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Perspective

Sulfur-chlorine redox chemistry towards sustainable electrochemical energy storage

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The sustainable development of modern society requires new battery systems constructed by abundant and low-cost materials. As the cornerstone of commercial batteries, lithium-ion batteries (LIBs) are widely employed in consumer electronics, electric vehicles, and grid energy storage applications [1]. The reliance on transition metals such as cobalt and nickel results in economic and sustainability concerns, especially for grid energy storage applications [2]. On the other hand, high-safety batteries are highly desired for real-world applications, which also drives the innovation of new materials and reaction pathways.

Conversion-type electrodes based on halogen conversion chemistries have emerged in recent years, due to the high element abundance with high redox potentials, enabling improvements in both energy density and cost-effectiveness [3]. Among various halogen elements, chlorine stands out as a unique candidate, owing to its high redox potential of 1.36 V versus standard hydrogen electrode (SHE) for the Cl^-/Cl^0 redox couple [4,5], and the high theoretical capacity of 756 mAh g^{-1} for Cl_2, outperforming conventional intercalation-type cathodes such as $LiFePO_4$ (170 mAh g^{-1}) and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (220 mAh g^{-1}). A pioneering work by utilizing Cl_2 was reported by Prof. Hongjie Dai from Stanford University, who developed rechargeable alkali metal||Cl_2 batteries based on a chloroaluminate electrolyte comprised of aluminium chloride ($AlCl_3$) in thionyl chloride ($SOCl_2$) with fluoride-based additives [6], shedding light on the potentials of Cl-based cathode chemistry (Fig. 1a). Based on a reversible Cl^-/Cl_2 redox chemistry, the resulting Na||Cl_2 batteries achieved a maximum specific capacity of 1200 mAh g^{-1} (based on the mass of carbon) at a discharge voltage of ~3.55 V. Moreover, the batteries exhibited stable cycling stability at 500 mAh g^{-1} over 200 cycles, achieving a Coulombic efficiency greater than 99% with energy efficiency exceeding 90%.

Despite the promising electrochemical performance of Cl-based redox chemistry, the complex solid-liquid-gas (carbon-electrolyte-Cl_2) triple interfaces pose significant challenges to efficient transport of both electrons and ions. The discontinuous transport pathways within conventional porous carbon nanoparticles lead to limited rate capability, for instance, a maximum charge capacity of only 150 mA g^{-1} [6]. To address this issue, we developed a bicontinuous-structured carbon cubosome to facilitate electron and ion transport, in mimicking the mass and energy transport of the sponge (Fig. 1b) [7]. This bicontinuous structure also enhances Cl_2 adsorption through the incorporation of nitrogen dopants (Fig. 1c). These innovations enabled a remarkable charge-discharge current of 16 A g^{-1} in Na||Cl_2 batteries, and the uniform NaCl deposition within the bicontinuous-structured carbon was confirmed using time-of-flight secondary-ion mass spectrometry. In a complementary strategy, Zhi and co-workers [8] optimized pore geometry by preparing a carbon host with "blocking pores", characterized by narrow pore necks and larger internal cavities (Fig. 1d). This structure enhanced the entrapment of both solid chlorides and gaseous Cl_2, thereby improving the cycling performance by mitigating the loss of active materials.

In addition to cathode design, the corrosive $SOCl_2$-based electrolytes remain a challenge for the practical applications of Cl-based batteries. Our recent work reported a low-corrosive electrolyte system based on organic solvents, such as methyl dichloroacetate (MDCA) [9]. By tuning the electron-withdrawing and electron-donating groups in the ester, we achieved appropriate coordination interactions between $AlCl_3$ and MDCA, enabling soluble and stable electrolyte system based on an organic ester solvent. Notably, this new electrolyte introduced an additional redox pathway associated with the cleavage/formation of the C–O bond of MDCA (Fig. 1e), enabling a reversible capacity of up to ~1200 mAh g^{-1} based on the mass of carbon. In addition, the resulting batteries could stably operate across a broad temperature range of –40 to 80 °C and showed decent cycling stability, e.g., 700 cycles at –40 °C. We further established a design principle of organic electrolytes for rechargeable Na||Cl_2 batteries based on solvent donor number and charge-transfer capability, which showed promise to further unlock the designability and sustainability of high-performance Na||Cl_2 batteries.

Another key bottleneck of Cl-based redox chemistry is the toxic Cl_2, leading to significant challenges in safety and electrochemical

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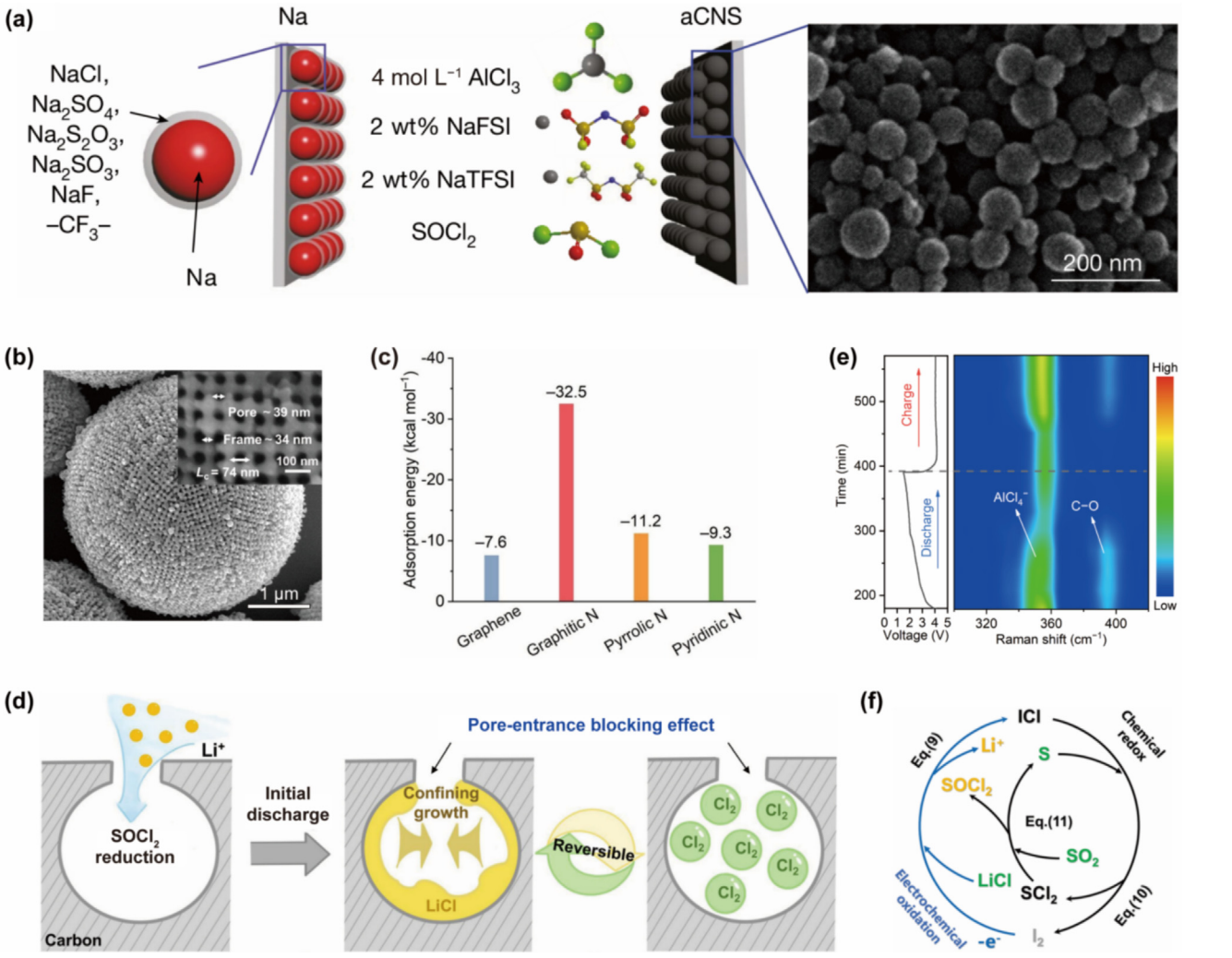

Fig. 1. Rational design of Cl-based redox chemistry. (a) Schematic of the Na||Cl_2 battery with initial electrolyte composition and scanning electron microscopy (SEM) image of the aCNS in the cathode [6]. Reproduced with permission from Ref. [6]. Copyright © 2021, Springer Nature. (b) SEM image of the N-doped bicontinuous carbon. The inset shows a locally magnified view. (c) Cl_2 adsorption energies on bare graphene, graphitic N, pyrrolic N, and pyridinic N [7]. Reproduced with permission from Ref. [7]. Copyright © 2023, Wiley-VCH. (d) Schematic of the blocking pores achieving strong confinement and highly reversible conversion of LiCl and Cl_2 [8]. Reproduced with permission from Ref. [8]. Copyright © 2025, Royal Society of Chemistry. (e) *In situ* Raman spectra of the ANM electrolyte during a continuous discharge-charge process in Na||Cl_2 battery [9]. Reproduced with permission from Ref. [9]. Copyright © 2025, Springer Nature. (f) Charge mechanism in the presence of I_2; green: charging reactants, yellow: charging products, black: intermediates, gray: catalysts [10]. Reproduced with permission from Ref. [10]. Copyright © 2023, American Chemical Society.

reversibility. A central challenge lies in the stabilization of gaseous Cl_2. Cui and co-workers [10] presented an innovative strategy by introducing I_2 into the $SOCl_2$-based electrolyte as a soluble catalyst to tailor the Cl^-/Cl_2 reaction (Fig. 1f). I_2 can facilitate the charge process by forming ICl as an intermediate at 3.85 V, which is lower than the Cl_2 formation potential of 4.15 V, resulting in a 21.07% improvement in energy efficiency. In addition, interhalogen compounds such as iodine trichloride (ICl_3) were introduced as the initial cathode material [11]. Upon oxidation, the generated Cl^0 species were chemically anchored through the reformation of interhalogen bonds with I, suppressing the formation of free Cl_2 gas. This "molecular-scale fixation" strategy thus enabled a highly reversible Li||Cl_2 electrochemistry, highlighting the effectiveness of precise mediation of Cl-based redox chemistry at the molecular level.

While the aforementioned strategies have improved the handling of Cl_2 gas, several fundamental limitations remain. For instance, the high toxicity of Cl_2 hinders the practical energy storage applications, particularly considering its gaseous state under ambient conditions, which raises safety concerns related to toxic gas leakage during operation. From an electrochemical aspect, the single-electron Cl^-/Cl^0 redox couple limits the achievable specific energy. These constraints underscore the need for innovative redox chemistries that offer improved safety and multi-electron transfer. Elemental sulfur (S_8) is a cathode in this regard. It is abundant, supports multi-electron reactions, and exhibits tunable conversion pathways that could enable new battery chemistries. Although sulfur can adopt oxidation states ranging from –2 to +6, high-valence S redox reactions remain largely unexplored, owing to the substantial oxidation barriers and the lack of suitable anion ligands. In conventional Na||S batteries based on the low-valence S^0/S^{2-} redox chemistry, discharge voltages are generally below 1.6 V, and the initial reduction process requires the preloaded Na metal at the anode, introducing safety concerns for practical battery manufacturing [12]. In this context, Cl^- anion may serve as a potential ligand to access high-valence S redox pathways in rechargeable alkali metal batteries, as the pioneering explores in aluminum (Al) metal batteries [13,14], and the prior advances in electrolyte design and mechanistic understanding of Cl-based batteries offer inspirable experience.

Very recently, we reported a high-voltage anode-free Na||S battery based on S^0/S^{4+} redox chemistry (Fig. 2a, b) [15]. This work addresses two key challenges in traditional Na||S batteries, including low discharge voltage and the reliance on largely excessive metallic sodium at the anode that causes safety concerns. Central to this new battery system is a sodium dicyanamide (NaDCA) salt in a chloroaluminate electrolyte, which not only enables reversible S/SCl_4 conversion at the cathode, but also ensures reversible Na metal plating/stripping on Al foil as the anode current collector. The reversible formation and consumption of SCl_4 during battery charge and discharge were confirmed by a variety of characterizations, and the role of DCA^- anion in accelerating the reaction kinetics and lowering the energy barrier of high-valence S oxidation was verified by density functional theory calculations. Differential charge density calculations confirmed the enhanced electron transfer between the sulfur species and the conductive matrix with the presence of the DCA^- anion. Furthermore, the formation of the $DCA^-\cdots SCl_x$ intermediates indicated that DCA^- can coordinate with high-valence sulfur intermediates, forming stabilized charge products that lower the overall reaction barrier. For Na plating and stripping at the anode, the NaDCA-based electrolyte showed significantly improved Coulombic efficiency from 43% to 96%, due to the formation of a nitrogen-rich solid-electrolyte interphase (SEI) layer, yielding uniform Na metal deposition with the maximum current density and areal capacity of 50 mA cm^{-2} and 12 mAh cm^{-2}, respectively.

The obtained high-voltage anode-free Na||S batteries demonstrated promising electrochemical performance, for instance, a high discharge voltage of ~3.6 V with a reversible capacity of 744 mAh g^{-1} based on the mass of sulfur. In addition, the maximum rate capability reached 16 A g^{-1}, delivering a power density of 23,773 W kg^{-1} calculated based on the total electrode mass of both cathode and anode. Furthermore, the incorporation of a bismuth-coordinated covalent organic framework (Bi-COF) in the cathode at a weight percentage of 8 wt% further improved the reversible capacity to 1206 mAh g^{-1} based on the total mass of sulfur and catalyst. We demonstrated the scalability of this battery concept by producing a 1.06 Ah battery, and the material cost was estimated as $5.03 per kWh (Fig. 2c), making it highly promising among current energy storage technologies. This battery

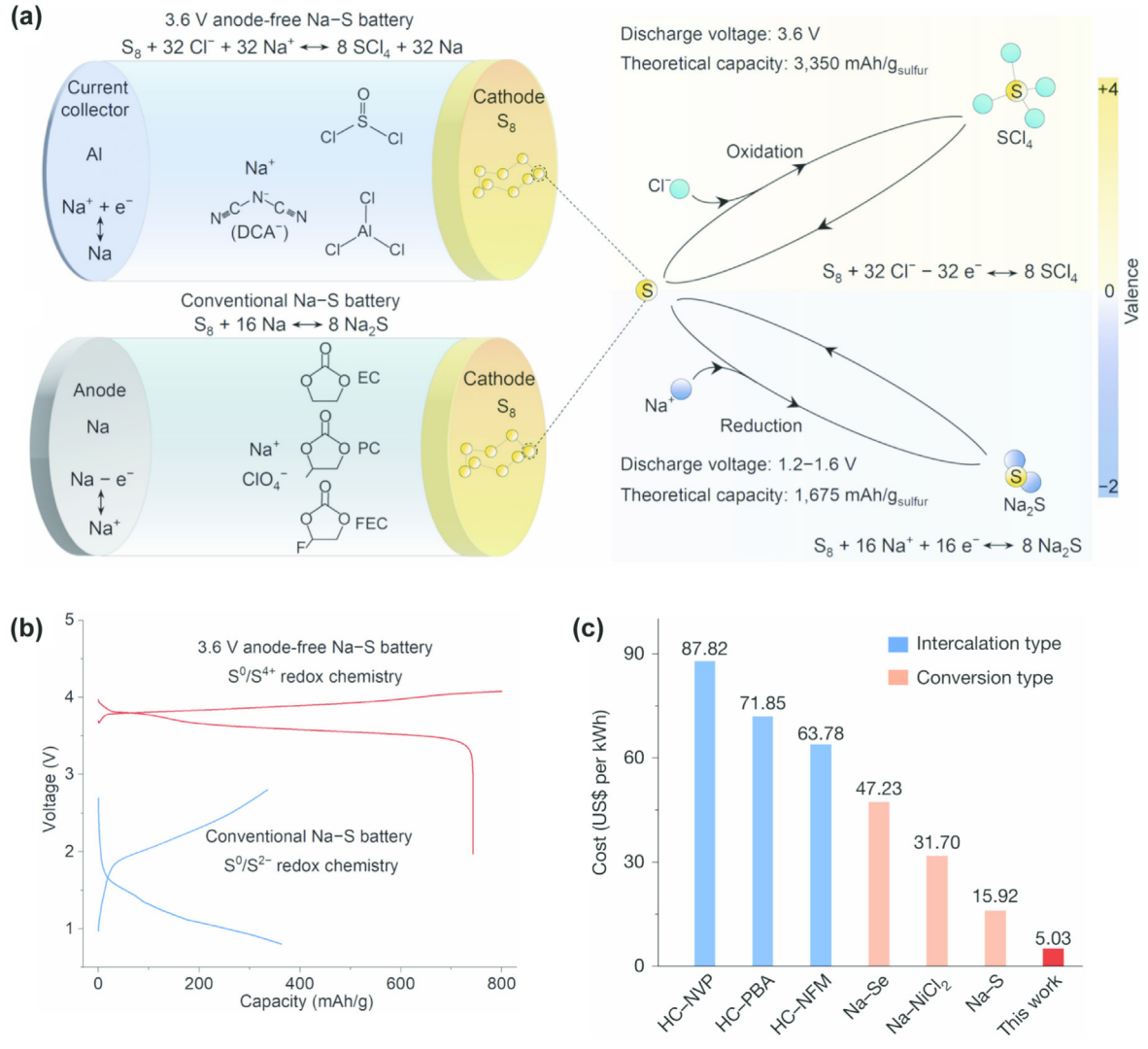

Fig. 2. Anode-free Na||S battery based on a reversible S/SCl_4 redox reaction and the conventional Na||S battery based on S/Na_2S redox chemistry using a conventional organic electrolyte [15]. (a) Schematic illustration of the anode-free Na||S battery based on the S/SCl_4 redox reaction with a chloroaluminate electrolyte. (b) Galvanostatic charge-discharge curves of our anode-free Na||S battery and the conventional Na||S battery based on the same S cathode. (c) Comparison of the unit price of the anode-free Na||S battery and state-of-the-art rechargeable batteries. HC, NVP, PBA and NFM represent hard carbon, $Na_3V_2(PO_4)_3$, $Na_2MnFe(CN)_6$ and $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$, respectively. Reproduced with permission from Ref. [15]. Copyright © 2026, Springer Nature.

concept can be generalized to high-voltage anode-free Li||S batteries, offering a promising route to develop high-voltage and high-safety Li||S batteries. Notably, considering the theoretical specific capacity of 3350 mAh g^{-1} for the 32 electron S redox reaction, the achieved S utilization requires further improvement. Several factors may account for this gap. The S/SCl_4 redox reaction involves a substantial kinetic barrier and relies strongly on the availability of Cl^- anions in the electrolyte. At higher sulfur utilization, depletion of Cl^- in the electrolyte may increase polarization, thereby limiting further reaction and restricting the attainable capacity. There is therefore considerable scope to improve the reversible sulfur capacity, which is now constrained by both the intrinsic cathode and anode chemistries, as well as their crosstalk. It is promising to develop more reversible anode reactions and to develop better cathode and electrolyte materials that suppress parasitic reactions and mitigate SCl_4 dissolution. Overall, these results offer a new approach for conventional alkali metal–sulfur batteries dominated by S^0/S^{2-} cathode chemistry and excessive alkali metal anode, opening a new avenue for sustainable and high-performance electrochemical energy storage.

The battery chemistries based on Cl, S, and their hybrids offer a new avenue for low-cost, sustainable, and high-performance electrochemical energy storage, but the following scientific and technological challenges remain to be solved considering their real-world implementation.

Advanced electrolyte and interface engineering. S- and Cl-based redox couples generally operate at high potentials of >3.5 V versus Li^+/Li or Na^+/Na, leading to electrolyte decomposition risks upon extended cycling and overcharge, which may cause gas evolution, impedance increase, and capacity decrease. To solve this issue, developing "dual-compatible" electrolytes may be a promising approach, which involves the design and synthesis of new salts, solvents, and additives that enable wide electrochemical windows. Developing localized high-concentration electrolytes and sacrificial additives that can form robust, conductive passivation layers at both cathode and anode may be highly promising.

Design of high-performance polymer materials. The dissolution and shuttling of active species remain a key challenge in all S-Cl chemistries, which undermine the Coulombic efficiency and cycle life, especially in anode-free configurations where the migrating species can poison the metal plating process. To this end, rational design of polymers with tailored chemical structures and excellent film-forming properties can be effective to address this issue. Future work can focus on the synthesis of functional polymer materials that combine high ionic conductivity, strong interactions with S- and Cl-based species, and decent electrochemical stability. By incorporating dynamic bonds or self-healing moieties, these polymers may form adaptive and robust interlayers on electrodes, suppressing active species shuttling and stabilizing electrode interfaces. For example, incorporating disulfide-containing polymers (e.g., poly(disulfide)s or disulfide crosslinked networks) onto the cathode and separator surfaces may improve the anchoring of S-Cl intermediates via the electrostatic interaction. Furthermore, the corrosive nature of Cl-based electrolytes can be alleviated through the development of polymer-based electrolytes, offering a potential approach to enhance the battery's practicability.

Practical battery fabrication and operando characterizations. For the practical battery applications of S-Cl redox chemistry, it is important to realize high-loading and lean-electrolyte conditions. This would require further improvements in electrical and ionic conductivities for thick electrodes, while ensuring the multi-phase reactions in the batteries. To this end, it is highly demanded to introduce advanced operando techniques to detect real-time dynamics of the reactions and interfaces, alongside multi-scale computational models to predict degradation and optimize cell design. These new insights can inspire the development of high-performance conversion-type batteries for real-world energy storage applications.

In summary, the S-Cl conversion chemistries open a promising avenue for sustainable, low-cost, high-safety, and high-performance energy storage. Some recent progresses in this emerging field have improved the practicability of the obtained batteries. With interdisciplinary cooperation of chemistry, materials science, energy, mechanical engineering, and artificial intelligence (AI), we believe S-Cl conversion chemistry can be an important candidate for the pursuit of next-generation energy storage technology, with potential applications in grid energy storage, electric vehicles, and consumer electronics.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2026.03.037.

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