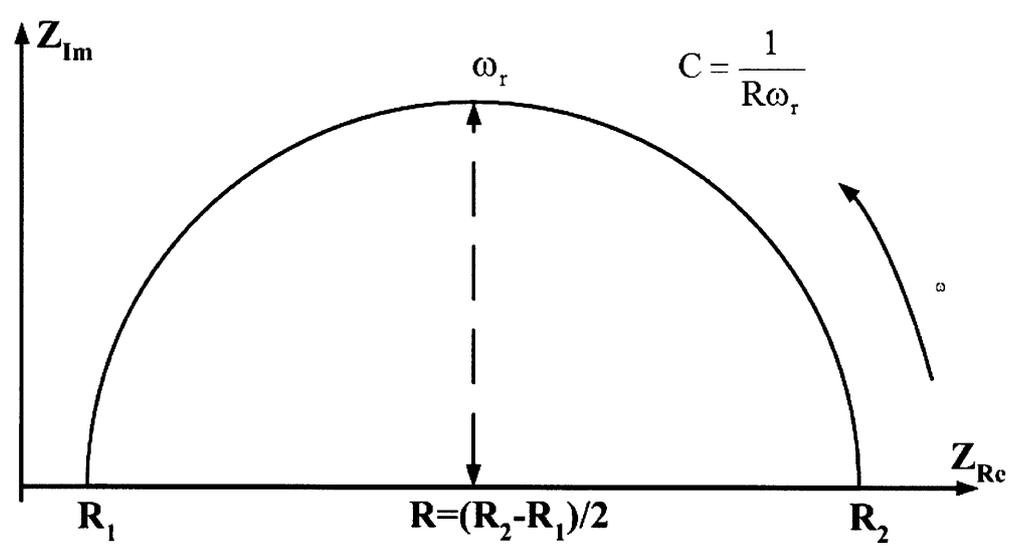


Figure 14. Complex-plane (Nyquist) plots of a capacitor with series R_1 and parallel R_2 resistances.

Additional information on the AC impedance behavior of electrochemical capacitors is best obtained from Chapter 16 of B.E. Conway's *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Application* (1999).

B Additional Data

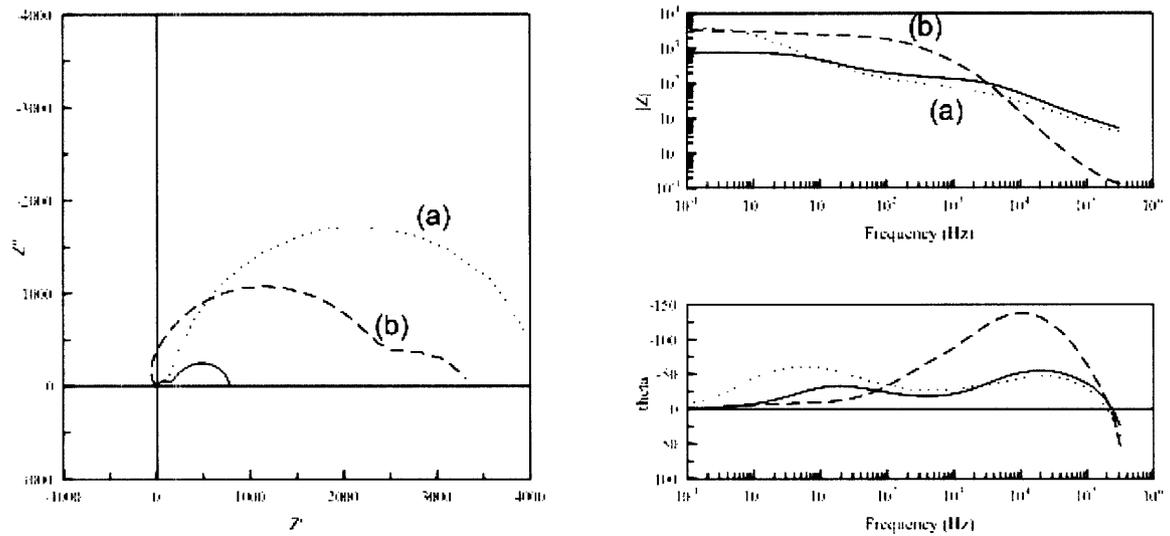


Figure 15. AC Impedance spectroscopy of three devices, all in 5N H₂SO₄: a) is the same device as in Figure 7, b) contains no active cell at all.

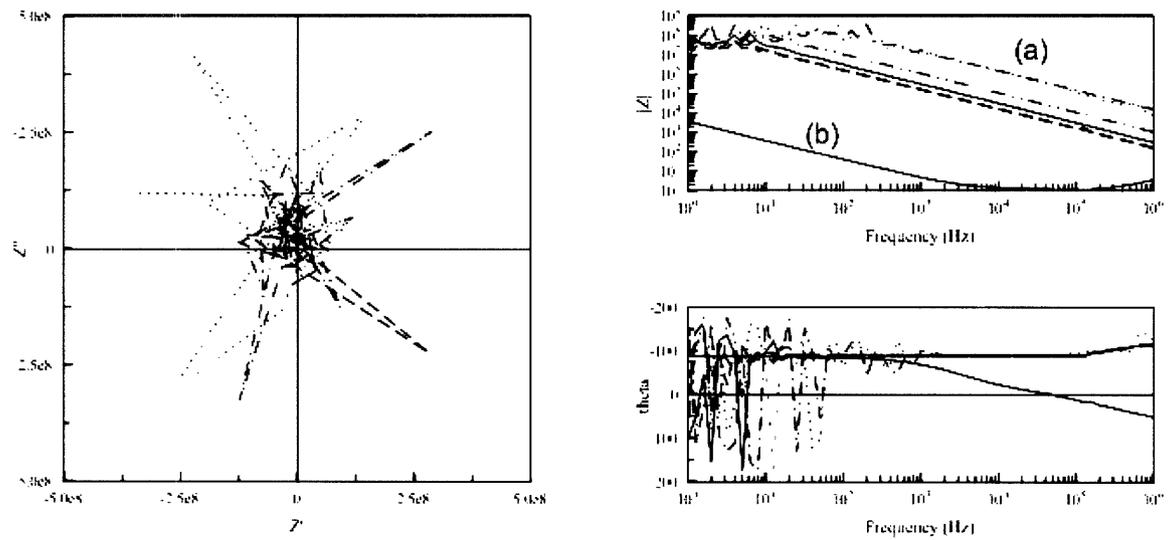


Figure 16. AC Impedance spectroscopy of 7 commercial traditional capacitors ranging in value from (a) 10 picoFarad to (b) 30 microFarad.