Understanding the Failure Mechanism of Rechargeable Aluminum Batteries: Metal Anode Perspective Through X-Ray Tomography

Ji Eun Wang, Alyssa Gilbert, Jason B. Harper,* and Dong Jun Kim*

Rechargeable aluminum batteries (AlBs), which represent cost-effective energy-storage devices due to the abundance of natural aluminum resources, have emerged as promising candidates for the next generation of rechargeable batteries. Although the electrochemical deposition of aluminum in ionic liquids (ILs) is well investigated for aluminum refining, the reversible electrochemical deposition/dissolution behavior of aluminum ions is not trivial. More specifically, the dendrite growth issue, which is common in Li metal anodes, is scarcer or vague. Herein, the electrochemical stability of the aluminum metal anode in IL electrolytes is investigated and the failure mechanism is discussed. It is confirmed that the inorganic anion of ILs mainly affects the electrochemical stability, whereas the organic cation influences the aluminum metal degradation. X-ray computed tomography results further identify deterioration of the surface morphology of the aluminum metal. The formation of “dead aluminum” is further confirmed, which indeed causes cell failure with repeated cycles. Finally, using the predeposited aluminum graphene paper as an alternative anode candidate for AlBs is further demonstrated.

1. Introduction

The increasing concern on climate change has created a considerable demand for more efficient and safe energy storage.[1] Such demands have propelled the rapid development of lithium-ion batteries (LIBs), and their use is now commonplace.[2] It is forecast that next-generation rechargeable batteries will require much-improved safety and energy density and will need to be made with abundant elements. Here, extensive research is under way to address these challenges, such as Li metal batteries, sodium- or potassium-ion batteries, and aluminum batteries (AlBs).[3–7] Among these, AlBs are attractive candidates for large-scale energy storage due to their high energy-to-price ratio.[8] AlBs feature one of the highest theoretical capacities, and the aluminum element is highly abundant.[8,9]

Most AlBs involve ionic liquids (ILs) as an electrolyte due to the highly oxidizing character of aluminum metal.[3–6] Furthermore, the nonvolatile and heat-resistant nature of ILs decrease their flammability.[10,11] Although aluminum deposition in ILs has been studied for more than decades,[12,13] fewer studies have been undertaken toward aluminum metal stability in a rechargeable battery configuration. This difference is noteworthy, especially considering that numerous Li metal studies have investigated various parameters, such as interface stability, failure mechanism, and electrochemical performance.[14–18] It is appreciated that understanding lithium–electrolyte interactions provides a basis for developing safe and stable Li metal batteries. Therefore, elucidating the interactions between the aluminum anode and ILs as analogous with those prevalent in Li anode–organic electrolyte systems is an essential step toward achieving high-performance AlBs.

The work described herein focused on gaining insight into the aluminum/IL interface, particularly the failure mechanism of the aluminum anode during electrochemical cycling. To this end, we prepared three different structural analogues of widely adopted [Emim]Cl ILs (Figure 1). The electrochemical characterization identified structural effects on the potential window of the electrolyte. To gain further insights, repeated aluminum deposition/dissolution electrodes were analyzed by scanning electron microscopy (SEM) and X-ray computed tomography (XCT). The results showed a distinct difference in surface deterioration behavior depending on the ILs. Finally, we demonstrated cathode-free AlBs with aluminum-predeposited graphene paper (GP) anode, which prevents cell failure caused by the build-up of “dead aluminum.”

2. Results and Discussions

2.1. Understanding Electrochemical Stability of ILs as Electrolytes

The general requirements for a reliable electrolyte include a wide electrochemical potential window, high ionic conductivity,
minimal side reactions, and moderate solvation/desolvation properties.\[^{[3]}\] In particular, the electrochemical potential window depends heavily on the types of cations, anions, and their concentrations.\[^{[19,20]}\] Up until now, aluminum chloride (AlCl\(_3\)) in 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) is the predominantly used electrolyte in AlBs.\[^{[21–25]}\] To investigate the structure–property relationships of the imidazolium-based ILs, we prepared three additional electrolytes by adding either aluminum halide salts (AlCl\(_3\) or AlBr\(_3\)) to corresponding imidazolium halides: 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-ethyl-3-methylimidazolium bromide ([Emim]Br), and 1-butyl-3-methylimidazolium bromide ([Bmim]Br). All electrolytes were prepared by mixing the imidazolium-based IL and the appropriate aluminum halide in a molar ratio of 1/1 or 1/1.5 at 75\(^\circ\)C, followed by slow cooling to room temperature. Cyclic voltammetry (CV) analysis was conducted with aluminum foil as a counter electrode and Mo foil as a working electrode to prevent reaction with the ILs.\[^{[26]}\] Detailed experimental conditions are described in the Experimental Section.

We first investigated the potential window of ILs comprising different cations and anions at various concentrations. The concentration of aluminum salts in the IL is a critical condition that determines the types of carrier ions and reactivity with the aluminum metal.\[^{[19,27]}\] For equal molar ratio of imidazolium halide and aluminum halide, the solution forms AlX\(_4^-\) anion and features a neutral condition. When the ratio is over 1, some of the Al\(_2X_7^-\) anion forms and the solution is basic. Note that [Emim]Br ([Emim]Br/AlBr\(_3\) = 1/1) dissolved as the liquid state at 75\(^\circ\)C but solidified upon cooling to room temperature.

Irrespective of the nature of the cation and the anion, when one equivalent of aluminum halide is present, ILs do not exhibit aluminum deposition/dissolution (Figure 2a–d) due to lacking higher-order chloroaluminate.\[^{[6,11,13]}\] The lack of intervention from aluminum-involved reactions allows us to analyze the potential window of ILs. Three imidazolium-based ILs displayed a cathodic peak approximately at −2 V versus Al/Al\(^{3+}\) due to the reduction of either the [Emim]\(^+\) or [Bmim]\(^+\) cation (Figure 2a,b,d). The similar cathodic potentials for all electrolytes reflect that the differences in the carbon chains or the halogen anions have a negligible effect on the reduction potential of the ILs. This outcome is not surprising given that the expected reaction at this potential would be reduction of the imidazolium center on the cation of the IL, which would be expected not to be affected to any significant extent by the length of the alkyl chain. The cathodic limit of −2 V is below the standard reduction potential of Al/Al\(^{3+}\), indicating that all three types of electrolytes would be stable concerning aluminum deposition/dissolution at 0 V.

Both [Emim]Cl/AlCl\(_3\) = 1/1 and [Bmim]–Cl/AlCl\(_3\) = 1/1 showed anodic peaks at around 4.5 V versus Al/Al\(^{3+}\) (Figure 2a,b), whereas [Bmim]Br ([Bmim]Br/AlBr\(_3\) = 1/1) appeared at around 4 V (Figure 2d). This anodic current peak difference unsurprisingly differs with the halogen involved, as shown in Equation (1).\[^{[6]}\]

\[
4\text{AlX}_4^- - 2e^- \rightarrow \text{X}_2 + 2\text{Al}_2\text{X}_7^- \quad (X = \text{Cl or Br})
\]

In addition, [Emim]Cl and [Bmim]Cl electrolytes displayed higher decomposition voltages than Br analogues, which implies that oxidative decomposition is mainly affected by the anion of the coordinating IL. This observation is consistent with the previous reports that oxidation of the anion is responsible for anodic decomposition of ILs.

![Figure 1. Chemical structures of 1-ethyl-3-methylimidazolium ([Emim]\(^+\), left) and 1-butyl-3-methylimidazolium ([Bmim]\(^+\), right)-based ILs. X = Cl or Br and Y = Cl or Br.](image)

![Figure 2. Cyclic voltammetry of prepared ILs. a–d) Electrochemical voltage stability window analysis of ILs with the ratio of imidazolium to aluminum salt of 1/1. e–f) Aluminum deposition/dissolution profile with the ratio of imidazolium to aluminum salt of 1/1.5.](image)
Next, we increased the molar ratio of AlX₃ (X = Cl) and achieved the cathodic and anodic ratios of [Emim]Cl/AlCl₃ = 1.1.5 and [Bmim]Cl/AlCl₃ = 1.1.5. Both of these mixtures were liquid at room temperature. The aluminum deposition/dissolution reaction and decomposition of the anion were investigated through CV in the voltage range from −0.5 to 2.5 V versus Al/Al³⁺. The CV data (Figure 2e,f) displayed the cathodic and anodic peaks from −0.5 to 0 V and 0 to 0.5 V, respectively. Each peak corresponds to the aluminum deposition and dissolution, which agrees with the previous reports.[20,28]

The equivalent processes evaluated in the corresponding bromide cases are shown in Figure 2g,h. The cathodic and anodic peaks are present in the −0.5 to 0.5 V range, referring to aluminum deposition and dissolution.

These data indicate that the acidic environment, containing the polymeric haloaluminate of Al₂X₇⁻, enables the reversible aluminum deposition/dissolution reaction, as follows.

$$4\text{Al}_2\text{X}_7^- + 3e^- \leftrightarrow \text{Al} + 7\text{AlX}_4^- \quad (X = \text{Cl or Br}) \quad (2)$$

In addition, all samples exhibited an anodic current flow exceeding 2 V on account of the decomposition and the evolution of halogens.[31] Similar to Equation (1), haloaluminate anions present in the ILs (Al₂X₇⁻) decompose as below.[6]

$$6\text{Al}_2\text{Cl}_7^- - 2e^- \rightarrow 2\text{X}_2 + 4\text{Al}_2\text{X}_{10}^- \quad (X = \text{Cl or Br}) \quad (3)$$

While there are subtle differences between the CV data at low potentials, we confirmed clear differences for the decomposition potential, depending on the type of cation and anion. The anionic decomposition of [Emim]Br and [Bmim]Br occurred at 1.95 and 1.87 V, respectively, slightly below the corresponding values for Cl-based ILs. It is foreseeable that the relatively weaker bond to aluminum and larger ionic radius of Br⁻ resulted in a narrower potential window.[20,32] Furthermore, we observed an additional cathodic peak in the 0.5–1.7 V range, implying the occurrence of side reactions in the IL electrolytes (Figure 2f,g). This degradation indicates the gradual removal of Al₂O₃ film and loss of aluminum metal due to the formation of “dead aluminum.” In Figure 3h, only region (1) of the aluminum foil was exposed to IL electrolyte during the electrochemical cycle. Apparent difference between region (1) and (2) explicitly shows severe degradation of aluminum foil due to electrochemical aluminum dissolution. Furthermore, the photo (Figure 3i) of aluminum electrode verifies the formation of dead Al and repeated loss of aluminum metal resulted in cell failure of AlBs.

2.3. Morphology Characterization of Aluminum Anode Via X-Ray Tomography

The morphological deterioration of the aluminum anode was reconstructed into a 3D image via X-ray tomography techniques (Figure 4 and S2, Supporting Information). Microcomputed tomography (μCT) uncovers a detailed degradation of the aluminum anode, whereas X-ray nanotomography provides high-resolution surface deposition and roughness images.

Following by initial aluminum deposition under the [Emim]Cl-based electrolyte, the sample retained (Figure 4a) a relatively smooth surface morphology. According to the X-ray nanotomography images, a partially covered layer was indicated, which suggests the deposition of a decomposed residual electrolyte (Figure 4b). In contrast, the aluminum dissolution process caused several pits of different sizes and depths scattered throughout the surface (Figure 4c). X-ray nanotomography further identified the rough and inconsistent surface morphology, verifying the pits up to 10 μm (Figure 4d). It is worth mentioning that we did not observe dendritic morphology throughout the cycling tests. The formation of pits after repeated cycles,
however, implies that aluminum metal continuously falls off, presumably forming “dead aluminum.”

We further analyzed the dependence of the morphology deterioration on the nature of the electrolyte. After the tenth cycle of aluminum deposition/dissolution, exposure of the electrodes to the [Bmim]Cl-based electrolyte induced larger and deeper holes (Figure 4e–h). Based on the SEM images, the sizes and distribution of the holes clearly differed from those observed for the electrodes exposed to the [Emim]Cl-based electrolyte. The difference in surface morphology indicates that the cation of the ILs used to form the electrolyte considerably affected the forming of a stable solid–electrolyte interphase (SEI) or electrical double-layer structure. The X-ray tomography images also confirmed less uniform aluminum deposition in the presence of the [Bmim]Cl-based electrolyte (Figure 4g,h). We could not fully determine the structure factor that induced an irregular interface or electrical double layer. However, the tomography images and high overpotential results imply that the structural effect from the organic cation and Al₂O₃ layer primarily triggered the formation of dead aluminum during battery cycling.

2.4. Aluminum Metal-Predeposited Anode on the graphene paper

As the most reported AlBs use aluminum metal as both current collector and anode, the build-up of dead aluminum possibly leads to the loss of contact and, inevitably, cell failure. Therefore, we searched for alternative anode candidates that 1) enable reversible aluminum deposition/dissolution, 2) avoid the potential formation of Al₂O₃ layer, and 3) prevent dead aluminum generation. To this end, we prepared an aluminum metal-predeposited anode on GP. Notably, conventional Cu, Ni, and stainless steel current collectors experience severe corrosion and consequently, could not be implemented in AlBs.

In an attempt to fabricate full-cell AlBs, we coupled aluminum-predeposited GP and free-standing GP as an anode
and cathode, respectively (Figure 5a). The aluminum-predeposited GP provides the aluminum complex source in the ALB, while pristine GP functions as cathode as well as current collector (Figure S3, Supporting Information). As the aluminum complex is stored only on the anode, while the cathode is free of any aluminum source, this cell can be defined as “cathode-free” ALBs, similar to the anode-free configuration in LIB analogues.[39,40]

The cathode-free ALB showed a capacity of 35 mAh g\(^{-1}\) (based on the total mass of the electrode) and good stability up to 60 cycles with high coulombic efficiency (CE) (Figure 5b). The voltage profile shown in Figure 5c corresponds to the intercalation reaction of AlCl\(_4\) with the GP.[22,41,42] The stable capacity retention suggests that the aluminum-predeposited GP could function as an anode in ALBs. SEM images of the aluminum-predeposited GP (Figure 5d) and ex situ GP anode after 60 cycles (Figure 5e–f) confirm that the surface morphology remains intact after repeated cycles. As the conventional aluminum anode cannot eliminate the formation of dead aluminum, the aluminum metal predeposition approach demonstrates a promising strategy for improving the anode stability in ALBs.

3. Conclusion

In summary, we investigated the compatibility and stability of electrolytes based on imidazolium-based ILs toward reversible aluminum deposition/dissolution. Although all tested acidic ILs displayed reversible aluminum deposition/dissolution, there...
were evident differences regarding electrochemical stabilities and aluminum metal degradation. The potential window and incidence of side reactions were largely affected by the types of organic cations and haloluate anions generated from the ILs. More importantly, even though the Al₂O₃ layer was removed by precycling, the initial presence of a stable oxide layer disrupts uniform deposition/dissolution. This inconsistent morphology possibly triggers the generation of dead aluminum, which accelerates the electrode surface deterioration. To this end, we prepared the predeposited aluminum metal electrode on GP and it exhibited stable cycle performance with minimal surface degradation. Our findings suggest that the aluminum metal predeposition approach is a potential solution to extend the cycle life of AlBs.

4. Experimental Section

Preparation of IL Electrolytes: [Emim]Cl and the aluminum salts were commercially available. The remaining imidazolium salts ([Bmim]Cl, [Emim]Br, and [Bmim]Br) were prepared through alkylation of N-methylimidazole with the appropriate alkyl halide under microwave irradiation at 100 °C, either 15 min [chlorides] or 5 min [bromides], followed by washing with ethyl acetate. The resultant salts were dried to constant weight under vacuum prior to use and showed physical and spectroscopic data consistent with literature reports.[43,44]

All chemicals were stored in an Ar-filled glove box, and electrochemical measurements were carried out using a potentialostat (BioLogic VSP potentiostat). CV analysis was conducted at a scan rate of 5 mV s⁻¹. Galvanostatic aluminium deposition/dissolution tests with Al-Al symmetric cells were conducted with a current density of 0.1 mA cm⁻² and areal capacity of 0.1 mAh cm⁻². Cathode-free AlBs were assembled using GP as a current collector of both anode (18 mm diameter with aluminum predeposition) and cathode (12 mm diameter), with glass fiber separator (18 mm diameter) and [Emim]Cl electrolytes (150 µL). Aluminum-predeposited GP anode was prepared by electrochemical deposition of aluminium under 0.1 mA cm⁻² current density for 10 h. Cathode-free AlB cell was cycled under 10 mA g⁻¹ current density based on the mass of GP cathode from a potential range of 1.0–2.15 V.

Ex Situ Characterization and X-Ray Microtomography: Ex situ electrode samples were retrieved by disassembling the cell in the Ar-filled glove box. SEM imaging was conducted with S3400 (Hitachi) after Pt coating on the sample surface (Emitech K575x Pt sputter coater). The X-ray tomography in microscale was conducted at the Tyree X-ray facilities at the University of New South Wales using HeliScanTM micro-CT (Mark I). The system had a Hamamatsu X-ray tube with a diamond window and a high-quality flatbed detector (3072 × 3072 pixels, 3.75 fps readout rate). The samples were scanned in a double-helix trajectory with the following setting: 80 kV, 82 µA (tube current), exposure time: 0.45 s, three accumulations, 1 Al filter, and 2880 projections per revolution. The voxel size obtained from this sample was 1.4 µm. The tomographic reconstruction was conducted using QMango software developed by the Australian National University.

X-ray nanotomography measurements were carried out at the 7C-XNI nanomaging beamline, at Pohang Light Source-II (PLS-II) in the Republic of Korea, which was designed for both spectral microscopy and nanotomography of ≈30 nm spatial resolution utilizing zone plate-based full-field transmission X-ray microscopy (TXM). Monochromatic X-rays, 9.3 keV, were selected by a liquid nitrogen-cooled double-crystal monochromator (DCM) and focused using a rhodium-coated horizontal focusing plane mirror (HFM) and a vertical focusing plane mirror (VFM). For X-ray
nanotomography, a golden objective zone plate of 30 nm outermost zone width, 300 μm diameter, and 0.9 μm thickness was used. To obtain a high-contrast image, Zernike phase-contrast method was applied using a holed golden film phase plate of 960 nm thickness (π/2 phase shift). As a detector, a scintillator-coupled optical microscope incorporating a thin scintillation crystal (20 μm-thick GAGG:Ce), a 20× optical objective, and a high-end charge-coupled device with 2048 × 2048 sensors of 15 μm pixel size was used. In this experiment, the field of view was 45 μm, and the effective pixel size (with two bins) was equivalent to 44 nm. For each tomography scan, 720 projections (0°–180°) were acquired with 1 s exposure time. Tomographic reconstruction was conducted based on the filtered back-projection algorithm method (Octopus software). The segmentation and visualization of the 3D data were conducted using a commercial software package known as Avizo.

Supporting Information

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

Acknowledgements

D.J.K. acknowledges support from the Australian Research Council (DE210101618). J.B.H. also acknowledges support from the Australian Research Council (DP180103682). The authors acknowledge the facilities and the scientific and technical assistance of Microscopy Australia at the Electron Microscope Unit (EMU) within the Mark Wainwright Analytical Centre (MWAC) at UNSW Sydney for the acquisition of scanning electron microscope images and the Tyree X-ray CT Facility, a UNSW network lab funded by the UNSW Research Infrastructure Scheme, for the acquisition of the 3D μCT images. In addition, the authors acknowledge the support of the 7C-XN1 beamline at Pohang Accelerator Laboratory (PAL), Pohang, Republic of Korea, regarding the acquisition of synchrotron X-ray nanotomography images.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

aluminum metal anodes, dead aluminum, ionic liquid electrolytes, rechargeable aluminum batteries, X-ray tomography

Received: October 1, 2021
Published online: October 28, 2021

[1] S. Chu, Y. Cui, N. Liu, Nat. Mater. 2017, 16, 16.
[2] B. Dunn, H. Kamath, J.-M. Tarascon, Science 2011, 334, 928.
[3] H. Yang, H. Li, J. Li, Z. Sun, K. He, H. Cheng, F. Li, Angew. Chem. Int. Ed. 2019, 58, 11978.
[4] G. A. Elia, K. Marquardt, K. Hoeppner, S. Fantini, R. Lin, E. Knipping, W. Peters, J.-F. Drillet, S. Passerini, R. Hahn, Adv. Mater. 2016, 28, 7564.
[5] P. K. Nayak, L. Yang, W. Brehm, P. Adelhelm, Angew. Chem. Int. Ed. 2018, 57, 102.
[6] N. Zhu, K. Zhang, F. Wu, Y. Bai, C. Wu, Energy Mater. Adv. 2021, 1.
[7] H. Kim, J. C. Kim, M. Bianchini, D. Seo, J. Rodriguez-Garcia, G. Ceder, Adv. Energy Mater. 2018, 8, 1702384.
[8] Q. Li, N. J. Bjerrum, J. Power Sources 2002, 110, 1.
[9] P. Canepa, G. Sai Gautam, D. C. Hannah, R. Malik, M. Liu, K. G. Gallagher, K. A. Persson, G. Ceder, Chem. Rev. 2017, 117, 4287.
[10] X. Tu, J. Zhang, M. Zhang, Y. Cai, H. Lang, G. Tian, Y. Wang, RSC Adv. 2017, 7, 14790.
[11] M. Galiński, A. Lewandowski, I. Stępiński, Electrochim. Acta 2006, 51, 5567.
[12] A. P. Abbott, K. J. McKenzie, Phys. Chem. Chem. Phys. 2006, 8, 4265.
[13] A. P. Abbott, G. Frisch, K. S. Ryder, Annu. Rev. Mater. Res. 2013, 43, 335.
[14] L. Liang, X. Sun, J. Zhang, J. Sun, L. Hou, Y. Liu, C. Yuan, Mater. Horizons 2019, 6, 871.
[15] M. He, R. Guo, G. M. Hobold, H. Gao, B. M. Gallant, Proc. Natl. Acad. Sci. 2020, 117, 73.
[16] A. A. Assegie, C.-C. Chung, M.-C. Tsai, W.-N. Su, C.-W. Chen, B.-J. Hwang, Nanoscale 2019, 11, 2710.
[17] B. Moorthy, R. Ponraj, J. H. Yun, J. E. Wang, D. J. Kim, D. K. Kim, ACS Appl. Energy Mater. 2020, 3, 11053.
[18] P. Muralidharan, J. H. Yun, R. Ponraj, J. E. Wang, D. J. Kim, D. K. Kim, J. Alloys Compd. 2021, 888, 161522.
[19] R. J. Gale, R. A. Osteryoung, Inorg. Chem. 1979, 18, 1603.
[20] H. Wang, S. Gu, Y. Bai, S. Chen, N. Zhu, C. Wu, F. Wu, J. Mater. Chem. A 2015, 3, 22677.
[21] X. Yu, M. J. Boyer, G. S. Hwang, A. Manthiram, Chem 2018, 4, 586.
[22] C.-J. Pan, C. Yuan, G. Zhu, Q. Zhang, C.-J. Huang, M.-C. Lin, M. Angell, B.-J. Hwang, P. Kaghazchi, H. Dai, Proc. Natl. Acad. Sci. 2018, 115, 5670.
[23] D. J. Kim, D.-J. Yoo, M. T. Otley, A. Prokofjevs, C. Pezzato, M. Owczarek, S. J. Lee, J. W. Choi, J. F. Stoddart, Nat. Energy 2019, 4, 51.
[24] T. Gao, X. Li, X. Wang, J. Hu, F. Han, X. Fan, L. Luo, A. J. Pearse, S. B. Lee, G. W. Rubloff, K. J. Gaskell, M. Noked, C. Wang, Angew. Chemie Int. Ed. 2016, 55, 9898.
[25] L. D. Reed, E. Menke, J. Electrochem. Soc. 2013, 160, A915.
[26] Y. Oh, G. Lee, Y. Tak, ChemElectroChem 2018, 5, 3348.
[27] T. Tsuda, G. R. Stafford, C. L. Hussey, J. Electrochem. Soc. 2017, 164, H5007.
[28] N. Canever, N. Bertrand, T. Nann, Chem. Commun. 2018, 54, 11725.
[29] M. Angell, C.-J. Pan, Y. Rong, C. Yuan, M.-C. Lin, B.-J. Hwang, H. Dai, Proc. Natl. Acad. Sci. 2017, 114, 834.
[30] A. Kitada, K. Nakamura, K. Fukami, K. Murase, Electrochim. Acta 2016, 211, 561.
[31] P. R. Gifford, J. B. Palmisano, J. Electrochem. Soc. 1987, 134, 610.
[32] H. Yang, L. Yin, L. Liang, Z. Sun, Y. Wang, H. Li, K. He, L. Ma, Z. Peng, S. Qiu, C. Sun, H.-M. Cheng, F. Li, Angew. Chem. Int. Ed. 2018, 57, 1898.
[33] H. Wang, S. Gu, Y. Bai, S. Chen, F. Wu, C. Wu, ACS Appl. Mater. Interfaces 2016, 8, 27444.
[34] T. Cai, L. Zhao, H. Hu, T. Li, X. Li, S. Guo, Y. Li, X. Xue, X. W. Xing, Z. Yan, L. Wang, Energy Environ. Sci. 2018, 11, 2341.
[35] X. Wen, J. Zhang, H. Luo, J. Shi, C. Tsay, H. Jiang, Y.-H. Lin, M. A. Schroeder, K. Xu, J. Guo, J. Phys. Chem. Lett. 2021, 12, 5903.
[36] J. Yang, C. Lian, H. Liu, Chem. Eng. Sci. 2020, 227, 115927.
[37] H. Chen, H. Xu, B. Zheng, S. Wang, T. Huang, F. Guo, W. Gao, C. Gao, ACS Appl. Mater. Interfaces 2017, 9, 22628.
[38] D.-J. Yoo, J.-S. Kim, J. Shin, K. J. Kim, J. W. Choi, ChemElectroChem 2017, 4, 2345.
[39] Y. Tian, Y. An, C. Wei, H. Jiang, S. Xiong, J. Feng, Y. Qian, *Nano Energy* 2020, 78, 105344.
[40] Z. Xie, Z. Wu, X. An, X. Yue, J. Wang, A. Abudula, G. Guan, *Energy Storage Mater.* 2020, 32, 386.
[41] H. Chen, F. Guo, Y. Liu, T. Huang, B. Zheng, N. Ananth, Z. Xu, W. Gao, C. Gao, *Adv. Mater.* 2017, 29, 1605958.
[42] H. Chen, H. Xu, S. Wang, T. Huang, J. Xi, S. Cai, F. Guo, Z. Xu, W. Gao, C. Gao, *Sci. Adv.* 2017, 3, eaao7233.
[43] L. Cammarata, S. G. Kazarian, P. A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* 2001, 3, 5192.
[44] W. E. Gardinier, G. A. Baker, S. N. Baker, F. V. Bright, *Macromolecules* 2005, 38, 8574.