ZINC BATTERIES

BASICS, DEVELOPMENTS, *and* APPLICATIONS

Edited by Rajender Boddula,
Inamuddin, & Abdullah M. Asiri

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Zinc Batteries

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Preface

The growing demand for electric energy storage has prompted many researchers to pursue advanced replacement batteries. Zinc-ion batteries have attracted widespread attention as a viable alternative to the lithium-ion batteries that dominate the market. Zinc is the 4th most abundant metal in the world, which can help to increase the popularity of electric vehicles (EVs) by diminishing the cost of the vehicles. Theoretically, a zinc battery possesses five times the energy density of a lithium battery. Primary Zn-air batteries were first introduced and commercialized in the 1930s. Since then, companies like Evercel, Fluidic Energy, Z-Power, EOS, Zinc Five, ZnR Batteries, ZAF, Zinium, etc., have patented and commercialized zinc-based battery solutions. However, Fluidic energy is currently producing reversible Zn-air technology. Zn-based batteries are preferred among all other metal-air batteries because of their salient features like low cost, lightweight, scale up, high energy density, safer battery technology, and environmental friendliness. These rechargeable batteries are very important rising energy storage systems because of their usability in portable electronic devices, grid management, and electric vehicles.

Zinc Batteries: Basics, Developments, and Applications is intended as a discussion of the different zinc batteries for energy storage applications. It also provides an in-depth description of various energy storage materials for Zn batteries. This book is an invaluable reference guide for electrochemists, chemical engineers, students, faculty, and R&D professionals in energy storage science, material science, and renewable energy. Based on thematic topics, the book contains the following fourteen chapters:

Chapter 1 details the various types of carbon structures used for the development of the zinc-ion battery (ZB). The major focus is on the ultimate design of ZBs using carbon to enhance oxygen reduction reaction for the better performance of ZBs.

Chapter 2 elucidates the different zinc batteries for energy-storage applications. The structure of a zinc battery is discussed. Also, the anode and cathode materials of zinc-carbon, zinc-cerium, and zinc–bromine batteries are highlighted for energy storage applications.

Chapter 3 discusses the fundamentals of zinc batteries and their scope of improvement by presence of metal additives like nickel and cobalt to prepare them as futurist batteries on a large scale. It focuses on their working, advantages and disadvantages, and the outlook and prospects of metal additives–based zinc batteries.

Chapter 4 focuses on how manganese-based material for Zn batteries will exhibit extensive properties for future use.

Chapter 5 discusses the different types of electrolytes, such as aqueous, nonaqueous, solid polymer and biopolymer electrolytes that are used in Zn-ion batteries. Additionally, it also highlights the different types of advancements in the electrolytes and recently reported electrolytes for the Zn-ion batteries.

Chapter 6 discusses zinc-ion batteries, their types and storage mechanisms. Several anodes for zinc-ion batteries with different morphologies and nanostructures are discussed and analyzed. A glimpse of the future of zinc-ion batteries is also discussed.

Chapter 7 discusses the cathode materials for zinc-air batteries. It also discusses the cathode definition, zinc cathode structure, non-valuable materials for cathode electrocatalytic, electrochemical specifications of activated carbon as a cathode, electrochemical evaluation of cathode substances $La_{1-x}Ca_xCoO_3$ zinc batteries and introduction of the other important synthesized cathode for zinc-air batteries.

Chapter 8 provides an up-to-date overview of research efforts on various zinc anode coatings to improve the stability of the charging cycle and design a new and improved zinc anode for increasing the battery energy efficiency and its lifetime. The challenges and problems facing zinc anodes of electrically rechargeable zinc-air batteries are discussed.

Chapter 9 discusses the basic principle and types of zinc-based batteries, along with their environmental effects. A detail discussion is presented on safety-related issues. Further, disposal and recycling methods are also highlighted.

Chapter 10 overviews the basic principles and developments of zinc-air batteries. This chapter elaborates on the public specifications, zinc-air electrode chemical reaction, zinc/air battery construction, primary Zn/ Air Batteries, principles of configuration and operation of Zn/air batteries, developments in electrical fuel Zn/Air batteries and Zn/air versus metal/ air systems.

Chapter 11 covers the widespread study of the history and advancements identified with Zinc batteries. Further, challenges confronting the advancement of new Zinc batteries are featured, along with future research viewpoints.

Chapter 12 discusses the effects of electrolyte selection, different electrolyte types, and anode selection on the inherent characteristics of the electrolyte, in rechargeable zinc-air batteries. Broad categories of electrolytes, e.g., acidic or alkaline electrolytes, polymers, and ionic liquids are investigated in this chapter with focus on the performance enhancement of zinc batteries by the proper electrolyte selection.

Chapter 13 overviews different issues associated with the zinc electrode. Safety, storage, handling, influences and disposal/recycling of zinc batteries are also discussed. The primary focus is given on the impacts on the ecological system.

Chapter 14 deals with the functioning principle and expansion of the nickel-zinc battery. The active material for nickel zinc batteries is a good approach to refining the life cycle of the nickel zinc battery. This chapter also includes different types of active material for a better life cycle in nickel zinc battery. The applications of nickel-zinc battery are also discussed.

Key Features

- Coverage on basic research and application approaches
- Explores challenges and future directions of Zn-based batteries
- Elaborates extensive properties of Zn batteries electrodes for future use

Editors
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1

Carbon Nanomaterials for Zn-Ion Batteries

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Abstract

The development of the zinc-ion battery (ZB) hindered due to the problem associated with the suitability of its design especially on the catalyst and electrodes parts. Modified surface of carbon can enhance oxygen reduction reaction significantly for the catalytic performances. An ultimate design of ZBs should contain proper synthesis along with a precursor-like nitrogen with carbon-metal support for enhanced performances of ZBs. Electrodes formed with N-doped carbon fiber network with Co_4N NPs not only provide high current density but also flexibility to ZBs. The ORR of ZBs can also be increased by using the N-doped carbon nanofiber (NCN). The enhancement of OER/ORR activity has been observed by coupling $NiCo_2S_4$ nanocrystals with nitrogen-doped carbon nanotubes (N-CNT/$NiCo_2S_4$) for electrocatalyst applications in ZBs. P and S co-doped C_3N_4 sponge with C nanocrystal (P-S-CNS) demonstrated good OER and ORR activity. The OER and ORR performance can also be enhanced with the use of carbon nanosheets because of its greater surface area. The morphology and the porous structure in the N-rGO/NC cathode surface OER and ORR activity in ZBs.

Keywords: Zinc-ion battery, carbon, nanocomposites, oxygen-reduction, oxygen-evolution

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1.1 Introduction

The demand of storage energy especially without depending much on fossil fuels has been accelerated recent years with the progress in the battery field technologies [1–7]. The use of lithium undoubtedly makes it the leader in this sector. But, for the sake of electric vehicles (EVs), the use of lithium increase the cost many folds which is one of the reasons of unpopularity of EVs in the consumer vehicle market [8, 9]. In these sense, zinc, the 4th abundant metal in the world, can help to increase the popularity of the EVs by diminishing the cost the vehicles [10]. Theoretically, the zinc battery (ZB) possesses five times the energy density with respect to the lithium batteries. Hence, they are much more superior to that of its lithium counterpart both theoretically as well as economically. Despite of all this the advantages of ZB technology, its development highly hindered due to the problem associated with the suitability of its design especially on the catalyst and electrodes parts [11]. Modified surface of carbon can enhance oxygen reduction reaction significantly for the catalytic performances [12]. Hence, an ultimate design should contain proper synthesis along with a precursor-like nitrogen with carbon-metal support for enhanced performances of ZBs.

1.2 Co_4N (CN) - Carbon Fibers Network (CFN) - Carbon Cloth (CC)

Electrodes formed with N-doped carbon fiber network with Co_4N NPs shown in Figure 1.1 [13]. Meng *et al.* observed enhanced catalytic performances of CN/CFN/CC as an electrode in ZBs [13]. The following design not only provides 1 mA cm^{-2} current density but also flexible nature to ZBs in contrast to the conventional metal electrodes. The design can withstand 408 cycles with 1.09-V discharge-charge gap at 50 mA per cm^2 with 20 h of retention of current density. Moreover, the flexible nature of the ZBs makes it a perfect power source for a wide range of wearable portable devices.

1.3 N-Doping of Carbon Nanofibers

The ORR of ZBs can enhance with the N-doped carbon nanofiber (NCN) as shown in Figure 1.2 [14]. Here, large surface area as well as the exposure of the NCNs increased the ORR activity. The use of NCNs can surpass the peak power density of available platinum/carbon catalyst of magnitude 192 mW cm^{-2} to by using NCNs in ZBs with a new magnitude of 194 mW cm^{-2} [14].

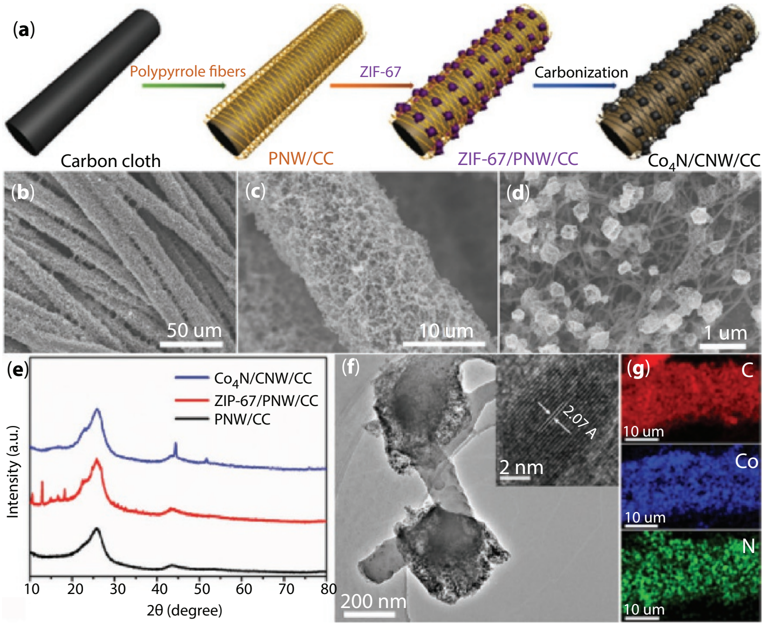

Figure 1.1 (a) Steps of Synthesis, (b)–(d) SEM images, (e) XRD, (f) TEM images and (g) EDS of CN/CFN/CC electrodes. Reprint with the permission from Reference [13]. Copyright 2016, ACS.

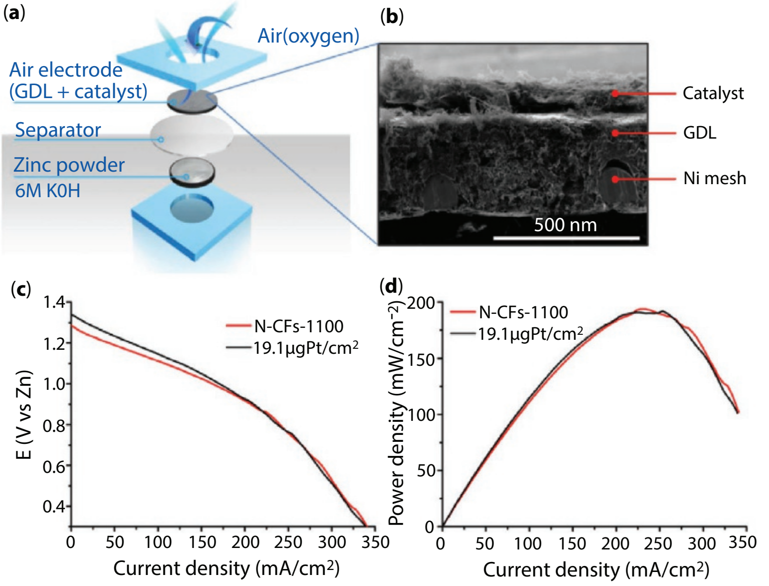

Figure 1.2 (a) ZB, (b) division of air electrode, (c) polarization graph, and (d) power density graph. Reprint with the permission from Reference [14]. Copyright 2013, Elsevier.

Moreover, the superiority of NCNs can also helps to achieve better electron numbers and hydrogen peroxide yields than that of the platinum/carbon catalyst.

1.4 $NiCo_2S_4$ on Nitrogen-Doped Carbon Nanotubes

The enhancement of OER/ORR activity has been observed by Han *et al.* by coupling $NiCo_2S_4$ nanocrystals with nitrogen-doped carbon nanotubes (N-CNT/$NiCo_2S_4$) for electrocatalyst applications in ZBs [15]. The

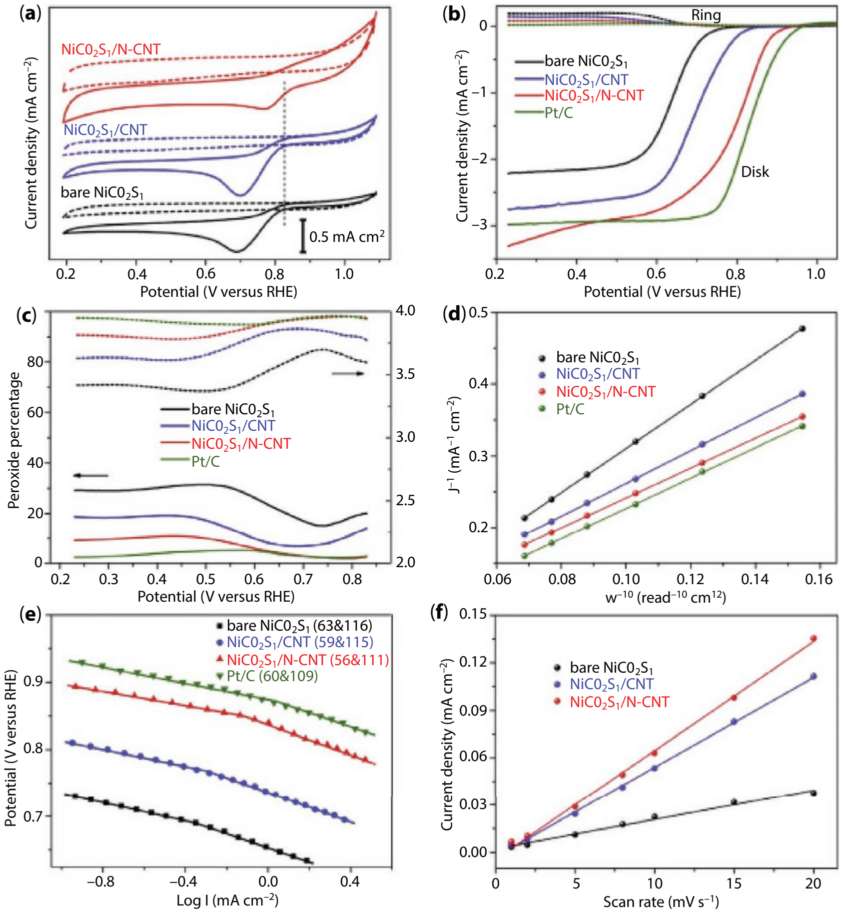

Figure 1.3 (a) Cyclic and (b) Linear voltammograms, (c) peroxide (solid) and no. of electrons (dotted), (d) K-L graph, (e) Tafel graph, (f) current densities of $NiCo_2S_4$, CNT/$NiCo_2S_4$, and N-CNT/$NiCo_2S_4$. Reprint with the permission from Reference [15]. Copyright 2017, Elsevier.

reversibility, stability, and bifunctional activity as shown in Figure 1.3 were up to the level of well-known metal catalysts performances. More positive cathode potential has been observed for N-CNT/$NiCo_2S_4$ in compression to its counterpart. Hence, this new design with carbon composites along with chalcogenides enables better performances for the ZBs.

1.5 3D Phosphorous and Sulfur Co-Doped C_3N_4 Sponge With C Nanocrystal

P and S co-doped C_3N_4 sponge with C nanocrystal (P-S-CNS) demonstrated good OER at 10 mA per cm^2 current density with 1.56 V. The ORR activity also enhanced up to 7 mA cm^{-2} with 1-V potential [16]. Figure 1.4 also showed that the power density with the use of P-S-CNS in ZBs can reach up to 200 mW per cm^2 at 200 mA per cm^2 current density. Not only that, it can provide emf of 1.5 V at a specific capacitance of around 830 mAh per g^1. The energy density also can reach up to 970 Wh per kg^1 at 5 mA per cm^2 current density. The reversibility and stability also enhances up to 500 cycles. Hence, the use of P-S-CNS in place of precious metals indeed demonstrates a cleaner and greener way of storage devices with respect to the conventional batteries.

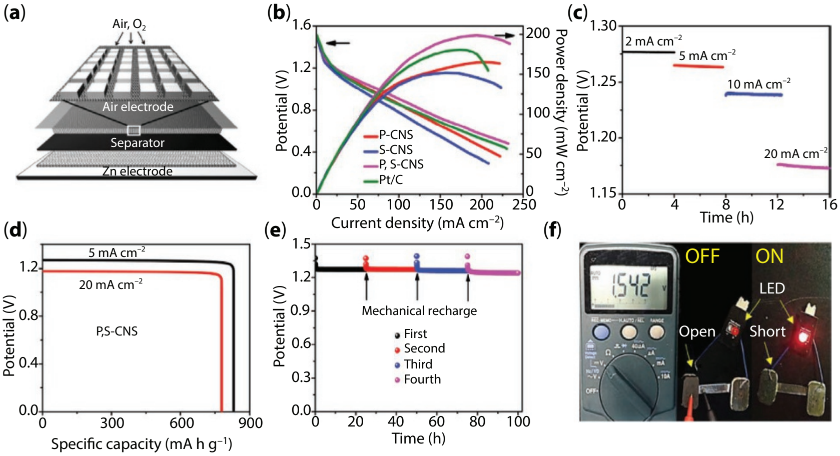

Figure 1.4 (a) ZBs; (b) Power density; (c) Galvanostatic discharge graphs; (d) Specific capacity; (e) Stability; (f) Simple demonstration with P-S-CNS. Reprint with the permission from Reference [16]. Copyright 2016, ACS.

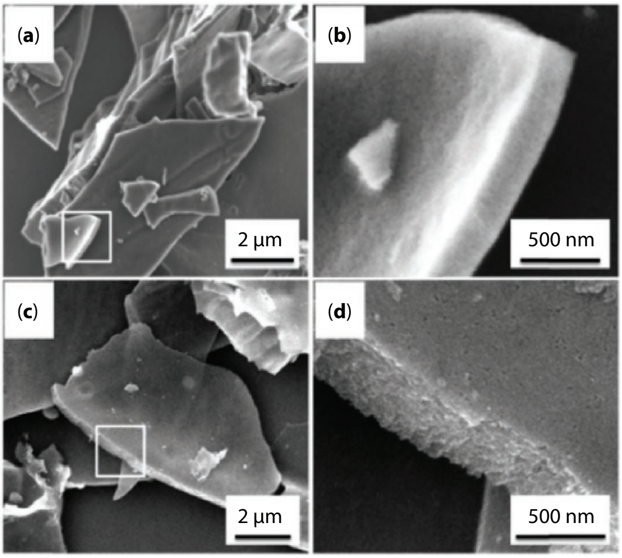

Figure 1.5 SEM images of 2D carbon nanosheets. Reprint with the permission from Reference [17]. Copyright 2015, RSC.

1.6 2D Carbon Nanosheets

The larger surface area of 1,050 m^2 per g of the nanosheets of carbon indeed makes it suitable for the application of the ZBs [17]. Figure 1.5 shows the SEM images of the 2D structure of the nanosheets. The OER and ORR performance can be enhanced with the use of carbon nanosheets because of its greater surface area which increase the oxygen absorption and enhance the catalytic activities in many folds. The platinum/carbon galvanic discharge voltage 1.2 V of current density of 5 mA per cm^2 can be achievable using the carbon nanosheets in ZBs. Hence, the competitive performances with the low cost of production indeed make it a suitable choice to use in the ZBs.

1.7 N-Doped Graphene Oxide With $NiCo_2O_4$

Graphene oxide with N-doped along with $NiCo_2O_4$ (N-rGO/NC) can be used as another stable cathode electrode for the ZBs applications [18]. The flower-like structure of the N-rGO/NC is shown in Figure 1.6. The flower-like structure helps to obtain 4-V plateau in the charge profile whereas

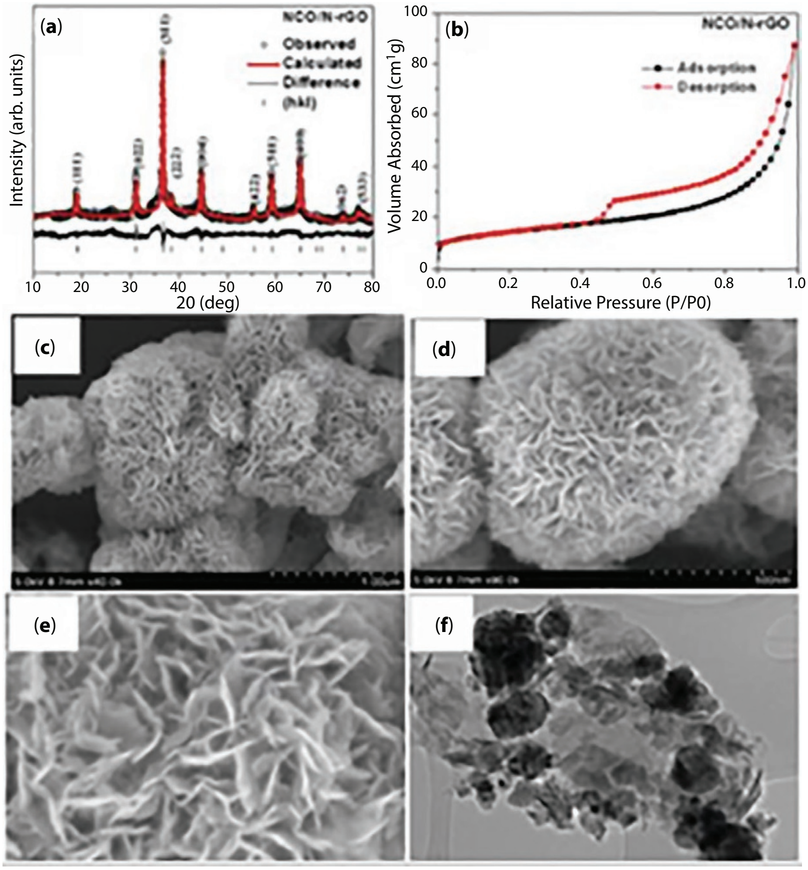

Figure 1.6 SEM, TEM, and XRD N-rGO/NC. Reprint with the permission from Reference [18]. Copyright 2017, RSC.

the plateau is situated around 2.6 V for the discharge profile. The capacity of the ZBs with the use of N-rGO/NC cathode can reach up to 7,000 mAh g^{-1} till 35 h. The morphology and the porous structure in the N-rGO/NC cathode surface help better flow of oxygen which enhances the OER and ORR activity.

1.8 Conclusions

In summary, the development of the zinc-ion battery (ZB) hindered due to the problem associated with the suitability of its design especially on the catalyst and electrodes parts. Modified surface of carbon can enhance oxygen reduction reaction significantly for the catalytic performances. An ultimate design of ZBs should contain proper synthesis along with a precursor-like nitrogen with carbon-metal support for enhanced performances of ZBs. For example, electrodes formed with N-doped carbon fiber network with Co_4N NPs not only provide 1 mA cm^{-2} current density but also flexibility to ZBs. The ORR of ZBs can also increase with N-doped carbon nanofiber (NCN). The enhancement of OER/ORR activity has been observed by coupling $NiCo_2S_4$ nanocrystals with nitrogen-doped carbon nanotubes (N-CNT/$NiCo_2S_4$) for electrocatalyst applications in ZBs. P and S co-doped C_3N_4 sponge with C nanocrystal (P-S-CNS) demonstrated good OER 10 mA per cm^2 current density with 1.56 V. The ORR activity also enhanced up to 7 mA cm^{-2} with 1-V potential. The OER and ORR performance can be enhanced with the use of carbon nanosheets because of its greater surface area which increase the oxygen absorption and enhance the catalytic activities in many folds. The morphology and the porous structure in the N-rGO/NC cathode surface help better flow of oxygen which enhances the OER and ORR activity in the ZBs.

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References

1. Skyllas-Kazacos, M., Chakrabarti, M.H., Hajimolana, S.A., Mjalli, F.S., Saleem, M., Progress in flow battery research and development. *J. Electrochem. Soc.*, 158, 8, R55–R79, 2011.
2. Park, M., Ryu, J., Wang, W., Cho, J., Material design and engineering of next-generation flow-battery technologies. *Nat. Rev. Mater.*, 2, 1, 16080, 2017.
3. Gaikwad, A.M., Arias, A.C., Steingart, D.A., Recent progress on printed flexible batteries: Mechanical challenges, printing technologies, and future prospects. *Energy Technol.*, 3, 4, 305–328, 2015.
4. Yuan, X., Liu, H., Zhang, J. (Eds.), *Lithium-ion batteries: Advanced materials and technologies*, CRC Press, 2011.
5. Wang, W., Luo, Q., Li, B., Wei, X., Li, L., Yang, Z., Recent progress in redox flow battery research and development. *Adv. Funct. Mater.*, 23, 8, 970–986, 2013.

6. Yoo, H.D., Markevich, E., Salitra, G., Sharon, D., Aurbach, D., On the challenge of developing advanced technologies for electrochemical energy storage and conversion. *Mater. Today*, 17, 3, 110–121, 2014.
7. Benson, C.L. and Magee, C.L., On improvement rates for renewable energy technologies: Solar PV, wind turbines, capacitors, and batteries. *Renewable Energy*, 68, 745–751, 2014.
8. Gaines, L. and Cuenca, R., *Costs of lithium-ion batteries for vehicles (No. ANL/ESD-42)*, Argonne National Lab., IL (US), 2000.
9. Nelson, P.A., Gallagher, K.G., Bloom, I.D., Dees, D.W., *Modeling the performance and cost of lithium-ion batteries for electric-drive vehicles (No. ANL-12/55)*, Argonne National Lab.(ANL), Argonne, IL (United States), 2012.
10. Li, Y., Gong, M., Liang, Y., Feng, J., Kim, J.E., Wang, H., Dai, H., Advanced zinc-air batteries based on high-performance hybrid electrocatalysts. *Nat. Commun.*, 4, 1805, 2013.
11. Rahmanifar, M.S., Mousavi, M.F., Shamsipur, M., Heli, H., A study on open circuit voltage reduction as a main drawback of Zn–polyaniline rechargeable batteries. *Synth. Met.*, 155, 3, 480–484, 2005.
12. Li, B., Chen, Y., Ge, X., Chai, J., Zhang, X., Hor, T.A., Zong, Y., Mussel-inspired one-pot synthesis of transition metal and nitrogen co-doped carbon (M/N–C) as efficient oxygen catalysts for Zn-air batteries. *Nanoscale*, 8, 9, 5067–5075, 2016.
13. Meng, F., Zhong, H., Bao, D., Yan, J., Zhang, X., In situ coupling of strung Co4N and intertwined N–C fibers toward free-standing bifunctional cathode for robust, efficient, and flexible Zn–air batteries. *J. Am. Chem. Soc.*, 138, 32, 10226–10231, 2016.
14. Park, G.S., Lee, J.S., Kim, S.T., Park, S., Cho, J., Porous nitrogen doped carbon fiber with churros morphology derived from electrospun bicomponent polymer as highly efficient electrocatalyst for Zn–air batteries. *J. Power Sources*, 243, 267–273, 2013.
15. Han, X., Wu, X., Zhong, C., Deng, Y., Zhao, N., Hu, W., NiCo2S4 nanocrystals anchored on nitrogen-doped carbon nanotubes as a highly efficient bifunctional electrocatalyst for rechargeable zinc-air batteries. *Nano Energy*, 31, 541–550, 2017.
16. Shinde, S.S., Lee, C.H., Sami, A., Kim, D.H., Lee, S.U., Lee, J.H., Scalable 3-D carbon nitride sponge as an efficient metal-free bifunctional oxygen electrocatalyst for rechargeable Zn–air batteries. *ACS Nano*, 11, 1, 347–357, 2016.
17. Li, B., Geng, D., Lee, X.S., Ge, X., Chai, J., Wang, Z., Zong, Y., Eggplant-derived microporous carbon sheets: Towards mass production of efficient bifunctional oxygen electrocatalysts at low cost for rechargeable Zn–air batteries. *Chem. Commun.*, 51, 42, 8841–8844, 2015.
18. Moni, P., Hyun, S., Vignesh, A., Shanmugam, S., Chrysanthemum flower-like NiCo 2 O 4–nitrogen doped graphene oxide composite: An efficient electrocatalyst for lithium–oxygen and zinc–air batteries. *Chem. Commun.*, 53, 55, 7836–7839, 2017.