

A review: conductive polymer-based aluminium current collector for Li-ion batteries

M. Goyal¹, S. N. Agarwal², K. Singh³, A. Shrivastava⁴, N. Bhatnagar^{1*}

¹Department of Chemistry, Manipal University Jaipur, India

²Department of Electrical Engineering, Manipal University Jaipur, India

³Department of Electronics and Communication Engineering, Manipal University Jaipur India

⁴Skill Faculty of Engineering and Technology, Shri Vishwakarma Skill University, Gurugram, Haryana, India

Received: March 14, 2022; Revised: July 22, 2022

Conductive polymers are favourable materials in lithium-ion batteries because of their high electrical conductivity and coulombic efficiency and their ability to be cycled hundreds or thousands of times with only slight degradation. This review paper presents an overview of the lithium ion batteries (LIB) fabricated by using various types of conductive polymers (CP) based on aluminum as a current collector (CC). More attention is paid to aluminum which can be used as a cathode current collector. The conductive polymer can minimize the interface resistance between the current collector and the active material to increase the performance of lithium batteries. Furthermore, it can help to lower the battery's internal resistance during usage. The most used conductive polymers are polyaniline (PANI), poly(ethylene glycol) (PEG), poly-dopamine (PDA), polyacetylene (PA), polypyrrole (PPy), polythiophene (PTH), PEDOT: PSS (poly(3,4-ethylenedioxythiophene)) and poly(styrene sulfonate), because of their ability to store and conduct lithium ions. The reason to use the conductive polymer binders is their high energy density, porous nature, high electrical conductivity and many other. This review article discusses the basic structure of the Li ion battery followed by analysis of various types of conductive polymers which can be used in lithium ion battery, and highlight the influence of aluminum as a cathode current collector.

Keywords: Conductive, Lithium; Aluminum; Resistance; Electrical; Sulfonate

INTRODUCTION

Lithium ion battery has high density, voltage stability, longevity, environmental security and low self-discharge rate [1, 2], which makes this battery more efficient and useful for electrical items such as phones, vehicles, portable devices, power tools, hybrid electric vehicles, etc. [3] The lithium ion batteries changed the area of energy storage and its production because of their dynamic properties. Flexible lithium ion battery is in progress which demands the high energy capacity in the development of the applications of soft mobiles [4]. Furthermore, in the periodic table, lithium is ranked on third number, implying that it contains the shortest radius of any single-charged ion, permitting lithium-based batteries to have an excellent power density and gravimetric capacity [5]. Li-ion batteries are known to be the common energy storage cells for powering handy electronic devices, and their use in automotive, defence, and aerospace applications is increasing. Despite their widespread use and commercial domination, LIBs have undergone extensive research and development in order to improve their features [6]. Electrochemical cell is defined as a device which converts chemical energy (C.E.) into electrical energy (E.E.). It is a redox process like in Daniel cell. In electrochemistry, the

substance which conducts electricity, causes the dissociation of ions, which generates the positive and negative terminals, i.e. cathode and anode of an electric circuit. In electrochemistry the anode behaves as a negative terminal while the cathode behaves as a positive terminal. Further, they are distributed into acids, bases and salts as they give ions while dissolving into aqueous or non-aqueous solvents. These solutions are known to conduct the electricity. When electrolytes are put between two electrodes and voltage is provided, the electrolytes conduct electricity through charge carriers or ions transfer. The selection of electrodes depends on the basis of process not on the charge and polarity. As a consequence, chemical reactions occur at the cathode, which contain e^- from the anode, and produce electrons for the cathode to take. Hence, in an electrolyte, negative charge occurs at cathode and positive charge occurs at anode [7]. The ions in an electrolyte cell are non-spontaneous which transfer electrical energy into chemical energy.

To replace graphite anode with Li metal produces higher energy density of Li-ion batteries and these batteries are called lithium metal batteries. Lithium metal batteries consist of four parts: anode material, cathode material, electrolyte, and separator [8].

* To whom all correspondence should be sent:
E-mail: niturbhatnagar@gmail.com

HIGH CONDUCTIVITY	HIGH THERMAL AND CHEMICAL STABILITY	LIGHTWEIGHT AND FLEXIBLE	INEXPENSIVE AND FEASIBLE
<ul style="list-style-type: none"> To collect and transfer electrons, electrical conductivity is required, which can increase the rate performance of lithium ion batteries. 	<ul style="list-style-type: none"> Current collector is stable and unaffected by active materials and electrolytes. 	<ul style="list-style-type: none"> Current collector should be strong and flexible enough to suit the demands of production. Since lightweight current collectors enhance the mass and volumetric specific capacity of lithium metal batteries has increased. 	<ul style="list-style-type: none"> Current collector should be inexpensive and simple to obtain so that it may be utilized in other applications.

Figure 1. Various properties of current collector used in lithium ion battery

The cathode current collector (CC) is largely utilized in battery creation, and it is mainly cycled into aluminium foil paper with a thickness of 10-20 μm [9, 10], whereas copper is employed as an anode current collector with a thickness of 5-8 μm [11].

Aluminum can be used as the best current collector (CC) due to its cheap cost, conductivity and availability [12, 13] In Figure 1, the properties of the current collector are explained. For the better performance and stability of the Li-ion battery, aluminum can be used as a carbon coating [14].

Conductive polymer is used in cathode material especially. Conductive polymers have also been explored for a variety of uses, including active electrode materials in LIB [15]. The reason to use conductive polymer is its electrochemically active stable nature, high electronic conductivity and the great porosity for electrolyte. For the battery performance, internal resistance is proportional to the depth of charge and discharge. It means that in battery discharge there is increment in internal resistance which further reduces the electrolyte concentration.

The review aims at examining and summarizing some of the research work on conductive polymer-based aluminum current collectors for lithium ion battery.

Basic structure of Li ion battery

Lithium ion battery is a secondary rechargeable battery. The cathode and anode of lithium ion batteries are separated by a polymer membrane and are all wetted by the electrolyte [16]. In a lithium ion battery, two electrodes with two distinct electron affinities can be used, with electrons flowing from one electrode to another outside the battery and the electrolyte ions closing the circuit within the battery [7]. In this case, the electrode reaction converts the chemical energy into electrical energy. During the charging phase, lithium ions are put into the anode after being extracted from the cathode, and the

opposite reaction happens during the discharging process. Hence, lithium ions move from cathode to anode as shown in Figure 2 [16]. The redox reactions occurred simultaneously with the advancement or retreating of the electrode surfaces in a conventional galvanic battery system.

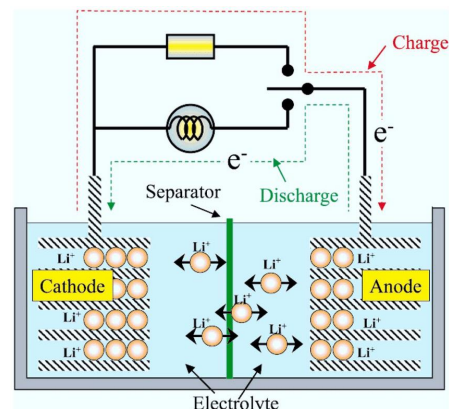
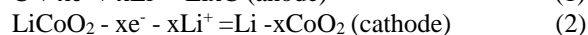
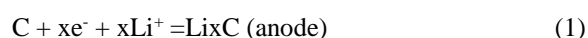


Figure 2. Mechanism of Li ion battery [17]

The first lithium ion battery was discovered by Yoshino using LiCoO_2 cathode and the discharged carbon anode as shown in equation below [18]:



Heterogeneous redox reactions in lithium ion batteries are invariably followed by volume expansion and solid-state mass diffusion [19]. One of the challenges that new materials try to overcome is voluminal variation. The most important materials that define the electrochemical parameters of a lithium ion battery are the anode, cathode, and electrolyte. Despite this, graphite has a specific capacity about is 372 mAhg^{-1} due to which every 6-C atoms combine with one lithium ion to form LiC_6 [20]. Figure 3 represents the properties of the Li ion battery [33]. The following factors influence Li storage capacity [21]:

- the sufficient space for admitting lithium

ions;

- the electrode material's ability to shift valence states.

Those key elements outlined above serve as motivation and guidance for learning about new and improved composite materials in order to address the growing need for energy storage.

The current collectors in lithium metal batteries should have high conductivity, high chemical and thermal stability, lightweight, flexibility, cheap cost and easy access. Figure 3 describes the advantages, limitations and applications in lithium metal batteries [22-24].

Li-ion batteries contain electrolyte salts such as

lithium perchlorate (LiClO₄), lithium hexafluoro arsenate (LiAsF₆), lithium tetrafluoroborate (LiBF₄), lithium hexafluorophosphate (LiPF₆), lithium trifluoromethanesulfonate (Li(CF₃SO₃)), lithium oxalyldifluoroborate (Li[BF₂(CO₂)₂]), etc. Brief discussion on some salts is given in Table 1. These salts should meet some criteria, as follows [7]:

1. Ionic conductivity is high in a variety of non-aqueous solvent systems.
2. Electrolyte solutions should be inert to anions.
3. Anion should be safe to use.
4. It should be able to prevent anodic breakdown of an aluminum current collector.

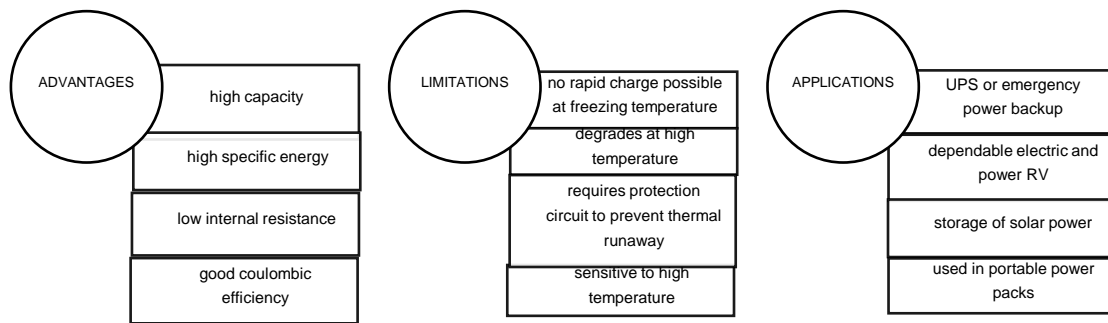


Figure 3. Advantages, limitations and applications of Li ion battery [33]

Table 1. Summary of some lithium salts

S. No.	Salt	Characteristics	Equations
1.	Lithium perchlorate [25,26] (LiClO ₄)	<ul style="list-style-type: none"> • Strong acid • High solubility • High anodic stability • Good ionic conductivity in non-aqueous solvents 	1. $\text{LiClO}_4 + \text{ne}^- + 2\text{nLi}^+ \rightleftharpoons \text{Li}_2\text{O} + \text{LiClO}_3, \text{LiClO}_2 + \text{LiCl}$
2.	Lithium tetrafluoroborate [27] (LiBF ₄)	<ul style="list-style-type: none"> • Smaller anionic size • High ionic conductivity • Moisture problem 	<ol style="list-style-type: none"> 1. $\text{Li}^+ + \text{BF}_4^- \leftrightarrow \text{LiF}\downarrow + \text{BF}_3\uparrow$ 2. $\text{BF}_3 + \text{H}_2\text{O} \rightarrow \text{BOF}\uparrow + 2 \text{HF}$
3.	Lithium hexafluoroarsenate [25,28] (LiAsF ₆)	<ul style="list-style-type: none"> • Higher ionic conductivity • Passivates the aluminum current collector on both sides of the electrode surface, which creates the solid electrolyte interface. 	<ol style="list-style-type: none"> 1. $\text{LiAsF}_6 + \text{H}_2\text{O} \rightarrow \text{HF} + \text{AsF}_5 + \text{LiOH}$ 2. $\text{LiAsF}_6 + 2\text{e}^- + 2\text{Li}^+ \rightarrow \text{AsF}_3 + 3\text{LiF}$ 3. $\text{AsF}_3 + 2\text{ne}^- + 2\text{nLi}^+ \rightarrow \text{Li}_n\text{AsF}_{3-n} + \text{nLi}^+$
4.	Lithium trifluoromethane sulfonate (Li(CF ₃ SO ₃)) [29]	<ul style="list-style-type: none"> • High dissociation constant • Low dielectric media • In non-aqueous solvents, ionic conductivity is poor 	<ol style="list-style-type: none"> 1. $2 \text{Li}(\text{CF}_3\text{SO}_3) + 2\text{e}^- + 2 \text{Li}^+ \rightarrow 2\text{Li}_2\text{SO}_3\downarrow + \text{C}_2\text{F}_6\uparrow$ 2. $\text{C}_2\text{F}_6 + 2\text{e}^- + 2\text{Li}^+ \rightarrow \text{CF}_3\text{CF}_2\text{Li} + \text{LiF}\downarrow$ 3. $\text{Li}_2\text{SO}_3 + 6\text{e}^- + 6\text{Li}^+ \rightarrow \text{Li}_2\text{S}\downarrow + 3 \text{Li}_2\text{O}\downarrow$
5.	Lithium bis(trifluoromethane sulfonyl)imide [30,31] (Li[N(CF ₃ SO ₂) ₂])	<ul style="list-style-type: none"> • Thermally stable • High conducting • Low dielectric constant • Higher dissociation 	<ol style="list-style-type: none"> 1. $\text{Li}[\text{N}(\text{CF}_3\text{SO}_2)_2] + 4\text{e}^- + 4\text{Li}^+ \rightarrow \text{Li}_3\text{N}\downarrow + 2 \text{Li}(\text{CF}_3\text{SO}_2)\downarrow$ 2. $2 \text{Li}(\text{CF}_3\text{SO}_2) + \text{ne}^- + \text{nLi}^+ \rightarrow \text{Li}_2\text{S}_2\text{O}_4\downarrow + \text{C}_2\text{F}_x\text{Li}_y + \text{LiF}\downarrow$ 3. $\text{Li}_2\text{S}_2\text{O}_4 + 6\text{e}^- + 6 \text{Li}^+ \rightarrow 2 \text{Li}_2\text{S}\downarrow + 4\text{Li}_2\text{O}\downarrow$
6.	Lithium tris(perfluoroethyl) trifluorophosphate [32] (Li[PF ₃ (CF ₃ CF ₂) ₃])	<ul style="list-style-type: none"> • Lower reactivity • Lower viscosity 	1. $(\text{CF}_3\text{CF}_2)_3\text{PF}_2 + \text{LiF} + 5 \text{H}_2\text{O} \rightarrow \text{Li}[(\text{CF}_3\text{CF}_2)_3\text{PF}_3] \cdot 5 \text{H}_2\text{O}$

Table 2. Cathode materials and conducting polymer binders: capacity adjusted by electrode weight [40]

Electrode	Speed of charging conventional Li-ion battery	Normalized discharge capacity (mAhg ⁻¹)	Cycles	Parameter variation of Li-ion battery after addition of conductive polymer
LFP/PEDOT:PSS/SBR-CTS/C [41] (90:3:4:3 wt%)	0.2	140	100	Increased electron density and best cyclic stability
LFP/PEDOT:PSS [15] (92:8 wt%)	0.2 1	110 97	100	No redox activity and better cyclic stability
LCO/PVDF/C (95:3:2 wt%) (<i>in situ</i> polymerized PANI/LiV ₃ O ₈)/PVDF/C (85:10:5 wt%) [42]	0.2 0.1 1	133 204 195 157 160	30 55	Cyclic stability increase and better rate capability
LFP/SA-PProDOT [43] (80:20 wt%)	0.1 1	136 96	400	Better binding capability and electronic conductivity
Hydrogel-derived Cu-PPy/C-LFP [44] (~15:85 wt%)	1	128	1000	Better cyclic performance

Table 3. Anode materials and conducting polymer binders: capacity adjusted by electrode weight [40]

Electrode	Speed of charging conventional Li-ion battery	Normalized discharge capacity (mAhg ⁻¹)	Cycles	Parameter variation of Li-ion battery after addition of conductive polymer
Si/PEDOT:PSS/CMC/C [45] (70:10:10:10 wt%)	~0.06 (0.2 Ag ⁻¹) ~2.8 (10 Ag ⁻¹)	2700 609	100	Better cyclic stability and rate performance
LTO/PEDOT:PSS/CMC/C [46] (90:2:2:6 wt%)	0.2 1	141 138	1000	Better cyclic stability
Hydrogel-derived Si/P-PPy/CNT [47] (~70 wt% Si:~0.2 wt% CNT)	0.78	1120	1000	Enhancement in performance
Si/FA/PEDOT:PSS [48] (80-20 wt%)	0.28	1542	100	Better electrochemical stability
Si/PF-COONa [49] (66.6:33.4 wt%)	0.1	2180 1852	100	Better electronic conductivity

Table 4. Some used current collectors

Material	Current collector		Properties
	Cathode	Anode	
Aluminum (Al)	Used in a variety of cathode materials	At low potential it reacts with Li	<ul style="list-style-type: none"> • High electrical conductivity • Low cost
Copper (Cu)	Oxidized at high potential	Used in a variety of anode materials.	<ul style="list-style-type: none"> • Lightweight • High electrical conductivity • Low cost
Nickel (Ni)	Cathode material made of LiFePO ₄	Used for NiO and Si/ C anode material	<ul style="list-style-type: none"> • In acidic and alkaline solutions, it is stable.
Stainless steel	Cathode material made of LiMnO ₄	Used for MnO ₂ and Fe ₃ O ₄ anode material	<ul style="list-style-type: none"> • The corrosion resistance of the surface oxide layer is excellent.

Conductive polymers for lithium ion batteries

Many groups have observed in recent years that thin coatings of conducting polymers such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PT) on the surface of active particles can significantly boost the capacity and rate capability of cathodes. PEDOT (poly(3,4-ethylenedioxy thiophene)) has been utilized to coat LiFePO_4 and LiCoO_2 particles and increase their performance [34-39]. PEDOT:PSS is a binder and conductive additive for Li ion battery and by adding the conductive polymer it behaves as current collector which decreases contact resistance. The following tables (Tables 2 and 3) summarize the normalized capacities of electrodes having poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) binders and other conductive polymers also.

Aluminum-based current collector for Li-ion battery

The basic step to use the current collector is performance, safety or stability in lithium ion battery, so aluminium foil is an important cathode current collector. Al foil has high conductivity, light weight, low price, and easy processing. However, it is easy to react with Li at low voltage, so it is often used in various cathode materials [50-52]. Current collector thickness of Al foil has decreases from 16 μm to 10 or 12 μm , but some manufactures even utilize 8 μm Al foil. Also, to increase the conductivity, cathode CC employs carbon coated Al foil [53, 54]. In Li-free cathode current collector, aluminium foil and carbon coated aluminium foil are the most used cathode materials. As a result, the most often utilized cathode current collectors are titanium, nickel, stainless steel, and carbon [55-58]. Nickel is quickly dissolved when exposed to high voltage, which limits its use. Like aluminum, titanium can form oxide coating on the surface. Stainless steel is a metal alloy composed mostly of iron, chromium, nickel, and manganese. Because of the passivation coating like chromium oxide (Cr_2O_3) on the surface, it has a strong corrosion resistance. Carbon materials have low density which can lower down the specific gravity of CC. Flexible battery systems with good flexibility are a suitable choice [8].

The restricted contact surface with active materials, along with interface resistance, are some drawbacks of using aluminum foil as a current collector. Surface treatment is the method which is commonly used for improving and enhancing the aluminum foil current collector (CC) [59-62]. In Table 4, a brief description of some used current

collectors with their properties is given [8].

CONCLUSION

In this paper we have highlighted the recent developments in the design and manufacturing of conductive polymer-based aluminum current collectors (CC) for Li-ion batteries. As a result, current collectors with high strength, lightweight, high flexibility, and ultrathin profiles will continue to be developed in the future [63]. Major focus on the increment of energy density should be increased, C-rate should be increased. If C-rate increases, then the chances of battery charging and discharging should be increased. Cycling rate also increases which leads to an increase of discharge rate. Further, research should be taken on various properties that should be optimized.

Acknowledgement: The authors gratefully acknowledge the facility provided by the Manipal University Jaipur.

Conflict of Interest: There is no conflict of interest.

REFERENCES

1. C. Liu, F. Li, L. P. Ma, H. M. Cheng, *Adv. Mater.*, **22**, 28 (2010).
2. Y. Luo, L. Guo, M. Xiao, S. Wang, S. Ren, D. Han, Y. Meng, *J. Mater. Chem. A*, **8**, 4629 (2020).
3. U. S. Kim, C. B. Shina, C. S. Kim, *J. Power Sources*, **189**, 841 (2009).
4. J. Y. Choi, D. J. Lee, Y. M. Lee, Y. G. Lee, K. M. Kim, J. K. Park, K. Y. Cho, *Adv. Funct. Mater.*, **23**, 2108 (2013).
5. H. Vikstrom, S. Davidsson, M. Hook, *Appl. Energy*, **110**, 252 (2013).
6. L. Lu, X. Han, J. Li, J. Hua, M. Ouyang, *J. Power Sources*, **226**, 272 (2013).
7. V. Aravindan, J. Gnanaraj, S. Madhavi, H. K. Liu, *Chem. Eur. J.*, **17**, 14326 (2011).
8. Y. Liu, D. Gao, H. Xiang, X. Feng, Y. Yu, *Energy Fuel*, **35**, 12921 (2021).
9. M. Wang, M. Tang, S. Chen, H. Ci, K. Wang, L. Shi, L. Lin, H. Ren, J. Shan, P. Gao, Z. Liu, H. Peng, *Adv. Mater.*, **29**, 1703882 (2017).
10. S. Yi, B. Wang, Z. Chen, R. Wang, D. Wang, *RSC Adv.*, **8**, 18597 (2018).
11. H. Chu, H. Tuan, *J. Power Sources*, **346**, 40 (2017).
12. C. Iwakura, Y. Fukumoto, H. Inoue, S. Ohashi, S. Kobayashi, H. Tada, M. Abe, *J. Power Sources*, **68**, 301 (1997).
13. A. H. Whitehead, M. Schreiber, *J. Electrochem. Society*, **152**, A2105 (2005).
14. H. C. Wu, H. C. Wu, E. Lee, N. L. Wu, *Electrochem. Comm.*, **12**, 488 (2010).
15. P. R. Das, L. Komsiyyska, O. Osters, G. Wittstock, *J. Electrochem. Society*, **162**, A674 (2015).
16. X. Meng, *IOP Conf. Ser.: Earth and Environ. Sci.*, *IOP Publishing*, **300**, 042039 (2019).
17. Y. Nishi, *The Chemical Record*, **1**, 406 (2001).

18. C. Liu, Z. G. Neale, G. Cao, *Mater. Tod.*, **19**, 109 (2016).
19. M. N. Obrovac, V. L. Chevrier, *Chem. Rev.*, **114**, 11444 (2014).
20. S. J. Dillon, K. Sun, *Curr. Opinion in Solid State and Mater. Sci.*, **16**, 153 (2012).
21. M. S. Islam, C. A. Fisher, *Chem. Soc. Rev.*, **43**, 185 (2009).
22. P. Zhu, D. Gastol, J. Marshall, R. Sommerville, V. Goodship, E. Kendrick, *J. Power Sources*, **485**, 229321 (2021).
23. L. Liu, H. Zhao, Y. Lei, *Small Methods*, **3**, 1800341 (2019).
24. L. Kong, H. Peng, J. Huang, Q. Zhang, *Nano Res.*, **10**, 4027 (2017).
25. O. Y. Chusid, E. E. Ely, D. Aurbach, M. Babai, Y. Carmeli, *J. Power Sources*, **43**, 47 (1993).
26. N. S. Choi, Y. M. Lee, J. H. Park, J. K. Park, *J. Power Sources*, **119**, 610 (2003).
27. S. Hossain, *Handbook of Batteries*, 2nd edn., 1995.
28. D. Guyomard, J. M. Tarascon, *Solid State Ionics*, **69**, 222 (1994).
29. D. Aurbach, A. Zaban, Y. Ein-Eli, I. Weissman, O. Chusid, B. Markovsky, M. Levi, E. Levi, A. Schechter, E. Granot, *J. Power Sources*, **68**, 91 (1997).
30. D. Aurbach, O. Chusid, I. Weissman, P. Dan, *Electrochim. Acta*, **41**, 747 (1996).
31. D. Aurbach, *Nonaqueous Electrochem.*, 289 (1999).
32. J. S. Gnanaraj, E. Zinigrad, M. D. Levi, D. Aurbach, M. A. Schmidt, *J. Power Sources*, **119**, 799 (2003).
33. M. Oswal, J. Paul, R. Zhao, University of Southern California, 2419 (2010).
34. D. Lepage, C. Michot, G. Liang, M. Gauthier, S. B. Schougaard, *Angew. Chem.*, **123**, 7016 (2011).
35. L. J. Her, L. J. Hong, C. C. Chang, *J. Power Sources*, **157**, 457 (2006).
36. C. Arbizzani, M. Mastragostino, M. Rossi, *Electrochem. Comm.*, **4**, 545 (2002).
37. A. V. Murugan, *Electrochim. Acta*, **50**, 4627 (2005).
38. X. Liu, H. Li, M. Ishida, H. Zhou, *J. Power Sources*, **243**, 374 (2013).
39. D. L. Ma, Z. Y. Cao, H. G. Wang, X. L. Huang, L. M. Wang, X. B. Zhang, *Energy Environ. Sci.*, **5**, 8538 (2012).
40. V. A. Nguyen, C. Kuss, *J. Electrochem. Society*, **167**, 065501 (2020).
41. H. Zhong, A. He, J. Lu, M. Sun, J. He, L. Zhang, *J. Power Sources*, **336**, 107 (2016).
42. H. Guo, L. Liu, Q. Wei, H. Shu, X. Yang, Z. Yang, M. Zhou, J. Tan, Z. Yan, X. Wang, *Electrochim. Acta*, **94**, 113 (2013).
43. M. Ling, J. Qiu, S. Li, C. Yan, M. J. Kiefel, G. Liu, S. Zhang, *Nano Letters*, **15**, 4440 (2015).
44. Y. Shi, X. Zhou, J. Zhang, A. M. Bruck, A. C. Bond, A. C. Marschilok, K. J. Takeuchi, E. S. Takeuchi, G. Yu, *Nano Letters*, **17**, 1906 (2017).
45. D. Shao, H. Zhong, L. Zhang, *Chem. ElectroChem.*, **1**, 1679 (2014).
46. S. N. Eliseeva, E. V. Shkreba, M. A. Kamenskii, E. G. Tolstopjatova, R. Holze, V. V. Kondratiev, *Solid State Ionics*, **333**, 18 (2019).
47. B. Liu, P. Soares, C. Checkles, Y. Zhao, G. Yu, *Nano Letters*, **13**, 3414 (2013).
48. T. M. Higgins, S. H. Park, P. J. King, C. Zhang, N. McEvoy, N. C. Berner, D. Daly, A. Shmeliov U. Khan, G. Duesberg, V. Nicolosi, J. N. Coleman, *ACS Nano.*, **10**, 3702 (2016).
49. D. Liu, Y. Zhao, R. Tan, L. L. Tian, Y. Liu, H. Chen, F. Pan, *Nano Energy*, **36**, 206 (2017).
50. G. Zhang, K. Lin, X. Qin, L. Zhang, T. Li, F. Lv, Y. Xia, W. Han, F. Kang, B. Li, *ACS Appl. Mater. Interfaces*, **12**, 37034 (2020).
51. S. Myung, Y. Hitoshi, Y. Sun, *J. Mater. Chem.*, **21**, 9891 (2011).
52. T. Ma, G. Xu, Y. Li, L. Wang, X. He, J. Zheng, J. Liu, M. Engelhard, P. Zapol, L. Curtiss, J. Jorne, K. Amine, Z. Chen, *J. Phys. Chem. Lett.*, **8**, 1072 (2017).
53. L. Luo, P. Zhao, H. Yang, B. Liu, J. G. Zhang, Y. Cui, G. Yu, S. Zhang, C. M. Wang, *Nano Letters*, **15**, 7016 (2015).
54. Y. Y. Zhang, S. J. Zhang, J. T. Li, K. Wang, Y. C. Zhang, Q. Liu, R. S. Xie, Y. R. Pei, L. Huang, S. G. Sun, *Electrochim. Acta*, **298**, 496 (2019).
55. S. Jin, S. Xin, L. Wang, Z. Du, L. Cao, J. Chen, X. Kong, M. Gong, J. Lu, Y. Zhu, H. Ji, *Adv. Mater.*, **28**, 9094 (2016).
56. D. Shin, Y. Song, D. Nam, J. H. Moon, S. W. Lee, J. Cho, *J. Mater. Chem. A*, **9**, 2334 (2021).
57. H. Xu, H. Jin, Z. Qi, Y. Guo, J. Wang, Y. Zhu, H. Ji, *Nanotech.*, **31**, 205710 (2020).
58. S. Jin, Y. Jiang, H. Ji, Y. Yu, *Adv. Mater.*, **30**, 1802014 (2018).
59. C. Jeong, S. Lee, J. Kim, K. Y. Cho, S. Yoon, *J. Power Sources*, **398**, 193 (2018).
60. C. Portet, P. L. Taberna, P. Simon, C. Laberty-Robert, *Electrochim. Acta*, **49**, 905 (2004).
61. J. Li, C. Rulison, J. Kiggans, C. Daniel, D. L. Wood, *J. Electrochem. Soc.*, **159**, A1152 (2012).
62. C. Busson, M. Blin, P. Guichard, P. Soudan, O. Crosnier, D. Guyomard, B. Lestriez, *J. Power Sources*, **406**, 7 (2018).
63. L. Liu, H. Zhao, Y. Lei, *Small Methods*, **3**, 1970023 (2019).