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Electrochemical energy storage in a β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ nanobelt network and its application for supercapacitors†

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We report a nanostructured oxide pseudocapacitor electrode utilizing a sodium-doped vanadium oxide (β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$) nanobelt network with a three dimensional framework crystal structure, which has been successfully synthesized under mild hydrothermal conditions and heat treatment. Cyclic voltammetry, galvanostatic charge-discharge and cycling tests have been carried out on the nanobelt network in 1 M LiClO_4 /propylene carbonate (PC) electrolyte for a 1 V potential window. A high specific capacitance of 320 F g^{-1} at 5 mV s^{-1} scan rate has been achieved with two sets of redox peaks being identified, corresponding to the half occupancy at M_3 and M_2 intercalation sites along the tunnel in the β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ crystal lattice. The β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ nanobelt electrode is able to deliver a high energy density of 47 W h kg^{-1} at a high power density of 5 kW kg^{-1} . Slight degradation in energy density at high power density has been observed. This can be attributed to the charge storage in the nanobelt network which is dominated by the fast surface dependent reaction. Superior cycling stability, with only 34% degradation in specific capacitance, is observed in the β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ nanobelts after 4000 cycles. The results clearly indicate the promising potential of these doped vanadium oxide electrodes for electrochemical energy storage devices.

Introduction

Supercapacitors, which can deliver significant energy with high power density, have attracted a lot of attention due to their potential application in energy storage. Among various oxide materials, vanadium oxide (V_2O_5) has been recognized as one of the most promising electrode materials for its high specific capacitance and accessible layered crystal structure for ion intercalation. The energy storage in V_2O_5 is mainly contributed from the Faradic charge transfer process in the reversible redox reaction, which usually involves the solid state diffusion of the ion. However, this slow diffusion-controlled redox reaction limits the reaction kinetics and results in significant degradation in specific capacitance at fast charging/discharging rate. Hence, an electrode material with a short ionic diffusion distance or containing fast diffusion pathways in the lattice will be beneficial for ion diffusion and energy storage.

Apart from the diffusion-controlled redox reaction, which occurs within the crystal lattice, the redox reaction also occurs at the oxide-electrolyte interface. This surface dependent process is another major component contributing to energy storage and possesses faster reaction kinetics than the diffusion controlled process. Thus, the energy storage at fast charging/discharging rate could be further improved if this surface dependent process is promoted and dominates the overall energy storage in the oxide electrode.

In order to achieve the delineated goals, two strategies have been adopted utilizing V_2O_5 as the starting base material. The

first strategy is to fabricate a V_2O_5 nanostructure network as the electrode material. Network configuration provides an effective electrolyte penetration while the high surface-to-volume ratio nanostructure creates sufficient oxide-electrolyte interfaces for surface reaction and ion injection. Moreover, short ionic diffusion distances in the oxide nanostructure will lead to shorter time required for the diffusion controlled redox reaction, hence improving the overall reaction kinetics. A similar strategy has been demonstrated in some recent works, for example ref. 1 reported a nanocomposite of carbon nanotubes and V_2O_5 nanowires, which can achieve a specific capacitance of 200 F g^{-1} at a high current density of 10 A g^{-1} . In addition, a porous network of $\text{VO}_x \cdot y\text{H}_2\text{O}$ has been demonstrated to have a specific capacitance of 167 F g^{-1} at 25 mV s^{-1} scan rate.²

The second strategy is to tailor the oxide lattice structure to create more intercalation sites or to provide fast diffusion pathways. V_2O_5 usually consists of VO_5 square pyramids layers with an intercalation site between the layers. Apart from the layered structure, a more rigid three dimensional (3D) framework structure with a tunnel can be achieved by doping with metallic species, such as Na into V_2O_5 , which forms the β phase $\text{Na}_{0.33}\text{V}_2\text{O}_5$.³ This β phase tunnel structure is expected to enhance the ion intercalation by introducing three different intercalation sites along the tunnel.⁴ Moreover, the tunnel can act as a fast diffusion path for ion diffusion, which can improve the overall charge storage kinetics.

Considering all these factors, we have synthesized a network nanostructure made of interconnected nanobelts of the desired β phase $\text{Na}_{0.33}\text{V}_2\text{O}_5$ through a hydrothermal process and annealing. The resultant nanostructures of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ are of high yield, with easy electrode fabrication without additives or binders, and exhibit promising supercapacitor properties by delivering high energy density at high power density. The charge

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storage mechanism is derived from the cyclic voltammetry scan rate analysis to provide further understanding of the enhancement in performances. The power density and energy density of the fabricated electrodes are being evaluated and correlated to the charge storage mechanisms and energy storage performances. The feasible concept of a three dimensional framework oxide phase in a nanostructured network form provides a general platform and directive strategy beneficial to the pseudo-capacitive enhancement in oxide electrodes at high charging/discharging rates.

Experimental

The Na-doped V_2O_5 nanobelt network structures were prepared through a hydrothermal process. 0.234 g NH_4VO_3 (Aldrich) and 0.478 g NaCl (Aldrich) were added into 20 ml of de-ionized water and stirred for 1 h until the solution became clear yellow in color. The solution was adjusted to pH 4 with 3 M HCl before being transferred into a Teflon-lined stainless steel autoclave. The solution was heated for 24 h at 180 °C. Brown colored nanobelts were formed and centrifuged in de-ionized water several times to remove any possible residual chemicals. The nanobelts were dispersed in de-ionized water and drop-cast ($30 \mu g cm^{-2}$ electrode area) onto the ITO substrate (Delta technologies, 15–25 Ω/sq). The nanobelts were then air-dried overnight at room temperature (as-synthesized samples) or annealed at 300 °C in air for 16 h (annealed samples).

X-Ray diffraction (XRD) patterns of the as-synthesized and annealed nanobelts were recorded with a Rigaku diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) over a 2θ angle ranging 10–70°. The size and morphology of the nanobelts were characterized by field emission scanning electron microscope (FESEM, JEOL 6340F) and transmission electron microscopy (TEM, JEOL 2010) with selected area electron diffraction (SAED). Thermogravimetric analysis (TGA) was carried out using TA Instruments TGA Q500 with a heating rate 10 °C min⁻¹ in N₂ environment. X-Ray photoelectron spectroscopy (XPS) measurements were made on a Kratos Analytical AXIS HSi spectrometer with a monochromatized Al K α X-ray source (1486.6 eV photons). Cyclic voltammetry was carried out in a typical three-electrode electrochemical cell using Autolab PGSTAT 302 with nanobelts/ITO glass as the working electrode, Ag/AgCl as the reference electrode and a Pt sheet as the counter electrode. The galvanostatic charge-discharge study was carried out in the same setup between $\pm 0.5 \text{ V}$ (vs. Ag/AgCl) for 0.1–50 A g⁻¹. Galvanostatic cycling testing was carried out for 1 V potential window at 10 A g⁻¹ in the same electrochemical setup. All the electrochemical measurements were carried out in one molar strength liquid electrolyte of lithium perchlorate in propylene carbonate (1 M LiClO₄/PC) at room condition.

Results and discussion

Structural characterization

Fig. 1 shows the X-ray diffraction (XRD) patterns of the as-synthesized and annealed products. The XRD pattern from the as-synthesized product exhibits a very strong intensity peak at 10.56° and another peak at 21.22°, corresponding to the 001/002 planes of the V_2O_5 -based hydrate with a lamellar structure and

Fig. 1 (a) X-Ray diffraction patterns of the as-synthesized and annealed nanobelts; (b) Thermogravimetric analysis (TGA) of the as-synthesized nanobelts from room temperature to 500 °C at 10 °C min⁻¹ heating rate.

a preferential orientation along the (001) crystal plane.⁵ In the lamellar hydrate, the water molecules are chemically bounded between the VO₅ square pyramid layers. The interlayer spacing of 8.36 Å can be calculated from the (001) reflection, which is close to the interlayer spacing of 8.75 Å in $V_2O_5 \cdot 0.5H_2O$ (PDF #40-1297). Dramatic changes were observed from the XRD pattern of the 300 °C air annealed sample, revealing the presence of a β -NaV₆O₁₅ or β -Na_{0.33}V₂O₅ phase (PDF #24-1155), which is a framework structure with a tunnel. This signifies that a phase change has occurred upon heat treatment at 300 °C, which is accompanied by water removal.

The removal of water can evidently be found from the thermogravimetric analysis (TGA) in Fig. 1b, where two significant weight losses are detected. The first weight loss between 120 °C to 150 °C is due to the removal of physical bounded surface water. The second weight loss around 200 °C to 300 °C can be attributed to the removal of chemically bounded water within the nanobelts. The amount of weight loss at this temperature region is found to be 5 wt%, which corresponds to 0.49H₂O and agrees well to the XRD analysis. The weight losses at different temperatures and the amount of chemically bounded water are consistent with the results found in V_2O_5 xerogels.⁶

X-Ray photoelectron spectra (XPS) wide range scan of the as-synthesized and annealed samples are shown in Fig. 2a. The

Fig. 2 XPS spectra of the as-synthesized and annealed nanobelts: (a) wide range scanning and (b) high resolution spectra of V 2p and O 1s.

survey spectra show the presence of elements of Na, V and O before and after annealing. This result confirms that Na has been doped into the nanobelts during the hydrothermal process. The binding energies (BE) of the V 2p_{3/2} and Na 1s are found to be 517.0 eV and 1070.5 eV, respectively, which are consistent with the reported BE of V(v)⁷ and Na.⁸ High resolution XPS data from the V 2p and O 1s region of the nanobelts are shown in Fig. 2b. The O 1s of the as-synthesized nanobelts exhibits two peaks, one at 529.9 eV and the other at 532.0 eV. The BE presented by the first peak (529.9 eV) can be associated to the metal–oxide bonding in the V₂O₅.^{7–9} The second peak (532.0 eV) can be related to the hydroxide bonding in the intercalated water molecule within the as-synthesized nanobelts.⁸ After heat treatment, the BE of the Na 1s and O 1s (metal–oxide bonding) increases to 1071.0 eV and 530.0 eV, respectively. On the other hand, the V 2p_{3/2} peak can be deconvoluted to two peaks after the heat treatment. The peak with higher BE of 517.3 eV can be attributed to V(v),^{7,9} while the peak at 516.0 eV can be related to V(IV).⁷ The results suggest that some electron densities have been transferred from Na and O ions to V(v) ions and reduced it to V(IV).^{7,10,11} The statistical distribution of V(IV) among the V sites in the framework structure has formed the electronic localization (within the VO₆ octahedra or VO₅ square pyramids layers)¹² and the Na sites within the tunnel of β-Na_{0.33}V₂O₅³ and resulted in the increase in the BE of V(v), which has also been found in previous reports.^{7,10} A O 1s peak at 532.0 eV is also observed in the annealed nanobelts (Fig. 2b), which corresponds to the hydroxide bonding. The presence of the peak could be due to the surface bound water on the annealed nanobelts. The

intensity of this peak is found to significantly decrease after heat treatment, which agrees well with the TGA result of water removal upon annealing.

The structure and morphology of the samples before and after heat treatment are investigated using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) and displayed in Fig. 3. The as-synthesized sample consists of interconnected nanobelts of 100–150 nm width, 50 nm thickness and more than 10 μm in length (Fig. 3a). The annealed nanobelts are shown in Fig. 3b for comparison. There is no structural breakdown or significant dimension variation observed in the annealed nanobelts after the water removal and phase change. The selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM) image of the annealed nanobelts in Fig. 3b inset show that the nanobelt is single crystalline with a clearly resolved lattice fringe of 7.2 Å spacing, which corresponds to the (002) plane of β-Na_{0.33}V₂O₅.

In summary, the hydrothermal process of the Na_{0.33}V₂O₅ nanobelts formation can be expressed as follows:

Fig. 3 Hydrothermally synthesized nanobelts: (a) as-synthesized nanobelts. Inset: lower magnification of the as-synthesized nanobelts; (b) 300 °C air annealed nanobelts. Inset: a HRTEM image of the annealed nanobelts with electron diffraction pattern inserted.

where Na was doped into the V_2O_5 nanobelts at elevated temperature during the hydrothermal process and the as-synthesized nanobelts are in the hydrated form. Similar doping effects into V_2O_5 can be found in ref. 13, where CTAB was doped into V_2O_5 during the hydrothermal process. It is worth noting that the NaCl used in this work also acts as the 1D structural growth directing agent or capping agent, as reported elsewhere in hydrothermally-formed oxide nanostructures.¹⁴

Upon annealing and water removal, the as-synthesized hydrated nanobelts are transformed from a layered structure with water intercalated between the VO_5 square pyramid layers to a $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ phase, which contains a tunnel within the 3D framework crystal structure. Thus, the annealing of the as-synthesized nanobelts (containing $0.49\text{H}_2\text{O}$) can be expressed as:

Electrochemical studies

Cyclic voltammetry was performed using 1.0 M LiClO_4 /propylene carbonate (PC) electrolyte to investigate the Li ion insertion/extraction behavior in the as-synthesized and annealed nanobelt network electrode without any binder. Well-resolved redox peaks are detected in the as-synthesized and annealed nanobelts at 5 mV s^{-1} scan rate (Fig. 4a). Insertion of Li ions in the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ involves the redox reaction of V and can be described as follows:

where x represents the Li intercalation level. The as-synthesized nanobelts contain one set of redox peaks at $-0.36\text{ V}/-0.21\text{ V}$ while the annealed nanobelts, $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$, contain two sets of redox peaks at $+0.08\text{ V}/+0.33\text{ V}$ and $-0.33\text{ V}/-0.21\text{ V}$. The difference in redox peaks could be due to the different crystal structure of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelts, which possess a 3D framework crystal structure with a tunnel. Three geometrically feasible intercalation sites have been identified along the tunnel,³ namely an intercalation site, M_1 , at the middle region of the tunnel, an eight coordinated site, M_2 , and a tetrahedral site, M_3 . Up to 1.6 moles of Na^+ ¹⁵ or Li^+ intercalation⁴ per $\text{Na}_{0.33}\text{V}_2\text{O}_5$ can be obtained by fully occupying the intercalation sites in three intercalation processes at different Li intercalation levels, x .^{4,15} The first intercalation occurs at $0 < x < 0.33$, which corresponds to half occupancy of Li in the M_3 site. The second intercalation occurs at $0.34 < x < 0.70$ with half occupancy of Li in the M_2 site. Lastly, the third intercalation occurs at $0.75 < x < 1.65$, which can be related to the filling of all the remaining vacancies in the M_1 , M_2 and M_3 sites. On the other hand, The Li intercalation levels among the three intercalations ($0.33 < x < 0.34$ and $0.70 < x < 0.75$) correspond to the transition region where Li intercalation continuously occurs. In the CV studies, our $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelt network shows an overall intercalation level, x , of 0.66 at 5 mV s^{-1} , which corresponds to an ion intercalation level up to the second intercalation step at $x < 0.70$. Moreover, two sets of redox peaks are observed in the CV curve, which can be attributed to the first and second intercalation step

Fig. 4 (a) Cyclic voltammograms of the as-synthesized and annealed nanobelts at 5 mV s^{-1} scan rate for $\pm 0.5\text{ V}$ vs. Ag/AgCl ; (b) the scan rate-dependence of the specific capacitance of the as-synthesized and annealed nanobelts ranging from 5 mV s^{-1} to 100 mV s^{-1} at $\pm 0.5\text{ V}$ voltage range. All cyclic voltammetry studies were carried out in 1 M LiClO_4 /PC electrolyte.

of $0 < x < 0.33$ and $0.34 < x < 0.70$, respectively.⁴ The third intercalation ($0.75 < x < 1.60$) is not detected in this study, likely due to the kinetics limitation in ion intercalation at $x > 0.70$, where the diffusion coefficient of Li ion for $x > 0.70$ is found to be 2 to 4 orders smaller than $x < 0.70$.⁴ This slow Li diffusion has resulted in the absence of the third intercalation in our CV testing at a scan rate of 5 mV s^{-1} .

Fig. 4b summarizes the specific capacitance (SC) of the as-synthesized and annealed nanobelts from scan rates of 5 mV s^{-1} to 100 mV s^{-1} for $\pm 0.5\text{ V}$ (vs. Ag/AgCl). The SC of the as-synthesized nanobelts ($\text{Na}_{0.33}\text{V}_2\text{O}_5 \cdot 0.49\text{H}_2\text{O}$) is found to be 191 F g^{-1} at 5 mV s^{-1} scan rate. On the other hand, the SC of the annealed nanobelts ($\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$) is found to be significantly enhanced to 320 F g^{-1} . Table S1 (ESI,† refs 16–18) summarizes the capacitive performances of crystalline V_2O_5 -based materials in the literature to date. The $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelts exhibit one of the highest SC among crystalline V_2O_5 -based nanostructures.

The SC of the as-synthesized and annealed nanobelts of 191 F g^{-1} and 320 F g^{-1} correspond to the overall Li intercalation levels of 0.38 and 0.66, respectively. This indicates that under the same scan rate and potential window ($\pm 0.5\text{ V}$), the electrochemical charge storage mechanism is different for the as-synthesized and annealed nanobelts. Hence, analysis of the scan rate-dependence of the current in CV was carried out to study the charge storage mechanisms and quantify the capacitance of each mechanism.

In general, the total stored charges within the metal oxide consist of three components: Li ion intercalation, charge-transfer at the oxide–electrolyte interface and electrical double layer. The first two components are Faradic reactions, which involve charge transfer and oxidation state variation. In contrast, the third component is a non-Faradic process, where the charges are stored within the electrical double layer. These three components exhibit different degrees of time dependence, which can be translated to a different scan rate dependence in the CV study. Li ion intercalation is a diffusion-controlled process and proportional to the square root of the scan rate.¹⁹ On the other hand, the charge-transfer process on the nanobelt surface and electrical double layer are surface-dependent processes with a capacitive response and directly proportional to the scan rate.²⁰ The current at a certain voltage, hence, is a contribution from the two mechanisms and can be expressed in terms of scan rate ν as:²¹

$$i(V) = k_1\nu + k_2\nu^{1/2} \text{ or } i(V)/\nu^{1/2} = k_1\nu^{1/2} + k_2 \quad (6)$$

where k_1 and k_2 are the proportionality constants for surface-dependent current and intercalation current. The surface-dependent capacitance and intercalation capacitance at a specific scan rate can hence be quantified by obtaining the k_1 and k_2 from the slope and the y -axis intersect point in the $i(V)/\nu^{1/2}$ versus $\nu^{1/2}$ plot. Fig. 5a shows the voltammetric responses for the as-synthesized and annealed nanobelts at 5 mV s^{−1} scan rate. The Li⁺ intercalation current dominates around the redox peak, while the surface-dependent current is the main contributor for the rest of the voltage range. The voltammetric surface-dependent capacitance and intercalation capacitance are quantified and normalized to the active mass, as shown in Fig. 5b. Surface-dependent capacitance is found to be the major component in both samples at 5 mV s^{−1}. This is due to the nanobelt network structure facilitating electrolyte penetration and providing a large oxide–electrolyte interfacial area at the reaction sites.

Fig. 5 (a) The voltammetric responses of the as-synthesized and annealed nanobelts at 5 mV s^{−1} scan rate. The surface-dependent current is shaded and the unshaded regions represent the intercalation current; (b) the capacitive contribution of the surface-dependent and intercalation capacitance in the as-synthesized and annealed nanobelts; (c) the scan rate dependence of the surface-dependent and intercalation capacitance in the annealed nanobelts (β -Na_{0.33}V₂O₅).

Comparing the as-synthesized and annealed nanobelts, the intercalation capacitance is doubled after the phase transition from layered structure to 3D framework structure, implying the enhancement in the diffusion-controlled intercalation process in the annealed nanobelts (β -Na_{0.33}V₂O₅). This enhancement can be attributed to the β -Na_{0.33}V₂O₅ crystal structure, which possesses a tunnel for fast ion diffusion and up to three different sites for ion intercalation. Fig. 5c shows the surface-dependent and intercalation capacitance of the annealed nanobelts from 0.5 mV s^{−1} to 20 mV s^{−1}. The surface-dependent capacitance is almost constant after 10 mV s^{−1} (due to the kinetic limitation in the interfacial charge transfer process)^{22,23} and dominates the overall capacitance at higher scan rates. On the other hand, the intercalation capacitance contributes the major portion of the overall capacitance at slow scan rates (*i.e.* less than 5 mV s^{−1}) and decreases with the increase in scan rate. These observations are in good agreement with the charge storage mechanisms as: (1) the surface reaction has a capacitive response with fast reaction kinetics, hence it dominates at fast scan rate and (2) the diffusion-controlled intercalation process is a slow reaction. It dominates at slow scan rates because longer times are required for effective ion intercalation.

Fig. 6a shows the galvanostatic charge-discharge study between ± 0.5 V vs. Ag/AgCl at 0.5 A g^{−1} for the β -Na_{0.33}V₂O₅ nanobelts. Symmetric charging and discharging curves are observed while two plateau regions are detected. These plateau regions can be attributed to the first and second intercalation step within the β -Na_{0.33}V₂O₅ nanobelts.^{4,15} The power density and energy density can be calculated from the charge-discharge plot, as follows:

$$P = \Delta E I / m \text{ (W kg}^{-1}\text{)} \text{ where } \Delta E = (|E_{\max} - E_{\min}|) / 2 \quad (7)$$

$$E = Pt / 3600 \text{ (W h kg}^{-1}\text{)} \quad (8)$$

where P is the power density, E is the energy density, $E_{\max}$ is the voltage at the end of charging (+0.5 V), while $E_{\min}$ corresponds to the voltage at the end of discharging (−0.5 V). I is the applied constant current, t is the charging or discharging time and m is the mass of the active material. The results are summarized in the Ragone's plot (Fig. 6b) for the current densities ranging from 0.1 A g^{−1} to 50 A g^{−1}. The highest energy density is found to be 62 W h kg^{−1} at 50 W kg^{−1}. Chen *et al.* have reported a V₂O₅/CNT network composite¹ with 16 W h kg^{−1} at a high power density of 75 W kg^{−1}. Similarly, Qu *et al.* have demonstrated an asymmetric supercapacitor of activated carbon and V₂O₅·0.6H₂O nanoribbons¹⁸ with 20.3 W h kg^{−1} at 2000 W kg^{−1}. As compared to these V₂O₅-based electrode, the β -Na_{0.33}V₂O₅ nanobelt network possesses higher energy density at a comparative power density. This observation shows that the β -Na_{0.33}V₂O₅ nanobelt network is more effective in energy storage under the same power density. As the charging/discharging rate (*i.e.* the current density) is increased, the Ragone's plot of the β -Na_{0.33}V₂O₅ nanobelt network reflects a gradual decline in energy density, but a fast increase in the power density. This superior performance can be explained by the results from the CV scan rate-dependence analysis. As shown in Fig. 5, two charge storage mechanisms contribute to the overall SC of the oxide. The ratio between the capacitances from these two mechanisms governs the overall reaction kinetics and hence affects the supercapacitor

Fig. 6 (a) A galvanostatic charge-discharge study of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelts between ± 0.5 V vs. Ag/AgCl at 0.5 A g^{-1} ; (b) Ragone's plot of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelt network; (c) the specific capacitance vs number of cycles of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelts at 10 A g^{-1} .

performances, such as the power density and energy density. At high scan rates, the energy storage is dominated by the fast surface reaction, which is capable of maintaining the charge storage amount at high power density. Hence, only slight degradation in the energy density is observed with the increase in current density and power density. However, significant degradation is detected after 5 kW kg^{-1} , where the energy density degrades from 47 W h kg^{-1} to 12 W h kg^{-1} . The degradation suggests that the kinetic limit of the surface reaction has been reached. Hence, the optimum operating condition of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelt network is around 5 kW kg^{-1} , where a high power density can be achieved with a small trade-off in the energy density (47 Wh kg^{-1}).

Fig. 6c shows the galvanostatic cycling of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelt network at 10 A g^{-1} for 4000 cycles. Degradation in SC occurs after 200 cycles and only around 34% degradation is observed after 4000 cycles. The initial increase in SC has been observed previously, but the reason is not yet fully understood.^{24–26}

Some possible reasons are due to the incomplete wetting at the initial cycles²⁵ or some vanadium is probably inaccessible for reduction at the starting cycle and is therefore not able to participate in the electrochemical process.⁷ Wei *et al.* have reported $\text{Cu}_{0.04}\text{V}_2\text{O}_5$ with 28% degradation in the energy storage after 60 cycles.²⁷ Zhan *et al.* have demonstrated the cycling testing on $\text{Cr}_{0.10}\text{V}_2\text{O}_5$ and 17% degradation in the energy storage was observed after 50 cycles.²⁸ As compared to these metal doped V_2O_5 , our $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelts are more robust and exhibit longer cycling lifetime. This could be due to the framework structure in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ which is superior in withstanding the stress induced during ion insertion and extraction.

Conclusion

In this communication, we have synthesized $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ phase network nanobelts by a hydrothermal process, followed by heat treatment at 300°C . The three dimensional framework crystal structure of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelt network electrode enables a high specific capacitance of 320 F g^{-1} and a Li intercalation level of 0.66 in 1 V potential windows. Two sets of redox peaks have been detected from the fabricated electrode, corresponding to the half occupancy at M_3 and M_2 intercalation sites along the tunnel. Detailed CV scan rate-dependent analysis has been carried out to quantify the surface-dependent and intercalation capacitive components. The $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelt network electrodes are shown to have been dominated by surface-dependent capacitance at scan rates higher than 10 mV s^{-1} , resulting in only a slight degradation in the energy density at a high power density and capable to deliver an energy density of 47 W h kg^{-1} at a power density of 5 kW kg^{-1} . Galvanostatic cycling testing has been carried out on the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelts with only 34% degradation in specific capacitance being observed after 4000 cycles. These superior performances suggest that the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ nanobelt network structure is a promising energy storage material for high energy and high power application.

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