A Novel Flexible Hybrid Battery–Supercapacitor Based on a Self-Assembled Vanadium-Graphene Hydrogel

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A novel flexible hybrid battery–supercapacitor device is proposed consisting of high specific surface area electrodes paired with an electrolyte, which contains a redox species that can exist in more than two oxidation states. The two initially equal half-cells of the device consist of a reduced graphene oxide hydrogel which encapsulates vanadium ions, synthesized with a single-step method. During charge, the oxidation state of the vanadium ions changes, resulting in two half-cells with different potentials which considerably increases the energy density. The achieved maximum capacity of more than 225 mAh g⁻¹ is roughly eight times higher than that of comparable graphene hydrogel supercapacitors without vanadium content, but the potentiostatic charging time is only double. Operated as a supercapacitor, it retains 95% of the initial capacitance over 1000 cycles. As battery, the losses are more significant, retaining around 50% of the initial capacity. However, these losses during battery operation can be almost entirely restored by electric measures. The vanadium ion addition also improves the self-discharge characteristics of the device. Moreover, the self-discharge does not permanently damage the hybrid device since both half-cells initially consist of the same vanadium graphene hydrogel and discharging resets it to initial conditions.

1. Introduction

Batteries and supercapacitors are deemed as reliable power sources for a multitude of mobile electronics devices ranging from cell phones, laptops to (hybrid) electric vehicles.^[1–3] They are also considered as a key technology for portable and wearable electronics which require lightweight, flexible, and highly efficient energy storage systems.^[4–6] Although batteries can store a high amount of specific energy, they deliver electricity at rather low current densities due to their intrinsically low power-handling capabilities.^[7,8] Another main disadvantage of batteries is their relatively short cyclic durability.^[7,8] In contrast, supercapacitors can provide high specific power with outstanding cyclic stability and efficiency.^[9,10] Various types of supercapacitors are reported in the literature, many of which are based on carbon electrodes,^[11] including activated carbon,^[12] carbon nanotubes

(CNTs),^[13] carbide-derived carbon,^[14] onion-like carbon,^[15] and graphene-based materials.^[16,17] However, their application is limited due to their low energy storage capacities compared to those of batteries. In addition, supercapacitors usually suffer from a relatively high self-discharge rate.^[9,10] Functionally, supercapacitor electrodes can be combined with battery electrodes to develop hybrid devices with desirable specific energy capacities and power densities.^[18–21]

From a general perspective, a hybrid battery–supercapacitor is defined as a device using two different charge storage mechanisms, i.e., electrical double layer (EDL) formation and faradaic reaction. The first mechanism is based on the potential difference between electrode and electrolyte. Ions in the vicinity of the electrode are, depending on their charge, attracted or expelled due to electrostatic forces. This results in a thin interfacial layer—the EDL—where the electroneutrality of the liquid is violated, or in other words, where the charges in the liquid are separated. The second mechanism is also based on the potential difference between electrode and electrolyte. However, additional to the EDL formation, a (electrochemical) redox reaction takes place where charge is transferred across the electrode–electrolyte interface. According to this definition, so-called pseudocapacitors are not hybrid battery–supercapacitor systems since they only employ faradaic adsorption of ions on a decorated surface of pseudocapacitive material such as RuO₂, MnO₂, and V₂O₅.^[22] Over the last decades, several hybrid battery–supercapacitor systems were introduced. These can be classified based on their level of hybridization as full-cell or electrode level hybridization.^[23] Devices combining a faradaic electrode along with a supercapacitive electrode are considered full-cell hybrids.^[24,25] For example, a full-cell hybrid device can use a zinc or lithium-based electrode as the faradaic electrode and activated or microporous carbon as the supercapacitor electrode.^[26–28] Due to the combined charge storage mechanisms, hybrid devices provide different specific charge storage and power handling characteristics compared to the corresponding supercapacitor and battery, respectively.^[29–31] The concept of hybridization can be extended to the electrode level by the combination of an electrochemical reaction of an redox-active electrolyte with the intrinsic EDL formation at a high specific surface area electrode.^[32–35] Here, it is beneficial that the redox couples remain dissolved in the electrolyte and

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the electrode only serves as electron donor/acceptor. Then, the charge storage capacity is not limited by the electrode material. Additionally, the electrodes do not experience a significant structural change during charge/discharge cycles leading to exceptional cyclic stability.^[23] Several redox couple electrolytes can be employed for such hybrid devices. Akinwolemiwa et al. categorized these redox electrolytes based on their electrical charge into cationic, anionic, and neutral redox couples.^[36] Neutral redox couples, such as hydroquinone, are less desirable since they do not participate in the EDL formation.

Currently, hybrid devices consist of either two equal hybrid electrodes (one redox couple with two redox states), two different hybrid electrodes (two redox couples with two redox states) or a combination of a hybrid electrode with a conventional (supercapacitor or battery) electrode.^[23] Generally, devices with two different electrodes offer higher power densities since they benefit from the different Galvani potentials, which mitigates the potential drop during discharge. These devices, however, feature performance losses over time due to the crossover of ions from one electrode compartment to the other. Separation of the electrode by an ion exchange membrane reduces the ion crossover,^[26–28,32–35] but this so-called redox shuttling still results in relatively short self-discharge times.

In this work, we propose a novel flexible hybrid device with high specific surface area electrodes paired with an electrolyte, which contains redox species that can exist in more than two oxidation states.^[37] Such a design has several advantages: The high specific surface area of the electrode and the ion content of the electrolyte leads to considerable EDL capacitances. The use of species with more than two redox states also offers considerable benefits and unique characteristics compared to other designs. The device is made from equal half-cells, which considerably simplifies manufacturing. Charging the device converts the half-cells into two (dissimilar) hybrid electrodes which encapsulate electrolytes with different oxidation states and therefore different Galvani potentials. The different electrode potentials induce a cell potential which increases the energy content and power density of the cell. The cell can also be easily regenerated in the event of self-discharge due to redox shuttling, since ions that cross the separator do not permanently harm the cell; they are converted to the desired redox states during the next charge cycle. Likewise, the simplicity of the cell design allows for restoration of cycle losses by simple (electrical) measures.

In detail, such a hybrid battery–supercapacitor can be realized by combining the high capacitance characteristics of a hydrogel made from reduced (multilayer) graphene oxide (rGO) and the ability of vanadium to exist with different oxidation states. This combination leads to a considerably higher specific capacity ($\approx 200 \text{ mAh g}^{-1}$ at 1 A g^{-1}) compared to other reported graphene hydrogel supercapacitors (27.7 mAh g^{-1} at 1 A g^{-1})^[38] and features unique power-handling capabilities which makes it suitable for a wide range of applications. At low current densities (relatively low power densities), this power source behaves like a battery. It stores electrical energy by means of the redox reaction of the vanadium species that are incorporated in the graphene hydrogel in addition to the EDL formation at the interface of the electrolyte and the graphene

sheets. At high current densities, this power source functions as a supercapacitor in which the energy is mainly stored in the EDL. In other words, the time scale of the charge transfer process controls the distribution between energy transferred by the EDL (capacitance) and the redox reactions (capacity). This behavior is in contrast to the existing hybrid systems, where the contribution of the faradaic reactions mainly depends on cell potential.^[23] This unique feature allows for fast charging and makes the device well-suited for both energy and power-based applications. The utilization of the vanadium redox electrolyte also significantly improves the self-discharge characteristic of the device compared to conventional supercapacitors. Furthermore, there are indications that capacitance losses during self-discharge are partially converted into (battery) capacity. In this device, all the charge storage phenomena take place at the surface of the rGO hydrogel matrix without any structural changes. This not only increases the durability of the electrodes but also preserves its flexibility which makes our device an excellent candidate for flexible energy storage applications.

2. Results and Discussion

The vanadium-graphene hydrogel (V-GHG) is synthesized through the single-step hydrothermal thermal reduction of a homogenous mixture of a concentrated GO (16 mg mL^{-1}) dispersion and vanadyl sulfate solution (2 M). In detail, vanadyl sulfate powder ($\text{VO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$) is dissolved in the 2 M sulfuric acid supporting electrolyte, aided by sonication at 50°C . This results in an electrolyte solution comprising 2 M of VO^{2+} . In the next step, 20 mL of the concentrated GO dispersion is mixed with 5 mL of the VO^{2+} -electrolyte by vigorously stirring for 5 min . The solution is transferred into a Teflon-lined autoclave for a hydrothermal reduction at 180°C for 16 h . The autoclave is then cooled down to room temperature and the as-prepared V-GHG is removed with tweezers (Figure S1, Supporting Information). The concentration of VO^{2+} in the electrolyte is found to be 0.4 M based on potassium permanganate titration. The lower concentration is a result of the dilution of the 2 M vanadium solution with the concentrated GO dispersion. The specific surface area of the V-GHG matrix is determined using the methylene blue dye adsorption method (Figure S3, Supporting Information). Typically, specific areas of $1335 \text{ m}^2 \text{ g}^{-1}$ are measured, which is similar to the typical surface area of an equivalent hydrothermally reduced GHG ($1286 \text{ m}^2 \text{ g}^{-1}$, Figure S4, Supporting Information) made without the addition of vanadium.

For material characterizations, the sample is first rinsed with deionized water to remove the excess electrolyte at the surface of the hydrogel and then dried (Figure S2, Supporting Information). The morphology of the dried V-GHG is further investigated by scanning electron microscopy (SEM) at different magnifications ranging from 50 to $5 \mu\text{m}$ (Figure 1a–c). These images reveal that the dried V-GHG has an interconnected 3D network consisting of porous walls. The pore sizes range from sub-micrometers to several micrometers, similar to those reported in refs. [38–40]. The larger magnifications in Figure 1b,c show that the porous walls are mainly composed

Figure 1. a–c) Cross-sectional SEM images of the dried V-GHG sample with different magnifications. d) XRD patterns of dried V-GHG, rGO, and vanadyl sulfate powder samples.

of ultrathin layers of stacked rGO. In addition to the wall-layers, some filaments are observed in the outer part of the V-GHG matrix. These filaments originate from the precipitation of vanadyl sulfate salt, which occurs during solvent evaporation. The structure and composition of the dried V-GHG is investigated by X-ray diffraction (XRD) via Cu- K_{α} radiation ($\lambda = 1.542 \text{ \AA}$). The results are compared to the spectra of a dried hydrothermally reduced GHG and of vanadyl sulfate powder ($\text{VOSO}_4 \cdot x\text{H}_2\text{O}$) (Figure 1d). We observe a broad diffraction peak at a diffraction angle of $2\theta = 23.71^\circ$ in the rGO spectrum indicating the existence of π - π stacking between the graphene layers, which is similar to results reported in refs. [38–41]. The peaks of the vanadyl sulfate powder are in good agreement with the standard pattern of $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$.^[42] The XRD spectrum of the dried V-GHG exhibits the characteristic diffraction patterns of rGO and $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$. The suppression of the broad rGO peak can be attributed to existence of the relatively high amount of vanadyl sulfate salts at the surface of the dried V-GHG. Additionally, the absence of the GO peak at scattering angles around $2\theta = 11^\circ$ indicates the hydrothermal reduction of GO and successful recovery of the π -conjugated systems of the mixture.

Most interestingly, the sharp peaks related to vanadyl sulfate confirm a significant encapsulation of vanadium electrolyte due to the residual hydrophilic oxygenated functional groups of the GO. The vanadium electrolyte content of the hydrogel is calculated using Equation (S1) in the Supporting Information and

found to be 96.4 wt%. The electrolyte uptake of the V-GHG is comparable to the water content of a GHG (97%), as reported in ref. [39].

Figure 2 is a sketch of an exploded view of a flexible hybrid battery-supercapacitor made with the V-GHG. In detail, we use two pieces of carbon cloths as current collectors. Polyimide sheets with a thickness of 182 μm, featuring a rectangular-shaped cavity (1 cm by 3 cm), are arranged on top of the current collectors. The V-GHG is cut into slices, which are placed in the polyimide cavities and pressed on the carbon cloth to remove excess electrolyte. The total mass loading for such an electrode is around 1 mg based on the V-GHG dried weight; this corresponds to around 3.3 mg cm^{-2} . A NEOSEPTA CMS membrane is used to establish ionic contact between the electrodes while preventing electronic contact. To assemble the V-GHG hybrid device, the stack consisting of current collectors, membrane, and electrodes are sealed with parafilm to maintain the water content (humidity) within the device. The entire arrangement is then pressed with an applied pressure of 500 kPa for 10 min. The so-fabricated device is mechanically robust and highly flexible.

The electrochemical performance of the device is evaluated using cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS) measurements. **Figure 3a** shows the cyclic voltammograms (CVs) of our V-GHG hybrid device within a potential window of 0–1.2 V and with scan rates ranging from 1 to 100 mV s^{-1} . Comparison of

Figure 2. Exploded view of the flexible hybrid battery–supercapacitor made from V-GHG (dimensions are not to scale).

the CVs reveals that the existence of the redox peaks and the underlying shape of the voltammogram is governed by the scan rate. At scan rates below 5 mV s^{-1} , the redox peaks are associated with the electrochemical conversion of the vanadium redox

couples in each electrode. This unique behavior distinguishes our V-GHG hybrid device from other supercapacitors,^[38–41] pseudocapacitors,^[43–45] and all hybrid systems reviewed by Lee et al.^[23] At relatively high scan rates, our device behaves like an ideal EDL supercapacitor featuring even and rectangular-shaped CV loops confirming the low contact resistances between electrodes and current collectors. In the case of considerable contact resistances, a rectangular CV profile is distorted to an oblique angle.^[38] The excellent capacitive performance at high scan rates is attributed to the intrinsically high surface area of the graphene-hydrogel matrix.^[38–41] The observation of this novel hybrid performance is supported by galvanostatic charge–discharge profiles recorded at different current densities (Figure 3b,c). At a relatively high current density of 5 A g^{-1} (Figure 3b), the correlation between time (transferred charge) and voltage is rather linear proving the capacitive performance of the system. In contrast, the redox activity of the encapsulated electrolyte leads to battery-like behavior (identified by plateau-like regions in the charge–discharge profile) when operated with low current densities such as with 0.5 A g^{-1} in Figure 3c.

Figure 3. a) Cyclic voltammetry of the V-GHG hybrid device at different scan rates. b) Galvanostatic charge–discharge curve at a current density of 5 A g^{-1} . c) Galvanostatic charge–discharge curve at a current density of 0.5 A g^{-1} . d) Comparison of specific capacity and coulombic efficiency of the hybrid device as a function of current density. e) Ragone plot of the V-GHG hybrid device and comparison with selected other electrochemical energy storage systems (Data for battery systems and electrical double-layer capacitors (EDLC) are adopted from ref. [46]). f) Nyquist plots at different open circuit voltages.

The battery-like characteristics are related to the difference in the Galvani potential of the electrodes. Initially, the hybrid device has an open circuit voltage (OCV) of around 0 V since it consists of two equal half-cells with the same content of vanadium ions (VO^{2+}). During charging, VO^{2+} ions are oxidized to VO_2^+ at the positive electrode. This reaction also generates protons which migrate through the cation exchange membrane to the negative electrode, where VO^{2+} ions are reduced to V^{3+} . The main redox reaction in both half cells is

Positive side

Negative side

In other words, the charging of the device results in EDL formation (capacitance) and differently changes the oxidation state of the vanadium ions in the two half-cells. Consequently, the two half-cells feature different Galvani potentials which induce a considerable electromotive force (capacity). The faradaic reactions lead to two half-cells with a standard reversible cell potential of 0.67 V. It should be noted that the OCV of the device can go beyond 0.67 V with further charging and increasing the state of charge (SOC) of the electrolytes. The SOC of the electrolyte is described either as the ratio of V^{3+} to all vanadium ions at the negative side or the ratio of VO_2^+ to all vanadium ions at the positive side.

The unique performance of the device is governed by the competition of the redox reactions and the EDL formation which have considerably different time scales. The kinetics of the vanadium redox reactions are rather slow and the rates are influenced by electrode overpotential and the diffusion of vanadium ions from the bulk of the encapsulated electrolyte to the surface of the gel matrices. The EDL formation is a rapid process since it does not involve an electron transfer across the electrode–electrolyte interface.^[23] This difference in time scales leads to the hybrid characteristics of the device. At relatively high current densities, the faradaic reactions are not fast enough to compete with the rapid charge transfer in the EDL. At lower current densities, the EDL is still charged but the process is slow enough that the redox reactions can occur to a significant extent, which increases the capacity of the device. The capacity and coulombic efficiency of the device is calculated according to Equations (S2) and (S3) in the Supporting Information, respectively. The device exhibits a high capacity of around 200 mAh g⁻¹ (normalized by the dried mass of electrode) at a current density of 1 A g⁻¹. Comparison with a similar unfunctionalized GHG supercapacitor (Figure S2, Supporting Information) indicates that the EDL formation provides a capacity of around 277 mAh g⁻¹. Thus, the capacity contributed by the redox reactions is calculated to be 172.3 mAh g⁻¹, corresponding to about 87.6% of its theoretical value (196.5 mAh g⁻¹), as discussed in Section 5 in the Supporting Information.

When the current density increases from 1 to 5 A g⁻¹ (Figure 3d), the capacity of the unfunctionalized GHG

supercapacitor drops to around 46 mAh g⁻¹. This value corresponds to a specific capacitance of around 277 F g⁻¹ per electrode (Equation (S4), Supporting Information). In comparison, our V-GHG hybrid device has more than two times the specific capacitance of an unfunctionalized GHG (130 F g⁻¹) at a current density of 5 A g⁻¹^[38] and is similar to a GHG where the gel matrix is decorated with vanadium pentoxide V_2O_5 .^[43,44] Our hybrid's capacitance leads to an outstanding areal capacitance of around 915 mF cm⁻² at a current density of 5 A g⁻¹. Note that the device performance at relatively low current densities should not be characterized with the capacitance. In fact, the existence of the plateau-like potential regime leads to an overestimation of the capacitance for this condition.^[23] Figure 3d shows that the coulombic efficiency—the ratio of discharge to charge in a charge–discharge cycle—increases with current density.

The efficiency of our V-GHG hybrid system is found to be 85% at a current density of 1 A g⁻¹, where the device is mainly operated as a battery. This efficiency loss is mainly due to ion redistribution after charging, which will discuss in more details below. It is noteworthy that this efficiency still compares favorably with other hybrid system which utilize different redox species. Specific data given in ref. [23], include $\text{Ce}_2(\text{SO}_4)_3$ (68%), $\text{K}_3\text{Fe}(\text{CN})_6$ (61–87%), $\text{KI}|\text{LiSO}_4$ (67%), ZnBr (85%), KBr (82%), and graphene hydrogel functionalized with hydroquinone (75%). As shown in the figure, the coulombic efficiency improves from 85% to 92% when the current density increases from 0.5 to 1 A g⁻¹. Further increase of the current density leads to a less pronounced increase in efficiency. This effect can be attributed to the capacitor-like behavior of our device at higher current densities. In general, supercapacitors have a higher coulombic efficiency compared to batteries due to the absence of charge transfer across the electrode interface.^[23] In the V-GHG hybrid device, as the current density increases, the contribution of EDL formation becomes more pronounced which increases the coulombic efficiency. This relatively high coulombic efficiency over a wide range of current densities confirms the enhanced power handling capability of this device compared to conventional batteries. The energy and power density of the V-GHG hybrid device is calculated by applying Equations (S5) and (S6) in the Supporting Information. For comparison purposes, the energy and power are normalized by the mass of active materials in the device. The results are plotted in a Ragone plot (Figure 3e) and compared with data for hybrid devices having activated carbon electrodes in contact with redox electrolytes^[47,48] and for regular and decorated GHG supercapacitors.^[38,49] As shown in Figure 3e, the GHG supercapacitor (without redox electrolytes) features a lower energy density which also decreases slightly with increasing power density. In contrast, hybrid devices with redox electrolyte provide higher energy densities. However, they have a lower power capability since their energy density drastically decreases with increasing power density. For our V-GHG hybrid system, regions of battery-like and capacitor-like behavior can be identified. The first region stems from the redox activity of the electrolyte at low power densities having a maximum energy density of 75.7 Wh kg⁻¹ at a power density of 1675 W kg⁻¹. This energy density is significantly higher than that of the conventional supercapacitors in Figure 3e and compares favorably with a tin/vanadium hybrid

device (59.8 Wh kg^{-1} and 182.2 W kg^{-1}).^[47] The second region is located at power densities greater than 1.35 kW kg^{-1} . Here, the energy density decreases only slightly with increasing power density. This behavior is similar to those of conventional supercapacitors. Nevertheless, our V-GHG hybrid device exhibits an energy density of 12.2 Wh kg^{-1} at a power density of 2.6 kW kg^{-1} , which is substantially higher than those of the GHG supercapacitors. These results indicate that the V-GHG hybrid device combines the excellent energy rating of a battery with the superior power handling of a supercapacitor. We also compare the performance of the hybrid device with conventional battery systems in Figure 3e. However, the energy and power density of noncommercialized (lab-scale) power sources are commonly normalized with the electroactive mass of the electrodes. This method overestimates the performance when compared to commercial devices which are normalized with the system mass. For a more realistic comparison, we also normalize the performance data of our device with the mass of electrodes, electrolytes and the separator. Then, the maximum energy density of the device is found to be 5.62 Wh kg^{-1} at a power density of 20 W kg^{-1} . This maximum energy density is superior to a solid-state flexible asymmetric supercapacitor made from graphene films (2.95 Wh kg^{-1})^[50] but is less than a tin/vanadium redox electrolyte device (17.2 Wh kg^{-1}).^[47] At a power density of 0.5 kW kg^{-1} , our device features an energy density of 0.71 Wh kg^{-1} which is similar to a flexible solid-state supercapacitor made from GHG films (0.67 Wh kg^{-1} and 0.61 kW kg^{-1}).^[38] Note that the energy density of the device can be increased by making a vanadium graphene hydrogel with higher vanadium concentrations.

The electrochemical characteristics of the device are further analyzed using EIS at different OCVs of 0.01, 0.60, and 1.10 V. EIS measurements are performed for a frequency range of 10 mHz to 100 kHz by applying a sinusoidal signal of 5 mV amplitude. The measured Nyquist diagrams are plotted in Figure 3f. Each plot features a semi-circle at high-to-medium frequencies followed by an inclined line in the low-frequency region. The semi-circle represents the electrolyte resistance in the porous structure of the electrode, the electrode resistance, and the contact resistances. Figure 3f shows that diameter of the semi-circle changes with the OCV. This should be associated with the different composition of the electrolyte for the different SOC. The impedance spectra for OCVs of 0.01 and 1.2 V approach respective phase angles of 80° at frequencies of 501 and 398 mHz, demonstrating the supercapacitor-like behavior of the device. However, the line spectrum for an OCV of 0.6 V is inclined at 45° which is typically described with a Warburg impedance element. Thus, this behavior should correspond to the diffusion of vanadium ions from the bulk electrolyte to the surface of the gel matrix, affirming the battery-like characteristics of the device. The charging performance is evaluated using a fast-charging technique where the device is charged at a range of current densities and then discharged at a current density of 0.5 A g^{-1} . The performance of the hybrid device is compared to that of a conventional GHG supercapacitor (Figure 4a). For the V-GHG hybrid device, a maximum capacity of 226 mAh g^{-1} is measured at a charge and discharge current density of 0.5 A g^{-1} . This capacity is chosen as the basis for the capacity fading caused by fast charging of the device. Doubling the charging

current to 1 A g^{-1} results in an approximate capacity drop of 10%. When the charging current density is increased from 0.5 to 4 A g^{-1} , the V-GHG device still maintains around 46% (102.5 mAh g^{-1}) of the slow charge capacity. The conventional supercapacitor features a maximum capacity of 45 mAh g^{-1} at a charging current density of 0.5 A g^{-1} but has a better capacity retention. When the charging current density is increased from 0.5 to 4 A g^{-1} , the conventional supercapacitor features a 66% capacity retention, albeit with a five times lower capacity than the V-GHG hybrid device. This test reveals that the coulombic efficiency of the V-GHG hybrid device is around 20% less than that of the GHG supercapacitor. This is understood since faradaic reactions with charge transfer across the electrode interface are associated with overpotentials. Figure 4b gives detailed insight into the fast-charging performance of the V-GHG hybrid device by comparing the results to that of the conventional supercapacitor. Initially, both cells are completely discharged at a current density of 0.25 A g^{-1} , then the cell potential is held at 0 V for 2 min to ensure complete discharge. Subsequently, both devices are charged with a current density of 4 A g^{-1} followed by discharge at a current density of 0.5 A g^{-1} . The upper and lower potential limits are 1.2 and 0 V, respectively. As can be seen in the figure, the V-GHG hybrid device charges for over 100 s until it approaches the upper potential limit. The discharge curve features a plateau-like region in the middle of the discharge process, which is attributed to the redox reactions and battery-like characteristics of the device. The discharge time is 738 s which corresponds to a delivered capacity of 102.5 mAh g^{-1} and a coulombic efficiency of 92.2%. For the conventional GHG supercapacitor, the charge–discharge curve shows a rather triangular shape with a charging time of 27 s followed by 211 s of discharge time. The capacity and coulombic efficiency of the conventional supercapacitor are found to be 29.3 mAh g^{-1} and 97.7%, respectively. The charge–discharge characteristics of the device are also investigated by potentiostatic charging at constant potential of 1.2 V, followed by discharging at a current density of 0.5 A g^{-1} . Figure S3 in the Supporting Information reveals that the conventional supercapacitor becomes fully charged after around 300 s, as the delivered capacity reaches a constant value of 30.5 mAh g^{-1} . The required charging time and discharge capacity of the V-GHG hybrid device corresponds to 720 s and 252 mAh g^{-1} , respectively. In conclusion, our V-GHG hybrid device delivers an 8.3 times higher discharge capacity with only a 2.4 times longer charging time, compared to a similar GHG supercapacitor without vanadium ions (Figure S4, Supporting Information). These data highlight the excellent synergetic effect of the incorporation of vanadium ions into high surface area GHG, resulting in high capacities of the device under fast charging conditions. The performance of the device under mechanical stress is investigated at various bending angles by galvanostatic charge–discharge measurements at a current density of 2.5 A g^{-1} . There is no noticeable difference in capacity for bending angles from 0 to 90° . Even at a bending angle of 135° , the device only shows a negligible capacity fading of around 3% (Figure 4c). Overall, the device demonstrates excellent integrity under mechanical stress. The durability of the device is evaluated by galvanostatic charge–discharge measurements at a current density of 10 A g^{-1} . The capacity retention and coulombic

Figure 4. a) Delivered capacity of the V-GHG device at current density of 0.5 A g⁻¹ after charging at different current densities. b) Galvanostatic charge–discharge profile at charging current density of 4 A g⁻¹ and discharge current density of 0.5 A g⁻¹. c) Galvanostatic discharge capacity of the device at current density of 2.5 A g⁻¹ for different bending angles. d) Cycling stability of the device at a current density of 10 A g⁻¹. e) Cycling stability of the device at a current density of 3.5 A g⁻¹, the inset compares the charge–discharge cycle profile of the as fabricated device with the profile measured after a restoring step. f) Capacity retention of the device at a current density of 3.5 A g⁻¹ with restoring cycles after every 250 cycles.

efficiency are plotted against the cycle number in Figure 4d. We observe that the device shows a capacity fading around 5% while the coulombic efficiency remains constant. This is in a good agreement with the performance of conventional supercapacitors made from GHGs reported in ref. [38]. Nevertheless, testing at these high current densities is only useful to examine the supercapacitor features of our hybrid device since the faradaic contribution to energy storage is minimized. Consequently, this testing needs to be performed at a lower current density where both redox reaction and EDL formation occur simultaneously. Therefore, another durability test is performed at a current density of 3.5 A g⁻¹ for 1000 cycles (Figure 4e). The device retains an excellent coulombic efficiency with an average 98% over 1000 cycles; however, the delivered capacity gradually decreases. We assume that this capacity decay is predominantly attributed to accumulation of faradaic reaction products in the EDL. This unwanted accumulation is a result of the interplay of continuous cycling and mass transfer limitations as described below. In the EDL, the ions are balanced by the cohesive electrostatic forces induced by the very large local electric field and the dispersing influence of the thermal energy (diffusion). In many electrochemical energy storage systems, the faradaic

reaction changes the polarity of the reactant. For example, the reduction of zinc ions results in electroplated zinc and the space in the EDL can be rapidly occupied by another zinc ion from the bulk electrolyte. In our case, we have reactant and product always dissolved in the electrolyte. Furthermore, the faradaic reaction does not change the polarity of the reactants. The vanadium species in the three oxidation states that we utilize are all cations. This has the disadvantage that the electrostatic force hinders the diffusion process of the product from the EDL back into the bulk so that the reactant transport to the electrode surface is hindered as well which constitutes a form of mass transfer polarization. We can use the ratio of thermal (diffusive) and electrostatic energy of an ion in the EDL to obtain some qualitative insight into this phenomenon; i.e., $\frac{RT}{zF\phi}$, where R is the universal gas constant, T is the temperature, z is the valency of the ion, F is the Faraday constant, and ϕ is the potential drop over the EDL. In case of V³⁺, the potential drop over the EDL must be less than roughly 10 mV so that diffusion can overcome the cohesive electrostatic attraction. Thus, a certain time at a low potential difference is required to achieve the equilibrium composition in the EDL; this time is not

granted during continuous charge–discharge cycling. This phenomenon is commonly known as relaxation time and is also observed for Li-ion batteries.^[51]

A quantitative value for this relaxation time is given by the potential recovery of the hybrid device immediately after discharge as can be seen in Figure S5a in the Supporting Information. Here, we first discharge the hybrid device at 0.5 A g^{−1} to the cutoff potential of 0 V which is then held for 15 min. The hybrid device is subsequently charged and discharged at a current density of 1 A g^{−1}. At the end of the discharge, the open circuit potential is recorded for 2 h. We observe that the open circuit potential very rapidly increases after discharge. This sudden change is followed by a slow increase to an asymptotic value of around 0.5 V. The test is repeated for different current densities of 2, 3, 4, and 5 A g^{−1}, results are plotted in Figure S5b in the Supporting Information. We find that the potential recovery and the asymptotic value depend on the charge–discharge rate. The higher the charge–discharge rate, the faster the recovery and the higher the asymptotic potential. It is obvious that all curves can be described with the same exponential form

$$V = A \exp\left(-\frac{t}{\tau}\right) + C, \text{ where } A \text{ is a pre-exponential coefficient, } C$$

is a constant, t is the time, and τ is the characteristic time scale of the potential recovery which is equal to the relaxation time as we derive in more detail in the Supporting Information. Evaluation of Figure S5b in the Supporting Information reveals that the relaxation time, depending on the current density, ranges from around 3 min for a current density of 5 A g^{−1} to around 6 min for a current density of 1 A g^{−1}. The experimental relaxation times are in good agreement with the characteristic time scale of the transport processes which are found from a magnitude of order analysis to be around 1 min, cf. Section 7 in the Supporting Information.

If this relaxation time is longer than the (off) time between a charge and discharge cycle, a (reversible) capacity decay over cycling occurs as evident by comparison of the charge–discharge profiles during the cycling test. At a current density of 3.5 A g^{−1}, both energy storage mechanism—the faradaic reactions and the EDL formation—take place as evident by the battery-like charge and discharge profile (Figure S6a, Supporting Information). However, as the cycle number increases the EDL is gradually enriched with confined ions. This changes the initial potential of the charge cycle as can be seen in Figure S6a–c in the Supporting Information. Likewise, since the amount of vanadium ions that can participate in the faradaic reactions is limited, the EDL formation becomes more prominent as the charge storage mechanism as evident by the suppression of the plateau-like part of the charge and discharge profile. If we grant the relaxation time to the device by a discharge at constant potential of 0 V for several minutes, which we call restoration step, we can restore the initial capacity. Another possibility for a restoration step is a low current charge and discharge cycle. This result proves that our capacity losses are not due to material degradation but are related to the confinement of ions in the EDL. The inset in Figure 4e compares two charge–discharge profiles at a current density of 1 A g^{−1}. One profile is obtained right after fabrication of the device. The other one is recorded after 1000 cycles (at 3.5 A g^{−1}) and one restoration step. We observe a very similar profile indicating that after restoration step we have almost no

capacity losses. Indeed, the measured capacity after restoration is found to be 186 mAh g^{−1} corresponding to a 98% capacity retention. In conclusion, allowing for relaxation during charge and discharge diminishes ion confinement and retains initial capacity. For further investigation of this hypothesis, another durability test is performed. Here, V-GHG hybrid device is cycled at a current density of 3.5 A g^{−1} for 1000 cycles with a restoring step after every 250 cycles; results are given in Figure 4f. We find restored capacities of 92%, 95%, 95%, and 95% after each restoration step. This test confirms that the losses are related to charge build-up and there is only a negligible degradation of the electroactive materials which is consistent with the observation of the relatively constant coulombic efficiency during cycling.

Self-discharge characteristics and leakage current are important parameters for the practical application of electrochemical storage systems.^[23] Particularly, systems with redox electrolytes are expected to suffer from higher self-discharge rates originating from ion-crossover, also called redox shuttling.^[23] The leakage current of the V-GHG hybrid device is measured using the current floating method at a cell potential of 1.2 V. In detail, the cell is first charged to a cell potential of 1.2 V at a current density of 1 A g^{−1}. Afterwards, the cell potential is kept at 1.2 V for 2 h while the current response of the device is recorded (Figure S7, Supporting Information). The floating current quickly drops to 80 $\mu\text{A mg}^{-1}$ (mass per electrode) in order to compensate for the leakage current in the device. The mass-based leakage current of our V-GHG hybrid device is higher compared to those reported for conventional GHG-based supercapacitors, which are typically 1.5 $\mu\text{A mg}^{-1}$.^[38] This higher value is mainly associated with the fact that during charge the faradaic reactions create new species and consume/produce protons in the respective half-cells. This results in considerable concentration differences which are depleted with a higher leakage current during the floating current experiment. However, the encapsulated vanadium ions significantly increase the capacity of the device, which is not considered in a mass-based leakage current definition. For better comparison with other systems, the leakage current can also be normalized by the charge capacity of the device. Then, our V-GHG hybrid device features a leakage current of 4.1 $\mu\text{A C}^{-1}$ which is significantly lower compared to that of comparable conventional GHG supercapacitor (51.9 $\mu\text{A C}^{-1}$)^[38] and of a functionalized graphene-based hybrid using hydroquinone (15 $\mu\text{A C}^{-1}$).^[33] The self-discharge characteristics of the device are also investigated based on OCV measurements; the performance is compared with that of a conventional GHG supercapacitor. For both cases, the device is charged at a current density of 0.5 A g^{−1} up to a cell potential of 1.2 V. The cell potential is kept at 1.2 V for 15 min and then the OCV is recorded, cf. Figure 5a. The V-GHG hybrid device features a rapid cell potential drop during the first hour followed by a further moderate potential decay over the rest of the experiment. After 14 h, the potential is 0.57 V which corresponds to a potential fading of 52%. This rate is significantly lower compared to that of the conventional GHG supercapacitor (Figure 5a) and those reported for GHG-based hybrids with redox electrolyte of hydroquinone in H₂SO₄ (96% cell potential fading after 12 h)^[52] or sulfonated polyaniline in H₂SO₄ (79% cell potential fading after 12 h).^[53]

Hence, to obtain further detailed insights into the self-discharge behavior of our hybrid, we perform further experiments to track the SOC of the electrolytes. However, it is not possible

Figure 5. a) Self discharge curve of the devices recorded after charging at a current density of 0.5 A g^{-1} to 1.2 V and holding the potential at 1.2 V for 15 min. b) State of charge of the electrolyte at open circuit voltage (self-discharge) over 7 h.

to track the SOC of a single hybrid device over time. Here, we make 14 V-GHG hybrid devices with almost equal internal resistances (average: $1.48 \pm 0.11 \Omega$) and connect them in parallel. The devices are charged up to 1.2 V and then operated at open circuit conditions. In such a parallel arrangement, the devices share their characteristics and the overall performance should be similar to a large equivalent device. Every half-hour, one device is disconnected and the SOC of the electrolyte is determined as described in the Supporting Information. As shown in the Figure 5b, the SOC of the electrolyte decreases over the first 1.5 h. However, after 2 h the SOC considerably increases again, decreases and then slightly increases again. We also observe the same qualitative behavior when we analyze the SOC of single hybrids after different times operated at OCV. We attempt to explain this by the following scenario: the main reason for the cell potential drop at OCV is the transfer of charge from one half-cell to the other, that is, the leakage current. The leakage current is initially very large (Figure S7, Supporting Information) and therefore causes the relatively sharp initial potential decay (Figure 5a). Due to the high capacitance of the electrodes, a considerable amount of the electrical energy is stored in the EDL. Once the device is at OCV, the charge in the EDL diffuses back into the bulk of the hydrogel. However, this diffusion is a relatively slow process due to the (cohesive) electrostatic forces in the EDL. The Galvani potential of the electrode is therefore, for a longer time, higher than the equilibrium potential of the redox reaction and triggers further faradaic reactions. In other words, the overpotential at the electrode (the capacitance) increases the SOC (the capacity) which mitigates the cell potential drop due to self-discharge over time. After a certain time, the overpotential at the electrode is no longer sufficient to (considerably) drive the faradaic reactions and the SOC consistently decreases due to the leakage current. These phenomena are transient, and the rates are varying and it seems that there are instances where the SOC increase is in favor compared to the rate self-discharge. This test shows a very interesting characteristic of the V-GHG hybrid device and indicates that losses in capacitance are buffered by their partial recovery as capacity.

3. Summary and Outlook

In summary, we report a facile method to synthesize a hybrid vanadium-graphene hydrogel having the redox activity of the

vanadium ions and the high-surface-area of the 3D graphene framework. The vanadium-graphene hydrogel is used as half-cells in a flexible power source with a cation exchange membrane as separator. Both half-cells are made from the same hydrogel which encapsulates vanadyl ions VO^{2+} . However, charging the device changes the oxidation states of vanadium ions in each half-cell and induces a cell potential. The characterization of the device shows that the incorporation of vanadium electrolyte not only increases the energy density of the device but also results in a hybrid performance. In detail, this device can be operated as a battery, supercapacitor, or hybrid, depending on the operating current density. This feature also provides an opportunity for fast charging of the device. Compared to a conventional graphene hydrogel supercapacitor, we arrive at an eight times higher capacity for only a twofold increase in charging time. The integrity of the device is investigated at different bending states. The device features the same charge–discharge profile and capacity despite the different mechanical stresses which indicates the excellent robustness. In terms of charge–discharge cycle durability, the device shows an excellent capacity retention of 98% at a high current density. At lower current densities, there is a minor real and a major but only apparent capacity decay. The real capacity decay is only on the order of several percent and could be related to degradation of the electroactive material or a change of the graphene structure over continuous charge–discharge cycling. This should be investigated in future work. The apparent capacity decay is due to mass transfer polarizations which origin from accumulation of reaction products in the electrical double layer. This phenomenon occurs when the (off) time between charge–discharge cycles is less than the relaxation time of the device. Nevertheless, the initial capacity of the device can be (mainly) reinstated by simple restoring steps such as a (very) low current charge–discharge cycle or operation at open circuit potential for several minutes. This observation suggests that the ideal charging method could be a pulse charging method, which may not only utilize the total capacity of the device but may also reduce the charging time. However, this needs more investigation in order to develop an optimal algorithm for a charging protocol. This remarkable cycling performance is made possible due to the simple design of our V-GHG hybrid. The incorporation of the vanadium electrolyte also improves the self-discharge characteristics of the device and monitoring the state of charge suggests a partial recovery of the losses through faradaic reactions. The

present concept of utilizing a redox species that can exist in more than two redox states results in a considerably simplified design of hybrid battery–supercapacitors which has outstanding features such as true hybrid performance with a wide range of power capability, flexibility, high energy density, and the ability to restore most of the capacity decay during operation by simple electrical means. In future work, we will further increase the energy density of the device by optimization of the one-step synthesis of the vanadium graphene-hydrogel. Likewise, it would be interesting to infer whether graphene hydrogels with other redox-active species can be synthesized.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

fast charging, flexible power sources, hybrid battery–supercapacitors, reduced graphene oxide, vanadium redox electrolytes

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