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## VS<sub>4</sub>–NiAl LDH composite electrodes for next-generation high-performance supercapacitors†

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Transition metal dichalcogenides (TMDs), particularly vanadium tetrasulfide (VS<sub>4</sub>), have demonstrated potential for versatile applications in photochemical, electrochemical, energy harvesting, and energy storage applications over a period of time owing to their unique structural and redox properties. In this study, VS<sub>4</sub> was integrated with nickel aluminium layered double hydroxide (LDH) at varying concentrations (2.5 wt%, 5 wt%, and 7.5 wt%) via a hydrothermal approach to enhance its capacitive performance. Among the composites, VS<sub>4</sub> + LDH(5%) exhibited superior electrochemical characteristics with a high specific capacitance of 740 F g<sup>−1</sup> at 0.4 A g<sup>−1</sup> in 3 M KOH. Furthermore, a symmetric supercapacitor device fabricated using this composition delivered an energy density of 6.65 W h kg<sup>−1</sup>, yielding a suitable power density of 598.5 W kg<sup>−1</sup> at a current density of 1 A g<sup>−1</sup> applied within an operating potential window of 1.2 V. For the validation of the practical application of the SC device, we powered small electronic devices, underscoring the potential of VS<sub>4</sub> + LDH composites as an active and viable electrode material for advanced supercapacitors, bridging the gap between novel material designs and real-world applications.

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## 1. Introduction

Fossil fuel-based technologies are increasingly being phased out in favour of more sustainable alternatives as their detrimental influence on human health and the environment becomes ever more apparent. The emergence of new energy sources and storage solutions driven by remarkable recent technological progress has gained paramount importance in addressing these challenges.<sup>1,2</sup> In particular, energy storage devices (ESDs) have become extremely catalytic in overcoming these challenges by enhancing the technologies of renewable energy sources and maximizing grid integration.<sup>3</sup> Some of the challenges that ESDs face today are high production costs and inconsistent reproducibility, which pose substantial impediments to their commercialization.<sup>4,5</sup> Therefore, recent research has focused on developing high-performance ESDs with enhanced power density and increased energy density using novel materials with unique structures for commercial producibility.<sup>6,7</sup>

Supercapacitors (SCs), also known as ultracapacitors or electrochemical capacitors, take the lead in the energy storage industry, presenting unique features that set them apart from other energy-storage systems and provide a distinct advantage.<sup>8</sup> They are widely recognized for their environmental friendliness, high power density, rapid charge–discharge capability, safety, and long cycle life.<sup>9–12</sup> Based on their energy storage mechanisms, SCs are classified as pseudocapacitors, electric double-layer capacitors (EDLCs), and hybrid supercapacitors.<sup>13–15</sup> EDLCs' charge storage process is defined by ion adsorption and desorption at the electrode–electrolyte interface, as opposed to pseudocapacitors', which rely on surface-driven ion or proton insertion and extraction. In the case of hybrid SCs, the mechanism combines pseudocapacitive ion insertion/extraction and electrical double-layer capacitance, enabling enhanced energy storage capabilities.<sup>16,17</sup> Among the various components, the electrode material plays a pivotal role in determining the performance characteristics of an SC. A well-designed, optimized electrode material can significantly enhance the energy storage capacity, power density, and cycle life of SCs.

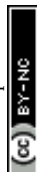
In this context, two-dimensional (2D) materials have received a great deal of attention as SC electrode materials in recent years.<sup>18–20</sup> As next-generation candidates for electrochemical energy storage devices, 2D materials offer several notable advantages: (i) the surface area is expanded in 2D nanosheets owing to the exposure of surface atoms; (ii) the edge sites of 2D nanosheets exhibit

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enhanced chemical reactivity, while the open van der Waals gaps facilitate electrolyte ion intercalation; and (iii) they possess exceptional mechanical strength and flexibility at the atomic scale.<sup>21,22</sup> Among these layered materials, transition metal-based compounds have emerged as particularly attractive for developing high-performance energy storage devices. A major competitor in the post-graphene era is the 2D transition metal dichalcogenide (TMD). Its huge surface area and varied oxidation states make it suitable for both faradaic and EDLC storage methods.<sup>23,24</sup>

Various types of layered materials, especially TMDs, are currently employed in SC applications. Among these materials, vanadium disulfide (VS<sub>2</sub>) features a 2D layered structure, with vanadium atoms snuggled between two layers of sulfur held together by weak van der Waals forces.<sup>23,25</sup> This structure has been extensively studied for energy storage applications due to its favorable properties, including an interlayer spacing of 5.76 Å that facilitates efficient ion and electron transport.<sup>26,27</sup> Furthermore, vanadium tetrasulfide (VS<sub>4</sub>) in its monoclinic form has a narrow band gap of 1.0 eV, allowing for comparatively strong electronic conductivity. The structural arrangement of VS<sub>4</sub>, with an interchain spacing of 5.83 Å, creates an abundance of active sites that promote efficient ion diffusion and storage. The sulfur atoms in VS<sub>4</sub> exist as S<sub>2</sub><sup>2-</sup> and are attached to the adjacent vanadium (V) atoms.<sup>28</sup> Consequently, VS<sub>4</sub> can be characterized as V<sup>4+</sup>(S<sub>2</sub><sup>2-</sup>)<sub>2</sub>, and due to its chain-like structure, this material enables rapid electrolyte ion transport, enhancing its reaction kinetics.<sup>29</sup> Moreover, VS<sub>4</sub>'s higher sulfur content plays a key role in electrochemical reactions in enhanced ionic intercalation and, therefore, has superior reaction capacity to VS<sub>2</sub>.<sup>30</sup> Its remarkable properties have made it a go-to electrode material for SC and lithium-ion battery manufacturers, fuelling its widespread commercial deployment as well.<sup>31,32</sup> However, despite its promises, pristine VS<sub>4</sub> faces limitations due to poor rate capability and cycling stability, stemming from inadequate electron conductivity and significant volume changes during cycling.<sup>33–35</sup> To address these issues, researchers have devised various strategies to boost the reaction kinetics and structural integrity.<sup>36</sup>

Composite materials, incorporating carbon nanotubes (CNTs), graphenes, and layered double hydroxides (LDHs), have been developed to amplify the properties of VS<sub>4</sub> and unlock its full potential. LDHs stand out among metal oxide/hydroxide materials as prospective electrodes for high-performance SCs. Their exclusive combination of high redox activity, cost-effectiveness, and environmental sustainability surpasses that of CNTs and graphenes, making LDHs attractive alternatives.<sup>37</sup> Moreover, their distinct sheet-like architecture facilitates rapid ion transport, enhances ion exchange flexibility, and allows for tailored composition.<sup>38</sup> LDHs feature a versatile, brucite-like host structure comprising tunable and oxidizable metal elements. This framework is interspersed with guest spaces containing interlayer anions and water molecules, enabling dynamic interactions and modifications.<sup>39</sup> LDHs, in general, can be explained with the following formula: [M<sub>1-x</sub><sup>2+</sup>M<sub>x</sub><sup>3+</sup>(OH)<sub>2</sub>](A<sup>n-</sup>)<sub>x/n</sub>·mH<sub>2</sub>O, where M<sup>2+</sup> indicates a divalent cation (e.g., Zn<sup>2+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup>), M<sup>3+</sup> indicates a trivalent cation (including Cr<sup>3+</sup>, Mn<sup>3+</sup>,

Fe<sup>3+</sup>, and Al<sup>3+</sup>), and A<sup>n-</sup> stands for the interlayer exchangeable anions (such as SO<sub>4</sub><sup>4-</sup>, OH<sup>-</sup>, and NO<sub>3</sub><sup>3-</sup>).<sup>40–42</sup>

In this study, we synthesized a VS<sub>4</sub> + NiAl LDH composite featuring a flower flake-like morphology composed of nanolayers *via* a rapid hydrothermal method. The composite capitalizes on its layered architecture to achieve a high surface area, enhancing the electrochemical activity. The VS<sub>4</sub> + NiAl LDH composite electrode delivers an outstanding electrochemical property, characterized by a specific capacitance of 740 F g<sup>-1</sup> at 0.4 A g<sup>-1</sup>, which significantly exceeds that of pure vanadium sulfide, demonstrating an excellent electrochemical performance for a 3-electrode set up with 3 M KOH as the aqueous electrolyte at a voltage window starting from 0 to 0.6 V. Furthermore, a symmetric flat cell was assembled using the VS<sub>4</sub> + NiAl LDH(5%) composite, which delivered an impressive energy density of 6.65 W h kg<sup>-1</sup> and a corresponding power density of 598.5 W kg<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>. Furthermore, we evaluated the composite electrode's cycling stability over 2500 cycles, observing 86.95% retention capacity after 1500 cycles at 1 A g<sup>-1</sup>. These results indeed highlight the potential of VS<sub>4</sub> in NiAl LDH composites with its high cyclability and cost-effectiveness for sustainable energy storage solutions. The fabricated symmetric supercapacitor in the form of a coin cell demonstrated its practical application by powering a watch and calculator for 200–250 seconds and a set of 3 LEDs for several seconds, showcasing its potential as a reliable and efficient energy storage solution.

## 2. Experimental

### 2.1. Materials

The analytical grade chemicals were used to synthesize VS<sub>4</sub> and VS<sub>4</sub> + NiAl LDH without any additional purification. Nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), aluminum nitrate nonahydrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), urea (CO(NH<sub>2</sub>)<sub>2</sub>), ammonium fluoride (NH<sub>4</sub>F), ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>), thioacetamide (TAA), potassium hydroxide (KOH), carbon black (super C<sub>65</sub>), and polyvinylidene fluoride (PVDF) were procured from Sisco Research Laboratories Pvt. Ltd (SRL). Double-distilled water (DI water), *N*-methyl-2-pyrrolidone (NMP) (C<sub>5</sub>H<sub>9</sub>NO), and ethanol (C<sub>2</sub>H<sub>6</sub>O) were used to prepare a homogeneous solution.

### 2.2. Preparation of VS<sub>4</sub>

The anemone-like VS<sub>4</sub> was synthesized by a solvothermal method as shown in step 1 of Fig. 1. NH<sub>4</sub>VO<sub>3</sub> (85.5 mmol) and CH<sub>3</sub>CSNH<sub>2</sub> (4 mmol) taken in a stoichiometric ratio were dissolved in 20 mL of NMP, helped by heating at 70 °C and held under magnetic stirring for 30 minutes for homogenous mixing of the precursors. Then, 20 mL of ethanol was added to the above solution with continuous stirring at 30 °C for 1 h. The mixture was then moved to a 100 mL autoclave lined with Teflon and heated to 160 °C for 24 h in an oven. The solid precipitate from the autoclave was collected by centrifugation at 8000 rpm and then repeatedly washed with water and ethanol. Ultimately, the precipitate was vacuum dried at



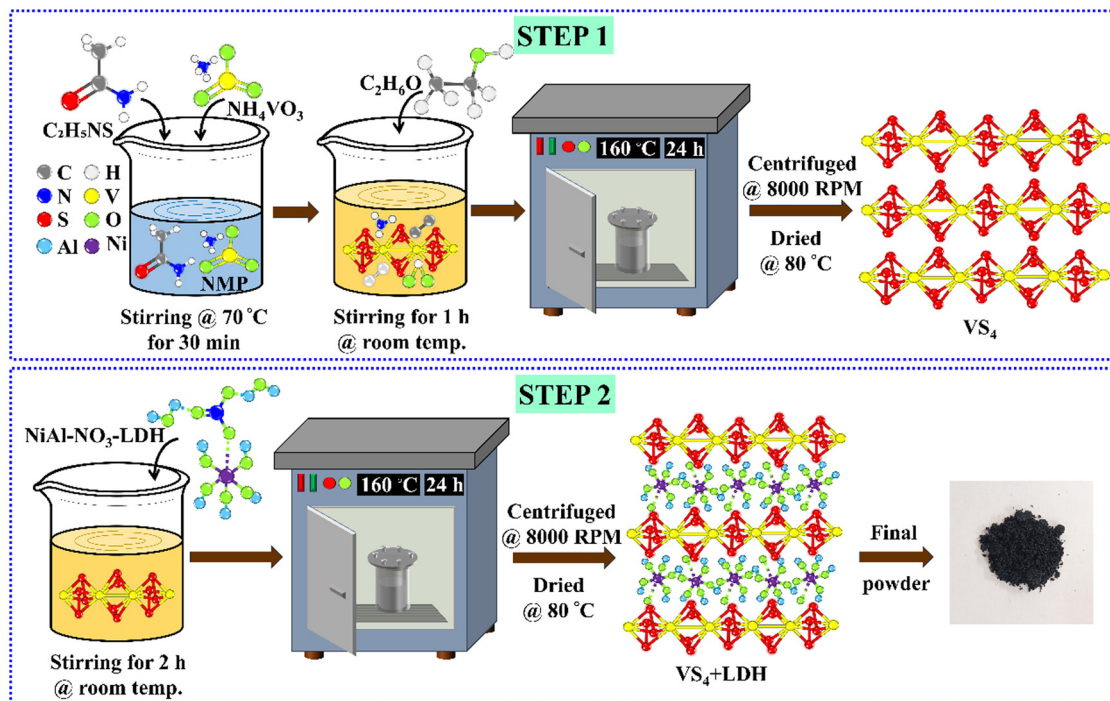
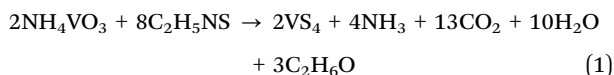


Fig. 1 Schematic of the hydrothermal synthesis of  $\text{VS}_4$  and  $\text{VS}_4$  + LDH composite material.

80 °C overnight. The solvents were used to increase the inter-atomic distance for better electrochemical performance of the metals used.<sup>43</sup> The following chemical equation represents the synthesis process:



### 2.3. Preparation of the NiAl LDH

The NiAl LDH compound was prepared by a hydrothermal method.  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (3 mmol) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1 mmol) were dissolved in 100 mL of DI water and kept under magnetic stirring till a homogeneous solution was formed. To the prepared solution,  $\text{CO}(\text{NH}_2)_2$  (2 mmol) and  $\text{NH}_4\text{F}$  (8 mmol) were added and kept under magnetic stirring for 1 h. The mixture was then placed in a 250 mL Teflon-lined autoclave and heated at 140 °C for 20 h. The precipitate was separated by centrifugation, washed sequentially with deionized water and ethanol, and dried at 60 °C for 12 h to obtain the NiAl LDH compound.

### 2.4. Preparation of the $\text{VS}_4$ + NiAl LDH composite

The  $\text{VS}_4$  + NiAl LDH composites were synthesized by a rapid solvothermal process; the schematic representation is shown in step 2 of Fig. 1. The stoichiometric ratio of  $\text{C}_2\text{H}_5\text{NS}$  and  $\text{NH}_4\text{VO}_3$  dissolution was achieved by treating the materials with 20 mL of NMP by stirring magnetically at 70 °C for 30 minutes. Subsequently, 20 mL of ethanol was added, and the solution was stirred at 30 °C for 1 h. Subsequently, concentration mass ratios of 2.5%, 5%, and 7.5% of the as-prepared LDH powder

were added to the mixture for three different solutions and stirred at room temperature for 2 h. The mixture was then transferred to a 100 mL Teflon-lined autoclave and hydrothermally treated at 160 °C for 24 h. The obtained black powder was recovered by centrifugation, rinsed with DI water and ethanol sequentially, and dried at 80 °C for 12 h to obtain the  $\text{VS}_4$  + NiAl LDH composite.

### 2.5. Material characterization details

The morphology of the  $\text{VS}_4$  + LDH composite materials was studied by field emission scanning electron microscopy (FESEM) (JEOL-JST-IT800) and high-resolution transmission electron microscopy (HR-TEM) (Fei TECNAI T20). To analyze the elemental composition and quantify the atomic and weight percentages of the constituent elements, energy-dispersive X-ray spectroscopy (EDX) was performed in conjunction with FESEM. Phase identification and crystallinity were assessed by powder X-ray diffraction (PXRD) measurements, conducted over a  $2\theta$  range of 10° to 80° using an Anton Paar diffractometer (model: XRDYNAMIC500). Raman spectra were acquired using a RAMAN 785 ER instrument to identify vibrational modes. Fourier transform infrared (FTIR) spectroscopy was conducted in the spectral range of 400–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  using a PerkinElmer spectrophotometer (model: 100S). The samples were prepared by a potassium bromide (KBr) pellet technique. Additionally, high-resolution X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha system to analyze the surface elemental composition and determine the oxidation states of the elements present in the composite.





## 2.6. Fabrication of Ni foam/VS<sub>4</sub> electrodes and electrochemical tests

Initially, the nickel foam (NF) substrate was thoroughly cleaned by sonication in 3 M HCl for 30 minutes to remove impurities. Following this, it was thoroughly rinsed with deionized water and ethanol until a neutral pH was achieved. The cleaned NF was then kept in an oven at 60 °C overnight for drying and weighed using a high-precision micro-digit balance before further processing. For the efficient transport of ions and for the optimization of the reaction environment, the design of the electrode is very crucial.<sup>44</sup> Therefore, the working electrode was constructed by adding VS<sub>4</sub>, carbon black, and PVDF in a mass ratio of 8/1/1, and the resulting mixture was homogenized with 1–2 mL of NMP. Usually, the capacitance of the materials depends on the thickness of the coating, which increases with the increase in the mass loading.<sup>45</sup> Therefore, the slurry was slowly coated optimally onto a nickel foam by a drop-casting method with the help of a micro pipette in an area of 1 cm<sup>2</sup> and was then heated at 80 °C overnight to vaporise the organic solvent. The same procedure was followed even for the VS<sub>4</sub> + LDH(*x*) (*x* = 2.5%, 5%, and 7.5%) composite electrodes. The composite mixtures contain between 1.2 and 1.4 mg of VS<sub>4</sub> or VS<sub>4</sub> + LDH(*x*) as the electroactive material. Electrochemical characterization was performed using an ORIGALYS electrochemical workstation (OGF-500). The evaluations included cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) using a 3 M KOH aqueous solution as the electrolyte. The platinum rod and Ag/AgCl were used as the counter and reference electrodes, respectively.

## 3. Results and discussion

### 3.1. Morphological analysis

The morphology of VS<sub>4</sub> and its composite NiAl-LDH was extensively characterized by FESEM, TEM, and HRTEM, as

shown in Fig. 2. These techniques provided valuable insights into the structural evolution and interface interactions between VS<sub>4</sub> and the LDH. VS<sub>4</sub> standalone of the FESEM revealed an intriguing anemone-like structure, comprising nanorods as shown in Fig. 2(a). This unique morphology suggests a high surface area and has potential for efficient electrochemical reactions. Upon the incorporation of NiAl + LDH(5%), the VS<sub>4</sub> structure underwent significant transformations, resulting in a nano-flower-flake type morphology shown in Fig. 2(b) and (c). However, as shown in Fig. S1 (ESI<sup>†</sup>), the 2.5% and 7.5% LDH concentrations lack the nanoflower-like structure, resulting in poorer electrochemical performance. Therefore, the overall flower-like hierarchical structure of VS<sub>4</sub> + LDH(5%) is beneficial for uses such as supercapacitors and batteries because of its inherent porosity. EDX analysis of the VS<sub>4</sub> + LDH(5%) composite confirms the presence of V, S, Ni, Al, and O elements, with their corresponding atomic and weight percentages presented in Fig. 2(d). TEM analysis reveals VS<sub>4</sub> + LDH(5%) nanoflakes with diameters of several tens of nanometers, as shown in Fig. 2(e). Further structural information obtained from HRTEM and SAED analyses is presented in Fig. 2(f) and (g) of the VS<sub>4</sub> + LDH(5%) composite. The SAED concentric ring patterns specify the Bragg reflection planes with their interplanar spacing of 0.57 nm for the VS<sub>4</sub> + LDH(5%) composite sample, as compared to the value of 0.56 for VS<sub>4</sub>,<sup>46</sup> respectively. It shows clear lattice fringes, increased interlayer spacing when compared to VS<sub>4</sub>, and homogeneous nanoflake distribution, facilitating ion/electron transfer and improving electrochemical kinetics.

### 3.2. Structural analysis

To determine the crystalline phase of VS<sub>4</sub> and VS<sub>4</sub> + LDH(*x*) (*x* = 2.5%, 5%, and 7.5%) composites, XRD analysis was performed, as shown in Fig. 3(a). The VS<sub>4</sub> + LDH(5%) composite has characteristic peaks at 21.4°, 23.6°, 31°, 35°, 38°, 45.15°,

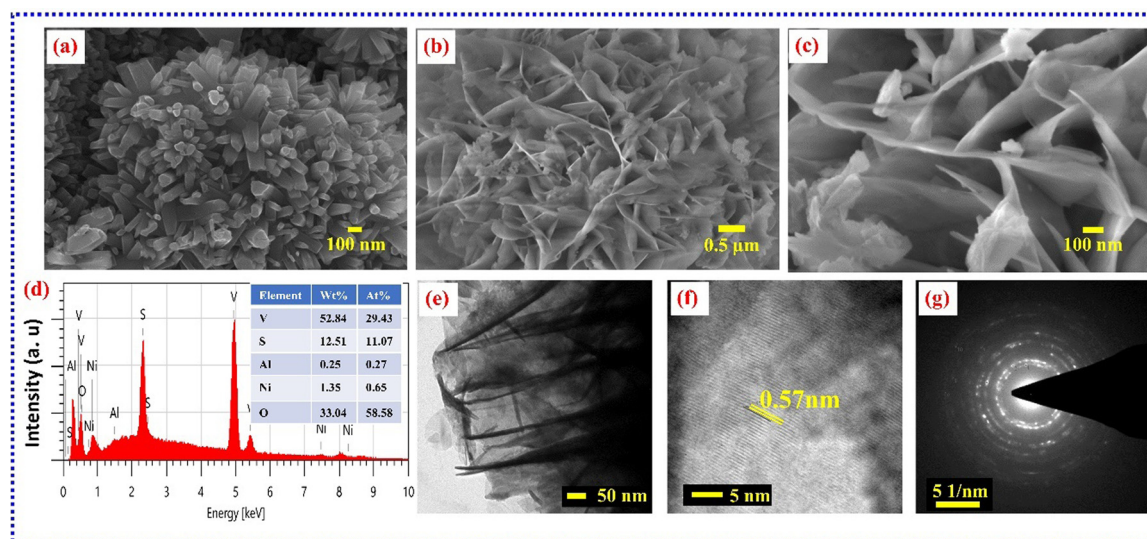


Fig. 2 FESEM images of (a) VS<sub>4</sub> and (b) and (c) VS<sub>4</sub> + LDH(5%) at low and high magnifications. (d) EDX spectra of VS<sub>4</sub> + LDH(5%) (inset shows the atomic and weight percentage). (e) Transmission electron microscopy (TEM) image, (f) high-resolution TEM (HR-TEM) image and (g) SAED pattern of the VS<sub>4</sub> + LDH(5%) composite.



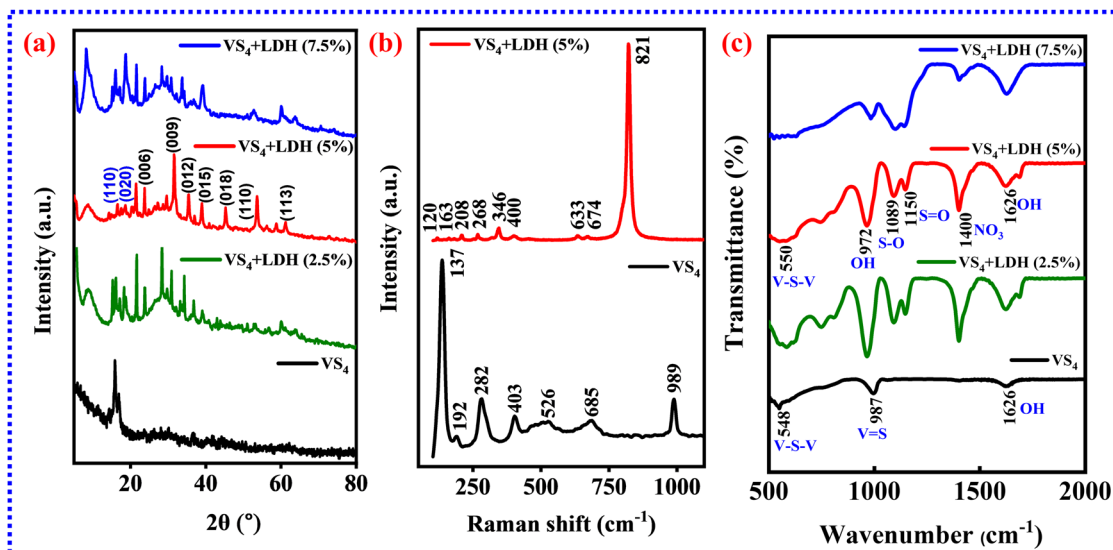


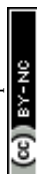
Fig. 3 (a) XRD pattern of VS<sub>4</sub> and VS<sub>4</sub> + LDH(*x* = 2.5%, 5%, and 7.5%). (b) Raman spectra of VS<sub>4</sub> and VS<sub>4</sub> + LDH(5%). (c) FTIR spectra of VS<sub>4</sub> and VS<sub>4</sub> + LDH(*x* = 2.5%, 5%, and 7.5%) composites.

and 53.52°, which belong to the (006), (009), (012), (015), (018) (110), and (113) planes of NiAl-LDH (JCPDS no. 15-0087). The planes correspond to the rhombohedral phase of NiAl-LDH.<sup>47</sup> The peaks at 15.93° and 16.92° for VS<sub>4</sub> belong to the (110) and (020) planes, and all observed diffraction peaks are indexed to the monoclinic phase of VS<sub>4</sub> (JCPDS no. 21-1434).<sup>48,49</sup>

Fig. 3(b) illustrates the Raman spectra of the prepared VS<sub>4</sub> and VS<sub>4</sub> + LDH(5%) composite. The two bands located at 137, 282, and 989 cm<sup>-1</sup> corresponded to the stretching and bending vibrations of the V-S bond, respectively. The peaks at 120, 163, and 346 cm<sup>-1</sup> correspond to the stretching and bending of the basal and non-basal planes of the NiAl-LDH. The functional groups present, chemical structure, and vibrational modes of the prepared materials were studied by FTIR spectroscopy. The FTIR spectra of VS<sub>4</sub> and VS<sub>4</sub> + LDH(*x* = 2.5%, 5%, and 7.5%) composites were recorded over the range of 500–2000 cm<sup>-1</sup>, as illustrated in Fig. 3(c). The absorption peaks occurred at 550, 972, 1089, 1150, 1400, and 1626 cm<sup>-1</sup> corresponding to VS<sub>4</sub> + LDH(5%). The vibrational modes of VS<sub>4</sub> also cause the expansion of the V-S-V metal ion group, giving rise to smaller peaks at 550 cm<sup>-1</sup>. The absorption bands at 1089 cm<sup>-1</sup> and 1150 cm<sup>-1</sup> correspond to the stretching vibrations of the S-O and S=O bonds, respectively. The broad band at 972 cm<sup>-1</sup> and a weaker band at 1626 cm<sup>-1</sup> are assigned to the stretching and bending vibrations of OH-groups from adsorbed water, respectively. The absorption peak at 1400 cm<sup>-1</sup> indicates the stretching vibration of the N-O bond of NO<sub>3</sub>. The FTIR confirms the bonding stretching vibration of the VS<sub>4</sub> and VS<sub>4</sub> + LDH(*x* = 2.5%, 5%, and 7.5% composites).

XPS was employed to study the composition, valence states, and purity of the synthesized VS<sub>4</sub> + LDH(5%) composite material.<sup>50</sup> Fig. 4(a) shows the VS<sub>4</sub> + LDH(5%) composite material survey spectrum, indicating the presence of primary elements, for instance, vanadium, sulfur, oxygen, nickel, and

aluminum, without any impurities. The XPS survey spectrum and the illustration of the corresponding elemental presence of VS<sub>4</sub> + LDH(2.5%) and VS<sub>4</sub> + LDH(7.5%) are illustrated in the ESI† (Fig. S2a and S3a). Fig. 4(b) depicts the binding energy (BE) of V 2p displaying two peaks: the first peak, at 517.51 eV, corresponds to V 2p<sub>3/2</sub>, while the second peak, at 524.97 eV, corresponds to V 2p<sub>1/2</sub>, respectively. The XPS spectra of VS<sub>4</sub> + LDH(2.5% and 7.5%) (Fig. S2b and S3b, ESI†) revealed shifts in the V 2p peaks. Specifically, the V 2p<sub>3/2</sub> and V 2p<sub>1/2</sub> peaks for V<sup>4+</sup> occurred at 517.38 eV and 524.11 eV (2.5% LDH), and 516.6 eV and 524.40 eV (7.5% LDH).<sup>51</sup> Fig. 4(c) illustrates the XPS spectra of the S 2p spectra, which confirms the presence of S<sub>2</sub><sup>2-</sup> dimer peaks at 164.00 eV and 162.84 eV, corresponding to S 2p<sub>1/2</sub> and S 2p<sub>3/2</sub>. The XPS spectra of VS<sub>4</sub> + LDH(2.5% and 7.5%) displayed shifts in the S 2p peaks, as illustrated in Fig. S2c and S3c (ESI†). The S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> peaks were observed at 162.82 eV and 164.18 eV for the 2.5% LDH and at 162.86 eV and 163.96 eV for the 7.5% LDH. This finding implies that the architecture of VS<sub>4</sub> can be adjusted effectively with the layered molecule-level regulation of the LDH structure at the optimised concentration. This observation underscores the superior structural and electrochemical performance of VS<sub>4</sub> + LDH(5%), highlighting its advantages over other composite materials.<sup>52,53</sup> In Fig. 4(c), the obtained VS<sub>4</sub> + LDH(5%) composite displays three characteristic peaks at 532.12 eV, 533.98 eV, and 535.80 eV, which correspond to V-O, defective O, and adsorbed O, respectively. The peak position and peak area ratio of the three types of oxygen species differ from those of the precursor VS<sub>4</sub> and the fully converted product V<sub>2</sub>O<sub>3</sub>, owing to the unique composition of the heterostructure. The XPS spectra of VS<sub>4</sub> + LDH(2.5% and 7.5%) showed shifts in the O 1s peaks (V-O, defective O, and adsorbed O), as depicted in Fig. S2d and S3d (ESI†). The analysis indicates that extrinsic adsorbed oxygen is crucial in the synthesis method of the VS<sub>4</sub> + LDH composite.<sup>54,55</sup> The VS<sub>4</sub>



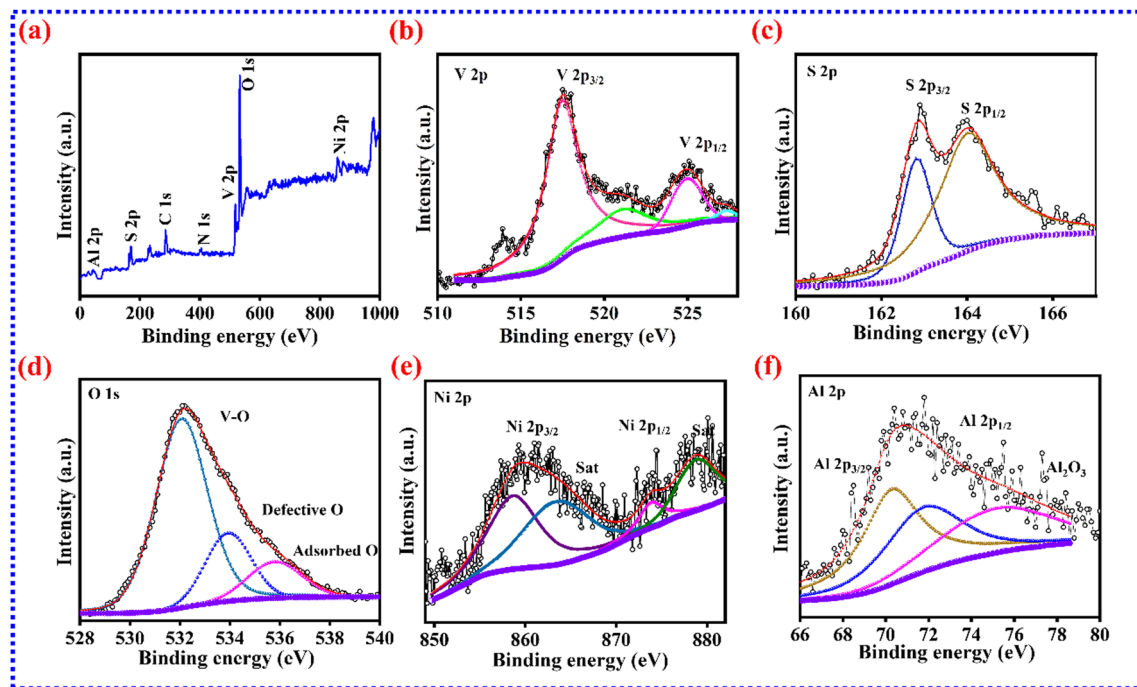


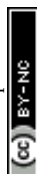
Fig. 4 (a) Wide-range XPS survey spectrum, (b) V 2p, (c) S 2p, (d) O 1s, (e) Ni 2p, and (f) Al 2p of the VS<sub>4</sub> + LDH(5%) composite material.

combination with the LDH has the potential to modify the distribution of surface charge, which may enhance electrostatic charge. This may lead to a significantly favourable change in binding energy. Furthermore, the specific quantities of the LDH added to the composite are 2.5%, 5%, and 7.5%. Consequently, the elements present in the LDH (Ni and Al) exist at very low concentrations, resulting in significantly low peak intensities in the corresponding XPS analysis. The VS<sub>4</sub> combination with the LDH has the potential to modify the distribution of surface charge, which may enhance electrostatic charge. This may lead to a significantly favorable change in binding energy. Furthermore, the specific quantities of the LDH added to the composite are 2.5%, 5%, and 7.5%. Consequently, the elements present in the LDH (Ni and Al) exist at very low concentrations, resulting in significantly low peak intensities of XPS spectra. Fig. 4(e) shows the Ni 2p high-resolution spectra. Around 858.90 eV, it deconvolutes into two peaks, which are identified as the Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub> orbitals of Ni<sup>2+</sup> at 855.71 eV, 855.83 eV, which are slightly higher than those of VS<sub>4</sub> + LDH(2.5%) and VS<sub>4</sub> + LDH(7.5%), respectively, as shown in Fig. S2 and S3 (ESI<sup>†</sup>). The peaks at 863.92 eV and 878.72 eV at VS<sub>4</sub> + LDH(5%) Fig. 4(e), 862.92 eV, and 876.54 eV at VS<sub>4</sub> + LDH(2.5%) (Fig. S2e, ESI<sup>†</sup>), 862.52 eV, and 878.98 eV at VS<sub>4</sub> + LDH 7.5% (Fig. S3e, ESI<sup>†</sup>) are supplemental satellite peaks of the Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub> orbitals. The Al 2p spectra (Fig. 4(f)) shows that the peaks at binding energies of 70.29 eV and 71.94 eV correspond to the Al 2p<sub>3/2</sub> and Al 2p<sub>1/2</sub> orbitals of Al<sup>3+</sup> in VS<sub>4</sub> + LDH(5%), while the peak at 75.57 eV indicates the presence of Al<sup>3+</sup> species in Al(OH)<sub>3</sub>. Furthermore, oxygen displays a peak with a B.E. value of 532.15 eV, which aligns with the metal–oxygen bonds.<sup>56</sup> The peaks at 67.81 eV and 73.40 eV,

and at 67.68 eV and 73.48 eV, correspond to the Al 2p<sub>3/2</sub> and Al 2p<sub>1/2</sub> orbitals of VS<sub>4</sub> + LDH (2.5%) and (7.5%) (Fig. S2f and S3f, ESI<sup>†</sup>), respectively.<sup>57</sup> The shifts in binding energies of V<sup>4+</sup>, S<sup>2-</sup>, Ni<sup>2+</sup>, and Al<sup>3+</sup> suggest a strong interfacial chemical interaction between VS<sub>4</sub> and the NiAl-LDH, indicating significant electronic coupling between the two components.

### 3.3. Electrochemical analysis

The electrochemical activity of the as-synthesized VS<sub>4</sub> and VS<sub>4</sub> + LDH(*x*) (*x* = 2.5%, 5%, and 7.5%) composite electrodes was investigated by CV, GCD, and EIS measurements using 3 M KOH electrolyte in a three-electrode cell configuration using an electrochemical workstation. The fundamental study of the current associated with the electrode as a function of time concerning the applied potential is interpreted from the CV.<sup>58</sup> The electrochemical behaviour of these electrodes was evaluated by the CV at a scan rate from 5 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup> in the potential window of 0 to 0.6 V using a three-electrode apparatus, as shown in Fig. 5(a)–(d). All these electrodes display two prominent redox peaks on the cathodic and anodic curves, corresponding to the continuous oxidation and reduction occurring within the VS<sub>4</sub> and VS<sub>4</sub> + LDH(*x*) (*x* = 2.5%, 5%, and 7.5%) composite electrodes. The peaks at 0.33 V, 0.35 V, 0.36 V, and 0.39 V are due to the oxidation of vanadium (V<sup>3+</sup> to V<sup>5+</sup>) and high sulfur content in VS<sub>4</sub> and VS<sub>4</sub> + LDH(*x*) (*x* = 2.5%, 5%, and 7.5%) composite materials. The cathode scan of the CV curves reveals peaks at 0.20 V, 0.21 V, 0.19 V, and 0.19 V in VS<sub>4</sub> and VS<sub>4</sub> + LDH(*x*) (*x* = 2.5%, 5%, and 7.5%) composite materials, corresponding to a reduction of high sulfur content and vanadium (V<sup>5+</sup> to V<sup>4+</sup>, and then to V<sup>3+</sup>). The CV measurement reveals identifiable redox peaks, indicating that the electrode





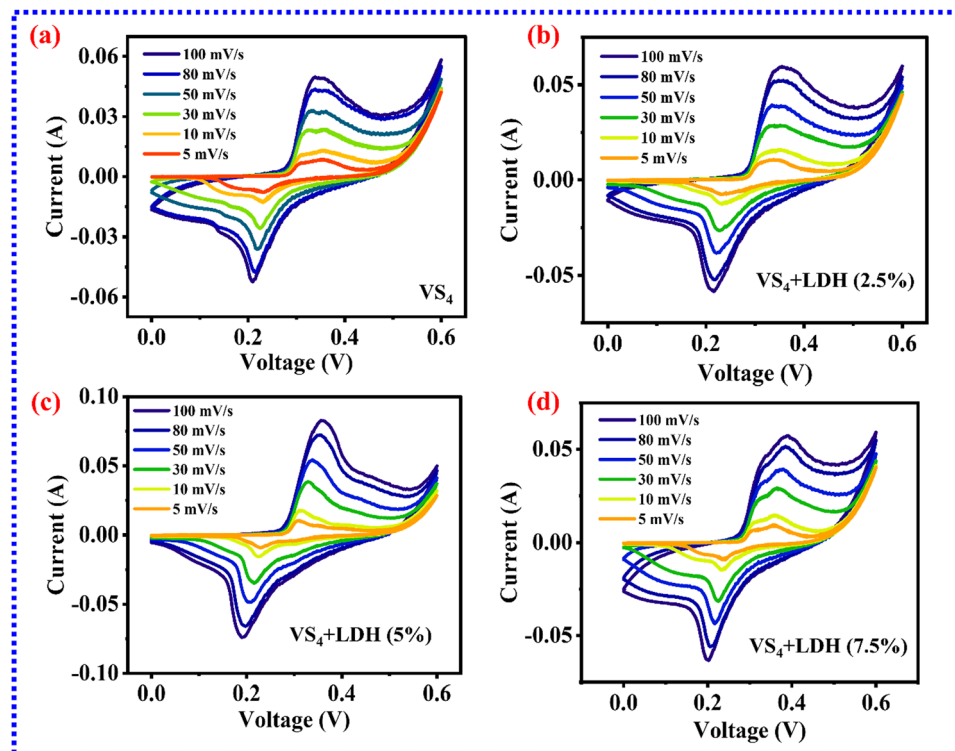


Fig. 5 CV of (a)  $\text{VS}_4$ , (b)  $\text{VS}_4 + \text{LDH}(2.5\%)$ , (c)  $\text{VS}_4 + \text{LDH}(5\%)$ , and (d)  $\text{VS}_4 + \text{LDH}(7.5\%)$  composite materials.

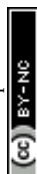
material functioned as a faradaic battery and was pseudocapacitive. Even at a higher scan rate, the CV curves stay constant, demonstrating a good rate of capability.

Notably, the  $\text{VS}_4$  nanosheets display two broad peaks, characteristic of their faradaic redox behaviour, underscoring their potential for pseudocapacitive energy storage. As the scan rates increase, the cathodic and anodic peaks shift due to the electrode's internal resistance. The rapid electron transfer or redox reactions occur at the electrode-electrolyte interface, facilitating efficient energy storage. Fig. 5(a) shows the CV measurements at different scan rates ranging from 5 to  $100 \text{ mV s}^{-1}$ . The resulting oxidation and reduction peaks are detected at 0.35 V and 0.23 V at a scan rate of  $5 \text{ mV s}^{-1}$ , and there is a peak shift as the scan rate is increased. Therefore, the observed peaks at a scan rate of  $100 \text{ mV s}^{-1}$  were at 0.33 V and 0.20 V, respectively. The  $\text{VS}_4$  electrode system exhibits reversible redox reactions, as evidenced by two distinct peaks. This phenomenon is attributed to the synergistic interaction between the electrode and hydroxide ions ( $\text{OH}^-$ ) in the electrolyte. Notably, increasing the scanning speed amplifies the anodic and cathodic peak currents, accompanied by an expansion of the enclosed area. This behavior is indicative of pseudocapacitive characteristics in the electrode. The peak shift is also observed in the  $\text{VS}_4 + \text{LDH}(x)$  ( $x = 2.5\%$ ,  $5\%$ , and  $7.5\%$ ) composite electrodes.

The GCD technique was employed to investigate further the electrochemical properties of  $\text{VS}_4$  and  $\text{VS}_4 + \text{LDH}(x)$  ( $x = 2.5\%$ ,  $5\%$ , and  $7.5\%$ ) composite electrodes. All measurements were performed in a 3 M KOH electrolyte within a potential window

of 0 to 0.6 V. For the pristine  $\text{VS}_4$  electrode, GCD curves were recorded at different current densities ranging from  $0.4 \text{ A g}^{-1}$  to  $3 \text{ A g}^{-1}$  to evaluate the rate capability and charge-discharge performance, as shown in Fig. 6(a). Similarly, GCD profiles of the  $\text{VS}_4 + \text{LDH}$  composites with different LDH loadings (2.5%, 5%, and 7.5%) were obtained across the same range of current densities, and are shown in Fig. 6(b)–(d). All GCD curves exhibit a characteristic non-linear behavior, which is a clear indication of pseudocapacitive charge storage mechanisms dominated by faradaic redox reactions involving vanadium ions ( $\text{V}^{5+}/\text{V}^{3+}$ ) and the high sulfur content in the structure. As the current density increases, a consistent decrease in discharge time is observed across all samples. This trend is attributed to the limited ion diffusion time at higher current densities, which restricts the full utilization of active sites within the electrode material, thereby reducing the total charge stored during each cycle.

When  $\text{K}^+$  and  $\text{OH}^-$  from the KOH electrolyte interact with  $\text{VS}_4$ , a chemical reaction occurs. The  $\text{K}^+$  ions, being highly electropositive, are attracted to the sulfur atoms in  $\text{VS}_4$ , leading to the formation of potassium sulfide ( $\text{K}_2\text{S}$ ). This reaction involves the transfer of sulfur atoms from the  $\text{VS}_4$  lattice to the  $\text{K}^+$  ions, resulting in the formation of a new compound. Simultaneously, the  $\text{OH}^-$  ions from the electrolyte react with the vanadium atoms in  $\text{VS}_4$ , leading to the formation of vanadium oxyhydroxide ( $\text{VO}_x(\text{OH})_y$ ). This reaction involves the incorporation of oxygen and hydrogen atoms from the  $\text{OH}^-$  ions into the  $\text{VS}_4$  lattice, resulting in the formation of a new vanadium-based compound. Overall, the reaction between  $\text{K}^+$  and  $\text{OH}^-$  with  $\text{VS}_4$  leads to the formation of new compounds,



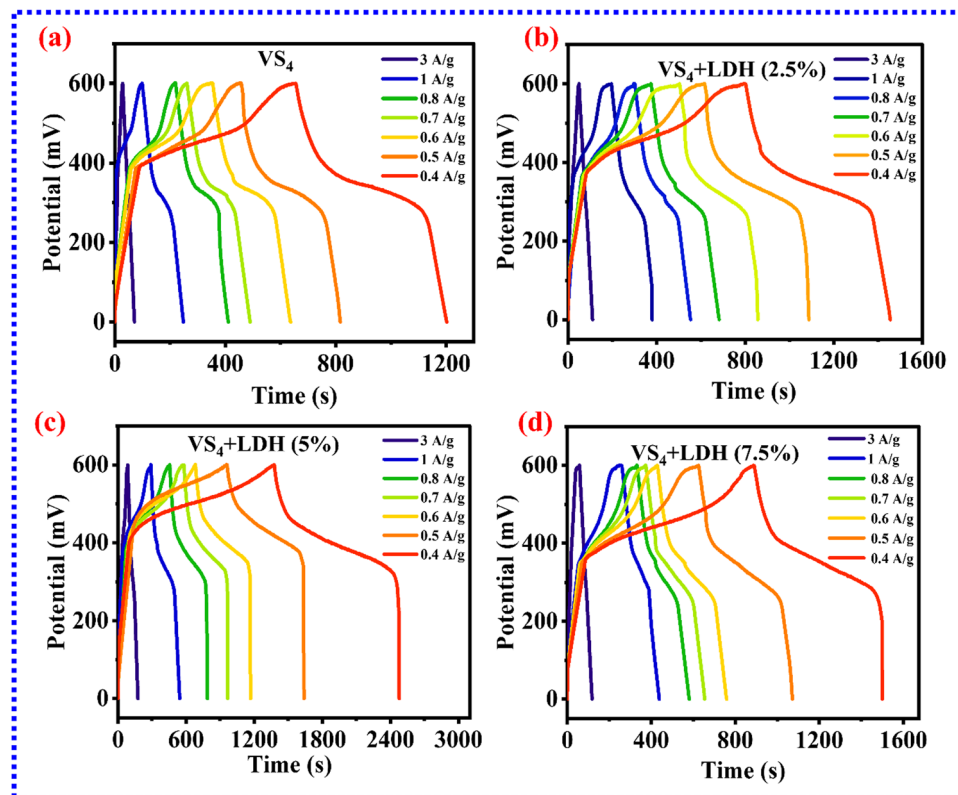


Fig. 6 GCD of (a)  $\text{VS}_4$ , (b)  $\text{VS}_4 + \text{LDH}(2.5\%)$ , (c)  $\text{VS}_4 + \text{LDH}(5\%)$ , and (d)  $\text{VS}_4 + \text{LDH}(7.5\%)$  composite materials.

including potassium sulfide and vanadium oxyhydroxide, taking forward the reactivity of the electrochemical kinetics.

The CV comparison of  $\text{VS}_4$  and  $\text{VS}_4 + \text{LDH}(x)$  ( $x = 2.5\%$ ,  $5\%$ , and  $7.5\%$ ) composite electrodes at  $100 \text{ mV s}^{-1}$  scan rate is shown in Fig. 7(a). The electrochemical analysis reveals that the  $\text{VS}_4 + \text{LDH}(5\%)$  electrode exhibits the highest specific capacity, surpassing  $\text{VS}_4$ ,  $\text{VS}_4 + \text{LDH}(2.5\%)$ , and  $\text{VS}_4 + \text{LDH}(7.5\%)$ , respectively. For comparison, the cyclic voltammetry (CV) curve at  $100 \text{ mV s}^{-1}$  for the bare Ni foam, which shows negligible activity, is also included in Fig. 7(a). This enhanced performance is attributed to the well-organized arrays and intimate integration of the NiAl-LDH and  $\text{VS}_4$ , facilitating efficient electron and ion transport and increased surface area in  $\text{VS}_4 + \text{LDH}(5\%)$ , allowing for greater ion intercalation and specific capacity. CV plots display distinct redox peaks, demonstrating pronounced faradaic reactions in the studied electrodes. The comparative GCD curves at  $0.4 \text{ A g}^{-1}$  current density of the four electrodes with the 0 to 0.6 V potential window in a 3 M KOH electrolyte solution were constructed. The results show that the  $\text{VS}_4 + \text{LDH}(5\%)$  composite material has high specific capacitance when compared to that of  $\text{VS}_4$ ,  $\text{VS}_4 + \text{LDH}(2.5\%)$ , and  $\text{VS}_4 + \text{LDH}(7.5\%)$  materials, as shown in Fig. 7(b). The results reveal that the composite electrode exhibits an extended discharge time, highlighting its outstanding electrochemical performance. Furthermore, it is noted that at elevated current densities, the discharge time decreases due to the impeded diffusion of  $\text{OH}^-$  ions within the electrode, which somewhat limits its high rate capability. The accelerated discharge at higher

currents curtails the intercalation process, resulting in under-utilization of the electrode's maximum charge storage potential.<sup>59</sup> The specific capacitance of the electrodes can be calculated from the CV (eqn (2)) and GCD (eqn (3)) curves as follows:<sup>60</sup>

$$C_s = \frac{\int I dV}{m \nu \Delta V} \quad (2)$$

$$C_s = \frac{I(A) \Delta t}{m \Delta V} \quad (3)$$

where  $C_s$  is the specific capacitance,  $V$  is the potential,  $I$  is the current,  $m$  is the mass loading of the material coated on the Ni foam,  $\nu$  is the scan rate,  $\Delta V$  is the potential window applied to the electrode, and  $\Delta t$  represents the discharge time.

The capacitance values for the  $\text{VS}_4$ ,  $\text{VS}_4 + \text{LDH}(2.5\%)$ ,  $\text{VS}_4 + \text{LDH}(5\%)$ , and  $\text{VS}_4 + \text{LDH}(7.5\%)$  electrodes at  $5 \text{ mV s}^{-1}$  scan rate were measured to be  $235.53 \text{ F g}^{-1}$ ,  $493.92 \text{ F g}^{-1}$ ,  $874.86 \text{ F g}^{-1}$  and  $462.36 \text{ F g}^{-1}$ , respectively. The capacitance values obtained for the  $\text{VS}_4$ ,  $\text{VS}_4 + \text{LDH}(2.5\%)$ ,  $\text{VS}_4 + \text{LDH}(5\%)$ , and  $\text{VS}_4 + \text{LDH}(7.5\%)$  electrodes were found to be  $364 \text{ F g}^{-1}$ ,  $437 \text{ F g}^{-1}$ ,  $740 \text{ F g}^{-1}$ , and  $405 \text{ F g}^{-1}$  at a current density of  $0.4 \text{ A g}^{-1}$ . The study found that  $\text{VS}_4 + \text{LDH}(5\%)$  has a much superior specific capacitance to  $\text{VS}_4$ ,  $\text{VS}_4 + \text{LDH}(2.5\%)$ , and  $\text{VS}_4 + \text{LDH}(7.5\%)$  nanosheets. As shown in Fig. 7(c), the value of  $C_s$  decreases with the increase in scan rate, indicating that the proper diffusion of electrolytic ions occurs at a lower scan rate when compared to the higher scan rate. The  $C_s$  value of all four electrodes is higher at a lower scan rate ( $5 \text{ mV s}^{-1}$ ), owing to the





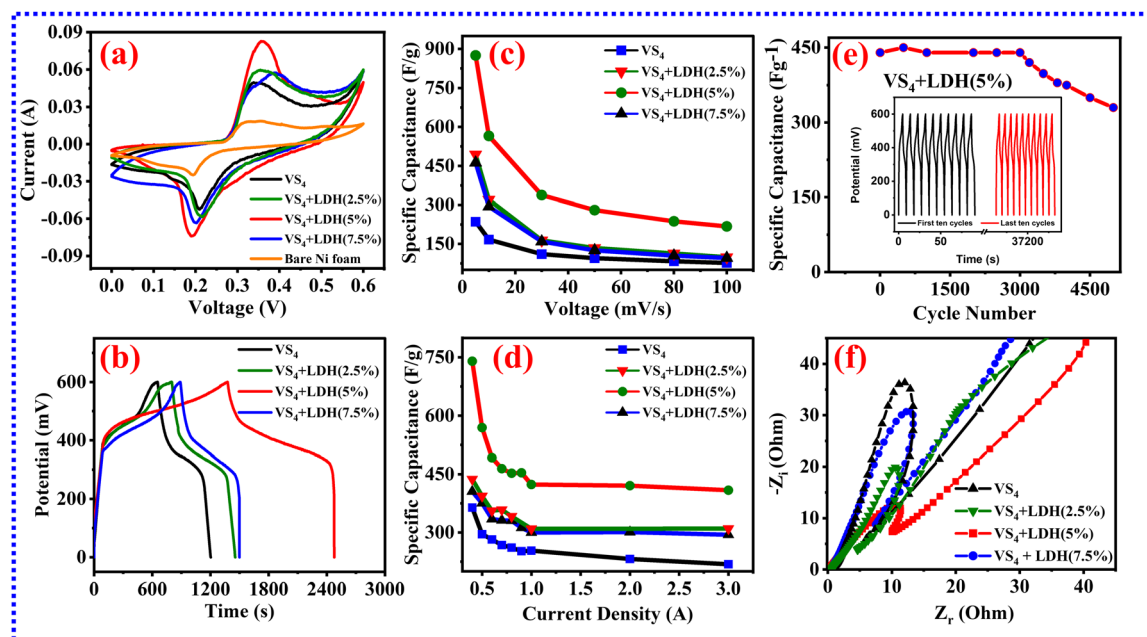
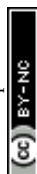


Fig. 7 (a) CV comparison of a bare Ni foam,  $\text{VS}_4$  and  $\text{VS}_4 + \text{LDH}(x)$  ( $x = 2.5\%$ ,  $5\%$ , and  $7.5\%$ ) composite electrodes at a  $100 \text{ mV s}^{-1}$  scan rate. (b) GCD comparison of the four electrodes at  $0.4 \text{ A g}^{-1}$ , rate capability curve of the four electrodes at (c) different scan rates ( $5\text{--}100 \text{ mV s}^{-1}$ ) and (d) different current densities ( $0.4\text{--}3 \text{ A g}^{-1}$ ), and (e) the specific capacitance vs. cycle number curve (inset: the initial and the final charge–discharge cycles of consecutive 5000 GCD cycles of the  $\text{VS}_4 + \text{LDH}(5\%)$  composite material at  $1 \text{ A g}^{-1}$ ). (f) Nyquist plots of  $\text{VS}_4$  and  $\text{VS}_4 + \text{LDH}(x)$  ( $x = 2.5\%$ ,  $5\%$ , and  $7.5\%$ ) composite electrodes.

electrolyte ions diffusing entirely into the electrode and having enough time to flow completely throughout the active area for charge storage. When the scan rate increases, the  $C_s$  value of the electrode decreases because of the time limit of the higher scan rates, resulting in the momentum of the electrolyte ions to interpolate the innermost sites of the  $\text{VS}_4 + \text{LDH}(5\%)$  composite electrode components in the electrode being limited. Moreover, the overall performance of the electrolyte is very much dependent on the intrinsic molecular properties, and it is increasingly evident that it plays a pivotal role in determining the conductivity and stability of the electrode.<sup>61</sup> This is the reason for the CV curve, with only the outer active surface resulting in charge storage. As a result, the variation identified in the response of the CV and the current performance of the  $\text{VS}_4 + \text{LDH}(5\%)$  composite electrode was determined by the ion's physical properties, including the ionic radius, conductivity, ion mobility, and ionic hydration sphere radius, and the  $\text{K}^+$  ion ionic radii and hydration number are  $1.33 \text{ \AA}$  and  $6.5$ , which are almost the same as  $\text{O}^{2-}$  ions, correspondingly. The  $C_s$  values of the materials were evaluated not only by the KOH electrolyte's ionic radii for improved diffusion but also by the mobility and conductivity of the ions ( $\text{K}^+$  or  $\text{OH}^-$ ). Hereafter, the  $\text{K}^+$  ions with a high molar conductivity of  $73.5 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$  float on the surface of the electrode/electrolyte to enable improved  $C_s$ . The existence of  $\text{OH}^-$  anions delays the mobility of  $\text{K}^+$  cations, which is the primary reason for the fluctuation of capacitance value in  $\text{VS}_4$  and  $\text{VS}_4 + \text{LDH}(x)$  ( $x = 2.5\%$ ,  $5\%$ , and  $7.5\%$ ) composite materials.

Fig. 7(d) illustrates the variation in  $C_s$  for different current densities for  $\text{VS}_4$  and  $\text{VS}_4 + \text{LDH}(x)$  ( $x = 2.5\%$ ,  $5\%$ , and  $7.5\%$ )

composite electrodes using a  $3 \text{ M KOH}$  electrolyte solution. At a higher charging and discharging rate of  $0.4 \text{ A g}^{-1}$ , the  $\text{VS}_4 + \text{LDH}(5\%)$  electrode retains significantly higher  $C_s$ , demonstrating its ability to withstand high charge rates during the intercalation and deintercalation processes. This behaviour underscores the excellent electrochemical stability and robustness of the  $\text{VS}_4$  structure under rapid charge–discharge conditions. The observed variability in  $C_s$  values derived from CV and GCD measurements arises because CV evaluates capacitance at specific potentials, whereas GCD considers the total potential range and averages the capacitance over this range based on the electrolyte behaviour and sample performance. The averaging of capacitance across the voltage range during GCD analysis can account for the slight differences in  $C_s$ . Here, the  $\text{VS}_4 + \text{LDH}(5\%)$  nanomaterial exhibits improved capacitive performance due to its unique structure. The proper incorporation of the NiAl LDH into the  $\text{VS}_4$  matrix can also be observed from the FESEM and the XPS data. Unlike the morphology of  $\text{VS}_4 + \text{LDH}(2.5\%)$  and  $\text{VS}_4 + \text{LDH}(7.5\%)$  (Fig. S1, ESI†), the nano-flower flake type morphology of  $\text{VS}_4 + \text{LDH}(5\%)$  provides a large surface area, allowing ions to access both surface and core regions, which enables efficient redox reactions. The composite's 2D ultrathin nano-sheet structure enables rapid charge transport and provides abundant active sites. The unique horn-like edge arrangement and positively charged LDHs facilitate efficient ion exchange and accessibility, enhancing charge storage. Additionally, sulfur in  $\text{VS}_4$  amplifies electrochemical activity, active sites, and electron transport, accelerating the electrochemical kinetics.<sup>62</sup> Moreover, the presence of sulfur in the host  $\text{VS}_4$  atoms enhances electrochemical activity, provides additional active



sites, and improves electron transport, ultimately boosting the electrochemical kinetics. These characteristics collectively improve the charge storage and overall electrochemical efficiency of the VS<sub>4</sub> + LDH(5%) electrode. As shown in the FESEM images, the homogeneous distribution of LDH within the VS<sub>4</sub> matrix leads to the formation of a flower-like structure with nanosheets that have an increased surface area and are interconnected in their framework, leading to increased reactivity, and creating a two-dimensional layered structure that facilitates the diffusion of electrolyte ions.

The VS<sub>4</sub> + LDH(5%) composite electrode's long-term cycling stability was tested during 5000 continuous charge and discharge cycles with a specific current of 1 A g<sup>-1</sup>. Fig. 7(e) depicts the charge and discharge curves for the first and last ten cycles, respectively. After 3500 cycles, the VS<sub>4</sub> + LDH(5%) composite electrodes preserved approximately 90.5% of their initial C<sub>s</sub>. As the number of cycles increases, the capacitance retention progressively decreases, and the deterioration process for the electrode begins at 3000 cycles. The cycling stability can be attributed to the following aspects: the interspace within the flower-like VS<sub>4</sub> + LDH(5%) composite helps relieve internal stress caused by volume expansion during electrolyte ion insertion and extraction. This relief mechanism mitigates structural damage, promoting stable cycling performance and enhancing cycle life by reducing internal stress and structural degradation, ultimately enabling more stable charge/discharge processes. Further, the specific capacitance *vs.* cycle number graph shown in Fig. 7(e), we can observe that there is a slight initial increase in capacitance, which can be attributed to the gradual activation of active material within the electrode. As the electrode undergoes repeated charge/discharge cycles, more electrochemically active sites, particularly Ni and V sites, become fully exposed and accessible. This increased exposure enables more efficient charge storage, contributing to the observed capacitance enhancement. As shown in Fig. 7(e), the prolonged cycling, however, leads to capacitance degradation. This decline may be due to structural changes, specifically the transformation of the LDH to β-Ni(OH)<sub>2</sub>, which occurs during the charge/discharge process.<sup>63</sup> This transformation potentially alters the electrode's electrochemical properties, ultimately affecting its performance. The material's stability declines progressively after 3500 cycles. Pre- and post-cyclic FESEM images are shown in the ESI† for reference (Fig. S4). Therefore, the VS<sub>4</sub> + LDH(5%) composite material crystal structure and shape are largely responsible for its better performance because of its numerous advantages such as high C<sub>s</sub>, good rate capability, and reasonable cycling stability. Finally, the VS<sub>4</sub> + LDH(5%) composite electrode promotes effective ion and electron transport and has high C<sub>s</sub> at ambient temperature, making it a promising choice for supercapacitor application.

EIS was employed to evaluate the electrical conductivity and charge-transfer characteristics of the electrode materials. The measurements were conducted over a frequency range of 0.01 Hz to 100 kHz with an applied AC amplitude of 10 mV. The resulting Nyquist plot, shown in Fig. 7(f), has a quasi-semicircular shape at high frequencies, where the x-intercept

represents the material's internal or ohmic resistance (R<sub>s</sub>). This resistance encompasses the ionic resistance of the electrolyte, the intrinsic material resistance, and the contact resistance between components. Notably, the diameter of the semicircle on the impedance spectrum indicates the charge-transfer resistance (R<sub>ct</sub>), providing insights into the material's conductivity, with a smaller diameter indicating higher conductivity. The Warburg resistance (W), reflected by the slope of the low-frequency linear segment, signifies the degree of ion diffusion and electrochemical interaction between the electrode material and the surrounding electrolyte.<sup>64</sup> As shown in Fig. 7(f), VS<sub>4</sub> + LDH(5%) has a lower R<sub>s</sub> value (0.33 Ω), representing the slope at low frequency, signifying that the VS<sub>4</sub> + LDH(5%) composite has a lower Warburg resistance (W) and a higher ion diffusion rate.

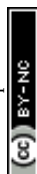
Given the pseudocapacitive behavior of the VS<sub>4</sub> + LDH(5%) composite electrode, its kinetic characteristics were elucidated by examining the corresponding CV plot. Fig. 8(a)–(f) illustrate the capacitive and diffusion role of the VS<sub>4</sub> + LDH(5%) composite electrode at different scan rates (5 to 100 mV s<sup>-1</sup>). As the scan rate increases, the diffusive contribution decreases while the surface-controlled capacitive phenomenon rises. This behaviour occurs because, at lower scan rates, electrolyte ions can fully diffuse into the microporous network, whereas at higher scan rates, the charge storage mechanism becomes dominated by surface phenomena. The oxidative and reductive peak currents exhibit a highly linear relationship, with values from the linear regression analysis being very close to 1. The linear regression analysis confirms the diffusion-regulated charge storage behaviour in the VS<sub>4</sub> + LDH(5%) electrode, highlighting the importance of both diffusion-controlled and capacitive processes in governing the electrochemical energy storage.<sup>65,66</sup> Eqn (4) can be used to explain the relationship between peak currents and scan rates.

$$i = av^b \quad (4)$$

where  $v$  is the scan rate,  $i$  is the achieved peak current,  $a$  is a constant, and  $b$  indicates the charge storage mechanism. The capacitance contribution is assessed by plotting  $\log(i)$  *versus*  $\log(v)$  of the anodic and cathodic peak current densities ( $I$ , A g<sup>-1</sup>), according to a power-law relationship with scan rate ( $V$ , mV s<sup>-1</sup>). The parameter ' $b$ ' is significant, as it represents the combined effects of capacitive electrochemical processes and ionic diffusion. Notably, ' $b$ ' values of 1 and 0.5 correspond to ideal capacitive and diffusive behaviors, respectively, in charge storage. Fig. 8(g) shows that the calculated  $b$  value of 0.61 for the VS<sub>4</sub> + LDH(5%) electrode suggests a combined mechanism, where both capacitive contributions and ion diffusion-controlled processes play a role. The immediate electrical current can be expressed as the proportion contribution of the capacitive and diffusion behaviour, and it can be determined using eqn (5):<sup>67</sup>

$$i = k_1v + k_2v^{1/2} \quad (5)$$

where ' $i$ ' is the peak current density and ' $v$ ' the scan rate;  $k_1$  and  $k_2$  are constant values. A distinct  $k_1$  value is derived for each



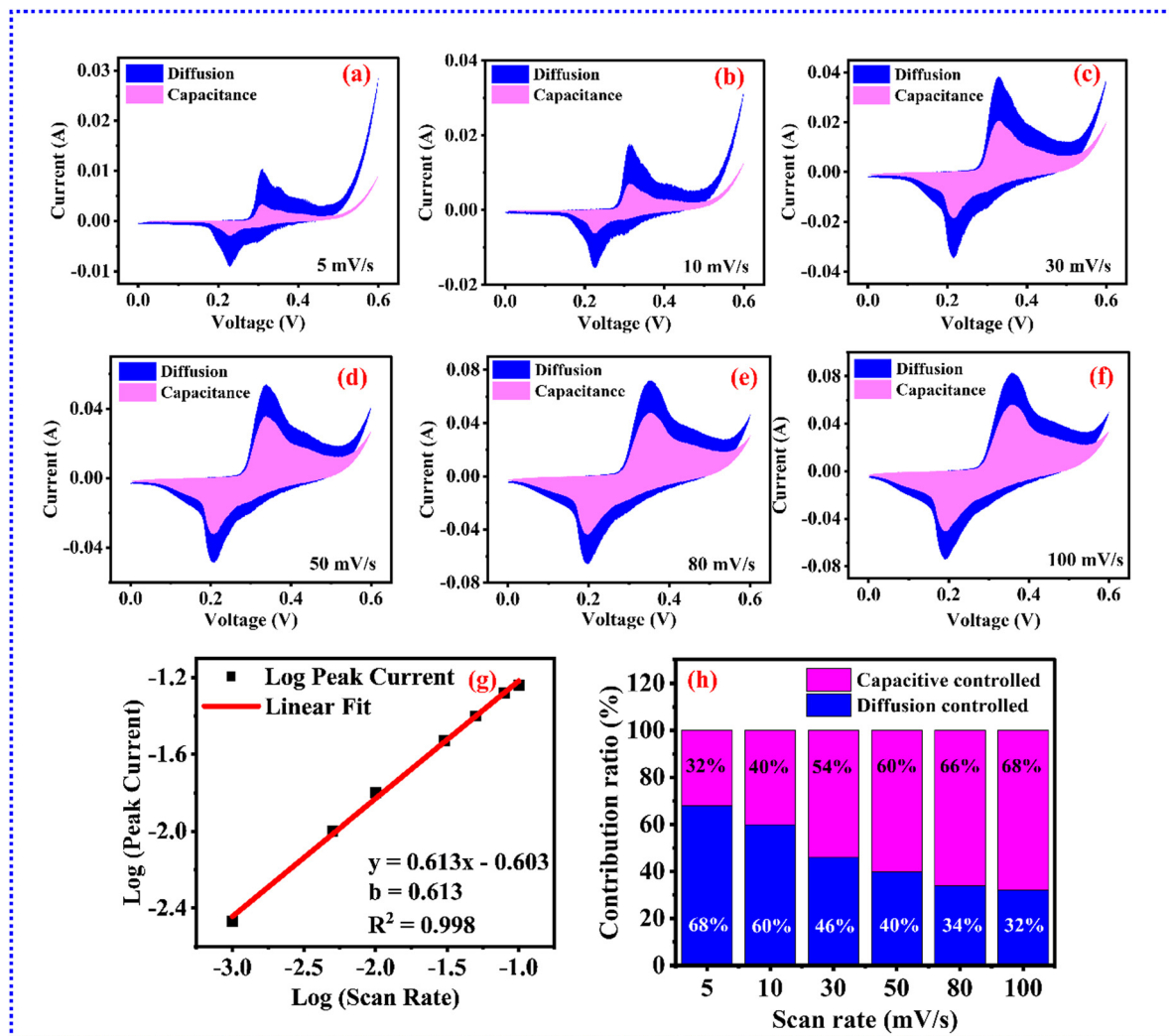


Fig. 8 (a)–(f) CV plots of the  $\text{VS}_4 + \text{LDH}(5\%)$  composite material at different scan rates extending from 5 to  $100 \text{ mV s}^{-1}$  in 3 M KOH with the contribution of diffusion and capacitive controlled surface process. (g)  $b$  value of the  $\text{VS}_4 + \text{LDH}(5\%)$  composite electrode material. (h) Plot illustrating the charge contribution from surface capacitive and diffusive processes as a function of scan rate.

specific voltage through a fitting analysis. Fitting analysis yields a  $k_1$  value for each specific voltage, where  $k_1v$  represents the capacitive current contribution and  $k_2v^{1/2}$  represents the diffusion-controlled current contribution. By determining  $k_1$  and  $k_2$  at a given potential, the relative contributions of pseudocapacitive and diffusive processes to the overall capacitance can be precisely determined. As shown in Fig. 8(h), the proportion of surface capacitive control in the charge storage process was evaluated at different scan rates of 5, 10, 30, 50, 80, and  $100 \text{ mV s}^{-1}$  as 32.0%, 40%, 54%, 60%, 66%, and 68%, respectively. The capacitive contribution increases progressively with the scan rate, indicating that the surface redox reaction plays a dominant role in the charge storage mechanism, particularly at high scan rates.

### 3.4. Device testing and application

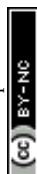
To comprehensively analyse and understand the electrochemical performance of the  $\text{VS}_4 + \text{LDH}(5\%)$  composite electrodes, a

symmetric two-electrode device that serves as both the cathode and the anode was fabricated with 6 M KOH used as the electrolyte solution. The CV of the symmetric cell shows a potential window ranging from  $-0.6$  to  $0.6 \text{ V}$  at different scan rates from 10 to  $40 \text{ mV s}^{-1}$ , as shown in Fig. 9(a). The CV profiles exhibit a quasi-rectangular shape at various scan rates, signifying an ideal capacitive behaviour.<sup>68</sup>

The GCD curves of the  $\text{VS}_4 + \text{LDH}(5\%)$  composite electrode at different current densities ranging from  $0.4 \text{ A g}^{-1}$  to  $2 \text{ A g}^{-1}$  are shown in Fig. 9(b). These curves show mostly pseudocapacitor behaviour, in correspondence with the CV of the sample. The specific capacitance values at different current densities were determined using eqn (6):<sup>69</sup>

$$C_s = \frac{2I(A)\Delta t}{m\Delta V} \text{ F g}^{-1} \quad (6)$$

The EIS analysis was performed to evaluate the resistive behaviour of the electrode material and the electrolyte solution



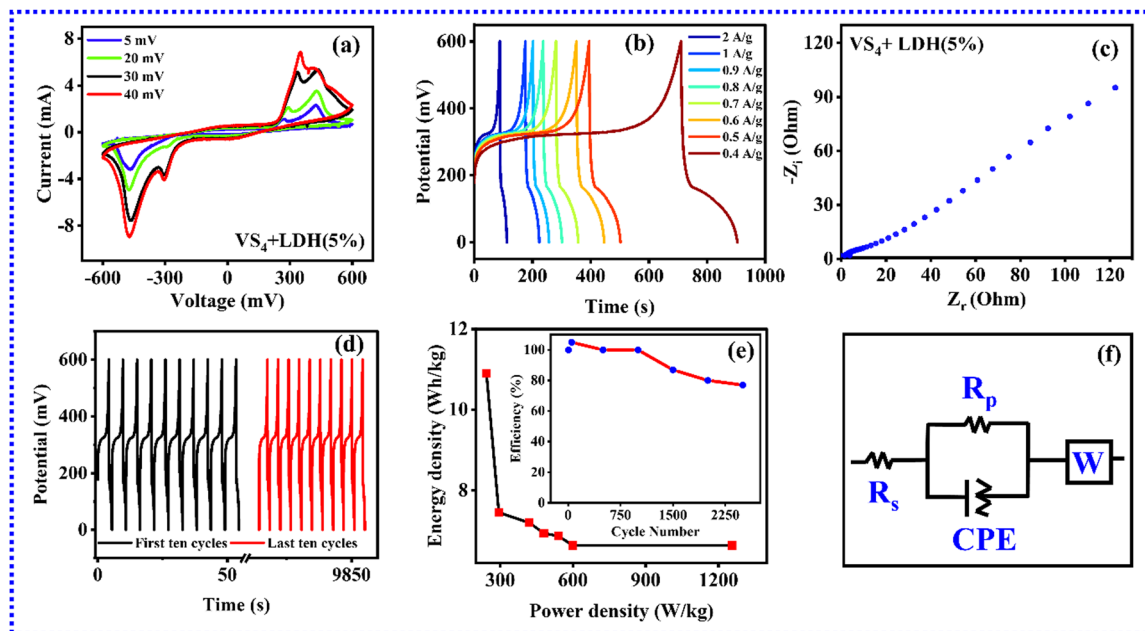


Fig. 9 (a) CV curves, (b) GCD curves, (c) Nyquist plot, (d) stability plot for 2500 cycles, (e) specific energy versus specific power profile (Ragone plots) of cells (inset: CS retention of material for 2500 cycles), and (f) circuit diagram.

in supercapacitor applications. The Nyquist plot was obtained from impedance measurements spanning a broad frequency range of 0.01 Hz to 100 kHz, as shown in Fig. 9(c).

A two-electrode system was employed to investigate the cyclic durability of the supercapacitor, a critical parameter for practical uses. As depicted in Fig. 9(d), the stability test results reveal a reasonable cycling stability, with the device maintaining 86.95% of its initial capacity over 2500 cycles at a current density of  $1 \text{ A g}^{-1}$ . In Fig. 9(e) (inset), the efficiency percentage per cycle for 2500 cycles is also included, and the FESEM image of the post-2500-cycles of the  $\text{VS}_4 + \text{LDH}(5\%)$  SC device active electrode material is depicted in Fig. S5 of the ESI†. The reduction in capacitance preservation in the device is caused by the mechanical stress on the electrode during the electrolyte intercalation, which weakens it and hence reduces the electrode stability. Moreover, during the charging–discharging cycles, an activation process occurs, similar to the three-electrode configuration, resulting in an initial increase and a subsequent gradual decline in specific capacity.

The performance metrics of the supercapacitor were evaluated in terms of energy density ( $E$ ) and power density ( $P$ ), which are the two important characteristics of supercapacitors. The  $E$  and  $P$  of the  $\text{VS}_4 + \text{LDH}(5\%)$  composite electrodes were calculated and represented in the Ragone plot, as shown in Fig. 9(e). The energy density ( $E$ ) and power density ( $P$ ) of the two-electrode system were derived from the specific capacitance according to eqn (7) and (8):<sup>70,71</sup>

$$\text{Energy density } (E) = \frac{1}{2} \frac{C_s \times \Delta V^2}{3.6} (\text{W h kg}^{-1}) \quad (7)$$

$$\text{Power density } (P) = \frac{E \times 3600}{\Delta t} (\text{W kg}^{-1}) \quad (8)$$

where  $\Delta V$  is the voltage window,  $\Delta t$  the discharge time, and  $C_s$  the specific capacitance of the cell. The maximum energy density of the device was  $6.65 \text{ W h kg}^{-1}$ , with a corresponding power density of  $598.5 \text{ W kg}^{-1}$  at a current density of  $1 \text{ A g}^{-1}$ . The symmetric device with  $\text{VS}_4 + \text{LDH}(5\%)$  electrodes achieves a substantial improvement in energy density, especially at elevated power densities. According to eqn (7), a reasonably high specific capacity and a wide potential window are necessary preconditions for reaching high energy density. The  $\text{VS}_4 + \text{LDH}(5\%)$  composite electrode with a high sulfur content, with the inclusion of LDHs at a specific concentration, has a high specific surface area, coupled with the radially grown nanoflake morphology, providing a high density of active sites, resulting in an improved specific capacity.

The equivalent circuit model shown in Fig. 9(f) comprises a resistor, a capacitor, and a constant-phase element (CPE), which collectively simulate the complex electrochemical behavior and reactions occurring within the system. The series resistance ( $R_s$ ), representing the ohmic drop between the electrode and the electrolyte, was determined to be  $1.33 \Omega$  from the intercept with the  $Z$ -axis at high frequencies, as shown in Table 1. The fitted Nyquist circuit confirms the predominance of pseudocapacitive behaviour, consistent with the CV and GCD data. These results highlight the excellent electrochemical performance of the  $\text{VS}_4 + \text{LDH}(5\%)$  composite electrode-based supercapacitor.

Further, a symmetric supercapacitor device was fabricated for real-world applications, as depicted in Fig. 10(a). The device was assembled using a  $\text{VS}_4 + \text{LDH}(5\%)$  composite electrode slurry coated onto two conductive copper sheets, with cellulose paper serving as the separator. The nano  $\text{VS}_4 + \text{LDH}(5\%)$  composite electrode slurry was applied to copper sheets





**Table 1** EIS fitted parameters from the Nyquist plot

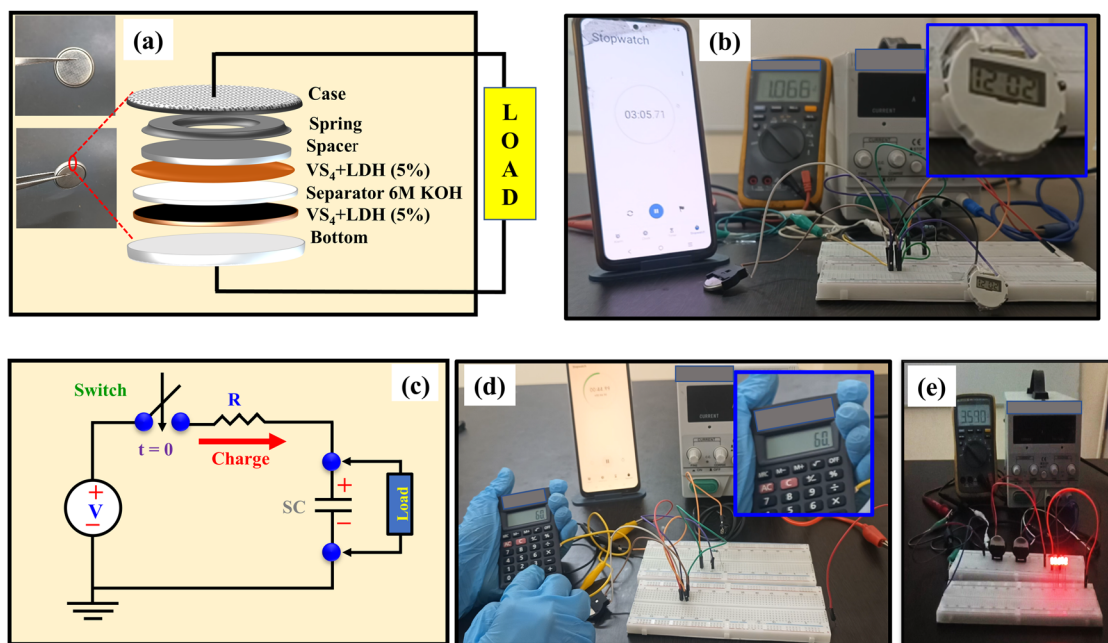
| Parameters                               | End values of VS <sub>4</sub> + LDH(5%) device |
|------------------------------------------|------------------------------------------------|
| Series resistance ( $R_s$ )              | 1.33 $\Omega$                                  |
| Constant-phase element CPE               | $Y_0 = 0.00761$ , $n = 0.69$                   |
| Charge transfer resistance ( $R_{p_i}$ ) | 48.6 $\Omega$                                  |
| Warburg impedance ( $W$ )                | 0.00853                                        |

through the doctor blade method and subsequently dried in a vacuum oven at 70 °C for 12 h. To complete the assembly, a few drops of 6 M KOH electrolyte solution were added to the separator arrangement. Further, the conductive sheets, spacer, and spring were packed into a coin cell. The fabricated symmetric cells were placed in a coin cell holder, as shown in the inset of Fig. 10(a), to prevent air exposure and evaporation during testing. The SC device was fabricated and connected to the resistance–capacitance (RC) circuit to form a combined energy storage system. Their charging and discharging behaviours were analysed using an RC circuit, as illustrated in Fig. 10(b). The devices were charged with a constant voltage

supply for 30 seconds, after which the power source was disconnected. The charged supercapacitor-powered devices, such as a watch and a calculator, are shown in Fig. 10(c) and (d), respectively. The charged supercapacitor successfully powered the watch and calculator for 200 to 250 seconds (see ESI,† Videos S1 and S2) and a set of 3 LEDs for a few seconds. This practical demonstration highlights the potential of VS<sub>4</sub> + LDH(5%) composite material-based supercapacitors for energy storage and portable applications. For the comparison study, we include some of the recent works conducted on VS<sub>4</sub> and its composites in Table 2.

## 4. Conclusions

A series of VS<sub>4</sub> + NiAl LDH nanocomposites with different weight percentages of NiAl LDH(2.5%, 5%, and 7.5%) were successfully synthesized *via* a facile solvothermal method. The incorporation of the NiAl LDH into the VS<sub>4</sub> matrix resulted in a significant enhancement of supercapacitor performance,



**Fig. 10** (a) Schematic of the fabrication of the coin cell (inset: fabricated coin cell). (b) Reference RC circuit for electrical connections. Illumination of (c) a watch, (d) a calculator, and (e) a 5-LED device powered by an SC.

**Table 2** Comparative study of VS<sub>4</sub> and its composites

| S. no. | Electrode material                  | Synthesis method | Specific capacitance (F g <sup>-1</sup> ) | Scan rate/current density (A g <sup>-1</sup> ) | Cycling stability         | Ref.      |
|--------|-------------------------------------|------------------|-------------------------------------------|------------------------------------------------|---------------------------|-----------|
| 1      | VS <sub>4</sub> /CNT                | Hydrothermal     | 330                                       | 1                                              | 51% after 5000 cycles     | 72        |
| 2      | VS <sub>4</sub> -CC@VS <sub>3</sub> | Hydrothermal     | 206                                       | 1                                              | 93% after 1000 cycles     | 73        |
| 3      | VS <sub>4</sub> /rGO                | Hydrothermal     | 877                                       | 0.5                                            | 90% after 1000 cycles     | 74        |
| 4      | VS <sub>4</sub> /Sb                 | Hydrothermal     | 539.4                                     | 3                                              | 174% after 10 000 cycles  | 75        |
| 5      | VS <sub>4</sub> /MXene              | Solvothermal     | 332.1                                     | 1                                              | 88.5% after 10 000        | 76        |
| 6      | VS <sub>4</sub>                     | Solvothermal     | 617                                       | 0.4                                            | 93.8% after 12 000 cycles | 77        |
| 7      | VS <sub>4</sub> + NiAl LDH          | Solvothermal     | 740                                       | 0.4                                            | 90.5% after 3500          | This Work |



demonstrating the potential of these nanocomposites for advanced energy storage applications. The optimised incorporation of the LDH into VS<sub>4</sub> led to enhanced performance, as evidenced by the improved specific capacitance values of the fabricated SCs. Among the composites, the VS<sub>4</sub> + LDH(5%) electrode exhibited the most promising electrochemical performance. The exceptional performance of the VS<sub>4</sub> + LDH(5%) composite, as evidenced by the FESEM data, can be attributed to its unique two-dimensional flower-like nanoflake morphology, which offers a high surface area for ion access, and to the presence of electronegative sulfur species that enhance electron transport and redox kinetics. The characterization techniques, especially XPS spectroscopic analysis, confirmed the formation of strong chemical bonds between VS<sub>4</sub> and the NiAl-LDH, resulting in enhanced electrochemical performance of VS<sub>4</sub>. The interfacial interaction between VS<sub>4</sub> and the LDH, along with the crucial role of the oxidation states of metal and sulfur ions, facilitates rapid charge transfer kinetics and improved capacitive behavior. Moreover, GCD analysis revealed a high specific capacitance of 740 F g<sup>-1</sup> at a current density of 0.4 A g<sup>-1</sup>. Furthermore, a symmetric supercapacitor device fabricated using the VS<sub>4</sub> + LDH(5%) composite achieved a maximum power density of 598.5 W kg<sup>-1</sup> and an energy density of 6.65 W h kg<sup>-1</sup>. These features collectively contribute to improved charge storage and transport dynamics, making the material highly suitable for next-generation electrochemical energy storage systems. The VS<sub>4</sub> composite, particularly with 2D materials, shows promise for enhancing the electrochemical performance and scalability. Besides energy storage devices, this composite material has potential applications in photocatalysts, biosensors, solar cells, and drug delivery systems, offering opportunities for future research and development. The electrochemical performance and cycling life of the VS<sub>4</sub> compound can still be improved by doping with other heteroatoms such as boron, phosphorus, nitrogen, oxygen, and fluorine, offering promising directions for future research and development.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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