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HIGH POWER SUPERCAPACITORS FOR HYBRID ENERGY STORAGE SYSTEMS FOR SOLDIERS AND VEHICLES

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ABSTRACT

Rechargeable Li-ion batteries such as BB-2590 are critical energy storage devices used for military applications. While these devices can have energy densities exceeding 150 Wh/kg, this energy is difficult to fully access in pulsed and high power applications due to the relatively slow kinetics associated with their redox processes[1]*. As the demands for power and energy increase in the battlefield soldiers to access to new power and energy sources rapidly. Energy efficiency and recharge rates are critical for maintaining and sustaining equipment and communications. Supercapacitors are a class of electrochemical energy-storage device that could complement batteries in hybrid energy storage systems for applications in military and transportation, and load-leveling or uninterruptible power supply. In terms of their specific energy and specific power, supercapacitors partially fill the gap between conventional capacitors and batteries. Accordingly, these devices can improve the performance of electronic power sources in applications where multiple cycles and high-power performance are required. Noticeably, supercapacitors can be included in a hybrid configuration to manage short, high power pulses, thereby minimizing stresses on the primary energy-storage device.*

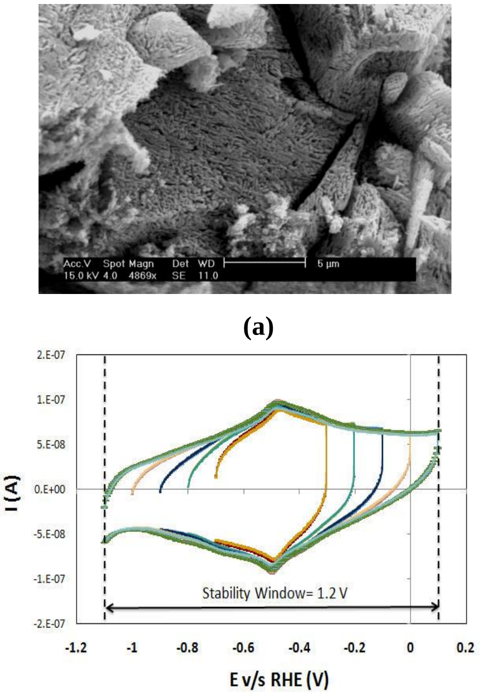
INTRODUCTION

Batteries are the principal devices used for most electrical energy storage, but they are inefficient in pulsed and high power applications. Supercapacitors, another type of electrochemical energy storage device, can be hybridized with a primary energy storage source to extend their run times and cycle-lives by handling these pulsed and high power events [1,2]. Currently available commercial-off-the-shelf (COTS) supercapacitors are expensive, have modest energy densities (~5 Wh/kg) and are suited to handle pulses of up to a few seconds [3]. With improvements in energy density and reductions in cost, the markets for supercapacitors are expected to grow rapidly [4]. To achieve broader application, supercapacitors will have to efficiently manage longer and repetitive pulses which translate to higher energy densities and smaller footprint.

Inmatech is commercializing next generation supercapacitor devices that incorporate low cost, high performance materials. We have demonstrated the technical feasibility of using proprietary nanostructured vanadium nitride (VN) based electrodes and an asymmetric cell architecture with non-flammable aqueous electrolytes (KOH) to manufacture commercially-attractive, high energy density supercapacitors (Funded by *NSF IIP 1113564, 1142998 and 1230387*). These devices use aqueous electrolytes which are safe (nonflammable), inexpensive and have much higher ion conductivities at low temperatures than organic electrolytes used in COTS devices.

BACKGROUND

Batteries are critical energy storage devices used for commercial and military applications. While these devices can have energy densities exceeding 100 Wh/kg, this energy is difficult to fully access in pulsed and high power applications due to the relatively slow kinetics associated with their redox processes [1]. Supercapacitors are a class of electrochemical energy-storage device that complements batteries in hybrid energy storage systems for transportation and military applications, and load-leveling or uninterruptible power supply applications [4]. In terms of their specific energy and specific power, supercapacitors partially fill the gap between conventional capacitors and batteries. Accordingly, these devices can improve the performance of electronic power sources in applications where multiple cycles and high-power performance are required. For example, supercapacitors can be included in a hybrid configuration to manage short, high power pulses, thereby minimizing stresses on the primary energy-storage device. Currently available supercapacitors have modest energy densities and are well suited to handle pulses of up to a few seconds [5]. To achieve broader application, supercapacitors will have to efficiently manage much longer pulses which translate to higher energy densities.



(a)

(b)

Figure 1: Micrograph of VN (a) at accelerating voltage 15 kV and 5000 times magnification and cyclic voltammogram of VN (b) in 0.1M KOH as electrolyte using scan rate of 50 mV/s at room temperature. Each voltammogram is superimposed with scan number 25 and 100 to show stability as the potential window widens.

There are two different storage mechanisms for supercapacitors. Currently available commercial supercapacitors store charge via formation of an ***electrical double layer*** on high surface area, engineered carbons. The high surface areas are due in large part to the presence of micropores that are not easily accessed by the electrolytes, therefore, there is a point of diminishing returns with respect to increasing the surface area. These carbon-based materials are typically used in a ***symmetric*** design with identical or very similar active materials in both electrodes, and possess specific capacitances of up to 300 F/g [5].

Table 1: Conductivities of various material.

Active Material	Conductivity ($\mu\Omega$ cm)$^{-1}$
RuO_2	0.0002
MnO_2	0.0005
VN	0.012
VC	0.017
Carbon	0.001

The ***pseudocapacitive*** mechanism exploits fast, reversible, faradaic redox reactions within the first few nanometers of the surface of the active materials [4], and materials with capacitances in excess of 1000 F/g have been reported. Pseudocapacitance is largely limited to aqueous electrolytes and charge storage is derived from either near surface redox reactions or underpotential deposition of atomic species on the electrode surface [4]. Materials that exhibit this pseudocapacitive behavior include metal oxides and hydroxides such as RuO_2 [6-12] and MnO_2 [13-17]. The high cost of Ru is unattractive for large-scale use and MnO_2 has a somewhat limited stability window for use in a typical symmetric design. Recently, early transition metal nitride-based materials have been reported to exhibit pseudocapacitive behavior [18-27]. These materials have electronic conductivities (see Table 1) that are much higher than those for transition metal oxides [22, 23], and can be produced with high surface areas and open pore structures [27, 28]. For example, highly porous vanadium nitride (VN) (Figure 1a) can be produced with surface areas exceeding 100 m^2/g. These materials are extremely stable during cycling over nearly 1.2 V in aqueous electrolytes including concentrated KOH (Figure 1b) and are inexpensive to produce. Researchers at the University of Michigan have worked more than 15 years with these materials and demonstrated that materials like high surface area VN can be used to produce devices with performance characteristics that are superior to those for high surface area carbons.

Despite their proven performance benefits, supercapacitors markets have been limited, largely due to the need for higher energy densities and lower cost. The United States Department of Energy has targeted energy and power densities of 15 Wh/kg and 700 W/kg, respectively [29], for supercapacitors to be more widely used for load-leveling and regenerative braking in hybrid and electric vehicles. State-of-the-art symmetric supercapacitors employing high area carbon electrodes and non-aqueous electrolytes can reach energy densities of 3-6 Wh/kg with power densities of 700

W/kg. These devices have been highly optimized, and only incremental gains in energy density are expected in the future.

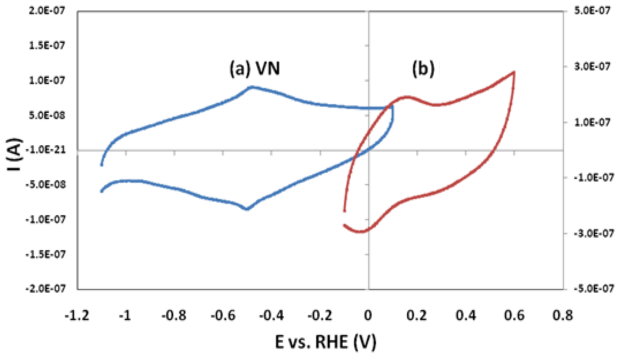


Figure 2: Cyclic voltammograms of (a) VN and (b) a metal oxide in 1M KOH as electrolyte using scan rate of 50 mV/s at room temperature. Each voltammogram was superimposed after 25 and 100 cycles, and overlaid here to demonstrate the widened potential window of ~1.8 V that is beyond the maximum voltage of 1 V (thermo-dynamic window is 1.23 V for water) for aqueous electrolytes.

Recently a new type of supercapacitor architecture has been demonstrated which combines two different types of electrode materials [4,17,30-32]. The voltage windows in these ***asymmetric*** devices are wider than that for conventional symmetric supercapacitors due to the use of two different materials with complementary operating potential windows. Potential windows as wide as 2 V have been reported for carbon-MnO_2 supercapacitors with aqueous electrolytes, however, the energy densities are limited due to the moderate capacitances of carbons in aqueous electrolytes [32]. We have developed next generation supercapacitor devices by incorporating high capacitance materials in asymmetric designs that optimize the operating potential window. Accordingly, the feasibility of this asymmetric design hinges on the successful pairing of two different types of electrodes to operate with high capacitances at the opposite ends of the potential spectrum. For example, VN is an attractive electrode material for energy storage in the negative potential region with KOH based electrolyte (Figure 2a) while metal oxides are attractive for use in the positive potential region (Figure 2b).

INNOVATION

The key figures of merit for supercapacitors are the power and energy densities. The power density is, all other factors being constant, a function of the electronic conductivity of the active materials. The energy, E, stored in a capacitor is given by [3]:

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

where C is the capacitance, and V, the operating voltage. For double layer capacitors, energy is stored through reversible ion adsorption on the surface of the electrode. This double layer capacitance is described by the Helmholtz model and is given by the following equation [3]:

$$C_{dl} = \frac{\varepsilon_r \varepsilon_0 A}{d}$$

where C_{dl} is the double layer capacitance, ε_0 is the dielectric constant of vacuum, ε_r is the dielectric constant of the electrolyte, A is the area of the electrode accessible to the ions and d is the effective thickness of the double layer in the electrolyte (see Figure 3). For the pseudocapacitive mechanism, the capacitance, C_ϕ is given by [3]:

$$C_\phi = \frac{d(\Delta Q)}{d(\Delta V)} = \frac{dQ}{dV}$$

where Q is the amount of charge stored. For both the double-layer capacitance and pseudocapacitance, charge storage predominantly relies on contact of the electrode surface with the electrolyte and the stability of the electrode-electrolyte system.

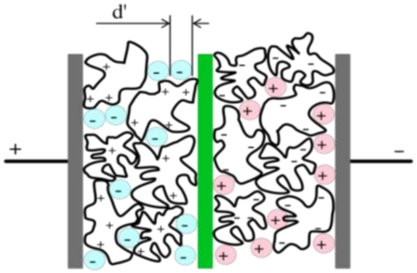


Figure 3: Schematic of the diffused double layer.

To improve the energy density, one can increase the capacitance, C, and/or expand the operating voltage, V. The key performance parameters are accessible electrode area and the operating voltage window within which the electrode material is stable in the electrolyte solution and over which the electrolyte solution does not undergo electrolysis.

We have incorporated the following innovations: (i) vanadium nitride based pseudocapacitive electrodes, (ii) an asymmetric cell design to significantly widen the operating voltage window and (iii) an aqueous electrolyte that eliminates fire hazards. Vanadium nitrides have been reported to have capacitances exceeding 1340 F/g in aqueous electrolytes although the scan rate was relatively low [23]. These innovations will ultimately lead to supercapacitors with specific energy densities approaching 15 Wh/kg with manufacturing costs an order of magnitude lower than those for currently available commercial products.

VN BASED SUPERCAPACITORS

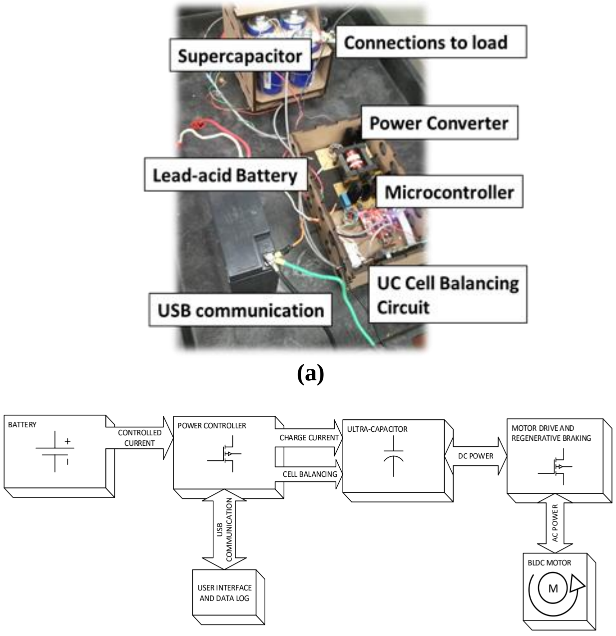
At Inmatech, we have focused on developing cells with low internal resistances which is critical to high power applications. Based on our prismatic cell performance, our target specification for supercapacitors in cylindrical format is summarized in Table 2. According to our survey, there is a demand for high power supercapacitors in cylindrical format for military applications, specifically for 18650s and 26650s that are currently used for Li-ion batteries. However, since these cells are designed for low power batteries, we are optimizing the placement and number of tabbing, as well as the welding to the can to achieve ESR value significantly below 1 mOhm using modelling software such as Battery Design Studio and/or COMSOL.

Table 2: Target specification for Inmatech's supercapacitors.

Prototype Cells		 18650	 26650	 D-Cell
Cell Voltage (V)	1.6	1.6	1.6	1.6
Cell Weight (g)	82	48	75	140
Cell Volume (cm^3)	45	16	34	53
Volumetric Energy Density (Wh/L)	14	13	14	14
Mass Energy Density (Wh/Kg)	6	5	6	6
Continuous Power Density (W/L)	7540	-	-	-

HYBRID ENERGY STORAGE (HES) SYSTEM

Recently we have assembled and evaluated a hybrid energy storage (HES) system (see Figure 4) that integrates supercapacitors in parallel with a commercially established 12 V lead-acid battery (PbA) (Funded by Next Energy). Specifically, a hardware-in-the-loop system was developed with a pulse-width modulation (PWM) based microcontroller for cell balancing and for integrating the supercapacitors with the battery with a current efficiency of ~86% demonstrated on a 12V HES. We have achieved 100% range extension with HES (with 60% regenerative energy) in a simulated New York City drive cycle (35% depth of discharge) compared to a battery alone system. Since HES is agnostic to specific battery chemistries, we envision Li-ion cells can readily be hybridized to provide high repetitive pulse power capabilities to various applications for military use and reduce the soldier burden with its smaller energy storage footprint.



(a)

(b)

Figure 4: Hardware in the loop system (a) for a hybrid energy storage system, and its control topology (b).

REFERENCES

[1] Miller, J.R. and Burke, A.F., *Electrochemical capacitors: challenges and opportunities for real-world applications.* Electrochem. Soc. Interface, 2008. **17**(1): p. 53-57.

[2] Song, Z., and Hoffman, H. and Li, J. and Han, X. and Zhang, X. and Ouyang, M. *A system comparison of different semi-active hybrid energy storage system topologies for electric vehicles*. J. Power Sources. 2015.

[3] *World Ultracapacitor Markets*, 2009. N661-27, Frost and Sullivan.

[4] Conway, B.E., *Electrochemical Supercapacitors*. 1999, New York: Plenum.

[5] Simon, P. and Gogotsi, Y., *Materials for electrochemical capacitors.* Nat. Mater., 2008. **7**(11): p. 845-854.

[6] Zheng, J.P., *Ruthenium oxide-carbon composite electrodes for electrochemical capacitors.* Electrochem. Solid-State Lett., 1999. **2**(8): p. 359-361.

[7] Hu, C.-C., Chang, K.-H., Lin, M.-C. and Wu, Y.-T., *Design and Tailoring of the Nanotubular Arrayed Architecture of Hydrous* RuO_2 *for Next Generation Supercapacitors.* Nano Lett., 2006. **6**(12): p. 2690-2695.

[8] Hu, C.-C. and Huang, Y.-H., *Cyclic voltammetric deposition of hydrous ruthenium oxide for electrochemical capacitors.* J. Electrochem. Soc., 1999. **146**(7): p. 2465-2471.

[9] Hu, C.-C., Chen, W.-C. and Chang, K.-H., *How to achieve maximum utilization of hydrous ruthenium oxide for supercapacitors.* J. Electrochem. Soc., 2004. **151**(2): p. A281-A290.

[10]Trasatti, S. and Buzzanca, G., *Ruthenium dioxide: a new interesting electrode material. Solid state structure and electrochemical behavior.* J. Electroanal. Chem. Interfacial Electrochem., 1971. **29**(2): p. 1-2.

[11]Juodkazis, K., Juodkazyte, J., Sukiene, V., Griguceviciene, A. and Selskis, A., *On the charge storage mechanism at* $RuO_2/0.5\ M\ H_2SO_4$ *interface.* J. Solid State Electrochem., 2008. **12**(11): p. 1399-1404.

[12]Ma, Z., Zheng, J.P. and Fu, R., *Solid state NMR investigation of hydrous ruthenium oxide.* Chemical Physics Letters, 2000. **331**(1): p. 64-70.

[13]Jiang, J. and Kucernak, A., *Electrochemical supercapacitor material based on manganese oxide: preparation and characterization.* Electrochim. Acta, 2002. **47**(15): p. 2381-2386.

[14]Lee, H.Y. and Goodenough, J.B., *Supercapacitor Behavior with KCl Electrolyte.* J. Solid State Chem., 1999. **144**(1): p. 220-223.

[15]Hu, C.-C. and Tsou, T.-W., *Ideal capacitive behavior of hydrous manganese oxide prepared by anodic deposition.* Electrochem. Commun., 2002. **4**(2): p. 105.

[16]Lee, H.Y., Kim, S.W. and Lee, H.Y., *Expansion of active site area and improvement of kinetic reversibility in electrochemical pseudocapacitor electrode.* Electrochem. Solid-State Lett., 2001. **4**(3): p. A19-A22.

[17]Toupin, M., Brousse, T. and Belanger, D., *Charge Storage Mechanism of* MnO_2 *Electrode Used in Aqueous Electrochemical Capacitor.* Chem. Mater., 2004. **16**(16): p. 3184-3190.

[18]Deng, C.Z. and Tsai, K.C., *Characterization of molybdenum nitride as an ultracapacitor material.* Proc. - Electrochem. Soc., 1997. **96-25**(Electrochemical Capacitors II): p. 75-84.

[19]Chen, C., Zhao, D., Xu, D. and Wang, X., *g-*Mo_2N/Co_3Mo_3N *composite material for electrochemical supercapacitor electrode.* Mater. Chem. Phys., 2006. **95**(1): p. 84-88.

[20]Liu, T.C., Pell, W.G., Conway, B.E. and Roberson, S.L., *Behavior of molybdenum nitrides as materials for electrochemical capacitors.* J. Electrochem. Soc., 1998. **145**(6): p. 1882-1888.

[21]Li, X.-l., Xing, Y., Wang, H., Wang, H.-l., Wang, W.-d. and Chen, X.-y., *Synthesis and characterization of uniform nanoparticles of g-Mo2N for supercapacitors.* Trans. Nonferrous Met. Soc. China, 2009. **19**(3): p. 620.

[22]Choi, D. and Kumta, P.N., *Chemically synthesized nanostructured VN for pseudocapacitor application.* Electrochem. Solid-State Lett., 2005. **8**(8): p. A418.

[23]Choi, D., Blomgren, G.E. and Kumta, P.N., *Fast and reversible surface redox reaction in nanocrystalline vanadium nitride supercapacitors.* Adv. Mater. (Weinheim, Ger.), 2006. **18**(9): p. 1178-1182.

[24]Glushenkov, A.M., Hulicova-Jurcakova, D., Llewellyn, D., Lu, G.Q. and Chen, Y., *Structure and Capacitive Properties of Porous Nanocrystalline VN Prepared by Temperature-Programmed Ammonia Reduction of V2O5.* Chem. Mater.: p. ACS ASAP.

[25]Zhou, X., Chen, H., Shu, D., He, C. and Nan, J., *Study on the electrochemical behavior of vanadium nitride as a promising supercapacitor material.* J. Phys. Chem. Solids, 2009. **70**(2): p. 495-500.

[26]Choi, D. and Kumta, P.N., *Synthesis, structure, and electrochemical characterization of nanocrystalline tantalum and tungsten nitrides.* J. Am. Ceram. Soc., 2007. **90**(10): p. 3113-3120.

[27]Parker, J., Wixom, M. and Thompson, L., *High Surface Area Nitride, Carbide and Boride Electrodes and Methods of Fabrication Thereof.* 1997: US Patent number 5,680,292.

[28]Kwon, H., Choi, S. and Thompson, L. T., *Vanadium Nitride Catalysts: Synthesis and Evaluation for n-Butane Dehydrogenation*, Journal of Catalysis, 1999. **184**: p 236.

[29]www.science.energy.gov/bes/reports/files/EES_rpt.pdf

[30]Salitra, G., Soffer, A., Eliad, L., Cohen, Y. and Aurback, D., *Carbon Electrodes for Double-Layer Capacitors 1. Relations Between Ion and Pore Dimensions.* J. Electrochem. Soc., 2000. **147**: p 2486.

[31]Sevilla, M., Alvarez, S., Centeno, T.A., Fuertes, A.B. and Stoeckli, F., *Performance of Templated Mesoporous Carbons in Supercapacitors*. Electrochim. Acta, 2007. **52**: p 3207.

[32]Kohmenko, V., Raymundo-Piñero, E. and Béguin, F., Journal of Power Sources, 2006. **153**: p 183.