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Necessity and Advantages of Developing Rechargeable Organic Batteries

1.1 Current Electrochemical Energy Storage Technologies

Li-ion battery (LIB) is well known as one of the electrochemical energy storage (EES) technologies, which can be seen in our daily lives, such as portable equipment and electric vehicles. LIBs have made great progress in the last 30 years, which can be traced back to 1991, when the first reversible LIB was commercialized by Sony Corp. [1]. The battery is based on $LiCoO_2$, graphite, and ester-solvents with $LiPF_6$ [2, 3]. Afterward, a series of ternary $LiNi_xCo_yMn_zO_2$ (NCM, $x + y + z = 1$) and $LiFePO_4$ spring out, considering the aspects of energy density and security [4–11]. Prior to LIBs, actually, lithium metal batteries (LMBs) were commercialized by Moli Energy Corp., based on lithium metal and metal sulfide as negative and positive electrodes, respectively [12]. However, the battery was in a tailspin after several safety incidents due to the lithium dendrites, which are easily generated after cycling [13, 14]. Note that for the discovery and development of LIBs, John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino were awarded the 2019 Nobel Prize in Chemistry.

Similar to LIB, sodium-ion battery (SIB) is also one of the state-of-the-art EES technologies. Actually, SIBs have a longer history compared with LIBs, with the layered oxides discovered toward the end of the 1960s [15, 16]. Considering the limited Li resource, SIB is a suitable alternative EES due to the relatively abundant Na resource (420 times more than Li). It is noted that the oxides Na_xMO_2 (M = 3d element) have some special structure by regulating deficient sodium [17–20], such as O2, O3, P2, and P3 types, according to the structural packing described by Delmas [17]. Therefore, the electrochemical performance can be modified in Na-based oxides, which has an evident advantage compared with the Li-based oxides used for LIBs. The energy density of SIB could climb to 200 $\mathrm{Wh\,kg^{-1}}$, as reported by Hu's group, which is a breakthrough [21]. However, the energy density is still limited with respect to LIBs, which could deliver over 300 $\mathrm{Wh\,kg^{-1}}$ [22].

The good news is that SIBs have been commercialized by some Chinese companies such as CATL Corp. and HiNa Battery Corp. Given the energy density difference among the typical EES, the different battery systems aim for different

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market orientation to share the energy pressure. For example, lead-acid batteries, Ni–Cd batteries, and supercapacitors are used for devices with short mileage or low energy density, which are still required by the market. Nonetheless, both LIBs and SIBs cannot satisfy our demand in the long term, considering the resource crisis accompanied by high costs and pollution. Moreover, the traditional batteries are restricted to a sealed system and organic electrolytes (aqueous electrolytes are still facing great difficulties [23, 24]). Herein, we need a new EES without (or with mitigatory) the concerns.

A rechargeable organic battery is a good choice because the active materials are low cost, and the battery has comparable energy density when compared with LIB and SIB [25–31]. Moreover, the properties of organic materials can be controlled by different functional groups, such as the charge/discharge potential, the reaction dynamics, and the structural stability [32–37]. Furthermore, the system is unrestricted which can be used in an aqueous system, typically redox flow batteries (RFBs) [38–42]. Actually, the organic battery has been studied for over 60 years [43]. At the initial stage, the electrochemical performance of the organic material is poor with an ambiguous reaction mechanism, which impedes the development of the battery. In recent years, the corresponding published papers have a manifest rising tendency which can be seen in Figure 1.1, which partially benefits from technological advancements and several outstanding contributions made by Chen's group and Schubert's group since 2012 [44–69]. Now, there are many kinds of organics with active centers based on O, N, and S, enriching the family of organic batteries, which could compete with the traditional metal-ion batteries.

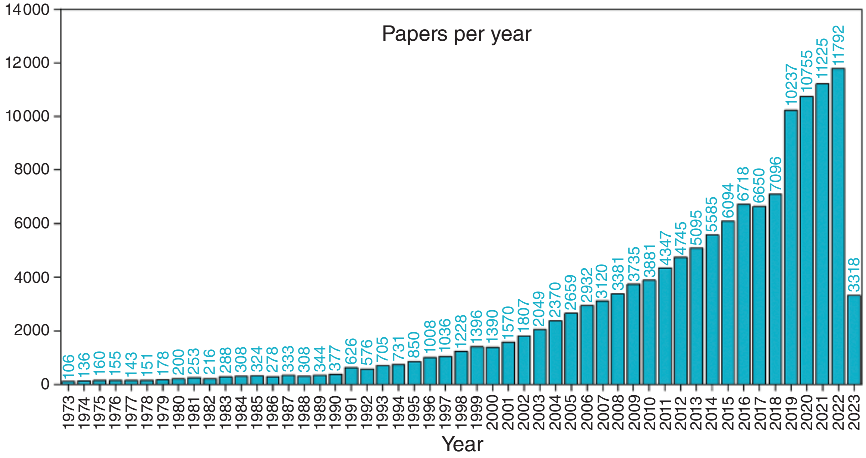

Figure 1.1 Published papers per year for the rechargeable organic batteries with keywords such as organic electrode, organic cathode, and organic battery. The time of the statistics is April 2023.

1.2 Rechargeable Organic Batteries

Organic batteries show different mechanisms from the typical LIBs, which mainly include insertion/extraction ($LiCoO_2$, NCM, etc.), alloying (Al, Si, etc.), and conversion mechanism (O, P, S-based composites, etc.) [70–79]. For the organic electrodes, the mechanism usually contains the repeated breaking and bonding of a bond (carbonyl, organosulfide, and radical materials in Chapter 2). A single bond (typically S—S bond) is broken during discharge, after which the broken bond receives an electron and bonds with a metal ion for charge balance. A double bond (typically carbonyl units) shows a similar mechanism. Note that during the reaction, radical materials are usually generated which has been applied in RFBs due to the fast kinetics [80–82]. There seems to be another mechanism not involved in bond breaking, which is based on electron transfer and anion compensation (typically N-containing active materials) [83].

The first investigation of organic materials is carbonyl compounds, which can be traced back to the 1960s [43]. However, the material shows high solubility in aprotic electrolytes, restricting the application although some other carbonyl composites are constructed [32]. Afterward, the direction was turned to conductive polymers in the 1970s because of their less solubility, such as polyacetylene and polypyrrole [83–89]. Unfortunately, these electrodes suffered from limited capacity due to incomplete reaction [88, 89]. A revival emerged when Armand and Tarascon depicted a bright future for organic batteries, attracting more attention [28]. Encouragingly, molecules with popular functional groups (quinones, carboxylates, radical centers, etc.) and other redox-active centers (imines, alkenes, alkynes, azo, etc.) have been investigated [90–97].

Another typical organic material is organosulfide with S as the redox center. Visco et al. initially studied tetraethyl thiuram disulfide (TETD) in 1988 [98]. However, the electrode delivered poor electrochemical performance, which cannot be used in a battery. Actually, the research of organosulfide battery mainly focused on polysulfides from the 1980s to 2015, such as naphtho[1,8-*cd*][1,2]dithiol and dibenzo[*c,e*][1,2]dithiin, which have not attracted full attention [99, 100]. The polysulfides have a large specific capacity (over 300 $mAh\,g^{-1}$), however, with poor stability due to the rigid framework in which the S—S bonds suffer from breaking and painful bonding, deteriorating the original structure which can be only used for lithium primary battery. Afterward, organosulfide with small molecule was investigated. However, the materials were considered hopeless because they easily dissolved into the electrolyte, leading to a shuttle effect that normally appeared in Li–S batteries. Until 2016, dimethyl trisulfide (DMTS) [101] was successfully applied in organic batteries with a reversible charge/discharge process (with 849 $mAh\,g^{-1}$) and cycling performance (50 cycles) with the assistance of a carbon paper which was also proposed for polysulfide in 2013 [102]. The creative idea has opened a broad perspective for the research of small-molecule organosulfur

[103–111]. Hereafter, molecules with more sulfur content (–Sn–) were studied to modify the specific capacity [112–116]. The performance of organosulfur can be regulated by heteroatom doping (such as Se, Te), combination with metal sulfides for good conductivity and stability, and the application of RFBs [117–126].

1.3 Goal, Scope, and Organization of this Book

It is obvious that a consequent and growing amount of literature is now easily available on organic batteries after years of silence. There is room for reversible electroactive organic systems in the future EES landscape in view of the application. However, it must be noted that there exists a certain disciplinary boundary between inorganic and organic compounds because the redox chemistry of organics is different from that of typical LIBs, making it challenging for nonspecialist readers when dealing with organic batteries. Therefore, it would be timely to provide a kind of "tutorial"-oriented book for a broader audience. Based on the latest selected and reliable data from both general and specialized scientific literature, this contribution also aims at providing the readers with a better understanding of the consecutive global demand for electrical energy sources and the evolution trends of organic batteries.

The following approach will be stepwise introduced in this book.

1.3.1 Working Principles and Fundamental Properties

First, the reader will have a concept of some prototypical organic materials, including the mechanisms and cell configurations. The organic electrodes as cathodes are the key point in this book, including the introduction of the mechanism (Chapter 2), carbonyl-based organic cathodes (Chapter 3), sulfur-containing organic cathodes (Chapter 4), radical-based organic cathodes (Chapter 5), organometallic complex-based cathodes (Chapter 6), polymer-based organic cathodes (Chapter 7), and other organic cathodes. The reader will know the basic types and reaction mechanisms of these organic electrodes. Afterward, some typical organic anodes are introduced (Chapter 8), which can be assembled as an all-organic battery counter to an organic cathode (Chapter 9).

1.3.2 A Selection of an Organic Electrode

After our introduction, the reader will know that the function of an organic electrode could be modified by applying a wealth of functional groups. Compared with the typical inorganic electrodes, organic electrodes can be considered cathodes (even working at high potential like P-type electrodes), anodes, and soluble agents for RFBs. Moreover, with the assistance of some special functional groups (such as N-based group), a battery with ultra-high-rate performance (e.g. thiuram monosulfide [TM]) and eutectic solution at low temperature as a special electrolyte (such as the interaction between 2,2′-dipyridyl disulfide (DPyDS) and lithium

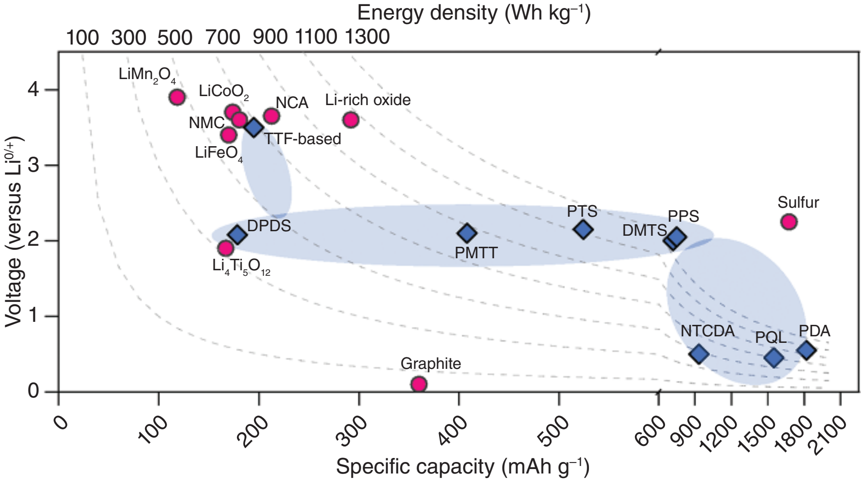

Figure 1.2 Typical organic materials with voltage, specific capacity, and energy density are compared with some typical traditional electrode materials.

bis(trifluoromethanesulfonyl)imide [LiTFSI]) can be achieved [107, 127]. The organic materials hold a wide range of voltage, specific capacity, and energy density (Figure 1.2). Thus, the reader will know how to choose an organic electrode based on the demand.

Note that TTF-based, DPDS, PMTT, PTS, DMTS, PPS, NTCDA, PQL, and PDA denote tetrakis(methylthio)-derivative cyclohexene-1,4-diylidenes (TTF-based) [128], diphenyl disulfide (DPDS) [119], dipentamethylenethiuram tetrasulfide (PMTT) [129], phenyl tetrasulfide (PTS) [118], dimethyltrisulfide (DMTS) [101], phenyl hexasulfide (PPS) [92], 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) [95], poly(1,6-dihydropyrazino[2,3g]quinoxaline-2,3,8-triyl-7-(2*H*)-ylidene-7,8-dimethylidene) (PQL) [130], and polydopamine (PDA) [131], respectively.

1.3.3 EES Applications

After the introduction, the reader will understand the concept of the organic electrodes in terms of the cost, resource availability, and stability. For the cost, the typical DMTS and TM have an obvious price advantage compared with $LiCoO_2$ and NCM. Notably, TM has an ultrahigh redox activity with long cycling performances (over 8000 cycles), making it a potential candidate [127]. As for availability, organic materials are based on plentiful elements such as C, N, O, and S. It is obvious from the price comparison that the organic electrodes have rich resources. Herein, taking the long view, the organic electrodes have a low cost. As for chemical stability, the typical inorganic electrodes always suffer from a phase transition during cycling; hereafter, the structure deteriorates until the end of the cycle life. By contrast, the solubility property of organic electrodes makes the electron transfer process faster through a new mechanism different from the insertion/extraction mechanism. Note that a moderate dissolution of the active material benefits the rate performance and mitigates the evolution of the bulk structure of the electrode.

1.3.4 Practical Applications

Although research on the organic electrodes is earlier than the typical LIBs, the development of LIBs is faster due to their successful commercialization by Sony Corp. LIBs have the advantages of high specific capacity and stable cycling lifespan. However, LIBs encounter the bottleneck at the point of long development. Herein, other types of batteries emerge as alternatives, such as SIBs and Zn-ion batteries. As a prototype post-LIB, the battery based on organic materials holds obvious advantages. On the one hand, a P-type organic electrode (e.g. ethyl viologen iodide) can deliver a capacity of 230 mAh g^{-1}, with a high output potential of 3.7 V. On the other hand, the TM electrode can hold a robust cycling lifespan, with a high capacity retention of 70% even after 8000 cycles. As for security, the electrolyte based on DPyDS and LiTFSI consists of a eutectic solution just by grinding together, being of incombustibility, which potentially matches the demands of safety for electrolytes. Moreover, RFBs can be designed based on organic electrodes applying their solubility. Therefore, it should be declared that organic electrodes have a high potential for practical application.

1.3.5 Key Challenges

- The solubility of the organic electrodes is one key challenge. Because the soluble organic material has a shuttle effect, the organic electrodes keep the silence for a long time. With the application of carbon paper for organosulfide in 2016, a reversible and long cycling performance of organic battery was achieved. A carbon paper has strong adsorption ability which restricts the dissolution of the organic electrodes, mitigating the shuttle effect to some extent. Recently, a functional MOF-based separator has been designed to hinder the shuttle of the active material for LIBs based on the organic electrode (5,5′-dimethyl-2,2′-*bis*-*p*-benzoquinone), prolonging the cycle life to 2000 cycles (capacity retention of 82.9%) [132]. However, the mentioned separator raises the cost. From the view of practical use, a more facile and low-cost method should be applied.
- The cycling stability is another challenge for the application of organic electrodes. Although the soluble property accelerates the reaction kinetics, it also leads to the loss of the active material, resulting in a capacity loss and a short cycle life. The dissolution degree of organic electrodes should be carefully regulated. Moreover, some organic electrodes have the intrinsic properties of electrochemical inertness, resulting in a large polarization, which should be a concern.
- Various mechanisms are involved in the organic reactions, which are different from the traditional mechanisms in LIBs. The reaction always involves the break and recombination of the active bond, free radical reaction, charge recombination,

and so on. Herein, the detailed reactions step by step are still indistinct due to the complex electron transfer, dissolution–diffusion, element, and steric-dependent properties involved in the processes. The details also depend on the advanced equipment.

- As discussed above, some organic electrodes have their advantages, such as long lifespan, high working potential, and robust stability. However, it is still hard to find one organic electrode that has its full advantages. The organic electrode should be comparable in the fields of energy density, lifespan, and cost.

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References

1 Li, M., Lu, J., Chen, Z., and Amine, K. (2018). *Adv. Mater.* 30: 1800561.
2 Mizushima, K., Jones, P.C., Wiseman, P.J., and Goodenough, J.B. (1980). *Mater. Res. Bull.* 15: 783–789.
3 Yazami, R. and Touzain, P. (1983). *J. Power Sources* 9: 365–371.
4 Padhi, A.K., Nanjundaswamy, K.S., and Goodenough, J.B. (1997). *J. Electrochem. Soc.* 144: 1188.
5 Choi, J. and Manthiram, A. (2005). *J. Electrochem. Soc.* 152: A1714.
6 Jiang, J., Shi, W., Zheng, J. et al. (2014). *J. Electrochem. Soc.* 161: A336.
7 Kang, B. and Ceder, G. (2009). *Nature* 458: 190–193.
8 Kim, U.-H., Park, G.-T., Son, B.-K. et al. (2020). *Nat. Energy* 5: 860–869.
9 Li, W., Erickson, E.M., and Manthiram, A. (2020). *Nat. Energy* 5: 26–34.
10 Logan, E.R., Hebecker, H., Eldesoky, A. et al. (2020). *J. Electrochem. Soc.* 167: 130543.
11 Sun, H.H., Ryu, H.-H., Kim, U.-H. et al. (2020). *ACS Energy Lett.* 5: 1136–1146.
12 Whittingham, M.S. (1976). *J. Electrochem. Soc.* 123: 315.
13 Liu, Y., Lin, D., Liang, Z. et al. (2016). *Nat. Commun.* 7: 10992.
14 Ye, H., Xin, S., Yin, Y.-X. et al. (2017). *J. Am. Chem. Soc.* 139: 5916–5922.
15 Thery, J. and Briancon, D. (1964). *Rev. Int. Hautes Temp. Refract.* 1: 221.
16 Delmas, C. (2018). *Adv. Energy Mater.* 8: 1703137.
17 Delmas, C., Fouassier, C., and Hagenmuller, P. (1980). *Phys. B+C* 99: 81–85.
18 Parant, J.-P., Olazcuaga, R., Devalette, M. et al. (1971). *J. Solid State Chem.* 3: 1–11.
19 Delmas, C., Braconnier, J.-J., Fouassier, C., and Hagenmuller, P. (1981). *Solid State Ionics* 3–4: 165–169.
20 Braconnier, J.-J., Delmas, C., Fouassier, C., and Hagenmuller, P. (1980). *Mater. Res. Bull.* 15: 1797–1804.

21 Li, Y., Zhou, Q., Weng, S. et al. (2022). *Nat. Energy* 7: 511–519.

22 Qiao, Y., Yang, H., Chang, Z. et al. (2021). *Nat. Energy* 6: 653–662.

23 Yue, J., Zhang, J., Tong, Y. et al. (2021). *Nat. Chem.* 13: 1061–1069.

24 Suo, L., Borodin, O., Gao, T. et al. (2015). *Science* 350: 938–943.

25 Sato, K., Ichinoi, R., Mizukami, R. et al. (2018). *J. Am. Chem. Soc.* 140: 1049–1056.

26 Kim, D.J., Yoo, D.-J., Otley, M.T. et al. (2019). *Nat. Energy* 4: 51–59.

27 Han, C., Li, H., Shi, R. et al. (2019). *J. Mater. Chem. A* 7: 23378–23415.

28 Armand, M. and Tarascon, J.M. (2008). *Nature* 451: 652–657.

29 Friebe, C., Lex-Balducci, A., and Schubert, U.S. (2019). *ChemSusChem* 12: 4093–4115.

30 Wang, S., Li, F., Easley, A.D., and Lutkenhaus, J.L. (2019). *Nat. Mater.* 18: 69–75.

31 Xie, J. and Zhang, Q. (2019). *Small* 15: 1805061.

32 Wang, D.-Y., Guo, W., and Fu, Y. (2019). *Acc. Chem. Res.* 52: 2290–2300.

33 Wang, D.-Y., Liu, R., Guo, W. et al. (2021). *Coord. Chem. Rev.* 429: 213650.

34 Wang, D.-Y., Si, Y., Guo, W., and Fu, Y. (2020). *Adv. Sci.* 7: 1902646.

35 Wang, D.-Y., Si, Y., Guo, W., and Fu, Y. (2021). *Nat. Commun.* 12: 3220.

36 Wang, D.-Y., Si, Y., Li, J., and Fu, Y. (2019). *J. Mater. Chem. A* 7: 7423–7429.

37 Wang, D.-Y., Wang, W., Li, F. et al. (2022). *J. Energy Chem.* 71: 572–579.

38 Alotto, P., Guarnieri, M., and Moro, F. (2014). *Renewable Sustainable Energy Rev.* 29: 325–335.

39 Sum, E. and Skyllas-Kazacos, M. (1985). *J. Power Sources* 15: 179–190.

40 Sum, E., Rychcik, M., and Skyllas-kazacos, M. (1985). *J. Power Sources* 16: 85–95.

41 Rychcik, M. and Skyllas-Kazacos, M. (1988). *J. Power Sources* 22: 59–67.

42 Xu, Y., Wen, Y., Cheng, J. et al. (2009). *Electrochem. Commun.* 11: 1422–1424.

43 Williams, D.L., Byrne, J.J., and Driscoll, J.S. (1969). *J. Electrochem. Soc.* 116: 2.

44 Liang, Y., Tao, Z., and Chen, J. (2012). *Adv. Energy Mater.* 2: 742–769.

45 Häupler, B., Wild, A., and Schubert, U.S. (2015). *Adv. Energy Mater.* 5: 1402034.

46 Janoschka, T., Hager, M.D., and Schubert, U.S. (2012). *Adv. Mater.* 24: 6397–6409.

47 Lee, S., Kwon, G., Ku, K. et al. (2018). *Adv. Mater.* 30: 1704682.

48 Leung, P., Shah, A.A., Sanz, L. et al. (2017). *J. Power Sources* 360: 243–283.

49 Luo, J., Hu, B., Hu, M. et al. (2019). *ACS Energy Lett.* 4: 2220–2240.

50 Muench, S., Wild, A., Friebe, C. et al. (2016). *Chem. Rev.* 116: 9438–9484.

51 Peng, H., Yu, Q., Wang, S. et al. (2019). *Adv. Sci.* 6: 1900431.

52 Schon, T.B., McAllister, B.T., Li, P.-F., and Seferos, D.S. (2016). *Chem. Soc. Rev.* 45: 6345–6404.

53 Song, Z. and Zhou, H. (2013). *Energy Environ. Sci.* 6: 2280–2301.

54 Wang, H. and Zhang, X. (2018). *Chem. Eur. J* 24: 18235–18245.

55 Wei, X., Pan, W., Duan, W. et al. (2017). *ACS Energy Lett.* 2: 2187–2204.

56 Winsberg, J., Hagemann, T., Janoschka, T. et al. (2017). *Angew. Chem. Int. Ed.* 56: 686–711.

57 Wu, Y., Zeng, R., Nan, J. et al. (2017). *Adv. Energy Mater.* 7: 1700278.

58 Xie, J., Gu, P., and Zhang, Q. (2017). *ACS Energy Lett.* 2: 1985–1996.

59 Xu, Y., Zhou, M., and Lei, Y. (2018). *Mater. Today* 21: 60–78.

60 Zhao, Q., Lu, Y., and Chen, J. (2017). *Adv. Energy Mater.* 7: 1601792.

61 Zhao, Q., Zhu, Z., and Chen, J. (2017). *Adv. Mater.* 29: 1607007.

62 Zhu, L., Ding, G., Xie, L. et al. (2019). *Chem. Mater.* 31: 8582–8612.

63 Zhu, Z. and Chen, J. (2015). *J. Electrochem. Soc.* 162: A2393.

64 Armstrong, C.G. and Toghill, K.E. (2018). *Electrochem. Commun.* 91: 19–24.

65 Casado, N., Hernández, G., Sardon, H., and Mecerreyes, D. (2016). *Prog. Polym. Sci.* 52: 107–135.

66 Ding, Y., Zhang, C., Zhang, L. et al. (2018). *Chem. Soc. Rev.* 47: 69–103.

67 Gong, K., Fang, Q., Gu, S. et al. (2015). *Energy Environ. Sci.* 8: 3515–3530.

68 Gracia, R. and Mecerreyes, D. (2013). *Polym. Chem.* 4: 2206–2214.

69 Oltean, V.A., Renault, S., Valvo, M.L., and Brandell, D. (2016). *Materials* 9: 142.

70 Abel, P.R., Lin, Y.-M., de Souza, T. et al. (2013). *J. Phys. Chem. C* 117: 18885–18890.

71 Gao, H., Zhou, T., Zheng, Y. et al. (2016). *Adv. Energy Mater.* 6: 1601037.

72 Li, L., Seng, K.H., Li, D. et al. (2014). *Nano Res.* 7: 1466–1476.

73 Li, X., Guo, S., Jiang, K. et al. (2018). *ACS Appl. Mater. Interfaces* 10: 16–20.

74 Mao, J., Fan, X., Luo, C., and Wang, C. (2016). *ACS Appl. Mater. Interfaces* 8: 7147–7155.

75 Wang, Y.-X., Seng, K.H., Chou, S.-L. et al. (2014). *Chem. Commun.* 50: 10730–10733.

76 Wu, L., Hu, X., Qian, J. et al. (2014). *Energy Environ. Sci.* 7: 323–328.

77 Xu, Y., Zhu, Y., Liu, Y., and Wang, C. (2013). *Adv. Energy Mater.* 3: 128–133.

78 Zheng, Y., Zhou, T., Zhang, C. et al. (2016). *Angew. Chem. Int. Ed.* 55: 3408–3413.

79 Zhou, T., Pang, W.K., Zhang, C. et al. (2014). *ACS Nano* 8: 8323–8333.

80 Nakahara, K., Iwasa, S., Satoh, M. et al. (2002). *Chem. Phys. Lett.* 359: 351–354.

81 Suga, T., Pu, Y.-J., Oyaizu, K., and Nishide, H. (2004). *Bull. Chem. Soc. J.* 77: 2203–2204.

82 Liu, M., Visco, S.J., and De Jonghe, L.C. (1990). *J. Electrochem. Soc.* 137: 750.

83 Ma, T., Liu, L., Wang, J. et al. (2020). *Angew. Chem. Int. Ed.* 59: 11533–11539.

84 Shirakawa, H., Louis, E.J., MacDiarmid, A.G. et al. (1977). *J. Chem. Soc., Chem. Commun.* 16: 578–580.

85 Chance, R.R., Shacklette, L.W., Miller, G.G. et al. (1980). *J. Chem. Soc., Chem. Commun.* 8: 348–349.

86 Ivory, D.M., Miller, G.G., Sowa, J.M. et al. (1979). *J. Chem. Phy.* 71: 1506–1507.

87 MacInnes, D., Druy, M.A., Nigrey, P.J. et al. (1981). *J. Chem. Soc., Chem. Commun.* 7: 317–319.

88 Novák, P., Müller, K., Santhanam, K.S.V., and Haas, O. (1997). *Chem. Rev.* 97: 207–282.

89 Jia, X., Ge, Y., Shao, L. et al. (2019). *ACS Sustainable Chem. Eng.* 7: 14321–14340.

90 Lu, Y., Hou, X., Miao, L. et al. (2019). *Angew. Chem. Int. Ed.* 58: 7020–7024.

91 Iordache, A., Delhorbe, V., Bardet, M. et al. (2016). *ACS Appl. Mater. Interfaces* 8: 22762–22767.

92 Bhargav, A., Bell, M.E., Karty, J. et al. (2018). *ACS Appl. Mater. Interfaces* 10: 21084–21090.

93 Hansen, K.-A., Nerkar, J., Thomas, K. et al. (2018). *ACS Appl. Mater. Interfaces* 10: 7982–7988.

94 Matsunaga, T., Kubota, T., Sugimoto, T., and Satoh, M. (2011). *Chem. Lett.* 40: 750–752.

95 Han, X., Qing, G., Sun, J., and Sun, T. (2012). *Angew. Chem. Int. Ed.* 51: 5147–5151.

96 Renault, S., Oltean, V.A., Araujo, C.M. et al. (2016). *Chem. Mater.* 28: 1920–1926.

97 Luo, C., Borodin, O., Ji, X. et al. (2018). *Proc. Natl. Acad. Sci. U.S.A.* 115: 2004–2009.

98 Visco, S.J. and DeJonghe, L.C. (1988). *J. Electrochem. Soc.* 135: 2905.

99 Liu, M., Visco, S.J., and De Jonghe, L.C. (1989). *J. Electrochem. Soc.* 136: 2570.

100 Inamasu, T., Yoshitoku, D., Sumi-otorii, Y. et al. (2003). *J. Electrochem. Soc.* 150: A128.

101 Wu, M., Cui, Y., Bhargav, A. et al. (2016). *Angew. Chem. Int. Ed.* 55: 10027–10031.

102 Fu, Y., Su, Y.-S., and Manthiram, A. (2013). *Angew. Chem. Int. Ed.* 52: 6930–6935.

103 Sun, J., Zhang, K., Fu, Y., and Guo, W. (2022). *Nano Res.* 16: 3814–3822.

104 Guo, W., Zhang, W., Si, Y. et al. (2021). *Nat. Commun.* 12: 3031.

105 Lian, J., Guo, W., and Fu, Y. (2021). *J. Am. Chem. Soc.* 143: 11063–11071.

106 Gao, M., Lan, J., Fu, Y., and Guo, W. (2022). *ChemSusChem* 15: e202200423.

107 Song, J., Si, Y., Guo, W. et al. (2021). *Angew. Chem. Int. Ed.* 60: 9881–9885.

108 Tang, S., Chen, Q., Si, Y. et al. (2021). *Adv. Mater.* 33: 2100824.

109 Tang, S., Guo, W., and Fu, Y. (2021). *Adv. Energy Mater.* 11: 2000802.

110 Li, F., Si, Y., Liu, B. et al. (2019). *Adv. Funct. Mater.* 29: 1902223.

111 Zhao, B., Si, Y., Guo, W., and Fu, Y. (2022). *Adv. Funct. Mater.* 32: 2112225.

112 Li, F., Guo, W., Si, Y. et al. (2021). *Electrochim. Acta* 370: 137757.

113 Zhao, J., Si, Y., Han, Z. et al. (2020). *Angew. Chem. Int. Ed.* 59: 2654–2658.

114 Li, F., Si, Y., Li, Z. et al. (2020). *J. Mater. Chem. A* 8: 87–90.

115 Sang, P., Si, Y., and Fu, Y. (2019). *Chem. Commun.* 55: 4857–4860.

116 Wu, M., Bhargav, A., Cui, Y. et al. (2016). *ACS Energy Lett.* 1: 1221–1226.

117 Chen, Q., Si, Y., Guo, W., and Fu, Y. (2022). *Chem. Commun.* 58: 10993–10996.

118 Lv, X., Guo, W., Song, J., and Fu, Y. (2022). *Small* 18: e2105071.

119 Ren, S., Si, Y., Guo, W., and Fu, Y. (2022). *ACS Sustainable Chem. Eng.* 10: 7526–7535.

120 Xie, K., Sun, J., Lian, J. et al. (2022). *Appl. Phys. Lett.* 121: 133904.

121 Cui, Y., Ackerson, J.D., Ma, Y. et al. (2018). *Adv. Funct. Mater.* 28: 1801791.

122 Wang, Z., Li, X., Guo, W., and Fu, Y. (2021). *Adv. Funct. Mater.* 31: 2009875.

123 Fan, Q., Guo, W., Si, Y. et al. (2021). *Adv. Funct. Mater.* 31: 2001493.

124 Chen, Q., Wang, W., Li, X. et al. (2022). *Proc. Natl. Acad. Sci. U.S.A.* 119: e2202449119.

125 Chen, Q., Guo, W., and Fu, Y. (2022). *Adv. Sci.* 9: 2104036.

126 Chen, Q., Guo, W., Wang, D., and Fu, Y. (2021). *J. Mater. Chem. A* 9: 12652–12658.

127 Chen, Q., Li, L., Wang, W. et al. (2022). *J. Am. Chem. Soc.* 144: 18918–18926.

128 Kato, M., Senoo, K.-I., Yao, M., and Misaki, Y. (2014). *J. Mater. Chem. A* 2: 6747–6754.

129 Bhargav, A., Ma, Y., Shashikala, K. et al. (2017). *J. Mater. Chem. A* 5: 25005–25013.

130 Wu, J., Rui, X., Long, G. et al. (2015). *Angew. Chem. Int. Ed.* 54: 7354–7358.

131 Sun, T., Li, Z.-J., Wang, H.-G. et al. (2016). *Angew. Chem. Int. Ed.* 55: 10662–10666.

132 Bai, S., Kim, B., Kim, C. et al. (2021). *Nat. Nanotechnol.* 16: 77–84.