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Supercapacitor Materials for Soldier Systems

Land Sustain (12S) Thrust Advisory Group Scoping Study

Colin G. Cameron

Defence R&D Canada – Atlantic

Technical Memorandum
DRDC Atlantic TM 2006-142
September 2006

Canada

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Abstract

Supercapacitor technology stands as a bridge between the high power output of capacitors and the high energy characteristics of batteries, fuel cells, and energy harvesters. Supercapacitors offer the promise of better designed power systems for soldier-based applications. Use of such technology will enable the improved design of conventional electronic equipment such as radios and targeting systems, as well as enabling futuristic weaponry such as electromagnetic pulse generators and magnetically launched projectiles.

This document introduces work being carried out at DRDC Atlantic. It explains how supercapacitors work and how they fit in with military applications. The work focuses on developing new materials to push supercapacitors to new performance levels, and with special consideration to Canadian needs.

Résumé

La technologie des supercondensateurs établit le lien entre la haute puissance de sortie des condensateurs et les niveaux élevés d’énergie que produisent les batteries, les piles à combustible et les capteurs d’énergie. Les supercondensateurs pourraient améliorer la conception des systèmes d’alimentation pour les applications destinées aux soldats. Le recours à cette technologie permettrait de perfectionner l’équipement électronique ordinaire, comme les systèmes radio et de choix d’objectifs, ainsi que de créer des armes futuristes, par exemple des générateurs d’impulsions électromagnétiques et des projectiles à lancement magnétique.

Ce document présente certains travaux entrepris à RDDC Atlantique. Il explique comment les supercondensateurs fonctionnent et comment ils s’adaptent aux applications militaires. Les recherches sont orientées vers le développement de nouveaux matériaux qui puissent accroître encore le rendement des supercondensateurs, dans le contexte particulier des besoins du Canada.

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Executive summary

Supercapacitor Materials for Soldier Systems: Land Sustain (12S) Thrust Advisory Group Scoping Study

Colin G. Cameron; DRDC Atlantic TM 2006-142; Defence R&D Canada – Atlantic; September 2006.

Background: Modern military operations rely heavily on electrical energy. Sensors, communications apparatus, sighting systems, and countless other equipment draw power. In many instances (for the dismounted soldier, for example) the power is provided by batteries. This in turn leads to an added weight penalty along with the logistical burden of providing a continuous supply of replacement cells. This is already an issue; the continuing development of electronic technologies in the field suggests that reliance on batteries will only continue to increase.

Principal Findings: There are two important considerations for any portable source of electrical power: total energy content, and how quickly the energy can be delivered (*i.e.*, power density). Generally speaking, batteries contain large quantities of energy, but have relatively low power density. On the other hand, supercapacitors offer high power output but with modest energy. Systems requiring large bursts of power must use either a large battery or a small battery in conjunction with supercapacitor. This underlines the concept of hybrid electrical supply systems, where the electrical demands of some apparatus is met by an rationally designed combination of a battery and a supercapacitor.

Significance of Findings: Supercapacitor-based hybrid power offer the possibility of better designed systems. Such a concept will facilitate deployment of electronic equipment, and will lead to significant improvements in weight burden. The flexibility of the supercapacitor system will also make environmental energy capture schemes more broadly applicable.

Future Work: DRDC Atlantic has recently started a Technology Investment Fund (TIF) program in developing new materials for supercapacitors. Since the performance of a supercapacitor is primarily a reflection of the electrode material, this is a key consideration. The TIF program intends to generate new high performance electrode materials with particular attention to the needs of the Canadian Forces.

Sommaire

Supercapacitor Materials for Soldier Systems: Land Sustain (12S) Thrust Advisory Group Scoping Study

Colin G. Cameron; DRDC Atlantic TM 2006-142; R & D pour la défense Canada – Atlantique; septembre 2006.

Contexte: Les opérations militaires modernes reposent largement sur l'énergie électrique. Les détecteurs, les appareils de communications, les systèmes de visée et nombre d'autres équipements consomment de l'énergie. Dans bien des cas (pour le soldat débarqué, par exemple), cette énergie provient de batteries et de piles. Il en résulte un accroissement de poids ainsi qu'un fardeau logistique résultant du constant besoin de batteries et de piles de rechange. Ce problème se fait déjà sentir, et le développement continu de technologies électroniques dans le domaine donne à penser que notre utilisation des batteries et piles ne cessera d'augmenter.

Résultats: Deux considérations importantes entrent en ligne de compte pour toute source transportable d'énergie électrique : son contenu total en énergie et la vitesse à laquelle cette énergie peut être fournie (*c.-à-d.* la densité de puissance). En général, les batteries contiennent de grandes quantités d'énergie, mais n'offrent qu'une densité de puissance relativement faible. Quant à eux, les supercondensateurs fournissent une puissance de sortie élevée, mais peu d'énergie. Les systèmes qui ont besoin de fortes salves de puissance doivent comprendre une grosse batterie ou une petite batterie avec un supercondensateur. Cette situation illustre le principe des circuits d'alimentation électrique hybrides, qui combinent une batterie et un supercondensateur de façon rationnelle afin de répondre à la demande d'un certain appareil.

Portée: Les circuits d'alimentation hybrides à supercondensateur offrent la possibilité d'améliorer la conception des systèmes. Ces circuits faciliteront le déploiement d'équipement électronique et mèneront à des réductions de poids considérables. La souplesse des systèmes à supercondensateur élargira également les possibilités de captage de l'énergie environnementale.

Recherches futures: RDDC Atlantique a récemment lancé, dans le cadre du Fonds d'investissement technologique (FIT), un programme visant à développer de nouveaux matériaux pour les supercondensateurs. Comme le rendement d'un supercondensateur dépend principalement du matériau utilisé comme électrode, il s'agit là d'un aspect essentiel. Le programme du FIT devrait permettre de produire de nouveaux matériaux à haut rendement pour les électrodes, dans le contexte particulier des Forces canadiennes.

Table of contents

Abstract . . . i

Résumé . . . i

Executive summary . . . iii

Sommaire . . . iv

Table of contents . . . v

List of figures . . . vi

List of tables . . . vi

1 Soldier systems energy requirements . . . 1

1.1 Short term soldier power requirements . . . 3

1.2 Long term soldier power requirements . . . 3

2 Strategies for the storage of electrical energy . . . 3

2.1 Batteries . . . 4

2.2 Fuel cells . . . 4

2.3 Capacitance . . . 5

2.4 Supercapacitors . . . 5

3 The supercapacitor materials program at DRDC Atlantic . . . 8

3.1 Approach . . . 8

3.2 Goals . . . 9

4 Further supercapacitor research ideas: enhancing Canadian soldier systems . . . 9

4.1 Materials optimized for arctic conditions . . . 9

4.2 Supercapacitors based on ionic liquids . . . 10

4.3 Improved device construction . . . 10

5 Conclusion . . . 10

Glossary 11

References 12

Distribution list 13

List of figures

Figure 1: (a) Energy density *vs.* power density for the DRDC supercapacitor, direct methanol fuel cells, and a variety of batteries. (b) Energy density *vs.* power density for various different power sources including conventional capacitors. 2

Figure 2: Charge accumulation in a parallel plate capacitor. 5

Figure 3: The double layer of a charged electrode and attracted ions, leading to electrochemical capacitance. 6

Figure 4: Negative ions surrounding a positively charged fibrous electrode, illustrating the concept of a large surface area electrode. 6

List of tables

Table 1: Some advantages and disadvantages of supercapacitors. 7

1 Soldier systems energy requirements

The Revolution in Military Affairs (RMA) [1] document outlines how military operations are undergoing rapid change, spurred to a large extent by the continuing evolution of technology. Since the document's publication in 1999, the world has seen changes in the political climate which could not have been easily predicted at that time. The corresponding redefinition of the combat environment serves to underline the RMA document's observation that change in the nature of warfare is concomitant with the application of new technologies, concepts, and doctrine. New developments in technology will put increased demands on power sources as outlined in a report on advanced power sources for the Canadian Forces [2].

Supercapacitors offer the possibility of designing power systems more efficiently. Today's soldier relies heavily on batteries for electrical power in the field. The proliferation of electronic equipment will increase the demand for battery power. This in turn will mean more weight for the soldier to carry and burden supply logistics, especially when numerous non-standard batteries are in use. The alternative is to design a more rational power distribution system for the soldier; better power management could satisfy power-hungry equipment without taking bigger, heavier batteries to the field. Supercapacitors could play an important role in such a system, providing bursts of power when needed.

The key concept is illustrated in Figure 1 where the energy density and power density of several electric power sources are compared.[1] For batteries, non-rechargeable alkaline cells and rechargeable NiMH cells are mature, readily available, and relatively inexpensive choices. The century-old lead-acid battery is a poor performer owing largely to the weight of its constituents, but it is still commonplace.

Batteries offer energy densities ranging from poor to good. The electrical current they can supply is limited, hence they suffer from poor power densities. Fuel cells offer excellent energy densities, but again limited current draw hampers their power density. Environmental energy harvesting devices offer nearly infinite energy density, but minuscule power density. High power output can be developed in conventional capacitors, but with tiny energy content. Supercapacitors on the other hand offer an excellent compromise of power and energy densities, as shown in Figure 1. Clearly, the best system is a hybrid one that offers the energy density of a fuel cell, battery, or harvester along with the power density of a supercapacitor.

[1] The performance values come from many sources, and can be somewhat optimistic. They are still useful in presenting an order-of-magnitude comparison of technologies. The DMFC value is an estimate based on several sources, and it will vary depending on the relative sizes of the cell and the fuel reservoir.

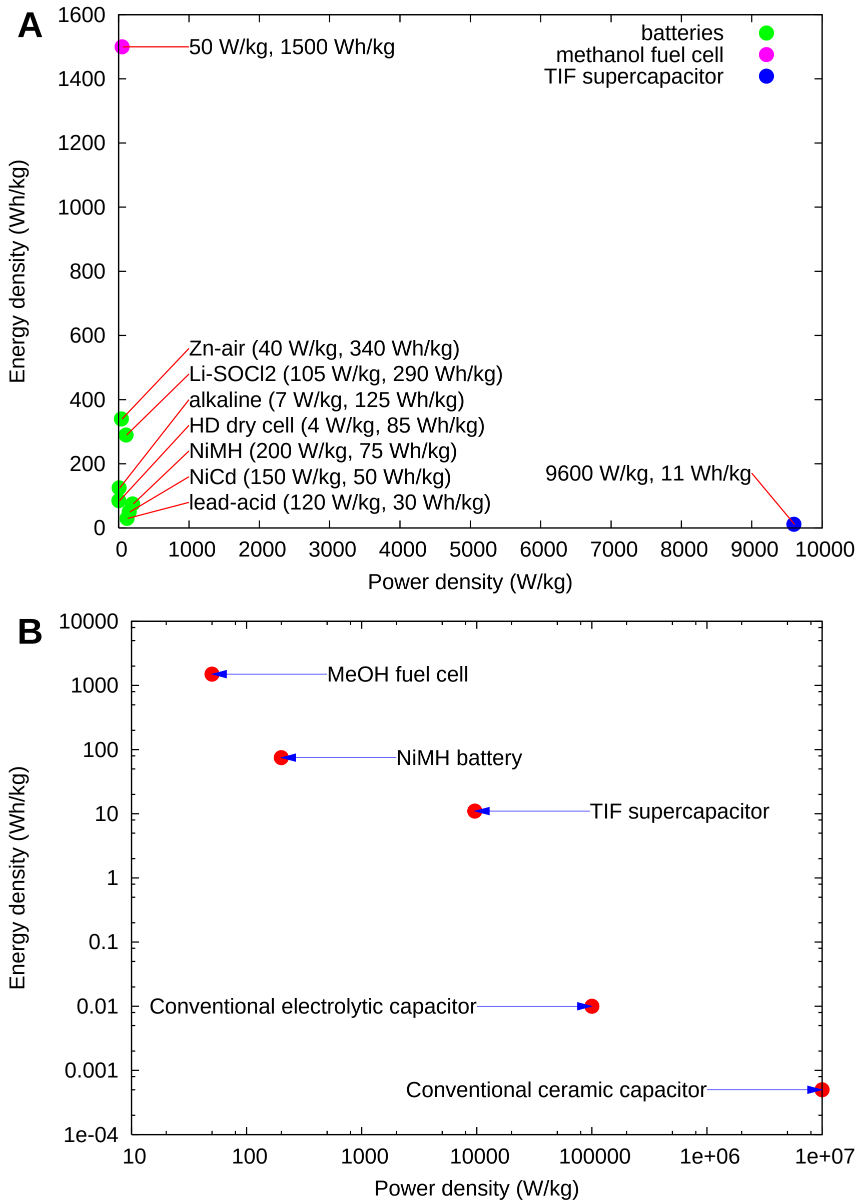

Figure 1: *(a) Energy density vs. power density for the DRDC supercapacitor, direct methanol fuel cells, and a variety of batteries. (b) Energy density vs. power density for various different power sources including conventional capacitors.*

1.1 Short term soldier power requirements

Supercapacitors have a role to play in rational design of better power systems for conventional soldier systems platforms. They are ideal for electronic devices that have high peak loads, such as radios, laser target designators, and so on. For example, a hypothetical radio might draw 50 W of power when transmitting. Using the values in Figure 1a, this implies at least 7 kg of alkaline batteries are needed to operate the device. However, if the radio is only transmitting occasionally, say a duty cycle of 10%, a supercapacitor weighing less than 10 g would provide sufficient power, and it could be recharged by a battery weighing less than 1 kg, representing approximately 85% weight savings.

There exists a Thrust 12sz project to produce handheld fuel cells that can fit in a munitions pouch, with a target output of 3 W at 5 V and 90 Whr reserve. Coupled with supercapacitors, this unit could run devices demanding much more power but for brief (under 1 minute) intervals.

1.2 Long term soldier power requirements

Other technologies could benefit from supercapacitors. LAV silent watch operations require noise-free power sources. Banks of batteries are currently used, and there is research into replacing these with regenerative fuel cells. Supercapacitors used in conjunction with such systems would provide for load-leveling, and hence more compact power or more versatile systems.

Futuristic weaponry such as RF pulse weapons, lasers, and electromagnetic projectile launchers will be impossible to implement without pulse power delivery such as that offered by supercapacitors.

The Integrated Soldier Systems Project (ISSP) is one which intends to develop and deploy soldier-based technology over the next ten to fifteen years. The intent is to use technological advances to increase the potency of the land force. Currently projected advances include concepts such as wearable computers, helmet-mounted displays, global positioning system (GPS) receivers, assorted radio transmitters, and targeting systems. The comparatively primitive soldier-mounted technology of today already requires the soldier to carry at least thirty-nine AA-size batteries for a seventy-two hour mission. Without better power management, these proposed soldier technologies will lead to an untenable battery burden.

2 Strategies for the storage of electrical energy

Fundamentally, there are two ways to store electrical energy. One approach involves the electrochemical transformation of chemical potential energy; electrical work is yielded when chemical agents flow to their respective electrodes and undergo oxidation or reduction. This reaction of bulk chemical species occurs in batteries and fuel cells, and collectively reactions of this nature are described as *Faradaic*. The second approach is electrostatic in nature, and involves the accumulation of charge without chemical transformation. The charging of a pair of metal plates is an example of this process, and in the absence of chemical transformation, such processes are deemed *non-Faradaic*.

2.1 Batteries

Primary (non-rechargeable) and secondary (rechargeable) batteries represent a safe, convenient, and usually inexpensive source of portable electric energy. In general, batteries have a high energy density, but suffer from relatively low current density. While current density can be maximized through cell design (*e.g.*, using large area electrodes), certain phenomena will always limit their current output. These limitations include transport of the active chemicals within the electrolyte, and the electrochemical kinetics associated with the electron transfer and the phase changes of the active material.

2.2 Fuel cells

Fuel cells are similar to batteries in that they involve the conversion of chemical energy to electric energy *via* a Faradaic process. Unlike a battery, a fuel cell produces electrical energy continuously as long as fresh fuel is provided. Like batteries, however, issues of molecular transport and electron transfer kinetics limit the power density of fuel cells. Fuel cells are characteristically high energy density devices.

While a number of different types of fuel cells are being developed in parallel, proton exchange membrane (PEM) hydrogen fuel cells and direct methanol fuel cells (DMFC) are the most likely candidates for soldier-based applications, owing to their portability and low temperature operation. The latter type has the added benefit of being liquid fuelled, and avoids the issues associated with storage of hydrogen gas under pressure. DMFC technology is generally considered to be still in its early stages, although the Taiwan high-tech firm Antig recently announced [3] plans to sell DMFC power units for laptops by 2007.

2.3 Capacitance

Non-Faradaic charge storage is achieved in capacitors, the simplest example of which is illustrated in Figure 2 in a parallel plate configuration. An applied voltage drives the accumulation of charge at the interface of each plate and the intervening vacuum or dielectric material. Since no chemical change occurs, charging and discharging tend to be very rapid processes, leading to high current densities. The stored electrical energy though is very low. It is related to voltage V and capacitance C:

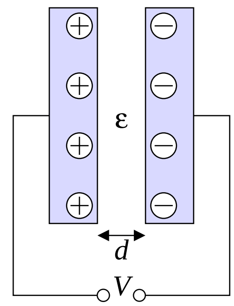

Figure 2: *Charge accumulation in a parallel plate capacitor.*

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

The capacitance is a function of the electrode area A, and the permittivity ε and the thickness d of the dielectric medium between the electrodes:

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

The key point is that the energy storage capacity increases with a greater electrode area and a diminished distance between accumulated charges.

2.4 Supercapacitors

Also known as *Ultracapacitors*, electrochemical supercapacitors also store electrical energy *via* the separation of charge. Unlike conventional capacitors, these devices operate on a microscopic scale.

Any electrode — a strip of metal, for instance — immersed in a solution of ions will attract ions of opposite charge when a voltage is applied to the electrode. The ions are surrounded by a shell of solvent molecules, and can normally approach the electrode only to a very small distance. This concept is illustrated in Figure 3, and the ensuing separation of charge leads to a phenomenon known as *double layer capacitance*. Often in electrochemical studies, this capacitance is a nuisance; it introduces spurious currents that must be separated from one's experiment. In the case of supercapacitors, this capacitance is exploited.

One advantage of such an electrochemical capacitor is that the charge separation distance d is very small, on the order of nanometers. This leads to large capacitance in accordance with Equation 2. Furthermore, it is possible to create electrode materials that are fibrous and porous, and hence with inherently high surface areas, Figure 4. This condition also leads to large capacitance.

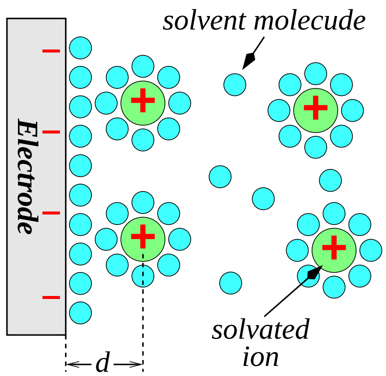

Figure 3: *The double layer of a charged electrode and attracted ions, leading to electrochemical capacitance.*

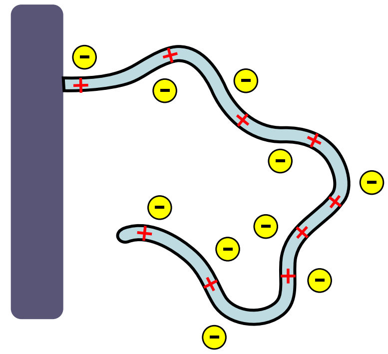

Figure 4: *Negative ions surrounding a positively charged fibrous electrode, illustrating the concept of a large surface area electrode.*

Further charge storage is available through a mechanism called *pseudocapacitance*. In such a system, the electrode material itself can undergo Faradaic charge transfer. Large capacitance ensues. It is important to differentiate pseudocapacitance from battery-based storage. In the former, charge transfer occurs within the electrode, and in the latter charge transfer occurs between the electrode and some species in solution, accompanied by some chemical transformation.

Some advantages and disadvantages of supercapacitors are summarized in Table 1.

Table 1: *Some advantages and disadvantages of supercapacitors.*

Advantages:

- High power density
- Simple principle
- Straightforward construction (similar to batteries)
- Long life, order of 10^6 cycles
- Inexpensive materials (for some cases)
- Linear discharge curve allows easy determination of state-of-charge
- Ideal for combined use in hybrid power systems with a second source

Disadvantages:

- Poor energy density
- Low working voltage: approximately 1.4 V aqueous, 3–4 V non-aqueous
- Nonaqueous systems more expensive.
- More exotic electrode materials can be expensive
- High voltage requires cell stacking, and hence careful cell matching

3 The supercapacitor materials program at DRDC Atlantic

A recent DRDC report [2] surveyed the advanced power requirements and opportunities needed to coincide with military technological developments until 2020. It emphasizes that future advanced military systems will be unable to deliver their full capabilities without the parallel development of adequate power source technology. For example, weaponry from Horizon 3 and beyond (*e.g.*, electromagnetic projectiles, RF pulse weapons, high intensity lasers, and so on) will not be possible without very high power burst energy sources. Likewise, many strategic objectives in diverse technology activities (*e.g.*, communications systems for distributed and/or remote sensors, denial and blinding apparatus in RF/electronic warfare, electro-optical weapons, and space systems) would clearly benefit from power sources capable of delivering transient spikes of high output, interspersed with periods of low power or standby. A quick discharge capacitance approach seems most reasonable to deliver the transient high power pulses such systems demand. However, the energy storage density of conventional capacitors leaves much to be desired. Generally speaking, the most promising approach for military applications would be a hybrid system [2, 4, 5] where a high energy density device such as a battery, a fuel cell, or a generator operates in series with a high power density component, such as a supercapacitor.[2]

3.1 Approach

This TIF-funded supercapacitor program takes a materials approach to improving supercapacitor performance. First generation technology has evolved to the point where commercial applications are now available. These are generally double-layer type capacitors using inexpensive amorphous carbon as the active material. There is much room to improve the performance by using better designed materials. The project includes world-class experts from Canadian academia and it consists of several concurrent threads:

- The development of ion and electron conducting sol-gel silica based materials having high surface areas and sulphonate derivatives of the same composited with conducting polymers
- High surface area metal oxides and carbons
- Conducting polymer – carbon nanotube composites

[2] It is possible to accomplish such hybrids using conventional capacitors; a common example of this is found in the common camera flash. For more powerful applications, conventional capacitors become impractical due to size and expense of constructing a bank capable of storing any significant quantity of energy (see Figure 1b). Conventional aluminum electrolytic capacitors can discharge on the microsecond timescale, but cost around \$200–\$400 per Farad. A supercapacitor costs less than \$20 per Farad (and probably below \$1/F) while occupying a much smaller volume.

- Production of diffuse networks of conducting polymers to facilitate ion flux and hence improve current densities
- Decreasing the impedance of the interface between the electrode material and the current collector. This will decrease the equivalent series resistance (ESR) of supercapacitors, and thereby enhance their rates of discharge.
- Exploring non-aqueous electrolytes
- Creating dielectric composites with high permittivity and/or high breakdown strengths for use in conventional capacitors
- Modeling at the molecular and at the device level.

3.2 Goals

The objectives of this project are to improve the power density and/or energy density of capacitive energy storage devices. The approach will be a ground-up one, developing materials specifically to address these needs, and focusing on issues such as manipulating meso- and micropore distribution to balance total surface area with ion transport requirements [6]. In doing so, we hope to achieve material specific capacitance on the order of 10^2 C/g and device performance in the range of 40 kJ/kg and 9 kW/kg, and stable over $> 10^5$ cycles. The final stages of the current project will see the construction of prototype devices for demonstration purposes in familiar packaging (button cells, for instance) using the most successful materials from the project.

4 Further supercapacitor research ideas: enhancing Canadian soldier systems

4.1 Materials optimized for arctic conditions

A number of solvent influences affect the capacitance behaviour of the electrode. These include the dielectric constant of the solvent, the dipole moment and size/shape of the solvent molecules, solvation energies of the electrolyte ions in the solvent, and so on. Additionally, the electrical resistance of the electrolyte and solvent influences the ESR of the capacitor, affecting the performance at high discharge rates. It turns out that water often has a number of desirable properties, not least of which is its non-toxicity. Its low electrochemical breakdown voltage (< 1.5 V) is a problem. A fatal problem for aqueous systems in cold environments is freezing. A research program in non-aqueous supercapacitor solvents might solve this issue. A Canada-specific supercapacitor could be developed, optimizing performance in arctic environments, perhaps at the expense of room-temperature behaviour.

4.2 Supercapacitors based on ionic liquids

Ionic liquids are molten salts at room temperature. Often based on ammonium and imidazolium cations, the molecules are designed so that they do not readily pack to form liquids. Possible advantages of using ionic liquids in supercapacitors are:

1. Being ionic, the liquid itself is the electrolyte

2. Ionic liquids have a near-zero vapour pressure. This means that there will be no pressure buildup in an ionic liquid cell even at elevated temperatures

3. The potential window will be wider, allowing for higher operating voltages. This implies a higher energy density in accordance with Equation 1.

4.3 Improved device construction

There is provision late in the current project to demonstrate the best materials in prototype supercapacitor devices. In order to reach the ultimate goal of improving soldier systems, follow-on work should include a small project devoted exclusively to optimizing device construction. For instance, careful matching of the electrodes is an important consideration, especially for stacked systems. Ultimately, such a project would lead to a program to demonstrate the technology.

5 Conclusion

Supercapacitors are devices of strategic interest to soldier technology in Canada. The supercapacitor research program intends to produce new electrode materials for high performance next generation supercapacitors. There exists the opportunity for further development of the products of the program. Materials refinement, optimized device construction, and specialization for cold climate deployment are worthwhile avenues for further exploration.

Glossary

DMFC: Direct methanol fuel cell, a fuel cell that consumes methanol directly without requiring an fuel reformer that generates hydrogen gas.

Energy density: The total electrical energy of a source per unit mass. Usually given as J/kg or W h/kg.

ESR: Equivalent series resistance

Faradaic: Describes an electrochemical reaction where chemical species undergo a transformation involving the transfer of electrons.

GPS: Global positioning system

ISSP: Integrated Soldier Systems Project

LAV: Light armoured vehicle

NiMH: Nickel-metal hydride

Oxidation: An electrochemical process where a species loses electrons.

PEM: Proton exchange membrane, a key component for a class of fuel cells that operate near room temperature.

Power density: The amount of electrical power available per unit mass of the source, usually in W/kg.

Reduction: An electrochemical process where a species gains electrons.

TIF: Technology investment fund

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Supercapacitor technology stands as a bridge between the high power output of capacitors and the high energy characteristics of batteries, fuel cells, and energy harvesters. Supercapacitors offer the promise of better designed power systems for soldier-based applications. Use of such technology will enable the improved design of conventional electronic equipment such as radios and targeting systems, as well as enabling futuristic weaponry such as electromagnetic pulse generators and magnetically launched projectiles.

This document introduces work being carried out at DRDC Atlantic. It explains how supercapacitors work and how they fit in with military applications. The work focuses on developing new materials to push supercapacitors to new performance levels, and with special consideration to Canadian needs.

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