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Tin/vanadium redox electrolyte for battery-like energy storage capacity combined with supercapacitor-like power handling†

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We introduce a high performance hybrid electrochemical energy storage system based on an aqueous electrolyte containing tin sulfate (SnSO₄) and vanadyl sulfate (VOSO₄) with nanoporous activated carbon. The energy storage mechanism of this system benefits from the unique synergy of concurrent electric double-layer formation, reversible tin redox reactions, and three-step redox reactions of vanadium. The hybrid system showed excellent electrochemical properties such as a promising energy capacity (ca. 75 W h kg⁻¹, 30 W h L⁻¹) and a maximum power of up to 1.5 kW kg⁻¹ (600 W L⁻¹, 250 W m⁻²), exhibiting capacitor-like galvanostatic cycling stability and a low level of self-discharging rate.

Electrochemical energy storage (EES) systems such as batteries and supercapacitors are key enabling technologies for a sustainable and efficient use of energy.1–3 With a growth in the demand for a reliable supply for renewable energy sources, EES systems have drawn more and more attention since the grid scale application of EES systems could resolve the intermittent power generation features of the renewable energy sources.4 In general, common batteries can provide high energy storage capacity (30–300 W h kg⁻¹) while suffering from low power performance (<1 kW kg⁻¹) and limited cycle lifetime (<50000 cycles). Supercapacitors are characterized by a high power performance (5–10 kW kg⁻¹) and extremely high stability (>100000 cycles), but exhibit low energy storage capacity (<8 W h kg⁻¹).5 These differences originate from different charge storage mechanisms.6 In principle, the charge storage mechanisms for EES devices can be classified into four categories (Fig. 1A): (1) electrical double-layer formation at the electrode/electrolyte interface (electrical double-layer capacitors), (2) redox intercalation through a layered structure via bulk reaction of the electrode (typical batteries), (3) solid phase redox reaction at the near surface of the electrode but not through the bulk material which can be pseudocapacitive,7 and (4) electrochemical reactions of soluble redox couples (redox electrolytes).8 Electric double-layer formation is accomplished by fast ion electroosorption and this purely physical charge separation process at the electrode/electrolyte interface enables rapid charge storage and recovery.9 Redox intercalation provides much higher charge storage capacity through the intercalation of ions (such as lithium, sodium, or potassium) into the layered structure of the electrode via a charge transfer process.10–12 The intercalation process, however, is severely limited by the diffusion kinetics of the ions and may degrade the layered structure of the electrode with increasing cycle numbers, particularly at a high rate.13 Nanoscale design and optimization of the electrode materials,14 or the use of novel nanotextured materials, like MXene,15 may provide unique

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possibilities to improve on this limitation, but alternative concepts are still in high demand. In particular, the non-ideal reversibility of chemical and/or structural changes in redox-active electrode materials complicates the achievement of longevity and stable performance.\(^\text{16}\)

While the use of redox-active electrode materials has attracted tremendous research interest, the field of redox-active electrolytes remains largely uncharted at present.\(^\text{17,18}\) Unlike the other mentioned charge storage mechanisms, energy storage via redox electrolytes is not exclusively confined to the electrode/electrolyte interface and encompasses the entire fluid volume. For instance, vanadyl sulfate (VOSO\(_4\)) will not only provide charge storage via double-layer formation at the electrode/electrolyte interface, but additional charge transfer is accomplished through a series of vanadium redox states.\(^\text{19,20}\) This dual (hybrid) energy storage mechanism brings along the need for the implementation of ion exchange membranes to avoid ion shuttling and rapid self-discharge.\(^\text{21}\) When no solid phase transition occurs and there are no electrolyte cross-contamination issues,\(^\text{22}\) a redox electrolyte based energy storage system can offer a cycling lifetime of over 10 000 cycles.\(^\text{23,24}\)

To maximize the volumetric and gravimetric energy storage capacity, an intriguing approach has been used to employ a synergistic combination of ultrafast ion electrosorption, fast redox-electrolyte charge transfer, and high-energy interfacial redox reactions. For that purpose, we introduce in this work, for the first time, the effective and stable coupling of tin and vanadium redox activities. Our work employs conventional nanoporous carbon to illustrate the facile implementation of the approach to already existing electrode technologies. A large energy capacity is expected based on the large standard potential difference between V\(_3^+/V_2^+\) and VO\(_2^+/VO_2^+\) reactions (ESI,\(^\dagger\) Fig. S1) in combination with the reversible Sn\(_{2+/Sn}\) phase transition inside carbon nanopores. The latter provides a large charge storage capacity involving the transfer of two electrons and the possibility of further oxidation to Sn[IV].\(^\text{25}\)

We prepared free-standing carbon film electrodes made from YP80F activated carbon (Kuraray Chemicals) with a specific surface area of 1756 m\(^2\) g\(^{-1}\) and an average pore size of 1.6 nm as characterized by nitrogen gas adsorption analysis (ESI\(^\dagger\)).\(^\text{26}\) The final hot-rolled films were produced with 200 \(\mu\)m thickness containing 5 mass% polytetrafluoroethylene (PTFE) as the binder (see ref. 27). For the redox electrolyte, vanadyl sulfate (VOSO\(_4\)) with 97% purity, tin sulfate (SnSO\(_4\)) with 95% purity, sodium sulfate (Na\(_2\)SO\(_4\)) with 99% purity, and H\(_2\)SO\(_4\) with 99.99% purity were purchased from Sigma Aldrich and mixed with deionized water. For the stability of the electrolyte and enhanced redox activity, all redox electrolytes were prepared by addition of 0.1 M H\(_2\)SO\(_4\). We used a type FAS15 anion exchange membrane (FuMa-Tech) to effectively prevent redox shuttling of vanadium and vanadium oxide ions between the two electrodes. As the reference electrode, we applied an Ag/AgCl electrode (Bioanalytical Systems, saturated, 3 M NaCl). For more information on electrochemical testing using a VMP300 potentiostat/galvanostat (Bio-Logic),
see the ESI† (esp. Fig. S2). For post-mortem analysis, electrode samples were collected after charging the working electrode to \(-0.2\) V and \(-0.57\) V vs. Ag/AgCl in chronocamperometry mode for 30 min. After cell disassembly, the samples were soaked in 0.1 M H₂SO₄ aqueous solution for a day, then subsequently soaked in deionized water for a day, and dried at room temperature in a desiccator in order to remove the dissolved ions. The possible contribution of the graphite current collector to the energy storage capacity (e.g., via intercalation) was excluded by comparative experiments with platinum current collectors (Fig. S4D, ESI†).

As seen from the cyclic voltammogram for a full cell presented in Fig. 1B, the aqueous VOSO₄/SnSO₄ redox electrolyte system with added 0.1 M H₂SO₄ is ideally suited to maximize the energy storage capacity over the entire range of accessible cell voltage (exemplified for up to 1.2 V). A large area under the discharging curve is indicative of a high-energy storage (recovery) capacity which can be quantified by integrating the discharging current. We obtained 42 mA h g⁻¹ (16.8 mA h mL⁻¹) for a mixture of 1 M VOSO₄/1 M SnSO₄, 38 mA h g⁻¹ (15.2 mA h mL⁻¹) for 3 M VOSO₄, and 29 mA h g⁻¹ (11.6 mA h mL⁻¹) for 1 M SnSO₄ at a slow rate of 1 mV s⁻¹. For a comparison, only 9.1 mA h g⁻¹ (3.6 mA h mL⁻¹) was achieved when using the same carbon material in 1 M Na₂SO₄ or 17 mA h g⁻¹ (6.8 mA h mL⁻¹) for 1 H₂SO₄ in the same voltage range. A clearly visible and broad redox peak pair at around 648 mV with small specific energy rating of 19.8 Wh kg⁻¹ was achieved by the 1 M VOSO₄/1 M SnSO₄ system, having a much larger voltage stability window of up to 1.4 V. This clearly implies a synergistic influence of the VOSO₄/SnSO₄ combination in terms of high specific energy. The individual application of VOSO₄ and SnSO₄ could not provide such high specific energy (Fig. 1C) due to their solubility limits (SnSO₄: 1.6 M in water at 20 °C in absence of vanadyl sulfate, VOSO₄: 3.3 M in water at 20 °C). Initially, we see an S-value (Fig. S4A, ESI†) above 0.1 from 0.5 V to 0.8 V. However, this value drops below 0.1 as the tin sulfate system becomes conditioned. This indicates that S-value analysis is to be carefully employed when adapting to redox systems.

A high amount of Faradaic charge transfer associated with redox reactions contributes to an enhanced specific energy and occurs at a fixed cell voltage. For instance, 3 M VOSO₄ exhibits two increases in specific energy at 0.5–0.8 V and >1.1 V (Fig. 1C), which correspond to the two large redox peaks observed in the cyclic voltammogram (Fig. 1B). As a result, a maximum specific energy rating of 19.8 Wh kg⁻¹ can be reached. For 3 M VOSO₄, however, no further increase in specific energy is possible because of the voltage stability window being limited to \(~1.25\) V, most probably due to water splitting. An even higher specific energy of 32 Wh kg⁻¹ was achieved by the 1 M VOSO₄/1 M SnSO₄ system, having a much larger voltage stability window of up to 1.4 V. This clearly implies a synergistic influence of the VOSO₄/SnSO₄ combination in terms of high specific energy. The individual application of VOSO₄ and SnSO₄ could not provide such high specific energy (Fig. 1C) due to their solubility limits (SnSO₄: 1.6 M in water at 20 °C in absence of vanadyl sulfate, VOSO₄: 3.3 M in water at 20 °C). Initially, we see an S-value (Fig. S4A, ESI†) above 0.1 from 0.5 V to 0.8 V. However, this value drops below 0.1 as the tin sulfate system becomes conditioned. This indicates that S-value analysis is to be carefully employed when adapting to redox systems.

The data so far relate to two-electrode cells. To gain a more detailed insight into the electrochemistry of the VOSO₄/SnSO₄ system, a three-electrode configuration was applied with an Ag/AgCl reference electrode (Fig. S2B, ESI†) to study the voltage development at each individual electrode. This particular configuration allows us to not only operate the cell voltage in a full-cell-like manner, but also access the potential information of the positive and negative electrode at the same time. Fig. S4B (ESI†) shows the potential profile of the positive and negative electrode while the voltage applied between the negative and positive electrodes was ranged from 0 V to 1.4 V. In the case of the 1 M VOSO₄/1 M SnSO₄ system, the potential at the positive electrode increases much faster than the potential at the negative electrode due to the strong redox activities at the negative potential at around \(-0.45\) V vs. Ag/AgCl.

Since the asymmetric potential development of the negative and positive electrode implies an inefficient utilization of the total charge storage capacity of a system, charge balancing is required. The performance can be severely impaired by balancing the charge storage capacity of both electrodes while keeping the potential of each electrode below their respective stability limits. One unique advantage of the redox electrolyte system is the highly facile charge balancing through concentration adjustment. In this way, charge balancing is much simpler as compared to the mass balancing commonly employed for supercapacitor devices, which brings complexity through imbalance in the geometrical shape of the electrodes. In order to maximize the specific energy of the system, the voltage imbalance of the negative and positive electrode can be adjusted by enhancing the charge storage capacity at the positive electrode. The 1 M VOSO₄/1 M SnSO₄ system already represented its maximum possible electrolytic concentration due to the low solubility of SnSO₄ (ca. 1.6 M) as compared to that of VOSO₄ (ca. 3.3 M). Further optimization of the electrochemical performance can be obtained...
by carefully increasing the VOSO₄-to-SnSO₄ ratio in order to balance the strong redox activity at the negative electrode. An array of different molar ratios is presented in the ESI,† Fig. S4C. The best performance was obtained for 0.75 M SnSO₄/2 M VOSO₄ in terms of high energy density as the potential increase at the positive electrode was suppressed by the redox activity of VOSO₄ at around +0.75 V and +0.14 V vs. Ag/AgCl and remained below the oxygen evolution potential (Fig. 1D). The specific energy of this system was 65.3 W h kg⁻¹ as calculated from the discharging potential profile shown in Fig. 1D, as compared to 37 W h kg⁻¹ for the 1 M SnSO₄/1 M VOSO₄ cell.

For a comprehensive understanding of the redox activities of the negative and positive electrode, we employed a three-electrode configuration with an oversized counter electrode (oversized by ca. 35 times compared to the working electrode; Fig. S2B, ESI†). In the case of the 0.75 M SnSO₄/2 M VOSO₄ system, the VO₂⁺/VO₄⁺ redox reaction was investigated at the working electrode while keeping the potential of the counter electrode outside the range of the other redox activities (Fig. S3, ESI†). As a first step, 1 M SnSO₄ and 1 M VOSO₄ redox electrolytes were individually studied at the potential range from around −0.6 V to +0.8 V (Fig. 2A). The vanadium system shows three distinguishable redox peaks, which can be identified as V³⁺/V⁴⁺ , VO₂⁺/VO₃⁻ , and VO₂⁺/VO₄⁺ at around −0.5 V, +0.1 V, and +0.75 V vs. Ag/AgCl.⁴

In the case of the tin system, a very sharp and large peak appears at around −0.47 V, which aligns with the reduction of Sn²⁺ to metallic tin (tin electroplating). As the scanning direction changes to the anodic scan, the metallic tin is expected to be oxidized to Sn⁴⁺ . A slightly broader anodic peak (−0.43 V) might indicate a series of tin oxidation reactions towards Sn[nv] (Fig. S1, ESI†). As a next step, two cells were prepared with 0.75 M SnSO₄/0.2 M VOSO₄ in order to study the electrochemical behavior of the positive and negative electrodes (Fig. 2B). Reversible reactions of the VO²⁺/V³⁺ and VO₂⁺/VO₄⁺ couples can be seen at the positive electrode. During the reduction of the negative electrode, a steep increase in cathodic current was observed at −0.43 V, which aligns with the reduction of Sn²⁺ to tin metal. The results of the post-mortem nitrogen gas adsorption test (Table S2, ESI†) are in excellent agreement with the results of the formation of metallic tin, possibly in the carbon nanopores with pore sizes below 3 nm (Fig. S5, ESI†). The formation of the metal is believed to block the carbon nanopores as supported by the lower specific surface area (minus 41%) and the total pore volume (minus 48%) of the reduced negative electrode as compared to the pristine electrode. A high cathodic peak at −0.5 V (Fig. 2B) indicates the contribution of the V⁵⁺ to V⁴⁺ reaction. During reverse polarization (Fig. 2B), a broad anodic peak arises at around −0.41 V, which aligns with the oxidation of V⁴⁺ to V⁵⁺ and tin metal to Sn²⁺ . The dissolution of the tin metal to Sn²⁺ is also evidenced by the higher specific surface area and the total pore volume of the oxidized negative electrode (Table S2, ESI†) from the post-mortem nitrogen gas adsorption analysis (Fig. S5, ESI†). During further oxidation from −0.36 V to −0.27 V, we still see a high anodic current, perhaps implying further oxidation of tin to Sn[nv],...
which aligns with the lower specific surface area and total pore volume from the post-mortem analysis of the oxidized negative electrode. We see a capacitive behavior of the electrode in the range where no specific redox reactions are expected (Fig. 2B, inset) as characterized by a rectangular shape in the cyclic voltammogram. This capacitive contribution aligns with the formation of the electric double-layer by vanadium (V$^{3+}$, V$^{2+}$), vanadium oxides (VO$^{2+}$, VO$_2^-$), and tin cations (Sn$^{3+}$) as well as sulfates (SO$^{4+}$), or by the pseudocapacitive mechanism of the redox species; the capacitive contribution can be also seen in the cyclic voltammogram obtained from a full-cell configuration (Fig. S4D, ESI†).

To confirm the oxidation states of the tin system, we carried out post-mortem characterization of the negative electrode. For that, the electrodes were charged to −0.2 V and −0.57 V vs. Ag/AgCl, washed with 0.1 M H$_2$SO$_4$ aqueous solution and deionized water, and dried in vacuum. The electron micrographs (Fig. 2C) show that the surface of the carbon particles became roughened after the electrode was exposed to −0.2 V vs. Ag/AgCl as compared to the pristine electrode (activated carbon with 5 mass% PTFE). The Raman spectra support the fact that no change in the carbon structure occurred, maintaining the same ID/IG ratio (1.08 ± 0.05) before and after electrochemical testing (Fig. S6A, ESI†). The XRD pattern of the pristine electrode shows the presence of amorphous carbon and PTFE binder (Fig. 2C). The negative electrode exhibits amorphous SnO$_2$ peaks, meaning that the metallic tin could have been possibly limited to the outer surface of the activated carbon. We assume that the PTFE was partially decomposed to fluorine and carbon.

As investigated so far, the SnSO$_4$/VOSO$_4$ electrolyte system provides battery-like specific energy (> 60 W h kg$^{-1}$) through a complex charge storage mechanism of tin and vanadium redox activities and electric double-layer formation. For broader applications of this promising energy storage system, a high power performance is required. For the characterization of rate handling, galvanostatic charge/discharge was applied to the 0.75 M SnSO$_4$/2 M VOSO$_4$ cells with a full-cell configuration (Fig. S2A, ESI†) up to 1.4 V (Fig. 3A). For comparison, we added the data for the performance of a double-layer capacitor in 1 M Na$_2$SO$_4$ aqueous solution with the same type of activated carbon electrode. At a low specific current of around 55 mA g$^{-1}$, the 0.75 M SnSO$_4$/2 M VOSO$_4$ system exhibited a battery-like energy specific energy of up to 75 W h kg$^{-1}$, which can be converted to ca. 30 W h L$^{-1}$ when normalized to the volume of the two electrodes, the membrane, and the electrolyte. At a low specific current, the double-layer capacitor employing 1 M Na$_2$SO$_4$ only provides a maximum of 5 W h kg$^{-1}$ (2 W h L$^{-1}$). At a specific current of 4 A g$^{-1}$, the 0.75 M SnSO$_4$/2 M VOSO$_4$ system shows much higher specific energy (8.2 W h kg$^{-1}$) than the 1 M Na$_2$SO$_4$ supercapacitor (3.1 W h kg$^{-1}$). The poor energy rating at higher specific currents (> 6 A g$^{-1}$) is possibly due to the solid phase transition of Sn$^{2+}$ ions to solid tin as also supported by the increase in ohmic resistance (see the ESI† for the calculation) at the specific current regime over 1 A g$^{-1}$, which indicates the
overpotential due to mass transfer. When the specific current is converted to specific power (Fig. S7, ESIF), the 0.75 M SnSO₄/2 M VOSO₄ system provides a maximum performance of up to ca. 1.5 kW kg⁻¹, which can be converted to ca. 600 W L⁻¹ or 250 W m⁻² when normalized to the volume of the two electrodes, the membrane, and the electrolyte, or to the membrane area, respectively.

An important but often not discussed property of energy storage systems is the self-discharge, or more specifically, the time-dependent loss of the open circuit voltage after charging up to a specific cell voltage. As reported in several studies, redox electrolyte based systems are expected to suffer from a large self-discharging rate due to redox shuttling when ions are not selectively separated, for instance, by application of an ion exchange membrane. To prevent the ion shuttling of the vanadium ions, we employed a type FAS15 ion exchange membrane and achieved a very stable behavior (Fig. 3B) After 10 h of OCV measurement, the initial voltage dropped to about 17%, which is only half the self-discharge of an aqueous supercapacitor operated in 1 M H₂SO₄. Interestingly, the redox electrolyte system yields a self-discharge superior to supercapacitors, possibly due to less effect of ion-redistribution on the potential loss as the system has a hybrid charge storage principle.

The high performance stability (Fig. 3B, inset) is particularly remarkable when we consider that battery-like electrochemical energy storage systems commonly feature poor cycling stability. However, our redox electrolyte system presents very stable performance and after 4500 cycles (ca. 400 h of continuous testing), the specific capacity of the 0.75 M SnSO₄/2 M VOSO₄ cell degraded only by ca. 15% compared to the initial capacity of the system. The comparably high cycling stability is complemented by a high Coulombic efficiency of almost 100%, which is in excellent agreement with the electrochemical stability determined by the S-value analysis (Fig. S4C, ESIF).

In summary, we demonstrated a new type of hybrid energy storage system by applying an aqueous redox electrolyte with SnSO₄ and VOSO₄ into a nanoporous carbon based electrode. Through a simple charge balancing by adjusting the relative molar concentration of SnSO₄ and VOSO₄, the best optimized cell exhibited a broad voltage stability window of up to 1.4 V in a full-cell configuration, a promising specific energy of 75.4 ± 2.3 W h kg⁻¹, and a maximum specific power of ca. 1.5 kW kg⁻¹ as well as a high cycling stability over 4500 cycles, and a low level of self-discharging rate. The origin of the high specific energy is the three-step redox activities of vanadium by changing the oxidation state from 2⁺ to 5⁺ and the large redox activities of tin at the negative electrode. From the XPS analysis, these tin redox activities are believed to be due to the formation of the metallic tin in the carbon micropores, further oxidation of metallic tin to Sn[IV], or a further reduction of metallic tin to tin fluoride on the outside of the carbon particles, where PTFE is accessible. As the solid phase transition through the redox activities of tin can narrow or block carbon micropores, studies regarding the detailed solid phase formation mechanism in the micropores are necessary which will allow the estimation of the best pore structure of the electrode material, thus, further improvement of the power performance is expected.

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