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Screening Protocol for the Electrochemical Characterization of Potential Supercapacitor Materials

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Defence R&D Canada – Atlantic

Technical Memorandum
DRDC Atlantic TM 2009-279
November 2009

Canada

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Abstract

A method for the preparation and measurement of potential active materials for supercapacitor electrodes was developed and validated. An ethanolic suspension of the active material was applied to carbon fibre fabric, and allowed to dry. The electrode (active material and carbon support) was affixed in a half cell assembly that allowed consistent placement of the reference electrode. The electrode was characterized in deaerated 0.5 M H_2SO_4 (aq) by cyclic voltammetry, electrochemical impedance spectroscopy, and constant current charge discharge experiments. The electrode preparation method, and half cell assembly was determined to be highly reproducible, resulting in accurate electrochemical characterization of the active material. Using this method, the capacitance of two potential supercapacitor materials was evaluated: PAni-PTSA was determined to have a capacitance of ~ 300 F/g and PAni-2NSA/MWCNT was found to have a capacitance of ~ 153 F/g.

Résumé

Une méthode de préparation et de mesure de matériaux actifs qui pourraient servir à réaliser des électrodes de supercondensateurs a été mise au point et validée. Une suspension éthanolique du matériau actif a été appliquée à un tissu de fibre de carbone, qu’on a ensuite laissé sécher. L’électrode (composé du matériau actif et du support de carbone) a été fixée dans un ensemble demi-cellule, ensemble qui permet un positionnement uniforme de l’électrode de référence. L’électrode a été caractérisée dans une solution aqueuse d’acide sulfurique (H_2SO_4) désaérée au moyen de la voltampérométrie cyclique, de la spectroscopie d’impédance électrochimique et d’expériences de charge et de décharge à courant constant. La méthode de préparation des électrodes et l’ensemble de cellule ont permis d’obtenir des résultats hautement reproductibles : il a donc été possible de réaliser une caractérisation électrochimique précise du matériau actif. Deux matériaux qui pourraient servir à réaliser des supercondensateurs ont été évalués : le PAni-PTSA (polyaniline-acide toluène-4-sulfonique) a une capacité d’environ 300 F/g, tandis que le PAni-2NSA/MWCNT (polyaniline-acide naphtalène-2-sulfonique/nanotube de carbone multiparoi) a une capacité d’environ 153 F/g.

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Executive summary

Screening Protocol for the Electrochemical Characterization of Potential Supercapacitor Materials

Trisha A. Huber; Michael C. Kopac; Felix Wong; DRDC Atlantic TM 2009-279; Defence R&D Canada – Atlantic; November 2009.

Introduction or background: The military has a need for high power energy sources. Supercapacitors are energy storage devices that exhibit higher energy density than conventional capacitors, and higher power density than batteries. The focus of the Supercapacitor TIF project was to develop and investigate novel materials as potential supercapacitor electrode materials. To determine whether a material exhibits supercapacitor potential, the electrochemical properties must be evaluated. This technical memorandum describes a protocol for electrode preparation, electrochemical cell set up, and methods utilized to evaluate the capacitance.

Results: A methodology for the preparation of electrodes and evaluation of capacitance has been developed. The capacitance of PAni-PTSA and PAni-2NSA/MWCNT was found to be ~ 300 F/g, and ~ 153 F/g, respectively.

Significance: In order to determine whether a material exhibits potential as a supercapacitor electrode material, it is necessary to properly evaluate its capacitance and other pertinent electrochemical parameters. A reproducible means of accurately determining the capacitance of chemically prepared active materials has been developed.

Future plans: Future work includes developing a methodology for the preparation of higher loaded electrodes (for power density measurements), as well as optimizing the supercapacitor assembly.

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Screening Protocol for the Electrochemical Characterization of Potential Supercapacitor Materials

Trisha A. Huber; Michael C. Kopac; Felix Wong; DRDC Atlantic TM 2009-279; R & D pour la défense Canada – Atlantique; Novembre 2009.

Introduction ou contexte : Les forces armées ont besoin de sources d'énergie à haute puissance. Les supercondensateurs sont des dispositifs de stockage d'énergie dont l'énergie spécifique est supérieure à celle des condensateurs classiques, tandis que leur puissance spécifique dépasse celle des piles. Le projet de FIT sur les supercondensateurs avait pour but de mettre au point et d'étudier de nouveaux matériaux qui pourraient servir à réaliser des électrodes de supercondensateur. Pour déterminer le potentiel d'utilisation d'un matériau dans cette application, il faut évaluer ses propriétés électrochimiques. Le présent mémoire technique décrit un protocole comprenant la préparation d'électrodes, la configuration d'une cellule et les méthodes servant à évaluer la capacité.

Résultats : Une méthode de préparation des électrodes et d'évaluation de la capacité a été mise au point. Les capacités mesurées du PAni-PTSA (polyaniline-acide toluène-4-sulfonique) et du PAni-2NSA/MWCNT (polyaniline-acide naphtalène-2-sulfonique/nanotube de carbone multiparoi) sont de 300 F/g et 153 F/g, respectivement.

Importance : Pour déterminer le potentiel d'utilisation d'un matériau en vue de réaliser des électrodes de supercondensateur, il faut évaluer correctement sa capacité et d'autres paramètres électrochimiques. Un moyen reproductible de déterminer avec précision la capacité de matériaux actifs préparés chimiquement a été mis au point.

Perspectives : Les travaux futurs comprendront notamment la mise au point d'électrodes à charge plus élevée (pour la mesure de la puissance spécifique) et l'optimisation de l'ensemble de supercondensateur.

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1 Introduction

The Canadian Forces require a wide range of energy storage to supply power for a variety of military applications. These power requirements span many orders of magnitude from milliwatts (mW) to Megawatts (MW). Examples of devices/platforms that require power include micro electro mechanical devices (MEMs), portable battery packs, unmanned aerial vehicles (UAVs), light armoured vehicles (LAVs), kinetic energy/directed energy (KE/DE) weapons, radiofrequency (RF) munitions, remote communications and surveillance, and portable electronics.[1]

Pulse power technology was identified as one of three areas in which significant R&D opportunities exist. Presently there is a deficiency of power sources capable of supplying adequate pulse power for many applications including portable electronics, future weaponry, and communications. High pulse power applications require that energy is supplied at a very high rate. Conventional high energy density sources, such as batteries can store a lot of energy, however the rate at which this energy can be accessed is relatively slow (low power density). Conversely, conventional capacitors can supply stored energy at very high rates (high power density), although the amount of energy that can be stored is relatively low (low energy density). Thus the capacitor can supply a transient power pulse, but the pulse is very short owing to the low energy density.

The performance of various devices are often compared in a Ragone plot (see Figure 1), in which power density and energy density are presented as a log-log plot. As illustrated, supercapacitors offer performance intermediate between batteries and capacitors in that they exhibit higher energy density than capacitors and higher power density than batteries. Hybrid energy devices, in which a supercapacitor is coupled to a high energy density device (battery or fuel cell), would satisfy high pulse power as well as high energy density requirements.

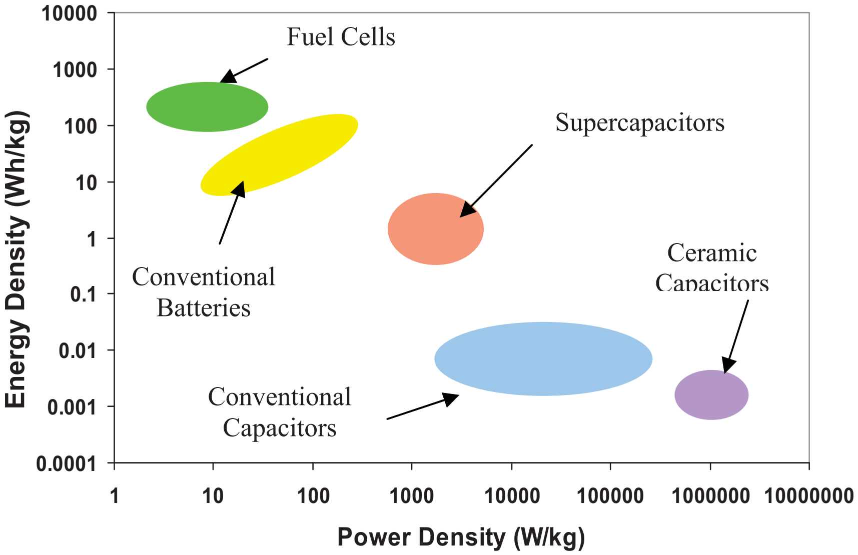


Figure 1: Ragone Plot comparing the Power Density and Energy Density of Various Energy Storage Devices.

The increase in capacitance offered by supercapacitors over conventional or parallel plate, capacitors may be easily understood by first considering the charge storage mechanism utilized by conventional capacitors. A parallel plate capacitor consists of two plates (or electrodes), which are connected to a voltage supply and separated by a dielectric material of thickness, d (see Figure 2). The energy that can be stored in the capacitor is dependent on the capacitance, C, and the square of the voltage difference between the plates:

$$E = \frac{1}{2}CV^2 \tag{1}$$

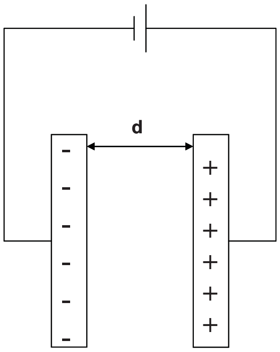
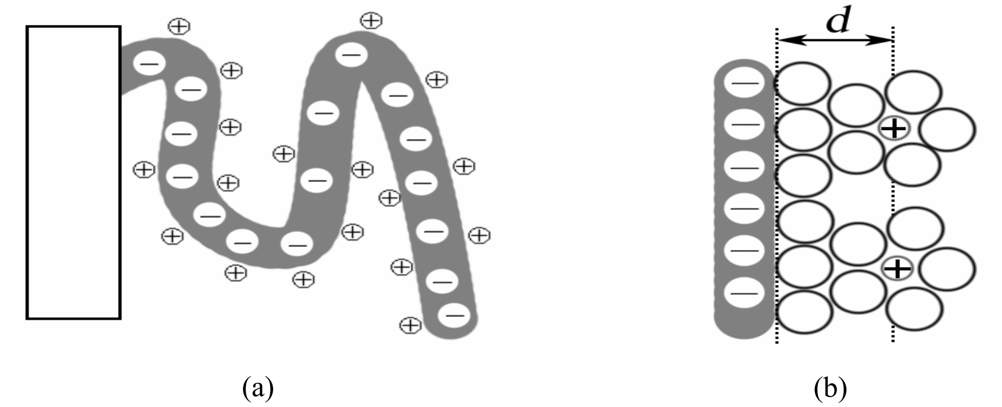


Figure 2: Diagram of a Conventional Capacitor.

The capacitance is dependent on the surface area of the plates, the dielectric constant of the dielectric material, and inversely proportional to the distance between the plates (thickness of the dielectric material), d:

$$C = \varepsilon \frac{A}{d} \tag{2}$$

Supercapacitors, also known as electrochemical capacitors, exhibit capacitances that are several (up to 8) orders of magnitude higher than conventional capacitors, as a result of increasing the surface area (A) and decreasing the charge separation (d). The use of highly porous or fibrous active materials increases the surface area considerably (Figure 3a). The reduction in charge separation distance is achieved through the use of an electrolyte which, upon charging of the cell, forms a layer of ions close to the surface of the active material (Figure 3b). This layer forms a virtual plate that is separated from the active material surface by solvent molecules, which are effectively the dielectric material. Thus, each electrode of a supercapacitor is in essence a conventional capacitor, separated by a membrane, which allows ionic, but not electronic, flow.



(a) (b)

Figure 3: Maximizing the surface area with a high porosity material (a). Electric double layer yields a charge separation in the order of several nanometers (b).

Thus, the entire supercapacitor cell is effectively two capacitors (having capacitance C_1 and C_2), connected in series; the total capacitance (C_{total}) of which is determined as follows:

$$\frac{1}{C_{total}} = \frac{1}{C_1} + \frac{1}{C_2} \tag{3}$$

In addition to electrochemical double layer capacitance (EDLC) illustrated above, materials that exhibit redox activity may utilize an additional charge storage mechanism that is pseudo-Faradaic in nature in which charge is stored through reduction or oxidation of the material itself. Materials that exhibit this type of capacitance, called pseudo-capacitance, include transition metal oxides which may be oxidized and reduced, and conducting polymers, in which the charge storage mechanism involves the reversible reduction and oxidation of the backbone chain.

To address the requirement for high power energy devices, the Supercapacitor TIF is geared toward developing pulse power technology. In this report, we present a screening protocol developed under the Supercapacitor TIF (12sz07) to assess the potential of materials as supercapacitor electrode materials. The protocol consists of the preparation and electrochemical measurement of electrodes. The protocol was developed in-house and incorporates work done during a co-op work term.

2 Experimental

2.1 Materials

Aniline (Sigma-Aldrich, > 99.5 %) was purified by distillation before use. Ammonium persulfate (APS, Fisher Scientific, 99%), N-phenyl-1,4-phenylenediamine (dianiline, Sigma-Aldrich, 98%), *p*-toluenesulfonic acid (PTSA, Sigma-Aldrich, 98%), and 2-naphthalenesulfonic acid (2-NSA, Sigma-Aldrich, 70%) were used as received. Industrial grade thin multi-walled carbon nanotubes (MWCNTs, Nanocyl-7000, diameter ~ 9 nm, ~90% C purity, Lot 257-1) were purchased from Nanocyl Inc and purified before use.[2]

Carbon fibre paper was purchased from EFT Fibres Technology; titanium (Ti) foil (0.25 mm thick) and platinum (Pt) wire (1.0 mm diameter) were purchased from Goodfellow Cambridge Limited. The Ti foil was cut into 7.5 mm x 12 mm pieces. Concentrated sulfuric acid (H_2SO_4) was purchased from Sigma-Aldrich and diluted with distilled water.

2.2 Preparation of Active Materials

2.2.1 PAni - PTSA

Polyaniline doped with PTSA (PAni-PTSA) was prepared by chemical oxidative polymerization as follows. Aniline (12 mL) and 0.638 g dianiline were dispersed in a solvent mixture of 10 mL ethanol and ~ 200 mL 1M PTSA (aq). To this, a solution of 23.1 g APS in ~ 100 mL 1M PTSA (aq) was added dropwise, and allowed to stir overnight. The reaction mixture was centrifuged at 5000 rpm for 5 minutes; the supernatant was decanted and the precipitate was washed with distilled water (twice by centrifugation). The washing process was performed twice with ethanol. The precipitate was collected by vacuum filtration (medium glass frit) and dried at ~ 70 ºC overnight.

2.2.2 PAni – 2NSA/MWCNT Composite

A composite of MWCNTs coated with polyaniline doped with 2-NSA (PAni-2NSA/MWCNT) was prepared by the chemical oxidative polymerization in the presence of dispersed MWCNTs (*in-situ* polymerization) as follows. A suspension of 29.55 mg of MWCNTs in 30 mL ethanol was sonicated for 15 minutes (50% duty cycle). To this, a solution of 100 µL of aniline in 10 mL ethanol was added dropwise, with stirring, followed by sonication for an additional 15 minutes (50% duty cycle). 30 mL of 0.8 M 2-NSA (aq) was added slowly, then 209 mg of APS in 10 mL 0.8 M 2-NSA (aq) was added dropwise. The reaction was allowed to proceed overnight covered by a watchglass. The reaction mixture was centrifuged at 5000 rpm for 5 minutes; the supernatant was decanted and the precipitate was washed with distilled water (twice by centrifugation). The washing process was performed twice with ethanol. The precipitate was collected by vacuum filtration (medium glass frit) and dried at ~ 70 ºC overnight.

2.3 Preparation of Electrodes

The electrodes consist of two components: the active material and the carbon fibre paper support. The carbon fibre paper used was Spectracarb 2050 (hereinafter referred to as 2050), which is a thin, conductive carbon paper. Small (13 mm) circles of 2050 were cut using a cork borer, washed several times in ethanol, followed by drying in a 70 ºC oven.

A small quantity of active material was dispersed in ethanol by sonication until a homogeneous suspension was attained (typically 20 – 60 min). The suspension was applied by pipette to the pre-weighed 2050 disc. Application of the suspension was limited to the centre of the carbon disc to ensure that none of the active material would be covered by the o-ring of the sample holder (*vide infra*). After a sufficient quantity of active material had been applied (~ 1 mg), the electrode was dried thoroughly at ~ 70 ºC. A drying time of 2 h was determined to be sufficient for this quantity of active material. To ensure reproducibility, and assess the uncertainty for the electrode preparation method, 3 – 5 electrodes were prepared for each active material.

2.4 Half Cell Assembly

The sample holder (see Figure 4) was fabricated in-house, and was fashioned after that used in the Pickup lab (at Memorial University). A large hole was drilled in the front piece to ensure electrolyte access to the active material, and a circular groove along the edge of this large hole, was milled to accommodate an o-ring. The presence of the o-ring was to ensure that the electrode was pressed tightly against the current collector; this o-ring covers the outer 2 mm of the carbon disc excluding ~ 48% of the nominal surface area of the carbon electrode. In the front side of the sample holder, a small hole was drilled perpendicular to the large hole, indicated by an arrow in Figure 4, to accommodate the reference electrode (RE). The reference electrode employed was a standard saturate calomel electrode (SCE) lengthened with shrink wrap tubing and terminated with a Vycor™ tip. The use of this modified Luggin capillary allowed the reference electrode to be positioned close to the working electrode, to ensure that the iR drop was not only minimized, but consistent from one sample to the next.

The sample holder was assembled with the Ti foil at the back, and the electrode was positioned such that the active material faced the front of the sample holder (see Figure 5). The front and back pieces were held together by 4 nylon nuts and bolts, and the entire assembly was immersed in deaerated 0.5 M H_2SO_4 (see Figure 6). The Ti was connected as the working electrode (WE), and the Pt wire was connected as the counter electrode (CE) to the potentiostat.

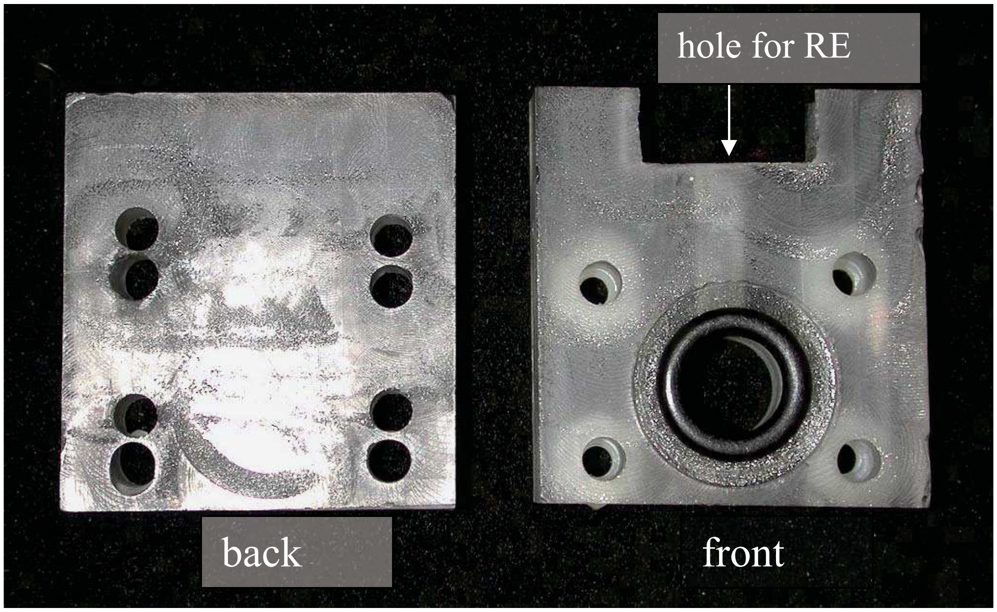


Figure 4: Half cell used for electrochemical measurements.

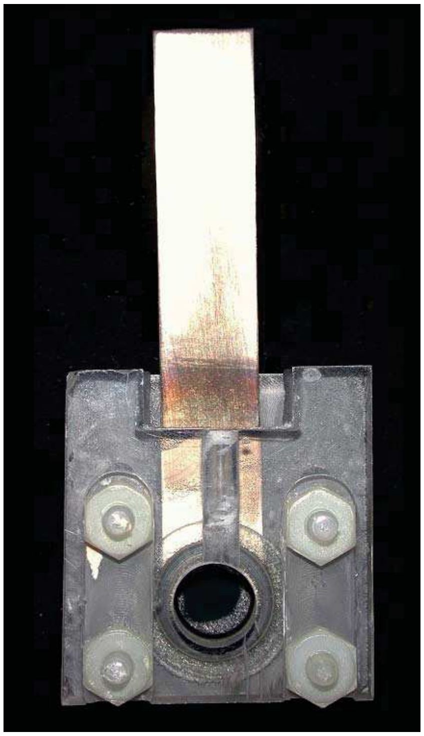


Figure 5: Assembled half cell.

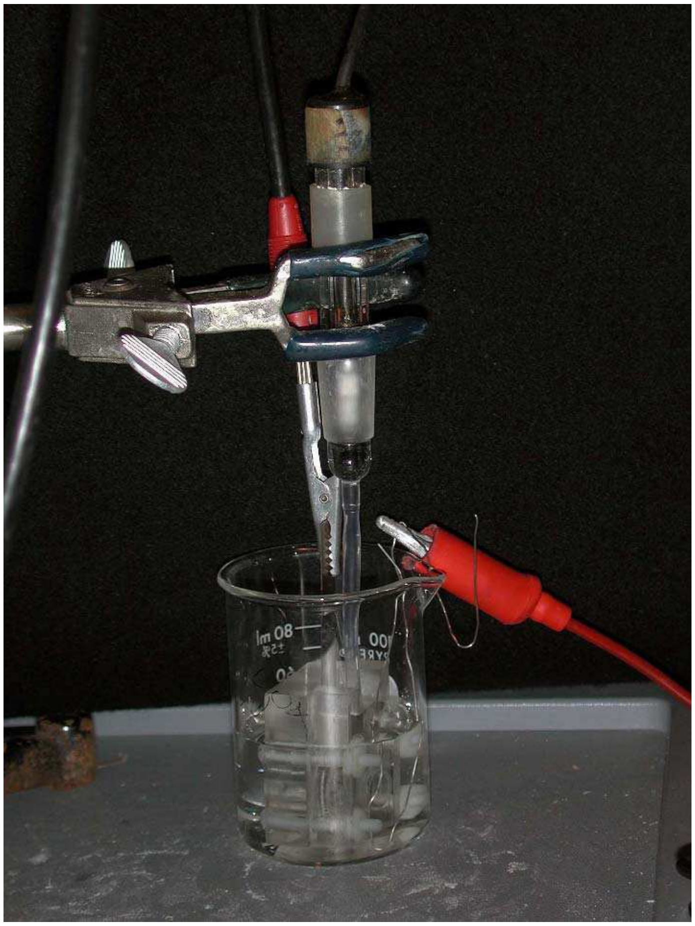


Figure 6: Experimental set up for electrochemical measurements (tubing for Ar flow omitted for clarity).

2.5 Electrochemical Measurements

Electrochemical measurements were performed with a PAR273A potentiostat and a Solartron 1255 HF frequency response analyzer controlled by CorrWare and ZPlot. CV measurements were typically acquired with a potential window of 0.1 to 0.5 V (vs RE), at a scan rate of 10 mV/s. For screening purposes, 20 scans were typically collected. EIS data were acquired from 0.1 Hz to 10 kHz, with an ac perturbation of 5 mV and a dc offset of 0.3V (vs RE). The samples were held at 0.3V for 10 minutes prior to data acquisition. Constant current discharge data were acquired at three different currents: 0.1, 0.2, and 0.5 mA.

3 Results and Discussion

3.1 Electrode Preparation

Since the active materials under investigation are in the form of powder, it is necessary to use some sort of support for electrode preparation. Carbon fibre paper is commonly used in the Pickup lab for this purpose, as well as to reduce the contact resistance between the active material and the current collector.[3] Spectracarb 2050 was found to work well with the active materials in terms of adhesion to the support and reduction of contact resistance. The Spectracarb 2050 (hereinafter referred to as 2050) is thin, conductive, exhibits low capacitance (~ 0.3 F/g, negligible compared to that of the active material), and small discs are easily punched out with a cork borer. It was necessary to wash the 2050 with ethanol to remove any ethanol-soluble sizing prior to active material application.

Application of the active material to the 2050 is performed by dropping a suspension of the active material in ethanol onto the surface, then drying in an oven (~70 ºC). The mass of the active material must be determined with great accuracy, as the only means to compare potential materials is by the specific capacitance, which is expressed in farads per gram of active material (F/g). Furthermore, the amount of active material must be large enough to enable accurate assessment, but small enough to ensure that all available surface area is accessible to the electrolyte; it is found that approximately 1 milligram is sufficient to minimize mass uncertainty and maintain accessible surface area.

When utilizing such small quantities of active material, the effects of several sources of uncertainty can be substantial and must be minimized. An accurate mass determination of the carbon fibre paper is important, as the mass of active material is determined by the difference between the mass of the 2050 and the mass of the 2050 + active material:

$$m_{\text{active material}} = m_{\text{2050+active material}} - m_{2050} \tag{4}$$

Sufficient time for the evaporation of the ethanol used in electrode preparation must be allowed. An experiment was performed in which the mass of two electrodes were monitored as a function of drying time. The electrodes were prepared using a material that absorbs a significant amount of ethanol, to ensure that the time determined would be suitable for all electrodes. The data are presented in Figure 7, and indicate that 2 hours should be sufficient for complete ethanol evaporation. The data also indicate a variation in the measured mass in the absence of the effect of adsorbed moisture; this variation may be attributed to the uncertainty in the balance, which is affected by its stability at the time of measurement. A variation of 0.01 to 0.06 mg has been observed with the same electrode, and introduces a relative uncertainty of several percent in the mass of the active material (assuming ~ 1 mg active material mass). To minimize this, multiple measurements are performed in determining the mass of both the unloaded 2050 and the loaded electrode. Typically the absolute uncertainty is no more than ± 0.02 mg, and is small compared to the standard deviation of capacitance values determined using multiple electrodes. In addition, the mass of 2050 and the electrodes should be determined soon after they have been removed from the oven, to minimize the effect of absorption of atmospheric moisture.

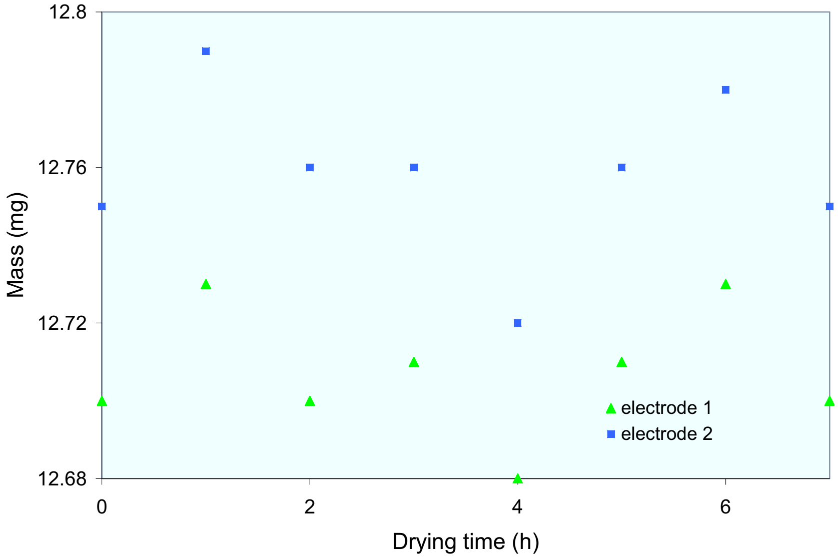


Figure 7: The effect of drying time on the mass of two electrodes.

Early experiments indicated that the concentration of the dispersion applied to the 2050 had an effect on the measured capacitance. The observed capacitance variation was attributed to the distribution of the active material on/in the 2050. Less concentrated dispersions led to some of the active material filtering through the 2050, and perhaps resulting in insufficient electrolyte access for measurement. Subsequently, care was taken to ensure that the dispersion was adequately concentrated (~ 1 mg active material in 10 drops of dispersion) to ensure that most active material remained on the surface of the 2050. As the electrode is held against the current collector with an o-ring (see Figure 4), it is important that the active material is not trapped beneath it, rendering a portion of the active material unavailable for measurement. Thus, the application of active material is restricted to the centre portion of the 2050 disc that will be accessible to the electrolyte.

The current collector used in these experiments is titanium (Ti) which should be sanded periodically to remove the titanium dioxide (TiO_2) layer that forms due to a natural passivation process. It was found that under the conditions utilized in this screening protocol it is not necessary to sand the Ti before each measurement; the currents employed are so small that the resistance introduced by the oxide coating does not noticeably affect the data.

The electrodes were characterized using three techniques: cyclic voltammetry, constant current charge-discharge experiments, and electrochemical impedance spectroscopy.

3.2 Cyclic Voltammetry (CV)

In CV, the potential applied to the working electrode is varied, and the current response is measured. The rate at which the potential is changed is known as the scan rate and is usually expressed in mV/s. The data are presented graphically as current response (y-axis, in amperes (A)) versus cell potential (x-axis, in volts (V)). Cyclic voltammetry is an effective method to measure capacitance, providing the scan rate is slow enough; slow is a relative term and is active-material dependent. The adequacy of the scan rate may be determined by investigating the response of the system at a range of scan rates. The capacitance, which is expressed in farads, F (1F = 1 A·s/V), is calculated by dividing the current (in A) by the scan rate (in V/s). Specific capacitance (abbreviated to capacitance, in this report), which is expressed in farads per gram (F/g) of active material, is calculated by dividing the capacitance (current/scan rate) by the mass of the active material. In addition to capacitance determination, the CV spectrum can provide an indication of the resistance of the active material, which is evident in the shape of the spectrum. Ideal capacitors exhibit rectangular CV spectra, thus any deviation from the rectangular shape indicates relatively high resistance, as evidenced by the slower current response (manifested in non-vertical current response at potential limits).

Validation of the experimental set up was performed by a series of experiments in which the effect of various factors was investigated. Factors such as the placement of the counter electrode (CE), the area of the CE, and sanding of the alligator clips and the Ti current collector, were found to make little difference in the CV spectrum of PAni-2NSA/MWCNT (see Figure 8).

The reproducibility of this method of fabricating electrodes is illustrated in Figure 9, which shows CV spectra for four electrodes prepared from PAni-2NSA/MWCNT. The overlaid spectra are very similar; in fact the average capacitance (calculated from 0.15 to 0.45 V vs SCE) exhibits a variation of 5%. In order to compare spectra acquired for different electrodes, the spectra must be normalized with respect to active material mass (loading), as the current response is dependent on the amount of electroactive material. Furthermore, the spectra must also be normalized with respect to scan rate, and in fact should be acquired at the same scan rate, as this has an effect on both the current response and the shape of the spectrum.

The effect of loading is illustrated in Figure 10 which shows cyclic voltammograms for a series of electrodes ranging in PAni-PTSA mass from 0.68 to 2.95 mg. Although the capacitance remains almost constant across the series, the effect of increased loading is evident by the increased resistance (indicated by the slower current response as the potential is varied). As mentioned previously, this slower current response manifests itself in deviation from the rectangular shape of an ideal capacitor.

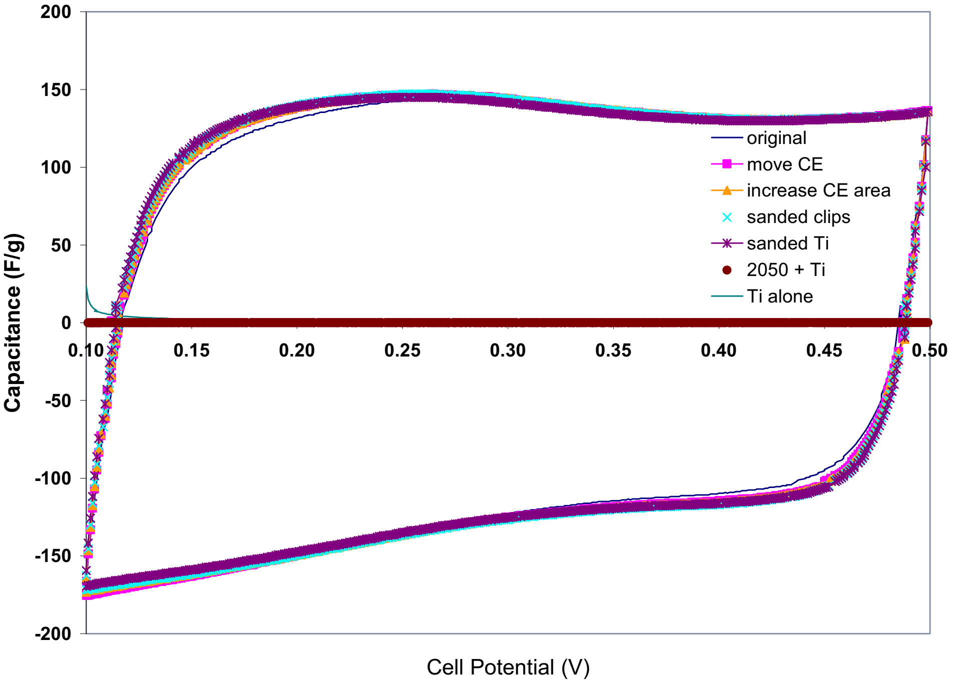


Figure 8: The effect of various experimental parameters at a scan rate of 10 mV/s.

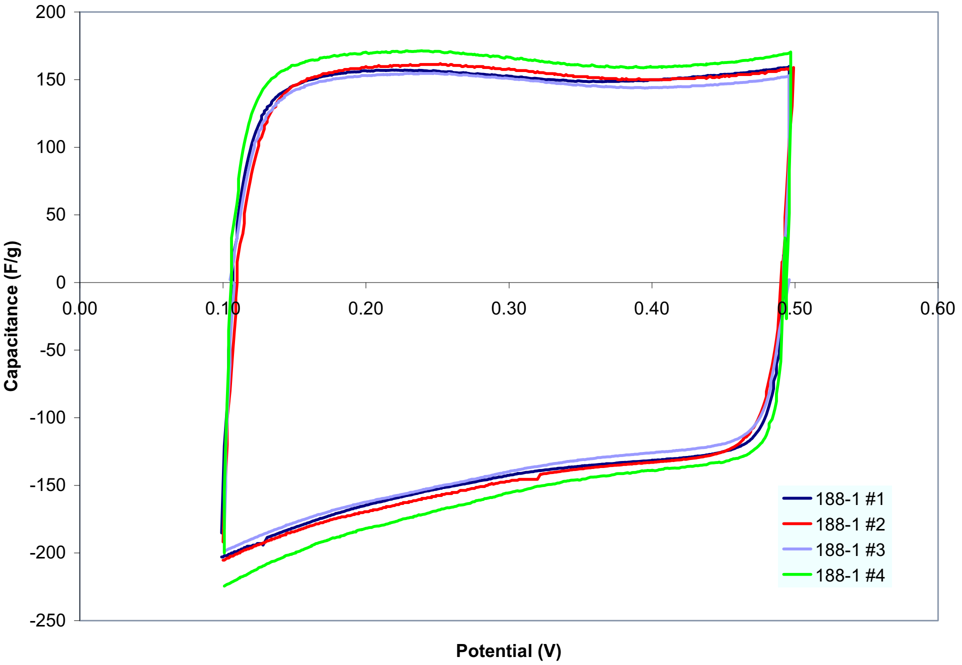


Figure 9: CV data demonstrate the reproducibility of the electrode preparation (scan rate 10 mV/s).

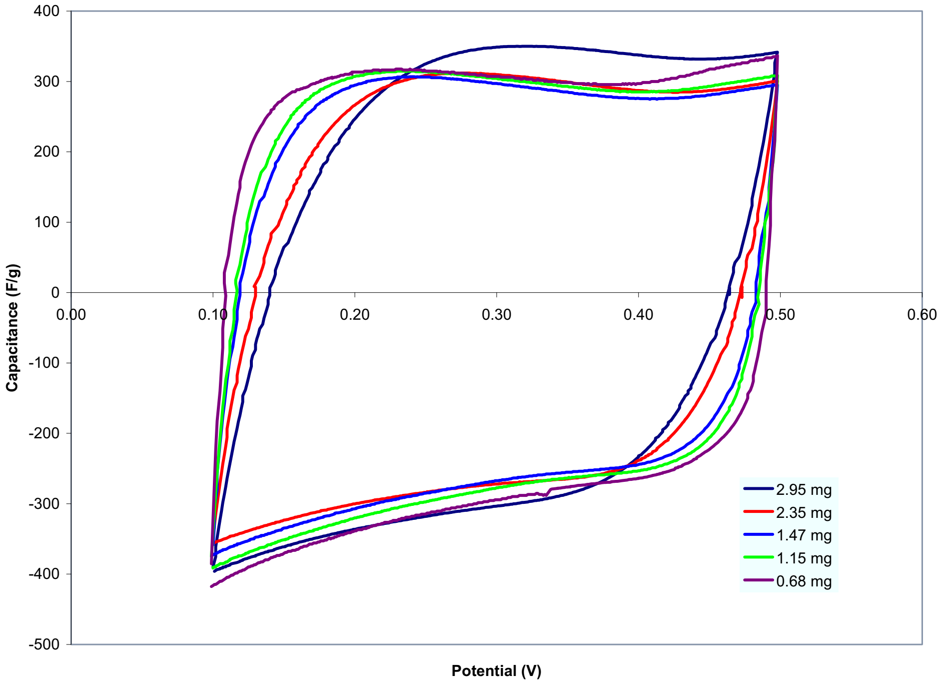


Figure 10: The effect of active material loading at a scan rate of 10 mV/s.

3.3 Electrochemical Impedance Spectroscopy (EIS)

Impedance, Z, is the opposition of alternating current (ac) flow in a complex system, and is similar to the resistance of direct current (dc) flow, and as such follows Ohm's law, Z = V/I, where V is the potential (in volts), I is the current (in amps), and Z is the impedance (in ohms). Impedance is comprised of resistance, R, and reactance, X.[4]

$$Z = \sqrt{R^2 + X^2} \tag{5}$$

The resistance is frequency-independent, but the reactance, which can be capacitive, X_C, and/or inductive, X_L, is frequency-dependent.

$$X_C = \frac{1}{2\pi f C} \tag{6}$$

where X_C = capacitive reactance (Ω)
f = frequency (Hz)
C = capacitance (F)

$$X_L = 2\pi fL \tag{7}$$

where X_C = inductive reactance (Ω)
f = frequency (Hz)
L = inductance (H)

Reactance causes a phase shift between the current and the voltage. The total reactance is the difference between the capacitive reactance and the inductive reactance.[4]

$$X = X_L - X_C \tag{8}$$

Impedance, Z, can be expressed as a complex number where the resistance, R, is the real component (Z') and the reactance, X is the imaginary component (Z"). Reactance causes a phase shift (with a phase angle of φ) between the current and the voltage, and is frequency-dependent.[4]

$$Z = R + jX = Z' + jZ'' \tag{9}$$

where $j = \sqrt{-1}$

$$Z' = |Z|\cos\phi$$

and $$Z'' = |Z|\sin\phi$$

For a resistor, the reactance term is zero, thus $Z_R = R$. For a capacitor, the resistive term is zero, and capacitive reactance is predominant at relatively low frequencies (i.e. when capacitance is high, inductance is relatively low due to their inverse dependence on frequency). Thus the impedance is inversely proportional to the frequency and the capacitance:

$$Z_C = \frac{1}{j\omega C} \tag{10}$$

Slow reaction kinetics and diffusion impede electron flow, thus electrochemical cells behave as a collection of resistors, capacitors, and inductors. Electrochemical impedance spectroscopy (EIS) investigates such systems in terms of circuit elements, and the EIS data aid in the evaluation of the equivalent circuit elements present, and their approximate connectivity (in series or parallel). In complex systems the exact circuit representation may be challenging, as more than one combination of circuit elements may give rise to similar data, however, knowledge of the system can help to deduce the most reasonable circuit element representation.

Electrochemical impedance data were acquired at a dc offset of 0.3V. This means that the working electrode (active material) was held at a potential of 0.3V versus the reference electrode, which is the midpoint of the potential window investigated in the CV experiments. At a wide range of frequencies (0.1 Hz to 10 kHz), the system was perturbed using a small amplitude signal

(5 mV), and the impedance (both real and imaginary components) at each frequency was measured. The EIS data may be plotted in several different ways: the Nyquist plot, in which Z’ is plotted on the x axis, and Z” is plotted on the y axis, as shown in Figure 11 for PAni-2NSA/MWCNT. In this plot, each data point represents the complex impedance at a different frequency. The shape of the curve, and where it intersects the Z’ axis (x axis) provides information about the system in terms of resistance and capacitance. The x-intercept represents the equivalent series resistance (esr) which incorporates electrolyte resistance (including separator), active material resistance, and the contact resistance at the active material/current collector interface. The shape of the curve provides information about the circuit elements present (resistors, capacitors, inductors), and their relative magnitude and arrangement (in series or parallel). Supercapacitors are typically porous and possess high surface area, thus the impedance behaviour is complex and must be represented by a distribution of capacitive and resistive elements (transmission line); the shape of the Nyquist plot typically contains an almost vertical portion at low frequencies (corresponding to the capacitive behaviour), and a linear region at a 45° angle to the real axis at higher frequencies. The impedance in the high frequency region corresponds to electrolyte resistance within the pores of the active material.[5]

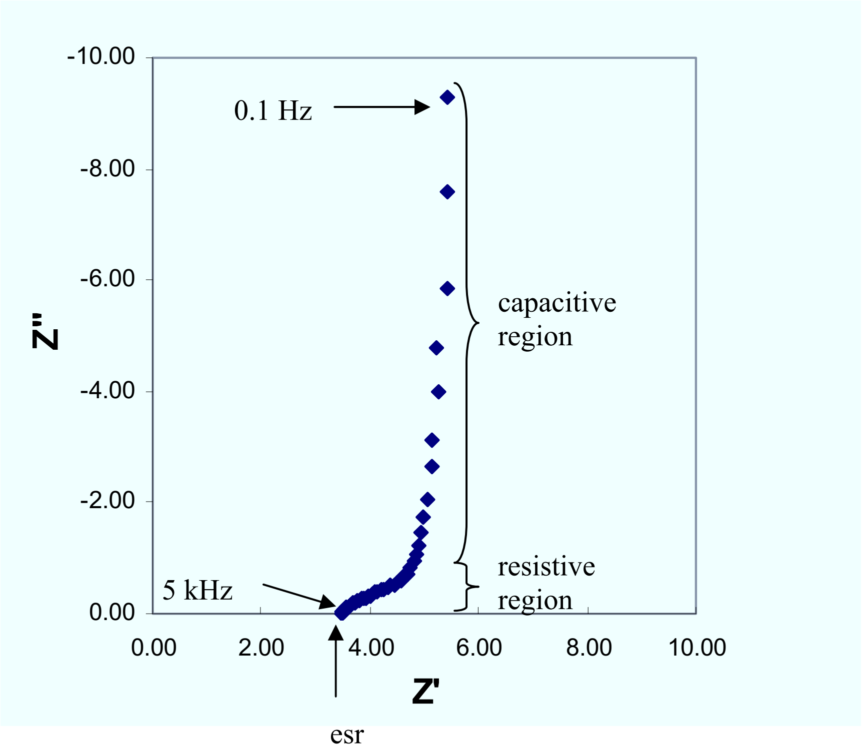


Figure 11: Typical Nyquist Plot of PAni-2NSA/MWCNT

Although the Nyquist plot is commonly employed to represent the data, a potentially more useful means involves calculating the capacitance using Z” (see equation 11), and plotting that against frequency (Figure 12). The capacitance is highest at low frequency, and drops off at higher frequency.

$$C = \frac{1}{-2\pi f Z''} \qquad (11)$$

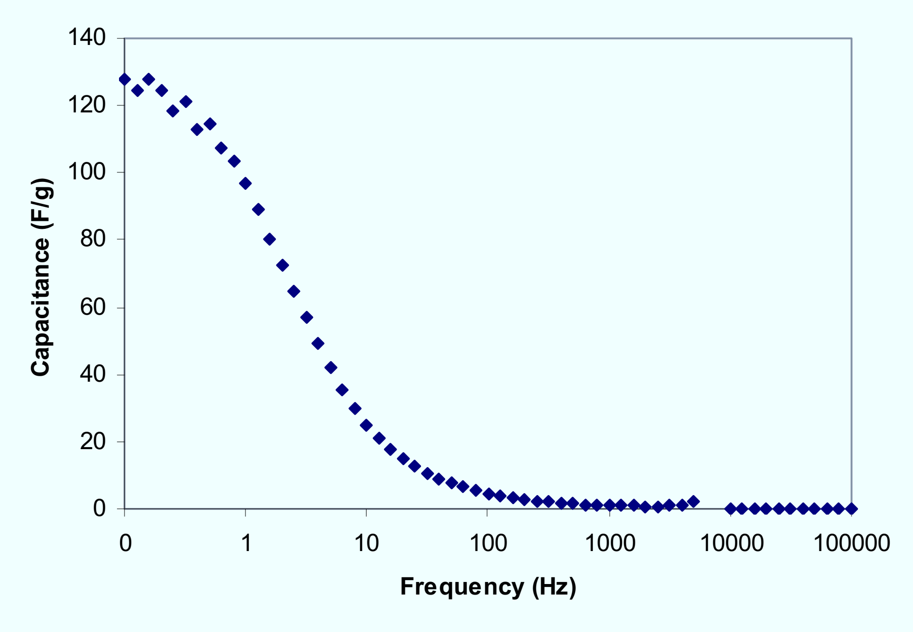


Figure 12: Capacitance versus Frequency Plot for PAni-2NSA/MWCNT.

3.4 Constant Current Charge-Discharge Experiments

The specific capacitance, C_s, can also be determined using constant current discharge data (neglecting the non-linear portion that results from the iR drop, attributable to the solution resistance):

$$C_s = \frac{I\Delta t}{m\Delta E} \qquad (12)$$

where I is the discharge current (in A), Δt is the discharge time (in s), ΔE is the change in potential (in V), and m is the mass (in g). Charge – discharge curves for supercapacitors are typically linear, with an iR drop portion visible at the start of each cycle (see Figure 13).

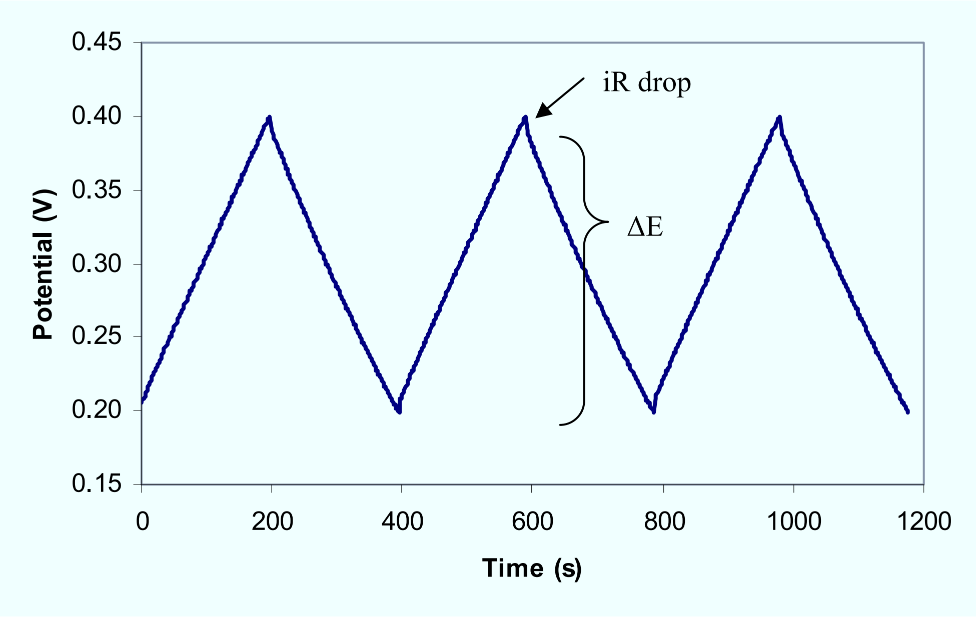


Figure 13: Typical Constant Current Charge-Discharge Curve for a 1.34 mg Electrode of PAni-2NSA/MWNT at a Constant Current of 0.2 mA

The capacitance of each electrode is determined by all three measurement methods. Capacitance values based on the CV data and the constant current discharge data are consistent, however the capacitance determined from the EIS data is typically lower (see Table 1). The apparent anomalous value resulting from the EIS experiment, is commonly observed and is attributed to the smaller perturbation (ac amplitude) utilized during measurement.[6] In this project, capacitance values quoted for a variety of active materials are based on the CV data, and are an average of several (3 – 6) electrodes prepared for each active material.

Table 1: Capacitance Values for the Same Electrode made with PAni-2NSA/MWCNT, Based on Different Measurement Methods

Method	**Capacitance (F/g)**
EIS	128
CV	152
Constant Current Charge-Discharge	152

In addition to determining the capacitance from constant current discharge curves, the power density (PD) can be calculated as follows:

$$PD = \frac{I\int_{t=0}^{V=0} Vdt}{m\Delta t} \tag{13}$$

where the integral ∫Vdt is the area under the discharge curve, I is the current, m is the mass of active material, and Δt is the discharge time. As mentioned earlier, the energy density (ED) is a measure of the amount of energy stored per mass unit, and is given by I∫Vdt/m; the power density is simply the length of time required to access that energy, so PD = ED/ Δt.

An important point to note is that the power density is dependent on the current utilized in the discharge experiments, thus one must ensure that data were acquired under the same conditions when comparing the power density of two materials. For example, using the charge-discharge data shown in Figure 13 the power density is determined to be 29 W/kg at a constant current of 0.2 mA, however the calculated power density for the same electrode is 100 W/kg at a current of 0.5 mA. Another point to note is that electrodes having very small amounts of active material (such as those used in this screening protocol) cannot withstand high currents (≥ 1 mA). Thus the calculated power density is likely not the maximum power density for this material, and is limited by the sample size. For comparison, a commercial supercapacitor, Maxwell Boostcap BCAP0140 E250, exhibits energy density on the order of 4.2 Wh/kg and a maximum power density of 15 kW/kg.

4 Conclusions and Future Work

Although all three electrochemical techniques may be utilized, CV is an excellent primary screening method to assess active material potential. Not only can the capacitance be easily calculated from the current response, but the shape of the CV spectrum provides information regarding the pseudo-capacitance and relative resistance of the active material. Pseudo-capacitance is evident by the presence of redox peaks, in addition to the typical rectangular shape. The only caveat is that the scan rate must be slow enough for the system to exhibit capacitance behaviour. If the scan rate is too high, then resistive behaviour dominates; this is evident when the spectrum resembles a rice grain, as opposed to a rectangle. The optimal scan rate is dependent on the electrochemistry of the active material, and can be determined by trial and error. Spectracarb 2050 is useful as a support for the active material as it facilitates the preparation of electrodes, and its light weight allows for a fairly accurate active material mass determination (a 13 mm diameter disk has a mass of ~ 12 mg). Furthermore, the 2050 does not contribute substantially to the overall capacitance, allowing an accurate evaluation of the active material capacitance, yet possesses high conductivity thereby reducing the contact resistance between the current collector and the active material.

The capacitance of the materials evaluated using this screening protocol are relatively high, ~ 300 F/g for PAni-PTSA and ~ 153 for PAni-2NSA/MWCNT, hence, these materials exhibit promise as lightweight energy storage materials. However, in order to assess their utility as a source of pulse power, it is necessary to scale up the sample quantity and reduce resistance wherever possible (leads, electrolyte, etc). The sample size limits the maximum viable current and can result in an erroneous conclusion regarding active material viability.

The next step in the project is to develop a method by which larger quantities of active material can be assessed, especially with respect to power density. In particular, the development of a prototype that can operate as a stand alone device is of interest. The fabrication of a functional prototype, as proof-of-concept based on the active materials developed within the TIF program, is the ultimate goal.

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List of symbols/abbreviations/acronyms/initialisms

A	area or ampere
ac	alternating current
aq	aqueous
aq	aqueous
C	capacitance or carbon
ºC	Celsius
CE	counter electrode
cm	centimeter
CV	cyclic voltammetry
dc	direct current
DE	directed energy
DND	Department of National Defence
DRDC	Defence Research & Development Canada
DRDKIM	Director Research and Development Knowledge and Information Management
EIS	electrochemical impedance spectroscopy
F	farad
g	gram
h	hour
HF	high frequency
H_2SO_4	sulphuric acid
Hz	hertz
I	current
KE	kinetic energy
kHz	kilohertz
L	inductance
LAV	light armoured vehicles
µL	microlitre
mA	milliampere
MEM	micro electro mechanical

mg	milligram
min	minute
mV	millivolt
mW	milliwatt
MW	megawatt
MWCNT	multi-walled carbon nanotube
2NSA	2-naphthalenesulfonic acid
PAni	polyaniline
Pt	platinum
PTSA	*p*-toluenesulfonic acid
R	resistance
R&D	Research & Development
RE	reference electrode
RF	radio frequency
SCE	saturated calomel electrode
Ti	titanium
TiO_2	titanium dioxide
UAV	unmanned aerial vehicle
V	potential or volt
WE	working electrode
X	reactance
Z	impedance
Z’	real component of impedance
Z”	imaginary component of impedance

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A method for the preparation and measurement of potential active materials for supercapacitor electrodes was developed and validated. An ethanolic suspension of the active material was applied to carbon fibre fabric, and allowed to dry. The electrode (active material and carbon support) was affixed in a half cell assembly that allowed consistent placement of the reference electrode. The electrode was characterized in deaerated 0.5 M H2SO4 (aq) by cyclic voltammetry, electrochemical impedance spectroscopy, and constant current charge discharge experiments. The electrode preparation method, and half cell assembly was determined to be highly reproducible, resulting in accurate electrochemical characterization of the active material.

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supercapacitor; polyaniline; carbon nanotubes

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