

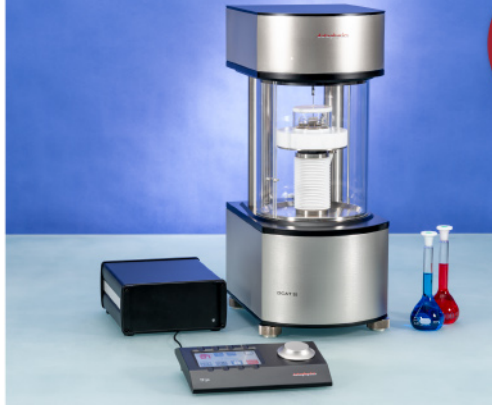


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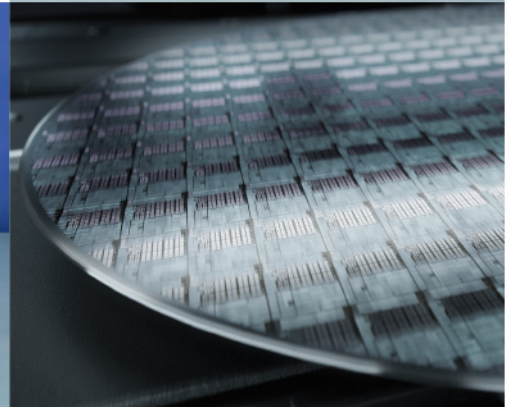


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Modified Solid Electrolyte Interphases with Alkali Chloride Additives for Aluminum–Sulfur Batteries with Enhanced Cyclability

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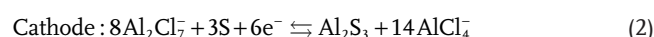
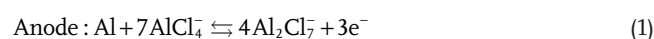
Aluminum–sulfur batteries employing high-capacity and low-cost electrode materials, as well as non-flammable electrolytes, are promising energy storage devices. However, the fast capacity fading due to the shuttle effect of polysulfides limits their further application. Herein, alkaline chlorides, for example, LiCl, NaCl, and KCl are proposed as electrolyte additives for promoting the cyclability of aluminum–sulfur batteries. Using NaCl as a model additive, it is demonstrated that its addition leads to the formation of a thicker, $\text{Na}_x\text{Al}_y\text{O}_2$ -containing solid electrolyte interphase on the aluminum metal anode (AMA) reducing the deposition of polysulfides. As a result, a specific discharge capacity of 473 mAh g^{-1} is delivered in an aluminum–sulfur battery with NaCl-containing electrolyte after 50 dis-/charge cycles at 100 mA g^{-1} . In contrast, the additive-free electrolyte only leads to a specific capacity of 313 mAh g^{-1} after 50 cycles under the same conditions. A similar result is also observed with LiCl and KCl additives. When a KCl-containing electrolyte is employed, the capacity increases to 496 mA h g^{-1} can be achieved after 100 cycles at 50 mA g^{-1} . The proposed additive strategy and the insight into the solid electrolyte interphase are beneficial for the further development of long-life aluminum–sulfur batteries.

1. Introduction

Aluminum metal batteries (AMBs) are potential energy storage devices complementary to the state-of-the-art lithium-ion batteries, due to the high theoretical capacity (2980 mA h g^{-1} , 8050 mAh cm^{-3}), low cost, and high abundance of aluminum

metal.^[1–3] The usually employed electrolytes for stripping/plating of aluminum metal at room temperature are nonflammable ionic liquids or deep eutectic liquids,^[4–9] which endows AMBs intrinsic safety. On the other hand, aluminum metal anodes (AMAs) exhibit a higher redox potential (-1.7 V vs standard hydrogen electrode, SHE) than other common metal anodes (-3.0 , -2.7 , -2.9 , and -2.4 V vs SHE for lithium, sodium, potassium, and magnesium, respectively),^[10] which limits the voltage output and consequently the energy density of AMBs. One feasible solution to mitigate this shortcoming for a higher energy density is to employ materials with high specific capacity as cathode material. In this context, elemental sulfur with high specific capacity (1672 mAh g^{-1}) and low cost is a promising cathode material for high-energy-density AMBs, that is, Al–S batteries.^[11–16]

When the sulfur cathode is dis-/charged in a potential window $<1.8 \text{ V}$ versus Al^{3+}/Al with the $[\text{AlCl}_3]_{1.3}[\text{EmimCl}]_1$ electrolyte, the reaction mechanism can be described by the following reactions:^[17–19]



Al–S batteries employing liquid electrolytes suffer from the notorious shuttle effect of polysulfides as other intensively investigated metal–sulfur batteries.^[20,21] During the discharge, the conversion of sulfur to Al_2S_3 at the cathode occurs via the stepwise formation of polysulfide intermediates.^[22] These are soluble and can diffuse through the electrolyte to AMA, where they are further reduced to Al_2S_3 and polysulfides with shorter chain length.^[23] The generated sulfides recombine with the dissolved polysulfides and diffuse back to the cathode to be oxidized during charge.^[12] This shuttle effect of the $\text{S}/\text{Al}_2\text{S}_3$ conversion reaction leads to poor cyclability of Al–S batteries. Additionally, Al_2S_3 and low-order polysulfides deposited on AMA are no longer available for further dis-/charge.

Up to now, several strategies have been proposed to improve the poor reversibility and lifespan of Al–S batteries. At the

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DOI: 10.1002/adfm.202214405

cathode side, materials that can adsorb polysulfides have been employed as the host material of sulfur to reduce the dissolution of polysulfides,^[24–26] for example, heteroatom-functionalized and/or hierarchical porous carbonaceous materials, metal-organic frameworks (MOFs), boron nitrides, and Mxenes.^[18,27] Catalysts that can further anchor the polysulfides and simultaneously promote the sluggish electrochemical conversion between S and Al_2S_3 are also embedded to the aforementioned host materials,^[28–30] for example, Mo_6S_8 ,^[31] and TiN .^[32] In addition to the cathode, electrolyte design approaches preventing the diffusion of polysulfides are also reported, resulting in remarkably enhanced cyclability.^[33–35] For example, modification of separators with materials exhibiting strong adsorption of soluble polysulfides are effective in hindering their diffusion to AMAs.^[29,36] Huang et al. recently reported that an ionic-liquid-impregnated MOF, that is, a quasi-solid-state electrolyte, can block the shuttling of polysulfide between the sulfur cathode and AMA.^[22] Nonetheless, AMAs, which also play an important role in the shuttle process, have received little attention up to now. Suitable engineering of electrolytes enabling an electronically insulating solid electrolyte interphase (SEI) on AMAs may suppress the deposition of low-solubility Al_2S_3 and/or short-chain polysulfides further promoting the cell cycling performance.

In this work, alkali chlorides are, for the first time, proposed as electrolyte additives to modify the SEI on AMAs and suppress the polysulfide shuttle in Al-S batteries. It is demonstrated that adding NaCl to the conventional $[\text{AlCl}_3]_{1.3}[\text{EmimCl}]_1$ electrolyte can enhance the cyclability of Al-S batteries. To

understand the improved performance, detailed characterization of sulfur cathodes and AMAs cycled in NaCl-containing electrolytes was conducted, showing that the improved cyclability mainly originates from a thicker, $\text{Na}_x\text{Al}_y\text{O}_2$ -containing SEI layer formed in the NaCl-modified electrolyte on AMAs. In addition to NaCl, LiCl and KCl as electrolyte additives also lead to improvement of Al-S batteries' lifespan. These findings provide a new path to suppress the detrimental polysulfides shuttle effect in Al-S batteries, resulting in their improved cycle performance.

2. Results and Discussion

NaCl and $[\text{AlCl}_3]_{1.3}[\text{EmimCl}]_1$ (AE) were selected as the model additive and electrolyte, respectively, to investigate the influence of alkaline chloride additives on the properties of the electrolytes for Al-S batteries. In the following, AE electrolyte with x wt. % NaCl addition is named AE- x Na (with $x = 1, 2$, and 4). The operation of Al-S batteries requires for the electrolyte to transport both AlCl_4^- and Al_2Cl_7^- between S cathodes and Al metal anodes (see Equations 1 and 2). A faster transport of these two ions in the electrolyte results in faster reaction kinetics and lower polarization. The ionic conductivity reflects the overall ionic transport ability of the electrolyte. Therefore, the ionic conductivity of these electrolytes at 20 °C have been measured and compared in Figure 1a. When 1 wt.% NaCl is added to the AE electrolyte, the ionic conductivity slightly increased from 13.7 to 14.2 mS cm^{-1} . In contrast, the samples with higher NaCl

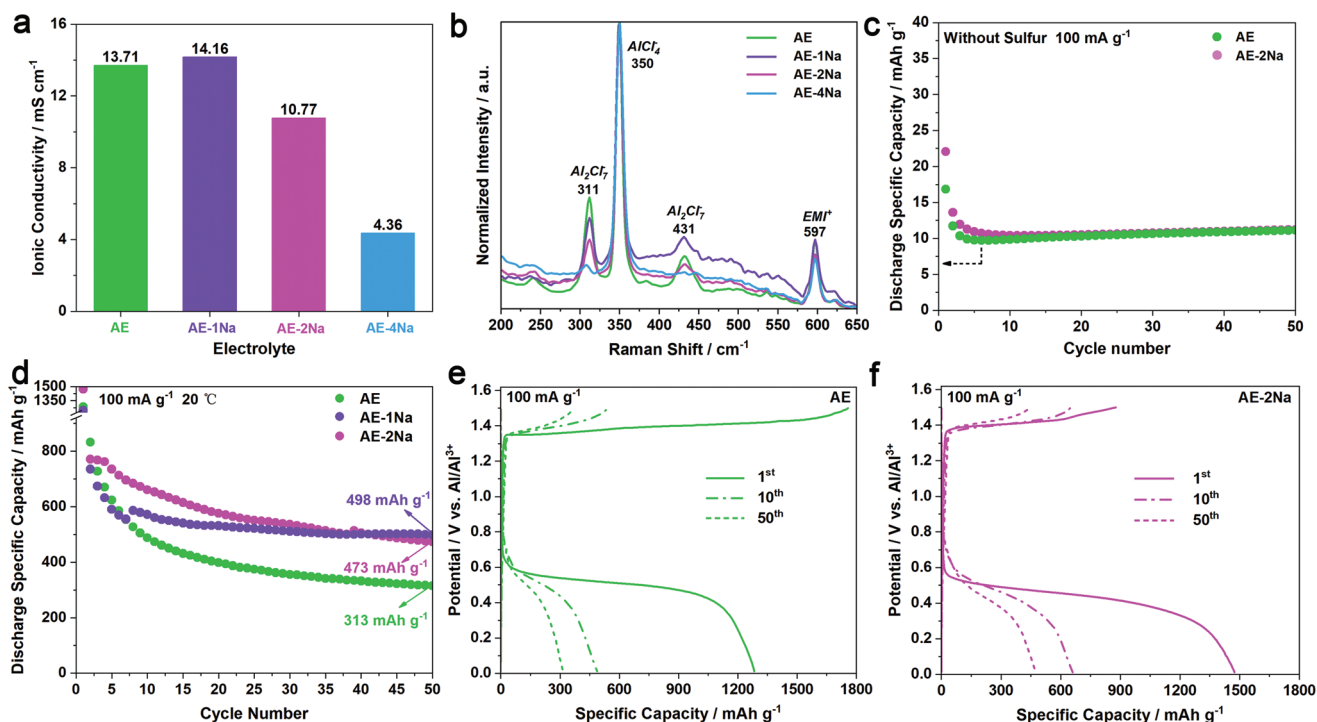


Figure 1. a) Ionic conductivity and b) Raman spectra of the AE and NaCl-containing electrolytes. c) Evolution of discharge specific capacity of Al-graphene batteries with AE and AE-2Na electrolyte upon dis-/charge cycling at 100 mA g^{-1} . d) Evolution of discharge specific capacity of Al-S batteries with the various electrolytes upon dis-/charge cycling at 100 mA g^{-1} . Dis-/charge profiles of Al-S batteries with e) AE and f) AE-2Na electrolytes at the 1st, 10th, and 50th cycle.

content exhibited lower ionic conductivity (e.g., the ionic conductivity of AE-4Na was only 4.4 mS cm^{-1}).

The dynamic equilibrium between Al_2Cl_7^- and AlCl_4^- in the electrolytes is of utmost importance since both ions are required for the operation of Al-S batteries (see Equations 1 and 2). As displayed in Figure 1b, the normalized Raman spectra clearly reveal that the addition of NaCl resulted in lower portion of Al_2Cl_7^- . When 4 wt.% NaCl was added to the AE electrolyte, the signal of Al_2Cl_7^- is barely observed.

To investigate the electrochemical performance of the electrolytes in the Al-S batteries at 20°C , three-electrode T-shaped cells were assembled employing aluminum foils as counter and reference electrodes and S/graphene as a model cathode material. All inert components used in these cells (mostly the cell case as well as cathode's current collector foil) were carefully selected to avoid any corrosion when in contact with the electrolyte. All details can be found in the **Experimental Section**. Without further notification, the sulfur content in the S/graphene composite was 34 wt.%, and the average sulfur loading was 0.5 mg cm^{-2} . The results of the structural and morphological characterization of the S/graphene electrodes can be found in Figures S1–S3, Supporting Information. GF/D membranes coated with multi-walled carbon nanotubes (MWCNT) were used as the separator, which characterization is shown in Figure S4 (Supporting Information). For reference, cells without sulfur were also assembled and tested; the received discharge capacity of such a cell of $\approx 10 \text{ mAh g}^{-1}$ (Figure 1c) indicates negligible capacity contribution of the materials, including the MWCNT coating on separator and the carbonaceous materials in the cathode.

The cyclic voltammetry (CV) profiles of the sulfur cathode in Al-S batteries employing AE and AE-2Na exhibited redox signals identical to previously reported cells (Figure S5, Supporting Information), validating the electrochemical activity of the prepared S/graphene cathode. Then, the assembled Al-S cells were further examined via galvanostatic cycling at 100 mA g^{-1} . The discharge specific capacity upon cycling is summarized in Figure 1d. A few selected dis-/charge profiles obtained with the AE and AE-2Na electrolytes are shown in Figure 1e,f, respectively, while the corresponding results with AE-1Na and AE-4Na can be found in Figure S6 (Supporting Information). The cell employing AE-4Na exhibited high polarization and negligible specific capacity, while the initial discharge capacity of the cells using other electrolytes was higher than 1200 mAh g^{-1} . As shown in Equations 1–3, Al_2Cl_7^- is required for the electrochemical reaction at the cathode side during the discharge of Al-S batteries. The low content of Al_2Cl_7^- in the electrolyte (Figure 1b) and the sluggish transport (Figure 1a) of Al_2Cl_7^- from anode to cathode limit the kinetics of the reaction leading to a significantly attenuated specific capacity when AE-4Na is employed. The specific capacity of the cell employing AE quickly dropped to 313 mAh g^{-1} at the 50th cycle. However, the electrolytes with 1 and 2 wt. % NaCl resulted in discharge specific capacity at the 50th cycle of 498 and 473 mAh g^{-1} , respectively. These results demonstrate that the addition of a suitable amount of NaCl, for example, 1 and 2 wt. %, can effectively promote the cycling performance of the Al-S batteries. In addition, it is noticed that the discharge specific capacity of AE-2Na based cell shows a slower decay than that of AE-1Na based cell in the

initial cycles, which is associated to the highest Na^+ content in AE-2Na facilitating the formation of a $\text{Na}_x\text{Al}_y\text{O}_z$ -containing SEI (to be discussed later). With the concern on the low concentration of Na^+ in AE-1Na, which may lead to the difficulty in characterize the difference of the interphase on Al metal anode, AE-2Na, which also leads to improved performance was selected for the subsequent characterization and tests.

In order to reveal the origin of the promoted cyclability, Al-S cells employing the AE electrolyte were assembled and tested using pre-cycled aluminum (pc-Al) electrodes extracted from Al|AE-2Na|S cells. Specifically, the pc-Al electrodes were recovered from Al|AE-2Na|S cells subjected to 40 dis-/charge cycles at 100 mA g^{-1} and cleaned with DMC. The pc-Al electrodes were then employed as anodes for pc-Al|AE electrolyte|S cells, which were dis-/charged with a specific current of 100 mA g^{-1} . The discharge specific capacity upon cycling of these cells is shown in Figure 2a while the dis-/charge voltage profiles of the pc-Al|AE electrolyte|S cell and an Al|AE electrolyte|S cell at the 50th cycle are compared in Figure 2b. The achieved specific capacity for the pc-Al|AE electrolyte|S cell was 507 mAh g^{-1} , that is, much higher than that of the Al|AE electrolyte|S cell, but very close to that of the Al|AE-2Na|S cell (Figure 1d). Surprisingly, a high specific capacity of 493 mAh g^{-1} was still observed for the pc-Al|AE electrolyte|S cell after 150 cycles. Despite the improved cyclability, rapid capacity fading in the initial 40 cycles is still observed when pc-Al was used as the anode, which can be attributed to the dissolution and insufficient re-oxidation of polysulfide at the cathode side upon discharge and charge, respectively. These results demonstrate that the improved cyclability of Al-S batteries upon addition of NaCl mostly originates from the interphase formed on the AMA electrode.

To further verify this evidence, Al||Al symmetric cells were assembled employing either AE or AE-2Na and cycled at 0.054 mA cm^{-2} with a cycling capacity of 0.27 mAh cm^{-2} for each cycle, that is, keeping the current density and cycling capacity roughly similar to those for Al-S cells shown in Figures 1d and 2a. The evolution of the voltage upon cycling is displayed in Figure 2c. The overvoltage of the Al|AE-2Na|Al cell decreased from 26 to 20 mV in the initial 8 cycles (80 h) to remain stable in the following 52 cycles (520 h). When the AE electrolyte was employed, the overvoltage increased in the initial 200 h from 15 to 24 mV to eventually stabilize at 22 mV. Overall, both AE and AE-2Na led to stable cycling of Al||Al symmetric cells, with the former electrolyte leading to the lowest overvoltage in the initial 10 cycles. However, the fastest capacity fading of Al-S cells with the two electrolytes occurred during the initial cycles (Figure 1d). Hence, the inferior cyclability of the Al-S cells employing AE unlikely originates from a compatibility issue between AMAs and electrolytes, for example, the corrosion of AMAs and/or the decomposition of the electrolytes, but rather from the cross-talking between the sulfur cathode and AMA, for example, the shuttling of polysulfides.

The sulfur cathodes and AMAs of the cells employing either AE or AE-2Na were removed after 40 dis-/charge cycles at 100 mA g^{-1} , washed, and further characterized to reveal the effect of the NaCl additive.

The X-ray diffraction (XRD) patterns of S in form of powder and pristine and cycled cathodes are compared in Figure S7 (Supporting Information). After cycling, the feature associated

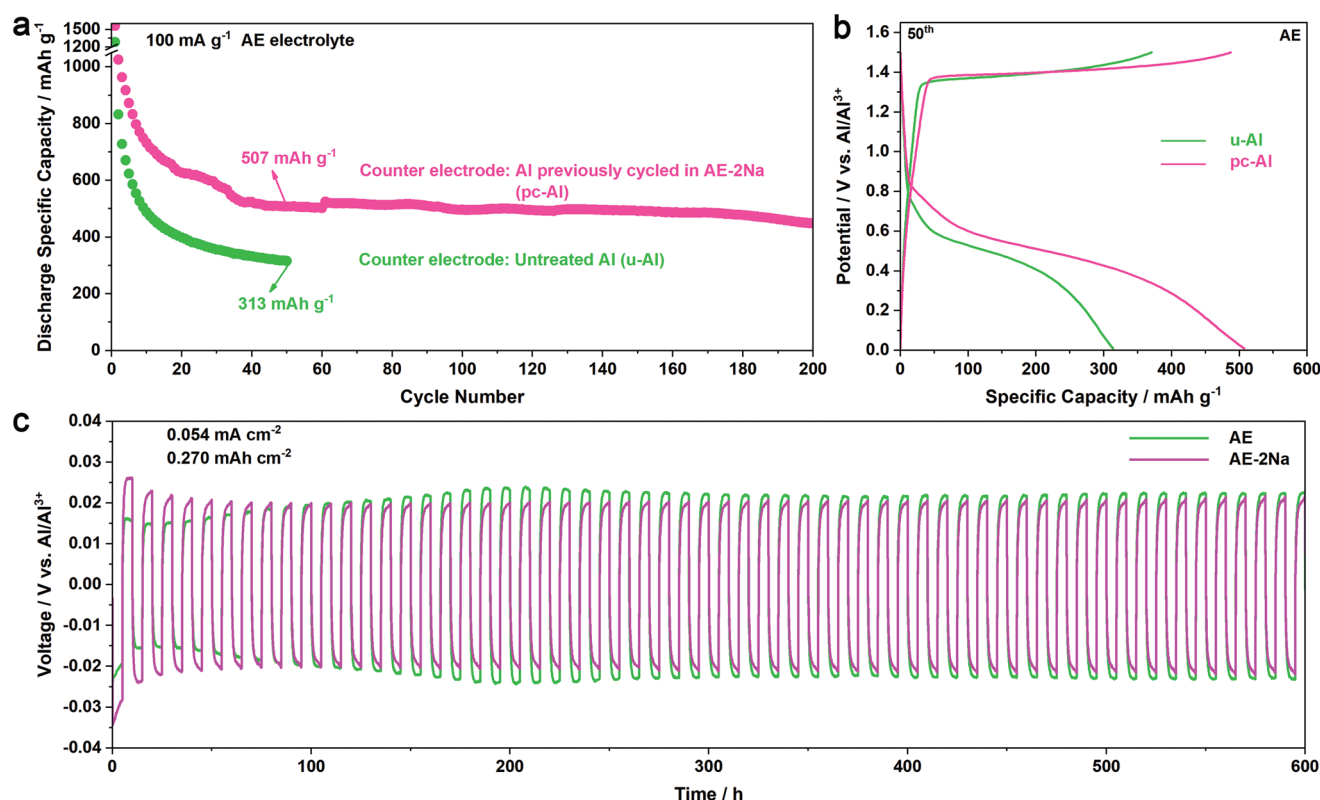


Figure 2. a) Evolution of discharge specific capacity of Al||AE|S cells upon dis-/charge cyclin. The cells were made using either pristine, that is, untreated, Al (u-Al) or previously cycled Al (pc-Al) in AE-2Na and b) the corresponding dis-/charge voltage profiles in the 50th cycle. c) Voltage evolution of Al||Al cells employing either AE or AE-2Na upon stripping/plating cycling at 0.054 mA cm⁻² with a cycling capacity of 0.27 mAh cm⁻² for each cycle.

with elemental sulfur are not observed, revealing the amorphization of the material. The cycled electrodes were also studied by scanning electron microscopy (SEM), revealing rather similar surface morphology for the electrodes cycled in AE and AE-2Na (compare Figure 3a,b). However, the energy dispersive X-ray (EDX) spectrum of the cathode cycled in AE-2Na shows a stronger S peak compared with that cycled in AE (Figure 3c), which indicates that more sulfur-based species remained in the cathode cycled with AE-2Na. The valence state of the elements in the cycled sulfur cathodes was examined with X-ray photoelectron spectroscopy (XPS). Figure 3d shows the S 2p XPS spectra whose intensity was normalized with respect to the main peak in the C 1s spectra. The detail spectra of both electrodes in the S 2p region showed the peak doublet of elemental S. Furthermore, the cathode cycled in AE electrolyte exhibited much lower signal intensity than that cycled in AE-2Na in agreement with the EDX results. The lower sulfur content observed in the electrode cycled in AE correlates well with its inferior retained capacity (Figure 1d). The XPS detail spectra for the other relevant elements (C 1s, Cl 2p, N 1s, Al 2p, and O 1s region, Figure S8, Supporting Information) did not reveal any significant differences (apart from the presence of the signal due to NaCl in the Na 1s spectrum), which indicates rather similar cathode electrolyte interphases on the sulfur cathodes cycled in AE or AE-2Na electrolytes.

In the next step, the focus is placed on the AMAs cycled in Al-S batteries as the electrochemical tests revealed the

improved cyclability to originate mostly from the anode side (Figure 2a). The surface SEM images of pristine AMAs and cycled in AE and AE-2Na are displayed in Figure 4a–c, respectively. The typical texture of aluminum foil was observed for the pristine AMA (Figure 4a). After 40 cycles, the surface morphology of the AMAs significantly changed due to the metal stripping/plating (Figure 4b,c) without, however, substantial differences caused by the electrolyte employed, AE or AE-2Na, which is in agreement to the similar performance of Al||Al symmetric cells employing both electrolytes (Figure 2c). The EDX spectra of these three AMAs, shown in Figure 4d, expectedly show a strong Al signal. The pristine electrode also showed a weak peak for O corresponding to the native oxide coating layer. The electrode cycled in AE additionally showed signals of C, N, and Cl, originating from the deposition of electrolyte species and/or their decomposition products, that is, the formation of the solid electrolyte interphase (SEI). For the electrode cycled in AE-2Na, peaks originating from Na appeared implying its presence in the SEI.

To further investigate the chemical differences in the SEI of AMAs recovered from Al-S batteries using AE and AE-2Na, XPS characterization was performed (see Figure 5). In the C 1s spectra (Figure 5a), the peaks located at 284.8, 286.3, and 289.0 eV are attributed to C–C, C–N/C–O,^[37] and C=O species,^[38] respectively. The peak doublet (199.0 eV for Cl 2p_{3/2} and 200.6 eV for Cl 2p_{1/2}) observed in the Cl 2p spectra (Figure 5b) results from the metal-chloride bond, that is, Al–Cl and/or

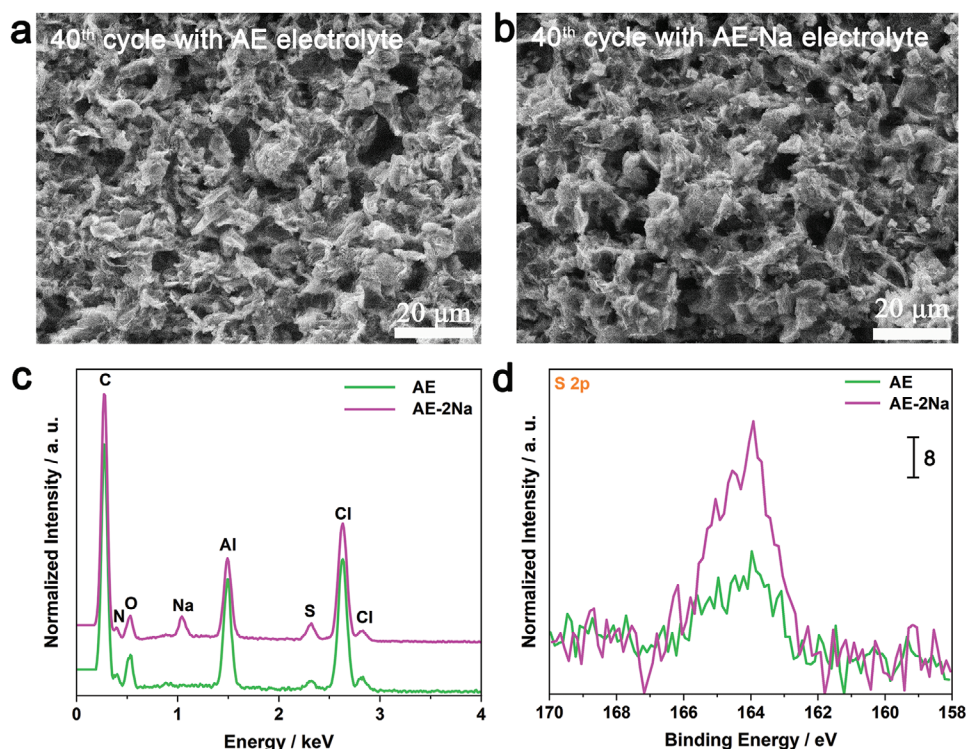


Figure 3. SEM images of sulfur cathodes cycled in a) AE and b) AE-2Na. c) EDX spectra of the cycled sulfur cathodes, normalized to C peak. d) S 2p XPS spectra of the cycled sulfur cathodes, normalized to the main peak in C 1s spectra.

Na–Cl.^[39,40] The higher intensity of this doublet in the spectrum of the electrode cycled in AE-2Na could result from the additional presence of NaCl. The peak at 401.8 eV in the N 1s spectra (Figure 5c) originates from N in Emim⁺.^[41] The Na 1s spectra of the AMA cycled in AE and AE-2Na are displayed in Figure 5d and Figure S9 (Supporting Information), respectively. As expected, no peak appeared in the Na 1s spectrum when AE was used as the electrolyte. Apart from the peak reflecting the Na–Cl bond at 1072 eV, a more intense peak at 1073.9 eV was observed in AE-2Na electrolyte. This peak, which can be assigned to Na_xAl_yO_z,^[42–44] results from the sodiation of the native surface oxide layer on Al, clearly demonstrating that NaCl participates in the formation of the SEI on AMAs. The Al 2p spectra in Figure 5e displays two doublets. The dominant peak doublet (74.7 eV for Al 2p_{3/2}) can be assigned to the Al–O bond in Al₂O₃ and/or Na_xAl_yO_z,^[45] while the less intense doublet (71.6 eV for Al 2p_{3/2}) corresponds to metallic aluminum.^[46] It is noticed that the peak doublet of metallic aluminum has higher intensity for the electrode cycled in AE than in AE-2Na sample, indicating that a thicker SEI is generated on the surface of the latter AMA. A lower intensity of Al₂O₃ and/or Na_xAl_yO_z for AE-2Na sample is caused by the presence of NaCl as indicated in Cl 2p and Na 1s (Figure 5b,d). More importantly, in the S 2p spectra (Figure 5f), the AMA cycled in AE exhibited more pronounced signals than that cycled in AE-2Na, demonstrating that fewer polysulfides are reduced and deposited on the AMA cycled in AE-2Na.

Based on the results, one can infer that the promoted cyclability in AE-2Na originates from the formation of a thicker,

Na_xAl_yO_z-containing SEI, which reduces the deposition of sulfides, including Al₂S₃, on the AMA. Therefore, a higher amount of sulfur remained available for the reaction at the cathode.

In addition to NaCl, two other alkaline chlorides, viz., LiCl and KCl, were also examined as electrolyte additives. In the following, [AlCl₃]_{1.3}[EmimCl]₁ (AE) with *x* wt. % LiCl or KCl is named AE-*x*Li or AE-*x*K, with *x* = 1, 2, and 4, respectively. The ionic conductivity of the electrolytes with different amounts of LiCl or KCl are shown in Figure 6a,d, respectively. Raman spectra of the electrolytes with different amounts of LiCl or KCl are displayed in Figure 6b,e, respectively. In general, the effects of LiCl and KCl on the ionic conductivity and the dynamic equilibrium between AlCl₄[−] and Al₂Cl₇[−] are very similar to that of NaCl. Figure S10 (Supporting Information) displays the ionic conductivity, Raman spectra and discharge profiles of AE, AE-4Li, and AE-4K. AE-4Li based cell presents the highest polarization, although the electrolyte has a high ionic conductivity. AE-4K based cell shows a much smaller polarization, compared with AE-4Na and AE-4Li, which is caused by the fact that AE-4K owns the highest content of Al₂Cl₇[−].

Al–S batteries with either AE-1Li or AE-1K electrolyte were assembled to explore the influence on the electrochemical performance. The discharge specific capacities upon cycling at 100 mA g^{−1} are shown in Figure 6c,f, respectively. Selected discharge voltage profiles can be found in Figures S11 and S12 (Supporting Information). After 50 cycles, the specific capacity delivered by the cells employing LiCl- or KCl-containing electrolytes was 391 and 485 mAh g^{−1}, respectively. Both modified

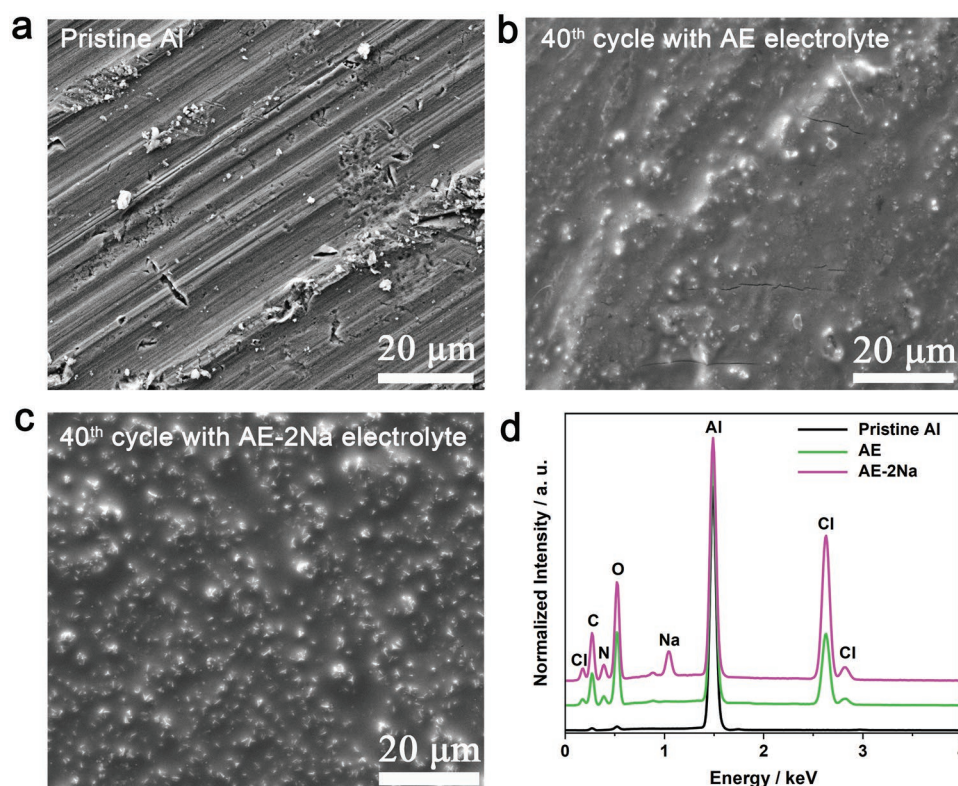


Figure 4. SEM images of a) pristine Al, and Al counter electrodes after 40 cycles with b) AE and c) AE-2Na. d) EDX spectra of the pristine and cycled AMAs, normalized to Al peak.

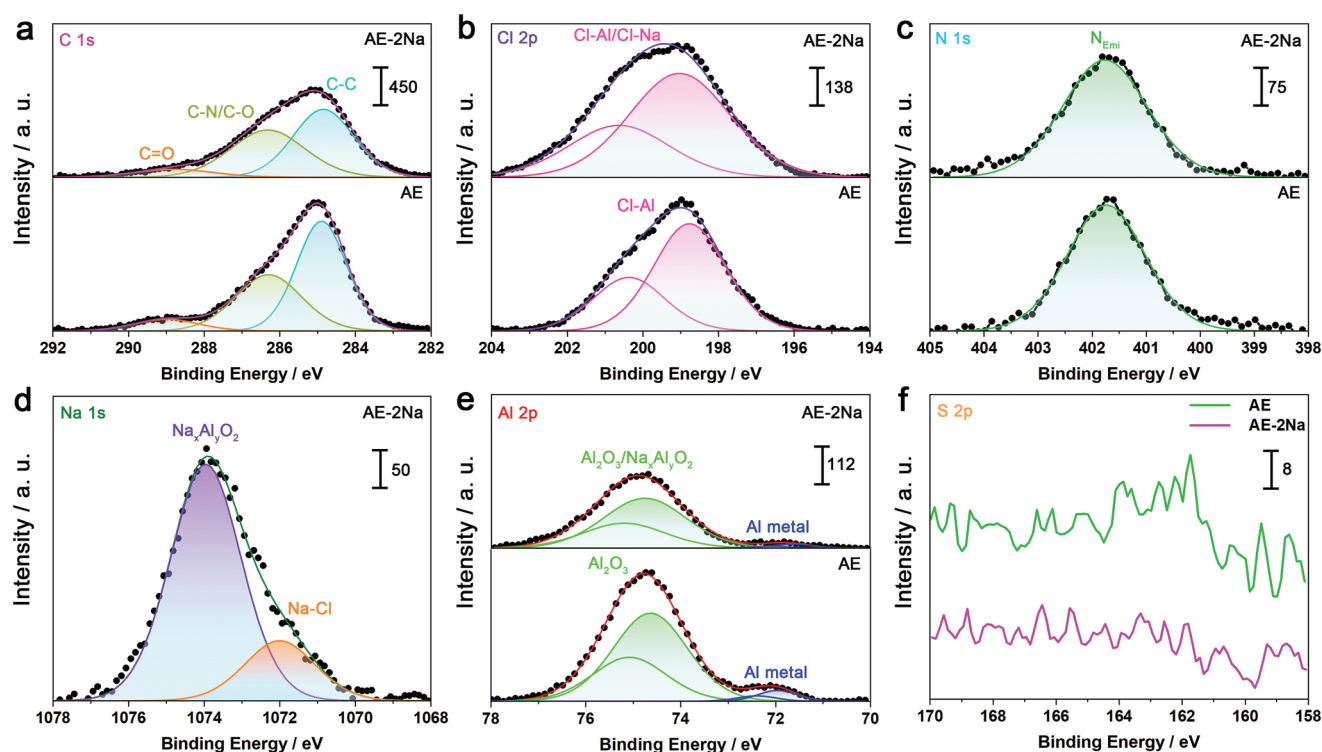


Figure 5. XPS detail spectra of Al counter electrodes recovered from Al-S batteries after 40 dis-/charge cycles from cells with AE or AE-2Na as electrolyte: a) C 1s, b) Cl 2p, c) N 1s, d) Na 1s, e) Al 2p, and f) S 2p region.

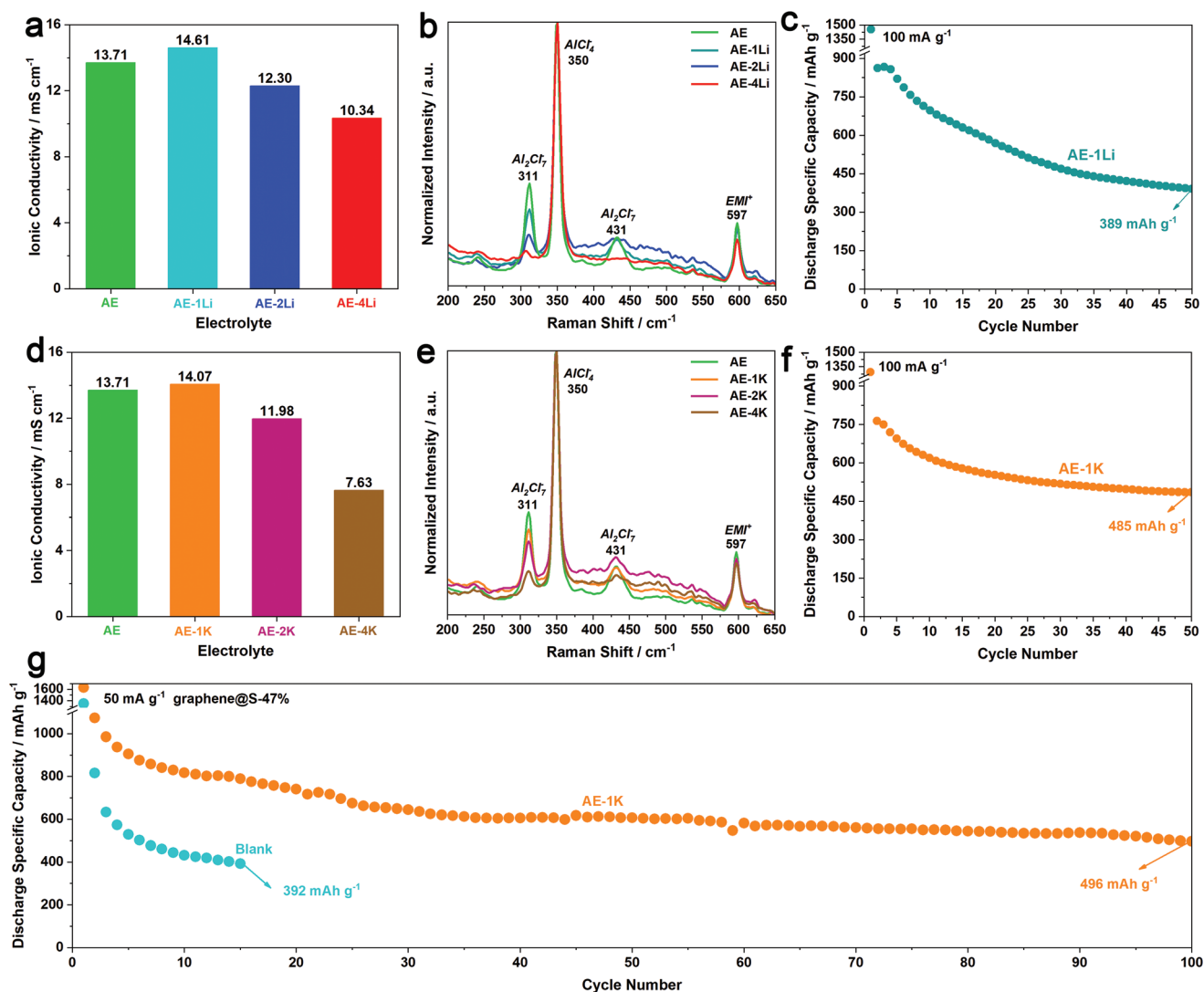


Figure 6. a) Ionic conductivity and b) Raman spectra of the AE and LiCl-containing electrolytes. c) Evolution of discharge specific capacity of Al-S battery with AE-1Li electrolyte upon cycling at 100 mA g⁻¹. d) Ionic conductivity and e) Raman spectra of the AE and KCl-containing electrolytes. f) Evolution of discharge specific capacity of Al-S battery with AE-1K electrolyte upon cycling at 100 mA g⁻¹. g) Evolution of discharge specific capacity of Al-S battery with S/graphene composite with a sulfur content of 47% upon cycling at 50 mA g⁻¹, the electrolyte was either AE or AE-1K.

electrolytes led to better capacity retention than AE, demonstrating the positive effects of the LiCl and KCl additives on the cyclability of Al-S batteries. In addition, it is noticed that the use of different alkali cations leads to different specific capacities in the initial cycles. The concentration of the additive is 1 wt.%, but LiCl has a lower molar mass with respect to KCl. So, the mole of the additives added to the electrolytes is different. Moreover, the charge density of Li⁺ and K⁺ is also different, which affects their interactions with anions. These two aspects could lead to the different structure (e.g., the dynamic equilibrium between Al₂Cl₇⁻ and AlCl₄⁻), physicochemical properties of the electrolytes (e.g., ionic conductivity), and, consequently, the different discharge specific capacity. Furthermore, when the sulfur content of S/graphene materials was increased from 34% to 47%, the battery with AE-1K electrolyte delivered a high capacity of 496 mA h g⁻¹ after 100 cycles at 50 mA g⁻¹ (Figure 6g), demonstrating an excellent cyclability.

Selected dis-/charge voltage profiles can be found in Figure S13 (Supporting Information).

3. Conclusions

The addition of a suitable amount (1 and 2 wt.%) of alkali chlorides (i.e., LiCl, NaCl, and KCl) to the [AlCl₃]_{1.3}[EmimCl]₁ (AE) electrolyte affects the ionic conductivity and the dynamic equilibrium between Al₂Cl₇⁻ and AlCl₄⁻ of the electrolyte and effectively promotes the cyclability Al-S battery. The detailed investigation of Al-S cells employing AE and NaCl-containing electrolytes demonstrates that the improved cyclability achieved with the use of NaCl as additive originates from the formation of a thick, Na_xAl_yO₂-containing SEI on the aluminum metal anode (AMA), which reduces the detrimental deposition of polysulfides and their reduction to Al₂S₃ on the AMA upon cycling.

4. Experimental Section

Materials: Sulfur (99.98%, Sigma–Aldrich), multi-walled carbon nanotubes (MWCNT, O.D. $\times$ L is 6–9 nm $\times$ 5 μ m Sigma–Aldrich), AlCl_3 ($\geq 99.99\%$, Alfa Aesar), polyacrylonitrile (PAN, average $M_w \approx 150\,000$ Sigma–Aldrich), graphene (The Sixth Element Inc.), Al metal (0.1 mm, 99.99%, Thermo Fisher), and dimethylformamide (analytical pure, VWR) were used as received. Molecular sieves (3 Å, Alfa Aesar) were activated at 300 °C under vacuum for one week. DMC ($\geq 99.9\%$, Sigma–Aldrich) was dried with the activated molecular sieves before use. 1-Ethyl-3-methylimidazolium chloride (EmimCl, $>98\%$, IoliTec) was dried at 110 °C under vacuum for 10 h before use. NaCl (analytical pure, VWR), LiCl (analytical pure, VWR), and KCl (analytical pure, Merck) were dried at 80 °C overnight under vacuum before use. Glass fiber separator (Whatman GF/D) was dried at 130 °C under vacuum overnight.

Synthesis of S/graphene: The S/graphene cathode materials were prepared via the following procedure: 0.11 g graphene and 0.35 g sulfur were mixed evenly in a mortar. The mixture was then encapsulated in a glass tube and heated at 155 °C in a vacuum of 1×10^{-1} mbar for 10 h, after which S/graphene with a sulfur content of 34 wt. % (S/graphene-34%) was obtained (see later for further details). By adjusting the proportion of sulfur in the procedure, S/graphene with 47% sulfur (S/graphene-47%) was also prepared.

Preparation of Electrolytes: All the electrolyte preparation was conducted in an Ar-filled glove box with O_2 and H_2O levels ≤ 0.1 ppm. $[\text{AlCl}_3]_{1.3}[\text{EmimCl}]_1$ was prepared via mixing AlCl_3 and EmimCl with a molar ratio of 1.3:1. For those with additives, an appropriate amount of LiCl, NaCl, or KCl (1%, 2%, or 4 wt. %) was added to the $[\text{AlCl}_3]_{1.3}[\text{EmimCl}]_1$. The mixture was stirred at 130 °C for 1 h in the Ar-filled glovebox. After cooling to room temperature, the electrolytes with additives were ready for use.

Electrochemical Measurements and Characterization: Three-electrode T-shaped cells employing aluminum metal foils as negative and reference electrodes, and S/graphene as cathode material were assembled. To avoid any corrosion by the electrolytes, polytetrafluoroethylene (PTFE) cell body and glassy carbon current collectors were used. The sulfur cathodes were prepared by casting the DMF-based slurry containing S/graphene, carbon black, and PAN^[47] in a weight ratio of 75:15:15 on non-graphitic carbon paper current collectors. After drying at 50 °C under vacuum for 10 h, discs with a diameter of 10 mm were cut and used as the positive electrodes, which S areal loading was $\approx 0.5 \text{ mg cm}^{-2}$. The negative and reference electrodes were Al discs (100 μm , 99.99%) with a diameter of 10 mm. 120 μL electrolyte were added into each cell. The MWCNT and PAN (4:1 wt. ratio) slurry (DMF as the solvent) was coated on one side of the GF/D membrane (MWCNT areal loading $\approx 0.25 \text{ mg cm}^{-2}$) was cut to discs with diameter of 10 mm as separator for the Al||S cells with the MWCNT-coated side facing to the sulfur cathodes.^[33] For Al||Al symmetric cells, Al discs with a diameter of 10 mm were used as the electrodes while bare GF/D separators were used.

The ionic conductivity of the electrolytes was determined via electrochemical impedance spectroscopy by an integrated liquid conductivity system MCS 10 (Material Mates-Biologic), using sealed high-temperature conductivity cells (HTCC, Material Mates) with Pt-black electrodes. The conductivity values averaged over 60 min (≈ 60 data points) were used. The cell constant was determined using a 0.01 m KCl standard solution. Sulfur content was determined by thermo-gravimetric analysis (TGA) with a heating rate of 10 °C min^{-1} in a temperature range of 30–600 °C under N_2 atmosphere. The cycling performance of Al–S batteries was tested using a MACCOR series 4000 battery cycler at 20 °C. Cyclic voltammetry (CV) was evaluated via the galvanostat/potentiostat VMP2 (Bio-Logic, France). Cycled electrodes extracted from Al–S cells were soaked in DMC for 2 mins and dried before further investigation. The morphology of graphene, MWCNT powder, and electrodes was investigated with scanning electronic microscopy (SEM, Zeiss LEO 1550 microscope equipped with a EDX detector). X-ray diffraction (XRD) patterns of the Al anodes were investigated using a Bruker D8 Avance diffractometer (Bruker, Germany) with Cu-K α radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried

out on a Specs XPS system with a Phoibos 150 energy analyzer using monochromatic Al-K α radiation (1486.6 eV), a take-off angle of 45°, and a pass energy of 30 eV at the analyzer for the detail spectra. The XPS data were analyzed by Casa XPS software and all spectra were calibrated to the main C 1s peak (of C–C species) at 284.8 eV.

Statistical Analysis: EDX spectra of S cathodes were normalized to the C peak (Figure 3c); EDX spectra of Al anodes were normalized to the Al peak (Figure 4d). S 2p XPS spectra of the sulfur cathodes were normalized in accordance with the main peak in the C 1s spectra (Figure 3d). The reported ionic conductivity is the average value with a relative standard deviation $<0.7\%$, which was analyzed via Excel software. Cell data were statistically analyzed using the MimsClient software. The voltage versus time curves are primary test data obtained from Maccor battery tester 4300, the corresponding capacity curves are secondary test data calculated and transformed from the primary test data. The presented capacity data of the cells in each graph correspond to one specific cell. However, each cell reported in this work has been reproduced for at least two additional cells with the relative standard deviation of the final capacity after cycling $<6\%$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

C.X. and X.L. gratefully acknowledge the financial support from the Chinese Scholarship Council (CSC). All authors acknowledge the basic funding of the Helmholtz Association.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

aluminum–sulfur batteries, cyclability, electrolyte additives, solid electrolyte interphases

Received: December 9, 2022

Revised: January 20, 2023

Published online:

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