A Mo$_5$N$_6$ electrocatalyst for efficient Na$_2$S electrodeposition in room-temperature sodium-sulfur batteries

Chao Ye$^{1,4}$, Huanyu Jin$^{1,4}$, Jieqiong Shan$^{1,4}$, Yan Jiao$^1$, Huan Li$^1$, Qinfen Gu$^2$, Kenneth Davey$^1$, Haihui Wang$^3$ & Shi-Zhang Qiao$^{1,6}$

Metal sulfides electrodeposition in sulfur cathodes mitigates the shuttle effect of polysulfides to achieve high Coulombic efficiency in secondary metal-sulfur batteries. However, fundamental understanding of metal sulfides electrodeposition and kinetics mechanism remains limited. Here using room-temperature sodium-sulfur cells as a model system, we report a Mo$_5$N$_6$ cathode material that enables efficient Na$_2$S electrodeposition to achieve an initial discharge capacity of 512 mAh g$^{-1}$ at a specific current of 1675 mA g$^{-1}$, and a final discharge capacity of 186 mAh g$^{-1}$ after 10,000 cycles. Combined analyses from synchrotron-based spectroscopic characterizations, electrochemical kinetics measurements and density functional theory computations confirm that the high d-band position results in a low Na$_2$S$_2$ dissociation free energy for Mo$_5$N$_6$. This promotes Na$_2$S electrodeposition, and thereby favours long-term cell cycling performance.
Sulfur is an attractive electrode material because of low cost and high-theoretical specific capacity of ~1675 mAh g\(^{-1}\). Sulfur electrodes can be conjugated with a range of metal anodes in rechargeable metal–sulfur (M–S) batteries, giving promise of practical energy-storage applications\(^2\)–\(^3\). However, sulfur reduction reaction (SRR) in M–S batteries is a complex conversion from elemental sulfur to insoluble metal sulfides\(^4\). Slugish SRR kinetics leads to incomplete conversion of the sulfur and “shuttle effect” of the polysulfides. This limits Coulombic efficiency (CE) and cycle-life and is therefore a deterrent to practical application\(^6\).

Metal sulfides electrodeposition from soluble polysulfides is the rate-determining step in practical sulfur electrodes\(^5\). Duan and co-workers demonstrated a slow conversion of soluble lithium polysulfides into insoluble lithium sulfides through studying the activation energy of various states of SRR in lithium–sulfur (Li–S) batteries\(^7\). This leads to accumulation of lithium polysulfides in the electrolyte, and is the primary reason for the shuttle effect, together with a rapid capacity fading\(^8\). Despite electronically conductive materials with active electrodeposition sites, such as heteromatom-doped carbon, typically applied as substrates to facilitate charge transfer, an atomic-level understanding of mechanism of metal sulfides electrodeposition in SRR is lacking\(^9\)–\(^12\). For example, although it is known that Li\(_2\)S electrodeposition is essential in Li–S batteries, the solid-solid conversion from Li\(_2\)S\(_2\) to Li\(_2\)S is unclear because it is difficult to distinguish various solid products in the complex process\(^13\)–\(^14\). Moreover, the correlation between the electrodeposition kinetics and geometric/electronic structure of the cathode materials remains unknown\(^15\)–\(^17\). Consequently, there is significant research interest in how to realize highly efficient metal sulfides electrodeposition in M–S batteries\(^18\).

Although SRR intermediates are too sensitive to be detected in air, advances in in-situ synchrotron characterizations with time resolution permit identification of specific polysulfides and metal sulfides and tracking of dynamic conversion\(^19\)–\(^21\). In-depth understanding can therefore be achieved for macroscopic polysulfides conversion kinetics\(^22\)–\(^23\). Nevertheless, atomic-level understanding of metal sulfides electrodeposition behavior is important and remains difficult to achieve experimentally\(^24\). Progress in density functional theory (DFT) computations that takes into account the geometric/electronic structure of the sulfur cathode materials is essential in investigating metal sulfides electrodeposition kinetics\(^25\). Therefore, combination of advanced in-situ synchrotron characterizations and computational quantum chemistry can reveal critical factors in metal sulfides electrodeposition kinetics\(^26\),\(^27\). Potential sulfur cathode materials with efficient metal sulfides electrodeposition kinetics can be engineered by tailoring geometric and electronic structures.

Here we present a Mo\(_5\)N\(_6\) cathode material that significantly catalyzes Na\(_2\)S electrodeposition and results in boosted performance for Na–S battery: 512 mAh g\(^{-1}\) capacity and long cycle life of 10,000 cycles under 1C (1675 mA h g\(^{-1}\)). Using a judicial combination of synchrotron-based characterizations, electrodeposition rate measurements and DFT computations, we evaluated the Mo\(_5\)N\(_6\) catalysts by linking extrinsic geometric structure with intrinsic reaction energetics in the Na\(_2\)S electrodeposition. With this research work we shed some light on the origin of high Na\(_2\)S electrodeposition reactivity and high SRR efficiency of this cathode material.

**Results**

**Atomic and electronic structures of molybdenum nitrides.** A series of molybdenum nitrides with varying atomic structure were selected as model cathode materials for investigation of correlation between the atomic structure, electronic structure and electrochemical performance in room-temperature sodium–sulfur (RT Na–S) batteries. Mo\(_5\)N\(_6\), MoN, and Mo\(_2\)N with varying stoichiometries were synthesized based on reported synthetic strategies\(^28\). The crystal phases of the as-prepared molybdenum nitrides were analysed by powder X-ray diffraction (XRD), and indexed to crystalline Mo\(_5\)N\(_6\), MoN, and Mo\(_2\)N, respectively (Supplementary Fig. 1). The scanning electron microscopy (SEM) images of these molybdenum nitrides confirm that the Mo\(_5\)N\(_6\) and the MoN show a two-dimensional (2D) morphology and that Mo\(_2\)N exhibits a homogeneous nanoparticle morphology (Supplementary Fig. 2). In addition, high-angle annular dark-field scanning transmission-electron microscopy (HAADF-STEM) imaging was performed to investigate the atomic structure of the molybdenum nitrides (Supplementary Fig. 3). As is shown in Fig. 1a, the Mo atoms are labeled as red-color spheres to aid visualization of the lattice fringes with a lattice distance of 0.24 nm, corresponding to the (2 1 0) and (1 1 0) facets of the Mo\(_5\)N\(_6\)\(^29\). In contrast, the MoN exhibits a lattice distance of 0.25 nm corresponding to the (200) and (2 1 0) facets. Mo\(_2\)N has two lattice distances of 0.24 nm and 0.21 nm, which are ascribed to the (2 0 0) facet and (1 1 1) facet, respectively (Fig. 1b, c). This observation confirms the crystal structures of the molybdenum nitrides determined by XRD results and demonstrates the different Mo atomic configurations in the molybdenum nitrides.

It is reported that sulfur redox kinetics is significantly affected by the d electron density of the materials, which regulates atomic structure\(^29\). Mo 3d X-ray photoelectron spectra (XPS) measurements showed that the Mo\(_5\)N\(_6\) has a higher dominant Mo valence state of 4+ with a binding energy of 230.0 eV, in contrast, the MoN and Mo\(_2\)N exhibit lower binding energies of Mo species at 229.2 and 228.9 eV, respectively (Fig. 1d)\(^30\). This finding is supported by synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) characterization that permits investigation of the impact on the surface electronic structures of the d electrons. The Mo L-edge white-lines originate from p electron transition to a vacant d electron state\(^31\). As is shown in the Mo L\(_{2,3}\) edge NEXAFS spectra (Fig. 1e), the intensity of adsorption edge peak decreases in the order Mo\(_5\)N\(_6\), MoN, and Mo\(_2\)N.\(^32\) Therefore, the XPS and NEXAFS results demonstrate the high Mo valence state and low d electron density of Mo\(_5\)N\(_6\), resulting from the unique atomic structure as is illustrated in Fig. 1f.

**Electrochemical properties of the molybdenum nitrides in the RT Na–S batteries.** To investigate electrocatalytic effects of molybdenum nitrides in RT Na–S batteries, we employed Mo\(_x\)Ny catalysts as an additive and carbon–sulfur composite containing 62.9 wt% sulfur as active material in assembly of the sulfur electrodes. The as-prepared electrodes were denoted as S/Mo\(_x\)Ny, S/MoN, and S/Mo\(_2\)N ( Supplementary Fig. 4). For comparison, a pure S/C electrode was also prepared. Long-term cycling experiments at a high rate of 1C were conducted to investigate cycling performance of the sulfur electrodes (Fig. 2a and Supplementary Fig. 5). The capacity loss during initial few cycles was observed and is attributed to the formation of stable solid electrolyte interphase (SEI) film because of side effects between carbonated-based solvents and highly reactive sodium anode surface\(^23\),\(^33\). A high capacity of 186 mAh g\(^{-1}\) was maintained by the S/Mo\(_5\)N\(_6\) after 10,000 continuous cycles under 1 C that refers to an capacity decay of 0.0064% per cycle, together with a stabilized CE held at around 100%. This performance significantly exceeds those of S/MoN (0.014%) and S/Mo\(_2\)N (0.024%). In contrast, the S/C electrode exhibited a low initial capacity of 201 mAh g\(^{-1}\) with a short cycle life of less than 200 cycles.
(Supplementary Fig. 6). Therefore, the S/Mo5N6 electrode has practical promise for a high-performance Na–S battery with high sulfur content, high capacity, small capacity decay and long cycling life in comparison with many reported sodium polysulfides cathodes, Na2S2 and Na2S cathodes, or hybrid of carbon and sulfur cathodes in Na–S batteries (Fig. 2b and Supplementary Fig. 7 and Supplementary Table 1)3,29,33–45. As is shown in Fig. 2c, S/Mo5N6 exhibited a series of advantageous discharge capacities of 513, 353, 304, 263, and 216 mAh g−1 when cycled at 0.1, 0.2, 0.5, 1, and 2 C (1 C = 1675 mA g−1), respectively. When the specific current was switched back to 0.2 C, a high discharge capacity of 325 mAh g−1 was maintained (Supplementary Fig. 8). Over the following cycling at 0.2 C (Supplementary Figs. 9 and 10), the S/Mo5N6 exhibited a capacity decay of 0.013% per cycle (298–179 mAh g−1 in 2970 cycles). However, S/MoN, S/Mo2N and S/C cathodes show relatively poor cycling and rating performance with limited capacities under high rates (Supplementary Figs. 8–11).

To explore the origin of high CE and stability under high rates of the S/Mo5N6 cathode, we investigated the Na+ diffusion of the three sulfur cathodes through cyclic voltammetry (CV) experiments under various scan rates from 0.1 to 5 mV s−1 in the potential range 0.5–2.8 V46. During the initial cathodic scan (Supplementary Fig. 12) there was a prominent peak corresponding to reduction of elemental sulfur and long-chain soluble polysulfides to less soluble Na2S2 and Na2S. For the anodic scan, one reproducible peak was observed. This corresponds to the oxidation of Na2S2 and Na2S to Na2Sx and elemental sulfur47. The slow oxidation kinetics of Na2S2 and Na2S to Na2Sx are likely the cause for the overlapping of the two oxidation peaks during the anodic scan. Based on the experimentally obtained slope between the peak current (i_p) and square root of the scan rate (ν1/2), the diffusion coefficient for sodium ions was estimated from: i_p ∝ n3/2AD1/2ν1/2, where i_p, n, D, A, c, and ν represent, respectively, peak current, number of electrons, diffusion coefficient, surface area of the electrode, concentration of the ion and voltage scanning rate (Fig. 2d)48. Because the number of electrons (n) and concentration of the sodium ion (c) are identical for the three sulfur electrodes, these cancel out in the i_p-ν1/2 slope. Based on the electrochemical active surface areas (ECSAs) for the sulfur electrodes (Supplementary Fig. 13) the i_p-ν1/2 slopes were normalized as is shown in Supplementary Fig. 14. It was confirmed that the S/Mo5N6 electrode exhibits greater sodium ion diffusion in comparison with that for S/MoN and S/Mo2N electrodes. This likely causes deposition of a thick Na2S layer on the electrode49,50.

To confirm the electrochemical measurements of diffusion rate, we computed the sodium ions diffusion barriers on the three molybdenum nitrides using climbing image nudged-elastic band (CI-NEB) method21. The three models were constructed based on the electron microscopy results, which are Mo5N6 exposing (0 0 4) facet, MoN with (0 0 2) facet, and Mo2N with (1 0 0) facet, as is shown in Supplementary Figure. 1551. The energy profiles for the ions diffusion on the three materials surface are shown in Fig. 2e, and the corresponding diffusion route in Supplementary Fig. 16. The diffusion barrier of sodium ions on the Mo5N6 (0 0 4) facet is 7 meV, which is significantly lower than those on the MoN (0 0 2) facet (65 meV) and Mo2N (1 0 0) facet (118 meV). Although the (0 0 4) facet for Mo5N6 and (0 0 2) facet for MoN can be regarded as the only primary exposed facets because of inherent 2D morphology, we considered other possible facets of Mo5N652,53. Given the 3D-morphology of Mo2N an additional major exposed facet of (1 1 1) was investigated. This showed a significantly greater sodium ion barrier of 246 meV over that for Mo2N (1 0 0) (Supplementary Figs. 17 and 18). Therefore, the computational results are consistent with the electrochemical results and confirm...
that the S/Mo$_5$N$_6$ electrode exhibits significantly greater sodium ion diffusion in comparison with the S/MoN and S/Mo$_2$N electrodes. These findings demonstrate that the Mo$_5$N$_6$ represents an increased sodium ion diffusion rate and significantly promotes reaction kinetics between sodium and sulfur.$^{55}$

**Kinetic investigations on Na$_2$S electrodeposition.** To determine the rate-determining step in overall SRR reaction, SRR kinetics were investigated on the S/C electrode via determination of the energy barrier ($E_a$) with electrochemical impedance spectra (EIS) measurements and analysis.$^{7}$ The measured EIS curve was fitted with an equivalent circuit as is shown in Fig. 3a, in which $R_{	ext{onf}}$ describes deposition of the adsorbed sodium polysulfides on the surface of the electrode, $R_{	ext{ct}}$ is the charge transfer process, and the “tail” is the Warburg resistance ($Z_{\text{Warb}}$ and $Z_{\text{new}}$)$^{55,56}$. The EIS curves for the S/C electrodes under varying voltage were measured at temperatures of 303, 313, and 323 K (Supplementary Fig. 19). By fitting $R_{	ext{ct}}$ values in the Arrhenius equation, $E_a$ at each voltage was evaluated (Supplementary Table 2). The conversion from S$_8$ to Na$_2$S$_2$ (x = 5–8) at 2.5 and 2.0 V results in low $E_a$ values of 0.63 and 0.57 eV, whilst the conversion following to Na$_2$S$_3$ and/or Na$_2$S$_4$ at 1.5 V exhibits an increased $E_a$ of 0.82 eV (Fig. 3b and Supplementary Table 3). During final conversion to Na$_2$S$_2$/Na$_2$S in the voltage range 1.0 to 0.5 V, $E_a$ increases from 0.79 to 0.89 eV. These findings confirm that conversion of the S$_8$ ring molecules to soluble Na$_2$S$_x$ is relatively facile, whereas the conversion of Na$_2$S$_2$ and/or Na$_2$S$_3$ to final insoluble Na$_2$S$_2$/Na$_2$S is significantly more difficult, making it the rate-determining step for SRR. Similarly, EIS curves for S/Mo$_{3.5}$N$_6$, S/MoN, and S/Mo$_2$N electrodes were measured at a temperature of 303, 313, and 323 K (Supplementary Figs. 20–22). As is shown in Fig. 3c, d, $E_a$ for S/Mo$_5$N$_6$ under each of 2.5, 2.0, and 1.5 V, is, respectively, 0.53, 0.57, and 0.60 eV. These values are less than for S/Mo$_2$N of, respectively, 0.64, 0.69, and 0.79 eV and for S/MoN of 0.67, 0.71, and 0.77 eV. Importantly, for the rate-determining step between 1.0 and 0.5 V, S/Mo$_5$N$_6$ exhibits significantly lower values of 0.73 and 0.74 eV in comparison with those for S/Mo$_2$N of 0.78 and 0.80 eV, and for S/MoN of 0.80 and 0.84 eV. These findings evidence significantly boosted overall kinetics and Na$_2$S electrodeposition on Mo$_5$N$_6$ compared with MoN and Mo$_2$N.

To further investigate the Na$_2$S electrodeposition kinetics on Mo$_5$N$_6$, in-situ synchrotron XRD measurements were conducted in transmission mode. A modified 2032-type coin cell with S/Mo$_5$N$_6$ as a cathode was discharged to 1.5 V (vs. Na$^+/Na$) using an in-house design to study the Na$_2$S electrodeposition, Fig. 4a (Supplementary Fig. 23)$^{20}$. As can be seen from the figure in the discharge from 1.5 V, two peaks at 12.8° and 15.7° are evident in the XRD patterns. These are assigned to soluble Na$_2$S$_5$ (No. 00-027-0792)$^{35,37}$. The other strong peak at 14.5° corresponds to Na$_2$S$_3$ (No. 04-003-2048). In addition, another peak at 11.9° is assigned to the Na$_2$S$_3$ (No. 00-044-0822)$^{35}$. This finding reveals that the reduction of elemental sulfur to the mixture of sodium polysulfides occurs from open-circuit voltage to 1.5 V in discharge. This is consistent with the CV findings. When the battery was discharged to ~1.0 V, a peak at 13.6° was observed. This is attributed to the (4 0 4) facet of Na$_2$S (No. 00-047-0178).
attributed to the charge transfer process, and the tail line represents the Warburg resistance (\(R_w\)) for SRR. The errors originate from the linear fitting of Arrhenius plots for \(R_w\). Values for \(R_w\) were obtained by fitting using an equivalent circuit as shown in the inset of panel a. The error bars represent relative errors of the fitted \(R_w\) values.

In the further discharge to \(\sim 0.8\) V, a peak located at 13.7° is assigned to the (1 0 2) facet of \(\text{Na}_2\text{S}_2\) (No. 04-007-3813). In the discharge from 1.5 to 0.5 V, most of the polysulfides in the battery were oxidized to \(\text{Na}_2\text{S}\). Importantly, the peak for \(\text{Na}_2\text{S}\) is seen before the appearance of the \(\text{Na}_2\text{S}_2\) phase. This unusual phenomenon leads to an assumption that \(\text{Mo}_5\text{N}_6\) exhibits very fast conversion kinetics from \(\text{Na}_2\text{S}_2\) to \(\text{Na}_2\text{S}\), that is, the conversion to \(\text{S}^2^-\) is highly efficient with \(\text{Mo}_5\text{N}_6\) compared to \(\text{MoN}\) and \(\text{Mo}_2\text{N}\). In addition, the highest peak current of 0.80 mA was observed during the electrodeposition on the \(\text{Mo}_2\text{N}\) as shown in the insets of Fig. 4b–d. The electrodeposition morphology of \(\text{Na}_2\text{S}\) on \(\text{CP}/\text{Mo}_2\text{N}_6\), \(\text{CP}/\text{MoN}\), \(\text{CP}/\text{Mo}_2\text{N}\), and \(\text{CP}\) was investigated by SEM imaging and energy-dispersive spectroscopy (EDS) mapping analysis (Fig. 4c–g). It was found that \(\text{Na}_2\text{S}\) is uniformly deposited on the surface of \(\text{CP}/\text{Mo}_2\text{N}_6\) with approximately 100% coverage. A three-dimensional (3D) deposition of \(\text{Na}_2\text{S}\) layers on the \(\text{CP}/\text{Mo}_2\text{N}_6\) highlights the high deposition efficiency. This is attributed to the low energy barriers of \(\text{Na}_2\text{S}\) nucleation and growth on \(\text{Mo}_2\text{N}_6\), \(\text{CP}/\text{MoN}\), \(\text{CP}/\text{Mo}_2\text{N}\), and \(\text{CP}\) exhibited an insufficient \(\text{Na}_2\text{S}\) deposition with discrete coating as was evidenced by low \(\text{Na}_2\text{S}\) coverage on the electrode surface (Supplementary Figs. 25–27). The sluggish \(\text{Na}_2\text{S}\) electrodeposition kinetics on \(\text{CP}/\text{MoN}\) and \(\text{CP}/\text{Mo}_2\text{N}\) are explained by the very high energy barriers for the redox reaction of polysulfides on them. The XPS spectra for the three sulfur electrodes discharged to 0.5 V were analyzed to confirm the electrochemical catalytic activity of \(\text{Mo}_2\text{N}_6\). It is seen in Supplementary Fig. 28 that the \(\text{S}/\text{Mo}_2\text{N}_6\) cathode exhibits dominate \(\text{S}^2^-\) species at the end of discharge, underscoring a highly efficient conversion of active sulfur species to \(\text{S}^2^-\). In contrast, \(\text{S}/\text{MoN}\) and \(\text{S}/\text{Mo}_2\text{N}\) cathodes show only partial conversion to \(\text{S}^2^-\). This finding is attributed to the strong adsorption of sodium polysulfides and low diffusion barrier of sodium ions. The EIS tests were conducted at 0.5 V, and
corresponding \( R_{\text{surf}} \) values which describe the deposition of insoluble sodium polysulfides on the electrode surfaces, and fitted to be \( \sim 485 \), \( \sim 281 \), and \( \sim 230 \) \( \Omega \) cm\(^2\) for S/Mo\(_5\)N\(_6\), S/MoN, and S/Mo\(_2\)N electrodes, respectively (Supplementary Fig. 29). This finding agrees well with those from the Na\(_2\)S electrodeposition test and the S 2p XPS analysis, confirming the highly efficient Na\(_2\)S electrodeposition on Mo\(_5\)N\(_6\) in comparison with the others\(^{41,63}\).

**Discussion**

To determine the origin of the significant deposition efficiency and cycling stability of S/Mo\(_5\)N\(_6\), DFT computations on thermodynamics and kinetics of Na\(_2\)S electrodeposition on various molybdenum nitride surfaces were carried out. The adsorption configurations and adsorption energies for Na\(_2\)S\(_n\) (\( n = 1 \)–\( 5 \)) on the three nitrides were investigated. As is shown in the adsorption configurations, Supplementary Figs. 30–32, S in Na\(_2\)S\(_n\) locates in the hollow sites on Mo\(_5\)N\(_6\) whilst Na in Na\(_2\)S\(_n\) locates away from the surface. This implies that Mo functions as a dominant adsorption site to interact with S in Na\(_2\)S\(_n\).\(^{64}\) The adsorption energies for Na\(_2\)S\(_n\) on Mo\(_5\)N\(_6\) were, respectively, \(-6.14\), \(-8.75\), \(-7.67\), \(-6.36\), and \(-9.23\) eV for \( n = 1, 2, 3, 4, \) and \( 5 \), Supplementary Fig. 33 (Supplementary Table 4). These high values confirm strong adsorption of Na\(_2\)S\(_n\) on Mo\(_5\)N\(_6\) when compared with reported materials in sulfur cathodes for lithium/sodium polysulfides adsorption\(^{65}\). Although adsorption energies for Na\(_2\)S\(_n\) on Mo\(_5\)N\(_6\) were (slightly) greater than those on MoN, it was not clear why there is faster deposition kinetics on Mo\(_5\)N\(_6\) compared with MoN.

To determine the origin of the fast Na\(_2\)S electrodeposition kinetics on Mo\(_5\)N\(_6\), we constructed a three-step reaction pathway for Na\(_2\)S\(_2\) conversion to Na\(_2\)S on the three molybdenum nitrides surfaces. The corresponding reaction steps are: 1) adsorption of Na\(_2\)S, 2) formation of adsorbed Na\(_{2}^{+}\) and Na\(_{2}S_{2}^{+}\) from Na\(_2\)S,
Fig. 5 Computational investigation of Na₂S electrodeposition. a Gibbs free energy diagram of conversion from Na₂S₂ to NaS⁺ on the three surfaces including adsorption of Na₂S₂, dissociation of Na₂S₂ to form adsorbed NaS (NaS₂*) and formation of adsorbed NaS (NaS⁺) from the NaS₂*. ΔGₕₐ₅₁ is dissociation free energy of Na₂S₂. ΔGₕ₆₅₂ indicates formation free energy of NaS⁺, and ΔG₉ indicates NaS⁺ formation free energy barrier. b Relationship between computed ΔGₕ₅₁ or ΔG₉ values and measured electrodeposition capacities on the three molybdenum nitrides surfaces. c Atomic configurations for NaS⁺ formation step on the surface of Mo₅N₆. The gray-color, light blue, orange, and blue spheres represent Mo, N, S, and Na atoms, respectively.

dissociation, 3) two NaS⁺ formation following simultaneous Na₂S₂ dissociation and a Na-S bond formation. For the Na₂S₂ dissociation step, Mo₅N₆ exhibits an optimal free energy (ΔGₕ₅N₆ₕ₅₁) value of -0.23 eV, whilst MoN and Mo₂N surfaces exhibit more positive values of ΔGₕ₅N₆ₕ₅₁ = 0.09 eV and ΔGₕ₅N₂₅₆ₕ₅₁ = 0.36 eV, respectively. However, for the NaS⁺ dissociation step, MoN shows the optimal free energy (ΔGₕ₅N₂₅₆ₕ₅₁) value of -0.05 eV, whilst Mo₅N₆ and Mo₂N surfaces exhibit more positive values of ΔGₕ₅N₆₂₅₆ₕ₅₁ = 0.04 eV and ΔGₕ₅N₂₂₅₆ₕ₅₁ = 0.39 eV, respectively. Therefore, from a thermodynamic point of view, Mo₅N₆ and MoN demonstrate similar Na₂S electrodeposition activity. However, these theoretical investigations based only on adsorption energetics do not agree with the experimental observation that CP/Mo₅N₆ sample demonstrates a significantly greater Na₂S electrodeposition capacity in comparison with CP/MoN. When the kinetics of NaS⁺ formation step is considered (Fig. 5a and Supplementary Table 5), the Mo₅N₆ surface exhibits a substantially lower energy barrier (ΔG₉ = 0.48 eV) than on MoN (ΔG₉ = 0.58 eV) and Mo₂N (ΔG₉ = 1.06 eV) (Fig. 5b and Supplementary Figs. 34–36). Therefore, from a kinetic viewpoint, Mo₅N₆ demonstrates the most favorable electrodeposition efficiency amongst the three molybdenum nitride structures. With the identification of large energy barrier of NaS⁺ formation on the MoN surface, in addition to the formation of the NaS⁺ state, the NaS⁺ formation kinetics also affect the overall deposition rate and lead to the experimentally observed activity trend (Fig. 5c). Therefore, association of the atomic reaction model (applying ΔGₕ₅₁ as a reactivity indicator) with the newly considered transition-state theory gives a qualitative confirmation of the deposition kinetics on the three molybdenum nitrides.

To investigate the origin of fast Na₂S electrodeposition kinetics on Mo₅N₆ from the aspect of electronic structure, spectroscopic measurements were carried out. The ex-situ NEXAFS characterizations were carried out on the three sulfur electrodes to investigate the dynamic change of the valence state of Mo in the three cathode materials. The Mo L₃-edge spectra for Mo₅N₆ (Fig. 6a) show that the valence state of Mo decreases gradually with the discharge and reaches lowest level at the discharge potential of 0.5 V. This is consistent with the adsorption configuration from DFT results and demonstrates the strong Mo–S interaction and high Na₂S electrodeposition capacity. During the following charge, the valence state of Mo increases to the original level until the end of charge at the potential of 2.8 V. This finding confirms the strong adsorption of sodium polysulfides and the high reversibility of Mo₅N₆ as electrode materials. As a comparison, similar measurements were performed on electrode with MoN. The NEXAFS spectra show that valence state of Mo decreases during discharge but remains unchanged during the following charge. This indicates that although MoN exhibits strong adsorption of sodium polysulfides, the high diffusion barrier of sodium ions on MoN leads to poor reversibility of the electrode. In contrast, the Mo₂N electrode shows a nearly unchanged valence state of Mo during the whole discharge/charge. These findings confirm that Na₂S electrodeposition kinetics on the molybdenum nitrides strongly depends on the valence state and d electron density of Mo.

To gain further fundamental insight into the low Na₂S⁺ dissociation barrier on Mo₅N₆, charge difference analyses on the transition state configurations on three surfaces were carried out (Fig. 6b–d). On MoN and Mo₂N surface, the interaction between the S (highlighted by red-color circles in Fig. 6c–d) and Na is strong, which represents electron accumulation between the two atoms. On the Mo₅N₆ surface, less electron accumulation is observed. This finding confirms a weaker interaction between the two atoms, which aids Na₂S⁺ dissociation with a lower
dissociation barrier. The weaker interaction between Na and S is attributed to the strong Mo–S interaction, also demonstrated in the NEXAFS and XPS findings. The relationship between the adsorption of an adsorbate on a surface and the electronic structure of the substrate is explained by the density of states (DOS) (Fig. 6e). When a polysulfide molecule from the electrolyte is adsorbed on the molybdenum nitrides surface to form Na₂Sn*, the electronic states of the Mo interact with those of sulfur. Consequently, the hybridized energy levels split into two groups: one is the anti-bonding states ($\sigma^*$) that normally go across the Fermi level ($E_F$); the other is the bonding orbital ($\sigma$) positioned under the $E_F$. The difference in the adsorption strength comes from the antibonding states, that is, with a higher location of the $E_F$ of the molybdenum nitrides, the antibonding states move to lower occupancy. This leads to a stronger interaction between Na₂Sn* and the molybdenum nitrides surface, and vice versa. In this work, the results of the DOS computations are consistent with the scheme, Fig. 6f. The low DOS peaks of the S 3$p$-Mo d antibonding orbitals (indicated by arrows) cause weak adsorption of S on MoN and Mo₂N. More importantly, the position of antibonding orbital is decided by the $d$-band position of Mo on the molybdenum nitrides; the $d$-band centers for the Mo atoms on the Mo₅N₆, MoN, and Mo₂N are −0.41, −1.56, and −2.41 eV, respectively. This is the same order as for the S–Mo antibonding

Fig. 6 Analyzes of Mo electronic structure in corresponding reaction transition state. a–c Ex-situ NEXAFS for the Mo L₃-edge of S/Mo₅N₆, S/MoN, and S/Mo₂N, for varying voltage during a discharge/charge cycle. b–d Charge difference analyzes from configurations of the transition states in the NaS⁺ formation step on the three cathode materials, in which yellow-color and cyan iso-surface represent electron accumulation and electron depletion, respectively, and the iso-surface value is 0.0015 e Å⁻³. Color code is the same as for Fig. 5c. e Energy level diagram showing orbital hybridization for adsorption sites and adsorbate. $E_F$ is the Fermi level of the substrate; $\sigma$ and $\sigma^*$ indicate bonding and anti-bonding states, respectively. f Solid lines represent DOS for S in the red-color circles in Fig. 6b–d. The DOS is projected onto the S 3$p$ state. Dashed lines represent surface Mo $d$-bands DOS of the three clean molybdenum nitrides surfaces.
peaks on the three surfaces. Therefore, the d-band position shows similar trends with the adsorption strength as is shown in Supplementary Fig. 37. The d-band center (applying as a descriptor) can be correlated with the Na2S5− dissociation energy as the underlying mechanism of the better electrodeposition reactivity of Mo3N6 in sulfur cathodes.

Using sodium-sulfur chemistry as an example, we correlated the Na2S electrodeposition reactivity on a Mo3N6 electrocatalyst with its reaction energetics and inherent electronic structure. By identifying the significant influence of Na2S dissociation on the overall SRR reactivity of various molybdenum nitrides surfaces, and theoretical computations demonstrates that Mo3N6 with favorable d-band position delivers significantly high Na2S electrodeposition reactivity and performance in Na-S battery. This advance in mechanistic understanding of metal sulfides electrodeposition will underpin rational design of efficient M-S batteries. Application has resulted in significant performance on an RT Na-S battery. Findings will be of immediate interest and practical benefit to a wide range of researchers in the rational design of electrode materials for accelerated applications in sustainable energy-storage and conversion.

Methods

Preparation of molybdenum nitrides. Mo powder (<150 μm, 99.99% trace metals basis) was purchased from Sigma-Aldrich without further purification. The 2D Mo3N6 nanosheets were synthesized through a Ni-induced salt-templated method as previously reported: 0.4 g of Mo powder was dispersed in 40 mL of ethanol with magnetic stirring for 10 min. 1.2 mL of H2O2 (30 wt%) solution was injected dropwise into the suspension. Following stirring for 12 h at room temperature, the solution turned into a dark-blue color. Separately, 10 mg of Ni(OOCCH3)2·H2O was dissolved in 10 mL of ethanol and mixed with the dark-blue suspension to form the precursor. The precursor solution was mixed with 640 g of NaCl powder and dried at 50 °C with continuous hand-stirring. The mixture was annealed at 750 °C for 5 h at a heating rate of 1 °C min−1 under 5% NH3/Ar atmosphere. The product was washed with deionized water and dilute hydrochloric acid several times to remove the NaCl template and Ni nanoparticles before being dried using vacuum filtration. The 2D Mo3N6 nanosheets were synthesized without addition of Ni. The Mo precursor was mixed with 640 g of NaCl and annealed at 750 °C for 5 h. The final product was obtained by removing NaCl using deionized water and vacuum filtration. The Ni3Mo nanoparticles were produced by annealing Mo powder under NH3 atmosphere. Fifty milligram of Mo powder was put into a porcelain boat uniformly. The powder was annealed at 650 °C for 5 h at the ramp rate of 1 °C min−1 under 5% NH3/Ar atmosphere.

Materials characterization. The morphology and structure of samples was characterized by SEM (FEI Quanta 250). HAADF-STEM images were recorded at 200 kV (Talos F200X). XRD data were recorded on a Rigaku MiniFlex 600 X-Ray Diffractometer. Sulfur content of the active material was determined by TGA (METTLER TOLEDO TGA/DSC 2) under N2. In-situ synchrotron XRD (with wavelength λ = 0.6888 Å) and NEXAFS data were recorded on the powder diffractometer and the soft X-ray spectroscopy beamline in the Australian Synchrotron, Clayton, Victoria.

Electrochemical characterization. For the battery performance measurement, active sulfur material containing elemental sulfur and conductive carbon (Kirjan Balck) with mass ratio of 2:1 was well-mixed and sealed in a quartz ampoule and thermally treated at 300 °C for 2 h under a Na2S atmosphere. 5 wt% Mo3N6 was used as the additive in the slurry with 80 wt% of active material, 5 wt% of conductive carbon and 10 wt% N-lauryl acrylate (LA133, purchased from Chengdu Yindile Power Supply Technology). For comparison, a pure S/C electrode was prepared with a slurry containing 80 wt% active material, 10 wt% conductive carbon and 10 wt% N-lauryl acrylate. The slurry mixture was cast on aluminum substrate. To stabilize voltage, the battery was discharged to the specific voltage under 0.1 C, then were dissembled in a glove box. The test electrodes were sealed in a sample-holder inside the glove box to transport the electrode samples.

Na2S electrodeposition experiments. The Na2S (97.0%), sulfur powder (reagent grade, 100 mesh particle size), tetraglyme (−99%) and glass fiber separator (Whatman glass microfiber GF/F) were purchased from Sigma-Aldrich Australia. The Na2S powder was stored in glove box. The carbon papers (CF) were purchased from Shanghai Hesens Electronics Co. Ltd. (HCPT01N). The original LiS electrodeposition tests are referred to for the Na2S electrodeposition tests11. The Na2S electrodeposition from soluble polysulfides was studied by potentiostatic deposition in Na2Sn tetraglyme solution on the CF current collectors. The Na2S tetraglyme solution was applied to compare the delicate kinetical differences for different samples with corresponding electrodeposition films and capacities. The test was conducted in a similar coin cell as for the electrochemical performance tests. The Na2S in tetraglyme solution added to the Mo3N6 on CF was the only source of sulfur active material. The 0.1 M Na2Sn solution was prepared by dissolving and mixing stoichiometric amounts of Na2S and sulfur in tetraglyme solvent at room temperature for 10 h. CF papers were punched into disks with a diameter of 12 mm and about 0.40 mg of Mo3N6, Mo2N, and MoN powders were separately dispersed on CF papers using pure ethanol as solvent. 25 μL Na2S was dropped onto the as-prepared current collectors as cathode. Sodium-foil was employed as the counter electrode, which was separated with cathode by glassfibre membrane and dropped with 15 μL electrolyte. The cells were galvanostatically discharged to 1.0 V at a constant specific current of 0.25 A, and kept potentiostatically at 0.5 V for Na2S to nucleate and grow until the current dropped below 10−5 A.

Computational methods. DFT computations were carried out using the Vienna Ab-initio Simulation Package (VASP)64,65. The exchange-correlation interaction was described by generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional66,67. The DFT-TS method of Grimme was employed to treat the VDW interaction68. All computations were carried out using a plane wave kinetic energy cut-off of 600 eV. All structures in the computations were spin-polarized and relaxed until the convergence tolerance of force on each atom was less than 0.01 eV. The energy convergence criteria were set to 10−4 eV for self-consistent calculations with a Gamma centered 2 × 2 × 1 K-points. All periodic slabs had a vacuum spacing of at least 15 Å. Density 10 × 10 × 1 k-points were used for the density of states (DOS) computations. All periodic slabs had a vacuum spacing of at least 15 Å. The structural model for Mo3N6 (0 0 4) facet contained five Mo-N layers with a supercell size of a = b = 11.44 Å, c = 20.60 Å, α = β = 90°, and γ = 120°. The structural model for Mo2N (0 0 2) facet contains five Mo-N layers with a supercell size of a = b = 11.36 Å, c = 20.70 Å, α = β = 90° and γ = 120° while the MoN (1 0 0) facet consisted of five Mo-N layers with a = b = 8.33 Å, c = 23.33 Å, α = β = γ = 90°. In computations the three bottom layers were kept fixed, all other atoms were allowed to relax. Na2Sn (n = 1−5) adsorption energies ΔE for each configuration were computed from:

$$\Delta E = E_{\text{total}} - E_{\text{Na2Sn}} - E_{i}$$

where $E_{\text{total}}$, $E_{\text{Na2Sn}}$, and $E_{i}$ are, respectively, the energies for the whole system, Na2Sn, and substrate.

Free energy diagram computation. Based on the experimentally obtained rate-determining step, the solid-solid conversion from Na2S2 to Na2S was proposed as three elementary steps, namely:

$$\text{Na}_2\text{S}_2 + \text{Na}^+ + 2e^- \rightarrow \text{Na}_2\text{S}_2$$

$$\text{Na}_2\text{S}_2 + \text{Na}^+ + 2e^- \rightarrow \text{Na}_2\text{S}_4 + \text{Na}^+ + 2e^-$$

$$\text{Na}_2\text{S}_4 + \text{Na}^+ + 2e^- \rightarrow \text{Na}_2\text{S}_2 + \text{Na}^+ + 2e^-$$

where $E_{\text{Na2S2}}$, $E_{\text{Na2S4}}$, and $E_{i}$ are, respectively, the energies for the whole system, Na2S2, and substrate.
and $\Delta G_{\text{diss-2}}$, respectively, and can be computed from:

$$\Delta G_{\text{diss-1}} = G(\text{NaS}_2^0 + \text{Na}) - G(\text{Na}_2\text{S}_2^0)$$

(3)

$$\Delta G_{\text{diss-2}} = G(2\text{NaS}) - G(\text{Na}_2\text{S}_2^0 + \text{Na})$$

(4)

in which

$$G = E + E_{ZPE} - TS$$

(5)

and where zero point energy corrections ($E_{ZPE}$) and entropic contributions ($TS$; $T$ was set to be 273.15 K). The free energy of the $\Delta G_{\text{diss-1}}$ and $\Delta G_{\text{diss-2}}$ were computed as:

$$\Delta G = \Delta E + \Delta E_{ZPE} - \Delta S$$

(6)

where $E_{ZPE}$ and $\Delta S$ are the binding energy, zero point energy change and entropy change, respectively. In this work the values of $E_{ZPE}$ and $\Delta S$ on the specific molybdenum nitrides surfaces were determined by vibrational frequency computation. Note that the exploration of active sites on the specific surface was conducted and chosen according to the most energetically stable adsorption site.

**Na$_2$S$_2$ dissociation barrier computation.** Following identification of the initial and final states for Na$_2$S$_2$ dissociation step on the three molybdenum nitrides surfaces, the energy barrier was located via searching for transition states by climbing image nudged-elastic band (CI-NEB) method implemented in VASP.$^{[2] 2}$

The transition states were obtained by relaxing the force below 0.05 eV Å$^{-1}$. The located transition states were confirmed by frequency analysis. The $d$-band center ($\epsilon_d$) was determined as the weighted DOS of $d$-band as:

$$\epsilon_d = \frac{\sum \epsilon_i n_i}{\sum n_i}$$

(7)

where $\epsilon_i$ is the DOS at energy $\epsilon_i$.

**Reporting summary.** Further information on research data is available in the Nature Research Reporting Summary linked to this article.

**Data availability**

Data that support findings from this study are available from the corresponding author on request.

Received: 26 March 2021; Accepted: 26 November 2021; Published online: 10 December 2021

**References**

1. Ji, X., Lee, K. T. & Nazar, L. F. A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. Nat. Mater. 8, 500–506 (2009).
2. Park, C.-W., Ahn, J.-H., Ryu, H.-S., Kim, K.-W. & Ahn, H.-J. Room-temperature solid-state sodium/sulphur battery. Electrochem Solid State Lett. 9, A123–A125 (2006).
3. Zhao, Q., Hu, Y., Zhang, K. & Chen, J. Potassium–sulphur batteries: a new member of room-temperature rechargeable metal–sulphur batteries. Inorg. Chem. 53, 9000–9005 (2014).
4. Kim, H. S. et al. Structure and compatibility of a magnesium electrolyte with a lithium-sulphur battery. Electrochim. Acta 57, 762–770 (2010).
5. Zhou, L., Danilov, D. L., Eichel, R.-A. & Notten, P. H. L. Host materials anchoring polysulides in Li–S batteries reviewed. Adv. Energy Mater. 11, 2001304 (2021).
6. Zhao, M. et al. Lithium–sulphur batteries under lean electrolyte conditions: Challenges and opportunities. Angew. Chem. Ed. 59, 12636–12652 (2020).
7. Zhang, L. et al. Design rules of heteroatom-doped graphene to achieve high performance lithium–sulphur batteries: both strong anchoring and catalysing based on first principles calculation. J. Colloid Interface Sci. 529, 426–431 (2018).
8. Fan, F. Y., Carter, W. C. & Chiang, Y. M. Mechanism and kinetics of Li$_2$S precipitation in lithium–sulphur batteries. Adv. Mater. 27, 5203–5209 (2015).
9. Liu, D. et al. Catalytic effects in lithium-sulphur batteries promoted sulphur transformation and reduced shuttle effect. Adv. Sci. 5, 1700270 (2018).
10. Yang, X. et al. Promoting the transformation of Li$_2$S$_2$ to Li$_2$S: significantly increasing utilization of active materials for high-sulphur-loading Li–S batteries. Adv. Mater. 31, 1901220 (2019).
11. He, J. & Manthiram, A. A review on the status and challenges of electrocatalysts in lithium-sulphur batteries. Energy Storage Mater. 20, 55–70 (2019).
12. Peng, L. et al. A fundamental look at electrocatalytic sulfur reduction reaction. Mater. Today 22, 33–44 (2019).
13. Zhao, M. et al. Lithium–sulphur batteries: both strong anchoring and catalysing based on first principles calculation. J. Colloid Interface Sci. 529, 426–431 (2018).
14. Song, Y. et al. Rationalizing electrocatalysis of Li–S chemistry by mediator design: progress and prospects. Adv. Energy Mater. 10, 1901075 (2020).
15. Lim, W.-G., Kim, S., Jo, C. & Lee, J. A comprehensive review of materials with catalytic effects in Li–S batteries: enhanced redox kinetics. Angew. Chem. Ed. 58, 18746–18757 (2019).
16. Pampel, J., Dörfler, S., Althues, H. & Kaskel, S. Designing room temperature sodium sulfur batteries with long cycle-life at pouch cell level. Energy Storage Mater. 21, 41–49 (2019).
17. Yan, Y., Cheng, C., Zhang, L., Li, Y. & Lu, J. Deciphering the reaction mechanism of lithium–sulfur batteries by in situ/operando synchrotron-based characterization techniques. Adv. Energy Mater. 9, 1900148 (2019).
18. Guo, Q., Kimpston, J. A., Brand, H. E., Wang, Z. & Chou, S. Solving key challenges in battery research using in situ synchrotron and neutron techniques. Adv. Energy Mater. 7, 1602831 (2017).
19. Li, S. et al. High performance room temperature sodium-sulfur battery by ionic acceleration in tellurium-doped sulfurized polycrystalline. ACS Appl. Energy Mater. 2, 2956–2964 (2019).
20. Kumar, A., Ghosh, A., Forsyth, M., MacFarlane, D. R. & Mitra, S. Free-radical catalysis and enhancement of the redox kinetics for room-temperature sodium–sulfur batteries. ACS Energy Lett. 5, 2112–2121 (2020).
21. Xu, X. et al. A room-temperature sodium-sulfur battery with high capacity and stable cycling performance. Nat. Commun. 9, 3870 (2018).
22. Yang, X. et al. Revitalising sodium-sulfur batteries for non-high-temperature operation: a crucial review. Energy Environ. Sci. 13, 3848–3879 (2020).
23. Chen, X., Hou, T., Persson, K. A. & Zhang, Q. Combining theory and experiment in lithium-sulfur batteries: current progress and future perspectives. Mater. Today 22, 142–158 (2019).
24. Li, P. et al. Chemical immobilization and conversion of active polysulﬁdes directly by copper current collector: a new approach to enabling stable room-temperature Li-S and Na-S batteries. Adv. Energy Mater. 8, 1800624 (2018).
25. Zhang, S., Yao, Y. & Yu, Y. Frontiers for room-temperature sodium–sulfur batteries. ACS Energy Lett. 6, 529–536 (2021).
26. Jin, H. et al. Single-crystal nitrogen-rich two-dimensional Mo$_2$N$_x$ nanosheets for efficient and stable seawater splitting. ACS Nano 12, 12761–12769 (2018).
27. Ye, C. et al. Electron-state confinement of polysulﬁdes for highly stable sodium–sulfur batteries. Adv. Mater. 32, 1907557 (2020).
28. Jin, H. et al. Constructing tunable dual active sites on two-dimensional C$_{32}$(CN)$_6$@Mo$_x$ hybrid for electrocatalytic hydrogen evolution. Nano Energy 53, 690–697 (2018).
29. Lede, E. J., Requejo, F. G., Pawelec, B. & Fierro, J. L. G. XANES Mo L-Edges and XPS study of Mo loaded in HY zeolite. J. Phys. Chem. B 106, 6902–6910 (2002).
30. Wei, S. et al. A stable room-temperature sodium/sulfur battery with dual-end binding sites. Energy Storage Mater. 6, 1080–1087 (2019).
31. Liu, D., Althues, H. & Kaskel, S. Designing room temperature lithium–sulphur batteries. Nanotechnol. 16, 166–173 (2020).
32. Peng, L. et al. A fundamental look at electrocatalytic sulfur reduction reaction. Nat. Catal. 3, 762–770 (2020).
33. Zhou, L., Danilov, D. L., Eichel, R.-A. & Notten, P. H. L. Host materials anchoring polysulﬁdes in Li–S batteries reviewed. Adv. Energy Mater. 11, 2001304 (2021).
34. Zhang, L. et al. Lithium–sulphur batteries under lean electrolyte conditions: Challenges and opportunities. Angew. Chem. Ed. 59, 12636–12652 (2020).
35. Zhang, L. et al. Design rules of heteroatom-doped graphene to achieve high performance lithium–sulphur batteries: both strong anchoring and catalysing based on first principles calculation. J. Colloid Interface Sci. 529, 426–431 (2018).
36. Fan, F. Y., Carter, W. C. & Chiang, Y. M. Mechanism and kinetics of Li$_2$S precipitation in lithium–sulphur batteries. Adv. Mater. 27, 5203–5209 (2015).
37. Liu, D. et al. Catalytic effects in lithium-sulphur batteries promoted sulphur transformation and reduced shuttle effect. Adv. Sci. 5, 1700270 (2018).
41. Lu, Q. et al. Freestanding carbon fiber cloth/sulfur composites for flexible room-temperature sodium-sulfur batteries. Energy Storage Mater. 8, 77–84 (2017).
42. Carter, R. et al. A sugar-derived room-temperature sodium sulfur battery with long term cycling stability. Nano Lett. 17, 1863–1869 (2017).
43. Chen, Y.-M. et al. A nitrogen doped carbonized metal–organic framework for high stability room temperature sodium–sulfur batteries. J. Mater. Chem. A 4, 12471–12478 (2016).
44. Fan, L., Ma, R., Yang, Y., Chen, S. & Lu, B. Covalent sulfur for advanced room temperature sodium-sulfur batteries. Nano Energy 28, 304–310 (2016).
45. Bauer, I., Kohl, M., Althues, H. & Kaskel, S. Shuttle suppression in room temperature sodium–sulfur batteries using ion selective polymer membranes. Chem. Commun. 50, 3208–3210 (2014).
46. Tao, X. et al. Balancing surface adsorption and diffusion of lithium-polysulfides on nonconductive oxides for lithium-sulfur battery design. Nat. Commun. 7, 11203 (2016).
47. Wang, Y.-X. et al. Room-temperature sodium-sulfur batteries: a comprehensive review on research progress and cell chemistry. Adv. Energy Mater. 7, 160829 (2017).
48. Hao, J. et al. Heterostructure manipulation via in situ localized phase transformation for high-rate and highly durable lithium ion storage. ACS Nano 12, 10430–10438 (2018).
49. Zhou, G. et al. Catalytic oxidation of Li2S on the surface of metal sulfides for Li–S batteries. Proc. Natl Acad. Sci. USA 114, 840–845 (2017).
50. Chao, D. et al. C-Plasma of hierarchical graphene survives SnS bundles for ultrastable and high volumetric Na-ion storage. Adv. Mater. 30, 1804833 (2018).
51. Sun, G.-D., Zhang, G.-H. & Chou, K.-C. Synthesis of molybdenum nitrides based on DFT studies. J. Phys. Chem. C 123, 554–564 (2019).
52. Altarawneh, M. et al. Conversion of NO into N2 over y-Mo2N. J. Phys. Chem. C 120, 22270–22280 (2016).
53. Xu, J. et al. Promoting lithium polysulfide/sulfide redox kinetics by the catalyzing of zinc sulfide for high performance lithium-sulfur battery. Nano Energy 51, 73–82 (2018).
54. Krewer, U. et al. Review—dynamic models of Li-ion batteries for diagnosis and operation: a review and perspective. J. Electrochem. Soc. 165, A3656–A3673 (2018).
55. Tan, G. et al. Burning lithium in Cs2, for high-performing compact Li–S/graphene nanocapsules for Li–S batteries. Nat. Energy 2, 17090 (2017).
56. Zhang, B.-W. et al. Long-life room-temperature sodium–sulfur batteries by virtue of transition-metal-nanocluster–sulfur interactions. Angew. Chem. Ed. 58, 1484–1488 (2019).
57. Xie, J. et al. Implanting atomic cobalt within mesoporous carbon toward highly stable lithium–sulfur batteries. Adv. Mater. 31, 1903813 (2019).
58. Zhang, G., Zhang, Z.-W., Peng, H.-J., Huang, J.-Q. & Zhang, Q. A toolbox for lithium–sulfur battery research: methods and protocols. Small Methods 1, 1700163–1700165 (2017).
59. Zhao, M. et al. Redox comodiation with organopolysulfides in Working lithium-sulfur batteries. Chem. 6, 3297–3311 (2020).
60. Yu, X. & Manthiram, A. Capacity enhancement and discharge mechanisms of room-temperature sodium-sulfur batteries. ChemElectroChem 1, 1275–1280 (2014).
61. Qiu, L. & Xu, G. Peak overlaps and corresponding solutions in the X-ray photoelectron spectroscopic study of hydrosulfurization catalysts. Appl. Surf. Sci. 256, 3413–3417 (2010).
62. Ma, D. et al. New strategy for polysulfide protection based on atomic layer deposition of TiO2 onto ferroelectric-encapsulated cathode: toward ultrastable free-standing room temperature sodium–sulfur batteries. Adv. Funct. Mater. 28, 1705337 (2018).
63. Chen, X. et al. An analogous periodic law for strong anchoring of polysulfides on polar hosts in lithium sulfur batteries: S or Li-binding on first-row transition-metal sulfides? ACS Energy Lett. 2, 795–801 (2017).
64. Pang, Q., Liang, X., Kwok, C. Y. & Nazar, L. F. Advances in lithium–sulfur batteries based on multifunctional cathodes and electrolytes. Nat. Energy 1, 16132 (2016).