Conformal Ultracapacitor Power Source Technology for the Miniature Kill Vehicle
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1. Introduction

Improvements in power technology are needed to accommodate advanced interceptor power requirements, enable advanced electronic packaging approaches, and reduce cost. Advances in all facets of missile technology have resulted in smaller, lighter components and ultimately smaller missiles. Despite this decrease in overall size however, power and energy requirements are increasing. Emerging system designs are pushing the envelope of current battery technology. Current battery technology for military systems is generally limited to single-use applications, is relatively inefficient, and is generally packaged in a cylindrical container, limiting the electronics packaging options available to the designer. High efficiency, multiple-use, arbitrarily shaped batteries could be a solution to this design constraint. The concept of a high-power conformal power source would allow designers more flexibility in locating the power source within the severely cramped avionics compartment.

The newly available ultracapacitor technology is making it easier for engineers to balance their use of both energy and power. The Multiple Kill Vehicle (MKV) program can take advantage of the ultracapacitor’s unique ability to deliver bursts of power to meet the demands of the system. MKV system applications will require that the ultracapacitors be connected together, in series and/or parallel combinations, to form a “bank” with a specific voltage and capacitance rating to meet its power requirement. This concept can also be extended to other programs such as THAAD and Advanced Precision Kill Weapon System (APKWS).

In this Phase I effort, we developed a conformal, stacked ultracapacitor for MKV based on the system requirements established with Lockheed Martin. The conformal ultracapacitor power source will be attached to the inside available surface of the individual miniature kill vehicle. The ultracapacitor will be charged through a charging system in the carrier vehicle using a reserve battery located in the booster interstage. The reserve battery is placed in the booster interstage because it has less stringent requirements for space and weight. The reserve battery will charge up the individual ultracapacitor during the fly out and the charged ultracapacitor will provide the required power to operate the individual MKV once it is deployed from its carrier vehicle. During system test, the ultracapacitor can be charged up with an external battery to perform individual MKV check out. The ultracapacitor stack will be placed in parallel with the reserve battery, the ultracapacitor will remain charged to the operational voltage, and any interruption in the power such as MKV separation and deployment will be seen as a load condition. As a result, the ultracapacitor will discharge, filling in the missing power and ensuring a continuous supply of power to the MKV to fulfill its mission requirement.

We also evaluated the feasibility of using carbon nanotubes as electrode material to further improve the performance of the ultracapacitor in the Phase 1 effort. We used a proprietary electrophoresis process to deposit the carbon nanotubes onto a thin flexible substrate. The flexible substrate can then be shaped to form a conformal power storage device to the shape of the MKV structure. The conformal ultracapacitor sheet can then be stacked in series and parallel to meet the power requirements of the MKV.

2. Kill Vehicle Power Requirements

Multiple Kill Vehicle’s preliminary design requirements were reviewed. Two 28V thermal batteries [Li(Si)/CoS2] in parallel are currently the baseline to provide power to the DC/DC converter, current regulator and laser drivers. The two batteries weighed 0.215
kg, and provide peak power of 500 W. The DC/DC converter is common to the electronics and avionics, which reduces kill vehicle weight and volume and provides for lower power density. The decision to add the current regulator allows for the seeker and avionics to share the battery. This reduces risk while improving the robustness of the system.

Figure 1 shows the power systems and lists the individual subsystem power requirement for the Kill Vehicle.

The battery performance specifications for THAAD (MIS-PRF-52041H) and APKWS (838235D) were also provided by Lockheed Martin and BAE Systems for review. A 24-35V power storage device capable of delivering up to 25Amps current over the required mission timeline will satisfy both programs’ need.

3. Electrode Material Development

The objective of this development effort is to demonstrate the feasibility of using stacked ultracapacitors as power source for MKV and we will improve the ultracapacitor performance by using carbon nanotubes as electrodes to increase specific energy and/or specific power beyond what is currently available.

The multi-walled carbon nanotubes (MWNTs) used in this study were produced by chemical vapor deposition (CVD). Synthesis of MWNTs was conducted in a horizontal quartz tube in a furnace. Catalyst powder (Fe/Al_2O_3) for producing MWNTs was placed in a ceramic boat which was then loaded into the tube furnace. Hydrogen was introduced into the furnace before it was heated up to 650°C. The temperature was held for 30 minutes during which ethylene was introduced into the quartz tube. Ethylene gas supply was then shut off and the system was cooled to room temperature.

The as-produced powder of Fe/Al_2O_3/MWNTs was treated with a HF aqueous solution and hydrochloride acid at room temperature successively to extract the nanotubes by dissolution of Al_2O_3 and iron particles. The nanotubes were then collected by filtration, washed with distilled water and dried.

The purified nanotubes were refluxed with concentrated boiling nitric acid for about 10 hours, and then washed with distilled water followed by rinsing with ethanol and drying at
The colloidal suspension of carbon nanotubes was prepared by adding a predetermined amount of refluxed carbon nanotubes in a scintillation vial containing 10 ml of dimethylformamide (DMF), and sonicated for 30 minutes. The colloidal suspensions remain stable for many months with no aggregated materials precipitating over time.

We compare the carbon nanotubes electrode performance with the state-of-the-art carbon (carbon blacks and carbon xerogel) materials used in the commercially available ultracapacitor. The performance is evaluated by measuring the cyclic voltammograms (CV curves) and constant current charge and discharge.

3.1 Carbon Nanotubes Electrode Preparation – Direct Deposition

Two electrodes were prepared by directly depositing 0.1 ml of the colloidal suspension (concentration: 5 mg of carbon nanotubes in 1 ml of DMF) on two 12 mm × 12 mm nickel foils (as current collector) followed by drying at room temperature. An Electrochemical Double Layer Capacitor (EDLC) test cell was then fabricated for electrochemical measurement. A glass fiber separator immersed in a 6N of KOH electrolyte was placed between two electrodes. The cyclic voltammetry and galvanostatic charge/discharge tests were performed with the Potentiostat/ Galvanostat (EG&G Princeton Applied Research, Model 263A).

A larger electrode was prepared by directly depositing 0.4 ml of colloidal suspension (concentration: 26.7 mg of carbon nanotubes in 1 ml of DMF) on 24mm×24mm (almost 1 inch by inch) nickel foils to study the feasibility of scaling up the electrode size. The same direct deposition procedure established for a quarter size electrode was used to prepare the larger electrode samples.

3.1.1 Test Results – Standard 12mm X 12mm Electrode

The microstructures of the direct deposited films were examined by scanning electron microscopy (FEI XL30-SFEG) and shown in Figure 3. The SEM image of nanotubes thin film shows dense packing and some local alignment.
The Cyclic Voltammogram (CV) measured at different scan rates of the assembled EDLC are provided in Figure 4. The CV at scan rates of 50 to 750mV/s shows mirror images with respect to the zero-current line and a very rapid current response to voltage reversal at each end potential. Nearly rectangular shape loops indicate that internal, interfacial and contact resistances are extremely small in the test sample. Higher resistance of the electrode tends to distort the CV loop, resulting in a narrower loop with an oblique shape, especially at a high scan rate.
The constant current charge/discharge curve for the carbon nanotubes thin film electrodes EDLC is shown in Figure 5. In both test samples, the E-t responses of the charge process shows almost the mirror image of their corresponding discharge counterparts, and no IR drop was observed, indicating that electrical series resistance (ESR) of the electrodes is small.

The specific capacitance of the electrode can be calculated from constant current charge/discharge curves using the following equation:

$$C = \frac{l}{m \times (\Delta V / \Delta t)}$$

Where \(l\) is the current, \(\Delta V/\Delta t\) is the slope of the discharge curve and \(m\) is the mass of the electrodes. A specific capacitance of approximately 36 F/g was obtained for the EDLC samples fabricated. The power density is estimated by integrating the inner area of the CV curve. A power density of about 16.7 kW/kg is achieved, indicating carbon nanotubes can be used to fabricate electrodes for ultracapacitor for fast power delivery application. We believe that the very large power density is attributed to the small internal resistance which is resulted from the coherent structure of the thin films fabricated using highly concentrated suspension.

### 3.1.2 Test Results – Larger 24mm X 24mm Electrode

The CV curves at 100mV/s scan rate of the two different size electrode made out of carbon nanotubes are shown in Figure 6. The maximum current that can be achieved is about 0.2A for a 24mm by 24mm electrode sample, whereas the maximum achievable current for a 12mm by 12mm electrodes is only 0.05A. In the 24mm by 24mm electrode, the amount of carbon nanotubes used is 4 times of that used in the 12mm by 12mm electrode. Thus the total current output can be increased by increase the surface area of electrode to include more active materials.
A constant current charge/discharge curve for this larger size EDLC is shown in Figure 7. Just like the current increase, the charge/discharge time also increased because more nanotubes were present at the electrode surface area. We measured power density as high as 30kW/kg when the amounts of carbon nanotubes in the electrode are increased. However, the specific capacitance did not change.

In conclusion, by increasing the surface area of electrodes and the amount of carbon nanotubes, the maximum current can be increased. But the current density and capacitance will not change.

3.2 Carbon Nanotubes Electrode Preparation – Electrophoretic Deposition

Carbon nanotubes electrodes were also fabricated using electrophoretic deposition (EPD) process and tested. In order to introduce a surface charge on the carbon
nanotubes, $10^{-5}$–$10^{-4}$ mol of Mg(NO$_3$)$_2$•6H$_2$O were added to the carbon nanotubes colloidal suspension as electrolyte prior to EPD. Nickel foils were used as the current collector. The EPD set-up is shown in Figure 8. A dc voltage of 20-40 volts was applied and a gravity assisted deposition technique was used to separate carbon nanotubes from impurity particle sediment in the solution. The EPD process was stopped until the suspension was almost clear indicating all tubes were deposited onto the nickel current collector. After deposition, the EPD electrodes were cut into small pieces of samples with a dimension of 0.9cm by 0.9cm for testing. The nanotubes on each electrode were about 0.02mg. The small samples were heated in tube furnace at 500°C for 0.5h under hydrogen environment prior to testing.

The microstructures of the films were investigated under scanning electron microscopy (FEI XL30-SFEG). For electrochemical measurement, a EDLC test cell was fabricated with a 6N KOH as electrolyte. A glass fiber filter paper immersed in the electrolyte was used as separator. The test samples were measured by itself and in series as a stack. The cyclic voltammetry and galvanostatic charge/discharge tests were performed using a Potentiostat/Galvanostat (EG&G Princeton Applied Research, Model 263A).

![Figure 8: Schematic of the electrophoresis process for the deposition of carbon nanotubes.](image)

### 3.2.1 Test Results

The SEM image of a nanotubes thin film electrode prepared by EPD is shown in Figure 9. The open porous structure provides a highly accessible surface area to the solvated ions at the electrode/electrolyte interface, which is crucial for charging/discharging of the electric double layer. The EPD carbon nanotubes film formed on the nickel foil has excellent adhesion to the foil and extremely low electrical contact resistance.
3.2.1.1 Test Results – Single EDLC Capacitor Cell

The CV curves of EPD carbon nanotubes electrode of a single cell EDLC is shown in Figure 10. Nearly rectangular shape of the curve indicates very small ESR of the electrodes and the fast diffusion of electrolyte in the films. These curves are very similar to the directly deposited carbon nanotubes electrodes, except they have charging/discharging current due to a smaller amount of carbon nanotubes deposited on the electrode.
The constant current charge/discharge curve for the single EPD capacitor is shown in Figure 11. Again, no IR drop was observed indicating that ESR of the electrodes is small. The capacitance of the EPD carbon nanotubes EDLC is the same as the number (36F/g) obtained from direct deposition method. Shorter discharge time is again due to fewer carbon nanotubes on the electrode.

The capacitor stack was also charged at a higher current (charge current was 5mA, but the discharge current was still 1mA) as shown in Figure 10b. It took a much shorter time to charge the capacitor to 1.7 V. The charging time is directly proportional to the charging current.
Figure 12: Charge/discharge curve of 2-cell capacitor stack in series

The CV test of the capacitor stack in series was carried out between 0 to 1.6V. Figure 13 shows the CV of the capacitor stack at different scan rates. Because of the contact resistance in the assembly, the shapes of the curves were not as ideal as those for single capacitor shown in Figure 8, but still show a relatively rectangular shape at scan rates up to 200mV/s, except there is an oxidation peak at higher voltages. At a higher scan rate (500mV/s), the CV shape became oblique.
Figure 13: CV of a capacitor stack consists of 2 EDLC cells in series at different scan rates

3.3 Carbon Nanotubes Electrode Preparation – EPD/Filtration

This experiment was aimed at increasing the output current of the EDLC. As demonstrated earlier, the EDLC built both from direct-deposition electrodes and EPD film electrodes have relatively low output currents. For example, the current was only about 2.5 mA for an EPD carbon nanotube EDLC, and 5 mA for a direct deposited carbon nanotube EDLC at a 500mV/S scan rate. Although increasing the carbon nanotubes in the electrode will increase the current output, it is time consuming to prepare mats or cakes using the EPD process and direct deposition of a thick film creates an interface problem at the nickel foil current collector due to mismatches of the thermal expansion coefficient. So a filtration technique was used to prepare thicker carbon nanotubes mats in this experiment. To prepare carbon nanotubes mats using filtration, there is no need to pre-treat carbon nanotubes, and no need to prepare stable suspension resulting in cost savings.

Two kinds of current collectors were used in this study. One is the regular nickel foils, and the other is nickel foils coated with a very thin layer of carbon nanotubes using EPD process. The carbon nanotubes mats were used as electrodes in both cases. The mats electrodes were first put in between two nickel foils to measure the electrochemical properties, and the then the same mats electrodes were put in between two carbon nanotubes coated nickel foils to measure the properties again.

3.3.1 Test Results – EPD/Filtration

Figure 14 shows the CVs of an EDLC fabricated using nickel foil as current collector and the filtered carbon nanotubes mats as electrodes. The CV curves are distorted even at a scan rate of 5mV/s. This is a clear indication that a high contact resistance exists between the carbon nanotubes mats and the nickel foil current collector.

![Figure 14: CVs with different scan rates of an EDLC fabricated using nickel foil as current collector and the filtered carbon nanotubes mats as electrodes](image)

However, when the nickel foil is coated with a very thin layer of carbon nanotubes, the CV curves shows the ideal rectangular shape as shown in Figure 15. It should be noted that the electrodes used in this test were the same mats corresponding to Figure 14. Therefore, the coated carbon nanotubes layer is crucial to lower the contact resistance at the interface. The maximum current output also improved to 50mA at 500mV/s scan rate as compared to the earlier measurement of 5 mA for a direct deposited carbon
nanotube EDLC at 500mV/S scan rate. Again, the higher current output is a direct result of more carbon nanotubes in the electrode.

Figure 15: CVs with different scan rates of an EDLC fabricated using an EPD coated nickel foil as current collector and filtered carbon nanotubes mats as electrode

3.4 Carbon Nanotubes Reinforced Carbon Black Electrode Development

The nanotubes used in this experiment are still those HNO$_3$-refluxed MWNTs used in earlier study. Carbon blacks used in this experiment are 36nm diameter particles, and were also refluxed in boiling concentrated nitric acid to remove all impurities. 50 mg of refluxed carbon nanotubes and 100 mg of refluxed carbon black were mixed in 15 ml of dimethylformamide (DMF) to prepare the colloidal suspension. These were prepared by direct depositing 0.1 ml of colloidal suspension on two 12mm $\times$ 12mm nickel foils (as current collector) followed by drying at room temperature. The weight percent of carbon nanotubes in the obtained composite electrode is 33.3wt%.

Another Carbon nanotubes/carbon black nanocomposite electrode test sample was prepared by the EPD process using a weight ratio of 1 parts by weight of carbon nanotubes to 4 parts by weight of refluxed carbon black. The electrode samples were processed the same as reported earlier for pure EPD carbon nanotubes samples.

3.4.1 Test Results – Carbon Nanotubes/Carbon Black Nanocomposite Electrode

The directly deposited carbon nanotubes/carbon black nanocomposite electrode showed an oblique CV shape indicting that the ESR of the electrodes is large. The large ESR of
the electrode was also evident during constant current charge/discharge test. An IR drop was observed.

A specific capacitance of 33F/g and a specific power density of 1kW/kg were obtained for the direct deposited carbon nanotubes/carbon black nanocomposite electrode. We speculate that the large ESR of the electrodes is due to the functional treatment of carbon black. It is possible that the refluxed carbon black had too much functional groups remaining on the carbon black particles, thus increasing the resistance of the active materials.

The EPD carbon nanotubes/carbon black nanocomposite electrode, on the other hand, showed a remarkable oxidation peak around 0.7-1.0 V. Although the peak around 1V was also observed with the EPD electrode with pure carbon nanotubes, the peak was relatively small. We attribute this large peak around 0.7-1.0 V to the presence of carbon black particles. The CV curves for EPD carbon nanotubes/carbon black nanocomposite electrode were also distorted, however, no IR drop was observed during the charge/discharge test indicating the ESR in the electrode is fairly small.

The specific capacitance estimated from the charge/discharge curve is close to specific capacitance of the EPD electrode with pure carbon nanotubes (35F/g). This suggests that partial replacement of carbon nanotubes with carbon black is a feasible way to reduce the cost without sacrificing the advantages of pure carbon nanotubes. The microstructure of EPD carbon nanotubes/carbon black nanocomposite electrode shows that the carbon nanotubes are coated with carbon black. In some area where the carbon black is even less, the carbon black particles just scattered on the nanotubes, as seen in Figure 16.

![Figure 16: SEM image of the EPD carbon nanotubes/carbon black nanocomposite electrode](image)

3.5 **Carbon Nanotubes Reinforced Carbon Aerogel Electrode Development**

A carbon nanotubes reinforced carbon aerogel composite electrode was prepared using the following process. This process involves the addition of carbon nanotubes (MWNTs)
into the sol resorcinol and formaldehyde, and the sol-gel polymerization of resorcinol with formaldehyde followed by the supercritical drying of the organic aerogel with liquid CO₂. First, a colloidal suspension (0.5mg/ml) of carbon nanotubes was prepared. Then predetermined amount of resorcinol and formaldehyde (molar ratio 1:2) was dissolved in this MWNTs suspension depending on the concentration of the nanotubes in the final product. 1wt% HCl (as catalyst) was then added into the suspension. The suspension was later transferred to a sealed mold and kept in the oven at 70 °C for 5 minutes to form gel with desired shape. After polymerization, the gel was aged at 75 °C for 2 days to increase the cross-linking density of the gel architecture. The composite gel was then supercritical dried with liquid CO₂ to produce a porous organic aerogel. Pyrolysis of the organic aerogel was carried out in argon at 1000°C for 3 hours to produce the porous carbon aerogel.

An EDLC test cell was assembled with the composite carbon aerogel derived nanostructured pads as electrodes. The same procedures were used to measure the CV curves and constant current charge/discharge characteristics.

### 3.4.1 Test Results – Carbon Nanotubes/Carbon Aerogel Nanocomposite Electrode

The SEM images of pyrolyzed nanotubes/carbon aerogel nanocomposite electrode (0.6wt% carbon nanotubes) is shown in Figure 17. The microstructure shown in Figure 17 is ideal because most of the nanosize carbon aerogel particles sit on the highly conductive carbon nanotubes, and the carbon nanotubes are also interconnected. At the same time, this composite is more porous than pure carbon aerogel due to the skeleton formed by the interconnected nanotubes, which is advantageous to the fast diffusion of electrolyte in the electrodes.

![Figure 17: SEM showing regular image of pyrolyzed nanotubes/carbon aerogel composite electrode](image)

The CV behavior of the composite carbon nanotubes/carbon aerogel electrodes is better than the capacitors built from pure carbon aerogel electrodes, especially at higher scan rate (100mV/s). On one hand, this can be attributed to the conductive nanotubes in the aerogel and the porous structure; on the other hand, the composite electrodes used in this experiment were much thinner that those pure carbon aerogel electrodes, so the diffusion of electrolyte in these composite electrodes probably was faster. The carbon nanotubes reinforcement allows us to make thinner carbon aerogel film by preventing the thin film from cracking.
Typical constant current charge/discharge curves for the ultracapacitor built from the carbon nanotubes/carbon aerogel composite electrodes still showed IR drops at higher discharge rate (10mA) indicating that ESR is not small enough to be ignored for this capacitor. We suspect that the contact resistance between composite electrodes and current collector is the major source of resistance.

A specific capacitance of 55F/g and 54F/g was obtained for the carbon aerogel electrode, and the composite carbon nanotubes/carbon aerogel electrode respectively. A maximum power density of 5kW/kg and 7.3kW/kg was calculated for obtained the carbon aerogel electrode, and the composite carbon nanotubes/carbon aerogel electrode respectively. Incorporating carbon nanotubes in the aerogel improved the power density by about 50%, however, the power density is still much lower than that of a pure carbon nanotube electrode (16.7 KW/Kg).

4 Conclusion

Electrophoresis deposition process opens a new door to fabicrate uniform carbon nanotubes films, in which charged nanotubes dispersed in a stable suspension are driven by a DC electric filed to move towards an oppositely charged electrode and build up a uniformly packed layer. It has the advantages of short formation time, simple deposition apparatus and suitability for mass production as in the plating industry. Most important, the porosity of the film can be tuned by changing the deposition parameters, and deposition of metal particles and formation of nanotubes films can be done all at once. Due to the higher conductivity in the film and lower ESR at the interface, the power capabilities are improved.

Based on Phase I study, following conclusions can be drawn:

- Carbon nanotube electrodes can be produced without any binders thus reducing the internal resistance in the electrode.
- The carbon nanotubes when added to the carbon aerogel as an electrode will improve its power density by 50% with 0.6 wt % of carbon nanotubes added without compromising the energy density.
- The carbon nanotubes provide a more uniform porosity for electrolyte access, and a conductive path network in a carbon nanotubes/carbon aerogel nanocomposite electrode.
- Carbon black can be use to replace some of the carbon nanotubes to reduce cost without sacrificing much of the carbon nanotubes performance. However, the optimum carbon black level must be determined.
- EPD coating of the current collector with carbon nanotubes and carbon nanotubes mats made with filtration technique appears to be the best approach to make electrodes for ultracapacitor application.
- The voltage of the ultracacpacitor can be increased by stacking individual EDLCs in series. Current output can be improved by increasing the electrode surface area and increasing the amount of active carbon nanotubes materials. However, the thickness of the electrode must be optimized for performance and handling purposes. Current output can also be increased by connecting the individual stacks in parallel.

5 Phase II Recommendation

The following recommendations are made for the Phase II efforts:
Complete a conformal power storage device (PSD) design based on a stacked ultracapacitors concept in series and parallel to meet system requirements of 24 - 35V, 1.4 A-hr, 25 Amp peak current capability.

Optimize the ultracapacitor design by using organic electrolytes instead of the aqueous electrolytes which have a maximum voltage limitation of 1 volt per individual cell. Organic electrolytes will increase the individual cell to 2.5 -3 volts and reduce the volume (thickness) of the stack.

Fabricate conformal arbitrary shaped prototype PSD for testing and capability demonstration by conducting functional performance tests in accordance with THAAD & MKV system specifications.