Identifying single-atom catalysts for boosted Al–S conversion reactions

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ABSTRACT

Aluminum–sulfur (Al–S) battery is a promising energy storage system owing to its safety, crustal abundance and high theoretical energy density. However, its development is hindered by the sluggish reaction kinetics and poor reversibility. Herein, a series of porous carbon supported atomic transition metal catalysts (SATM@NC) were considered to evaluate the catalytic activities in Al–S applications. Both theoretical and experimental results indicated that stable SATM@NC all promote the Al–S conversion reactions. Batteries assembled with SACo@NC/S demonstrated a high specific capacity of 509.4 mA h g−1 at 1 A g−1 after 200 cycles. In mechanism, atomic metal species weakened Al-S bonds of AlPSs and increased their reactivity. Particularly, distinctive Al-binding interaction between AlPSs and SACo@NC was critical for its superior catalytic activity. This work gives a systematically understanding of single-atom catalyst for Al–S chemistry, and provides enlightenment for high performance Al–S batteries.

1. Introduction

Benefit to the low cost, high specific capacity (2890 mAh g−1) and reliable safety, aluminum is regarded as a promising next-generation anode material [1]. And rechargeable aluminum-ion batteries (RABs) working with aluminum metal anode and ionic liquid-based electrolyte have attracted great attention. What hinder their applications are the unsatisfactory electrochemical performances of cathode materials [2]. In the past few years, much effort have been put into the developments of carbonaceous materials and metallic compounds [3, 4]. However, the electrochemical performances of the reported RABs are rarely to obtain both high specific capacity and long cycle life [5]. It is highly desired to develop potential cathode materials with favorable electrochemical properties.

Sulfur is a promising cathode material owing to its high theoretical specific capacity (1675 mAh g−1) and natural abundance [6, 7]. Since the reversible Al–S battery was reported in 2016, it has drawn great attention [8]. Nevertheless, the insulating nature of sulfur and aluminum polysulfides (AlPSs), sluggish electrochemical kinetics and poor reversibility of Al–S conversion reactions hinder its popularization and application [9]. In recent years, much efforts have been devoted to improving the electrochemical performances of Al–S batteries [10]. Electrolyte additive such as N-butyl-N-methylpyrrolidinium bromide and lithium salt have been successfully used in the previous studies [11, 12]. And a more recent study revealed that a quasi-solid-state electrolyte could contribute to the decreased voltage gap and improved reversibility, thus establishing high-energy Al–S batteries [13, 14].

The introduction of catalysts is another effective strategy to promote the Al–S conversion reactions. In 2019, carbonized HKUST-1 was employed to load sulfur, and the in-suit generated Cu nanoparticles were demonstrated to increase the conductivity and decrease the kinetic barrier for the Al–S conversion reactions [15]. Subsequently, Co/C compound was explored as sulfur host and the CoS2 nanoparticles could improve the reaction kinetics and sulfur utilization [16]. Compared with bulk catalysts, single-atom catalysts (SACs) are monodispersed single atoms supported on solid substrates with theoretical 100% atom utilization efficiency, high electrical conductivity and superior activity [17]. The catalytic activity of single-atom Co for Al–S chemistry has been demonstrated by recent studies, where the initial capacity was increased and the voltage hysteresis was reduced [18]. Nevertheless, the research of catalysis on Al–S chemistry is still in its infancy, and a systematical investigation for the catalytic performance and catalytic mechanism of

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various metal catalysts, particularly for SACs, are deficient.

Inspired by the applications of SACs in various metal–sulfur batteries, the catalyst support with porous framework, for example porous carbon, does play a critical role in promoting catalytic efficiencies and electrochemical properties [19, 20]. In addition to provide sufficient active catalytic sites, a porous material with a large specific surface area could also ensure metal polysulfide confinement and improve the contact between catalysts and electrolyte. Therefore, in this paper, SACs comprising different transition metal atoms interacting with a nitrogen moiety in porous carbon, denoted as SATM@NC (TM = Ti, V, Cr, Mn, Fe, Co, Ni, Cu), were considered as electrocatalysts and sulfur host. Density functional theory (DFT) calculations revealed that atomic Co could promote the conversion reactions by making the Gibbs free energy more negative. Among them, SACo@NC was regarded as the most promising catalyst, which exhibited the lowest Gibbs free energy for Al–S conversion reactions. Based on the DFT results, the catalytic effects of SATM@NC on the Al–S conversion reactions were confirmed by electrochemical characterizations. Combined with the catalysis of atomic Co and the nanoconfinement of porous carbon, the SACo@NC with 50 wt.% S loaded sample exhibited impressive rate performance (a specific capacity of 485.8 mAh g⁻¹ under current density up to 2 A g⁻¹) and excellent cyclic stability (a reversible specific capacity of 517.2 mAh g⁻¹ after 200 cycles under 1 A g⁻¹). Finally, the catalytic mechanism for SACs facilitating both the formation and decomposition of AlPSs was revealed on the basis of computational and experimental results. Benefiting from the distinctive Al-binding configurations, SACo@NC could maximize the deformation of AlPSs and minimize the decomposition energy barrier, which was believed to be the key to its excellent catalytic performance. This work provides comprehensive view and fresh insights for designing SACs with superior catalytic properties in Al–S batteries.

2. Experimental section

2.1. Preparation of TM–ZnO

In a typical procedure, 2.13 g Zinc acetate dihydrate, 0.3 mmol cobalt tetrahydrate (or Ferric nitrate nonahydrate, nickel acetate trihydrate, cupric acetate monohydrate, manganous acetate), and 6 g sodium citrate were dissolved in 90 ml deionized water under 60 °C water bath and stirred for 30 min. Then 2 g sodium hydroxide was added and maintained for 30 min. After vacuum filtration and washing with deionized water and ethanol for three times, the Co-ZnO (or Ni-ZnO, Cu-ZnO, Mn-ZnO) template with nanosheet structures was dried in the oven at 50 °C overnight and collected.

2.2. Materials characterizations

XRD patterns were collected using the CuKα line at a scan rate of 10° min⁻¹ (Rigaku D/max 2000 diffractometer). SEM images were collected with acceleration voltage of 1 kV (Hitachi S4800), TEM images were performed on a Hitachi HT-7700. HAADF-STEM and EDX were performed on a Titan Themis 60–300 “cubed” microscope fitted with aberration-correctors for the imaging lens and the probe forming lens, Super-X EDX system, operated at 300 kV. The BET surface area and pore structure were collected using Quantachrome Autosorb-IQ instrument. Element contents were determined by ICP measurements conducted on Agilent 7800 instrument. XPS measurements were conducted using Thermo Scientific K-Alpha instrument. The XAS measurement at Mn, Fe, Co, Ni and Co K-edge was performed at the beamline BL08B2 (bending magnet source) of SPring-8 with electron energy of 8 GeV and average current of 99.5 mA. The radiation was monochromatized by a Si (111) double-crystal monochromator. The detector was ion chamber (pure N₂ for I₀, N₂; Ar = 17:3 for I₁). All the measurements were carried out in the air and all spectra were collected in transmission mode. XAS data were processed and analyzed using the Demeter software package [21].

2.3. Preparation of cathode

SATM@NC/S were prepared as active materials by mixing SATM@NC with sulfur powder at the mass ratio of 1:1 under argon atmosphere and then heating at 155 °C for 12 h. By mixing the active materials (70%), carbon black (20%) and polyvinylidene fluoride (10%), the slurries were obtained. This slurries were then coated on a high pure molybdenum (Mo) foil current collector and dried in a vacuum oven at 55 °C overnight, which was used as working electrode. Without special instructions, the average loading mass density of sulfur per cathode was about 0.8 mg cm⁻². To evaluate the potentiality for practical application, cathode with sulfur loading of 2.3 mg cm⁻² was prepared as well. The separator is glass fiber (GF/D), and the ionic liquid electrolyte is the mixture of 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) and anhydrous AlCl₃ with the molar ratio of 1:1.3. About 12 µL cm⁻² electrolyte was added to wet the separator and cathode.

2.4. Electrochemical measurements

Electrochemical tests were performed using Swagelok-type cells assembled with high purity aluminium foil as the counter electrode in an argon-filled glovebox. Galvanostatic charge/discharge tests in the voltage range 0.01–1.8 V were performed on a Land battery testing system (CT2001A). The current density and specific capacity were recorded based on the mass of sulfur in the cathode. Cyclic voltammetry (CV) measurements were performed between 0.1–2.0 V at the scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) tests were performed in the frequency window of 100 kHz–10 mHz. Both the CV and EIS tests were achieved on the electrochemical workstation (CHI 660D).

2.5. Computational methods

Density Functional Theory (DFT) calculations were carried out using projector-augmented wave (PAW) method as implemented in Vienna ab initio simulation package (VASP) [22–25]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional was employed to describe the exchange-correlation interaction, and the van der Waals (vdW) correction DFT-D3 proposed by Grimme was chosen to describe the dispersion interaction [26, 27]. For all surface systems, vacuum slab in c direction was set to be more than 20 Å to avoid interaction between periodic images. The plane wave energy cut-off was set as 500 eV, and Gamma centered 3 × 3 × 1 k-points mesh was applied to surface calculations. The Gaussian smearing method was used with a width of 0.05 eV, and spin polarization was included in all calculations. The structures were relaxed until the forces and total energy on all atoms were converged to less than 0.05 eV Å⁻¹ and 1 × 10⁻⁵ eV. The decomposition of Al₂S₃ on SATM@NC surface is simulated using the climbing-image nudged elastic band (CI-NEB) method [28, 29]. 6 images were applied to these calculations.

2.6. Stability calculations in sulfur-rich environment

The binding strength between transition metal atom and nitrogen doped carbon materials (NC) in SATM@NC is described by Eₙ, and the average cohesive energy of each transition metal atom in corresponding sulfides TMₙSₓ is defined as Eₐ₂, Eₙ, and E₂ are calculated by

\[ E_{\text{Total}} = E_{\text{TM@NC}} - E_{\text{TM}} - E_{\text{NC}} \]  (1)

and

\[ E_{\text{ΔS}} = (E_{\text{TM@Sₙ}} - xE_{\text{TM}} - yE_{\text{Sₙ}}) / x \]  (2)

where \( E_{\text{TM@Sₙ}} \), \( E_{\text{TM}} \), \( E_{\text{Sₙ}} \) are the total energies of SATM@NC, transition metal atom and NC, respectively. \( E_{\text{TM@Sₙ}} \), \( E_{\text{TM}} \) and \( E_{\text{Sₙ}} \) are the energies per formula unit of TMₙSₓ and energy of per atom in bulk S phase,
respectively. When $E_{S1} < E_{S2}$, transition metal metals are dispersed as single atoms embedded in NC substrate. Otherwise, transition metal atoms would react with sulfur or AlPSs during charge-discharge or sulfur loading process to generate corresponding TM$_2$S$_y$ [30]. For instance, $E_{S1}$ for SACo@NC is $-7.73$ eV, which is more negative than the $E_{S2}$ for CoS ($-6.10$ eV) and CoS$_2$ ($-6.82$ eV). These results indicate that Co could be dispersed in NC to form stable SACo@NC.

### 2.7. Calculations of the Gibbs free energies

The binding energies ($E_b$) of sulfur and AlPSs on SATM@NC substrates are calculated as

$$E_b = E_{\text{Total}} - E_{\text{AlPSs}} - E_{\text{Substrate}}$$

(3)

where $E_{\text{Total}}$, $E_{\text{AlPSs}}$, and $E_{\text{Substrate}}$ are the energies of the SATM@NC complex with AlPSs adsorbed, AlPSs molecule and catalytic substrates, respectively. The relative free energy of the discharging process from $S_8$ to the Al$_2$S$_3$ on the substrate was calculated following the reaction sequence of

$$S_8 + Al \rightarrow AlS_{14} \rightarrow AlS_{12} \rightarrow AlS_6 \rightarrow Al_3S_1$$

The corresponding reaction energies for these five steps were calculated using the Eq. (4)-(7), with previous report as a reference [31], respectively. The relative free energy of the discharging process from $S_8$ complex with AlPSs adsorbed, AlPSs molecule and catalytic substrates, as given by the follow equations [32]:

$$E_{\text{AlS}_{14} \text{substrate}} - E_{\text{AlS}_{12} \text{substrate}} - 2E_{\text{Al}} - \frac{12}{8}E_{\text{S8}}$$

(4)

$$E_{\text{AlS}_{12} \text{substrate}} - E_{\text{AlS}_{6} \text{substrate}} + \frac{6}{8}E_{\text{S8}}$$

(5)

$$E_{\text{AlS}_{6} \text{substrate}} - E_{\text{AlS}_{1} \text{substrate}} + \frac{6}{8}E_{\text{S8}}$$

(6)

$$E_{\text{AlS}_{1} \text{substrate}} - E_{\text{Al} \text{substrate}} + \frac{3}{8}E_{\text{S8}}$$

(7)

where $E_{\text{AI}}$ is the energy of aluminum metal per atom and $E_{\text{S8}}$ is the energy of $S_8$ molecule.

### 3. Results and discussion

#### 3.1. Potential single-atom catalysts screening

According to the previous report, the charge-discharge process of Al-S batteries involved the formation of a serious of polysulfides and sulfide, as given by the follow equations [32]:

$$(1/8)S_8 + (1/3)e^- \rightarrow (1/6)S_{6x}^-$$

(8)

$$(1/6)S_{6x}^- + (2/x-1/3)e^- \rightarrow (1/x)S_{7x}^- (1 \leq x < 6)$$

(9)

In order to simulate these conversion reactions by DFT calculations, discharge product $S_{6x}$ with $x = 6, 4, 2$ and 1 were represented by Al$_2$S$_{14}$, Al$_2$S$_{12}$, Al$_2$S$_8$, and Al$_2$S$_3$ molecules, respectively. As illustrated in Fig. 5a, $S_8$ and aluminum polysulfides (AlPSs) molecules were constructed by referring to the previous results [33]. To evaluate the catalytic effect of SACs on the Al-S conversion reactions, one of the most typical SACs were applied to describe SATM@NC. The catalytic substrates were modeled as a series of atomic transition metal embedded in defective graphene in coordination with four nitrogen atoms. Pristine graphene (Gr) was chosen for comparative study. These substrate models are illustrated in Fig. 5b.

Before simulating the Al-S conversion reactions, the stabilities of different SATM@NC substrates were explored. Although the intrinsic stabilities of these SACs have been demonstrated in previous studies, it is essential that they would not be sulfurized into sulfides during cycling in sulfur-rich environments [34, 35]. The computational details of the stability computation are provided in the Experimental Section, and the calculated results are summarized in Table S1 and S2. In this scenario, SATi@NC, SAV@NC and SACr@NC are excluded in this research. Besides, the adsorption configurations of $S_8$ and Al$_2$S$_3$ on these materials were calculated to verify the above implications. As demonstrated in Fig. S2, SATi@NC, SAV@NC and SACr@NC show deformed atomic lattice after $S_8$ or Al$_2$S$_3$ adsorption, that is, bonds between single atom and coordinated N atoms break. It should be noted that these thermodynamic calculations have some limitations, for example, some of the unqualified samples mentioned above have been reported in lithium-sulfur (Li-S) batteries [36]. However, in the scope of this paper, any factors that may affect the stability should be removed as much as possible because of the poor cycling performance of Al-S batteries. Given that the stability calculations reflect the reaction trend of TM atoms with sulfur, it could be used as a criterion to rudimentarily screen a series stable SATM@NC for Al-S batteries. Therefore, only five SATM@NC (TM = Mn, Fe, Co, Ni, Cu) catalysts that are stable in sulfur-rich environment will be considered for further investigations.

According to the stability results, pristine Gr and five SATM@NC were considered to understand the catalytic mechanism and screen out a promising catalyst with the best performance. Fig. 1a, b and Fig. S3 show the optimized configurations of these catalytic substrates with $S_8$ and AlPSs adsorbed, and their corresponding binding energies were calculated. Then, following the order of intermediates in Eq. (8) and Eq. (9), the relative free energy profiles of the discharge process on these substrates could be plotted as illustrated in Fig. 1c. The computational details of the Gibbs free energies are provided in the Experimental Section, and this calculation concept is convincing as evidenced by successfully application in various metal–sulfur batteries [37, 38]. The data clearly shows that after spontaneous exothermic conversion from $S_8$ to Al$_2$S$_{14}$, the subsequent step to from Al$_2$S$_{12}$ is exothermic on SATM@NC while endothermic on Gr. This indicates that the reduction of Al$_2$S$_{12}$ is promoted by the single-atom catalysts. Afterwards, the formation of Al$_2$S$_8$ and Al$_2$S$_3$ are endothermic for all substrates. For the reduction of $S_8$ and AlPSs, the lower Gibbs free energy on all SATM@NC than that on Gr surface suggests that the discharge process is more thermodynamically favorable on SATM@NC surface [31]. All these results demonstrate the catalytic effect of atomic transition metal site. For the exothermic steps, reactions on SACo@NC possess highest Gibbs free energy change. While for the endothermic steps, the reduction from Al$_2$S$_{12}$ to Al$_2$S$_8$ exhibits the largest positive reaction free energy, which is determined to be the rate-limiting step. SAFe@NC delivers a lower reaction free energy of the rate-limiting step. This phenomenon demonstrates their advantages in catalysis compared with other SACs. Specifically, considering the whole discharge process, SACo@NC always has the most negative Gibbs free energy, and the energies needed in the rate-limiting step is moderate. As a result, SACo@NC is believed to catalyze the reduction of sulfur more effectively, indicating that it is one of the most potential catalysts to facilitate the Al-S conversion reactions [31].

#### 3.2. Synthesis and characterization of SATM@NC

Directed by the DFT calculations, five representative SATM@NC (TM = Mn, Fe, Co, Ni, Cu) with similar morphology and catalyst loading were prepared by the chemical vapor deposition (CVD) and MOF-derived method. The overall preparation procedure of SATM@NC is illustrated in Fig. 2a. Various transition metal ion doped ZnO solid solutions (TM-ZnO), which was synthesized by simple precipitation method, were treated with 2-methylimidazole vapor. Thus ZIF-8 doped with transition metal ion was thus formed on the surface of TM-ZnO. These samples were named as TM-ZnO@ZIF. After annealing TM-ZnO@ZIF at 650 °C and etching ZnO template, porous carbon matrix with atomic catalyst site, i.e., SATM@NC, were finally obtained. Without the addition of transition metal atoms, NC was also synthesized for comparison.
The morphology characterizations of SATM@NC and NC are shown in Fig. 2 b-d and Fig. S4. As demonstrated in the scanning electron microscopy (SEM) image in Fig. 2 b, a petal-shaped morphology is observed for SACo@NC. The transmission electron microscopy (TEM) image of SACo@NC in Fig. 2 c displays a clear porous carbon framework. And this image clearly demonstrates an interconnected microporous structure with a pore diameter of ~ 5 nm. High-resolution TEM (HRTEM) image (Fig. 2 d) confirms that no obvious nanoparticles or clusters exist in the porous carbon matrix. Admittedly, the morphologies for NC and other SATM@NC are not exactly the same as SACo@NC, but they all have similar porous structures. As depicted in Fig. 2 e, nitrogen sorption isotherms were conducted to evaluate their porosity, and detailed curves are shown in Fig. S5 and Fig. S6. The Brunner-Emmet-Teller (BET) surface area for NC, SAMn@NC, SAFe@NC, SACo@NC, SANi@NC and SACu@NC are in the range of 800~1000 m$^2$ g$^{-1}$. And their average pore diameters are 4~5 nm. It is obvious that the porous features of all these samples are similar and their pore sizes are quite large. The hierarchical meso-microporous architecture would bring multi benefits for high sulfur loading, well-accommodated volume expansion, efficient confinement of AlPSs and the exposure of catalytic sites.

Energy-dispersive X-ray spectroscopy (EDS) analysis results are shown in Fig. 2 f and S7, which illustrate the uniform distribution of C, N and TM elements in the porous carbon framework. Quantitatively, the loading contents of catalyst on SATM@NC were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). As shown in Fig. 3 a, the SACs loadings of SAMn@NC, SAFe@NC, SACo@NC, SANi@NC and SACu@NC are in the range of 0.6~0.8 wt%. These results indicate that SATM@NC all exhibit ultra-low and comparable metal content. In the XRD pattern of SATM@NC and NC in Fig. 3 b, a broad and weak diffraction peak at around 25° could be indexed to the porous carbon. Besides, there are no peaks of metal or oxide nanoparticles phase, which coincide with the TEM results. In general, all these results further identify the similarity on material morphology and catalyst content of SATM@NC. Thus, their catalytic activity differs only by the different catalytic atoms.

Further characterizations were performed to confirm the coordination structure of transition metal atoms in SATM@NC. As illustrated in Fig. 3 c and S8, aberration-corrected high-angle annular dark-field
scanning TEM (AC HAADF-STEM) images of SATM@NC samples all display well-dispersed atomic sites as brighter dots in the darker porous carbon matrix, which is direct evidence for the enrichment of single atoms. Then, taking SACo@NC as a typical representative, the X-ray absorption near-edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy of SACo@NC were performed. As illustrated in the XANES spectra in Fig. 3d, the near-edge absorption of Co K edge in SACo@NC drop between Co$_3$O$_4$ and Co foil. The detailed structure is further analyzed by EXAFS spectroscopy in R space (Fig. 3e). A major peak at ~1.4 Å is observed in the spectrum of SACo@NC, which is different from Co-O peak at ~1.72 Å and Co-Co peak at ~2.2 Å, corresponding to Co-N bonding. This result suggests that Co atoms are atomically dispersed on the porous carbon matrix without formation of Co cluster. The EXAFS fitting results in Fig. 3f and Table S3 provide quantitative structural parameters of Co atoms in SACo@NC, corroborating that atomic Co coordinates with four N atoms. Moreover, Wavelet Transform (WT) was adopted to analyze the Co k-edge EXAFS signal of SACo@NC (Fig. 3g). Only one intensity maximum at ~4 Å$^{-1}$, which is attributed to the Co–N bonding, is detected in the contour plot of SACo@NC. Considering the similarity of synthetic route and characterization results, the other SATM@NC are supposed to have similar catalytic center. Therefore, combining the above analysis, the local atomic structure around TM atoms in SATM@NC is TM-N$_4$ moieties.

3.3. Electrochemical properties of sulfur loaded SATM@NC

SATM@NC/S and NC/S were fabricated by infiltrating sulfur into SATM@NC and NC. The representative TEM-EDS maps of SACo@NC/S and NC/S are shown in Fig. S9 and S10, which demonstrate homogeneous dispersion of C, N, Co and S in the porous carbon supporter. XRD patterns of SACo@NC/S and NC/S show similar diffraction characteristic, where sulfur is amorphous and no sulfides are observed (Fig. S11). These results suggest that sulfur is uniformly dispersed without apparent aggregation in SATM@NC/S and NC/S. Thermogravimetric analysis (TGA) measurement reveals a high sulfur loading of ~50 wt.% in these
composites (Fig. S12). The mass loading of sulfur for SATM@NC/S and NC/S cathodes were all about 0.8 mg cm$^{-2}$. With NC/S electrode serving as reference, a series of electrochemical measurements were conducted on SATM@NC/S electrode to investigate the catalytic effect of single atoms.

The cycling performance in Fig. 4 a compares the cyclic stability of SATM@NC/S and NC/S cells. Under a current density of 500 mA g$^{-1}$, the discharge capacities after 100 cycles are in the order of SACo@NC/S > SAMn@NC/S > SAFe@NC/S > SANi@NC/S > SACu@NC/S > NC/S. An improved specific capacity retention compared with NC/S illustrates the catalytic effect of SATM@NC, and atomic Co site is believed to have the best catalytic activity. The SACo@NC/S cell could maintain a discharge specific capacity of 567.2 mAh g$^{-1}$ after 100 cycles, demonstrating an advanced electrochemical performance. Cyclic voltammetry (CV) tests in symmetric cells were also carried out to study the catalytic activity of SATM@NC/S in Al–S batteries (Fig. 4 b and Fig. S13) [30, 39]. Under identical test conditions, SATM@NC/S all exhibit higher current densities than NC/S, implying that more rapid redox conversion reactions occur on their surface. The accelerated kinetics is ascribed to the catalytic properties of single atoms seeded on the porous carbon. Among them, the maximal current density is achieved in SACo@NC/S, further confirming that SACo@NC could facilitate the conversion reaction more effectively. Moreover, the Nyquist plot in the electrochemical impedance spectra (EIS) of SATM@NC/S cells show smaller semicircle diameter than that of NC/S, indicating the faster charge transfer on SATM@NC/S (Fig. 4 c and Fig. S14). This phenomenon further revealing the fast redox kinetics of AlPSs accelerated by the SACs. Therefore, the catalytic effects of single atoms are proved experimentally, and SACo@NC is the optimum catalyst in this study. All these results are consistent with the theoretical calculations.

Further studies were conducted to evaluate the electrochemical properties of SACo@NC/S. From the galvanostatic charge-discharge profiles under 500 mA g$^{-1}$ in Fig. 4 d, with the assistance of single-atom Co, the voltage hysteresis is reduced and the discharge capacity in first cycle is increased. These results suggest that atomic Co enhance the reaction activity of sulfur electrode. Similar phenomena are observed in other SATM@NC/S cells (Fig. S15). CV profiles of SACo@NC/S and NC/S are shown in Fig. 4 e. One cathodic peak at ~ 0.5 V and one anodic peak at ~ 1.7 V are observed for the SACo@NC/S, and a larger polarization is observed in the CV profile of the NC/S, indicating that single-atom Co sites reduce the hysteresis of the full cell. Fig. 4 f demonstrates the rate capability of SACo@NC/S. The single-atom Co enables the battery an outstanding high-rate performance, delivering a specific capacity of 485.8 mAh g$^{-1}$ even at a higher current density of 2 A g$^{-1}$. When the current density is recovered to 0.4 A g$^{-1}$, high specific capacity of 663.1 mAh g$^{-1}$ could still be achieved, illustrating the superior rate capability of SACo@NC/S. In addition, long-term cyclic test at 1 A g$^{-1}$ was employed as plotted in Fig. 4 g. The discharge specific capacity of SACo@NC/S is 1097.4 mAh g$^{-1}$ at the first cycle, and
remains 517.2 mAh g\(^{-1}\) after 200 cycles with Coulombic efficiency (CE) of ~ 110%. As comparison, the specific capacity of NC/S after 200 cycles is only 160.7 mAh g\(^{-1}\). The CE > 100% means a higher charge specific capacity, which might be attributed to the side reactions in the electrolyte. This phenomenon has been mentioned in the previous studies as well [40]. It is worth further discussion but beyond the scope of this article. Furthermore, in order to demonstrate the capability of SACo@NC/S in practical applications, the sulfur loading was increased to 2.3 mg cm\(^{-2}\) and the corresponding cyclic performance was evaluated. After steadily cycling for 120 times, an areal capacity of 0.75 mAh cm\(^{-2}\) is obtained at 1 A g\(^{-1}\) (Fig. S16).

As shown in Fig. 4h and Table S4, the electrochemical performance of currently reported sulfur cathodes from RABs are summarized [10, 14-16, 37, 41-43]. Under current densities from 0.5 to 2 A g\(^{-1}\), the rate capability in this work is significantly enhanced compared with the previous studies, demonstrating the improvement of reactions kinetics with the assistance of SACs. In terms of cyclic stability, although the specific capacities in some reported data are appreciable, their cycle life is limited to only 50 cycles, and some of the results were evaluated under a current density of less than 0.1 A g\(^{-1}\), which are far from practical applications. After a long-term cycling, the specific capacity retention in this work clearly represents an advance. In addition, for achieving comparable cycling stability, the catalyst’s content of different single atoms in this work are all below 1.0 wt.%, significantly decreased compared to previous studies (> 30 wt.%), which reflects the cost advantage and high catalytic efficiency of SACs [15, 16]. Therefore, combined the superior catalytic effect of SACs and porosity of carbon matrix, improved Al-S batteries with high specific capacity and long cycling life are realized.

3.4. Catalytic mechanism of SATM@NC

In order to gain further insight into the catalytic chemistry, X-ray photoelectron spectroscopy (XPS) was used to analyze the sulfur cathodes at discharged/charged state. Fig. S17 presents the XPS Al 2p spectra of SACo@NC/S and NC/S. The appearance of intensive Al 2p peak after discharging suggests the Al-S conversion chemistry in the electrochemical process. According to the S 2p XPS spectra in Fig. 5a, b, peaks for S\(^0\) (2p\(_{3/2}\): 164.2 eV and 2p\(_{1/2}\): 165.4 eV) are observed at the pristine state for both samples. At the discharged state, the S 2p peaks for both samples shift to relatively lower binding energies, indicating that sulfur is reduced to lower oxidation states. Characteristic peaks for S\(^2-\) (2p\(_{3/2}\): 161.3 eV and 2p\(_{1/2}\): 162.5 eV) are detected and the doublets locating between 161.3 and 164.2 eV are assigned to the S\(^2-\) of AlPSs. In this scenario, a higher content of S\(^2-\) and less content of S\(^0\) are observed on SACo@NC/S than NC/S, which means that the reductions of sulfur species are much more complete with the help of single-atom Co catalysts. At the charged state, the binding energies of S peak shift in a positive direction, indicating the oxidation of the sulfur species. The fact that S\(^2-\) peaks disappear for SACo@NC/S but still exist for NC/S...
Further confirms the catalytic effect of SACo@NC in the oxidation process. As validated by these XPS results, atomic Co acts as effective catalyst and significantly promotes the bidirectional conversions of AlPSs.

The catalytic mechanism was investigated by DFT calculations as well. The optimized adsorption configurations of AlPSs on SATM@NC and Gr were compared firstly using Al$_2$S$_3$ molecule as an example. As demonstrated in Fig. 1a, only tiny changes are observed when it is adsorbed on Gr surface. On the surface of SATM@NC, as shown in Fig. 1b and Fig. S3, the deformations of Al$_2$S$_3$ molecule are more pronounced. One Al atom in Al$_2$S$_3$, which is denoted as mAl, shifts towards the substrates resulting in the elongation of the attached mAl-S bonds. A more significant deformation of Al$_2$S$_3$ molecule indicates that it is more reactive under the influence of SACs. Noticeably, the optimized adsorption configurations of Al$_2$S$_3$ on SATM@NC are different. On SAMn/Fe/Cu@NC, mAl sits on the top of N atom with forming TM-N interaction. It is obvious that the deformation of Al$_2$S$_3$ molecule on the surface of SACo@NC is as long as 2.179 Å, indicating that the deformation of Al$_2$S$_3$ molecule on the surface of SACo@NC is the most significant. This trend is consistent with the analysis about binding configurations. The longer bond length of Al$_2$S$_3$ means the greater weakening of the mAl-S bond, benefiting to the decomposition of Al$_2$S$_3$ [36]. Based on the above discussions, the breaking of mAl-S bond in Al$_2$S$_3$ molecule to generate an Al$_2$S$_3$ cluster and a single Al atom on SATM@NC substrates are exemplified to evaluate the AlPSs decompositions in oxidation process. The simulated pathways along decomposition process of Al$_2$S$_3$ on different substrates are demonstrated in Fig. 5e and Fig. S24, and the corresponding energy profiles are plotted in Fig. 5f. The energy barrier of Al$_2$S$_3$ decomposition on Gr is calculated to be 3.61 eV, while on SATM@NC the energy barriers are all much smaller, suggesting that the decompositions of Al$_2$S$_3$ are effectively facilitated by SATM@NC. Compared with SACo/Ni@NC, relatively large activation energies at the beginning of the decomposition on SAMn/Fe/Cu@NC is observed in the energy profiles, which may be attributed to the additional need to break mAl-N bonds. Among
SATM@NC, Al$_2$S$_3$ on SACo@NC exhibits the smallest decomposition barrier of 2.54 eV, illustrating the superior catalytic activity of atomic Co on reducing the energy barrier. In general, the results and discussions above reveal that the distinctive Al-binding configurations of AlPSs on SACo@NC is the key to guarantee its superior catalytic performance.

4. Conclusion

In order to develop SACs for Al–S conversion chemistry and uncover the reaction mechanism, a series of SATM@NC catalysts were evaluated by theoretical simulations and prepared for high performance Al–S batteries. In the light of DFT calculations, the catalytic effects of SACs were predicted and SACo@NC was chosen as the most promising catalyst for its most negative Gibbs free energy along S reduction process. Under the guidance of theoretical results, various SATM@NC were synthesized as sulfur hosts and electrocatalysts, and their catalytic properties were confirmed experimentally. Among them, SACo@NC exhibited superior rate performance (a specific capacity of 485.8 mAh g$^{-1}$ under current density up to 2 A g$^{-1}$) and long cycling stability (a reversible specific capacity of 517.2 mAh g$^{-1}$ at 1 A g$^{-1}$ after 200 cycles). The great improvement in the specific capacity, reaction kinetics and cycling life should be attributed to the combination of catalytic effects of SACs and nanoconfinement of porous carbon. According to the computational and experimental results, the catalytic mechanism that SATM@NC weaken Al–S bonds of AlPSs was uncovered. And distinctive Al-binding between AlPSs and SACo@NC was believed to contribute to its favorable catalytic activity. This study provides systematic and valuable insight for developing highly active SACs for high performance Al–S batteries.

Conflict of interest

The authors declare that they have no competing interests.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at CRediT authorship contribution statement


Declaration of Competing 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.

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Supplementary materials

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