VO₂ nanoflake arrays for supercapacitor and Li-ion battery electrodes : performance enhancement by hydrogen molybdenum bronze as an efficient shell material

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VO₂ Nanoflakes Array for Supercapacitor and Li-Ion Battery Electrodes: Performance Enhancement by Hydrogen Molybdenum Bronze As an Efficient Shell Material

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Abstract

Hydrogen molybdenum bronze (HMB) is electrochemically deposited as a homogeneous shell to VO₂ nanoflakes grown on graphene foam (GF), forming a GF+VO₂/HMB integrated electrode structure. Asymmetric supercapacitors based on the GF+VO₂/HMB cathode and neutral electrolyte are assembled and show enhanced performance with weaker polarization, higher specific capacitance and better cycling life than the unmodified GF+VO₂ electrode. Capacitances of 485 F/g (2 A/g) and 306 F/g (32 A/g) are obtained because of the exceptional 3D porous architecture and conductive network. In addition, the GF+VO₂/HMB electrodes are also characterized as the cathode of lithium ion batteries. Very stable capacities at rates up to 30 C are demonstrated for 500 cycles. This new type of shell material is expected to have its generic function in other metal oxide based nanostructures.

Conceptual Insights

Electrochemical supercapacitors/lithium ion batteries (LIBs) based on nanostructured metal oxides are receiving increasing attention. The performance of supercapacitors/LIBs is mainly determined by the electrochemical activity and kinetic feature of the electrode materials. High performance relies largely on scrupulous design of nano-architectures and smart hybridization of bespoke active materials. Also, a direct growth of aligned core/shell nanostructures on conductive substrates is highly desirable. Herein, we demonstrated a new shell material, hydrogen molybdenum bronze (HMB), for the construction of metal oxide based core-shell nanoarray electrodes and their enhanced electrochemical performances. The HMB shell may be a promising component in high-performance supercapacitors/LIBs because of its interesting properties with both high electrical conductivity and ionic conductivity.

Introduction

Supercapacitors, known as a high-power electrochemical device, emerge as a promising supplementary to the existing lithium ion batteries, or even a replacement in certain applications requiring fast charging and discharging processes.¹⁻⁵ The early studies of supercapacitors are heavily focused on carbon materials because of its chemical stability, low cost, high power density and long cycling life.^{3, 4, 6, 7} However, it is still beset with relatively low capacitance leading to low energy density. To achieve both high energy and power densities, researchers spare no efforts in searching metal oxide-based materials for pseudo-capacitor electrodes.⁸⁻¹¹ Compared with various forms of carbon that are used for electric double layer capacitors (EDLCs), pseudo-capacitive materials can store much more specific energy arising from electrochemical redox reactions. Up to now, various pseudo-capacitive materials (such as transition metal oxides/hydroxides, binary metal oxides, metal sulfides, conducting polymers)⁸⁻²³ have been explored and remarkable progress is reported in the single pseudo-capacitive material or their composite systems.

Of the candidate materials for pseudo-capacitors, neutral active materials are more preferable than the alkaline or acid ones because they are active in neutral electrolyte,⁹⁻¹¹ which will reduce the risk of corrosion of device components and be more compatible to commercial production. Vanadium oxides belong to this type. Currently, vanadium oxides have been widely investigated as electrode materials for neutral pseudo-capacitors by single nanoporous design,^{14, 24-28} and conductive or protective modification with reduced graphene oxides,^{29, 30} CNTs,³¹⁻³³ metal oxides,^{34, 35} and conducting polymers.^{36, 37} However, the majority of the prior research about vanadium oxides is focused on V₂O₅, while little attention is paid to VO₂, which is another stable neutral pseudo-capacitive material with high capacitance and excellent reactivity. To date, only VO₂/rGO,^{29, 30} VO₂/CNTs,³¹ and hydrogen treated VO₂ composite powder materials³⁸ have been reported with improved pseudo-capacitance. But most of the above VO₂ composite powder materials showed poor cycling stability with 30–35 % capacitance degradation after 1000 cycles. Hence, it becomes necessary to improve the long-term cycling performance and high rate capability

of VO₂. For this purpose, one promising approach is to design integrated structure together with appropriate surface engineering.

In recent years, the concept of lightweight electrodes has been widely adopted to boost the power/energy densities of both supercapacitors and batteries.³⁹⁻⁴² For this purpose, superlight and highly conductive substrates (such as graphene and their derivatives) are rationally combined with the electrochemical active materials, which eliminate the traditional polymer binders and post-preparation processing of electrode.⁴³⁻⁴⁶ To date, there is no report yet on integrating VO₂ to GF for application as supercapacitor electrodes. In this paper, we report our successful bottom-up growth of VO₂ nanoarray directly on GF as the integrated binder-free electrode for pseudo-capacitors as well as Li-ion batteries. In addition, it is found that such combination is still insufficient for high-rate performance because of a poor electrical conductivity of VO₂. It would be beneficial to form a thin and conductive sheath to the VO₂ to enhance the electron/ion transport kinetics and also structural stability.

Different from previous modification methods using carbon, conducting polymers and metals, in the present work, we adopt hydrogen molybdenum bronze (HMB) as a new conductive shell material. Our integrated electrode consists of GF supported VO₂/HMB core/shell nanoflake arrays. It is reported that HMB is not only an n-type semiconductor with high electrical conductivity up to 10³–10⁵ S/m, but also a fast ionic conductor with ionic conductivity of 0.001–0.01 S/m.⁴⁷⁻⁵¹ In view of these interesting properties, the HMB shell can provide a high conduction path for electrons, and in the meantime allows the transport of ions. In addition, the graphene foam and HMB can work together to afford a three-dimensional conductive network for fast charge collection. To prove the advantage of this design, we characterize the integrated electrodes for both asymmetric supercapacitors and lithium ion batteries. For both functions, evidently improved performance with higher specific capacity and better cycling life especially at high rates (up to 30 C) are achieved compared to the unmodified counterpart (GF+VO₂). Our research provides a new surface modification method for electrochemical active materials for applications in batteries, oxygen reduction reaction and catalysis.

Experimental

Preparation of GF+VO₂ Nanoflake Arrays. Firstly, 1.5 mmol V₂O₅ powder (Sigma-Aldrich) and 5 mmol H₂C₂O₄ powder (Sigma-Aldrich) were dissolved with 10 mL of distilled water at 75 °C until a dark blue solution was formed. Then 1.5 mL of 30 % H₂O₂ and 30 mL ethanol was added and kept continuously stirring for about 20 min. The obtained solution was transferred into 50 mL Teflon-lined stainless steel autoclave liners. And then, one piece of 3D GF (~0.6 mg cm⁻², prepared by chemical vapour deposition method according to our previously results^{52, 53}) was immersed into the reaction solution. The autoclave liners was kept at 180 °C for 3 h, and then the sample was collected and rinsed with ethanol and distilled water in turn for several times. Finally, the samples were annealed at 400 °C in Ar+H₂ (5 %) for 2 h to obtain VO₂ nanoflakes array (~0.8 mg cm⁻²).

Preparation of GF+VO₂/hydrogen molybdenum bronze (HMB) Core/Shell Arrays. The GF supported VO₂ nanoflakes array were acted as the skeleton for the growth of HMB shell. The electrolyte for electro-deposition of HMB was obtained by dissolving 0.5 g Na₂MoO₄ and 0.6 g H₂O₂ in 100 mL DI water, and adjusted with pH value of 3 by 0.1M H₂SO₄. The HMB layer (~10 % weight of

VO₂ arrays, the weight was determined using an analytical balance with high measure resolution 0.001 mg) was deposited by applying two-electrode constant cathodic current density of 0.5 mA cm⁻² and followed by a heat treatment at 150 °C in vacuum for 2 hours. The above VO₂ nanoflakes array worked as the working electrode and a Pt foil as the counter-electrode. As a comparison sample, HMB was also electrodeposited directly on GF.

Preparation of GF+VO₂/hydrogen tungsten bronze (HWB) Core/Shell Arrays. We also prepared GF supported VO₂/HWB core/shell arrays by the same methods using Na₂WO₄ as the starting material.

Characterization of GF Supported VO₂/HMB Core/Shell Arrays. The crystal structures of the samples were identified using X-ray diffraction (XRD, RigakuD/Max-2550 with Cu K α radiation). Raman spectra were obtained with a WITec-CRM200 Raman system (WITec, Germany) with a laser wavelength of 532 nm (2.33 eV). The Si peak at 520 cm⁻¹ was used as a reference to calibrate the wavenumber. The morphologies of the samples before and after cycles were characterized by field emission scanning electron microscopy (FESEM, FEI SIRION). The nanostructures of the samples were investigated by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F) operating at 200 kV. The XPS measurements were performed by a VG ESCALAB 220i-XL system using a monochromatic Al K α 1 source (1486.6eV). FT-IR spectra were recorded by a Perkin-Elmer 1760X FT-IR spectrometer with grinding the composite film into powder and diluting in KBr.

Electrochemical Measurements of GF Supported VO₂/HMB Core/Shell Arrays. Electrochemical measurements were performed in asymmetric supercapacitors with GF+ VO₂/HMB as the cathode, commercial activated carbon as the anode and 1 M K₂SO₄ as the electrolyte. The load weight of VO₂ was ~0.8 mg/cm² and the HMB layer was about 10 % weight of VO₂ arrays. Electrochemical performance was evaluated by galvanostatic charge/discharge tests (LAND battery testing system) and cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) measurements (CHI electrochemical potentiostat). CV measurements were carried out at between 0.3 and 1.5 V at 25 °C. For EIS, the amplitude of the sine perturbation signal was 5 mV, and the frequency was scanned from the highest (100 kHz) to the lowest (10 mHz). In this experiment, the designed capacitance of cathode and anode in the device was almost the same, so the specific capacitance (C_g) of the cathode could be calculated as follows: $C_g = 2C/M = 2I\Delta t/M\Delta V$, where C was the measured capacitance for the two-electrode cell, I (mA), Δt (s), ΔV (V) and M (mg) represented discharge current, total discharge time, potential drop during discharge, mass of active materials in cathode, respectively. The energy density (E) of the supercapacitor was calculated by the following equation: $E = 1/2 C_s \times (\Delta V)^2$, where C_s was the specific capacitance of device, and ΔV is the voltage range. The power density (P) was calculated using the following equation: $P = E/\Delta t$, where E and Δt was the energy density and discharge time, respectively.

Results and discussion

Fabrication and characterization of the integrated electrode

The fabrication process of GF supported VO₂/HMB core/shell nanoflake arrays is shown in Fig. 1a, d and g. Based on the CVD-derived GF substrate (Fig. 1a-c), the VO₂ nanoflake arrays are grown

onto both sides (inner and outer sides) of the GF via a facile solvothermal method (SS). This double-side growth can effectively improve the load weight of active materials. Shown in the cross-sectional image, the GF is completely covered by the quasi-vertical VO₂ nanoflakes with diameters of ~200 nm (Fig. 1d-f). Interestingly, the VO₂ nanoflakes show a star-fruit shape similar to

Fig. 1 (a, d, g) Schematic illustration of fabrication process of graphene foam (GF) supported VO₂/HMB core/shell arrays. SEM images of (b, c) GF, (e, f) VO₂ nanoflake arrays on GF (cross-sectional image and fine structure in inset) and (h, i) VO₂/HMB core/shell arrays on GF (cross-sectional image and fine structure in inset).

the V₂O₅ nanoflakes that were grown using similar method.²¹ After the subsequent electro-deposition (ED) of HMB shell, the core/shell nanoflake arrays are formed and the whole 3D porous structure is well preserved (Fig. 1g-i). In our case, the shell thickness is about 15 nm after ED at 0.5 mA cm⁻² for 1200 s. The shell thickness of HMB on VO₂ can be tuned by the ED time. The involved reactions of SS and ED are very complex. In the SS reaction, V₂O₅ powder, H₂C₂O₄ powder and H₂O₂ are used as the starting materials. The simplified formation reactions of SS-VO₂ are probably as follows.

During the annealing process,

It is noticed that a characteristic blue color appears during the ED of HMB. The electro-deposition reactions of the HMB shell can be simplified as follows.

Further insight into the microstructures and phases at different stages is obtained by TEM and HRTEM. The GF exhibits homogeneous texture with scrolling edge and a lattice spacing of ~

0.34 nm corresponding to (002) planes of graphitic carbon (JCPDS 75–1621) (Fig. 2a). The TEM images indicate that the as-prepared VO₂ nanoflakes are quite smooth and the average diameter is about 200 nm (Fig. 2b). Additionally, a single crystalline selected area electronic diffraction (SAED) pattern of VO₂ nanoflakes is observed. Furthermore, the measured lattice spacing of 0.58 nm is consistent with the (200) planes of VO₂ (B) phase (JCPDS 81-2392) (Fig. 2b). For the core/shell nanoflakes, a rougher surface is noticed. From the HRTEM image, it is seen that the HMB shell thickness is ~15 nm. In our TEM examination, some of the HMB shells are amorphous, in general agreement with results in literature.^{48, 49, 51} However, as we conducted post-annealing (150 °C in vacuum for 2 h), certain level of crystallization can be observed as revealed by incomplete fringes in Fig. 2d. Such core/shell nanoflake structure is also demonstrated by the energy dispersive X-ray spectroscopy (EDS) elemental mapping of O, V and Mo (Fig. 2e) and EDS spectrum (Fig. S2). The phase evolution is monitored by the XRD measurement (Fig. 3a). Comparing the XRD patterns of different products, it is observed that, expect for the peaks of GF, the strong diffraction peaks can be assigned to the monoclinic phase of VO₂ (B) (JCPDS 81-2392). No peaks of HMB are observed because of the small thickness and partial crystallization.

Fig. 2 TEM-HRTEM characterizations: (a) GF (HRTEM image in inset); (b) VO₂ nanoflake (SAED pattern and HRTEM image in inset); (c, d) VO₂/HMB core/shell nanoflake (SAED pattern and HRTEM image in inset); (e) EDS mapping of Mo, O and V.

To further verify the components of the core/shell structure, FTIR and XPS measurements were conducted. It is seen that the characteristic FTIR peak of VO₂ is located at 539 cm⁻¹,^{24, 30} while the HMB shows typical peaks at around 766 and 987 cm⁻¹ (Fig. 3b).⁴⁸ The core/shell VO₂/HMB contains all the above typical vibration peaks of both VO₂ and HMB. In addition, the composition is also supported by the XPS analysis (Fig. 3c and d). As shown in Fig. 3c, the XPS peaks of V2p and O1s are observed. For the V 2p spectra, the binding energy separation between core levels V 2p_{1/2} (524.4 eV) and V 2p_{3/2} (516.9 eV) is ~7.5 eV, which matches with the electronic states of VO₂.³⁰ For the Mo 3d core level, a mixed valence of Mo⁶⁺ and Mo⁵⁺ exists (Fig. 3d). These are the typical electronic states of HMB.⁵¹ Two peaks at 535.8 and 532.7 eV are assigned to Mo⁶⁺ (3d_{3/2}) and Mo⁶⁺ (3d_{5/2}), and 534.6 and 531.6 eV are due to Mo⁵⁺ (3d_{3/2}) and Mo⁵⁺ (3d_{5/2}). In O1s spectra (inset in Fig. 3c), the peak 530.5 eV is related with the metal-O bond (V-O and Mo-O). The small peak at 532.5 eV is associated with H₂O adsorbed on the surface.⁵⁴ Based on the results above, it is justified that the HMB is

successfully coated on the surface of VO₂ forming core/shell arrays on GF substrate.

Fig. 3 (a) XRD patterns and (b) FTIR spectra of GF, GF+VO₂ and GF+VO₂/HMB. (c) XPS spectra: (c) V (2p) and O (1s) regions of VO₂/HMB; (d) Mo (3d) spectra.

Using similar electro-deposition method, we also prepared GF supported VO₂/HxWO₃ core/shell arrays with different starting precursors (Fig. S3). A similar morphology is observed for the GF+VO₂/HxWO₃. In addition, in our experiment, a noteworthy phenomenon is that the VO₂ nanoflake arrays act as a strong backbone for the growth of HMB. In a control experiment, the single HMB could not be uniformly electrodeposited directly on the GF substrate; instead, it forms a dense but discontinuous film (Fig. S4). This is indicative of a poor adhesion of HMB film on GF. Hence, the nanostructure 3D surfaces of VO₂ nanoflakes provide effectively lower-energy sites for the preferable anchoring of HMB layer. This perfect matching allows the construction of VO₂/HMB core/shell nanoflakes array electrode for ultra-stable and high-rate electrochemical energy storage. Last but not least, there is no principle limit for the core oxide materials to VO₂; other pseudo-capacitive materials such as MnO₂ should also apply.

Performance enhancement as Supercapacitor electrodes

In order to evaluate the electrochemical properties of GF+VO₂/HMB core/shell arrays, asymmetric supercapacitors (GF+VO₂/HMB as the cathode and activated carbon as the anode) have been assembled and comprehensively characterized. First, in the cyclic voltammograms (CVs) at various current densities (Fig. 4a and S5a, b), both GF+VO₂/HMB and the uncoated GF+VO₂ electrodes show weak redox peaks and their CV behavior is similar to quasi-rectangular CV curves of EDLCs.¹¹ It should be highlighted that the scanning rates of CV for supercapacitors need to be higher than 10 mV s⁻¹; scanning rates lower than this are less meaningful for supercapacitors,¹ as they do not reflect the high charge/discharge characteristics. In our integrated electrode, VO₂ plays a dominating role in the electrochemical energy storage. The charge storage mechanism of VO₂ in the neutral K₂SO₄ electrolyte involves incorporation of electrolyte cation K⁺,

Meanwhile, the K⁺ ions could be incorporated in the HMB according to the simplified reaction:^{10, 55, 56}

However, the HMB mainly serves as a transport channel for ions between the electrolyte and inner VO₂ core; The ion storage contribution is very small because of its low weight ratio in the composite; which can be seen from the CV curve of GF+HMB (Fig. 4a). It is well accepted that the specific capacitance and electrochemical activity of active materials are proportional to the enclosed CV area. From the CV experiments, a higher current density and a bigger CV area are noticed for the GF+VO₂/HMB than the uncoated GF+VO₂ electrode at the same current density (Fig. 4a).

Fig. 4 Electrochemical characterizations of asymmetric supercapacitors with GF+VO₂ and GF+VO₂/HMB as the cathode material (activated carbon as anode for both cells): (a) CV curves at the scanning rate of 25 mV/s; (b) Nyquist plots at fully discharge state; (c) Charge/discharge curves at the current density of 2 A/g; (d) Specific capacitances; (e) Cycling life at different current densities.

The improved reaction reactivity of the GF+VO₂/HMB electrode is supported by the electrochemical impedance spectrum (EIS) test (Fig. 4b). Comparatively, the GF+VO₂/HMB electrode has lower electrode series resistance (derived from the high frequency intersection of the Nyquist plot in the real axis) and smaller semi-arc originated from the charge transfer process of Faradaic reactions in the high-medium frequency region. It is indicated that the GF+VO₂/HMB electrode has faster reaction kinetics than the GF+VO₂ counterpart due to more efficient conductive network constructed by the HMB shell. Fig. 4c shows the typical charge/discharge profiles of two electrodes at 2 A/g. The GF+VO₂/HMB electrode exhibits lower charge voltage and higher discharge voltage than the GF+VO₂ electrode, indicating that the former has a smaller polarization during the charge/discharge process, supported by the voltage drop at the initial discharge

process. Note that the initial voltage drop of the GF+VO₂/HMB electrode (0.5 V) is much smaller than the GF+VO₂ electrode (0.93 V). The energy density (E) of supercapacitor is $E=1/2CU^2$, where C is capacitance and U is the discharge voltage. Generally, a high polarization leads to a low discharge voltage, which will decrease the energy and power densities. In our experiment, the integrated conductive network helps to transport the charge efficiently and diminish the polarization, resulting in higher discharge voltage.

Discharge curves and corresponding specific capacitances of two electrodes are presented in Fig. S5c, d and 4d. The GF+VO₂/HMB electrode exhibits much better high-rate capability with specific capacitances from 485 F/g (2 A/g) to 306 F/g (32 A/g) (based on the mass of cathode), higher than those of the GF+VO₂ (350 F/g at 2 A/g and 170 F/g at 32 A/g). The obtained values are also higher than CNT/GF (100 F/g at 1 A/g),⁵⁷ ZnO/GF (316 F/g at 6 A/g),⁵⁸ and PANI/GF (346 F/g at 4 A/g),⁵⁹ and other vanadium oxides powder counterparts such as CNTs/VO₂ (250 F/g at 2 A/g),³¹ hydrogen treated VO₂ (300 F/g),³⁸ and RGO/VO₂ composites (225 at 1 A/g).^{29, 30} The corresponding comparison is shown in Table S1 in the supporting information. Additionally, we also tested the thickness effect of HMB on the capacitance. Fig. S5e shows the discharge curves of GF+VO₂/HMB electrodes with four different HMB thicknesses (~5, ~10, ~15, and ~20 nm corresponding respectively to electrodeposition time of 400, 800, 1200, and 1600 s). It is found that, while the difference is insignificant, the electrode with 15 nm-HMB shows the highest capacitance (450 F/g) compared to other thicknesses (409 F/g for 5 nm-HMB, 420 F/g for 10 nm-HMB and 426 F/g for 20 nm-HMB). The power and energy densities of the assembled asymmetric supercapacitor were also calculated (based on the mass of cathode, separator and anode). Fig. S5f shows the Ragone plot (energy density vs. power density) measured in the voltage window of 0.3 to 1.5 V at different current densities. The supercapacitor with GF+VO₂/HMB presents an energy density range from 14.5 to 9.2 Wh/kg when the power density changes from 0.72 to 11.5 kW/kg, superior to the GF+VO₂ (from 10.5 to 5.1 Wh/kg).

These results reveal the high specific capacitance and notable high-rate capability of the GF+VO₂/HMB electrode for high-performance supercapacitors. The enhanced properties of GF+VO₂/HMB electrode mainly come from the integrated porous conductive architecture. The VO₂ nanoflakes are not only directly grown on the GF substrate, but also homogeneously wrapped by thin HMB shell, which can provide both high electron and ion transfer path. This intimate binding and conductive network can provide fast and short electron/ion transfer path, thus leading to fast reaction kinetics with good high-rate performance. Meanwhile, "dead" mass could be avoided and most of the active materials are electrochemically active in the integrated electrode. Furthermore, the 3D porous structure with large inner space and reaction surface could facilitate the efficient contact between active materials and electrolytes, leading to improved utilization of active materials and high capacitance.

Cycling stability is a critical parameter for high-performance supercapacitors. Fig. 4e presents the cycle characteristics of two electrodes at 2 and 12 A/g. During the cycle processes, the GF+VO₂/HMB exhibits higher specific capacitance and better cycling stability than the GF+VO₂. The GF+VO₂/HMB electrode shows stable capacitances of 473 F/g at 2 A/g after 5000 cycles and 340 F/g at 12 A/g after 11000 cycles, respectively, and no obvious capacitance decrease is observed. These values are much higher than the corresponding GF+VO₂ electrode (333 F/g at 2 A/g and 163 F/g at 12 A/g). As the cycle life is highly related with the structural stability of the electrode, we disassembled the supercapacitors to

check the morphology of the electrodes after 11000 cycles (Fig. S6). It is found that the GF+VO₂/HMB electrode preserves its array structure, whereas the uncoated nanoflakes in the GF+VO₂ electrode are prone to aggregate into bundles and tend to collapse. Therefore, it is inferred that the introduction of HMB shell not only provides an electrical conductive path, but also helps to alleviate the structure damage.

Li-ion storage properties of VO₂/HMB core/shell nanoflake electrode

To further demonstrate the potential application of the GF+VO₂/HMB electrode, we also tested its electrochemical properties as cathode of lithium ion batteries. Fig. 5a shows CV curve of the GF+VO₂/HMB electrode at a scanning rate of 0.1 mV s⁻¹ between 1.5 and 3.5 V at the second cycle. The simplified reaction between lithium ion and VO₂ is expressed as follows.^{21, 60, 61}

Fig. 5 Electrochemical characterizations of the GF+VO₂/HMB electrode as cathode of lithium ion battery: (a) CV curves at the scanning rate of 0.1 mV/s at 2nd cycle; (b) Charge/discharge curves at the different current densities and (c) rate capability; (d) Cycling life at different current densities.

In our case, two pairs of redox peaks are noticed in the CV curve, both of which can be ascribed to the Li-ion reaction with VO₂. In comparison, the CV intensity of the HMB along (namely, GF+HMB) is very small. This means a negligible CV contribution (lower than 1.5 %) and subsequent capacity contribution from HMB. During the anodic process, two peaks at about 2.30 and 2.71 V are observed corresponding to the desertion of lithium from host structures. For the cathodic process, there are two reduction peaks at 2.42 and 2.07 V attributed to the insertion of lithium into VO₂. However, the detailed reaction mechanism between VO₂ and lithium ion is still unclear. One or two redox peaks can be observed in their CV curves according to the literature.^{21, 60-64} This different CV behavior is supposed to be associated with the multiple reversible insertion/desertion of lithium in the VO₂ host structure.

The charge/discharge curves of the GF+VO₂/HMB electrode at different rates and high-rate capability are shown in Fig. 5b and c. The charge/discharge plateaus observed are in consistent with the CV result. The GF+VO₂/HMB electrode delivers a specific capacity of 415 mAh g⁻¹ at 0.2 C and 380 mAh g⁻¹ at 1 C. Impressively, the GF+VO₂/HMB electrode exhibits excellent high-rate capability with specific capacity of 280 mAh g⁻¹ at 10 C and 219 mAh g⁻¹ at 30 C, respectively. The corresponding charge/discharge coulombic efficiency is about 99 %. The obtained values are much higher than the commercial LiCoO₂,⁶⁵ LiFePO₄,⁶⁶ LiMnO₄,⁶⁷ and other VO₂ powder materials,⁶¹⁻⁶⁴ and comparable to graphene/VO₂ ribbon.⁶⁰ It should be noted that when the current rate is decreased to 0.2 C, a high discharge capacity of 415 mAh g⁻¹ can be regained. In addition, the GF+VO₂/HMB electrode presents superior high-rate cycling stability (Fig. 5d). After 500 cycles, a high reversible capacity of 305 mAh g⁻¹ at 5 C (a capacity retention of 91.8 %) and 209 mAh g⁻¹ at 30 C (a capacity retention of 95.4 %) is obtained, respectively, superior to those VO₂ powder materials.⁶¹⁻⁶⁴ Based on the results above, it is justified that integrated electrode design and HMB modification can work together to achieve high-performance cathode for electrochemical energy storage devices.

Conclusions

In conclusion, we have demonstrated a new shell material, hydrogen molybdenum bronze (HMB), for the construction of metal oxide based core-shell nanoarray electrodes and their enhanced electrochemical performances. The HMB shell is proven to be a promising shell material for high-performance supercapacitors because of its interesting properties with both high electrical conductivity and ionic conductivity. Due to the unique composition and integrated conductive architecture, the GF+VO₂/HMB integrated electrode shows excellent electrochemical performances in asymmetric supercapacitors with higher capacitance, weaker polarization, and better cycling performance as compared to the GF+VO₂ electrode. Moreover, the GF+VO₂/HMB integrated electrode is also demonstrated as a superior cathode of lithium ion battery with noticeable high-rate capability. Prospectively, the electrodeposited HMB can be an effective shell material for a wide range of metal oxides to enhance their performance in batteries, supercapacitors and fuel cells.

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Electronic Supplementary Information (ESI) available: [Materials preparation and synthetic details. Fig. S1, 2: Photo and EDS spectrum of GF supported VO₂/HMB core/shell array electrodes. Fig. S3: SEM-TEM images of GF supported VO₂/HxWO₃ core/shell arrays. Fig. S4: SEM images of GF supported HMB film. Fig. S5: Electrochemical characterizations of asymmetric supercapacitors with GF+VO₂/HMB and GF+VO₂ as the cathode material. Fig. S6: SEM-TEM images of two electrodes after 11000 cycles. See DOI: 10.1039/c000000x/]

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