Vanadium pentoxide/carbide-derived carbon core–shell hybrid particles for high performance electrochemical energy storage†

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A novel, two step synthesis is presented combining the formation of carbide-derived carbon (CDC) and redox-active vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) in a core–shell manner using solely vanadium carbide (VC) as the precursor. In a first step, the outer part of VC particles is transformed to nanoporous CDC owing to the in situ formation of chlorine gas from NiCl\textsubscript{2} at 700 °C. In a second step, the remaining VC core is calcined in synthetic air to obtain V\textsubscript{2}O\textsubscript{5}/CDC core–shell particles. Materials characterization by means of electron microscopy, Raman spectroscopy, and X-ray diffraction clearly demonstrates the partial transformation from VC to CDC, as well as the successive oxidation to V\textsubscript{2}O\textsubscript{5}/CDC core–shell particles. Electrochemical performance was tested in organic 1 M LiClO\textsubscript{4} in acetonitrile using half- and asymmetric full-cell configuration. High specific capacities of 420 mA h g\textsuperscript{-1} (normalized to V\textsubscript{2}O\textsubscript{5}) and 310 mA h g\textsuperscript{-1} (normalized to V\textsubscript{2}O\textsubscript{5}/CDC) were achieved. The unique nanotextured core–shell architecture enables high power retention with ultrafast charging and discharging, achieving more than 100 mA h g\textsuperscript{-1} at 5 A g\textsuperscript{-1} (rate of 12C). Asymmetric cell design with CDC on the positive polarization side leads to a high specific energy of up to 80 Wh kg\textsuperscript{-1} with a superior retention of more than 80% over 10 000 cycles and an overall energy efficiency of up to 80% at low rates.

1. Introduction

Supercapacitors are electrochemical energy storage devices, which present ultrafast charge–discharge rates leading to higher power compared to conventional batteries, but suffer from relatively low specific energies.\textsuperscript{1–4} The high specific power of \textasciitilde 10 kW kg\textsuperscript{-1} benefits applications with charge- and discharge rates in the order of seconds and minutes, such as flashlights, high power machinery, or emergency doors in airplanes, to name just a few.\textsuperscript{2,5} Depending on the energy storage mechanism, we can differentiate between two types of supercapacitors, namely electrical double-layer capacitors (EDLCs) that store energy by ion electroosorption, and pseudocapacitors that accomplish a capacitor-like charge-voltage behavior by fast redox reactions.\textsuperscript{6} Today, most EDLCs employ activated carbon (AC) electrodes with surface areas between 1500 and 2000 m\textsuperscript{2} g\textsuperscript{-1}, leading to typical capacitance values of 100–200 F g\textsuperscript{-1} and specific energies of up to ca. 20 Wh kg\textsuperscript{-1}, depending on the electrolyte and the cell configuration.\textsuperscript{6} By virtue of these values, the energy storage capacity of supercapacitors is significantly smaller than conventional batteries (e.g., lithium ion batteries: \textasciitilde 100 Wh kg\textsuperscript{-1}).\textsuperscript{6} A facile way to enhance the electrochemical performance is to increase the specific surface area of the electrode material and to optimize the pore size distribution.\textsuperscript{7} This is particularly effective for a material with very high pore tunability, as presented in the case of carbide-derived carbons (CDCs).\textsuperscript{6} However, this strategy is limited by the minimum pore size required for ion accessibility and the charge screening ability of carbon.\textsuperscript{7,9,10} Further enhancements of the energy storage capacity can be accomplished by employing redox-active materials for faradaic charge transfer.\textsuperscript{11,12} The latter can be either in the form of fast redox processes of surface groups, ion intercalation in the electrode material, or redox reactions of the electrolyte.\textsuperscript{13,14} Depending on the charge-voltage profile of the involved faradaic reaction(s), one differentiates between capacitor-like (i.e., pseudocapacitive) or battery-like behavior.\textsuperscript{15} Pseudocapacitive materials, exhibiting a constant ratio of charge and voltage (i.e., capacitance, unit: farad), are, for example, ruthenium oxide,\textsuperscript{16} manganese oxide,\textsuperscript{17} or MXene.\textsuperscript{18} Battery-like systems, exhibiting distinct redox peaks

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in the cyclic voltammogram, are, for example, quinone surface
groups\textsuperscript{18,20} or many metal oxides working as cathodic lithium-
intercalation hosts (such as LiFePO\textsubscript{4}, LiCoO\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4}, and
LiFeSO\textsubscript{4}F; ref. 21).

A very promising electrochemical system employs the
hybridization of carbon materials with vanadium pentoxide
(V\textsubscript{2}O\textsubscript{5}).\textsuperscript{22–26} By this way, the beneficial electrical conductivity and
nanotextured surface of carbon is complemented by the high,
battery-like charge storage capacity of vanadia with a theoretical
capacity of 147 mAh g\textsuperscript{-1} for intercalation of 1 M of Li in the
V\textsubscript{2}O\textsubscript{5} structure.\textsuperscript{27} Several studies have investigated vanadium
pentoxide as a cathode material in lithium ion batteries,
exhibiting high capacities between 350 and 750 mA h g\textsuperscript{-1}.\textsuperscript{28–30}
Furthermore, other types of vanadia in different oxidation states
can be used in batteries, such as VO\textsubscript{2},\textsuperscript{31} and also dissolved as an
electrolyte in redox-flow batteries.\textsuperscript{32} In a previous study, we used
atomic layer deposition (ALD) for highly controllable decoration
of carbon onions with V\textsubscript{2}O\textsubscript{5}, achieving defined thickness,
morphology, and crystallinity of the metal oxide phase.\textsuperscript{33} A high
specific energy (38 Wh kg\textsuperscript{-1}) was achieved for a full-cell using
V\textsubscript{2}O\textsubscript{5}/carbon onion vs. activated carbon (asymmetric cell), which is
cia. 2-times higher than that of standard activated carbon in
organic electrolytes.\textsuperscript{33} Even higher values for the specific energy
were found for interpenetrating networks of CNTs and V\textsubscript{2}O\textsubscript{5}
nanowires (40 Wh kg\textsuperscript{-1})\textsuperscript{32} and vanadia-coated reduced gra-
phone oxide sheets (76 Wh kg\textsuperscript{-1}).\textsuperscript{34} While promising, the practical adaptation of microfabrication and ALD remains
limited and more facile synthesis routes for V\textsubscript{2}O\textsubscript{5}/carbon hybrid
materials remain in high demand.

The combination of redox-active metal oxides with conduc-
tive and porous carbons in a hybrid device can be achieved by
mechanical mixing (thus exhibiting strongly reduced conduc-
tivity), or the decoration of the carbon with metal oxides. For the
latter, especially when using highly porous carbons, issues of
pore clogging may arise, leading to a strong decrease in
capacitance and specific energy. These complications are avo-
ded by not coating the carbon with the metal oxide, but rather
fabricating a metal oxide core with a porous carbon shell.
Inspired by carbon only core–shell architectures, which can be
obtained for CDCs,\textsuperscript{35,36} we present a novel two-step synthesis for
V\textsubscript{2}O\textsubscript{5}/CDC composites in a core–shell arrangement. Our
approach requires only one precursor (vanadium carbide),
which is first partially transformed to nanoporous CDC by
chlorine treatment of carbide, and then partially calcined,
yielding core–shell V\textsubscript{2}O\textsubscript{5}/CDC particles. The chlorination step
was needed as it is an effective way to transform a metal carbide
to carbon. The nanoporous carbon shell makes the vanadium
pentoxide core accessible for ion intercalation and works as a
conductive additive. This was accomplished by a high level of
control over the synthesis steps, which prevented a completion of
both the chlorination and the oxidation processes. Rigorous
structural and electrochemical characterization was carried out
to establish the high energy storage capacity of the material in
organic electrolytes. The combination of carbon and vanadia is
of mutual benefit: carbon contributes electrical conductivity
(and, to a lesser extent, double-layer capacitance) and vanadia
provides a large energy storage capacity. However, the design of
the two phases and their nanoscopic arrangement are of high
importance for the resulting electrochemical performance. As
our data will show, the firm of transformed VC-derived V\textsubscript{2}O\textsubscript{5} and
VC-CDC enables attractive electrochemical performances.

2. Materials and methods

V\textsubscript{2}O\textsubscript{5}/porous carbon core–shell particles were synthesized using
a two-step approach: (1) VC/CDC core–shell particles are produced by etching vanadium from the outside to the inside of
VC particles with a remaining VC core. (2) The residual VC core
inside the CDC matrix is calcined by oxidation in synthetic air,
resulting in V\textsubscript{2}O\textsubscript{5}/CDC core–shell particles. These two steps are
explained in detail in the next sections.

2.1 Synthesis of vanadium carbide/carbide-derived carbon
core–shell particles

Vanadium carbide (VC)/CDC core–shell particles were syntheti-
ized by reactive extraction of vanadium using in situ generation
of chlorine. 1 g VC powder (purity 99.9%, <2 \mu m, Sigma Aldrich)
was thoroughly mixed with NiCl\textsubscript{2}·6H\textsubscript{2}O (purity 99.95%, Alfa
Aesar) and filled into a graphite crucible placed in an isothermal
zone of the reactor (Ø = 32 cm, length = 1 m). The reactor was
evacuated to 0.01 mbar and then heated to 700 °C at a heating
rate of 2.5 °C min\textsuperscript{-1}. After a holding period of 3 h at this
temperature, the reactor was cooled to room temperature under
a helium purge. The resulting product was then poured into
500 mL of 1 M HCl and the solution was vigorously stirred using
a magnetic stir bar. After filtration, the acid washing was
repeated with similar procedures to ensure the removal of
nickel species. The product was finally washed using distilled
water until neutral pH and then dried in an oven (60 °C)
night.

To achieve incomplete carbide-to-CDC conversion, we used
molar ratios of NiCl\textsubscript{2}·6H\textsubscript{2}O-to-VC of 1.4, 1.8, and 2.7. It is
assumed that chlorine (Cl\textsubscript{2}) is released during vacuum decom-
position of NiCl\textsubscript{2} and reacts with VC in a stoichiometric reaction
to produce VCl\textsubscript{4} via eqn (1) and (2).

\begin{equation}
[NiCl\textsubscript{2}·6H\textsubscript{2}O]\text{solid} \rightarrow [Ni]\text{solid} + [Cl\textsubscript{2}]\text{gas} + [6H\textsubscript{2}O]\text{gas}
\end{equation}

\begin{equation}
[VC]\text{solid} + [2Cl\textsubscript{2}]\text{gas} \rightarrow [C]\text{solid} + [VC\textsubscript{2}]\text{gas}
\end{equation}

Based on these reactions and assuming that all chlorine
reagents with carbide the theoretical conversion (X\textsubscript{theo}) can be
derived from eqn (3) assuming full reaction of VC with Cl\textsubscript{2}
release.

\begin{equation}
X\text{theo} = \frac{0.5n_{\text{Cl}_2}}{n_{\text{VC}}} \times 100\% = \frac{0.5n_{\text{NiCl}_2·6\text{H}_2\text{O}}}{n_{\text{VC}}} \times 100\%
\end{equation}

where n is in molar units. Ratios of 1.4 and 1.8 correspond to
a theoretical value (X\textsubscript{theo}) of the conversion of 70\% and 90\%,
respectively. A ratio of 2.7 provides a surplus of evolving chlo-
rine to facilitate complete CDC formation, theoretically 100%.
The resulting samples are labelled VC-X70, VC-X90, and
VC-X100.
To produce a reference material through the “classical” and not in situ chlorine generation route, VC was exposed to chlorine gas diluted in helium at 700 °C for 5 h, as described elsewhere. The resulting material is labelled VC-CDC.

2.2 Synthesis of V2O5/carbide-derived carbon core–shell particles
Calcination of the VC/CDC particles was performed at 450 °C for 30 min in a VG Scienta furnace using synthetic air. Additionally, VC particles without prior chlorine gas treatment were oxidized at different temperatures (450, 500, and 600 °C) for 4 h to produce V2O5 without an additional carbon shell.

2.3 Chemical and structural characterization
The chemical composition of all samples was measured by energy-dispersive X-ray analysis (EDX) using a X-Max-150 detector from Oxford Instruments in a JSM-7500F (JEOL) scanning electron microscope. Spectra were taken at ten different positions with an acceleration voltage of 10 kV.

Transmission electron microscopy (TEM) was carried out with a JEOL 2100F microscope using 200 kV acceleration voltage. Powders were dispersed in isopropanol, tip sonicated for 10 s and dropcast on a copper grid with a lacey carbon film (Gatan) support.

Chemical composition maps were acquired by energy filtered transmission electron microscopy (EF-TEM) using a FEI Titan Themis 60-300 at an acceleration voltage of 300 kV. Electron energy loss spectra (EELS) were recorded using a Gatan GIF Quantum ERS energy filter at an energy resolution of ~1.1 eV. From the acquired EELS the edge onsets of the carbon K-edge, the vanadium L-edge and the oxygen K-edge were determined and the three-window method applied to acquire the respective elemental maps. A slit width of 10 eV was utilized for the pre- and post-edge images. Since the vanadium and oxygen edges overlap, the exact same pre-edge windows were taken for both images. More information can be found in the ESI.

Thermogravimetric analysis (TGA) was carried out with a TG 209 F1 Libra system (Netzsch). Samples were heated up to 900 °C in synthetic air with a rate of 20 °C min⁻¹ as well as isothermally at 450 °C for 30 min. The sample mass ranged between 10 mg and 20 mg.

The nitrogen gas sorption analysis at ~196 °C was carried out with a Quantachrome Autosorb iQ system and the calculations were performed with ASiQwin-software 3.0. The samples were degassed at 100 °C for 1 h and subsequently heated to 150 °C and kept at this temperature for up to 20 h at a relative pressure of 0.1 Pa to remove volatile molecules from the surface. The relative pressure with nitrogen was 5 × 10⁻⁷ to 1.0 in 76 steps. The specific surface area (SSA) was calculated using the Brunauer–Emmett–Teller equation (BET) in the linear regime of the measured isotherms, typically 3 × 10⁻² to 2 × 10⁻¹ (relative pressure), with a Quantachrome Autosorb 6B.

Raman spectra were recorded with a Renishaw inVia Raman Microscope equipped with a Nd–YAG laser (532 nm). A 50× objective was used with a power of 0.02 mW at the surface of the sample. The spectra of CDC samples were recorded with 10 accumulations and 20 s acquisition time. Vanadium pentoxide and vanadium carbide spectra were recorded with 1 accumulation and 10 s acquisition as well as in two separate measurements for the full wavenumber range (0–4000 cm⁻¹). All spectra were normalized and background corrected by subtracting a linear baseline.

X-ray diffractograms were collected with a Bruker D8 Discover diffractometer using Cu-Kα radiation (0.154 nm) with a step size of 0.02° and a measurement time of 1 s per step. The system was calibrated with a corundum standard. The free-standing PTFE-bound electrodes were placed on a sapphire single crystal for the measurement.

2.4 Electrochemical characterization
For electrochemical characterization, free-standing, polymer-bound electrodes were used. The powder materials were dispersed in isopropanol and stirred in a mortar until most of the isopropanol was evaporated and a carbon slurry was obtained. For all samples, 10 mass% PTFE (60 mass% aqueous solution, Sigma Aldrich) was added and mixed in a mortar until a dough-like paste was formed. For the electrodes with pure V2O5 (VC-500) an additional conductive additive (see also the ESI, Table S1†), in this case 25 mass% VC-CDC was added to achieve the same amount of carbon as in the core–shell electrodes. Using a rolling machine (MTI HR01, MTI Corp.) electrodes with a thickness of 60 μm (±10 μm) were fabricated and dried overnight at 90 °C and 20 mbar.

Electrochemical characterization was carried out in 1 M LiClO4 in acetonitrile (ACN) from BASF. For all measurements, a two- and three-electrode setup was used, corresponding to full- and half-cell configuration, respectively. The electrodes were punched out to obtain discs with a diameter of 6 mm (1–3 mg) and were separated by a glass-fiber disc with a diameter of 13 mm (type GF/A, GE Healthcare). The electrode/separater/electrode arrangement was compressed between two carbon-coated aluminum discs (diameter 12 mm, type Zifo 2653, Coveris Advanced Coatings) using spring-loaded titanium pistons, sealed by a polyether ether ketone (PEEK) body. The cells were dried at 90 °C and 20 mbar before they were put in an argon-filled glove box (MBraun Labmaster 130; O2, H2O <1 ppm). The cells were vacuum back-filled with a syringe containing the electrolyte. Full-cell measurements were carried out in an asymmetric configuration with a charge-balanced counter VC-CDC electrode by measuring the discharge capacity at 0.05 A g⁻¹ in a half-cell setup for both, working and counter electrodes, and adjusting the mass of the VC-CDC electrode. In the half-cell setup, a ca. five times oversized AC counter electrode was used together with a reference electrode; the latter was PTFE-bound activated carbon YP-50F from Kuraray.

Electrochemical characterization was performed using a VSP300 and VMP300 potentiostat/galvanostat from Bio-Logic in cyclic voltammetry (CV) and galvanostatic mode with potential limitation (GCPL). In the half-cell configuration a potential window from −1.2 V to +1.2 V vs. carbon was used. For data obtained with cyclic voltammetry, a scan rate of 1 mV/s.
Eqn (5) and (6): the asymmetric full-cells (two electrodes) were calculated using

\[
\text{Specific capacity} = \int_{t_1}^{t_2} \frac{I dt}{m}
\]

with \(m\) the active mass of the working electrode (i.e., without the binder), \(I\) the applied current, and \(t_1\) and \(t_2\) the start and end of discharging (from +1.2 V to −1.2 V vs. carbon), respectively. The charge efficiency was calculated by dividing the discharge by the charge capacity and is presented in percent.

The specific energy (\(E_{\text{specific}}\)) and specific power (\(P_{\text{specific}}\)) of the asymmetric full-cells (two electrodes) were calculated using eqn (5) and (6):

\[
E_{\text{specific}} = \int_{t_1}^{t_2} U dt \times I / M
\]

\[
P_{\text{specific}} = E_{\text{specific}} / (t_2 - t_1)
\]

with \(M\) the active mass of both electrodes (i.e., without the binder), \(I\) the applied current, \(U\) the applied cell voltage, \(t_1\) and \(t_2\) the start and end of charging or discharging. Charging is in this case defined as the potential step from 0 V to 2.5 V cell voltage.

Long-time stability was measured by galvanostatic cycling at 1 A g \(^{-1}\) from 0 V to 2.5 V cell voltage for 10 000 times. The energy efficiencies, as well as the energy retention, were calculated dividing the respective value from discharging by the value from the charging part of the curve and are presented in percent.

### 3. Results and discussion

#### 3.1 Structure, chemical composition, and porosity

In this study, a novel two-step process is presented, which can be used for the synthesis of vanadium oxide combined with porous carbide-derived carbon hybrid structures in a core–shell arrangement: (1) VC/CDC core–shell particles are produced by etching vanadium from the outside to the inside of VC particles with a remaining VC core. (2) The residual VC core inside the CDC matrix is calcined by oxidation in synthetic air, resulting in \(V_2O_5/\text{CDC}\) core–shell particles. The resulting samples are labelled VC-X70, VC-X90, and VC-X100 for a theoretical conversion of 70%, 90%, and 100%. For additional calcination the samples were labelled VC-X70-air, VC-X90-air, and VC-X100-air. Complete transformation from VC to CDC (i.e., VC-CDC) was achieved by conventional chlorine gas treatment at 700 °C, resulting in highly disordered carbon (Fig. 1A). Minor amounts of VC are still visible in VC-CDC (Fig. 1A) but not quantitatively significant according to the chemical analysis (Table 1). For the synthesis of VC/CDC core–shell particles with different ratios of VC to CDC, the amount of NiCl\(_2\) was varied for \textit{in situ} chlorine formation during thermal treatment. As expected from the stoichiometric calculation presented in eqn (3), VC-X70 had the largest amount of VC in the composite with 40.2 ± 5.3 mass%. Larger amounts of NiCl\(_2\) led to lower VC contents of 29.0 ± 7.5 mass% and 6.9 ± 2.4 mass% for VC-X90 and VC-X100, respectively (Table 1). Although a stoichiometric surplus of chlorine in VC-X100 should result in complete transformation to CDC, TEM analysis still shows a small core region of residual VC. We explain this by a reduced vanadium etching rate because of the graphitic carbon layers wrapped around the carbide domains.

The calcination temperature of 450 °C was chosen to completely transform residual VC to vanadium oxide after initial benchmarking of the samples via thermogravimetric analysis (see the ESI, Fig. S1†). After calcination, vanadium oxide cores inside the carbon shell are clearly visible (Fig. 1D, G and J). The smallest vanadia cores are measured for VC-X100-air (\(d_{100} = 150 ± 100\) nm), similar to VC-X90-air (\(d_{100} = 160 ± 110\) nm), much smaller than for VC-X70-air (\(d_{100} = 410 ± 190\) nm) and the calcined VC particles (VC-500 °C) (\(d_{100} = 520 ± 200\) nm). As seen in Table 1, EDX measurements are in qualitative agreement with TEM and show \(V_2O_5\) contents of 98.1 ± 6.2 mass% for the precursor VC particles oxidized at 500 °C and lower amounts from 78.2 ± 2.3 mass% for VC-X70-air to 67.4 ± 4.1 mass% for VC-X100-air.

To show the structure and morphology in more detail, the two-step synthesis process is illustrated in Fig. 2 using energy filtered TEM (EF-TEM) based chemical mapping. As exemplified for VC, VC-X90, and VC-X90-air, we first see how VC particles were successively transformed to CDC from the outside to the inside retaining a VC core. Calcination of VC inside the composite particles leads to \(V_2O_5\) domains engulfed in nanoporous VC-CDC. EF-TEM chemical mapping confirms the distribution of carbon around the \(V_2O_5\). During calcination, a partial cracking of the carbon shell is induced due to expansion of the core, as a result of the different skeletal densities of 3.36 g cm \(^{-3}\) for \(V_2O_5\) and 5.48 g cm \(^{-3}\) for VC.\(^{38,39}\)

By use of Raman spectroscopy, we can track the structural changes after CDC synthesis (Fig. 3A) and calcination (Fig. 3C). It is shown that the VC signal intensity at 269 cm \(^{-1}\) decreases with successive transformation from VC to CDC (see the inset in Fig. 3A).\(^{40}\) In addition to the VC signal, the Raman spectra show incompletely graphitized carbon, with the D-mode at ca. 1340–1350 cm \(^{-1}\), the G-mode at ca. 1580–1600 cm \(^{-1}\), and a pronounced second order spectrum at 2200–3500 cm \(^{-1}\). The degree of carbon ordering in VC/CDC core–shell particles is significantly higher than for the fully transformed CDC by chlorine treatment (VC-CDC). This is evidenced by the broader peak shapes and transition between D- and G-mode due to amorphous carbon at ~1520 cm \(^{-1}\), as well as the less distinct second order spectrum for the VC-CDC sample (Fig. 3A).\(^{41,42}\) However, the process stemming from NiCl\(_2\) also leads to the local emergence of metallic Ni, which, in turn, catalyzes the formation of graphitic carbon arranged in onion-like shells (Fig. 11 and J).\(^{43}\)

As seen from Fig. S1 (ESI†), precise control over the calcination process temperature and duration is required to avoid
either incomplete carbide oxidation or complete CDC burn-off. For this reason, we conducted first oxidation experiments only on the initial VC powder. The increase in mass of the initial VC particles, without prior NiCl₂ treatment, is ~40 mass% (ESI, Fig. S1†) for an annealing at 600 °C, leading to crystalline V₂O₅ (Fig. 3B). However, using this calcination temperature, more than 50 mass% of the CDC was burned-off. Therefore, the synthesis was repeated at a lower temperature of 450 °C for a duration of 30 min. With this annealing process, the same mass increase (~40 mass%) was achieved, expecting the same vanadia phase, and only ~20 mass% of the CDC material was removed. Synthesis at 450 °C for 30 min results in a mixture of V₂O₅, amorphous V₂O₅, and VO₂ (ref. 46) because of the large size of the precursor VC particles (~1 μm) (Fig. 3B). The particles with the VC/CDC core–shell arrangement present much smaller cores than the initial VC particles (Fig. 1B), which leads to the formation of V₂O₅ already at 450 °C applied for 30 min (Fig. 3C). These findings are supported by X-ray diffraction (XRD), shown in the ESI, Fig. S2.† Transformation from VC to VC/CDC is clearly evidenced by the emergence of the (002) graphite signal at 26.4° 2θ for VC-X70 and the continuous increase of its intensity up to the highest degree of
transformation for VC-X100 (ESI, Fig. S2A†). The fully transformed VC-CDC presents a less distinct carbon signal, coming from nanocrystalline and amorphous carbon, in agreement with Raman spectroscopy. After calcination, only V$_2$O$_5$ is identified (ESI, Fig. S2B†).

Highly nanoporous materials with high specific surface areas typically result from chloride treatment of VC (i.e., VC-CDC). The nitrogen gas sorption isotherm of VC-CDC shows a characteristic type I(b) shape related to microporous materials with pore sizes <2.5 nm (ESI, Fig. S3A†). Both micro- and mesopores are found for the partial transformation of VC with type I(b) isotherms, related to the internal microporosity, combined with type IV(b) isotherms related to mesopores with a small H4 hysteresis (Fig. S3B†). The combination of micro- and mesopores has been reported in other studies on carbon core–shell structures. The BET surface area increases from 120 m$^2$ g$^{-1}$ for VC-X70 to 577 m$^2$ g$^{-1}$ for VC-X100, and to 1466 m$^2$ g$^{-1}$ for VC-CDC (Table 2). Calcination of VC/CDC core–shell particles does not change the pore type (micro- and mesopores), but leads to oxidation of the high surface area carbon, with consequent decrease in surface area. For VC-X100-air and VC-X90-air, the surface area collapses to 61 m$^2$ g$^{-1}$ (~89%) and 124 m$^2$ g$^{-1}$ (~38%), respectively, due to oxidation of the CDC shell. The surface area of VC-X70-air is even larger than before calcination with 310 m$^2$ g$^{-1}$ (+158%; Table 2). The high content of VC in VC-X70 (40 mass%), which is turned into the lower density V$_2$O$_5$, has a stronger impact on the surface area than the CDC, compared to VC-X90 and VC-X100 with lower VC contents.

### 3.2 Electrochemical performance

As seen from the previous section, partial chlorination of VC to VC/CDC and successive calcination to V$_2$O$_5$/CDC in a facile two-step approach leads to highly crystalline V$_2$O$_5$ embedded graphitic and porous carbon. This combination is promising for electrochemical hybrid energy storage applications, which was benchmarked in our study in 1 M LiClO$_4$ in ACN as the electrolyte. Cyclic voltammetry of VC-CDC using the half-cell setup shows a nearly ideal double-layer capacitor behavior with a rectangular CV shape without any redox reactions. This behavior is expected from nanoporous carbons in general and CDC materials in specific. VC-X70-air is characterized by double-layer capacitance on the positive side between +0.5 V and +1.2 V vs. carbon. In the negative range, a very broad redox peak emerges (Fig. 4B and ESI, Fig. S4B†). This broad peak correlates with the larger V$_2$O$_5$ core of VC-X70 compared to the nanotextured V$_2$O$_5$ particles in VC-X90-air and VC-X100-air. Due to longer ion pathways in the V$_2$O$_5$ crystal, the system presents slower redox reactions and broader redox peaks.

In stark contrast to the capacitor-like behavior of VC-CDC, the CVs of VC-X90-air and VC-X100-air are characterized by several, very sharp redox peaks from Li-ion intercalation. The occurring electrochemical Li$^+$ insertion process for V$_2$O$_5$ can be expressed by eqn (7):  

$$V_2O_5 + xLi^+ + xe^- \leftrightarrow Li_xV_2O_5$$

with $x$ as the mole fraction of Li-ions.

Table 1  Elemental composition measured with EDX. “n.d.” denotes not detected

| C (mass%) | V (mass%) | O (mass%) | Cl (mass%) | Ni (mass%) | VC (mass%) | V$_2$O$_5$ (mass%) |
|-----------|-----------|-----------|------------|------------|------------|------------------|
| VC        | 22.0 ± 0.5| 77.6 ± 0.7| n.d.       | n.d.       | 95.9 ± 1.1 |                   |
| VC-X70    | 60.6 ± 4.1| 32.5 ± 4.7| 6.3 ± 1.1  | 0.6 ± 0.1  | 40.2 ± 5.3 |                   |
| VC-X90    | 58.2 ± 9.5| 23.5 ± 7.1| 6.9 ± 2.1  | 0.5 ± 0.2  | 29.0 ± 7.5 |                   |
| VC-X100   | 74.8 ± 8.0| 5.6 ± 2.3 | 4.5 ± 0.9  | 0.4 ± 0.1  | 6.9 ± 2.4 |                   |
| VC-CDC    | 97.8 ± 0.4| 0.2 ± 0.1 | 1.8 ± 0.5  | 0.1 ± 0.1  | n.d.       |                   |
| VC-500    | 1.9 ± 0.4 | 69.0 ± 3.2| 29.1 ± 3.0 | n.d.       |           |                   |
| VC-X70-air | 20.0 ± 2.2| 57.9 ± 1.1| 22.1 ± 1.2 | n.d.       | 78.2 ± 2.3 |                   |
| VC-X90-air | 23.3 ± 3.4| 53.3 ± 4.2| 22.8 ± 2.0 | 0.6 ± 0.2  | 74.3 ± 6.2 |                   |
| VC-X100-air| 30.7 ± 1.7| 48.5 ± 2.4| 20.7 ± 1.7 | n.d.       | 67.4 ± 4.1 |                   |

Fig. 2  Transmission electron micrographs and schematic illustration of the transformation process from VC to V$_2$O$_5$/CDC core–shell particles. (A) VC, (B) VC-X90, and (C) VC-X90-air. Panel (C) shows the TEM image (filtered ±5 eV around the zero loss peak) and the corresponding chemical EELS mapping.
Typically, a set of two peaks for inter- and deintercalation is observed between +2 and +4 V vs. Li/Li$^+$ or −1.2 V and +0.8 V vs. carbon. The structural changes during Li$^+$ intercalation into V$_2$O$_5$ involve several phases like α, ε, δ, and γ for $x \leq 2$, with three voltage plateaus at 3.4, 3.2, and 2.3 V vs. Li/Li$^+$ (−0.7 V, 0 V, and +0.2 V vs. carbon) (Fig. 4B). The plateaus seen from the galvanostatic curves (Fig. 4B) and the pairs of redox peaks in the CVs (Fig. 4A) belong to the two-phase regions α/ε, ε/δ, and δ/γ. Larger lithium contents ($x > 2$) for potentials below 2 V vs. Li/Li$^+$ (−1.2 V vs. carbon) would lead to irreversible reactions and the formation of the γ-phase. A detailed discussion of the structural changes is already given in ref. 48 and 51–53. The first set of redox peaks emerges between −0.25 V and +0.8 V vs. carbon for inter- and deintercalation of the first Li-ion. A second lithiation step occurs between −1.2 V and 0 V vs. carbon (ESI, Fig. S4A†). For potentials above +0.8 V vs. carbon, only double-layer capacitance of the porous carbon is encountered. Calcined VC without the core–shell structure, but the same V$_2$O$_5$ phase, shows very broad sets of redox peaks in the CV compared to the core–shell structure. It is expected that longer ion intercalation paths of the larger size of V$_2$O$_5$ domains in VC-500 °C result in slower redox reactions of the electrode, similar to VC-X70-air. In contrast, the core–shell structures present much smaller V$_2$O$_5$ particles due to partial transformation into porous carbon.

Galvanostatic charge/discharge cycling (GCPL) in half-cells was further employed for assessing the power handling ability of the electrode materials. As seen from Fig. 4B, GCPL curves of VC-X100-air and VC-X90-air exhibited several voltage plateaus between −1.2 V and +1.2 V vs. carbon, in agreement with the redox peaks in the CVs. Nearly ideal double-layer behavior with triangular-shape GCPL curves was observed for VC-CDC. The Li$^+$ intercalation and deintercalation leads to phase transitions during cycling and is kinetically enhanced for nanoscopic materials because of better accessibility of intercalation pathways. Therefore, smaller V$_2$O$_5$ core sizes of V$_2$O$_5$/CDC core–shell samples show superior rate handling compared to VC-500 with a more than 2-times larger V$_2$O$_5$ particle size (Fig. 4C). This is especially seen for VC-X100-air with more than 100 mA h g$^{-1}$ capacity at 5 A g$^{-1}$ (equivalent to a rate of ca. 28C).

The lower vanadium oxide content of VC-X100-air limits the maximum capacity at low rates. The highest value is achieved

### Table 2: Porosity data from nitrogen gas sorption analysis

| Sample       | BET SSA (m$^2$ g$^{-1}$) | DFT SSA (m$^2$ g$^{-1}$) | Pore volume (cm$^3$ g$^{-1}$) |
|--------------|---------------------------|---------------------------|--------------------------------|
| VC-X70       | 120                       | 100                       | 0.185                          |
| VC-X90       | 200                       | 208                       | 0.224                          |
| VC-X100      | 577                       | 485                       | 0.424                          |
| VC-CDC       | 1466                      | 1535                      | 0.673                          |
| VC-500       | 42                        | 23                        | 0.053                          |
| VC-X70-air   | 310                       | 269                       | 0.254                          |
| VC-X90-air   | 124                       | 66                        | 0.171                          |
| VC-X100-air  | 61                        | 38                        | 0.108                          |
for VC-X90-air with more than 300 mA h g$^{-1}$. Typically, in the literature capacity values are normalized to the active mass, in this case the mass of V$_2$O$_5$ in the composite electrode. Using this way of normalization, the highest capacity for VC-X90-air is 415 mA h g$^{-1}$. Even for higher specific currents of 5 A g$^{-1}$ the specific capacity reaches more than 100 mA h g$^{-1}$ (comparable to a C-rate of 12 C). The normalized values are given as an inset in Fig. 4D for comparison. Cycling in the potential window of $-1.2 \text{ V to } +1.2 \text{ V vs. carbon}$ is expected to be completely reversible, and this behavior was confirmed for all V$_2$O$_5$/CDC core–shell particles with a coulombic efficiency of ca. 100% (Fig. 4D). The VC particles calcined at 500 °C with much larger particle sizes (Fig. 1B) and without CDC shells, present a lower charge efficiency of less than 80% at 20 A g$^{-1}$. This might be the result of V$_2$O$_5$ degeneration due to kinetic limitations.

Electrochemical properties on a device level were measured using an asymmetric full-cell setup with nanoporous VC-CDC as the counter electrode. Typically, symmetric setups for electrode

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**Fig. 4** (A) Cyclic voltammograms at 1 mV s$^{-1}$, (B) galvanostatic charge–discharge curves at 0.05 A g$^{-1}$, (C) capacity values dependent on the specific current, and (D) the charge efficiency and capacity retention. All measurements were performed in the half-cell configuration with activated carbon counter and reference electrodes from $-1.2 \text{ V to } +1.2 \text{ V vs. carbon}$.

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**Fig. 5** (A) Ragone plot with energy efficiency values and (B) specific energy retention for 10,000 galvanostatic cycles at 1 A g$^{-1}$ (rate of ca. 2.4C) with cyclic voltammograms recorded before and after stability testing. All measurements were performed in the full-cell configuration with a charge-balanced VC-CDC working electrode and V$_2$O$_5$/CDC composite electrode with a cell voltage of 2.5 V.
Table 3  Literature values for full-cell measurements (two-electrodes) in symmetric and asymmetric fabrication. OLC: onion-like carbon; CNT: carbon nanotube; NW: nanowire; rGO: reduced graphene oxide; ACC: activated carbon fabric; NS: nanosheet; PPy: polypyrrole; sym.: symmetric; asym.: asymmetric; ACN: acetonitrile; PC: propylene carbonate; LiTFSI: lithium bis(trifluoromethylsulphonyl)imide; WE: working electrode; CE: counter electrode

| Material (WE) | Setup | CE | Electrolyte | Specific energy $\frac{W h}{kg}$ | Specific power $\frac{W}{kg}$ | Ref. |
|--------------|-------|----|-------------|---------------------------------|----------------------------|-----|
| V$_2$O$_5$/CDC core–shell | asym. | CDC | 1 M LiClO$_4$ in ACN | 84 (51) | 166 | This study |
| V$_2$O$_5$/OLC | asym. | AC | 1 M LiClO$_4$ in ACN | 38 | 57 | 33 |
| V$_2$O$_5$/CNTs | asym. | AC | 1 M LiClO$_4$ in PC | 40 | 200 | 22 |
| V$_2$O$_5$/nanowires | asym. | AC fabric | 0.1 M LiTFSI in ACN | 46 | 662 | 59 |
| Li$^+$ exchanged V$_2$O$_5$ NWs | asym. | AC fabric | 0.1 M LiTFSI in ACN | 66 | 720 | 59 |
| V$_2$O$_5$/NWs/rGO | asym. | MnO$_2$/rGO | 1 M LiTFSI in ACN | 15 | 437 | 60 |
| V$_2$O$_5$/Pin/ACC | asym. | rGO/ACC | LiNO$_3$/PVA gel | 39 | 900 | 65 |
| V$_2$O$_5$ NS | asym. | rGO | 1 M KCl | 76 | 900 | 34 |
| V$_2$O$_5$ 0.6H$_2$O | asym. | AC | 0.5 M K$_2$SO$_4$ | 29 | 70 | 58 |
| Layered V$_2$O$_5$ aerogel | asym. | AC | 1 M Na$_2$SO$_4$ | 20 | 200 | 66 |
| V$_2$O$_5$/MWCNTs | sym. | WE | 1 M Na$_2$SO$_4$ | 87 | 250 | 56 |
| V$_2$O$_5$ nanofibers | sym. | WE | 1 M LiClO$_4$ in PC | 78 | 1800 | 55 |
| V$_2$O$_5$ | sym. | WE | 2 M KCl | 15 | 1500 | 55 |
| V$_2$O$_5$/PPy core–shell | sym. | WE | LiNO$_3$/PVA gel | 10 | 5000 | 67 |
| V$_2$O$_5$/graphene | sym. | WE | 1 M Na$_2$SO$_4$ | 68 | 250 | 57 |

4. Conclusions

This study, for the first time, demonstrates a two-step in situ synthesis of hybrid particles consisting of porous carbon and redox-active V$_2$O$_5$ by solely using VC as the precursor. The materials with battery-like behavior (e.g., intercalation/deintercalation) are disadvantageous due to their polarization dependent redox-reactions. Yet, several studies used different types of V$_2$O$_5$ or V$_2$O$_5$/carbon composites, such as electrospun V$_2$O$_5$ nanofibers,$^{25}$ V$_2$O$_5$/MWCNT core–shell aerogels,$^{26}$ and V$_2$O$_5$/graphene aerogels$^{27}$ with the symmetrical full-cell setup. However, in some of these studies, negative and positive polarization in the full-cell arrangement was used (e.g. −1 V to +1 V in an aqueous electrolyte), instead of 0 V to 1 V. In these cases the capacitance and specific energies are much larger reaching misleading high values of 87 W h kg$^{-1}$ in aqueous 1 M Na$_2$SO$_4$ (ref. 56) and 78 W h kg$^{-1}$ in organic 1 M LiClO$_4$ in PC.$^{35}$

Enhanced electrochemical performance can be obtained by use of an asymmetric two-electrode setup (Fig. 5). Studies so far have shown, for aqueous systems, the highest specific energy of 29 W h kg$^{-1}$ (Table 3) for hydrothermally prepared V$_2$O$_5$·0.6H$_2$O with activated carbon as the counter electrode.$^{28}$ Due to the improved voltage stability of organic electrolytes, much higher energies can be achieved, ranging from 15 to 76 W h kg$^{-1}$ with MnO$_2$/rGO, AC fabric, or rGO as the counter electrode in an asymmetric arrangement.$^{34,35,60}$ In this study, an asymmetric full-cell setup with V$_2$O$_5$/CDC on the negative polarization side and charge-balanced VC-CDC on the positive polarization side was used. VC-X90-air as a negative electrode material presents superior performance with a specific energy in excess of 80 W h kg$^{-1}$ for charging and more than 50 W h kg$^{-1}$ for discharging (Fig. 5A). Even at higher rates, with a specific power of ~6.7 kW kg$^{-1}$, the specific energy is 27 W h kg$^{-1}$ (12 W h kg$^{-1}$ for discharging). In agreement with half-cell measurements, VC-X100-air shows a lower specific energy of 66 W h kg$^{-1}$ with comparable power handling because of the lower V$_2$O$_5$ content. The energy and power performance of this core–shell system is highly competitive with current literature values and is, to the best of our knowledge, the only core–shell system reaching 50–80 W h kg$^{-1}$ specific energy when using asymmetric full-cell measurements and proper application of the cell voltage.$^{61}$

The high attractiveness of this material for electrochemical energy storage is underlined by the high cycling stability with an energy retention of more than 80% and 70% over 10 000 galvanostatic cycles for VC-X90-air and VC-X100-air, respectively, measured at 1 A g$^{-1}$ (Fig. 5B). The nearly ideal charge efficiency of the half-cell measurements (100%) translates to a still attractive energy efficiency of the asymmetric devices between 60 and 80% for low rates. For comparison, standard double-layer capacitors using activated carbon electrodes only reach slightly higher values of 80–95% dependent on the electrode.$^{62}$
particles present a V$_2$O$_5$/CDC core–shell structure with nanoscopic V$_2$O$_5$ cores, completely accessible to electrolyte ions and inter-connected by highly conductive carbon. High specific energies of 50 and 80 Wh kg$^{-1}$ for discharging and charging, respectively, were measured in a facile asymmetric full-cell setup, while simultaneously retaining ultrafast cycling. The asymmetric cell design with CDC on the positive polarization side leads to superior stability over 10,000 cycles and comparably high energy efficiency of 60–80% at low rates. The novel synthesis procedure can easily be scaled up by means of larger precursor mass and may also be very attractive for other redox-active compounds.

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