

REVIEW



Cite this: *Mater. Chem. Front.*,
2022, 6, 280

Received 15th September 2021,
Accepted 3rd December 2021

DOI: 10.1039/d1qm01267c

rsc.li/frontiers-materials

Cation-intercalation and conversion-type cathode materials for rechargeable aluminum batteries

Tianming Liu,^a Guocheng Lv,^{*b} Meng Liu,^b Changchun Zhao,^{ID *a} Libing Liao,^{ID b} Hao Liu,^{ID a} Jiayan Shi,^c Jian Zhang^d and Juchen Guo^{ID *cd}

The current research on cation-intercalation and conversion-type cathode materials for rechargeable aluminum batteries (RABs) is discussed in this critical review. The experimental evidence for Al^{3+} intercalation in transition metal oxides, chalcogenides, MXene, and Prussian blue analogues in both chloroaluminate ionic liquids and aqueous electrolytes is analyzed to identify the true reaction mechanisms. Chevrel phase molybdenum sulfide (Mo_6S_8) is the only proven intercalation material for RABs with unambiguous evidence, different understandings of the Al^{3+} intercalation mechanism in Mo_6S_8 are discussed. For conversion-type cathode materials, the discussion is focused on the conversion mechanism of metal chalcogenides, and the unique reversible oxidation mechanism of sulfur and selenium enabled by the chloroaluminate ionic liquid electrolytes. The reaction mechanisms of organic cathode materials are also discussed.

1. Introduction

Rechargeable aluminum (Al) batteries are considered as an alternative electrochemical energy storage technology for large-scale applications.¹ Despite the low battery voltage due to the high reduction potential of Al (-1.7 V vs. SHE),² the high theoretical energy (8046 mA h cm^{-3} and 2981 mA h g^{-1}),³ low cost, and high abundance of Al make rechargeable Al batteries (RABs) worth investigating.^{4,5} The majority of the research activities on RABs has been focused on cathode materials, which can be categorized into three groups based on different reaction mechanisms: AlCl_4^- intercalation materials, Al^{3+} intercalation materials, and conversion-type materials. AlCl_4^- is the Lewis neutral anion in the benchmark chloroaluminate ionic liquid electrolytes for RABs. It can reversibly intercalate into graphitic carbon materials with excellent rate capability and cycle stability.⁶ To date, the AlCl_4^- intercalation cathode materials are overwhelmingly carbon materials including graphite, few-layer graphene, and reduced graphene oxide. The Al^{3+} cation-intercalation and conversion-type cathode materials include a

wide variety of materials, of which most are inspired by their application as electrode materials in lithium-ion (Li-ion) batteries. Although the ionic size of Al^{3+} (0.39 Å) is smaller than that of Li^+ (0.59 Å), one can expect much more difficult Al^{3+} intercalation due to the large charge density of trivalent Al^{3+} cations. The potential and extent of the conversion reactions in RABs can also be very different from those in Li-ion batteries due to the higher redox potential of Al^{3+}/Al . Furthermore, for either Al^{3+} intercalation or conversion, the active species in the electrolyte are complex chloroaluminate anions, which have distinctly different reaction mechanisms from monovalent cations such as Li^+ . In recent years, numerous investigations have been devoted to Al^{3+} intercalation or conversion-type cathode materials for performance improvement and mechanism analysis. However, certain discrepancies still exist in the current literature and the mechanisms were not always rigorously validated. This review provides a comprehensive overview of the reported intercalation and conversion-type RAB cathode materials with emphasis on the clarification of reaction mechanisms. It is worth noting that the intercalation-type and conversion-type materials in this review are categorized based on the claims in the publications, not necessarily reflecting their true mechanisms as discussed below.

2. Al^{3+} intercalation cathode materials

The intercalation cathode materials can host Al^{3+} cations in their crystal lattice *via* reversible electrochemical intercalation, and the host lattice must sustain a stable crystal structure.

^a School of Science, China University of Geosciences, Beijing, 100083, China.
E-mail: zhaocc@cugb.edu.cn

^b Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China.
E-mail: guochenglv@cugb.edu.cn

^c Department of Chemical and Environmental Engineering, University of California, Riverside, California, 92521, USA. E-mail: jguo@engr.ucr.edu

^d Materials Science and Engineering Program, University of California, Riverside, California, 92521, USA

A unique challenge for Al^{3+} intercalation is the strong coulombic interaction between the trivalent Al^{3+} cation and the anionic framework of the host structure. Theoretical calculations indicated that it would be extremely difficult if not impossible for Al^{3+} to intercalate in transition metal oxides or sulfides.⁷ Nevertheless, transition metal oxides,^{8–13} chalcogenides,^{14–18} and their carbon-based composites^{19–24} have been reported as Al^{3+} intercalation cathode materials. It must be pointed out that Al^{3+} intercalation in the current chloroaluminate ionic liquid electrolytes involves chloroaluminate anions, since there are no simple Al^{3+} cations existing in these electrolytes.

2.1 Transition metal oxides

The reported intercalation-type transition metal oxide cathodes for RABs include vanadium dioxide (VO_2), vanadium pentoxide (V_2O_5), lithium vanadate (Li_3VO_4), and tin(IV) oxide (SnO_2). Wang *et al.* studied VO_2 with a metastable monoclinic structure as the host for Al^{3+} intercalation–extraction based on first-principles calculations.⁸ The authors simulated that Al occupied the interval of the V–O tunnel in the VO_6 octahedron, and increased the number of x from 0 to 4 in the $[\text{Al}_x(\text{V}_4\text{O}_8)]$ structure. The crystal structure remained stable when the number of intercalated Al was from 0 to 2. However, when 3 or 4 Al^{3+} were inserted, the excessively strong ionic bond would cause

serious structural distortion and chemical bond cleavage. A capacity of 165 mA h g^{-1} in the first discharge was experimentally demonstrated, and it is equivalent to a formula of $\text{Al}_{0.17}\text{VO}_2$. The capacity retention was 116 mA h g^{-1} after 100 cycles between 0.01 and 0.9 V *versus* Al under 50 mA g^{-1} . Despite the demonstrated performance, unambiguous experimental evidence for the intercalation mechanism was lacking in this study. The X-ray photoelectron spectroscopy (XPS) results indicated the reduction of V^{4+} to V^{3+} after discharge. However, the change in valence state of V cannot validate the intercalation mechanism.

Jayaprakash *et al.* first reported V_2O_5 nanowire as an Al^{3+} intercalation cathode for RABs with promising performance.²⁵ However, a later study by Reed and Menke suggested that the battery-like behavior of the Al– V_2O_5 cells could be the result of the electrochemical corrosion of the stainless steel current collector (iron and chromium) in the chloroaluminate ionic liquid electrolyte.²⁶ Nevertheless, a number of studies of V_2O_5 as the RAB cathode material have been reported since.^{9,10,12,25–28} Gu *et al.* attempted to elucidate the intercalation mechanism and the phase transformation induced by Al^{3+} in V_2O_5 .¹⁰ The galvanostatic discharge–charge curves in their study show a stable discharge slope at 0.6 V and a charge slope around 1.0 V *versus* Al as displayed in Fig. 1a. The XPS indicated that V^{5+} was reduced to V^{4+} during discharge. V^{3+} was detected during

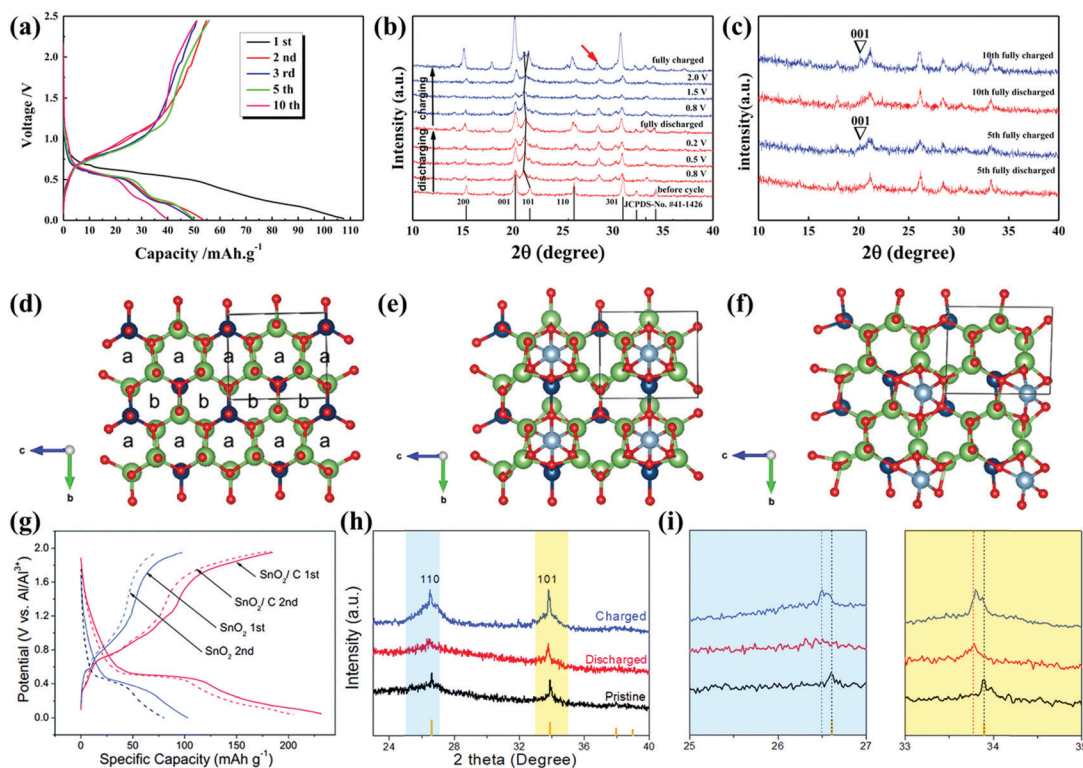


Fig. 1 (a) Galvanostatic charge–discharge curves of V_2O_5 nanowires *versus* Al under 10 mA g^{-1} ; (b) *ex situ* XRD of V_2O_5 nanowires during the first cycle at various voltages showing the shift of the (101) peak of orthorhombic V_2O_5 ; (c) *ex situ* XRD of V_2O_5 nanowires after the 5th cycle and 10th cycle showing the change in the (001) peak attributed to Al intercalation. Reproduced with permission from ref. 10. Copyright (2017) Elsevier. (d) The optimized crystal structure of Li_3VO_4 projected along the a -axis illustrating the a and b sites: Li, green; V, dark blue; O, red; Al, light blue; the structure model of inserting Al into the (e) a site and (f) b site. Reproduced with permission from ref. 11. Copyright (2017) American Chemical Society. (g) The 1st and 2nd discharge–charge potential profiles of SnO_2 and SnO_2/C at 500 mA g^{-1} ; (h) *ex situ* XRD of SnO_2/C at different stages; (i) enlarged XRD pattern from (h) showing the shift of the (110) and (101) planes. Reproduced with permission from ref. 13. Copyright (2019) The Royal Society of Chemistry.

the charging process, and it was attributed to the disproportionation. The authors also utilized *ex situ* X-ray diffraction (XRD) to characterize V_2O_5 at different stages during discharging and charging (Fig. 1b and c). The XRD results showed a shift of the (101) peak and changes in the (001) peak of the orthorhombic V_2O_5 , which was interpreted as the reversible structural change induced by the Al^{3+} intercalation. However, discrepancies were presented in the study: the galvanostatic intermittent titration technique (GITT) was used to measure the near-equilibrium discharge and charge potentials. The results showed that the equilibrium potentials of discharge (intercalation) and charge (extraction) changed drastically during cycling. This observation suggests that the structure of V_2O_5 was significantly altered by cycling, which is inconsistent with the intercalation mechanism. The transmission electron microscopic (TEM) characterization revealed an amorphous layer on V_2O_5 after discharge, indicating an irreversible structural change in V_2O_5 . Finally, the use of nickel (Ni) foam as the current collector is questionable. Shi *et al.* demonstrated that Ni is not stable in the chloroaluminate ionic liquid electrolyte, and the discharge-charge behavior in the Al-Ni cell can be obtained due to the corrosion reaction to form active nickel chloride ($NiCl_2$).²⁹ The complexity of the V_2O_5 cathode was further revealed by Wen *et al.*, who studied the chemical compatibility between V_2O_5 and the chloroaluminate ionic liquids.³⁰ Their results concluded that V_2O_5 chemically reacts to both Lewis neutral $AlCl_4^-$ and Lewis acidic $Al_2Cl_7^-$ anions to produce V-containing electrochemically active species in the electrolyte. Therefore, the feasibility and true reaction mechanism of V_2O_5 as the RAB cathode requires further clarification.

A $Li_3VO_4@C$ composite was demonstrated as a cathode material for RABs with an initial capacity of 137 mA h g^{-1} at a current density of 20 mA g^{-1} .¹¹ *Ex situ* XRD, XPS, ^{27}Al nuclear magnetic resonance (NMR), and first-principles calculations were applied to study the Al^{3+} intercalation mechanism in Li_3VO_4 . The discharge-charge curves and cyclic voltammogram (CV) clearly indicated redox reactions despite lower coulombic efficiency (CE) in the first cycle. The XPS data indicated that the oxidation state of V was reversibly changed between V^{5+} and V^{4+} during discharge and charge. Moreover, the XRD analysis of Li_3VO_4 at various stages during the first discharge-charge cycle revealed a reversible structural change that was attributed to Al intercalation and extraction. Two possible sites in the Li_3VO_4 crystal structure that can host Al^{3+} cations were proposed (a-site and b-site shown in Fig. 1d). First-principles calculations indicated that the a-site is more stable for intercalated Al^{3+} cations (Fig. 1e and f), and the crystal structure change from XRD was consistent with the intercalation of Al into the a-site. However, long-term cycling results from XRD clearly indicated deterioration of the crystallinity, resulting in a decreased capacity. Although the results and interpretations of this study are self-consistent, the change in the XRD pattern of Li_3VO_4 during the first cycle, which was the main evidence of Al^{3+} intercalation, was too subtle to be fully convincing. Interestingly, the ^{27}Al NMR spectra indicated that the molar ratio of $AlCl_4^-$ to $Al_2Cl_7^-$ in the electrolyte changed during discharge and charge,

which is inconsistent with the conventional assumption that the same amount of chloroaluminate anions would be consumed and generated at the opposite electrodes. A plausible explanation was not provided in this study, however, based on the understanding of the reactions between chloroaluminate anions and V_2O_5 ,³⁰ it is possible that the vanadate anion VO_4^{3-} can chemically react with $AlCl_4^-$ and/or $Al_2Cl_7^-$.

Lu *et al.* reported SnO_2 as a cathode material for RABs.¹³ Relatively high specific capacity was demonstrated for both SnO_2 and its carbon-supported composite as shown in Fig. 1g. The CV curves of SnO_2/C show a reduction peak at 0.5 V and an oxidation peak at 0.8 V *versus* Al, corresponding to the plateau of the galvanostatic discharge and charge curves. XPS spectra show that Sn^{4+} was partially converted to Sn^{2+} during discharge, and then oxidized to Sn^{4+} after charging. *Ex situ* XRD patterns show that the diffraction intensity of SnO_2 decreased after discharging and recovered after charging, and the (110) and (001) crystal planes shifted to the left about 0.1° after the charge/discharge process, which is attributed to the increase in the interlayer space (Fig. 1h and i). Unfortunately, the crystallographic evidence of Al^{3+} intercalation was not fully convincing due to the low resolution of the XRD patterns.

Transition metal oxides such as titanium dioxide (TiO_2),^{31–33} manganese oxides,^{34,35} vanadium oxides,^{36,37} molybdenum trioxide (MoO_3),^{38,39} and molybdenum-tantalum oxide⁴⁰ were also studied as the Al^{3+} intercalation cathodes in RABs based on aqueous electrolytes, which are either $AlCl_3$, Al trifluoromethanesulfonate ($Al(OTf)_3$), Al sulfate ($Al_2(SO_4)_3$), or Al nitrate ($Al(NO_3)_3$) solutions in water. Although battery-like discharge and charge performance were always demonstrated in these studies, unambiguous evidence of Al intercalation in these transition metal oxides was generally lacking. It is also worth noting that all the aqueous electrolytes used in these studies are very acidic due to the hydronium H_3O^+ generated from the hydrolysis of the hydrated Al^{3+} cations. Transition metal oxides are known for reversible electrochemical intercalation of protons as demonstrated in the studies of V_2O_5 ,⁴¹ TiO_2 ,⁴² and MoO_3 ,⁴³ in acidic electrolytes. Therefore, the true mechanisms of transition metal oxide cathodes in aqueous RABs need further scrutiny and clarification.

2.2 Spinel or layered transition metal chalcogenides

Compared to transition metal oxides, the analogous chalcogenides generally have a lower specific capacity and lower potential *versus* Al. However, they could be better host structures for Al^{3+} intercalation compared to oxides due to their more polarizable anion framework and larger lattice sites. Therefore, spinel and two-dimensional (2D) layered metal chalcogenides are natural selections due to their proven applications as hosts for monovalent and divalent cations.^{44–52}

The general formula of cubic thiospinel is AB_2X_4 (A, B = divalent and trivalent metals, respectively, and X = chalcogen), and the arrangement of X is cubic close packing. The divalent cation is filled in one-eighth of the tetrahedral void, and the trivalent cation is filled in one-half of the octahedral void. Li *et al.* studied porous Co_3S_4 microspheres from solvothermal

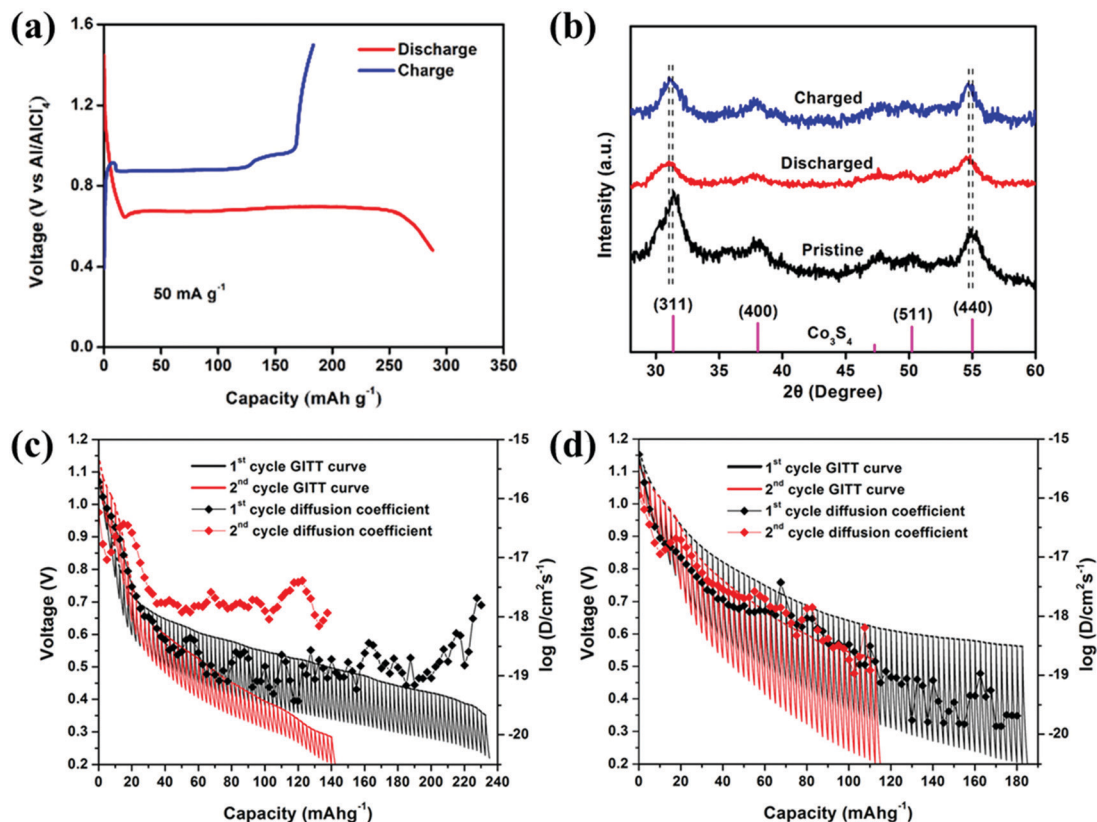


Fig. 2 (a) The first discharge–charge potential curve of Co_3S_4 microspheres versus Al at 50 mA g^{-1} ; (b) *ex situ* XRD patterns of Co_3S_4 at different charging and discharging states. Reproduced with permission from ref. 17. Copyright (2018) Elsevier. The GITT profiles of (c) TiS_2 and (d) $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ at 50°C with a calculated Al^{3+} diffusion coefficient as the function of capacity (*i.e.*, extent of Al intercalation). Reproduced with permission from ref. 15. Copyright (2017) American Chemical Society.

synthesis as the cathode material for RABs.¹⁷ Co atoms occupy both the tetrahedral and octahedral positions in the Co_3S_4 spinel structure. The evaluation of the electrochemical properties of Co_3S_4 was performed with polytetrafluoroethylene (PTFE) cells and glassy carbon current collectors to avoid the potential side reactions due to the chloroaluminate ionic liquid electrolyte. The first cycling curve displayed very distinct discharge and charge potential plateaus at 0.68 V and 0.88 V versus Al (Fig. 2a), respectively. Flat potential plateaus in the discharge and charge curves typically indicate phase transformation of the host crystal structure, thus a strong implication of the intercalation mechanism. The CE of the first cycle is only 64%, which was hypothesized as that part of the intercalated Al^{3+} was trapped in the crystal structure due to the strong interaction between Al^{3+} and the sulfide framework. Furthermore, the XRD pattern showed that the peak intensity of the (311) and (400) planes was reduced and shifted by 0.24° to the left after the first discharge (Fig. 2b), which might be attributed to the Al^{3+} intercalation. However, due to the low resolution of the XRD patterns before and after discharge, no crystal structural information could be obtained. The distinct plateaus in the discharge–charge curve disappeared after only 5 cycles, indicating that the Co_3S_4 crystal lattice could not sustain a repeated discharge and charge process, thus the phase transformation induced by Al^{3+} intercalation was irreversible. It is interesting that the *in situ* Raman spectra of the electrolyte indicated the

consumption of the Al_2Cl_7^- anion and generation of the AlCl_4^- anion after discharge; and *vice versa* after the charging process. This observation is consistent with the finding in the study by Jiang *et al.* on Li_3VO_4 ,¹¹ again indicating that the chloroaluminate ionic liquid may be actively involved in the RAB reactions.

Geng *et al.* reported two types of titanium sulfides (thiospinel $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ and layered TiS_2) as Al^{3+} intercalation cathode materials for RABs.¹⁵ The spinel $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ has an $Fd\bar{3}m$ space group. Assuming the Cu^{2+} position remains unchanged after discharge, the Rietveld refinement of the XRD patterns suggested that 9% of Al^{3+} occupied the same position as Cu^{2+} , resulting in a composition of $\text{Al}_{0.09}\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$. The Rietveld refinement of the XRD pattern of TiS_2 after Al intercalation indicated that the intercalated Al^{3+} cations occupied 11% of the octahedral intercalation position between the TiS_2 layers ($\text{Al}_{0.11}\text{TiS}_2$). The unit cell volume of the Al-intercalated TiS_2 is reduced, which was attributed to the strong attraction to the TiS_2 layers from the highly charged Al^{3+} cations. The analysis of the GITT discharge at 50°C showed the diffusion coefficients of Al are 10^{-18} to $10^{-20} \text{ cm}^2 \text{ s}^{-1}$ in $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ and 10^{-18} to $10^{-19} \text{ cm}^2 \text{ s}^{-1}$ in TiS_2 (Fig. 2c and d). The low diffusion coefficient is clearly the main obstacle to the Al intercalation in these two sulfides.

Overall, the layered TiS_2 cathode demonstrated a higher reversible capacity than the cubic spinel $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$, indicating that the 2D layered structure may be preferable for Al^{3+}

intercalation. To date, a number of other 2D transition metal dichalcogenides including vanadium disulfide (VS_2),²⁰ molybdenum disulfide (MoS_2)²¹ and molybdenum diselenide (MoSe_2)²³ have been reported as cathodes of RABs. Wu *et al.* reported a nanosheet VS_2 -graphene composite that exhibited a reduction peak at 0.45 V and an oxidation peak at 1.6 V *versus* Al in CV as displayed in Fig. 3a. The discharge and charge curves of the VS_2 cathode are slope-like, and the incorporation of graphene improved the capacity and capacity retention (Fig. 3b and c). *In situ* XRD revealed that the intensity of the (001) and (011) peaks of VS_2 were gradually weakened during discharge until diminished at 0.3 V. After charging to 1.7 V, the diffraction peaks re-appeared. *Ex situ* XRD indicated that the intensity of the VS_2 characteristic peak (001) became lower during the discharge, and slightly shifted to the left, which suggested the layer spacing of (001) was increased. However, the *in situ* and *ex situ* XRD analysis is not fully consistent, and the crystallographic data were not distinct enough to draw conclusions on the crystal structure change. Therefore, it is not

clear if the reaction mechanism between $\text{Al}^{3+} and VS_2 is intercalation.$

Yang *et al.* reported MoS_2 as the cathode material for RABs.²¹ The composite composed of MoS_2 and carbon nanofibers (CNFs) showed two pairs of redox peaks (0.55 and 0.8 V of reduction and 1 and 1.15 V of oxidation *versus* Al) in the CV curve at 0.5 mV s^{-1} , which corresponded well to the plateaus in the discharge-charge curve. The MoS_2 /CNFs composite exhibited a good rate performance, and maintained a specific capacity of 112 mA h g^{-1} after 50 cycles at 250 mA g^{-1} (Fig. 3d-f). It is worth noting that the distinct plateaus in the discharge-charge curve are consistent with the intercalation-extraction mechanism. The XPS Mo 3d spectra indicated reversible reduction and oxidation of Mo during discharge and charge. The *ex situ* XRD also showed that the (002) plane disappeared after full discharge and reappeared when charged to 1.8 V, which was interpreted as evidence of the intercalation mechanism. However, the amount and position of intercalated Al could not be determined due to the low crystallinity of the nanosized MoS_2 .

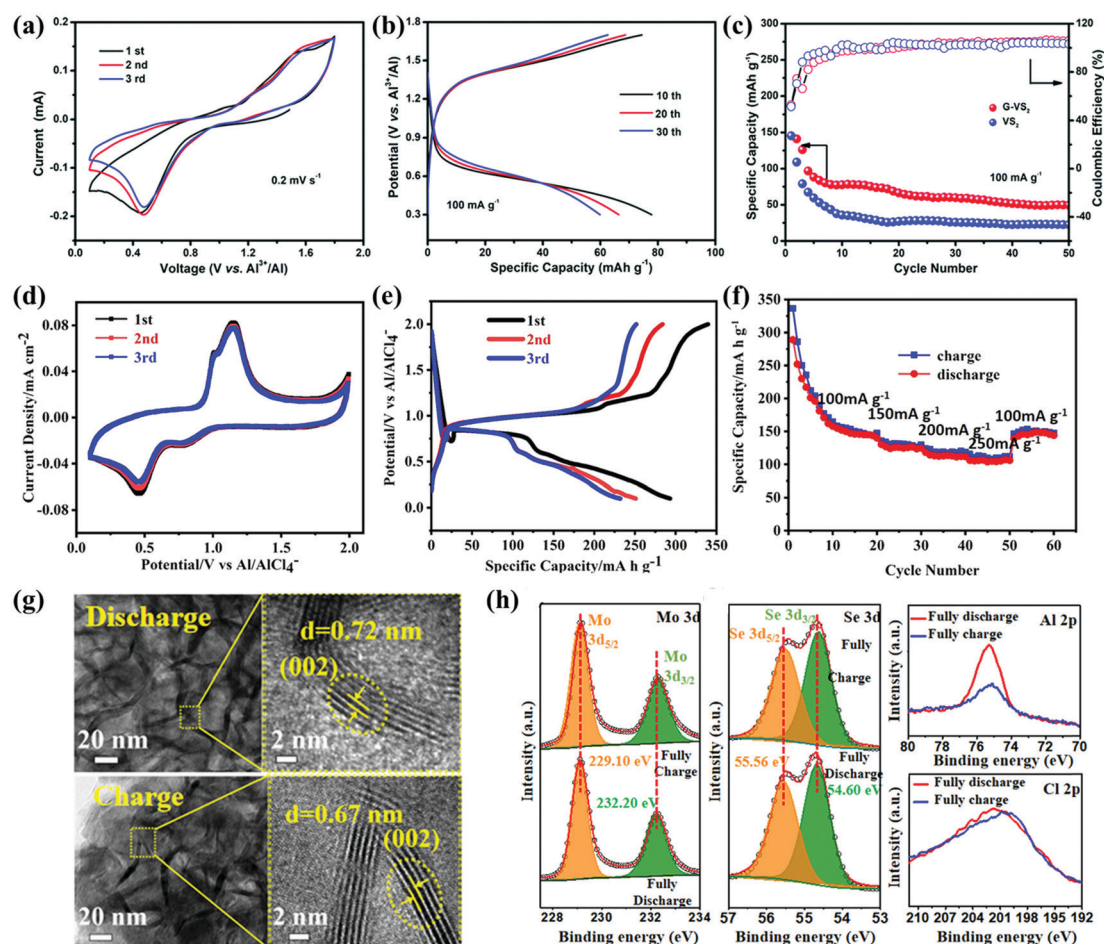


Fig. 3 (a) The CV curves of the VS_2 -graphene composite at a scan rate of 0.2 mV s^{-1} *versus* Al; (b) the 10th, 20th, and 30th discharge-charge curves of the VS_2 -graphene composite at a current density of 100 mA g^{-1} ; (c) comparison of the cycle stability and CE from VS_2 and VS_2 -graphene at 100 mA g^{-1} . Reproduced with permission from ref. 20. Copyright (2018) The Owner Societies. (d) The CV curves of MoS_2 /CNFs at a scan rate of 0.5 mV s^{-1} *versus* Al; (e) the discharge-charge curves of MoS_2 /CNFs at a current density of 100 mA g^{-1} ; (f) rate performance of MoS_2 /CNFs. Reproduced with permission from ref. 21. Copyright (2019) American Chemical Society. (g) HRTEM images of MoSe_2 after discharge and charge showing the reversible change of the (002) plane spacing; (h) the Mo 3d, Se 3d, Al 2p, and Cl 2p XPS spectra of the fully charged and discharged MoSe_2 . Reproduced with permission from ref. 23. Copyright (2021) American Chemical Society.

MoSe₂ was also investigated as the cathode for RABs by An and coworkers.²³ High-resolution transmission electron microscopy (HRTEM) analysis indicated that the *d*-spacing of MoSe₂ was increased from 6.7 Å to 7.2 Å after full discharge, and it returned to the original state after charging (Fig. 3g). However, the XPS spectra indicated that the oxidation state of Mo was not changed during the discharge and charge (Fig. 3h), which was clearly contradictory to the conventional understanding of the intercalation mechanism. One possible explanation is that selenium (Se) is the active element in MoSe₂ following a conversion mechanism. Interestingly, the Se 3d XPS spectra were not changed either after discharging and charging. This observation suggests that not only was Se active but also soluble species were produced from the electrochemical reaction of Se. The electrochemical activity of Se in metal selenides in chloroaluminate ionic liquids was demonstrated by a number of studies, which will be discussed in the section on conversion-type cathode materials.

2.3 Chevrel phase molybdenum sulfide (Mo₆S₈)

In 2015, Geng *et al.* first reported Chevrel phase Mo₆S₈ as an Al³⁺ intercalation cathode material for RABs. The Chevrel phase has a unique crystal structure composed of octahedral Mo atoms in the cubic sulfur anion unit cell. There are two positions in the

Mo₆S₈ lattice that can allow intercalation of monovalent and divalent cations.^{14,53–58} The first is at the center of the rhombohedron with eight Mo₆S₈ vertices (denoted as Al₁), and the second is a smaller site at the face center of the rhombohedron (denoted as Al₂). The CV scan demonstrated two pairs of cathodic/anodic peaks indicating that the two-step electrochemical reaction occurred in the Mo₆S₈ electrode. Consistent with the CV scan, the constant current cycling curves showed two distinct potential plateaus during discharge and two plateaus during charge (Fig. 4a and b), which typically implies an intercalation mechanism. The most unambiguous evidence of Al intercalation came from the XRD of Mo₆S₈ before and after discharge as displayed in Fig. 4c. The XRD pattern after discharge was distinctly different from the pristine Mo₆S₈, and the Rietveld refinement revealed that Al indeed intercalated into the two lattice sites previously mentioned. Following this original study, the same group performed a more detailed study on the phase transformation of Mo₆S₈ induced by Al intercalation. *Ex situ* XRD was performed at a different stage of Al³⁺ intercalation in Mo₆S₈, and the obtained XRD patterns were analyzed with Rietveld refinement combined with electrochemical and TEM characterizations.¹⁶ The Al³⁺ intercalation initially prefers the larger site of Al₁ over the smaller site of Al₂. However, the

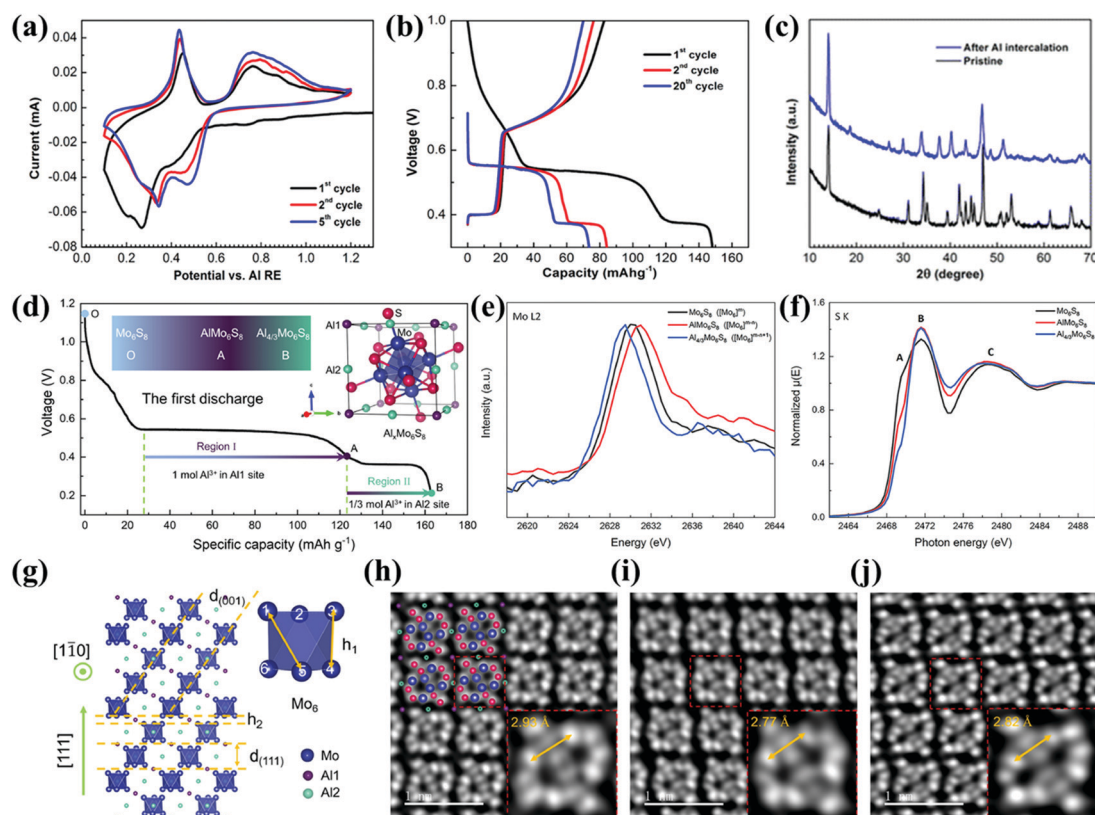


Fig. 4 (a) The CV curves of Mo₆S₈ at 0.1 mV s⁻¹ and 50 °C; (b) the representative discharge-charge curves of Mo₆S₈ at a current density of 12 mA g⁻¹ at 50 °C; (c) XRD patterns of the Mo₆S₈ cathode before and after full discharge. Reproduced with permission from ref. 14. Copyright (2015) American Chemical Society. (d) The first discharge profile of Mo₆S₈ at 10 mA g⁻¹ and 55 °C; the insets illustrate the crystal structure of Al_xMo₆S₈ and the stages of Al intercalation; (e) Mo L₂-edge of EELS spectra; (f) S K-edge of XAS spectra; (g) the crystal structure of Mo₆S₈ along (110) defining the Mo₁ to Mo₅ distance; (h-j) the STEM images of Mo₆S₈, AlMo₆S₈, and Al_{4/3}Mo₆S₈ along (001) showing the bond length of Mo₁-Mo₅ varies with Al intercalation, Mo: blue, S: red, Al₁: purple, Al₂: green. Reproduced with permission from ref. 18. Copyright (2021) Elsevier.

preference quickly diminishes because the strong repulsion between Al^{3+} cations forces the intercalating Al^{3+} cation into the Al_2 sites, resulting in equal occupation in these two sites at the end of the first discharge plateau. During the second discharge plateau, Al^{3+} cations exclusively intercalate into the larger Al_1 sites due to the strong repulsion between the cations.

Lee *et al.* proposed a different Al^{3+} intercalation mechanism based on *in situ* XRD characterization:⁵⁹ Al^{3+} cations intercalate into Mo_6S_8 following a two-step phase change reaction the same as the known Mg^{2+} and Li^+ intercalation in Mo_6S_8 .^{60–67} Al^{3+} cations first exclusively intercalate in the Al_1 site. Once the Al_1 sites are fully occupied resulting in a formula of AlMo_6S_8 at the end of first discharge plateau, the Al^{3+} cations start to intercalate into the Al_2 sites leading to the fully intercalated formula of $\text{Al}_{4/3}\text{Mo}_6\text{S}_8$. Tong *et al.* further revealed that the S anions in Mo_6S_8 also undergo a transient redox reaction during Al intercalation and extraction.¹⁸ The two plateaus of the first discharge curve of Mo_6S_8 at 10 mA g^{-1} and 55 °C contributed 95 mA h g^{-1} and 35 mA h g^{-1} capacity respectively, corresponding to 1 mole and 1/3 mole Al^{3+} intercalation in $\text{Al}_x\text{Mo}_6\text{S}_8$ (Fig. 4d). Electron energy loss spectroscopy (EELS) (Fig. 4e) and X-ray absorption spectroscopy (XAS) (Fig. 4f) were used to analyze the change in the valence state of Mo and S during the Al^{3+} intercalation, respectively. In the pristine Mo_6S_8 , the S^{n-} anion is not in the fully reduced state ($0 < n < 2$). During the first stage of Al intercalation (Mo_6S_8 to AlMo_6S_8), S^{n-} is fully reduced to S^{2-} and simultaneously Mo is oxidized. During the second stage of Al intercalation (AlMo_6S_8 to $\text{Al}_{4/3}\text{Mo}_6\text{S}_8$), Mo is subsequently reduced meanwhile the valence state of S^{2-} remains unchanged. The synergistic redox of Mo and S is correlated to the change of the crystal structure. The XRD analysis indicates that the interplanar space of (111) decreases after the first Al intercalation (AlMo_6S_8), and then it increases after further 1/3 Al intercalation ($\text{Al}_{4/3}\text{Mo}_6\text{S}_8$). The change of the interplanar spacing of (111) can be quantified by the Mo–Mo distance (Mo_1 to Mo_5) in the Mo octahedron as defined in Fig. 4g. The Rietveld refinement of XRD revealed the Mo_1 – Mo_5 bond length in $\text{Al}_1\text{Mo}_6\text{S}_8$ shrinks from the original 2.842 Å to 2.675 Å. When the rest of Al (1/3) was inserted, the bond length increased to 2.709 Å. The change of the Mo_1 – Mo_5 bond length was also confirmed by the measurement with scanning transmission electron microscopy (STEM). As displayed in Fig. 4h–j, the Mo_1 – Mo_5 length in the pristine Mo_6S_8 is 2.93 Å, which decreases to 2.77 Å after the first Al intercalation, and then increases to 2.82 Å after further 1/3 Al intercalation.

In addition to the spectroscopic and microscopic techniques described above, solid-state ^{27}Al NMR was also used by Jadhav *et al.* to analyze the Al^{3+} intercalation in Mo_6S_8 .⁶⁸ The quantitative ^{27}Al NMR spectra of Mo_6S_8 at different discharge and charge stages indicate simultaneous intercalation of Al^{3+} into the Al_1 and Al_2 sites. This conclusion is consistent with the finding from Geng *et al.* from their *ex situ* XRD study. The solid-state ^{27}Al NMR also revealed the reversible formation of an amorphous layer on the surface of Mo_6S_8 , which can be related to the desolvation process of chloroaluminate anions. This is a significant finding since the desolvation (breaking the Al–Cl bonds) prior to Al^{3+} intercalation has not been understood in

any intercalation-type cathode materials for RABs. It is clear from the studies above that the site occupation dynamics of Al^{3+} intercalation in Mo_6S_8 is still not fully understood to date.

2.4 MXene

MXene is a new group of 2D carbide or nitride materials derived from the mother MAX phase ($\text{M}_{n+1}\text{AX}_n$ where $n = 1$ to 4, M represents early transition metals, A is group 13 or 14 elements, and X is C or N). Typically acidic etching is used to remove the A elements from the MAX phase to obtain MXene with a general formula of $\text{M}_{n+1}\text{X}_n\text{T}_x$, where T represents the surface functional groups such as oxide, fluoride, chloride, and hydroxide resulting from the etching process.^{69,70} MXene materials recently attracted tremendous research efforts in applications such as catalysis and electrochemical energy storage.^{71,72} Beidaghi and coworkers reported V_2CT_x MXene as an Al-intercalation cathode for RABs.¹⁹ The V_2CT_x MXene is a layered vanadium carbide with many different functional groups on the surface, synthesized by etching Al from the V_2AlC MAX phase. At a current density of 10 mA g^{-1} within a voltage range of 0.1–1.8 V, the capacity of the 1st discharge is 178 mA h g^{-1} . *Ex situ* XRD showed weakening of the (0002) peak intensity of V_2CT_x during discharge, and the (0002) peak also downshifted from 9.21° to 9.11°, which corresponded to 0.1 Å increase in the d-spacing. Moreover, HRTEM images indicated that the interlayer spacing of V_2CT_x is increased by 0.2 Å after discharge. The XPS spectra show a reversible change of the vanadium oxidation state between V^{4+} and V^{3+} . Clearly these active V sites are on the surface of V_2CT_x enabled by the functional groups. The V_2CT_x MXene layers were further exfoliated using tetrabutylammonium hydroxide to increase the interlayer spacing by 5.73 Å. The exfoliated V_2CT_x has a high specific capacity of 392 mA h g^{-1} in the first cycle at a current density of 100 mA g^{-1} , which should be attributed to the enriched active surface sites containing V with a high oxidation state. In principle, MXene materials should not be categorized as Al^{3+} intercalation cathode materials since their electrochemical activity is provided by the surface functional groups resulting from the etching process.

2.5 Prussian blue analogues

Prussian blue analogues (PBAs) are three-dimensional open framework structures with large interstitial sites,^{73–75} which are capable of accommodating the intercalation of guest ions such as Li^+ , Na^+ , K^+ , Mg^{2+} , Zn^{2+} , and Al^{3+} .^{76–83} PBAs were mainly studied as Al^{3+} intercalation type electrodes in RABs based on aqueous electrolytes similar to the ones used in the studies of transition metal oxide cathodes (AlCl_3 , $\text{Al}(\text{OTf})_3$, $\text{Al}_2(\text{SO}_4)_3$, or $\text{Al}(\text{NO}_3)_3$ in water). Reversible discharge and charge behaviors were demonstrated, and the redox of the transition metal centers during discharge and charge was confirmed in these studies. However, evidence of Al intercalation was lacking. Similar to transition metal oxide cathodes, PBA compounds are also known for highly reversible proton intercalation in acidic electrolytes.⁸⁴ Furthermore, research shows that the same PBA compound had drastically different behavior toward Al intercalation in aqueous electrolyte *versus* organic electrolyte:

Liu *et al.* reported that copper hexacyanoferrate (CuHCF) nanoparticles in aqueous $\text{Al}_2(\text{SO}_4)_3$ electrolyte could exhibit reversible intercalation of Al^{3+} in the voltage range of 0.2 to 1.2 V *versus* a saturated calomel reference electrode with a specific capacity of 58.9 mA h g^{-1} at 50 mA g^{-1} . On the other hand, Menke and coworkers demonstrated that CuHCF had a very low reversible capacity (between 5 and 14 mA h g^{-1}) in $\text{Al}(\text{OTf})_3$ electrolyte in diglyme within an electrochemical window between 0.1 and 0.7 V *versus* Al.⁸⁵ These discrepancies suggest that the mechanism of PBAs in aqueous RABs requires further investigation.

3. Conversion mechanism cathode materials

Unlike intercalation-type cathode materials that require feasible crystal structures, conversion-type cathodes are more straightforward, at least theoretically. Most of the reported cathode materials for RABs to date are conversion-type. For example, the transition metals in CuO ,⁸⁶ Co_3O_4 ,⁸⁷ FeS_2 ,⁸⁸ NiS ,⁸⁹ and Ni_3S_2 ⁹⁰ electrodes can be reduced to a low valence state after discharge and generating Al_2O_3 or Al_2S_3 . The transition metals in Ni_2P ,⁹¹ Co_2P ,⁹² $\text{Co}_3(\text{PO}_4)_2$ ⁹³ and CoSe_2 ⁹⁴ cathodes will be reduced to the zero-valent state during conversion.

3.1 Transition metal oxides

CuO porous microspheres from hydrothermal methods were reported as cathode materials for RABs.⁸⁶ A reduction peak at 0.6 V and an oxidation peak of 0.8 V *versus* Al were detected in

the CV curves. However, the charge–discharge curves demonstrate one additional discharge plateau at 0.2 V and one additional charge plateau at 2.0 V, which were not clearly explained. But one can speculate that the reductive decomposition of the chloroaluminate ionic liquid electrolyte could be the reason for the low discharge plateau, and chlorine generation could be the reaction for the high charging plateau.²⁹ Monovalent Cu^+ was detected in the XPS spectra, confirming the reduction of Cu^{2+} . The authors claimed Cu_2O and Al_2O_3 as the products from the complete discharge to 0.1 V, however, the XRD pattern of the discharge products was inconclusive. Jiao and coworkers reported a metal organic framework (MOF)-derived Co_3O_4 polyhedral cathode for RABs.⁸⁷ The CV curves demonstrated two reduction peaks at 0.6 V and 0.4 V and one oxidation peak at 0.97 V *versus* Al. The XPS Co 2p spectra indicated the existence of metallic Co in fully discharged Co_3O_4 (at 0.1 V). The XPS Al 2p spectra after discharge displayed the enhancement of the Al peak, which was attributed to the Al_2O_3 product.

3.2 Transition metal sulfides and selenides

Most of the conversion-type cathode materials for RABs are transition metal sulfides and selenides. Mori *et al.* studied FeS_2 as a cathode material for RABs at 55°C .⁸⁸ The *ex situ* XRD detected the FeS diffraction peak after the discharge of FeS_2 , and the FeS peak disappeared after full charging. The S K-edge XANES spectra indicate that the peak at 2472 eV decreases during discharging, and the S 1s is gradually transformed to the S 3p bond, which is reversed during the charging process

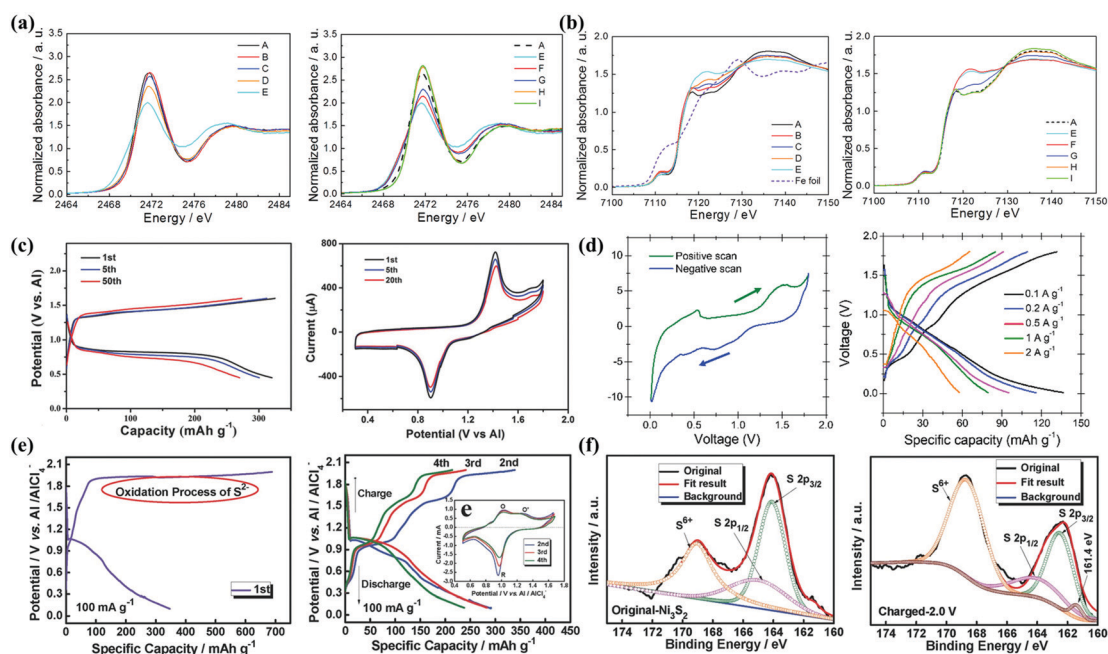


Fig. 5 (a) S K-edge and (b) Fe K-edge XANES spectra of FeS_2 during discharge and charge at 55°C ; potential decreases from A (OCP 1.2 V) to E (0.01 V) during discharge, and increases from E to I (1.8 V) during charge. Reproduced with permission from ref. 88. Copyright (2016) Elsevier. (c) The discharge–charge curves of binder-free Co_9S_8 @CNT–CNF at 100 mA g^{-1} and CV curves at 0.5 mV s^{-1} . Reproduced with permission from ref. 95. Copyright (2017) WILEY. (d) CV curves of Co_9S_8 versus Al at a scan rate of 0.25 mV s^{-1} and the discharge–charge curves at different current density. Reproduced with permission from ref. 96. Copyright (2019) Elsevier. (e) The discharge–charge curves of Ni_3S_2 /graphene at a current density of 100 mA g^{-1} ; (f) S 2p XPS spectra of Ni_3S_2 in the pristine state and after full charge. Reproduced with permission from ref. 90. Copyright (2016) WILEY.

(Fig. 5a). On the other hand, no shift is detected in the absorption edge of the Fe K-edge XANES spectra (at 7115 eV), indicating that the oxidation state of Fe is unchanged during discharge and charge (Fig. 5b). The isosbestic point at 7130 eV reveals the coexistence of the two iron compounds in the electrode with no presence of metallic iron, which is consistent with the *ex situ* XRD results. Furthermore, S and Al K-edge XANES proved the existence of amorphous Al_2S_3 . Therefore, the conversion reaction mechanism is described as the redox reaction between S_2^{2-} and S^{2-} (i.e., FeS_2 and FeS) accompanied by the formation of amorphous Al_2S_3 . It is worth noting that the authors found that FeS_2 and Al_2S_3 were readily soluble in the chloroaluminate ionic liquid, which would certainly complicate the discharge-charge process.

Zhuang and coworkers reported a binder-free cobalt disulfide and carbon nanofiber composite ($\text{CoS}_2@\text{CNFs}$) cathode.⁹⁷ The XPS analysis indicated that the oxidation state of Co in the pristine CoS_2 is Co^{2+} , and the anion is S_2^{2-} disulfide. Interestingly, Co^{3+} was detected from the XPS spectra after discharge, indicating that S_2^{2-} must be reduced during discharge. Based on the XRD pattern of the discharge product, the authors proposed AlCo_2S_4 as the discharge product, although unknown peaks were detected. Co_9S_8 is another cobalt sulfide material being investigated for RABs. Wang and coworker reported a binder-free $\text{Co}_9\text{S}_8@\text{CNT-CNF}$ cathode with an ultra-long cycle performance.⁹⁵ The charge plateau (1.30 V) and discharge plateau (0.95 V) of the charge-discharge curve are consistent with the anodic and cathodic peaks of the CV curve (Fig. 5c). The XPS spectra indicates the reversible redox of Co during discharge and charge. Hu *et al.* also demonstrated a two-dimensional porous Co_9S_8 nanosheet cathode with a capacity of 120 mA h g^{-1} after 250 cycles at 0.2 A g^{-1} .⁹⁶ However, the electrochemical characteristics of the porous Co_9S_8 nanosheets are quite different from the $\text{Co}_9\text{S}_8@\text{CNT-CNF}$ reported by Wang as illustrated from the CV scan and the discharge-charge curves in Fig. 5d. It is clear that the detailed mechanism of Co_9S_8 needs further clarification.

Wang *et al.* reported two types of nickel sulfides including $\text{Ni}_3\text{S}_2/\text{graphene}$ composite⁹⁰ and NiS nanobelts⁸⁹ as the cathode materials for RABs. It is worth noting that the Ni_3S_2 cathode is charged first before discharging due to the low valent states of Ni (Ni^0 and Ni^{2+} coexist in Ni_3S_2). Peculiarly, the first charging curve is a long voltage plateau at 2.0 V *versus* Al with a capacity two times higher than that of the discharge (Fig. 5e). The XPS Ni 2p spectrum of the charged Ni_3S_2 indicates the disappearance of metallic Ni (characteristic peak at 852.8 eV), confirming the oxidation of Ni^0 in Ni_3S_2 . As displayed in Fig. 5f, the S 2p spectrum after charging shows a new peak at 161.4 eV, which is attributed by the authors to a small amount of NiS .⁹⁸ Furthermore, the S 2p spectrum after charging indicates reduced population of S^{2-} anions and increased population of oxidized sulfur species. Therefore, the authors speculate that the long charging plateaus are due to the oxidation of S^{2-} . The high plateau at 2.0 V also appears in the subsequent cycles, but with lower capacity. It is necessary to point out that the deconvolution of the XPS S 2p spectra in this work has some flaws: S $2\text{p}_{1/2}$ and S $2\text{p}_{3/2}$ peaks must appear in pair

with a fixed peak separation of 1.16 eV and intensity ratio of 0.51. The S 2p spectra shown in Fig. 5f are not rigorously deconvoluted, therefore the interpretation may be questionable. Nevertheless, *ex situ* XRD showed that the charging products contain Al_2S_3 , NiCl_2 , and NiS . NiS can be rationalized as the oxidation product of Ni_3S_2 (due to the oxidation of Ni^0), however the origin of Al_2S_3 and NiCl_2 is not explained. The TEM images and selected area electron diffraction (SAED) after the reaction showed the transfer of Ni_3S_2 to amorphous structure, which is consistent with the conversion-type mechanism and may be the cause of the decrease in capacity. The same group subsequently studied hexagonal NiS nanobelt cathodes,⁸⁹ which is supposed to be the charging product of Ni_3S_2 according to their previous study. Indeed, the demonstrated electrochemical properties of NiS are consistent with Ni_3S_2 .

Based on the experimental data presented in the two studies above, there is an alternative explanation for the redox mechanism of Ni_3S_2 in the chloroaluminate ionic liquid electrolyte: during the charge of Ni_3S_2 , the metallic Ni is oxidized to NiCl_2 represented by the high charging plateau, which can explain the origin of the NiCl_2 identified by XRD. NiCl_2 is electrochemically active in the chloroaluminate ionic liquid. Shi *et al.* demonstrated that metallic Ni foil can function as an active cathode in Al-Ni cells by forming NiCl_2 through charge-first cycling.²⁹

Wang *et al.* prepared a hierarchical CuS microsphere cathode for RABs with a reversible capacity of 90 mA h g^{-1} at a current density of 20 mA g^{-1} after 100 cycles.⁹⁹ The XPS Cu 2p spectra demonstrate a reversible redox reaction between Cu^{2+} and Cu^+ during discharging and charging. The XRD pattern of the discharged electrode indicates the existence of Cu_2S and Al_2S_3 . The Raman peak of CuS at 473.56 cm^{-1} also shifted to 470.57 cm^{-1} after discharge, indicating the conversion of CuS to Cu_2S .¹⁰⁰

Transition metal selenides were also investigated as the cathode materials for RABs including the cobalt selenide-carbon composite ($\text{CoSe}@\text{C}$) derived from MOF ZIF-67,²⁴ cobalt diselenide-carbon composite in a reduced graphene oxide framework ($\text{CoSe}_2-\text{C}@\text{rGO}$),⁹⁴ and 3D ordered microporous (3DOM) $\text{CoSe}_2@\text{C}$ also derived from MOF ZIF-67.¹⁰¹ Despite their different chemical compositions and structures, these three cobalt selenides demonstrated very similar electrochemical properties, evidenced by the same feature in the charge-discharge curve and CV scan: a distinct charging plateau (or oxidation peak in CV) at approximately 2.0 V *versus* Al. It is also worth noting that none of the studies clearly stated whether charging (oxidation scan) or discharging (reduction scan) was applied first in their cycling (CV) experiments, which is critical to understand the reaction mechanism. All three studies provided XPS Co 2p spectra after cycling, but they are not fully self-consistent: the Co 2p spectrum of CoSe indicated that the valent state of Co (Co^{2+}) does not change throughout charge and discharge; while the Co 2p spectra of CoSe_2 indicated the existence of metallic Co after both discharge and charge, which can be confusing, particularly without knowing if CoSe_2 was charged first or discharged first. However, what is consistent in all three studies is the XPS Se 3d spectra, which all indicate that Se anions (Se^{2-} in CoSe and Se_2^{2-} in CoSe_2) were oxidized in

the charging process. The authors of the CoSe study speculated that the Se^{2-} anion was oxidized to the positive valence state of Se^{x+} (x may be 4 or 6) after charging. Instead, the authors of the 3DOM $\text{CoSe}_2@\text{C}$ study believed that Se_2^{2-} is oxidized to elemental Se. Nevertheless, it seems that redox of Se may be the main contributor to the demonstrated capacity of these cobalt selenides. Elemental Se has been demonstrated to be electrochemically active toward Al in the chloroaluminate ionic liquid electrolyte,^{102–105} therefore the working mechanism of cobalt selenides (particularly the role of Co) needs further clarification. It is also worth mentioning that the high potential charge plateau and the corresponding discharge plateau resembles the charge and discharge plateaus from the AlCl_4^- intercalation in graphitic carbon, thus whether Cl^- is involved in the charge and discharge reactions of the cobalt selenides also needs further investigation.

3.3 Phosphides and phosphate

Tu *et al.* studied nickel phosphide–reduced graphene oxide (Ni_2P -rGO) nanosheets as the cathode in RABs.⁹¹ The distinct potential plateau of the initial charging curve at 1.9 V was attributed to potential side reactions of the electrolyte. Three oxidation peaks (0.99 V, 1.35 V and 1.80 V) and two reduction peaks (0.53 V and 0.85 V) were detected in the CV scans, corresponding to the multi-step platform of charge and discharge curves. *Ex situ* XRD showed that the peak intensity of the Ni_2P was significantly lowered after discharge, and the crystallinity increased after charging. The XPS spectra after discharge indicated the peaks of metallic Ni (853.4 eV and 871.0 eV) and Ni^{2+} (856.2 eV and 874.4 eV). TEM image and SAED after discharge confirmed the formation of metallic Ni. The change in the valence state of P indicates that Ni^{2+} is partially irreversibly reduced to metallic Ni after discharge.

Lu *et al.* synthesized a Co–P compound supported on carbon cloth (Co–P/CC) as the cathode for RABs.⁹² XRD analysis confirmed the Co–P/CC is composed of polycrystal Co_2P and mellitic Co nanoparticles. The Co–P/CC composite demonstrated higher reversible capacity and lower voltage hysteresis compared to the commercial crystalline Co_2P . The oxidation peak at 1.0 V and two reduction peaks of 0.55 and 0.7 V in the CV curves corresponded to the potential plateau of the charge and discharge curve, while the 1.9 V charge plateau (not detected in CV) might be attributed to side reactions of the electrolyte. The XPS spectra showed the binding energy of metallic Co increased slightly (781.2 and 797.0 eV) when discharged to 0.01 V, and the peaks of Co^{2+} (781.2 and 797.0 eV) were detected after charging to 2.4 V, and the peaks of metallic Co disappeared. There was no change in the P 2p spectra, which confirmed that Co^{2+} in the Co–P/CC electrode is partially reduced to metallic Co during discharge. In addition, the peak intensity of Al 2p after discharge is increased, and the peak intensity of Cl 2p remained the same before and after discharge. Thus, the Co–P/CC cathode underwent a conversion reaction between Al^{3+} and Co_2P during discharge to generate $\text{Al}_m\text{Co}_n\text{P}$ and a small amount of metallic Co, which in turn was oxidized to Co_2P during the charging process. However, the contribution of the metallic Co in the pristine Co–P/CC composite to the charge/discharge capacity is unknown.

Yin and coworkers reported a cobalt phosphate–carbon composite ($\text{Co}_3(\text{PO}_4)_2@\text{C}$) as the cathode of RABs.⁹³ This composite was obtained by carbonization of ZIF-67@RF (resorcinol formaldehyde) followed by $\text{NH}_4\text{H}_2\text{PO}_4$ etching and heat treatment. The *in situ* XRD indicated a new peak (24.7°) was generated during discharge from 1.8 V to 0.9 V, and the peak intensity of the (210) plane at 25.9° was reduced. The appearance of the new peak during discharge is attributed to the generation of $\text{Al}_m\text{Co}_n(\text{PO}_4)_2$, and the *in situ* XRD patterns confirm the reappearance of the characteristic peaks of $\text{Co}_3(\text{PO}_4)_2$ after charging. Moreover, the XPS spectra showed the peak intensity of Co 2p_{1/2} and Co 2p_{3/2} is reduced after discharge, and the signal of Co^0 was detected at 0.5 V. The Co 2p spectrum returned to the argininal state after charging to 2.3 V.

3.4 Sulfur and selenium electrodes

The conversion reaction between Al^{3+} and sulfur has a relatively high theoretical potential (about 1.3 V *versus* Al) and an excellent theoretical specific capacity of 1675 mA h g^{-1} .^{106,107} Therefore, sulfur has been regarded as the most promising cathode for RABs. The main challenges of the sulfur cathode in RABs include the high hysteresis of the discharge and charge voltage and the slow reaction kinetics.¹⁰⁸ Transition metals have been demonstrated as effective catalysts for Li–S electrochemical reactions.^{109,110} Similarly, MOF-derived Cu-containing hosts were used as the sulfur host in Al–S batteries to improve the kinetics of sulfur species conversion. Guo *et al.* reported a S@HKUST-1-C composite cathode decorated with Cu nanoparticles (Fig. 6a).¹¹¹ The first discharge capacity reached 1200 mA h g^{-1} , and the capacity retention was 460 mA h g^{-1} after 500 cycles under 1 A g^{-1} (Fig. 6b). The same group subsequently reported a ZIF-67 derived Co-containing carbon host material for Al–S batteries.¹¹² The demonstrated capacity retention of the S@Co/C electrode was 500 mA h g^{-1} after 200 cycles at 1 A g^{-1} . The CV curve indicated a lower discharge–charge hysteresis of S@Co/C compared to S@C without the Co, confirming the catalytic effect of the Co content (Fig. 6c and d). In addition to the conventional redox reaction between elemental sulfur and sulfide anion (S^{2-}), a unique sulfur redox mechanism in which sulfur can be reversibly oxidized to the positive valent state in chloroaluminate ionic liquids was recently demonstrated by Qiao and coworkers.¹¹³ This work demonstrated redox of sulfur in two distinct windows: redox between S^0 and S^{2-} with Al_2S_3 as the reduction product and the redox between S^0 and S^{4+} with AlSCl_7 as the oxidation product (Fig. 6e and f). *In situ* near-edge X-ray absorption fine structure spectroscopy confirmed SCl_3^+ as the intermediate product of the electrochemical oxidation of sulfur. This finding lays the groundwork for high-voltage rechargeable Al–S batteries.

The electrochemical properties of Se and S are considered similar, however Se has a great advantage of being significantly more conductive ($1 \times 10^{-3} \text{ S m}^{-1}$ of Se *versus* $0.5 \times 10^{-27} \text{ S m}^{-1}$ of S). It is interesting that similar to sulfur, Se can also be reversibly oxidized in chloroaluminate ionic liquid electrolytes. Huang *et al.* constructed a Se/CMK-3 composite as the cathode for Al–Se

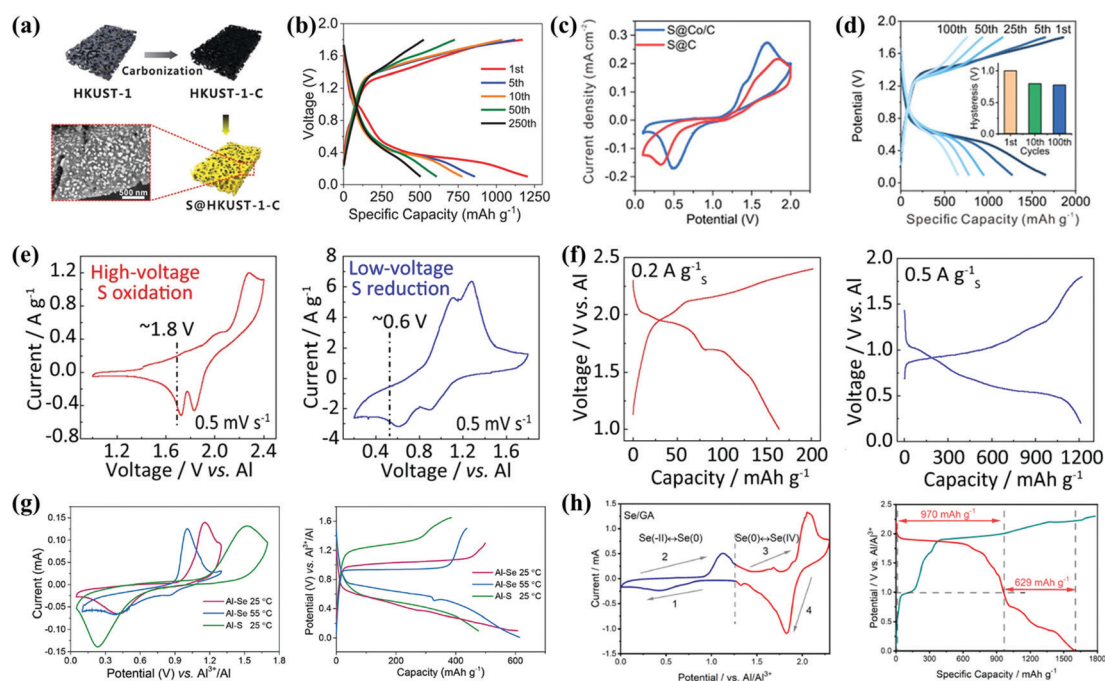


Fig. 6 (a) Schematic diagram of the synthesis of S@HKUST-1-C; (b) discharge–charge curves of S@HKUST-1-C at a current density of 1 A g^{-1} . Reproduced with permission from ref. 111. Copyright (2018) WILEY. (c) CV curves of S@Co/C and S@C cathodes at 0.2 mV s^{-1} ; (d) discharge–charge curves of S@Co/C at 1 A g^{-1} ; the inset shows the discharge–charge hysteresis at different cycles. Reproduced with permission from ref. 112. Copyright (2020) WILEY. (e) CV curves and (f) discharge–charge potential profiles of the S/CNT cathode in electrochemical windows with different cutoff potentials. Reproduced with permission from ref. 113. Copyright (2021) The Author(s). (g) CV scans and the discharge–charge curves of S@CMK-3 and Se@CMK-3 cathodes at 25°C and 55°C . Reproduced with permission from ref. 104. Copyright (2019) Elsevier. (h) CV curves of Se/GA at a scan rate of 0.2 mV s^{-1} and discharge–charge curves at 100 mA g^{-1} , the capacity is contributed from the two-stage reaction between Se^{2-} and Se^{4+} . Reproduced with permission from ref. 105. Copyright (2021) Elsevier.

batteries,¹⁰² in which it was charged first to 2.3 V versus Al in the charge–discharge tests. The charge product was identified as selenium chloride (Se_2Cl_2). Therefore, the electrochemical mechanism is the redox reaction between Se^0 and Se_2^{2+} . A reversible capacity of 178 mA h g^{-1} at 100 mA g^{-1} was demonstrated for 50 cycles with a nominal discharge voltage of 1.8 V versus Al. Interestingly, Liu *et al.* studied the redox reaction of the same Se@CMK-3 cathode using a discharge–first protocol with a cut-off charging voltage at 1.5 V versus Al (Fig. 6g).¹⁰⁴ It was found that the reversible redox reaction is between Se^0 and Se^{2-} anions with Al_2Se_3 as the discharge product. Li *et al.* reported a Se–carbon nanotube (Se@CT) composite cathode.¹⁰³ The reversible Se oxidation was also demonstrated in this study with a capacity of 163 mA h g^{-1} at 500 mA g^{-1} for 200 cycles. However, the authors argued a high valence state of Se such as Se^{4+} and Se^{2+} in addition to Se_2^{2+} could be the products of charging, which could lead to higher capacity. It is clear that Se is capable of a wide range of redox reactions between positive and negative valence states enabled by the chloroaluminate ionic liquid electrolyte. Yan and coworkers demonstrated a selenium/graphene aerogel composite (Se/GA) cathode in $\text{AlCl}_3/\text{triethylamine}$ hydrochloride ionic liquid electrolyte.¹⁰⁵ The authors proved that different electrochemical reactions occur in the two voltage ranges of 0.01 to 1.5 V and 1.0 to 2.3 V versus Al. The 6-electron transfer mechanism of Se ($\text{Se}^{2-} \leftrightarrow \text{Se}^0 \leftrightarrow \text{Se}^{4+}$) was demonstrated with a theoretical capacity of 2036 mA h g^{-1} .

In fact, the Se/GA cathode delivered a specific capacity of 1599 mA h g^{-1} ($\text{Se}^0 \leftrightarrow \text{Se}^{4+}$ contributing $\sim 970 \text{ mA h g}^{-1}$ and $\text{Se}^{2-} \leftrightarrow \text{Se}^0$ contributing $\sim 629 \text{ mA h g}^{-1}$) at a current density of 100 mA g^{-1} , reaching a utilization of 78.5% (Fig. 6h). It is worth noting that the high redox potential (approximately 1.85 and 2.06 V versus Al) between Se and the oxidized Se species are very similar to that of some transition metal selenide cathodes for RABs.^{24,94,101,114,115} The similarity implies that these transition metal selenides may have Se_x^{2-} anions as the active species contributing to the demonstrated reversible capacity.

3.5 Organic cathode materials

Organic redox materials have been extensively studied as cathode materials for rechargeable Li-ion batteries. RABs can also potentially benefit from the organic cathodes due to their robust redox mechanisms and high redox potential relative to Al compared to the inorganic materials. Conducting polymers, specifically polypyrrole and polythiophene, were studied by Hudak as the cathode materials for RABs.¹¹⁶ It was found that both polymers can be reversibly oxidized and reduced in the chloroaluminate ionic liquid electrolytes with chloroaluminate anions functioning as the dopants for the conducting polymers. Stable specific capacity between 30 to 100 mA h g^{-1} was demonstrated. More recent organic cathodes for RABs are based on the reversible reduction of the quinones and the coordination of chloroaluminate cations, including monovalent

AlCl_2^+ and divalent AlCl_2^{2+} , to the quinones after reduction. Stoddart and coworkers studied a phenanthrenequinone (PQ) based cathode in a Lewis acidic chloroaluminate ionic liquid electrolyte, and confirmed the reversible reduction of the quinone and the coordination of monovalent AlCl_2^+ in PQ.¹¹⁷ This organic cathode demonstrated superior capacity retention and rate capability compared to typical inorganic cathodes: retaining 53 mA h g⁻¹ after 5000 cycles at 2 A g⁻¹. Lu and coworkers studied a polyimide/MOF composite cathode with a capacity of 73 mA h g⁻¹ after 2800 cycles under 1 A g⁻¹.¹¹⁸ A similar reaction mechanism involving monovalent AlCl_2^+ was proposed. Dominko and colleagues revealed the redox reaction of anthraquinone (AQ) in the chloroaluminate ionic liquid, and they further developed an anthraquinone-based poly(antraquinonyl sulfide) (PAQS) cathode for RABs.¹¹⁹ The PAQS cathode demonstrated an initial discharge capacity of 190 mA h g⁻¹ at 0.5C and a 60% retention after 500 cycles. The authors proposed that the electrochemical mechanism was the reduction of the quinone accompanied with the coordination of the divalent AlCl_2^{2+} . Choi and coworkers reported a tetradiketone (TDK) macrocyclic molecule, which can reversibly react with AlCl_2^{2+} to achieve a high initial capacity of 350 mA h g⁻¹ and excellent stability of 8000 cycles.¹²⁰ Compared with PQ that reacts with the monovalent AlCl_2^+ , the authors proposed that TDK prefers coordination with divalent AlCl_2^{2+} due to its low stabilization after reduction from the lower ratio of benzene ring to carbonyl. The DFT calculation of binding energy, calculated IR vibration peaks of TDK, and the achieved specific capacity all supported the hypothesis that TDK coordinated with divalent AlCl_2^{2+} .

4. Conclusion and outlook

In summary, a number of challenges exist in the current field of Al^{3+} intercalation and conversion-type cathode materials for RABs. For intercalation-type cathodes, Chevrel Phase Mo_6S_8 is the only material that has been proven to follow this kind of mechanism with unambiguous evidence. Other Chevrel phase materials can also be expected to host Al *via* intercalation, however, with the low specific capacity (due to high molecular mass) and low intercalation-extraction potential *versus* Al, their practical value is questionable. Although many intercalation-type materials for monovalent cations have been claimed to be capable of hosting Al^{3+} *via* intercalation too, unambiguous experimental evidence such as crystallographic data is lacking in current studies. XPS has become a conventional technique to characterize the claimed intercalation-type cathode, however, XPS can only reveal the valence state of surface elements and cannot provide crystal structural information. It is critical for studies on Al^{3+} intercalation materials to show unambiguous crystallographic evidence. Furthermore, the desolvation of chloroaluminate anions during Al^{3+} intercalation must be understood.

We believe most of the reported RAB cathode materials are conversion-type based on our analysis of literature. The conversion mechanism may be straightforward in Li-ion batteries, but it can be

complex in RABs due to the involvement of the chloroaluminate ionic liquid electrolytes. The first question that has not been clearly answered is the chemical compatibility of the transition metal oxides, chalcogenides, and phosphides with the ionic liquids. A number of studies clearly demonstrate that some metal oxides and sulfides either dissolve in or react with the chloroaluminate ionic liquids. It is important for researchers to check the chemical compatibility of the cathode materials prior to the study of their electrochemical properties. Some studies on conversion-type cathodes indicated the existence of a metallic transition metal such as Ni or Co, thus it must be realized that these metals can be either corroded or electrochemically active in the ionic liquids. For instance, Ni, Ti, and Cu can be oxidized to form their chloride salts in the charging process in the chloroaluminate ionic liquids, and these chloride salts can be cycled in the charge-discharge tests demonstrating battery-like behavior. The true electrochemical reactions during the cycling of the RABs may not be the intended ones. A good example of this statement is the RABs based aqueous electrolytes. Another question about conversion-type cathodes is the role of chalcogenide anions, particularly selenides. A number of studies suggest that selenide anions can be oxidized (charged) to positive valence states, which would significantly improve the specific capacity of these materials.

Sulfur and selenium are more promising conversion-type cathode materials compared to the ones based on transition metals due to their clear advantage in capacity. The cycling performance of Al-S batteries has been demonstrated, but the reaction mechanism involving the intermediate products is not fully understood. An analogous reaction mechanism to that in Li-S batteries cannot be assumed in Al-S batteries due to the chloroaluminate ionic liquid electrolytes. Some interesting electrochemical properties of Al-S and Al-Se batteries have been demonstrated, specifically in the wide redox range of S and Se from negative to positive valence states, which can provide an additional boost to their specific capacity. The current studies suggest that the oxidation of S and Se to the positive valence state is enabled by the chloroaluminate anions (*i.e.*, forming AlSCl_7 and Se_2Cl_2) featured by a high charging plateau around 2 V *versus* Al. However, this potential is very close to the chlorine generation potential, particularly on cathodes using carbon materials with a high surface area, which can lower the overpotential of chlorine generation. Therefore, it may be possible that the charging products of S or Se in a high oxidation state such as Se_2Cl_2 are not directly from electrochemical oxidation of Se^0 , instead, they may be a result of the chemical reaction between Se and the chlorine generated during the charging process at high potential. The performance degradation of Al-S and Al-Se batteries also originates from the shuttle effect, dissolution of intermediate products in the chloroaluminate ionic liquid electrolytes.^{113,121} How to suppress the shuttle effect is the key to improving the cycle stability of Al-S and Al-Se RABs.

All current studies indicate that the chloroaluminate ionic liquid electrolyte is a universal problem for RABs. Although it is not the focus point of this critical review, it is clear that chloroaluminate ionic liquids are not feasible electrolytes for

practical RABs. They are expensive, corrosive, prone to oxidation (chlorine generation), and actively react with many cathode materials. Research and development of new Al electrolytes is crucial for RAB technologies.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

This work was supported in part by the National Natural Science Foundation of China (No. 21875223). J. G. acknowledges the support from the U.S. National Science Foundation through grant CBET-1751929.

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