

CHAPTER II

LITERATURE REVIEW

2.1 Aluminum-sulfur batteries

The success of lithium-ion batteries leads to the development of high-performance batteries with cost-effective and safety energy storage. Among many types of batteries, metal–sulfur batteries (Na, K, Mg, or Al) have been recently focused as promising commercial batteries which provide higher capacity than traditional ion batteries. (Klimpel et al., 2022) The high theoretical volumetric capacity of the Al anode ($8046 \text{ mAh}\cdot\text{L}^{-1}$) and theoretical energy density equal to $3177 \text{ Wh}\cdot\text{L}^{-1}$ comparing to Na-S batteries ($3079 \text{ Wh}\cdot\text{L}^{-1}$), Mg-S batteries ($3115 \text{ Wh}\cdot\text{L}^{-1}$), and Li-S batteries ($3290 \text{ Wh}\cdot\text{L}^{-1}$) as shown in Figure 2.1a and Figure 2.1b. Aluminum is the most abundant metal in the Earth's crust and the least expensive compared to other metal–sulfur batteries in Figure 2.1c.

For historical development of Al-S batteries, Marassi et al invented the very first Al-S batteries in the 1980s which studied sulfur in NaCl-AlCl molten electrolyte (Marassi et al., 1985; Tanemoto et al., 1982). After that, Licht and Peramunage invented Al-S batteries using an aqueous alkaline electrolyte. Due to the great potential of Li-ion batteries and Li-S batteries, the development of Al-S batteries remained untouched until 2015 shown in Figure 2.2 (Licht & Peramunage, 1993). The ionic liquid as the electrolyte for Al-S batteries represented a very high efficiency which can create rechargeable Al-S batteries (Cohn et al., 2015; X. Yu & Manthiram, 2017). After that the number of publications on Al–S batteries have increased in experimental and computational studies.

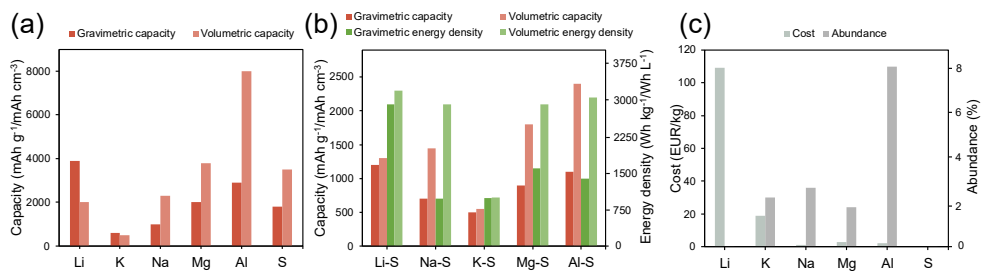


Figure 2.1 Comparison of metal-sulfur batteries and their components. (a) capacities of different metal including Li, K, Na, Mg, Al, and S in terms of gravimetric and volumetric. (b) Theoretical capacities and energy densities of each metal-sulfur batteries. (c) Comparison of abundance and cost of metal and S (Klimpel, Kovalenko et al. 2022).

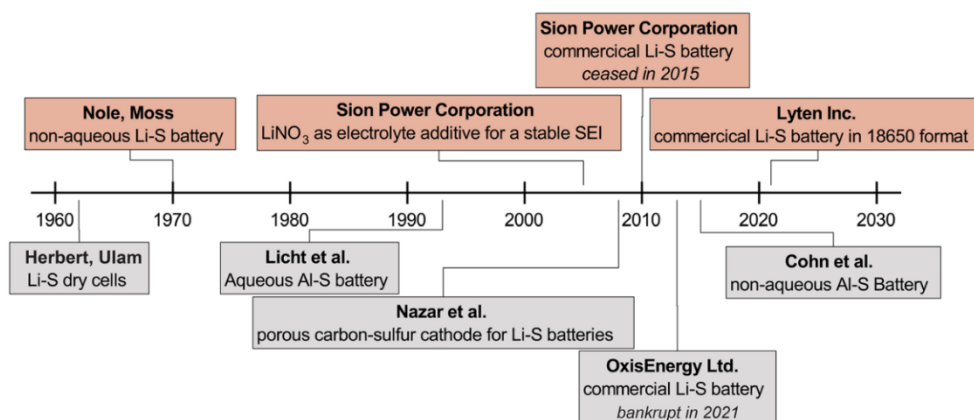
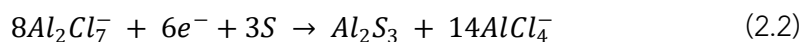
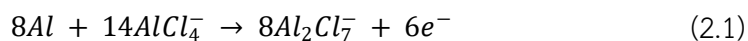


Figure 2.2 Development of Li-S and Al-S batteries and expectation (Klimpel et al., 2022).

Electrolyte of Al-S batteries normally contain chloroaluminate melts, which are the mixtures of aluminum chloride and other chlorides containing an organic cation, such as, 1-butyl-3-methylimidazolium chloride (MIM) and 1-ethyl-3-methylimidazolium chloride (EMIM). These electrolytes are called room temperature ionic liquid.

The mechanism of Al-S batteries using chloroaluminate ionic liquid electrolyte can be summarized as given equations (1) and (2). (Appiah et al., 2022; Bhauriyal et al., 2020)



During the discharge process, at the anode-electrolyte interface, Al reacts with AlCl_4^- to produce Al_2Cl_7^- species. Then Al_2Cl_7^- species transport from the anode through the bulk electrolyte to the cathode, shown in Figure 2.3. At the cathode, solid sulfur changes into dissolved polysulfide (S_8). Then the ligand exchange reactions in which polysulfide replaces chloride ions of Al_2Cl_7^- species result in the formation of aluminum polysulfide species (Al_2S_n). (Appiah et al., 2022; Bhowmik et al., 2022) This process is called sulfur reduction reaction. The key intermediates of Al_2S_n or S_8 initially start from S_8 , Al_2S_{18} , Al_2S_{12} , Al_2S_6 to Al_2S_3 shown in Figure 2.4.

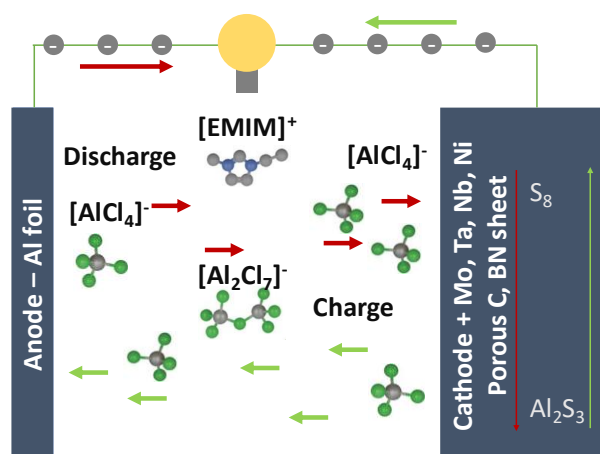


Figure 2.3 The charge and discharge mechanism of Al-S batteries.

During sulfur reduction reaction, the high orders of Al_2S_n species including Al_2S_{18} , Al_2S_{12} , Al_2S_6 prefer to dissolve into the bulk electrolyte. They could diffuse back and react with Al at the anode which is one of the main challenges in developing metal-sulfur batteries called shuttle effect. Furthermore, Al_2S_n species are difficult to change into lower order of Al_2S_n . These lead to the development of promising cathode material for Al-S batteries.

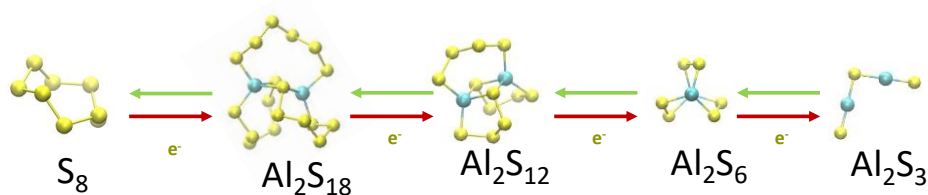


Figure 2.4 The sulfur reduction process and key intermediates.

2.2 Cathode materials for Al-S batteries

The information on the cathode materials is summarized in Table 2.1. In the initial stages of research, carbon was commonly used as cathode materials because of tunable properties, low cost, and abundance. The first cathode for rechargeable Al-S batteries made from Ketjen black carbon/S (Cohn et al., 2015). It was used as the sulfur host for the cathode because of the high surface area. The result showed a remarkably high specific capacity of more than $1400 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at $30 \text{ mA}\cdot\text{g}^{-1}$ which is more than 80% of the theoretical capacity. However, the inability to oxidize and the dissolution of the discharged products are the obstacle in capacity decay and low cycle life of the rechargeable batteries. Other carbon materials, such as activated carbon cloth/S (Gao et al., 2016), CNF/S (X. Yu & Manthiram, 2017), SWCNT/S (Smajic et al., 2020), and Graphene/CoS₂/S (Zheng et al., 2020), are also used as cathodes. However, their performance is not remarkable, and they exhibit low discharge cycles shown in Table 2.1.

The exponential improvement of cathode materials began since 2D materials were applied in experimental studies as cathodes. For example, 2D-BN nanosheet/S/C demonstrated a high specific capacity more than $300 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 250 discharge cycle (K. Zhang et al., 2019). For other 2D materials also including SATM@NC, S@Ti₃C₂T_x, S @ NO-C, S @ Fe-N-C, and S@Fe-NO-C also exhibited impressive performance comparable to 2D-BN nanosheet/S/C.

For the computational studies, the DFT study proposed a 2D copper-based MOF (Cu-BHT) monolayer as a potential cathode material in Al-S batteries. It revealed the reason behind better performance of Cu-BHT than that of graphene since Cu-BHT show a better performance of suppress the high orders of Al₂S_n species (Bhauriyal & Pathak, 2020). These findings suggest that DFT can provide insightful information and details at the atomistic level. Furthermore, DFT study can cooperate with experimental study. The combination of the experimental and computational techniques used to identify the single-atom catalysts for boosted Al-S conversion reaction. Computational models play an important role in the selection of candidate materials for the synthesis. Their catalytic properties were confirmed experimentally. Among them, SACo@NC/S exhibited rate performance with a specific capacity of $485.8 \text{ mAh}\cdot\text{g}^{-1}$ and long cycling

stability with a reversible specific capacity of $517.2 \text{ mAh}\cdot\text{g}^{-1}$ at $100 \text{ mA}\cdot\text{g}^{-1}$ after 200 cycles (Ju et al., 2022).

Table 2.1 Studied sulfur cathode materials for Al–S batteries.

Materials	Synthesis or Modeling References	Initial discharge capacity ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$)	Discharge cycle ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$) at n cycles
Ketjen black carbon/S (2015)	Solution-processed slurry based method (Cohn et al., 2015)	1200 @ 120 $\text{mA}\cdot\text{g}^{-1}$	<50 after 4 cycles
S (2015)	Commercial S-powder (Xia et al., 2015)	113.64 @ 15 $\text{mA}\cdot\text{g}^{-1}$	104.69 after cycles
Mo ₆ S ₈ (2015)	Chemical intercalation process (Geng et al., 2015)	148 @ 12 $\text{mA}\cdot\text{g}^{-1}$	70 after 50 cycles
Activated carbon cloth/S (2016)	Melt diffusion method (Gao et al., 2016)	1320 @ 50 $\text{mA}\cdot\text{g}^{-1}$	1000 at 20 cycles
NiS (2016)	Hydrothermal method (Z. Yu et al., 2016)	104.7 @ 200 $\text{mA}\cdot\text{g}^{-1}$	100 after 100 cycles

Table 2.1 (Continued) Studied sulfur cathode materials for Al–S batteries.

Materials	Synthesis or Modeling References	Initial discharge capacity ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$)	Discharge cycle ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$) at n cycles
Ni_3S_2 /graphene micro flakes (2016)	Mixing (S. Wang et al., 2016)	350 @ 100 $\text{mA}\cdot\text{g}^{-1}$	60 after 100 cycles
CNF/S as cathode and SWCNT coated separator (2017)	Vacuum filtration and vacuum drying (X. Yu & Manthiram, 2017)	>1200 @ 0.05 C	>450 after 10 cycles
S@CMK-3 (2018)	Melt diffusion method (H. Yang et al., 2018)	1390 @ 251 $\text{mA}\cdot\text{g}^{-1}$	>400 after 30 cycles
SPAN (2018)	Thermal polymerization (C. Wang et al., 2018)	343 @ 0.025 $\text{mA}\cdot\text{g}^{-1}$	201 after 20 cycles
2D-BN nanosheet/S/C (2019)	Ball milling mixing (K. Zhang et al., 2019)	532 @ 100 $\text{mA}\cdot\text{g}^{-1}$	300 after 250 cycles

Table 2.1 (Continued) Studied sulfur cathode materials for Al–S batteries.

Materials	Synthesis or Modeling References	Initial discharge capacity (mA·h·g ⁻¹)	Discharge cycle (mA·h·g ⁻¹) at n cycles
Co ₃ S ₄ (2019)	Solvothermal process (H. Li et al., 2019)	287.9 @ 50 mA·g ⁻¹	90 after 150 cycles
Carbonised-ZIF/S (2020)	Solvothermal synthesis (Hu et al., 2020)	1410 @ 200 mA·g ⁻¹	420 after 30 cycles
SWCNT/S (2020)	Non-destructive sublimation–deposition method (Smajic et al., 2020)	>900 @ 100 mA·g ⁻¹	1024 @ 2 cycles
Graphene/CoS ₂ /S as cathode and rGO coated separator (2020)	Melt diffusion method and hydrothermal method (Zheng et al., 2020)	680 @ 50 mA·g ⁻¹	1145 after 37 cycles
Cu-BHT MOF (2020)	VASP, DFT-D3 (Bhauriyal & Pathak, 2020)	Theoretical study	Theoretical study

Table 2.1 (Continued) Studied sulfur cathode materials for Al-S batteries.

Materials	Synthesis or Modeling References	Initial discharge capacity ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$)	Discharge cycle ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$) at n cycles
S@ZIF-67 and S@Z-67- 700 (2021)	Solvothermal synthesis (Xiao et al., 2021)	1675 @ 100 $\text{mA}\cdot\text{g}^{-1}$ Theoretical study	180 after 50 cycles Theoretical study
SATM@NC (2022)	Mixing (Ju et al., 2022)	1097.4 @ 100 $\text{mA}\cdot\text{g}^{-1}$	517.2 after 200 cycles
S@Ti ₃ C ₂ T _x (2022)	Conventional slurry- coating (Zheng et al., 2022)	489 @ 300 $\text{mA}\cdot\text{g}^{-1}$	415 after 280 cycles
(Ti ₃ C ₂ O ₂)@SA (2022)	VASP, DFT-D3 (Z. Wang et al., 2022)	Theoretical study	Theoretical study
S@NO-C, S @ Fe-N-C, S@Fe-NO-C (2023)	Solvothermal process (Luo et al., 2023)	352.1 at 300 $\text{mA}\cdot\text{g}^{-1}$	550.1 after 400 cycles Theoretical study

2.3 MXene for as electrode material for batteries

MXene is a type of 2D material that consists of thin layers of transition metal carbides, nitrides, or carbonitrides. MXene is in $M_{n+1}X_nT_x$ form, which includes transition metals (M elements), e.g., Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, carbon, and nitrogen (X elements) along with the functional surface termination groups (T_x elements).

They can be synthesized by the selective etching of the “A” element in the MAX phase. Figure 2.5a shows elements that commonly occur in the formation of MXenes. Normally, These Strong acids such as HF, LiCl, HCl are used to etch the MAX phase resulting in the delamination of MXenes (Mahmud et al., 2022). Then, the intercalation of MXenes occurs as shown in Figure 2.5b. To achieve selective layer. Top-down processes are used to etch and exfoliate using strong acids. For example, the production of Ti_3C_2 can achieve from Ti_3AlC_2 with a top-down method shown in Figure 2.5c (Naguib et al., 2011).

The fascinating properties of MXenes are high conductivity, mechanically robust, hydrophilicity, reactivity, and corrosion resistance. These characteristics make MXenes suitable for various applications such as biosensors, antibacterial agents, catalysis, and energy storage. The table below shows the MXenes and their synthesis conditions in Table 2.

The application for energy storage has become more interesting because their metallic or narrow bandgap characteristics are highly advantageous for batteries. They are usually used as electrodes for batteries. Several studies have shown an impressive performance shown in Table 3. For examples, Ti_3C_2 nanosheet as the anode material provide an impressive initial capacity of $1112 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ over 2000 cycles for Na-ion batteries (R. Zhao et al., 2019). $V_2O_x@V_2CT_x$ as the cathode material provide initial capacity of 304 over 200 cycles for Zn-ion batteries (Venkatkarthick et al., 2020). For Al-S batteries, there is a study that use $Ti_3C_2T_x$ as the cathode The results show an impressive performance which provide initial capacity of $489 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at $300 \text{ mA}\cdot\text{g}^{-1}$ and retained a value of $415 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 280 stable cycles. However, they are usually applied for metal-ion batteries. There is a long way to improve the performance of MXenes for other batteries.

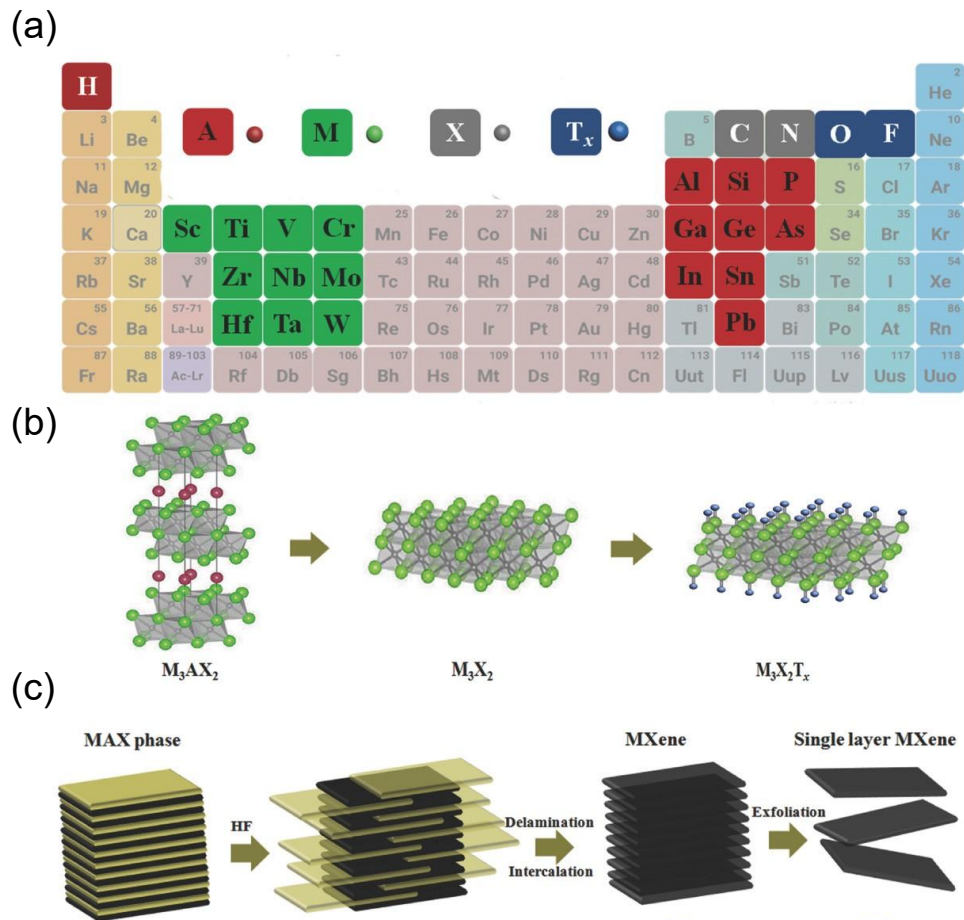


Figure 2.5 (a) Synthesizable elements used in MAX processes. (b) The illustration of MXene synthesis process. (c) The step of etching Ti_3AlC_2 using HF etchant (Mahmud, Hasan et al., 2022)

Table 2.2 Synthesis conditions for different MXene and their potential application.

MXene	Etchant (time, temperature)	Purpose/application	References
Nb ₂ C	50 wt % HF (90 h, RT)	anode material for LIB	(Naguib et al., 2013)
V ₂ C	50 wt % HF (90 h, RT)	anode material for LIB	(Naguib et al., 2013)
Ti ₃ C ₂	40 wt % HF (48 h, 60 °C) + Ti ₃ C ₂ calcinated high temp., 200–1200 °C	vacuum calcination for better electrochemical and thermal properties for LIB	(Lipatov et al., 2016)
Zr ₃ C ₂	1 M NaHF ₂ (12 h, RT)	comparison between structural stability of Zr ₃ C ₂ T _z and Ti ₃ C ₂ T _z MXenes	(Zhou et al., 2016)
(Nb,Ti) ₄ C ₃	50 wt % HF (90 h, 50 °C)	Nb ₄ C ₃ T _x multilayer MXene for energy storage applications	(J. Yang et al., 2016)
V ₂ C	3.35 M NaF in 12 M HCl (48 h, 90 °C)	preparation with NaF at high temperature as anode for LIB	(Liu et al., 2017)
Ti ₂ C	13.5 M LiF in 6 M (15 h, 40 °C)	hybrid Li-ion battery (LIB)	(Kajiyama et al., 2017)
Nb ₂ C	50 wt % HF (48 h, 25 °C)	chemical sensor	(Lin et al., 2017)

Table 2.2 (Continued) Synthesis conditions for different MXene and their potential application.

MXene	Etchant (time, temperature)	Purpose/application	References
Ti ₃ C ₂	2 M HCl (24 h, 40 °C)	PH sensor	(X. Chen et al., 2018)
Ti ₃ C ₂	40 wt % HF (24 h, RT)	Sn ⁴⁺ ion decorated nanocomposites for LIB	(Kong et al., 2018)

Table 2.3 Studied MXenes as Electrode Material for Batteries.

Structure	Battery type	electrode	Initial capacity (mAh g ⁻¹)	Current density (mA g ⁻¹)	Number of cycles	ref
2DTi ₂ CT _x nanosheets	Li-ion	anode	1015	100	50	(Ahmed et al., 2016)
V ₂ O _x @V ₂ CT _x	Zn-ion	cathode	304	2	200	(Venkatkarthick et al., 2020)
SnO ₂ -Ti ₃ C ₂	Li-ion	anode	1030.1	100	360	(F. Wang et al., 2017)
V ₂ CT _x	Al-ion	cathode	335	10	20	(VahidMohamadi et al., 2017)
PDDA-BP/Ti ₃ C ₂ nanosheet	Na-ion	anode	1112	0.1	2000	(R. Zhao et al., 2019)
MoS ₂ /MXene	K-ion	anode	453.5	50	50	(J. Li et al., 2020)

2.4 Single atom as catalyst on MXenes

A single-atom catalyst (SAC) is a type of catalyst that consists of isolated atoms of a metal or a non-metal on a supported substrate or an alloy. The catalysts are tunable to maximize atomic efficiency, the activity, and selectivity of catalytic reactions. The studies of SACs usually focus on metal-based catalysts, especially the late transition metals, such as Pt, Pd, Fe, Co, Ni, and Cu for their high catalytic activity and selectivity since d orbitals play an important role for their performance.

SACs work by providing active sites for chemical reactions to occur on the surface of a substrate or an alloy. The isolated atoms act as the centers of electron transfer, adsorption, and activation of the reactants and products. The substrate or the alloy supports the single atoms and stabilizes their electronic structure and geometry. The performance of single-atom catalysts depends on the type, size, and coordination of the single atoms, as well as the interaction with the substrate or the alloy (X.-F. Yang et al., 2013).

The preparation of SACs on supported materials still poses challenges due to the tendency of aggregation of single metal atoms. Two major techniques have been developed for synthesizing SACs. The first is mass-selected soft-landing techniques. These methods focus on precise control during the deposition of single metal atoms onto the support material. By carefully selecting and placing individual atoms, aggregation is minimized. The second is improved wet chemistry methods. These approaches enhance wet chemical processes to achieve better control over the placement of single metal atoms. The aim is to prevent aggregation and maintain the unique properties of SACs (N. Cheng et al., 2019).

For MXenes, SACs can be synthesized by different methods depending on the positions on MXenes including. These methods include adsorption on the surface, anchoring at the M vacancies, and anchoring at the T Vacancies.

2.4.1 Adsorption on the surface

In experimental studies, SAs on the surface of MXene are normally synthesized by electrostatic adsorption and in situ reduction in two steps (Y.-H. Chen et al., 2021). Firstly, metal cations are absorbed on the negatively charged functional groups of MXene to form ionic bonds driven by electrostatic attraction. Secondly, the metal

cations are reduced and fixed on the MXene to form covalent bonds with functional group by adding reducing agents or annealing at high temperatures. The successful of this method shows in Figure 2.6a. The presence of NaBH_4 avoided the excessive oxidation of MXene and leading Co^{2+} ions bond to O on MXene under the drive of electrostatic attraction.

The other efficient strategy is annealing in hydrogen atmosphere which can induce the morphologic transformation of SAs species on MXenes (Dai et al., 2022). For example, Ir species in hydrogen atmosphere can change from nanoparticles to single atoms on Mo-based MXene with the increase of annealing temperature shown in Figure 2.6b. Furthermore, there are the method that quaternary MAX phase which includes four different atoms. The sublimation of AlCl_3 , Zhao et al. selectively etched Al from the quaternary MAX phase $\text{Ti}_3(\text{Al}_{1-x}\text{Cu}_x)\text{C}_2$, which contained a mixed A layer, and obtained Cu single atoms on the surface of MXene shown in Figure 2.6c (Q. Zhao et al., 2021).

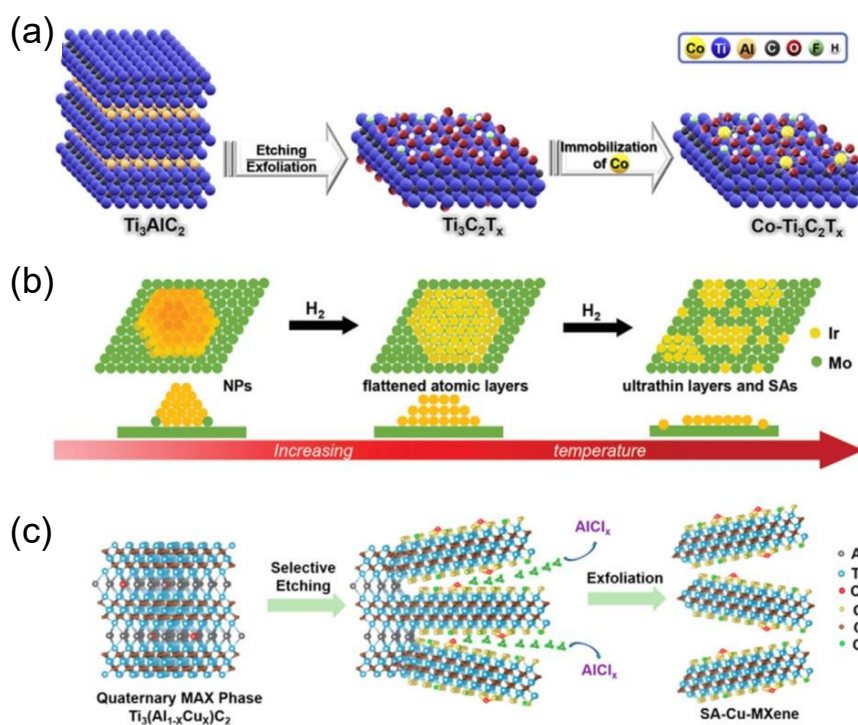


Figure 2.6 Illustrations of MXene synthesis. (a) Schematic of Co- $\text{Ti}_3\text{C}_2\text{T}_x$ single-atom catalysts (SA) (Y.-H. Chen et al., 2021). (b) Synthesis of Ir from nanoparticles to flattened layer and on $\text{Mo}_2\text{TiC}_2\text{T}_x$ (Dai et al., 2022). (c) The production of SA-Cu-MXene with selective etching quaternary MAX.

In computational studies, the adsorption of single atoms (SAs) mainly occurs at four possible sites: top site (T), two different hollow sites fcc and hcp, and bridge sites (B), where the sites of hcp and fcc are the preferred adsorption sites shown in Figure 2.7a and 2.7b.

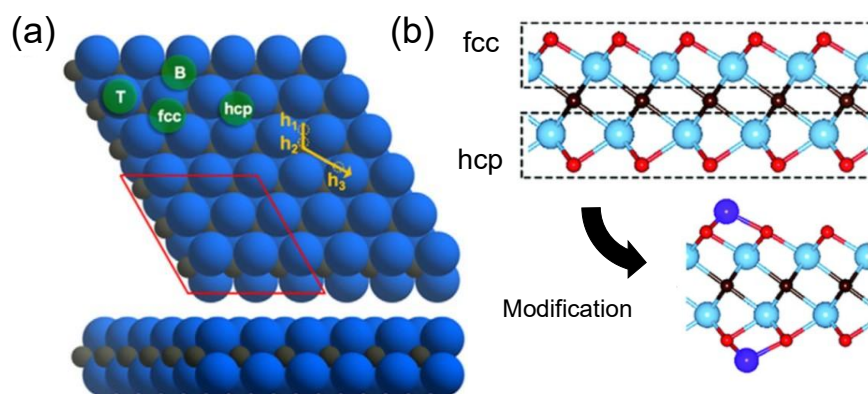


Figure 2.7 (a) All possible binding sites of single-metal atoms on M_2C . (b) An atomistic model of transition metal (TM) on M_2C .

2.4.2 Anchoring at the metal vacancies

In the synthesis process, forming metal vacancies (M vacancies) is inevitable because the surfaces normally have unsaturated coordination and certain reducibility called “self-reduction method”. Zhao et al. demonstrated Pt onto the Ti vacancy of Ti-based MXene with 0.2 wt% of Pt shown in Figure 2.8a (D. Zhao et al., 2019). The Pt atom was anchored at the Ti site rather than the lattice gap. The clear Pt spots located at the lattice plane walls of the Ti columns shown in Figure 2.8b and 2.8c. The one factor that involves to the M vacancy of MXene is the concentration of etching agent and etching time. Another study from Park et al., V_2CT_x with 49% HF for 5 days can provide V vacancies that can use to anchor-isolated Pt atoms by self-reduction (Park et al., 2022). There is a study that used CO_2 atmosphere as an addition process after adsorption step. Zhao et al. demonstrated CO_2 promoted the formation of Ti vacancy and conducive Se to Ti vacancy shown in Figure 2.8d.

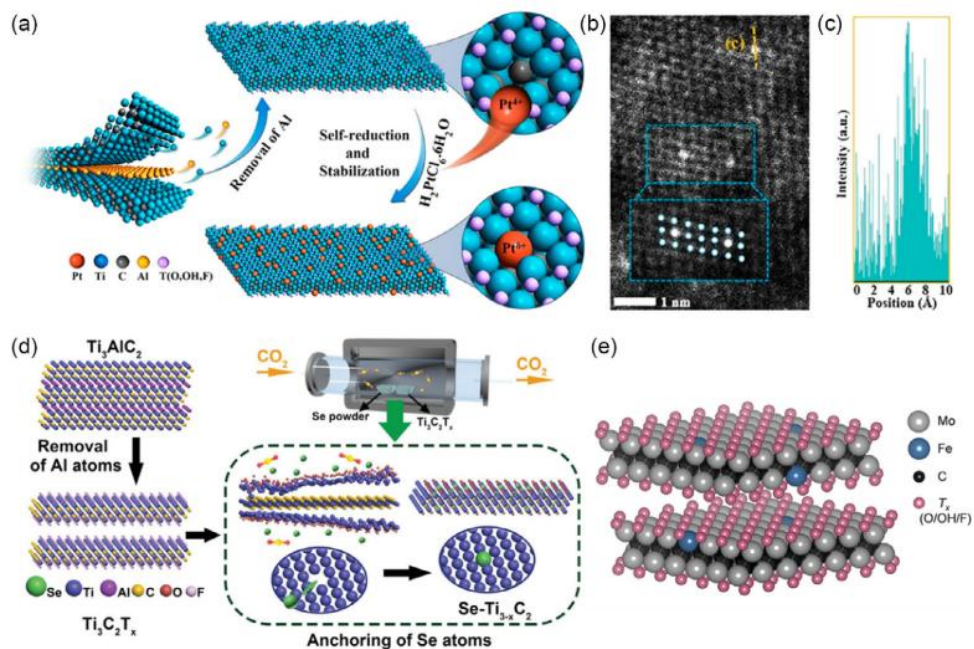


Figure 2.8 (a) Self-reduction-stabilization process for the preparation of $\text{Pt}_1/\text{Ti}_{3-x}\text{C}_2\text{T}_y$ (D. Zhao et al., 2019). (b) Magnified HAADF image of $\text{Pt}_1/\text{Ti}_{3-x}\text{C}_2\text{T}_y$. (c) Corresponding intensity maps. (d) Synthesis process of the $\text{SASE-Ti}_3\text{C}_2$. (e) Schematic representation of the $\text{Mo}_2\text{CT}_x:\text{Fe}$ structure.

For computational studies, M vacancies are natural sites on MXene and can be used to anchor individual atoms. Li et al. demonstrated calculated formation energy of Zr, Hf, Ta W, Re, and Os filling on the bimetallic MXene $\text{Mo}_2\text{TiC}_2\text{O}_2$ with Mo defects, which were -1.89, -2.24, -1.64, -0.10, 1.29, and -1.96 eV, respectively (L. Li et al., 2019). The study indicates that the experimental preparation for the structures with negative formation energy is possible.

2.4.3 Anchoring at the T Vacancies

TM atoms can prefer to be anchored to T vacancies or substituted for the T atoms to form SACs. There are various methods depending on materials and the conditions. For example, Bao et al. reduced $\text{Ti}_3\text{C}_2\text{T}_x$ with NaBH_4 , then added Cu ions to obtain $\text{Cu SA}/\text{Ti}_3\text{C}_2\text{T}_x$ by vacuum freeze-drying shown in Figure 2.9a (Bao et al., 2021). Zhao et al. added CoCl_2 solution in the form of ice cube to V_2CT_x solution and maintained the condition of 0 °C to ensure the slow release of Co^{2+} to avoid the formation of clusters (X. Zhao et al., 2023). The mixture was then exposed to ultraviolet light for 1 h to reduce and fix the Co onto the MXene shown in Figure 2.9b.

In computational studies, the functional groups O, F, and Cl are easy to form defects or be replaced in the reaction. The studies usually focused on oxygen vacancies because of the high stability of O terminated. The study of oxygen vacancies in $\text{Mo}_3\text{C}_2\text{O}_2$, Pd anchored onto these vacancies exhibited high stability and good CO oxidation activity (C. Cheng et al., 2018). Furthermore, the binding energy of Fe, Co, Ni, Cu, Zn, Ru, Rh, Ag, Ir, Pt, and Au atoms on the oxygen vacancies of Mo_2CO_2 was calculated by Cheng et al (C. Cheng et al., 2018). Four initial sites for anchoring TMs were calculated, including B, H1, H2, and oxygen vacancy shown in Figure 2.9c. The study revealed that TMs (except Fe) would always move to more stable oxygen vacancy during optimizations.

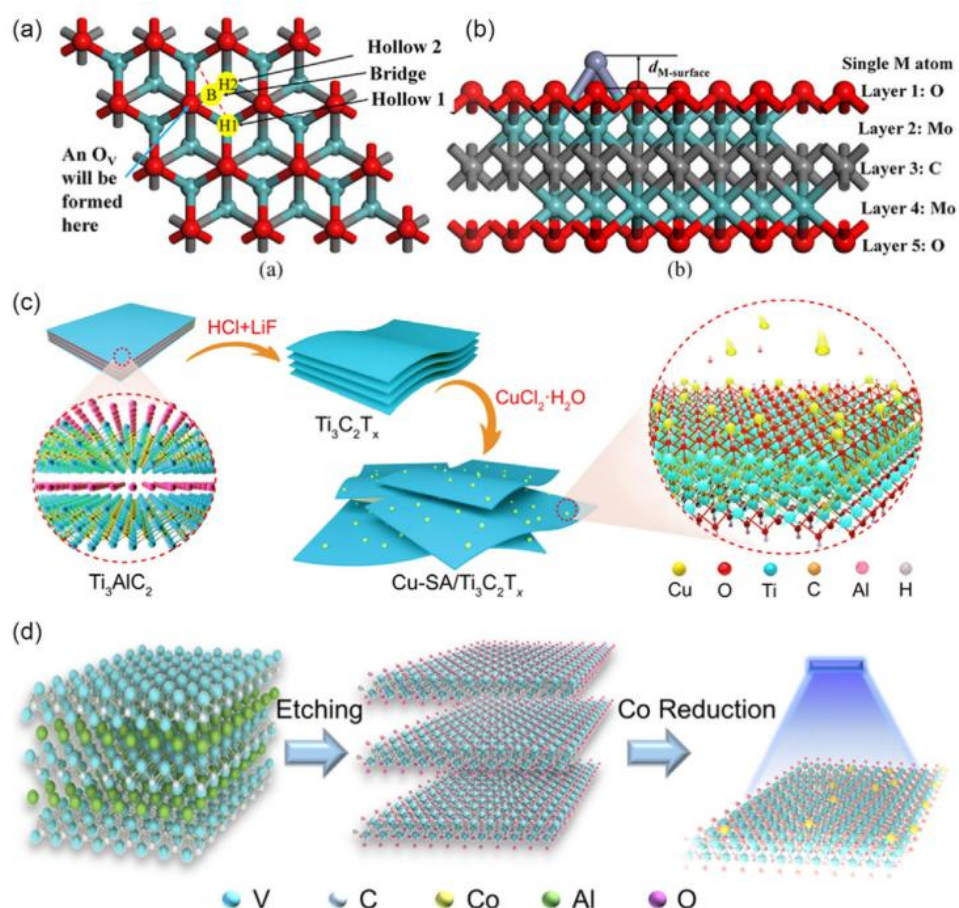


Figure 2.9 (a) Top view of the pristine Mo_2CO_2 sheet. (b) Side view of the optimized $\text{M}/\text{Mo}_2\text{CO}_2\text{-sigma}$ structure. (c) The synthesis of $\text{Cu-SA}/\text{Ti}_3\text{C}_2\text{T}_x$. (d) The synthesis of $\text{Co@V}_2\text{CO}_2$ (Bai & Guan, 2023).

For applications in energy storage, several studies demonstrate that MXene modification improves better performance in the batteries. In Li-ion batteries, Co/V₂C doubled capacity of the electrode material from 686.7 to 1117.3 mA·h·g⁻¹ at 0.1 A·g⁻¹ (C. Wang et al., 2018). Furthermore, Sn/V₂C electrode achieved 1284.6 mA·h·g⁻¹ at 0.1 A·g⁻¹ for 1600 cycles (C. Wang et al., 2019). In Li-S batteries, several studies demonstrated that SAs on MXenes can inhibit the dendrite of Li. Gu et al. demonstrated that Li could form an alloying phase with Zn rather than dendrite of Li on Zn/Ti₃C₂Cl_x (Gu et al., 2020). Furthermore, Zn-MXenes can improve reversible capacity and reduce the rate-limiting reaction barrier from 0.91 to 0.17 eV (D. Zhang et al., 2020).

However, there has been only one computational study on SAs-MXene for Al-S batteries. The study focused on Al-S batteries by Wang et al (Z. Wang et al., 2022). The study demonstrated that they use adsorption energy and the free energy diagram to explore and evaluate the performance of SAs on MXene. The study offered valuable insights and recommended candidate material for experimentalists shown in Figure 2.10.

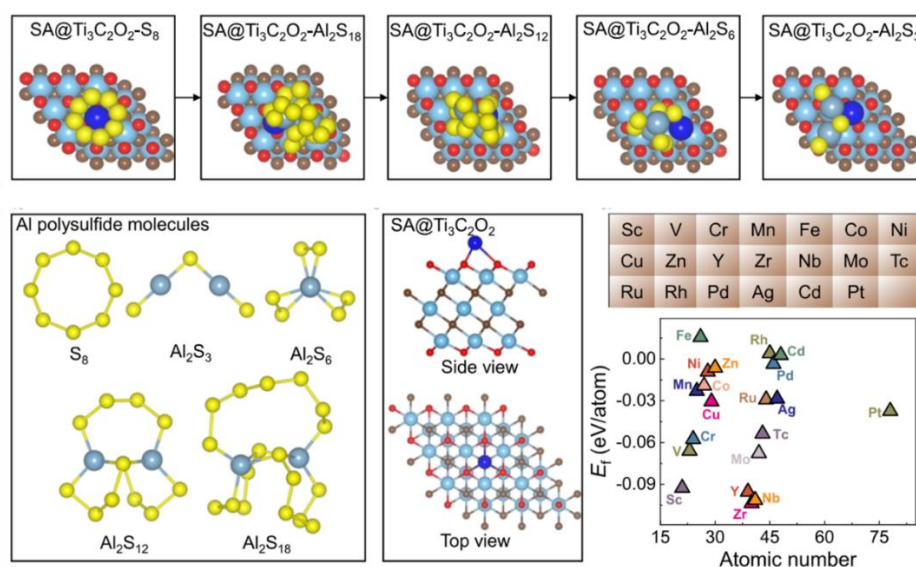


Figure 2.10 Key intermediates and reduction steps of S₈ and Al₂S_n on SA@Ti₃C₂O₂ with. Structural details and SA@Ti₃C₂O₂ (Z. Wang et al., 2022).

2.5 The studies of suppression of shuttle effect for metal-sulfur batteries

The shuttle effect is one of the main challenges in developing metal-sulfur batteries, leading to rapid capacity decay and low cycle life. The mechanism of this phenomenon occurs during the discharge process within the electrolyte. At the cathode, solid sulfur changes into dissolved polysulfide (S_8). The reduction process results in the formation of metal polysulfide species such as Li_2S_n or Na_2S_n . The key intermediates initially start from solid S_8 to large cluster of polysulfides such as Li_2S_8 and Li_2S_6 which are soluble in the electrolyte. However, these high-order species prefer to dissolve into the bulk electrolyte rather than remaining at the cathode. Driven by the concentration gradient, they could diffuse back and react with the metal anode.

This problem reduces the active material and corrodes the anode. Furthermore, the dissolved polysulfides are difficult to change into lower order insoluble sulfides. These issues result in the loss of active sulfur and poor electrochemical performance.

For computational studies, Density Functional Theory (DFT) provides insightful information and details at the atomistic level. To analyze the problem of the shuttle effect, the studies usually focus on the binding energy or adsorption energy of the polysulfide species on the cathode materials. This calculation reveals the reason behind the better performance of materials, such as the superior anchoring effect which prevents the dissolution of polysulfides. For example, the study of Li-S batteries by Wang C et. al. demonstrated that the adsorption strength of Li polysulfides on 2D- $Ti_3C_2O_2$ is stronger than that of with electrolytes including DME and DOL shown in Figure 2.11a. In the case of Al-S batteries, there is a work by Bhauriyal P. et. al that show the comparison between adsorption energy of Al_2S_n ($x=6, 12$, and 18) molecules with graphene, the Cu-BHT monolayer and EMIM⁺AlCl₄ electrolyte shown in Figure 2.11b. While other computational studies normally compare graphene or their pristine model to visualize the better anchoring effect (Ju et al., 2022; Z. Wang et al., 2022; Zheng et al., 2022).

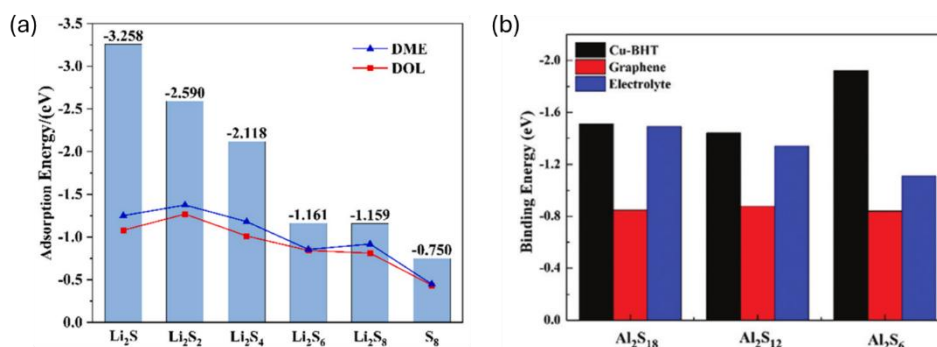


Figure 2.11 (a) The adsorption energy of Li polysulfides on 2D-Ti₃C₂O₂ cathode material for Li-S batteries (Dong et al., 2025). (b) Comparative binding energy of Al₂S_n (x =6, 12, and 18) molecules with graphene, the Cu-BHT monolayer and EMIM⁺AlCl₄ electrolyte (Bhauriyal et al., 2020).

In there case of Al-S batteries, most of computational studies did not

2.6 The studies of sulfur reduction reaction and conversion of small polysulfides for metal-sulfur batteries

In studies of the sulfur reduction reaction (SRR), the conversion of small polysulfides is considered the rate-determining step in metal-sulfur batteries. The mechanism involves the transition from soluble large cluster species to insoluble solid products (such as Li₂S or Na₂S). However, the conversion of small polysulfides (such as Li₂S₂) to the final product is rather sluggish due to the high activation energy barrier and the insulating nature of the solid discharge products. This phenomenon leads to the incomplete utilization of active sulfur (often limiting capacity to 50% of the theoretical value) and the premature termination of the discharge process.

To analyze this problem, computational studies usually focus on the Gibbs free energy profile of the reduction pathway. These calculations reveal the Gibbs free energy landscape of each reaction step. For example, Zhang et al. (D. Zhang et al., 2020) demonstrated that the initial reduction of S₈ is relatively favorable with a low energy barrier, whereas the subsequent conversion of polysulfides into insoluble products represents the kinetic bottleneck with the highest energy barrier, as shown in **Figure 2.12a**. Furthermore, DFT calculations can identify the catalytic effect of host materials. The study demonstrated that the introduction of electrocatalysts could

significantly lower the dissociation energy of Li_2S_2 , thereby accelerating the solid-solid conversion kinetics and improving sulfur utilization.

This method of investigating the SRR does not take the potential into account and is a common approach. However, there are a few computational studies that account for potential by using the oxygen reduction reaction as a reference (Feng et al., 2022; L. Wang et al., 2022). For example, the study by Yang et. al. examined the equilibrium, limiting potential and overpotential from SRR. The results show that there is no overpotential in electronic step of Ga doped SmMn_2O_5 (001) from SRR providing maximum theoretical limiting potential while there is the challenge in Li_2S desorption shown in Figure 2.12b and c. This suggests that the Ga-doped material is a promising candidate compared to other transition metals, as shown in Figure 2.12c.

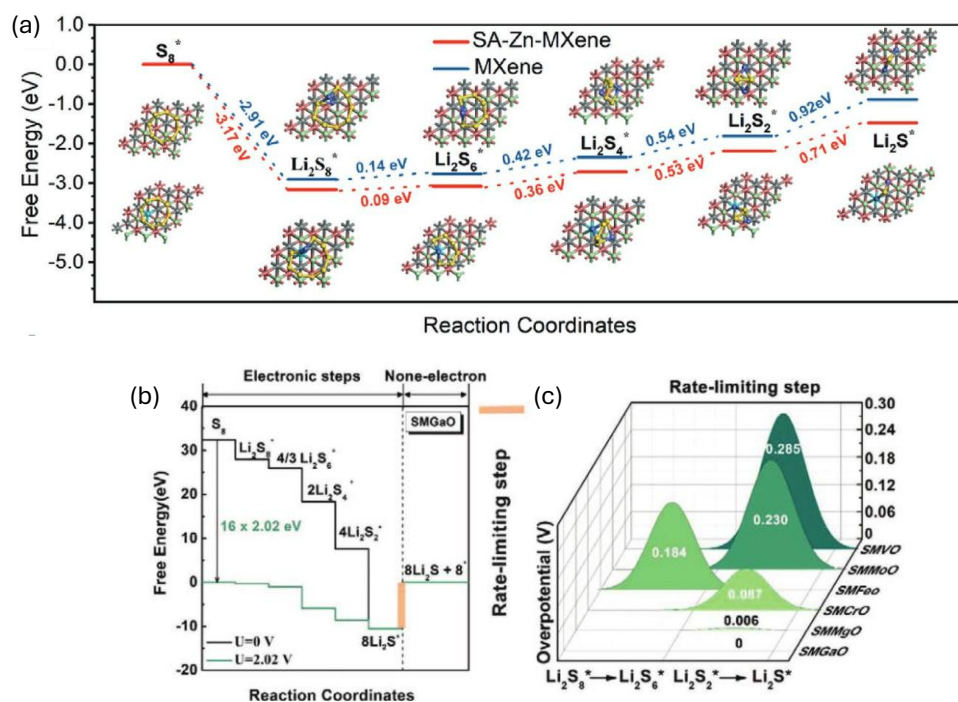


Figure 2.12 (a) The Gibbs free energy profiles of lithium polysulfides on SA-Zn-MXene and its pristine (D. Zhang et al., 2020). (b) Free energy diagram of SRR for Ga-doped SmMn_2O_5 (001) slab at $U = 0$ V and equilibrium potential ($U = 2.02$ V). (c) SRR overpotential and rate-limiting step of SmMnMO ($M = \text{V}, \text{Mo}, \text{Fe}, \text{Cr}, \text{Mg}, \text{Ga}$) system.

In the case of Al-S batteries, most computational studies regarding the SRR have not taken the potential into account (Bhauriyal & Pathak, 2020; Ju et al., 2022; Z. Wang et al., 2022). This is due to the complexity of the SRR mechanism and the limited

number of studies on Al-S batteries. Regarding the decomposition of small polysulfides (Al_2S_3), We observe that they attempt to dissociate the Al atom, similar to the approach taken by the community for breaking the Li atom from Li_2S , as shown in Figure 2.13a and b. The results indicate that this reaction is thermodynamically unfavorable with high energy barriers in both Li-S and Al-S batteries (Figure 2.13c and d).

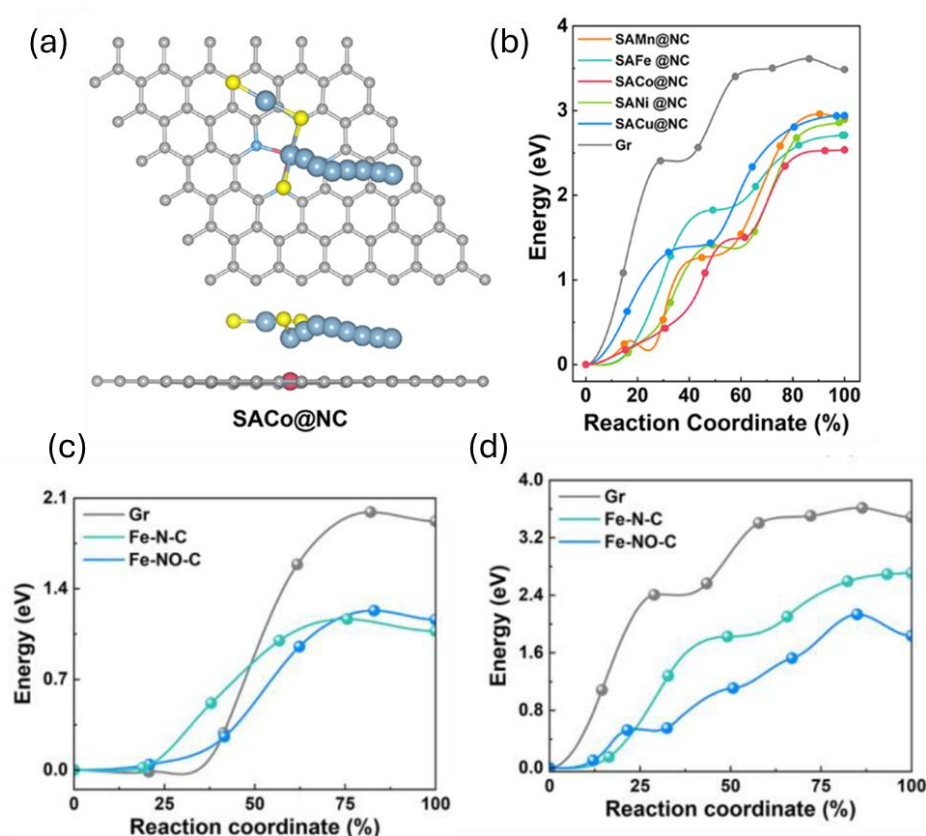


Figure 2.13 (a) The simulated decomposition pathway of Al_2S_3 on SACo@NC . (b) The calculated energy curves for the decomposition of Al_2S_3 on Gr and SATM@NC (Ju et al., 2022). (c) Li_2S and (d) Al_2S_3 molecules on Gr, Fe-N-C and Fe-NO-C (Ju et al., 2023).

2.7 References

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