

ZnAl Alloy and Organosulfur Hybrid Energy Storage for a Long Term Cyclability

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Abstract

This research introduces a novel aqueous aluminum-sulfur (ZnAl alloy-organosulfur) hybrid battery, distinct from conventional organic electrolyte-based systems. Addressing the limitations of slow kinetics and anode degradation in traditional ZnAl alloy-organosulfur batteries, our approach integrates a cathode made of organosulfur compounds bonded with reduced graphene oxide (rGO) and a zinc-aluminum (ZnAl) alloy anode. The system employs an electrolyte of aluminum trifluoromethanesulfonate ($\text{Al}(\text{OTf})_3$) in deionized water ($\text{DI-H}_2\text{O}$) and organic solvent of acetonitrile (ACN), enhancing cycle stability and Coulombic efficiency. Demonstrating over 99.98% efficiency after 2000 cycles, extending to 5720 cycles, this development marks a significant advancement in ZnAl alloy-organosulfur battery technology. It highlights the potential of aqueous systems in achieving high performance while maintaining environmental safety, offering a noteworthy contribution to the field of energy storage.

Keywords: ZnAl alloy-organosulfur batteries, Organosulfur, ZnAl anode, Cycle stability

1. Introduction

Electrochemical capacitors (ECs) are considered as a promising energy storage technology owing to their fast charging rate, high power density, and long cyclability [1-3]. However, a low energy density of ECs limits their practical applications [4, 5]. In order to resolve this bottleneck, hybrid energy-storage devices that have different charge-storage mechanisms on each electrode in an asymmetric manner have been developed for a larger energy density than ECs and a larger power density and longer cyclic stability than batteries [6-9]. In particular, multivalent metal ion capacitors, including zinc [10-12], magnesium [13, 14], calcium [15], and aluminum ion carriers [16, 17], are regarded as an emerging hybrid energy storage device beyond the typical hybrid ECs, such as lithium ion capacitors [19, 20]. When the activated carbon electrodes of metal ion capacitors are replaced by other faradaic electrodes that have a fast charge storage kinetics and long cyclability comparable to those of ECs [3, 4, 9], the energy density can be further improved. Therefore, the high-capacity faradaic electrode reacting with multivalent metal ion carriers should be developed to achieve a large energy density of hybrid energy storage devices.

Recently, we have demonstrated two types of hybrid energy storage devices integrating the conversion-based sulfur electrodes with lithium and sodium ion carriers [20]. Sulfur has advantages in terms of its high theoretical capacity of 1675 mAh g^{-1} , arising from multi-electron conversion reactions, and low cost [4, 21, 22]. However, sulfur active materials are limited by the dissolution of polysulfide intermediates in polar solvents, low electronic conductivity, and volume expansion. Organosulfur is

considered an alternative to resolve this issue through the immobilization on the nanostructured carbons [20]. The conversion reaction kinetics of organosulfur confined on the surface of nanostructured carbon could be facilitated to be comparable to that of capacitive electrodes [20].

Al metal anodes are very attractive owing to their high theoretical capacity (2980 mAh g⁻¹ and 8040 mAh cm⁻³), good safety and natural abundance [23-25]. Despite the recent progress on the electrolyte and interfacial engineering [26-28], the reversible Al plating/stripping is still challenging due to the irregular deposition and uncontrollable reaction. The reversibility of Al deposition on Zn foil could be dramatically improved in aqueous/organic hybrid electrolytes through the formation of ZnAl alloy anodes.²⁹ However, the proper cathode counterparts pairing with ZnAl alloy anodes are required for the development of hybrid full cells. Considering high theoretical capacity and appreciable electrode potential of both Al anode and S cathode [30], the Al-organosulfur hybrid full cells are expected to be emerging energy storage devices.

Herein, we first demonstrate hybrid energy storage devices based on ZnAl alloy and organosulfur/reduced graphene oxide (rGO) for a long cyclability (>2000 cycles) and high energy density. 4-aminophenyl trisulfide organosulfur (SOS) was chemically immobilized onto the surface of rGO to construct SOS@rGO cathode, where the fast and reversible surface conversion reaction was revealed as verified by *in situ* and *ex situ* spectroscopic characterizations. Furthermore, the dissolution of aluminum polysulfides was inhibited in hybrid electrolytes containing 1.2 mol L⁻¹ aluminum trifluoromethanesulfonate (Al(OTf)₃) salt and a mixture of deionized water (DI H₂O)

and organic solvent of acetonitrile (ACN).

2. Results and discussion

In this work, SOS@rGO organosulfur composite was prepared in virtue of the formations of --CO--NH--R and --C--NH--R bonds between the surface oxygen functional groups of rGO and SOS (**Figure 1A**). The structure of SOS@rGO was verified using ^{13}C NMR and XPS methods. As shown in **Figure 1B** and **Figure S1**, the ^{13}C NMR presents specific chemical environments of four carbons, where C-1 (122.7 ppm) corresponds to --C--S-- chemical bond and the peak positions of C-2 (136.1 ppm), C-3 (118.0 ppm), and C-4 (146.8 ppm) are consistent with the carbons in benzene ring located at the ortho, meta, and para positions of --C--S-- , respectively [20, 31]. Moreover, both SOS@rGO and rGO show the typical sp^2 carbon peak of rGO at 116.8 ppm. Compared to the pristine rGO, the incorporation of SOS into the SOS@rGO composites enables to achieve the weaker intensities of --C--O--C-- and --C--OH-- peaks shielded [32]. The chemical bonding of SOS@rGO is further excavated by XPS in **Figure 1C-D** and **Figure S2**. The S 2p spectrum of SOS@rGO shows two types of the sulfur atoms, viz. terminal-S (S_T) connected to carbon at the end of the chain and bridging-S (S_B) connected to another S atom (**Figure 1C**) [20, 22, 33-34]. The peak located at 164.7 eV is assigned to the S_B of SOS@rGO, while the peak at 163.5 eV is attributed to the S_T of SOS@rGO. In **Figure 1D**, the N 1s spectra of SOS@rGO present two peaks at 399.6 and 400.5 eV, corresponding to secondary amine (--C--NH--R) and amide (--CO--NH--R) chemical bonds, respectively, while the peak of the C--NH_2 chemical bond is located at 399.2 eV. Comparably, SOS is endowed with the existence of C--NH_2 group from

molecular formula, while SOS@rGO possesses three C-N chemical bonds. As shown in the C 1s spectra of SOS@rGO (**Figure S2**), two main peaks are observed at 284.6 and 285.5 eV, corresponding to C-C and C-N bonds. Moreover, three small peaks are located at 287.0, 288.0, and 289.2 eV, which are assigned to C-OH , C-O (carbonyl), and $\pi-\pi^*$, respectively. As confirmed by XPS and NMR analyses, this chemical bonding is attributed to the chemical reaction between the amine functional groups of SOS and epoxy and acid groups of rGO [20, 35]. In addition, the content of sulfur is estimated as $\sim 32\%$, as investigated by thermogravimetric analysis in **Figure 1E**.

The morphology and microstructure of SOS@rGO composites were characterized collecting SEM and TEM images. As exhibited in **Figure 2**, the layered structure of SOS@rGO is clearly observed. The surface of the ultrathin rGO is relatively rough and full of wrinkles, which contributes to the large accessible surface area, indicating the existence of ample oxygen functional groups (see **Figure S3A-B**). The surface roughness of rGO is further changed after the generation of SOS@rGO using SEM and TEM (**Figures 2A and 2B** and **Figure S4**). Even after the formation of SOS@rGO composite, the exfoliated structure of rGO was preserved. The rGO surface is well wrapped with a uniform layer of SOS as shown in HR-TEM image (**Figure 2C**). The STEM EDX elemental mapping images of SOS@rGO demonstrates the homogenous distributions of carbon, sulfur, oxygen, and nitrogen atoms, indicating the uniform coating of SOS groups on the whole rGO surface (**Figure 2D** and **Figure S5**).

The as-prepared SOS@rGO was used as an active material of cathode for ZnAl alloy-organosulfur hybrid batteries. The coin type full cells were assembled paring

SOS@rGO with Zn foil in a hybrid electrolyte of DI-H₂O and ACN with Al(OTf)₃ salt. In order to maximize the energy density of the full cell, the potential window range and concentration of electrolyte were optimized as follows. As displayed in **Figure 3A**, the cyclic voltammogram (CV) curves of the cell shows there is an apparently larger current response in the range of 0.3 to 1.8 V than those of others at the same scan rate of 0.5 mV s⁻¹. Moreover, a cathodic peak at 1.07 V and an anodic peak at 1.34 V are clearly observed, and these peaks are overlapped in the subsequent cycles, which confirms the reversible redox reaction of ZnAl alloy-organosulfur hybrid batteries (**Figure S6**). Furthermore, the electrolyte concentrations of 0.8, 1.2, 1.6, and 3.0 mol L⁻¹ were optimized varying the amount of Al(OTf)₃ salt. The galvanostatic charging and discharging (GCD) profiles of ZnAl alloy-organosulfur hybrid batteries were measured in a 1.2 mol L⁻¹ of electrolyte at the constant current density of 200 mA g⁻¹ (**Figure 3B**). The curve shape of the sloped plateau was consistent with the CV profile (**Figure S6**). A higher capacity of ~190.4 mAh g⁻¹ was delivered at the first cycle compared with that of ZnAl alloy-organosulfur hybrid batteries with the electrolyte concentrations of 0.8, 1.6, and 3.0 mol L⁻¹ (**Figure S7**).

As shown in **Figure 3C**, ZnAl alloy-organosulfur hybrid batteries in a 1.2 mol L⁻¹ of electrolyte delivered the much higher capacities of 190 and 100 mAh g⁻¹ at 200 and 2000 mA g⁻¹, respectively, and better reversibility compared with those in 0.8, 1.6, and 3.0 mol L⁻¹ of hybrid electrolytes (**Figures S8 and S9**). More importantly, ZnAl alloy-organosulfur hybrid batteries retains a higher reversible capacity of ~134 mAh g⁻¹ after 450 cycles when current density keeps at 200 mA g⁻¹ in **Figure 3D**. The long-term

cycling performance of ZnAl alloy-organosulfur hybrid battery was further verified, as shown in **Figure 3E**. The ZnAl alloy-organosulfur hybrid battery achieved an initial discharge capacity of 154.9 mAh g⁻¹ at a current density of 400 mA g⁻¹. A low capacity fade rate of only 1.6% per cycle was achieved even over 5720 cycles, along with a high Coulombic efficiency of 99.98%.

In order to explore the charge storage behavior of the SOS@rGO electrode, *in situ* Raman spectra and the relevant GCD profile for ZnAl alloy-organosulfur hybrid battery are achieved in **Figure 4**. The Raman spectrum of the SOS@rGO electrode reveals characteristic peaks of -S-S-S- and -C-S- bonds at around 470 and 650 cm⁻¹, respectively (**Figure 4A**). Notably, the peak intensity of the -S-S-S- decreases as a new peak appears at 570 cm⁻¹ upon a discharging from 1.8 to 0.3 V (**Figure 4B**). This new peak is indicative of the formation of -NH-C₆H₄-S-S-Al. Conversely, the -S-S-S- peak reappears during the charging phase from 0.3 to 1.8 V, indicating the reconversion of -NH-C₆H₄-S-S-S-C₆H₄-HN-, accompanied by a reduction in the -S-S- peak intensity.

X-ray photoelectron spectroscopy (XPS) was further used to analyze the postmortem ZnAl alloy-organosulfur hybrid battery. The cathodes underwent examination at different stages of their discharge and charge cycles. Following discharge, the SOS@rGO cathode was carefully extracted and subjected to XPS analysis. As shown in **Figure 4C**, the peaks at 164.7 and 163.5 eV are identified as bridging sulfur (S_B) and terminal sulfur (S_T) in the SOS@rGO structure. These peaks correspond to fully reduced sulfur (S²⁻) and partially reduced sulfur (S⁻), respectively [34, 36-39]. When

the cathodes were charged to 1.80 V, the S2p spectra revealed a negative shift of 0.95 eV for S_B and 1.5 eV for S_T. This shift indicates a change in the S_T/S_B ratio, which is due to the conversion reactions of the SOS@rGO with Al³⁺ ions. Additionally, the detection of elemental sulfur species is evidenced by the S2p spectral peaks at 170.0 eV and 168.8 eV, corresponding to O₂S-CF₃ and S-O bonds, which is characteristic of the electrolyte salt. Moreover, the Al2p and Zn2p single was also detected from the electrode surfaces during all processes (**Figure S10** and **S11**), revealing a distinct interfacial chemistry upon cycling of the Zn–Al alloy anodes. Specifically, the Al 2p peaks observed in the Zn–Al alloy anodes exhibited a shift towards higher binding energies compared to those of pure metallic Al. This shift indicates an electron transfer from Al to Zn atoms during alloy formation, leading to an electron deficiency in the Al atoms (**Figure S10**). Meanwhile, the Zn 2p peaks demonstrated a shift towards lower binding energies compared to metallic Zn, which is attributed to the electron softening effect in Zn atoms (**Figure S11**) [28]. The above evidences doubtless confirm the existence and anode role of Zn–Al alloy.

3. Conclusions

In this research, we present a groundbreaking aluminum-sulfur (ZnAl alloy-organosulfur) battery system, utilizing a novel SOS@rGO organosulfur composite cathode and a zinc foil anode in an aqueous-based electrolyte. This system showcases superior electrochemical performance, characterized by a high initial discharge capacity of 190 mAh g⁻¹ at 400 mA g⁻¹ current density and an exceptional cycle life, maintaining a capacity fade rate of only 1.6% per cycle over 5500 cycles with a

Coulombic efficiency of 99.98%. The optimized 1.2 mol L⁻¹ Al(OTf)₃ electrolyte significantly contributes to this performance, enhancing stability and reversibility. This ZnAl alloy-organosulfur battery system marks a significant advancement in battery technology, setting new standards for capacity, longevity, and efficiency. Its development is pivotal for future energy storage solutions, offering a sustainable, high-performance alternative that could revolutionize energy systems worldwide. This research paves the way for further innovations in eco-friendly and efficient energy technologies, addressing global energy challenges.

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Conflict of Interest

The authors declare no conflict of interest.

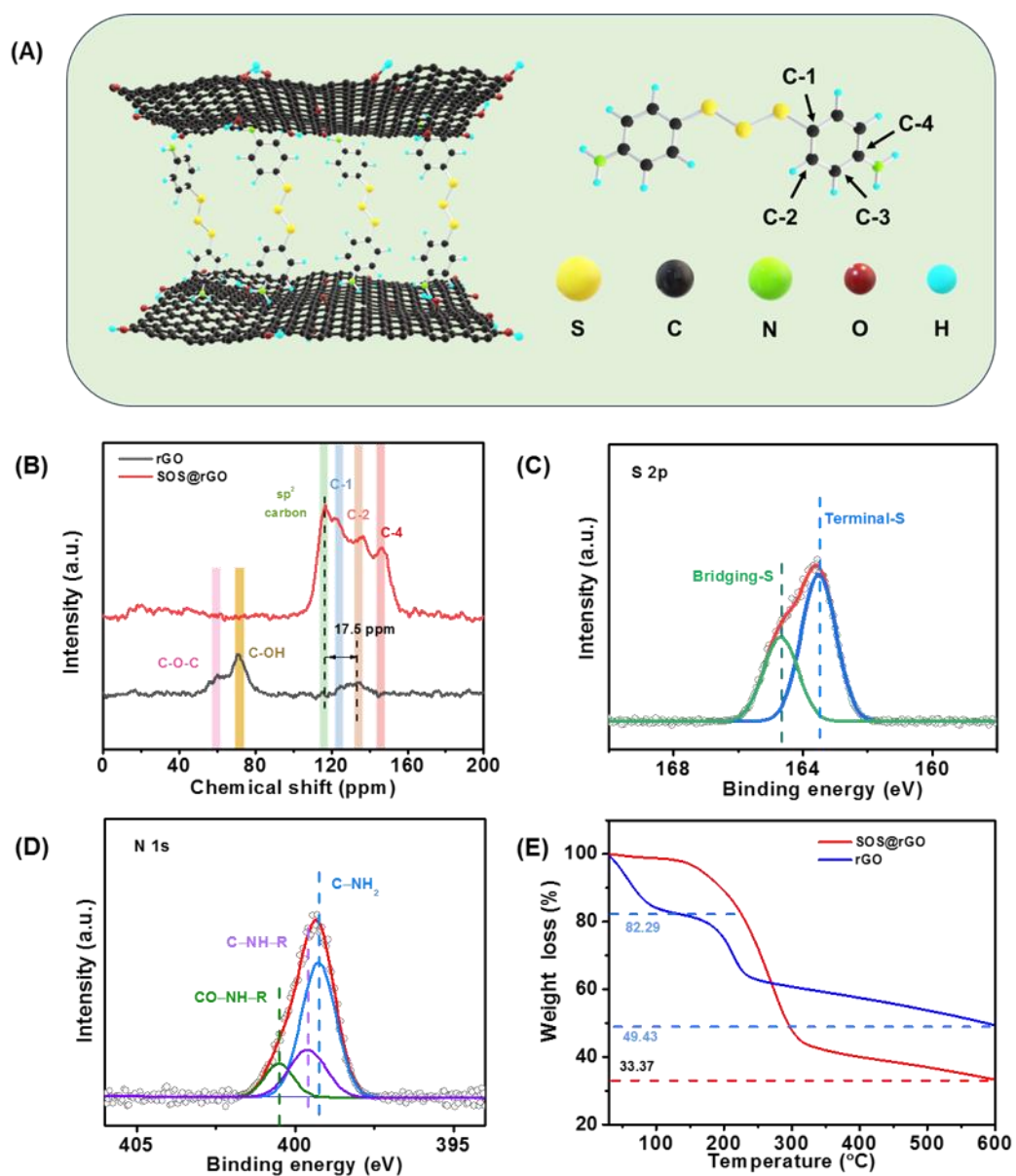


Figure 1. (A) Schematic illustration of SOS@rGO and the SOS molecule. (B) ¹³C MAS NMR spectra of SOS@rGO and rGO. (C) S 2p and (D) N 1s XPS curves of SOS@rGO. (E) TGA plot of SOS@rGO and rGO.

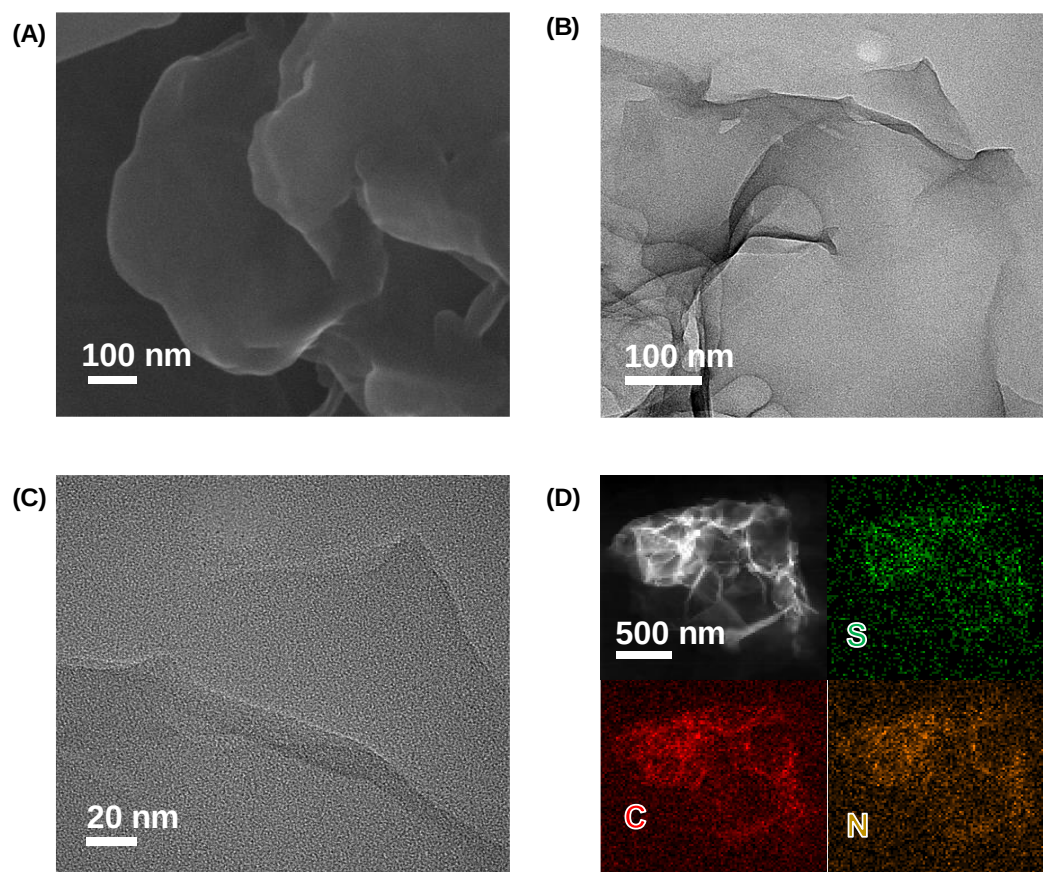


Figure 2. Structure and morphology of the SOS@rGO. (A) SEM image of SOS@rGO. (B) TEM image, (C) HR-TEM image of SOS@rGO. (D) STEM EDX mapping images of SOS@rGO.

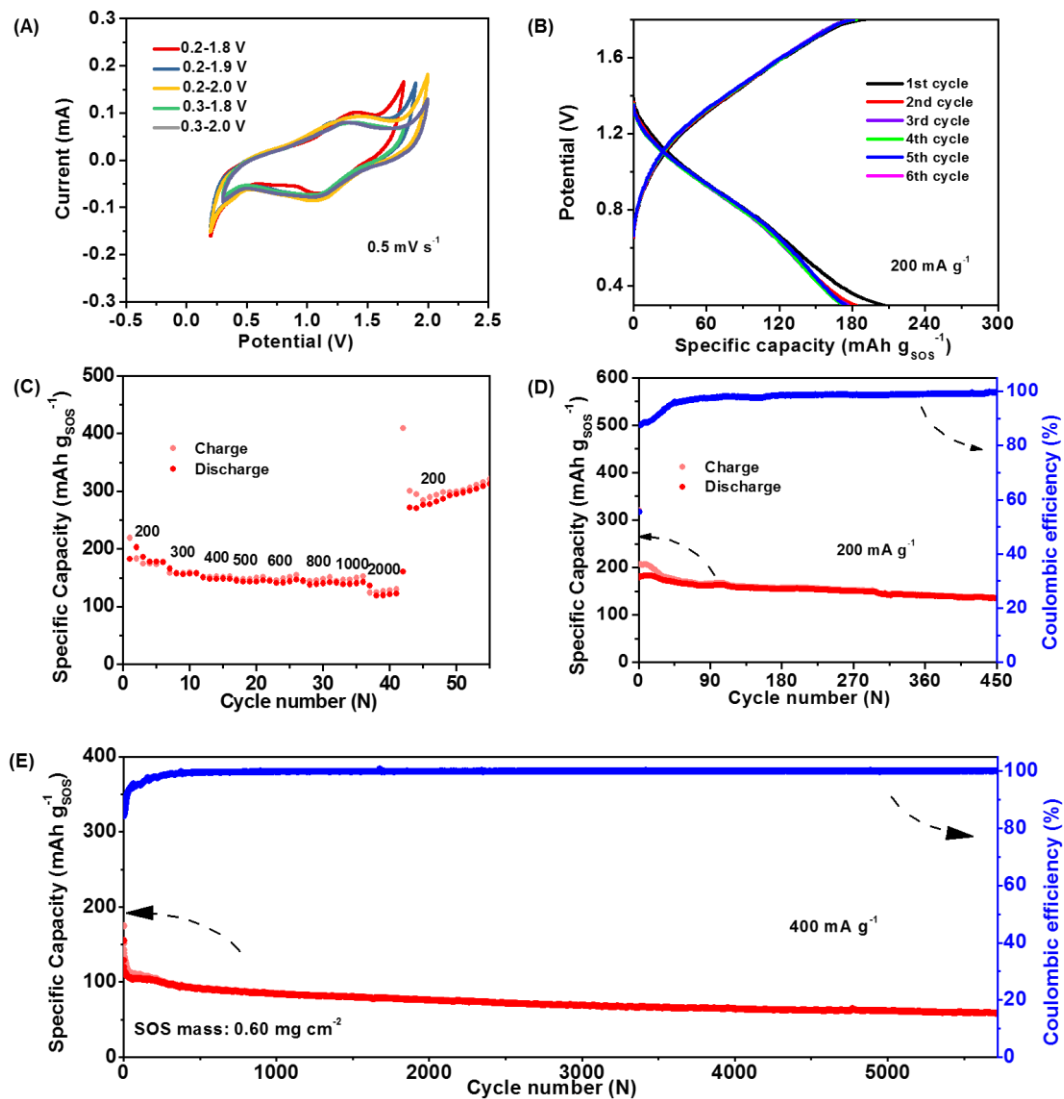


Figure 3. (A) CV curves of ZnAl alloy-organosulfur hybrid battery varying voltage windows at 0.5 mV s^{-1} . (B) GCD plots of ZnAl alloy-organosulfur hybrid battery at 200 mA g^{-1} . (C) Rate performance plots of ZnAl alloy-organosulfur hybrid battery at different current densities. (D) Cyclic stability of ZnAl alloy-organosulfur hybrid battery at 200 mA g^{-1} . (E) Cyclic stability of ZnAl alloy-organosulfur hybrid battery at 400 mA g^{-1} .

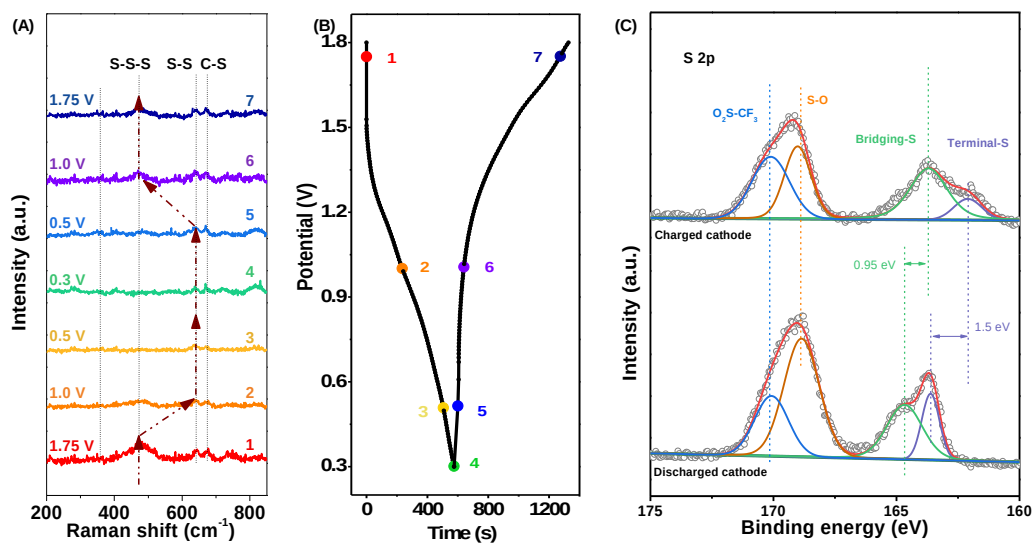


Figure 4. Surface redox charge-storage process of SOS@rGO. (A) *In-situ* Raman and (B) corresponding charge-discharge cycles of ZnAl alloy-organosulfur hybrid battery with 1.2 mol L⁻¹ Al(oTf)₃. (C) S 2p XPS spectra of cathode disassembled from ZnAl alloy-organosulfur hybrid battery.

Reference

- [1] B. Dunn, H. Kamath, J.-M. Tarascon, Electrical energy storage for the grid: A battery of choices, *Science* 334 (2011) 928–935.
- [2] J. R. Miller, P. Simon, Electrochemical capacitors for energy management, *Science* 321 (2008) 651–652.
- [3] Y. Shao, M. F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn, R. B. Kaner, Design and mechanisms of asymmetric supercapacitors, *Chem. Rev.* 118 (2018) 9233–9280.
- [4] C. Choi, D. S. Ashby, D. M. Butts, R. H. DeBlock, Q. Wei, J. Lau, B. Dunn, Achieving high energy density and high power density with pseudocapacitive materials, *Nat. Rev. Mater.* 5 (2020) 5–19.
- [5] M. R. Lukatskaya, S. Kota, Z. Lin, M.-Q. Zhao, N. Shpigel, M. D. Levi, J. Halim, P.-L. Taberna, M. W. Barsoum, P. Simon, Y. Gogotsi, Ultra-high-rate pseudocapacitive energy storage in two-dimensional transition metal carbides, *Nat. Energy* 2 (2017) 17105.
- [6] X. Yu, S. Yun, J. S. Yeon, P. Bhattacharya, L. Wang, S. W. Lee, X. Hu, H. S. Park, Emergent pseudocapacitance of 2D nanomaterials, *Adv. Energy Mater.* 8 (2018) 1702930.
- [7] R. Hou, G. S. Gund, K. Qi, P. Nakhanivej, H. Liu, F. Li, B. Y. Xia, H. S. Park, Hybridization design of materials and devices for flexible electrochemical energy storage, *Energy Storage Mater.* 19 (2019) 212–241.
- [8] J. M. Park, M. Jana, P. Nakhanivej, B.-K. Kim, H. S. Park, Facile multivalent redox chemistries in water-in-bisalt hydrogel electrolytes for hybrid energy storage full cells, *ACS Energy Lett.* 5 (2020) 1054–1061.
- [9] X. Gao, H. Wu, C. Su, C. Lu, Y. Dai, S. Zhao, X. Hu, F. Zhao, W. Zhang, I. P.

Parkin, C. J. Carmalt, G. He, Recent advances in carbon-based nanomaterials for multivalent-ion hybrid capacitors: A review. *Energy Environ. Sci.* 16 (2023) 1364–1383.

[10] X. Tian, S. Zhao, Y. Gao, H. Li, W. Cao, B. Xu, 3D printing-directed synergistic design of high-performance zinc-ion hybrid capacitors and nanogenerators for all-in-one self-powered energy wristband, *Adv. Func. Mater.* 33 (2023) 2300381.1–2300381.8.

[11] B. D. Boruah, B. Wen, S. Nagane, X. Zhang, S. D. Stranks, D. Boies, M. D. Volder, Photo-rechargeable zinc-ion capacitors using V_2O_5 -activated carbon electrodes, *ACS Energy Lett.* 5 (2020) 3132–3139.

[12] X. Li, M. Li, Q. Yang, H. Li, H. Xu, Z. Chai, K. Chen, Z. Liu, Z. Tang, L. Ma, Z. Huang, B. Dong, X. Yin, Q. Huang, C. Zhi, Phase transition induced unusual electrochemical performance of V_2CT_x MXene for aqueous zinc hybrid-ion battery, *ACS Nano* 14 (2020) 541–551.

[13] G. Pan, J. Li, L. Han, W. Peng, X. Xu, T. Lu, M. A. Amin, Y. Yamauchi, M. Xu, L. Pan, MoS_2 nanosheets with expanded interlayer spacing for ultra-stable aqueous Mg-ion hybrid supercapacitor, *Inorg. Chem. Front.* 9 (2022) 1666–1673.

[14] Y. Ding, S. Zhang, J. Li, Y. Sun, B. Yin, H. Li, Y. Ma, Z. Wang, H. Ge, D. Su, T. Ma, Enhanced elastic migration of manganese dioxide tunnels locally tuned by aluminium substitution, *Adv. Funct. Mater.* (2022) 2210519.

[15] N. Wu, W. Yao, X. Song, G. Zhang, B. Chen, J. Yang, Y. Tang, Calcium-ion hybrid energy storage device with high capacity and long cycling life under room temperature, *Adv. Energy Mater.* 9 (2019) 1803865.

[16] H. Ma, H. Chen, Y. Hu, B. Yang, J. Feng, Y. Xu, Y. Sun, H. Cheng, C. Li, X. Yan, L. Qu, Aqueous rocking-chair aluminum-ion capacitors enabled by a self-adaptive

electrochemical pore-structure remolding approach, *Energy Environ. Sci.* 15 (2022) 1131–1143.

[17] Z. Li, K. Xiang, W. Xing, W. C. Carter, Y.-M. Chiang, Reversible aluminum-ion intercalation in Prussian Blue analogs and demonstration of a high-power aluminum-ion asymmetric capacitor, *Adv. Energy Mater.* 5 (2015) 1401410.

[18] M. Jana, J. M. Park, M. Kota, K. H. Shin, H. H. Rana, P. Nakhanivej, J.-Q. Huang, H. S. Park, Surface redox-active organosulfur-tethered carbon nanotubes for high power and long cyclability of Na–organosulfur hybrid energy storage. *ACS Energy Letters* 6 (2021) 280–289.

[19] M. Jana, R. Xu, X.-B. Cheng, J. S. Yeon, J. M. Park, J.-Q. Huang, Q. Zhang, H. S. Park, Rational design of two-dimensional nanomaterials for lithium–sulfur batteries, *Energy Environ. Sci.* 13 (2020) 1049–1075

[20] P. Jeżowski, O. Crosnier, E. Deunf, P. Poizot, F. Béguin & T. Brousse, Safe and recyclable lithium-ion capacitors using sacrificial organic lithium salt, *Nat. Mater.* 17 (2018) 167-173. DOI: 10.1038/nmat5029

[21] Q. Liu, X. Han, H. Park, J. Kim, P. Xiong, H. Yuan, J. S. Yeon, Y. B. Kang, J. M. Park, Q. Dou, B.-K. Kim, H. S. Park, Layered double hydroxide quantum dots for use in a bifunctional separator of lithium–Sulfur batteries, *ACS Appl. Mater. Interfaces* 13 (2021) 17978.

[22] Q. Liu, X. Han, Z. Zheng, P. Xiong, R.-G. Jeong, G. Kim, H. Park, J. Kim, B.-K. Kim, H. S. Park, Crystallinity regulation of FeNi alloy nanoparticles for improvement of polysulfide suppression and electrochemical kinetics in lithium sulfur batteries, *Adv. Funct. Mater.* (2022) 2207094.

[23] G. A. Elia, K. Marquardt, K. Hoeppe, S. Fantini, R. Lin, E. Knipping, W. Peters, J.-F. Drillet, S. Passerini, R. Hahn, An overview and future perspectives of aluminum

batteries, *Adv. Mater.* 28 (2016) 7564-79. DOI: 10.1002/adma.201601357.

[24] Y. Wang, R. Chen, T. Chen, H. Lv, G. Zhu, L. Ma, C. Wang, Z. Jin, J. Liu, Emerging non-lithium ion batteries, *Energy Storage Mater.* 4 (2016) 103-129. DOI: 10.1016/j.ensm.2016.04.001.

[25] W. I. Sadat, L. A. Archer, The O₂-assisted Al/CO-electrochemical cell: A system for CO₂ capture/conversion and electric power generation, *Science Adv.* 2 (2016) e1600968. DOI: 10.1126/sciadv.1600968.

[26] N. Jayaprakash, S. K. Das, L. A. Archer, The rechargeable aluminum-ion battery, *Chem. Commun. (Camb)* 47 (2011) 12610-2. DOI: 10.1039/c1cc15779e.

[27] M. C. Lin, M. Gong, B. Lu, Y. Wu, D. Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B. J. Hwang, H. Dai, An ultrafast rechargeable aluminium-ion battery, *Nature* 520 (2015) 325-8. DOI: 10.1038/nature14340.

[28] S. Wang, Z. Yu, J. Tu, J. Wang, D. Tian, Y. Liu, S. Jiao, A novel aluminum-ion battery: Al/AlCl₃-[EMIm]Cl/Ni₃S₂@graphene, *Adv. Energy Mater.* 6 (2016) 1600137. DOI: <https://doi.org/10.1002/aenm.201600137>.

[29] Q. Dou, N. Yao, W. K. Pang, Y. Park, P. Xiong, X. Han, H. H. Rana, X. Chen, Z.-H. Fu, L. Thomsen, B. Cowie, Y. Kang, Q. Liu, D. H. Min, Y. M. Jung, Z. Guo, Q. Zhang, H. S. Park, Unveiling solvation structure and desolvation dynamics of hybrid electrolytes for ultralong cyclability and facile kinetics of Zn – Al alloy anodes, *Energy Environ. Sci.* 15 (2022) 4572-4583.

[30] T. Gao, X. Li, X. Wang, J. Hu, F. Han, X. Fan, L. Suo, A. J. Pearse, S. B. Lee, G. W. Rubloff, K. J. Gaskell, M. Noked, C. Wang, A rechargeable Al/S battery with an ionic-liquid electrolyte, *Angew. Chem. Int. Ed.* 55 (2016) 9898-9901. DOI: 10.1002/anie.201603531.

[31] M. Wu, A. Bhargav, Y. Cui, A. Siegel, M. Agarwal, Y. Ma, Y. Fu. Highly

reversible diphenyl trisulfide catholyte for rechargeable lithium batteries, *ACS Energy Letters* 1 (2016) 1221-1226. DOI: 10.1021/acsenergylett.6b00533.

[32] Y. Chen, S. Manzhos, A comparative computational study of lithium and sodium insertion into Van Der Waals and covalent tetracyanoethylene (TCNE)-based crystals as promising materials for organic lithium and sodium ion batteries, *Phys. Chem. Chem. Phys.* 18 (2016) 8874-80. DOI: 10.1039/c5cp07474f.

[33] L.-P. Hou, Y. Li, Z. Li, Q.-K. Zhang, B.-Q. Li, C.-X. Bi, Z.-X. Chen, L.-L. Su, J.-Q. Huang, R. Wen, X.-Q. Zhang, Q. Zhang, Electrolyte design for improving mechanical stability of solid electrolyte interphase in lithium-sulfur batteries, *Angew. Chem. Int. Ed.* 62 (2023) e202305466 doi: 10.1002/anie.202305466.

[34] Q. Liu, X. Han, Q. Dou, P. Xiong, Y. Kang, S. W. Kang, B. K. Kim, H. S. Park. Multiphase and multicomponent nickel-iron oxide heterostructure as an efficient separator modification layer for advanced lithium sulfur batteries, *Batteries & Supercaps* 4 (2021) 1843-1849. DOI: 10.1002/batt.202100156.

[35] O. C. Compton, D. A. Dikin, K. W. Putz, L. C. Brinson, S. T. Nguyen, Electrically conductive "Alkylated" graphene paper via chemical reduction of amine-functionalized graphene oxide paper, *Adv. Mater.* 22 (2010) 892-896. DOI: 10.1002/adma.200902069.

[36] Y.-W. Song, L. Shen, N. Yao, S. Feng, Q. Cheng, J. Ma, X. Chen, B.-Q. Li, Q. Zhang, Anion-involved solvation structure of lithium polysulfides in lithium-sulfur batteries, *Angew. Chem. Int. Ed.* (2024) e202400343. doi: 10.1002/anie.202400343.

[37] M. Zhao, H. J. Peng, B. Q. Li, X. Chen, J. Xie, X. Liu, Q. Zhang, J. Q. Huang, Electrochemical phase evolution of metal-based pre-catalysts for high-rate polysulfide conversion, *Angew. Chem. Int. Ed.* 59 (2020) 9011.

[38] W. J. Qu, Z.Y. Lu, C. N. Geng, L. Wang, Y. Guo, Y. B. Zhang, W. C. Wang, W. Lv, Q. H. Yang, Targeted catalysis of the sulfur evolution reaction for high-

performance lithium-sulfur batteries, *Adv. Energy Mater.* 12 (2022) 202202232. DOI: 10.1002/aenm.202202232

[39] B. Zhang, C. Luo, G. Zhou, Z.-Z. Pan, J. Ma, H. Nishihara, Y.-B. He, F. Kang, W. Lv, Q.-H. Yang, Lamellar MXene composite aerogels with sandwiched carbon nanotubes enable stable lithium-sulfur batteries with a high sulfur loading, *Adv. Func. Mater.* 31 (2021) 2100793.

