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Electron-delocalization catalyzers for high performance, low-temperature Li–S batteries†

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The extremely depressive conversion kinetics of polysulfides due to sluggish Li⁺ diffusion kinetics remain to be resolved for low-temperature Li–S batteries (LT-LSB). Herein, the strategy for electron-delocalization of nanocatalysts has been designed through introducing oxygen defects on vanadium trioxide that was anchored on a porous carbon network (ODVO@PCN). The reconstructed active sites of the V²⁺ state tend to interact with sulfur species more easily due to the stronger hybridization between V²⁺ sites and S sites in sulfur species, allowing enhanced Li⁺ transformation kinetics across the electrolyte/electrode interface for a fast redox reaction in the low-temperature surrounding. Consequently, at a low temperature of 0 °C, the cell with the ODVO@PCN kinetic promotor exhibits 501 mA h g⁻¹ at 1C and a long life time of up to 400 cycles at 0.5C. Reduced to ultralow –10 °C, the cell still provides a capacity of 706 mA h g⁻¹ and stabilizes a remarkable capacity retention of 85% after 100 cycles.

The development of low-temperature lithium–sulfur (Li–S) batteries for next-generation energy storage systems has attracted increasing attention due to their high theoretical capacity (1675 mA h g⁻¹) along with low cost and environmental friendliness, ensuring a relatively high energy density output under low temperature.^{1–4} Unfortunately, the practical application of low-temperature Li–S batteries (LT-LSBs) is significantly hindered by extremely sluggish conversion kinetics of polysulfides (LiPSs) due to depressive Li⁺ diffusion kinetics at low temperature, leading to low capacity with unsatisfactory sulfur utilization and inferior rate performance.^{5–9}

To address the above challenges, current strategies are mainly concentrated on electrolyte engineering by tuning the freezing point of electrolytes or modulating the solvation shell structure of Li⁺ to increase the diffusion kinetics.^{10–13} However, for the specific commercial electrolytes, the sluggish Li⁺ diffusion kinetics is the dominance due to increased viscosity and enlarged solvation shell structure at a low operation temperature, resulting in an extremely high Li⁺ transport barrier.^{14–18} To this end, employing electrocatalysts to decrease energy barrier to promote interfacial and bulk Li⁺ kinetics become more viable.^{19,20} In comparison with perfect crystal catalysts, the electron-delocalization engineering has been put forward to adjust electronic density of catalysts, aiming at enhancing the numbers of catalytic sites and generating a higher density of free delocalized electrons for reactions.^{21–25} Meanwhile, it has been revealed that introducing defects into metal-based catalysts offers an effective way to regulate electron orbitals of central atoms, triggering abundant structure aberration for higher catalytic efficiency as well.^{21,26–29} However, such an electron-delocalization catalyzer with high activity toward Li⁺ kinetics to promote the redox reactions of LiPSs remains unknown at low temperature. Therefore, constructing catalysts with electron-delocalization tunability is being urgently pursued to enhance the sulfur utilization and electrochemical performance of LT-LSBs.

Herein, a strategy of electron-delocalization with high electron state tunability is proposed toward high-performance low-temperature-tolerant Li–S batteries through introducing oxygen defects on vanadium trioxide that anchored on a porous carbon network (ODVO@PCN). As certified by X-ray analysis with electrochemical evaluations, the dominant active sites of V²⁺ derived from electron-delocalization ODVO@PCN provide a more favorable interaction with sulfur species in virtue of the stronger orbital hybridization between V²⁺ sites and sulfur species, enabling strong adsorption on LiPSs and remarkable catalytic activity in Li⁺ transformation across the interface for fast redox kinetics. The cell with ODVO@PCN demonstrates a high rate capacity of 501 mA h g⁻¹ at 1C and low decaying rate

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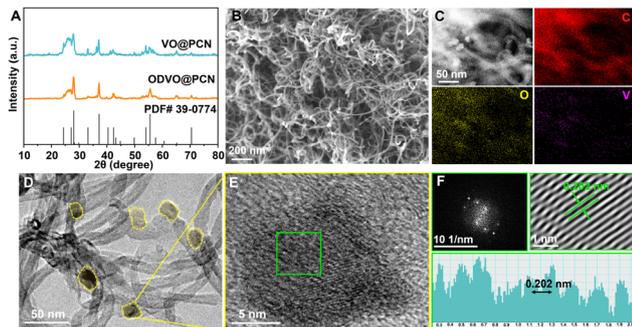


Fig. 1 (A) XRD curves of VO@PCN and ODVO@PCN nanocomposites; (B) SEM image and (C) STEM image, and corresponding EDX elemental mappings; (D) TEM image, (E) HRTEM image, and (F) FFT and IFFT images of the highlighted area of the ODVO@PCN nanocomposite.

of 0.069% after 400 cycles at 0.5C under 0 °C. Decreasing to an ultralow temperature of −10 °C, the cell still stabilizes with a capacity retention of 85% after 100 cycles, indicating bright prospects for application of LT-LSBs.

The ODVO@PCN was obtained *via* hydrothermal synthesis with thermal reduction, forming the nanosized morphology and porous structure. As shown in Fig. 1A, characteristic peaks located at 28.0°, 37.2° and 55.6° can be easily identified as the planes of (401), (303) and (205) of the V₂O₃ (JCPDS 39-0774) phase. At the same time, the wide and broad diffraction peaks centered at 26.6°, 43.5° and 54.8° are attributed to the amorphous nanocarbon (JCPDS 75-2078) in the ODVO@PCN. Similar to VO@PCN, the ODVO@PCN nanocomposites shows an interconnected morphology without apparent agglomeration (Fig. 1B and Fig. S1, ESI[†]). The uniform and homogeneous distributions of elemental V, O and C in the ODVO@PCN are obtained from the energy-dispersive X-ray spectroscopy (EDX) mappings (Fig. 1C), verifying the homogeneous dispersion of V₂O_{3-x} nanoparticles within the porous carbon networks. In the TEM images (Fig. 1D and Fig. S2, ESI[†]), morphological similarity from V₂O₃ to V₂O_{3-x} is further disclosed without obvious morphological evolution in spite of experiencing reduction. These nanoparticles are tightly anchored on the carbon tube walls with a domain size of around 15 nm (Fig. 1E and Fig. S3, ESI[†]). Combined with high-resolution TEM (HRTEM) images in Fig. 1E and F, the lattice spacing of 0.202 nm is assigned to the (420) crystal plane of the ODVO@PCN, which is in good agreement with XRD results.

Accordingly, ODVO@PCN affords the specific surface area of 121 m² g⁻¹ with hierarchical pore structures within the pore size of 2–50 nm to facilitate the physical and chemical adsorption to LiPSS (Fig. 2A and Fig. S4, ESI[†]). Such micropores (2–5 nm) with mesopores (10–50 nm) in the ODVO@PCN is advantageous for the simultaneous confinement and conversion of short-chain and long-chain LiPSS. Therefore, the ODVO@PCN-S after sulfur infiltration retains the specific surface area of 14 m² g⁻¹ with partial pore structures centered around the pore size of 50 nm (Fig. S5, ESI[†]). Beneficially, thermogravimetric analysis confers a V₂O_{3-x} content of 20.6 wt% in ODVO@PCN and high sulfur content of 75 wt%

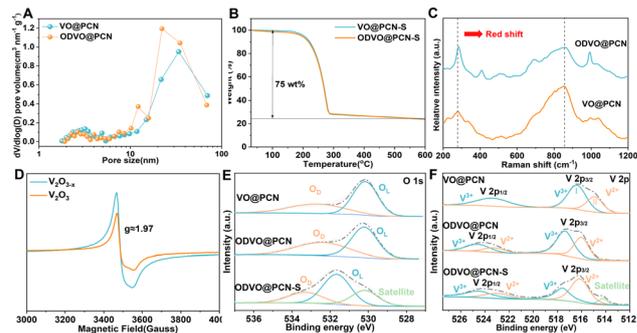


Fig. 2 (A) Pore size distribution of ODVO@PCN and VO@PCN; (B) thermogravimetric analysis (TGA) curves of ODVO@PCN-S and VO@PCN-S nanocomposites; (C) characteristic Raman spectra of the ODVO@PCN and VO@PCN nanocomposites; (D) EPR spectra of the as-synthesized ODVO@PCN and VO@PCN nanocomposites; high-resolution spectra of (E) O 1s and (F) V 2p of the ODVO@PCN, ODVO@PCN-S and VO@PCN nanocomposites.

in ODVO@PCN-S (Fig. 2B and Fig. S6, ESI[†]), respectively. The typical peaks in the Raman spectra of both defective ODVO@PCN and perfect VO@PCN are recognized at around 282.6, 404.4, 509.8, 690.6, 860.5, and 991.5 cm⁻¹ (Fig. 2C),^{30,31} which belong to various modes of V–O bond vibrations. Upon the electron-delocalization of defects in V₂O_{3-x}, the redshift of the V–O bond vibration peaks at 282.6 and 860.5 are created and observed, respectively. Also, I_D/I_G varies from 1.12 of VO@PCN to 1.23 of ODVO@PCN (Fig. S7, ESI[†]), suggesting the reformation of the electronic state in the carbon.³² The ODVO@PCN in the EPR spectra of Fig. 2D shows a more pronounced response than the VO@PCN nanocomposite around a *g*-factor of ≈1.97 between the values of the V-defect and the O-defect, which verifies the leading electron-delocalizing state of the V²⁺ species formed by removing some of the oxygen atoms within the ODVO@PCN sample.³³ Furthermore, the characteristic peaks of elemental V, O, C and N were exhibited in the wide XPS spectra (Fig. S8, ESI[†]). The high-resolution O 1s spectra of these three composites in Fig. 2E mainly exhibit two main characteristic peaks at 530.2 and 532.5 eV, assigned to lattice oxygen (O_L) and surface defect oxygen (O_D), respectively.²¹ The intensity ratio of I_{O_D}/I_{O_L} in ODVO@PCN is calculated to be 0.72 while that in VO@PCN is 0.59, suggesting that ODVO@PCN composites contain more oxygen defects. After loading of sulfur, there is a slight decrease of the I_{O_D}/I_{O_L} value to 0.68 with a red shift of both the O_L and O_D peaks due to the effective interaction with the sulfur. Meanwhile, the two main peaks centered around 516.1 and 517.4 eV in the high-resolution V 2p spectrum are attributed to the two species of V 2p_{3/2} (V²⁺) and V 2p_{3/2} (V³⁺) (Fig. 2F), respectively.³⁴ Accordingly, the evolution in the intensity ratio of I_{II}/I_I from 0.79 for VO@PCN to 0.88 for ODVO@PCN well demonstrates the electron-delocalization state, caused the valence changes and the emergence of the V 2p_{1/2} (V²⁺) peak at 523.3 eV with an apparent red shift for peaks of the V species. A surge in I_{II}/I_I to 1.1 for the ODVO@PCN-S nanocomposite further confirms the dominant active sites built by V²⁺ position due to stronger



hybridization of electron orbitals between V^{2+} sites and sulfur species (Fig. S9, ESI[†]). These results well confirm the successfully constructed electron-delocalization state within the ODVO@PCN nanocomposite *via* the formation of oxygen defect.

Benefiting from the abundant catalytic sites created by electron-delocalization state, the ODVO@PCN displays better ion conductivity than that of VO@PCN (1.78 vs. 0.82) to allow faster Li^+ diffusion kinetics (Fig. 3A and Fig. S10, S11, ESI[†]). In comparison to the electrochemical impedance spectroscopy (EIS) of the VO@PCN-S cathode (Fig. 3B), the ODVO@PCN-S cathode possesses a remarkably smaller charge transfer resistance (R_{ct}) (53 vs. 272 Ω) and a higher ion diffusion coefficient with a lower fitting slope (11.3 vs. 13.1) (Fig. 3B and C), so is the ODVO@PCN-S cathode after cycling (Fig. S12, ESI[†]), suggesting a much higher kinetics and faster lithium-ion mobility. In the cyclic voltammetry (CV) curves, the ODVO@PCN-S cathode exhibits a lower potential polarization (300 vs. 350 mV) and a higher response current than the VO@PCN-S cathode, demonstrating that ODVO@PCN can effectively strengthen the redox reaction of LiPSs (Fig. 3D). In the following three cycles, the ODVO@PCN-S cathode displays excellent repeatability, certifying the good electrochemical reversibility (Fig. S13, ESI[†]). Meanwhile, the Tafel slopes in Fig. S14 (ESI[†]), simulated from the second reduction peak in the CV curve of the ODVO@PCN-S cathode, are obviously smaller than those of the VO@PCN-S cathode (16.7 vs. 21.1 $mV\ dec^{-1}$). In addition, Li-ion diffusion capability can be evaluated on the scan rate dependent CV curves from the Randles-Sevcik equation:

$$\left(i_p = 0.4463nFAC \left(\frac{nFvD}{RT} \right)^{1/2} \right).$$

The simulated slope of ODVO@PCN-S is higher than that of VO@PCN-S (4.7 vs. 3.4), further proving that ODVO@PCN-S does possess faster redox conversion kinetics (Fig. 3E, F and Fig. S15, ESI[†]).

Thanks to the enhanced redox conversion kinetics of the ODVO@PCN catalyzer, the ODVO@PCN@S cathode acquires higher sulfur utilization with improved initial capacity of

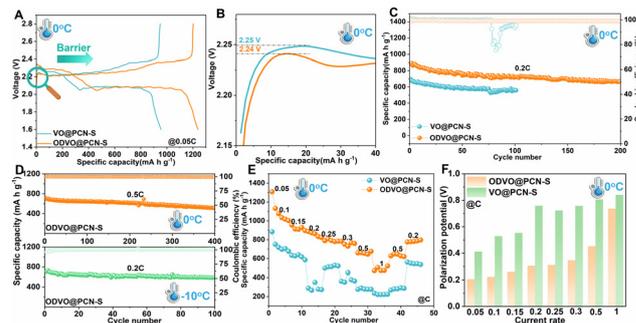


Fig. 4 (A) Initial charge–discharge profiles of the ODVO@PCN-S and VO@PCN-S cathodes at 0.05C; (B) comparison of the corresponding decomposition potential of Li_2S on the two cathodes; (C) cycle performance of the cathodes at 0.2C; (D) cycle performance of the ODVO@PCN-S cathodes at 0.5C (0 °C) and at 0.2C (–10 °C), respectively; (E) rate performance of the cathodes; (F) comparison of the overpotential at rates varying from 0.05 to 1C under low temperature.

1240 $mA\ h\ g^{-1}$ at 0.05C under 0 °C (Fig. 4A). As is well known, the cycling and rate reversibility of sulfur cathode is markedly determined by the ion diffusion kinetics due to the ionic/electronic insulating properties of Li_2S at low temperature.^{35–37} The ODVO@PCN@S cathode displays the smaller delithiation potential barrier of 2.24 V against 2.25 V of VO@PCN@S at 0 °C, directly reflecting the catalytic effect for the increased Li ion transport in Li_2S (Fig. 4B). Upon further cycling at 0.2C, the ODVO@PCN@S cathode delivers an initial capacity of 890 $mA\ h\ g^{-1}$ and stabilizes at 661 $mA\ h\ g^{-1}$ with high coulombic efficiency of 99% after 200 cycles (Fig. 4C), while the cell with the VO@PCN@S cathode only provides 695 $mA\ h\ g^{-1}$ and even failed within 100 cycles at 0 °C. Increasing to 0.5C, the ODVO@PCN@S cathode can maintain a high reversible capacity of 512 $mA\ h\ g^{-1}$ with a low decay rate of 0.069% at CE approaching 100% after 400 cycles (Fig. 4D and Fig. S16, ESI[†]). Lowering the operation temperature to –10 °C, the ODVO@PCN@S cathode still exhibits an initial capacity of 706 $mA\ h\ g^{-1}$ and displays a remarkable capacity retention rate of 85% with stable discharge plateaus after 100 cycles (Fig. 4D and Fig. S17, ESI[†]), verifying the excellent cycling stability of the catalyzed ODVO@PCN@S cathode at ultra-low temperature. Switching the current rate from 0.05 to 1C under 0 °C, the ODVO@PCN@S cathode exhibits stable rate performance with obvious discharge plateaus (Fig. 4E and Fig. S18, S19, ESI[†]), much lower than overpotentials at each current rate of VO@PCN@S (Fig. 4F). At 1C, the ODVO@PCN@S maintains a capacity of 501 $mA\ h\ g^{-1}$, while the capacity of VO@PCN@S declines rapidly to as low as 234 $mA\ h\ g^{-1}$, suggesting that highly active ODVO@PCN can catalyze the Li^+ diffusion kinetics to realize fast redox kinetics of LiPSs even at low temperature. Increasing to room temperature, the ODVO@PCN catalyzed sulfur cathode displays high-rate performance to 6C (727 $mA\ h\ g^{-1}$) with a continuously low overpotential (Fig. S20, ESI[†]). In addition, the cell with the ODVO@PCN catalyzer stabilizes 721 $mA\ h\ g^{-1}$ after 200 cycles at 1C (Fig. S21, ESI[†]). Even at 5C, a high reversible capacity of 421 $mA\ h\ g^{-1}$ after 1000 cycles with a decay rate of as low as 0.048% per cycle is realized (Fig. S22, ESI[†]), thereby verifying a remarkable electrochemical stability of the ODVO@PCN catalyzed sulfur cathode.

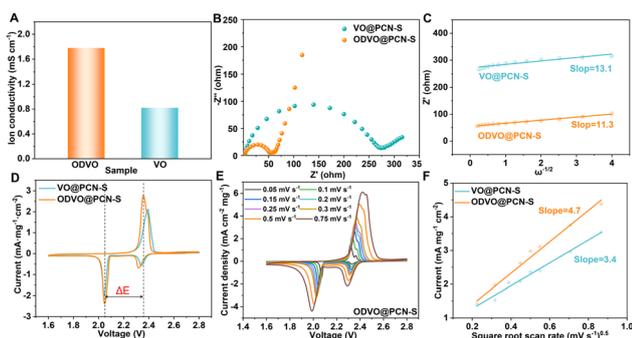


Fig. 3 (A) Ionic conductivity test at the electrode/electrolyte interface; (B) comparison of EIS between ODVO@PCN-S and VO@PCN-S electrodes and (C) the corresponding Li ion transport; (D) the CV curves of the two cathodes tested at 0.1 $mV\ s^{-1}$; (E) scan rate-dependent CV curves on the ODVO@PCN-S cathode; (F) current density at the lower cathodic peaks of the cathodes versus the square root of the scan rate.



In summary, we have successfully synthesized the electron-delocalized ODVO@PCN nanocatalyst as sulfur hosts for low-temperature Li-S battery, featuring strong electron regulation capability for high catalytic efficiency toward the polysulfide reaction and Li⁺ transformation kinetics for fast low temperature redox reaction. At a low temperature of 0 °C, the cell with the ODVO@PCN-S cathode exhibits a high-rate capacity of 501 mA h g⁻¹ at 1C and high CE approaching 100% after 400 cycles at 0.5C. Impressively, the cell still provides a high initial capacity of 706 mA h g⁻¹ and a stabilized capacity retention rate of 85% after 100 cycles at 0.2C even under ultralow temperature of -10 °C, much superior to that in most of the literature reports (Table S1, ESI†). Our ODVO@PCN nanocatalyst strongly shows the bright prospects of using electron-delocalized catalysts for high-performance LT-LSBs.

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Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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