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High-Energy Density Asymmetric Supercapacitor Based on Electrospun Vanadium Pentoxide and Polyaniline Nanofibers in Aqueous Electrolyte

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Vanadium pentoxide nanofibers (VNF) and polyaniline nanofibers (PANF) nanofibers are synthesized by electrospinning and rapid chemical polymerization routes, respectively. The electrochemical performances of synthesized nanofibers are evaluated in symmetrical (VNF-VNF, PANF-PANF) and asymmetrical (VNF-PANF) configurations in aqueous KCl (3 M) medium by cyclic voltammetry (CV) and galvanostatic measurements. Both VNF and PANF fibers exhibit pseudocapacitive behavior at the electrode/electrolyte interface. The VNF-PANF asymmetrical device is capable of delivering an energy and power densities of 26.7 Wh kg⁻¹ at 0.22 kW kg⁻¹, respectively which is higher than that of symmetrical configuration of VNF-VNF (5.2 Wh kg⁻¹ at 0.22 kW kg⁻¹). In addition, VNF-PANF asymmetrical supercapacitor retained 73% of specific capacitance after 2000 cycles. These results clearly show that high energy density supercapacitor can be constructed utilizing transitional metal oxides with conducting polymers as electro-active materials in an asymmetrical configuration in aqueous medium.

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Growing global energy demands have led to increased research efforts worldwide on both energy conversion and storage technologies. Supercapacitors are one such electrochemical energy storage device that are promising because of their high power density (~5 kW kg⁻¹), long cycle life and high charge/discharge rates.^{1,2} They are presently used in high power applications such as memory backup systems and would be excellent candidates for hybrid electric vehicles (HEV), portable electronic devices and renewable energy storage if the energy density is improved.³ Based on the charge storage mechanism, supercapacitors are broadly categorized into two different classes namely, pseudocapacitors and electrical double layer capacitors (EDLC). Pseudocapacitors fundamentally involve fast faradaic redox reactions occurring at the interface between the active material and electrolyte,¹ whereas EDLC involves electrostatic charge separation (non-faradaic) across electrode/electrolyte interfaces.² Predominantly commercial supercapacitors³ are EDLC type based on various carbon electrodes (eg. activated carbon, AC) and capable of delivering high power densities in the range of ~3 to 5 kW kg⁻¹, but possess lower energy density (2-5 Wh kg⁻¹) as compared to rechargeable batteries (~50-100 Wh kg⁻¹).⁴ For instance, AC derived from the coal and activated with KOH in the presence of 1 M H₂SO₄ electrolyte provides maximum specific capacitance of ~320 F g⁻¹ in two electrode configuration.⁴ Mesophase pitch activated with KOH enables the specific capacitance of ~200 F g⁻¹ in two electrode configuration and 6 M KOH as electrolyte. SBA-16 templated furfuryl alcohol derived carbon exhibited the specific capacitance of ~205 F g⁻¹ in two electrode configuration with 6 M KOH solution.⁴ Pseudocapacitor electrodes based on either electronically conducting polymers (ECP) (polyaniline (PANI),^{5,6} poly(3,4-ethylenedioxythiophene) (PEDOT),⁷ and polypyrrole (PPy)⁸) or transition metal oxides (TMO)⁹ (RuO₂,^{10,11} NiO_x,¹² Co₃O₄¹³ and V₂O₅ have been extensively investigated as electrode materials for supercapacitor applications.¹⁴⁻¹⁷ Pseudocapacitors based electrodes are often provide higher specific capacitance as the charge storage redox mechanism involves the entire electrode active mass as compared to EDLC carbon electrodes wherein primarily only the electrode surface contributes to the specific capacitance via double layer formation.

Energy density of supercapacitor is proportional to square of voltage ($E = 1/2CV^2$), where C is the specific capacitance (F g⁻¹) and V is the voltage window (Volts). In aqueous electrolytes, both EDLC and pseudocapacitors have lower working voltages (<1.23 V) which severely discounts their energy density. Although pseudocapacitors

exhibit higher specific capacitance and hence greater energy density, such increment is often inadequate and long term cycleability is also questionable. One approach to further increase the energy density is to widen the working voltage (~2-3 V) of both EDLC and pseudocapacitor by employing organic electrolytes instead of aqueous solutions.³ However, such aprotic organic solutions not only entail detrimental costs from fabrication processes which require water free environment, but also possess safety and toxicity issues remains. Another approach to increase the working voltage is to construct an asymmetric supercapacitor (ASC) in an aqueous medium by employing two different kinds of electrodes. Employing electrodes of different nature in ASC for positive and negative polarization allows both electrodes to operate in an optimal voltage range.^{9,18-22} It has been reported that ASC consisted of TMO-AC^{9,23-25} or ECP-AC^{26,27} pair is capable of relatively higher operating voltage.

Among the transition metal oxides, amorphous hydrous ruthenium oxide (RuO₂·xH₂O) exhibits pseudocapacitive behavior with large specific capacitance, but it is too expensive for the commercialization. V₂O₅ is one of the attractive candidates because of its layered structure, multiple oxidation states of vanadium which allows surface/bulk redox reactions leading to high capacitance in symmetric supercapacitor configuration.¹⁵ Similarly in ECP, polyaniline (PANI) is considered as a promising electrode materials for supercapacitor applications owing to its environmental stability, controllable electrical conductivity multiple intrinsic redox states and excellent processability.²⁸ In addition, nanostructured active materials are capable of providing higher power density than bulk counterparts owing to shorter diffusion pathways, increased accessible surface area leading to facile flow of ions at electrode/electrolyte interface. Indeed, polyaniline nanofibers (PANF) have been shown to exhibit a high specific capacitance of 428 F g⁻¹ in three electrode configuration.¹⁶ However, there is no report on the two electrode device performance of polyaniline nanofibers till date.

Herein, we have constructed an ASC based on a combination of nanostructured TMO and ECP to study the capacitive properties and widen the operating voltage in aqueous medium. A schematic illustration of the ASC utilizing electrospun VNF and PANF is shown in Figure 1. To the best of our knowledge, there is no work has been reported on ASC based on both nanostructured TMO and ECP in a single device. In the present work, an attempt has been made to construct an ASC comprising of electrospun vanadium pentoxide nanofibers (VNF) as negative electrode and polyaniline nanofibers (PANF) as positive electrodes in aqueous medium.²⁹ Electrospinning is a simple, low cost scalable facile route for making high aspect ratio 1D nanofibers with controllable diameter using electrostatic force.³⁰

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Figure 1. Schematic illustration of an asymmetrical supercapacitor comprising of VNF and PANF as positive and negative electrodes, respectively.

Also, electrospinning often results in highly porous interconnected three dimensional fibrous electrode that provides both a continuous conduction pathway and increased electrode/electrolyte contact surface.³¹ In addition, structure, surface morphology and diameter of the electrospun fibers was easily controlled by varying the parameters like applied potential, precursor concentration, viscosity and flow rate of the solution. Likewise, the length, diameter and morphology of the ECP nanofibers were tailored. The detailed electrochemical studies of both VNF and PANF electrodes are conducted and analyzed in both symmetric and asymmetric configurations and described in detail.

Experimental

Preparation of electrospun VNFs.— The detailed synthesis procedure of VNFs was reported elsewhere by Cheah et al.³² and we slightly modified and optimized to yield single phase V_2O_5 with fibrous morphology. Briefly, 1.6 g Polyvinylpyrrolidone (PVP) (Mw 3, 60,000 Fluka) was dissolved in mixture of absolute ethanol (Sigma-Aldrich) and acetic acid (Tedia Company Inc.) (1:3 volume ratio). 0.6 g vanadyl acetylacetonate ($VO(acac)_2$, 98%, Sigma-Aldrich) was added, and stirred for 24 h to obtain a homogenous solution. All chemical reagents were used as received. In the electrospinning procedure, the $VO(acac)_2$ precursor solution was transferred into a 10 mL syringe mounted on a electrospinning apparatus. The feeding rate was set to 1 mL h^{-1} by a syringe pump (KDS Scientific Model 210). A positive potential of 10 kV was applied to the 25 G needle tip through a high voltage source (Gamma High Voltage Research). The distance between needle tip and collector (aluminum foil) was maintained at a distance of 10 cm. By applying electric field, fibers were ejected from the Taylor cone formed at the needle tip and deposited on the collector as a mat. The as-spun mat was annealed at 470°C for 30 min, and cooled (2°C min^{-1}) to room temperature to yield VNF. The obtained fibers were yellowish in color indicating the V^{5+} oxidation state of vanadium.

Preparation and purification of PANF.— It is challenging to fabricate pure PANI fibers by electrospinning technique and hence we adopted chemical rapid mixing polymerization technique to form PANF.²⁹ Briefly, oxidant dopant solution was prepared by dissolving 25 mmol. of ammonium persulfate (98% Sigma-Aldrich) in 50 mL deionized water, and stirred for 30 min. Aniline dopant solution was made by adding 20 mmol of aniline (Sigma-Aldrich) into 50 mL deionized water, and stirred for 30 min. The oxidant solution is then quickly added to the aniline solution and stirred vigorously for a minute, and left to polymerized for an hour. After the polymerization, the dark green residue was washed with 300 mL of 0.2 M HCl solution followed by 300 mL of acetone to remove residual ammonium persulfate and aniline monomers respectively. The dark green residue was then dried at 50°C in vacuum for 12 hours.

Characterization of VNF and PANF.— Morphological features of synthesized nanofibers were characterized by Field emission scanning

electron microscope (FE-SEM, JEOL JFM-6340F) with an accelerating voltage of 5 kV and transmission electron microscope (TEM, JEOL 2100F) in high resolution mode operating at 200 kV. Software, Image J was used to measure the diameter of the fibers. Powder X-ray diffraction (XRD) was performed using Bruker diffractometer ($\text{Cu K}\alpha$) with step scanning (0.02° , 1 s dwell time) over 10 to 80° (2θ range). Rietveld method^{33–35} contained within TOPAS V3 (Bruker-AXS) was used to analyze the XRD pattern using the fundamental parameters approach. Brunauer-Emmett-Teller (BET) surface area analysis was performed by using NOVA 3200e system. The VNF and PANF samples were degassed at 373 K under vacuum for 10 h before conducting BET surface area measurements.

Electrochemical measurements.— The test electrodes were prepared by dispersing VNFs or PANFs, super P (99%, Alfa Aesar) and poly-vinylidene fluoride (PVdF) (Sigma-Aldrich) in *N*-methylpyrrolidone (NMP) (Sigma-Aldrich) with a weight ratio of 75:15:10, respectively to form slurry. Resultant slurry was then coated onto a 1 cm^2 area of graphite paper and subsequently dried. The mass loading of electrode material was $\sim 2 \text{ mg}$ and aqueous 3 M KCl (Sigma-Aldrich) was used as electrolyte (pH value is 6.4). The thickness of the electrode is approximately $200 \mu\text{m}$. Specific capacitance of individual components (VNF and PANF) were investigated using a three-electrode cell set-up, in which saturated calomel electrode (SCE, 0.242 V vs. NHE) and platinum foil ($5 \text{ cm} \times 5 \text{ cm}$) were used as counter and reference electrodes, respectively. At the same time, device (both symmetric and asymmetric) performance was monitored by two-electrode configuration. Cyclic voltammetry (CV, scan rate from 2 to 100 mV s^{-1}) and galvanostatic charge-discharge cycling studies (current rate from 0.15 to 3.1 A g^{-1}) were carried out in these three-electrode and two electrode configurations at ambient conditions. Electrochemical impedance spectroscopy (EIS) was measured in the asymmetrical device configuration (open circuit potential of $0.15 \sim 0.2 \text{ V}$) using the frequency response analyzer from Solartron (SI 1255B Impedance/gain-phase analyzer with Zview software) in potentiostatic mode with an AC amplitude of 10 mV from 105 to 0.01 Hz .

Results and Discussion

Figure 2 illustrates typical X-ray diffraction (XRD) patterns of electrospun VNF after annealing at 470°C for 30 min and PANF. XRD pattern of VNF reveal highly intense reflections that corresponded to orthorhombic Shcherbinaite structure with $Pmn2_1$ space group (JCPDS card no. 41-1426). Lattice parameters of VNF calculated from Rietveld crystal structure refinement was found to be $a = 11.513(2) \text{ \AA}$, $b = 3.5656(2) \text{ \AA}$ and $c = 4.3727(3) \text{ \AA}$. The XRD pattern of PANF revealed several broad reflection peaks (2θ) at

Figure 2. XRD patterns of PANF and electrospun VNF annealed at 470°C for 30 min in the range of 2θ from 10 to 60° .

Figure 3. (a) FE-SEM images of electrospun VNF, (b) electrospun VNF annealed at 470°C for 30 min. (c) PANF by rapid chemical polymerization. Insets: Magnified HR-TEM images and (d) Schematic representation of flexible supercapacitor.

15°, 20.6°, 25.2° and 26.8° which confirms the formation of polyaniline by rapid polymerization procedure. These reflections indicate the presence of crystalline order in the bulk PANF samples, which is consistent with literature.³⁶

Field emission scanning electron microscopic (FE-SEM) images of as-spun VNF shown in Figure 3a (with the inset showing the magnified view of the respective images) revealed smooth surface of the fibers with diameters ranging from 800 to 1000 nm and fiber length over 200 μm (See supplementary information). As spun VNF were annealed at various temperatures between 300 and 500°C to remove the polymer and to crystallize V₂O₅ nanocrystals in the VNF. Heating at higher temperature (> 500°C) leads to destruction of the fibrous structure, while at lower temperature (300–400°C) resulted in incomplete removal of PVP polymer. The synthesis condition mentioned here to prepare the VNF is slightly contrary than our previous report on VNF based symmetric supercapacitor, in which as-spun fibers were optimized at 400°C for 15 min with temperature interval of 100°C (300–500°C).¹⁵ In the present case, calcination temperature was further fine tuned to 470°C for 30 mins and still fibrous morphology maintained, which is presumably due to the less concentration of the vanadium precursor (40 mg less) and much slower flow rate to form the as-spun fibers. Figure 3b illustrates the VNF after annealing at 470°C for 30 minutes. The annealed VNF exhibited a more spiral like structure, with diameter of 300–500 nm, lower than that of as spun VNF. This change in fibrous morphology is mainly attributed to the decomposition of PVP polymer during sintering. Vaporization of the polymer during this process left behind pores and the surface seems

to have a spiral like morphology, which allows facile movement of electrolyte during the electrochemical reaction. It is worth noting that, sintering of as spun VNF was conducted at relatively low temperature (~470°C) to achieve a high performance V₂O₅ electrode. Figure 3c displays the morphological features of the PANF, showing interwoven structure with shorter fibers compared to electrospun VNF. The PANF fiber length and diameter PANF estimated from FE-SEM images with length of ca. 100–600 nm and diameter ranging from 30–200 nm. Transmission electron microscopy (TEM) was conducted to study the morphology of PANF (inset Figure 3c) clearly depicts nanostructured smooth surface of PANI. Such nanofibers can be readily utilized to fabricate flexible paper thin energy storage devices as shown in Figure 3d).

Nitrogen adsorption/desorption isotherms of both VNF and PANF at 77 K presented in Figure 4a and exhibited type II isotherm (according to IUPACS classification³⁷) with type H3 hysteresis showing absence of limiting adsorption at high relative pressure for both adsorption and desorption isotherm. Hysteresis loop extending down to low pressure region was observed indicating the presence of micropores which is advantageous for double layer charge storage. Desorption isotherm of PANF shows hysteresis loop at the relative pressure of 0.8–0.9, indicating meso-porosity (high surface area) which is beneficial for the movement of ions throughout the nanofibers. The gradual increase in adsorption curves of both VNF and PANF in the middle relative pressure region can be attributed to multi-layer adsorption of nitrogen in the mesopores and macropores. The leap (plunge) close to the saturation pressure in adsorption (desorption) isotherm suggests pores filling of large mesopores and macropores which is favorable as they allow ions to amass in the proximity of electrode permitting high power capability.

Brunauer-Emmett-Teller (BET) analysis³⁸ of the isotherms yields specific surface area of 9.5 and 36.8 m² g⁻¹ for VNF and PANF, respectively. The obtained values are consistent with the previous reports on these material (VNF: 10 m² g⁻¹, PANF: 34.4 m² g⁻¹).^{15,39} To investigate the pore size distribution, Barrett-Joyner-Halenda (BJH) analysis was applied on the desorption isotherms.⁴⁰ Figure 4b depicts the pore volume distribution curves obtained by BJH analysis. Much of the surface area is attributed to pores from the micropores range (<2 nm, IUPAC classification).⁴¹ These micropores are readily accessible to the hydrated K⁺ (0.3 nm) and Cl⁻ (0.3 nm) ions and would certainly enhance both the electrical double layer and pseudocapacitive contribution of the nanofibers.⁴²

Three electrodes setup was utilized to study the electrochemical stability of individual electrodes, in which platinum sheet and standard calomel electrode (SCE) were used as counter and reference electrodes, respectively. The CV curves (Figure 5 reveal that PANF electrode exhibited high electrochemical stability under positive polarization, giving a high electrochemical reversibility up to +1 V vs. SCE, whereas VNF electrode shows stability under negative polarization with reversibility of -1 V vs. SCE. These results illustrate that VNF is more stable being a negative electrode, while PANF is more

Figure 4. (a) Nitrogen adsorption-desorption isotherms of VNF and PANF at 77 K. (b) BJH plot depicting pores sizes distribution of VNF and PANF.

Figure 5. Cyclic voltammograms (CV) three-electrode cell of VNF and PANF at 10 mV s⁻¹ vs. SCE.

stable as a positive electrode. Hence, a working voltage window of 2 V ($E_{\text{PANF}} - E_{\text{VNF}} = 1.0 \text{ V} - [-1.0 \text{ V}] = 2 \text{ V}$) is viable if the two materials are judiciously paired in an asymmetric system with 3 M KCl as the common electrolyte. Generally, the aqueous system is stable up to $\sim 1.23 \text{ V}$ and said potential electrolysis takes place. However, in the asymmetric combination provides wider operating potential up to 2 V. This extension of the working potential in the aqueous medium is mainly due to the combination of the high hydrogen overpotential offered by VNF under negative polarization together with high oxygen overpotential when PANF is used as positive electrode.²³

Another factor to be considered is the optimization of desired capacity of such asymmetric configuration which is crucial to achieve

high energy density. It is important to note that in a symmetric configuration, the applied voltage is split equally between the two electrodes; however, if the two electrodes are different in nature as in a system, the voltage will be split depending on the capacitance of individual electrode. The capacitance of each electrode is related to the respective mass and intrinsic pseudocapacitance. In order to optimize the cell voltage in an asymmetric capacitor, mass balances between the two electrodes are necessary. The capacity balance will enlist the conservation of charges (i.e. $q^+ = q^-$) and can be obtained via the following equation,

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta E_-}{C_+ \times \Delta E_+} \quad [1]$$

where m_+ , m_- , C_+ , C_- , ΔE_+ , and ΔE_- are the respective mass, specific capacitance and potential windows of three electrodes configuration of the individual positive and negative electrode. Optimization of the mass ratio was done based on Equation 1 to be 1.2:1 for PANF : VNF.

Cyclic voltammetric (CV) and galvanostatic charge-discharge studies have been employed to evaluate the supercapacitive behavior of electrospun VNF and PANF materials in symmetric device configuration. The CV traces given in the present work is the average of 10 cycles at each scan rate. Figure 6a and 6b illustrates the CV traces of VNF-VNF and PANF-PANF symmetric device as a function of scan rate with respect to its current density in 3 M KCl aqueous solution. Generally, it is observed that the CV curves of the VNF electrodes exhibited a more rectangular shape when compared to PANF electrodes. This indicates that charging and discharging processes in VNF electrode are relatively faster. The current which depicts the direction of the charge flow, showed some delay upon the reversal of the potential sweep, suggesting resistance for the VNF-VNF symmetrical device possibly due to the diffusion process of ions through the pores. On the other hand, higher degree of deviation from a rectangular CV traces

Figure 6. (a) CV curves for annealed VNF and (b) PANF electrodes measured at various scan rates in 3 M KCl in two-electrode symmetric configurations, respectively. Galvanostatic charge-discharge curves for (c) annealed VNF, and (d) PANF electrodes measured at various current densities under the same conditions.

is noted for PANF electrodes and this suggests a higher resistance. On the other hand, higher degree of deviation from a rectangular CV traces is noted for VNF electrodes and this suggests a higher resistance similarly.

Galvanostatic charge-discharge measurements were carried out for VNF and PANF with symmetric configurations in 3 M KCl electrolyte and given in Figure 6c and 6d. The symmetry of the charge-discharge curves indicates good capacitive behavior in symmetric configurations. In such configurations the specific capacitance were calculated to be as high as 213 and 176 F g⁻¹ were obtained for VNF and PANF electrodes, respectively. The obtained values for VNF and PANF electrodes in aqueous medium are consistent with the previous reports.^{6,43} The high capacitance can be attributed to the high surface area provided by the porous and fibrous structure of VNFs, which eased the diffusion of ions into the pores thus contributing to the enhanced pseudocapacitance. The relatively lower specific capacitance obtained for PANF electrodes could be attributed to the absence of reversible doping process of PANFs which usually occurred in acidic media.⁴⁴

In order to fabricate VNF and PANF electrodes in asymmetrical configuration (ASC), a common aqueous electrolyte needs to be utilized. We have tested ASC consisting of VNF-PANF in various aqueous electrolytes. Although PANF results in higher capacitance in aqueous electrolyte like H₂SO₄,¹⁶ VNF dissolved in such acidic medium. Hence, KCl was chosen as the optimum electrolyte after several electrochemical trials of VNF-PANF in various aqueous electrolytes including H₂SO₄, KCl, H₃PO₄, NaOH, and KOH.

Figure 7a shows the CV curves of VNF-PANF asymmetric device in two electrode configuration measured at different potential windows as shown in the figure at 10 mV s⁻¹. In an aqueous medium, a CV curve of less oblique rectangular geometry is noted for PANF-VNF asymmetric device with working voltage below 2 V. With higher working voltage, the overall energy storage capability of the asymmetrical device is greatly enhanced. However, an undesirable drastic current surge is observed if working voltage exceeds 2.5 V which may be attributed to hydrogen evolution at the negatively polarized VNF electrode. Thus, we chose a potential window of 2 V in our subsequent experiments to investigate the overall electrochemical performance of the asymmetrical device. Further investigation is undergoing to investigate the origin of the irreversible reduction peak observed at 0.25 V (vs. VNF).

The CV of PANF-VNF asymmetric device, measured in two-electrode configuration between 0-2 V at various scan rates ranging from 2 to 100 mV s⁻¹ is depicted in Figure 7b. This figure indicates the fast charge/discharge capability at the measured scan rate. The CV curves resemble an ideal rectangle at low scan rate, and exhibit a slightly distorted trapezium as scan rate increases. Higher deviation is observed at higher scan rate which may be due to both kinetically limited charge storage process and the resistivity of the electrode, which will be verified by EIS measurements later. It is worth mentioning that the specific capacitance was calculated based on the total mass of active material instead of that of a single electrode. A device capacitance of 41 F g⁻¹ is obtained at 5 mV s⁻¹ which is slightly lower capacitance than VNF-VNF and PANF-PANF symmetric configurations. However, such asymmetrical configuration enables a working voltage up to 2 V, thereby enhancing energy density according to the following equation:

$$E = \frac{1}{2} CV^2 \quad [2]$$

where E is the specific energy density, C is the specific device capacitance and V is the working voltage of the device.

Galvanostatic charge-discharge studies were conducted for VNF-PANF asymmetric device with different current densities. Figure 7c depicts the typical charge-discharge curves of a PANF-VNF asymmetric supercapacitor. The symmetrical charging and discharging characteristics indicates good capacitive behavior of ASC. Figure 8 summarizes the specific capacitance calculated from galvanostatic

Figure 7. (a) Cyclic voltammograms (CV) of two-electrode cell of VNF and PANF at 10 mV s⁻¹ in the presence of 3 M KCl electrolyte solution with different operating potentials (b) CV traces of an asymmetrical PANF-VNF device measured between 0-2 V at various scan rates ranging from 2-100 mV s⁻¹. (c) Galvanostatic charge-discharge curves of an asymmetrical PANF-VNF device measured between 0-2 V at various current densities.

Figure 8. Plot of specific capacitance vs. cycle number obtained from galvanostatic charge/discharge curves with current density.

charge-discharge curves for both symmetric (VNF-VNF and PANF-PANF) and asymmetric configuration (VNF-PANF). For symmetric configuration, galvanostatic values are extracted from Figure 6 and ASC, values are extracted from Figure 7. In general, the specific capacitance gradually decreases with higher current density due to a larger IR drop at high current density. Decrease in specific capacitance values were observed with increasing current density. As charge/discharge rate increases, fewer ions are able to diffuse into the sub-surface resulting in less numbers of redox reactions, which leads to reduced charge storage. Nevertheless, the promising results from both CV and galvanostatic charge-discharge measurements of VNF-PANF asymmetric system indicates a higher working voltage, good pseudocapacitive properties.

Energy and power densities are used to characterize the performance of energy storage devices. To demonstrate the electrochemical performance of our device, energy and average power densities were evaluated from galvanostatic charge-discharge curves according to Equations 2 and 3,

$$P = \frac{E}{t} \quad [3]$$

where P is the specific power density, E is the specific energy density and t is the time to discharge. Figure 9a shows the Ragone plot of both symmetrical and asymmetrical devices. VNF-PANF supercapacitor exhibited much higher energy and power density than its symmetrical configuration counterparts. This is ascribed to the synergistic effect endowed by the combination of PANF and VNF namely; (1) the nanostructure of both PANF and VNF that facilitates diffusion of electrolyte ions and enables higher capacitance; (2) the asymmetrical configuration that widens the operating potential window thus enabling redox process from different oxidations states of vanadium. Figure 9b is a comparison of energy density and average power density of ASC constituted of nanofibers with commercial powder of V₂O₅ and PANI.⁴⁵ Nanostructured ASC exhibited higher power and energy densities when compared to their conventional commercial counterparts. This is owing to the better utilization of the active material in the nanostructured ASC.⁴⁴ Moreover, nanostructure morphology can facilitate the diffusion of electrolyte ions, while the intrinsic high electroactive surface area enables larger electrode/electrolyte interface thus leading to higher specific capacitance. In addition, the optimization process for the fabrication of electrodes by mass loading based on the specific capacitance obtained in the three electrode configuration. However, the obtained energy density depends on the nature of material and its morphology. We believe that owing to the open porous one dimensional nature of fibers, the entire mass is involved in the

Figure 9. (a) A Ragone plot of symmetrical and asymmetrical devices. (b) Performance comparison of nanostructured fibers ASC with commercial micron sized particles counterpart.

electrochemical process resulting in high energy density, whereas in commercial powders only surface of the materials are involved owing to the micron sized particles thus providing lower values irrespective of the applied current density.

Long cycling life is also another important requirement for supercapacitors especially for pseudocapacitors wherein faradaic redox process are involved. Figure 10 shows the capacity retention of the asymmetrical capacitor cycled at 5 mV s⁻¹ up to 2 V. Capacity of device is normalized with respect to the first discharge capacitance. The asymmetrical device displayed an initial specific capacitance of 42.7 F g⁻¹ with good cycling stability up to 2000 cycles, with capacity retention of ~73% after 2000th cycle. Supercapacitors are fundamentally expected to have long cycle life as energy is stored physically via electrical double layer formation. Whereas in the case of pseudocapacitor, cycle life is often limited by the parasitic chemical reactions and mechanical breakdown of structures due to swelling of electrode materials, both of which will be more pronounced at higher voltage. Here, the initial capacity degradation can be ascribed to the stabilization of the crystal structure. Minor fading was observed once the structure was stabilized (after 150 cycles) during electrochemical cycling. High energy density of 21.7 Wh kg⁻¹ is still maintained despite the fade. This finding shed new insights on coupling conducting polymer and nanostructured transition metal oxides to attain high energy density

Figure 10. Cycle performance of asymmetrical device with a voltage of 2 V at scan rate of 5 mV s^{-1} .

storage devices through careful selection of electrode materials and morphology tuning.

In order to better understand the resistive behavior of the device, an Electrochemical Impedance Spectroscopy (EIS) was performed between the frequency range 10^5 to 0.01 Hz at open circuit conditions ($0.15 \sim 0.2 \text{ V}$). Typical Nyquist plot for ASC before and after 1000 cycles are shown in Figure 11. Similar EIS is noted both before and after cycling. In the low-frequency region, before cycling, the impedance plot of PANF-VNF becomes inclined to a vertical line (Warburg), characteristic of a capacitive process.¹⁵ Equivalent series resistances (R_{ESR}) can be obtained from the intersection at the real axis, which are $2.8 \Omega \text{ cm}^{-2}$ and $2.5 \Omega \text{ cm}^{-2}$ before and after 1000 cycles respectively. This low value of series resistance further strengthens the earlier hypothesis that the distortion in the CV curves at higher scan rates may be attributed to limitations from other process such as the kinetics at the electrode/electrolyte interface. Additionally, to demonstrate the practical application of the fabricated asymmetric device, a red light emitting diode (1.6 V LED) is connected. During such testing, the asymmetrical device is galvanostatically charged at low current rate and discharged via LED, the lighting of LED is shown in Figure 12. Tandem cells of asymmetrical devices can be employed to increase the working voltage to the required level.

Figure 11. Nyquist plot of asymmetrical device at open circuit conditions before and after 1000 cycles. Inset showed the expanded high-frequency region. Area of the electrode is 1 cm^2 .

Figure 12. Photo image of red LED connected in series with asymmetrical device.

Conclusions

Symmetric and asymmetric supercapacitor devices based on electrospun long and porous interwoven network of VNF and PANF synthesized by rapid chemical polymerization process have been fabricated. X-ray diffraction spectra confirmed the formation of single phase materials. Pseudocapacitive behaviors of the synthesized materials were demonstrated in both symmetrical and asymmetrical configurations with aqueous KCl solution. An asymmetrical flexible device based on PANF and VNF as positive and negative electrodes, respectively. The asymmetric device (ASC) exhibited higher working voltage of 2 V, compared to the $\sim 1.23 \text{ V}$ limitations in symmetrical devices resulting in a high energy density of 21.7 Wh kg^{-1} as compared to symmetrical PANF and VNF devices. Furthermore, using an aqueous electrolyte makes the device more environmental friendly and undercut the hazards of working with organic counterparts. Capacitance retention of 73% up to 2000 cycles was also observed. Such ASC can be promising in conformal flexible printed electronics and high performance energy storage systems.

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