

AFRL-MN-EG-TR-1999-7078

ALKALINE ELECTROCHEMICAL CAPACITOR AND  
ELECTRODE FABRICATION

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NOVEMBER 1999

FINAL REPORT FOR PERIOD JANUARY 1997 - NOVEMBER 1999

DTIC QUALITY INSPECTED 4

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Form Approved  
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE November 1999	3. REPORT TYPE AND DATES COVERED Final Report January 1997 – November 1999
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4. TITLE AND SUBTITLE  Alkaline Electrochemical Capacitor and Electrode Fabrication	5. FUNDING NUMBERS  JON: 25020816    PE: 62602F PR: 2502 TA: 08 WU: 16
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6. AUTHOR(S) D. Finello
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory, Munitions Directorate, Fuzes Branch 306 West Eglin Blvd. Bldg. 432 Eglin AFB FL 32542-5430	8. PERFORMING ORGANIZATION REPORT NUMBER
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory, Munitions Directorate, Fuzes Branch 306 West Eglin Blvd. Bldg. 432 Eglin AFB FL 32542-5430  Program Manager: Dr. Duane Finello / (850) 882-2005 x-227	10. SPONSORING/MONITORING AGENCY REPORT NUMBER  AFRL-MN-EG-TR-1999-7078
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11. SUPPLEMENTARY NOTES Availability of this report is specified on the verso of front cover.
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12a. DISTRIBUTION/AVAILABILITY STATEMENT  Approved for public release; distribution is unlimited.	12b. DISTRIBUTION CODE
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13. ABSTRACT:  Highly capacitive (high surface area) electrodes that are electrochemically stable in strong alkaline electrolyte will form the basis for a new generation of electrical and electrochemical energy storage and conversion devices. A new type of electrochemical capacitor is described in addition to procedures for making the required electrodes. The subject low cost alkaline electrochemical capacitor designs are based upon titanium nitride electrodes which exhibit 125 mF/cm <sup>2</sup> surface capacitance density and remarkable electrochemical stability over a relatively wide (-55°C to +100°C) temperature range in aqueous potassium hydroxide of approximately 15 pH alkalinity. With energy density in excess of 300 mJ/cc and the potential to exceed a power density of 100 W/cc, the alkaline electrochemical capacitor represents a significant advancement in technology for high power energy storage.
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14. SUBJECT TERMS:  Electrochemical capacitor, alkaline electrolyte, titanium nitride, electrode	15. NUMBER OF PAGES  10
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR
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## PREFACE

This report describes an in-house effort conducted by personnel of the Fuzes Branch (MNMF), Ordnance Division (MNM), Munitions Directorate of the Air Force Research Laboratory, Eglin Air Force Base, Florida, under exploratory development project funds. The work reported herein was performed during the period 21 January 1997 to 12 November 1999 under the direction of Dr. Duane Finello (AFRL/MNMF), project engineer.

# ALKALINE ELECTROCHEMICAL CAPACITOR AND ELECTRODE FABRICATION

## INTRODUCTION

The subject work relates generally to alkaline capacitors, batteries, fuel cells, electrochemical synthesis reactors, sensors, and other energy storage/conversion devices, and more specifically to high surface area electrodes and electrolytes for use in such devices.

## BACKGROUND

Electrodes and electrolytes are the major constituents in several classes of energy storage and conversion devices, including capacitors, batteries, and fuel cells. Technological advances in the electronics industry have been associated with an on-going need to reduce electrode volume and weight to achieve increased energy density and power density for such devices. In general, such efforts towards miniaturization have not been as successful as those which have resulted in significant miniaturization of a variety of other electronic components.

Electrical and electrochemical energy storage density is typically proportional to the total electrode surface area accessible to the electrolyte. Therefore, one way to increase the amount of stored energy per unit volume (or weight) is to increase the surface area of the electrodes without physically increasing their size.

Prior art describes a number of ways to fabricate material with high specific area (total surface area divided by the volume or mass of the bulk material). US. Pat. No. 4,515,763 and US. Pat. No. 4,851,206 teach the preparation of such materials as powder catalysts. They do not concern electronic properties of the materials, such as conductivity or electrochemical stability in an electrolyte, nor do they address coatings of the materials in high surface area form as planar electrodes.

Prior art identifies three basic types of high surface area electrodes. One type is a metal which is mechanically or chemically etched to provide a roughened surface and high specific surface area. High surface area electrodes based on this principle are cited in U.S. Pat. No. 5,062,025. A second type of high surface area electrode is cited in U.S. Pat. No. 5,079,674 and U.S. Pat. No. 4,327,400 concerning carbon powder and foam. The third type of high surface area electrode is based upon noble (or platinum group) metal oxides as described in U.S. Pat. No. 5,185,679. While each type of electrode has found commercial application, none can provide optimal high density energy storage that is cost effective.

Electrochemical stability is a serious limitation for cost effective high surface area metals. Low cost metals are susceptible to electrochemical oxidation in aqueous electrolyte, and may only be suitable for the cathode or negative electrode. Low cost, high surface area carbons generally have extremely small pores (approaching atomic diameter) and relatively large pores (a few hundred times larger than atomic diameter) and this can limit the surface area accessible to nonaqueous (or less chemically aggressive) electrolytes. The spatially averaged electronic conductivity of carbon is a few orders of magnitude lower than that of most engineering metals, which is another disadvantage. The nature of the carbon bond to metal substrates is poorly understood and is still another deterrent to widespread application of planar high surface area carbon electrodes. Of course, the more costly precious metal oxide electrodes can satisfy the engineering requirements in some applications despite their cost; in the energy storage arena it is always advisable to avoid use of such materials, since they limit the mass marketability of the end product. Use of alkaline rather than acid electrolyte has been shown to be a wise choice where practical in the commercial battery marketplace; the same will ultimately hold true for electrochemical capacitors, at least until nonaqueous electrolytes can be used to make superior devices of lower cost.

For optimum performance in alkaline electrolyte, electrodes with special chemical and physical characteristics are required. The electrode material, whether in the form of powder or planar film, must possess high electrical conductivity in addition to high specific surface area. The electrode material must also be electrochemically stable in the electrolyte over the maximum operating voltage window the electrolyte can withstand (1.2 volt in the case of alkaline electrolyte, which is a common type of aqueous electrolyte). The

high surface area electrode, and its associated microporous (or nanoporous) structure, must suffer no deterioration in the presence of the electrochemically aggressive, ion-conducting electrolyte at any potential of up to +1.2 volt. Over this operating voltage range, it is required that the electrochemical interaction between electrode and electrolyte allow complete chemical, electronic, and physical reversibility over a relatively wide range of temperatures (-55°C to +100°C). This can be most readily verified by the technique of cyclic voltammetry, which is a measure of electrode current as the potential is gradually scanned across a desired voltage range.

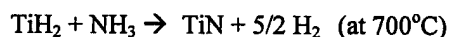
The present innovation provides a new type of high surface area electrode for use in alkaline electrical and electrochemical energy storage and conversion devices. The electrode comprises any conductive titanium compound, including titanium nitride (TiN), titanium (Ti), titanium hydride (TiH<sub>2</sub>), titanium suboxides (Ti<sub>4</sub>O<sub>7</sub> and Ti<sub>5</sub>O<sub>9</sub>), and titanium oxynitride (TiON). Any of these materials can be used as both anode and cathode in a bipolar (symmetric with regard to polarity) electrochemical capacitor design. This greatly simplifies device construction and manufacture.

In another embodiment there is provided a method of manufacturing the bipolar electrode of this invention, either by forming high surface area powder or by directly growing a high surface area layer, where the precursor compound is typically titanium hydride. The only practical route to formation of the desired high surface area electrode material requires elevated temperature ammonia (NH<sub>3</sub>) nitriding of titanium hydride at controlled ammonia flow rate. Programmed elevated temperature reduction of titanium oxide (TiO<sub>2</sub>) with ammonia is considered impractical since reduction does not readily occur at temperatures below 1200°C. Sintering accompanies such high temperature thermal exposure, which is associated with minimization of specific surface area and is useless for high surface area electrode fabrication.

In another embodiment there is provided an alkaline electrochemical capacitor incorporating the subject high surface area electrode material having a specific capacitance of 125 mF/cm<sup>2</sup> and an energy density of 312 mJ/cc. It offers relatively low (< 0.5Ω) internal resistance in conjunction with an electrochemical stability comparable to or exceeding that of any currently available electrochemical capacitor.

## RESULTS AND DISCUSSION

It has been determined that powdered high surface area titanium compounds are uniquely derived via decomposition of titanium hydride at temperatures above 400°C. In order to form high surface area titanium nitride powder by purely thermal means, a one-hour thermal treatment at 700°C in ammonia is required. The reaction is simply described as follows:



For ammonia flow rates of in excess of 2 liters per minute (l/min), titanium nitride was the reaction product. For ammonia flow rates below 1 l/min, other conductive titanium compounds formed. These included titanium oxynitride and titanium suboxides, all of which have lower conductivity than titanium nitride. (On a comparative conductivity scale, TiN has a conductivity of 46,000 Ω<sup>-1</sup>cm<sup>-1</sup>, while the suboxide Ti<sub>4</sub>O<sub>7</sub> has a conductivity of only 2,000 Ω<sup>-1</sup>cm<sup>-1</sup>). For this reason, high surface area TiN is the preferred electrode material for the alkaline electrochemical capacitor.

As mentioned in the preceding section, cyclic voltammetry can be used to reveal the overall stability of a given electrochemical system. Referring to Figure 1, cyclic voltammetry data for a pair of to reveal the overall stability of a given electrochemical system. Referring to Figure 1, cyclic voltammetry data for a pair of titanium nitride electrodes in 7 molar potassium hydroxide (strongly alkaline) electrolyte, it is apparent that this system is stable over a bipolar potential window of 1.2 volt.

In order to illustrate the construction of the alkaline electrochemical capacitor, Figure 2 provides an enlarged view of a portion of the device. (Only one of any number of bipolar cells is detailed since each is identical. A multi-cell stack type of alkaline electrochemical capacitor would be designed to operate at some given voltage. Since each alkaline cell can operate at one volt, a ten-cell capacitor would be designed for ten-volt operation, for instance). Capable of being readily permeated by electrolyte, an electrically insulating

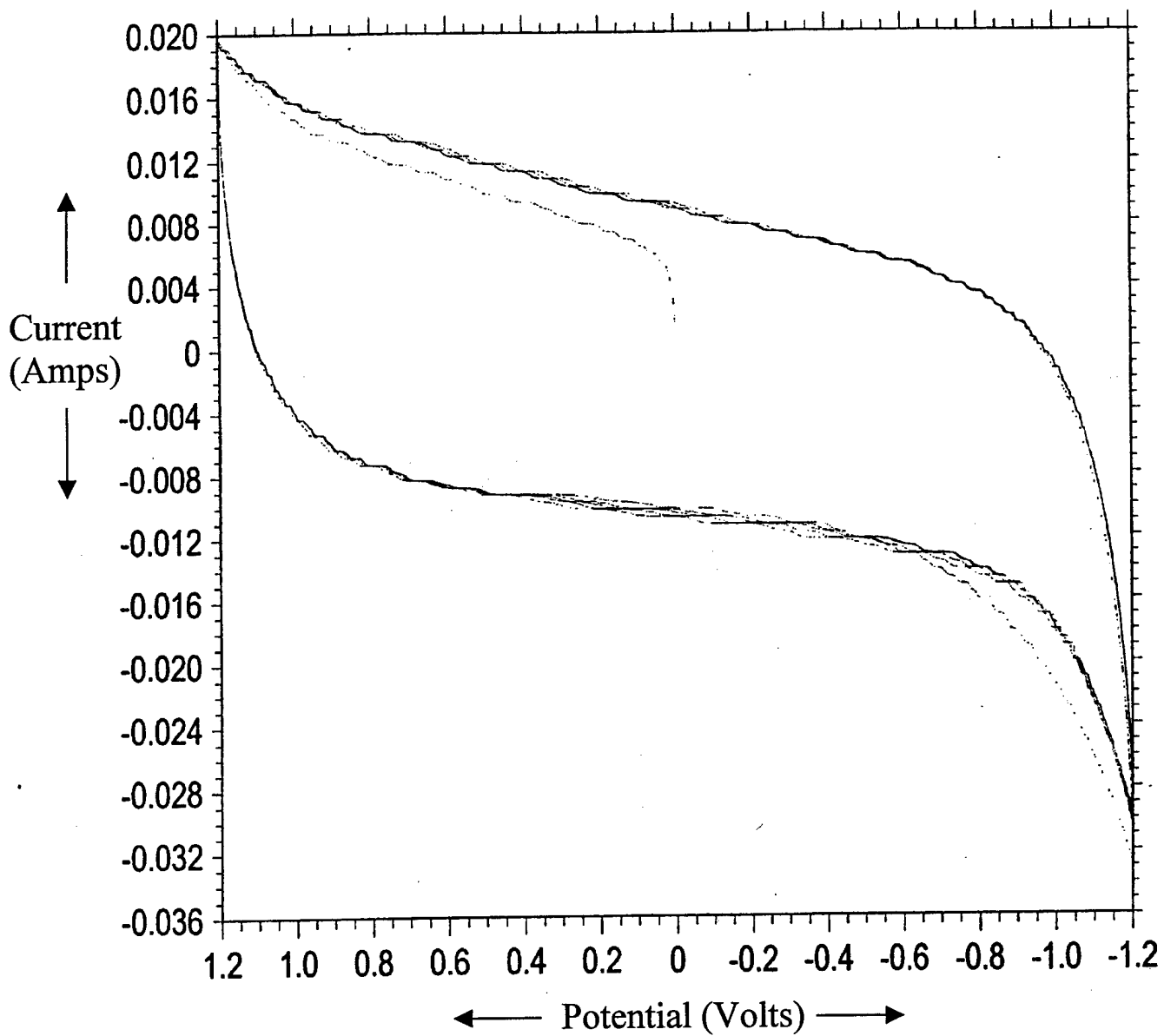


Figure 1. Cyclic Voltammogram for a Pair of TiN Electrodes in Alkaline Electrolyte

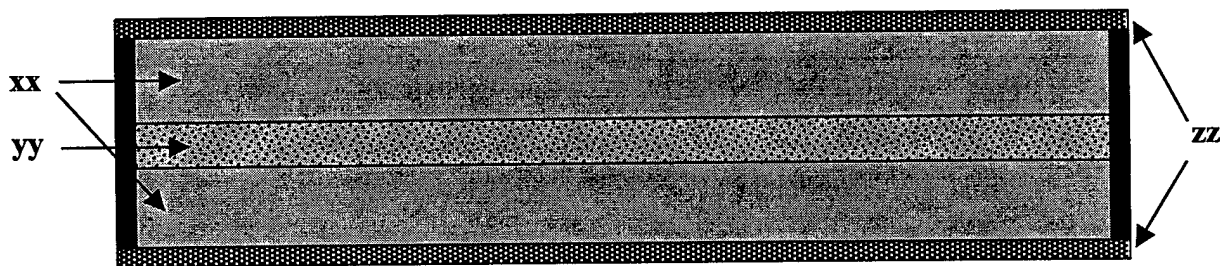


Figure 2. View of a Portion of Multi-Cell Alkaline Electrochemical Capacitor

separator membrane yy is applied to high surface area electrode (either powder or planar film) material xx. A second unit of electrode material xx is used adjacent to the separator membrane yy. The first and second electrodes consist of identical material. The separator membrane (of approximately 1-mil thickness) may be made of any alkaline electrolyte solution compatible polymer, such as polypropylene, polyethylene, or nylon; however, the membrane pore size must be considerably finer than the average particle size for the powder electrode. Separator membrane pore size is not critical for planar film electrodes. They have metal film substrates (i.e., sections of foil made of titanium, zirconium, iron, nickel, or stainless steel or alloys thereof). Here, the separator is required simply to prevent adjacent electrodes from touching and shorting out one or more capacitor cells within the multi-cell stack.

When planar film electrodes are used, coating both sides of the metal foil substrate facilitates construction of the multi-cell alkaline electrochemical capacitor. If powder electrodes are used instead of planar film electrodes, individual cells may be physically reinforced and sealed using conductive elastomeric end terminations zz. Such terminations can be made from any conductive particle loaded elastomer and bonded to an insulating elastomeric shell which constitutes the remainder of the cell housing prior to final device wire attachment and packaging. Carbon loaded elastomers (such as carbon filled rubber) can be used for alkaline electrochemical cell termination, but bulk TiN powder would serve as a filler that would give the elastomer greater conductivity. It is important that all materials used must be compatible with the strongly alkaline electrolyte and exhibit long term electrochemical stability in it.

A ten-gram sample of titanium hydride (99% pure, 325 mesh powder) was placed in a shallow stainless steel tray in a split core tube furnace and thoroughly dried at 175°C for two hours in 99.97% pure nitrogen gas at controlled flow rate (2 l/min). Thermal exposure was performed in 99.99% pure anhydrous ammonia at controlled flow rate (2 l/min) using a ramp-up temperature profile which increased the specimen temperature to 700°C within two hours. Without interrupting the controlled flow of anhydrous ammonia, the temperature was held at 700°C for two additional hours, followed by cooling to room temperature within one hour. High surface area titanium nitride powder was the product of the reaction, and the material was stored for subsequent usage.

A small (one-inch diameter) circular piece of 40% porous polypropylene membrane (Celgard 3400, 40 nm average pore diameter) was epoxied between a pair of rubber gaskets of 0.625-inch inner diameter. A sample (several milligrams) of the high surface area titanium nitride powder was placed into one side of the gasket/membrane assembly, and it was plugged with a nitrided disk of titanium metal of 2-millimeter thickness. The half cell was flipped in order to place an equal amount of powder into the other side of the assembly. After wetting this powder with 7.6 M (14.7 pH) potassium hydroxide solution, this side of the assembly was similarly plugged with a disk of nitrided titanium metal. The alkaline electrolyte wicked evenly across the membrane within the assembly, and the single cell electrochemical capacitor was soon ready to be tested.

A small pinch clamp was used to hold a strip of copper foil to each of the opposite faces of the assembly. Test wires were attached to a one-volt power source in order to charge the alkaline capacitor cell, and the amount of charge stored was subsequently measured with a Princeton Applied Physics Model 379 digital coulometer. In addition, the internal resistance (equivalent series resistance, or ESR) of the alkaline capacitor cell was measured with a GenRad Model 1658 RLC digital impedance bridge at a frequency setting of 1 kHz. With a measured ESR of 0.47Ω, the alkaline capacitor cell exhibited a capacitance of 0.25 farad. With a specific capacitance of 125 mF/cm<sup>2</sup>, the alkaline capacitor offers a capacitive energy density of 312 mJ/cc based upon the volume of active material. In addition, no loss in performance was observed upon operation at 90°C temperature, and it was apparent from cyclic voltammetry analysis that electrochemical stability was maintained over the bipolar potential window of 1.2 volts.

Design modifications of the alkaline electrochemical capacitor involving different types of electrode configurations for various electrical and electrochemical energy storage/conversion devices not addressed herein, obvious to those with ordinary skill in the art, are conceivable ramifications of the subject technology. For example, one practiced in the state-of-the-art of electrochemistry will also be aware of the unique electrode design configurations that will be most likely to be optimal for alkaline fuel cells, batteries, electrochemical synthesis reactors, catalysts, and sensors.



## CONCLUSION

Low cost alkaline electrochemical capacitors based upon powdered titanium nitride electrodes exhibit  $125 \text{ mF/cm}^2$  surface capacitance density and remarkable electrochemical stability over a relatively wide ( $-55^\circ\text{C}$  to  $+100^\circ\text{C}$ ) temperature range in aqueous potassium hydroxide of approximately 15 pH alkalinity. With energy density in excess of  $300 \text{ mJ/cc}$  and the potential to exceed a power density of  $100 \text{ W/cc}$ , the alkaline electrochemical capacitor represents a significant advancement in technology for high power energy storage.

In planar electrode configuration, the alkaline electrochemical capacitor holds promise of extremely high ( $10 \text{ J/cc}$ ) energy density in conjunction with extremely low (several milliohm) ESR. Using chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD), it will become possible to mass produce planar electrode material of very high (one-farad per square centimeter) surface capacitance density. Within the general concept of ultracapacitor construction, the extremely small interelectrode spacing could make it possible to achieve extremely high ( $100 \text{ W/cc}$ ) power density as well.

High surface area ( $1 \text{ F/cm}^2$ ) films of titanium nitride can be grown on 1-mil titanium foil using a high vacuum ( $10^{-5}$  torr) ammonia PECVD system equipped with a  $300^\circ\text{C}$  titanium hydride vapor generator (or bubbler). Hot ( $700^\circ\text{C}$ ) filament CVD provides an alternative means for growing such films from the titanium hydride vapor in the presence of ionized ammonia. Ammonia partial pressures ranging from 10 to 50 torr are used in either case so as to provide an adequate source of reactive nitrogen and balance the partial pressure of titanium hydride generated from the bubbler. High surface area titanium nitride films can be grown in less than an hour, and either PECVD or hot filament CVD can be scaled appropriately for mass production of planar film electrode material.

It is conceivable that a powerful alkaline capacitor resembling a standard D-cell battery could be manufactured through use of this technology. It would require a pair of twelve-foot strips of planar film electrode material of approximately 2-inch width. With both sides of half-mil substrate foil coated with 0.75-mil titanium nitride, a single rolled D-cell would offer over 7400 farads of capacitance and theoretically be capable of providing a 1.4 kW burst of power. Although such quantities of planar film electrode material are far from being commercially available, the cost of materials required does not preclude such development within the next decade.

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