batteries

MDPI

Editorial

Research in Nickel/Metal Hydride Batteries 2017

Kwo-Hsiung Young [1,2]

[1] BASF/Battery Materials—Ovonic, 2983 Waterview Drive, Rochester Hills, MI 48309, USA; kwo.young@basf.com; Tel.: +1-248-293-7000

[2] Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202, USA

Academic Editor: Andreas Jossen

Received: 2 January 2018; Accepted: 26 January 2018; Published: 12 February 2018

Abstract: Continuing from a special issue in Batteries in 2016, nineteen new papers focusing on recent research activities in the field of nickel/metal hydride (Ni/MH) batteries have been selected for the 2017 Special Issue of Ni/MH Batteries. These papers summarize the international joint-efforts in Ni/MH battery research from BASF, Wayne State University, Michigan State University, FDK Corp. (Japan), Institute for Energy Technology (Norway), Central South University (China), University of Science and Technology Beijing (China), Zhengzhou University of Light Industry (China), Inner Mongolia University of Science and Technology (China), Shenzhen Highpower (China), and University of the Witwatersrand (South Africa) from 2016–2017 through reviews of AB_2 metal hydride alloys, Chinese and EU Patent Applications, as well as descriptions of research results in metal hydride alloys, nickel hydroxide, electrolyte, and new cell type, comparison work, and projections of future works.

Keywords: nickel-metal hydride battery; rechargeable alkaline battery; metal hydride alloy; electrochemistry; electrolyte; core-shell structure

1. Introduction

The Nickel/metal hydride (Ni/MH) battery continued to be an important energy storage source in 2017. Recent demonstrations of Ni/MH batteries in a few key applications, such as new hybrid electric vehicles manufactured in China [1], an integrated smart energy solution in Sweden [2], a Ni/MH battery system with a high robustness at high temperature in Middle East [3], fast charge (3–5 min) [4] and a wide temperature range (between −55 and 70 °C) [5] for bus transportation, the introduction of Mega Twicell for larger scale energy storage [6], and Cellect 600 for telecommunication backup power [7]. This progress pushed research and development work into multiple directions with targets of higher gravimetric energy, higher delivered power at low temperature, prolonged cycle life at high temperature, and lower material and manufacturing costs. Continuing from the work established in a United States Department of Energy funded program—Robust Affordable Next Generation Energy Storage System (RANGE) in 2015–2016 [8], further development, especially in the implementation of the advanced materials at the cell level, were accomplished by BASF and its collaborators. These accomplishments are reported in this special issue of Batteries.

2. Contributions

The selected papers presented in this Special Issue are highlighted in this section. They are mainly results obtained through international collaborations with other institutes, and can be divided into six general categories: reviews (three papers), metal hydride (MH) alloys used as negative electrode active materials (seven papers), nickel hydroxide as the positive electrode active materials (one paper), electrolyte (two papers), cell performance (five papers), and special analytic tools (one paper).

2.1. Reviews on Related Work

Three review papers are included in this Special Issue of Batteries: one on the C14-predominated AB_2 MH alloys [9] and two on Patent Applications related to Ni/MH batteries filed separately in China [10] and Europe [11]. AB_2 MH alloy has a 20% higher capacity than that from the conventional used misch-metal based AB_5 MH alloy, and is absent from the rare earth elements and immune from their price volatilities. However, the relatively lower performances in high-rate dischargeability and cycle stability in AB_2 require refinements in both the chemical composition and fabrication process, which are reviewed and discussed here. In the intellectual property area, related patents (or applications) are important to the researchers and companies in the field in addition to regular academic publications. Continuing from the reviews of patents from United States [12] and Japan [13] published last year, we focused on patent applications filed in the country that produces the most Ni/MH batteries—China—and the third largest consumer market—Europe. While the Chinese Patents focus more on the battery components and fabrication method, the European ones concentrate on applications, such as for the button cell and bipolar design.

2.2. Metal Hydride Alloys

There are studies of three families of MH alloys included in this Special Issue of Batteries, AB_2 (both C14 and C15), body-centered-cubic (BCC), and superlattice alloys. In the Laves phase-based AB_2 family, doping effects of Pd [14] and B [15] to a C14-predominated alloy were studied and a comparison between C14- and C15-MH alloys was also presented [16]. The preliminary conclusions are both Pd and a newly formed V_3B_2 phase improve the surface catalytic ability and C15 alloy is more suitable for high-rate application. In the BCC area, thermal annealing was found to be beneficial to the corrosion resistance of a Fe-containing alloy by introducing a new Ti-rich phase [17]. Lastly, the effects of annealing [18], addition of Fe [19], and alkaline etch were reported in superlattice based MH alloys [20]. Optimization of the annealing condition and Fe-content were obtained. Additionally, a superlattice MH alloy with high La-content treated by an alkaline etching was recommended for high-rate application.

2.3. Nickel Hydroxide

The discovery of a core-shell structured high-capacity $Ni(OH)_2$ used as active material in the positive electrode of Ni/MH batteries was a major accomplishment in the RANGE program [8]. This Special Issue includes a paper that further elaborates on the manufacture, properties, and half-cell results of the high-capacity α-β $Ni(OH)_2$ as compared α-$Ni(OH)_2$ fabricated by other means [21]. After the phase transformation step (initial cycling), a core (β-$Ni(OH)_2$)-shell (α-$Ni(OH)_2$) structured spherical powder with an excellent cycle stability in the flooded half-cell configuration was formed. The shell portion (higher Al-content) of the particle is composed of α-$Ni(OH)_2$ nano-crystals imbedded in a β-$Ni(OH)_2$ matrix, which helps to reduce the stress originating from the lattice expansion in the β-α transformation. A review of the research on α-$Ni(OH)_2$ is also included.

2.4. Electrolyte

Finding an alternative electrolyte with a less corrosion to the MH alloy and expanded voltage window was the top priority of the RANGE program [8]. In 2016, we reported that the reduction of the corrosion nature of the alkaline KOH electrolyte can be accomplished by selection of both adequate combination of alkaline species [22] and salt additives [23]. In this Special Issue, the effects of adding Cs_2CO_3 salt in the electrolyte was further investigated, and a newly formed surface amorphous oxide was credited for the reduction of surface oxidation of the MgNi-based MH alloy [24]. Another breakthrough was using the ionic liquid to replace the aqueous KOH solution as the electrolyte [8]. The non-aqueous ionic liquid enabled the use of ultrahigh-capacity Si anode (3635 mAh g^{-1}) [25] and expansion of the voltage window. A paper about the fundamental principle and selection of ionic liquid used in the proton-conducting MH battery is included in the Special Issue of Batteries [26].

2.5. Cell Performance Comparison

Sealed cells were built and tested to verify the results obtained from half-cell testing. In the C-size cell, performances of AB_2 (between C14 and C15) [27], a Fe-free [28] and a Fe-doped [29] superlattice MH alloys were measured, and that results can be summarized as follows: C15-based MH alloy was more suitable for high-rate application comparing to those from C14 alloy and confirm previous half-cell results [16], superlattice alloy showed better high-rate and low-temperature performances comparing to those of AB_5 MH alloy, and Fe in the superlattice alloy can extend the cycle life by preventing Al-leaching from the negative electrode. In the newly developed pouch type cell, the high-capacity core-shell $Ni(OH)_2$ was compared to the conventional single-phase $Ni(OH)_2$, and lower impedance and better charge retention were observed [30]. Lastly, the high-temperature storage characteristics of Ni/MH battery module based on superlattice MH alloy were compared to those from nickel-cadmium and valve-regulated lead-acid batteries, and favorable results were obtained [31].

2.6. Analytic Methodology

Continuing from previous reports on the crystallographic orientation alignments in phases in an AB_2-predominating alloy [32] and a BCC-C14 alloy [33], electron backscatter diffraction (EBSD) was applied to a series of La-Mg-Ni-based superlattice metal hydride alloys produced by a novel method of interacting a $LaNi_5$ alloy with Mg vapor [34]. Mg formed discrete grains and then diffused through the *ab*-phase of $LaNi_5$ and transformed it into AB_2, AB_3, and A_2B_7 phases. According to EBSD mapping, diffusion of Mg stops at the grain boundary of the host $LaNi_5$ alloy. A prefect alignment in the *c*-axis between the newly formed superlattice phases and $LaNi_5$ was observed. Understanding of Mg-$LaNi_5$ solid-state reaction contributes directly to development work for a low-cost fabrication method to produce high-value superlattice alloys for battery applications.

3. Conclusions

In this Special Issue of Batteries, the joint research efforts from BASF-Ovonic and their collaborators in 2016–2017 are highlighted by reviewing nineteen papers focused on the area of Ni/MH batteries. The majority of the works focused on the implementation of the advanced material/cell design developed from the previous year, including both the superlattice MH alloy and BCC-based multi-phase MH alloys used as negative electrode active materials, high-capacity core-shell β-α $Ni(OH)_2$ as positive electrode active materials, ionic liquid as electrolyte, and pouch cell design. Future research activities of the team aim to commercialize high-capacity Si-based negative electrode, development of high-capacity Mn-based positive electrode, thin separator to reduce the impedance of the ionic liquid electrolyte, and continuous improvement in the low-and high-temperature performance of Ni/MH batteries.

Acknowledgments: The Guest Editor (K.Y.) thanks both the colleagues who made impressive and important contributions to the articles and the editorial team at the publisher MDPI for providing precious guidance. K.Y. is also obliged to R.F. Jordan at the Rockefeller University for refinement of his writing.

Conflicts of Interest: The author declares no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

Ni/MH	Nickel/metal hydride
RANGE	Robust Affordable Next Generation Energy Storage System
MH	Metal hydride
BCC	Body-centered-cubic
EBSD	Electron backscatter diffraction

References

1. Ogawa, K. Toyota to Start Local Production of NiMH Battery Cells in CHINA by end of 2016. Available online: http://techon.nikkeibp.co.jp/atclen/news_en/15mk/030900433/ (accessed on 8 December 2017).
2. Ferroamp EnergyHub Powered by Nilar. Available online: http://www.nilar.com/wp-content/uploads/2017/09/Ferroamp-Customer-Case-NIL17.pdf (accessed on 8 December 2017).
3. Alpha Innovations, Arts Energy and Grolleau Showcase NiMH Solution for Telecom at GITEX, in Dubai. Available online: http://www.alphainnovations.eu/news/alpha-gitex-dubai (accessed on 8 December 2017).
4. Domestic Super Battery Debut: 3–5 Minutes is Full. Available online: http://www.bestchinanews.com/Science-Technology/4877.html (accessed on 8 December 2017).
5. NiMH Battery with an Extreme Temperature Range. Available online: http://www.sohu.com/a/150492105_117460 (accessed on 8 December 2017). (In Chinese)
6. Large Capacity "MEGA TWICELL" Ni-MH Battery Developed by FDK. Available online: http://www.fdk.com/whatsnew-e/release20170215-e.html (accessed on 8 December 2017).
7. Cellect^{TM} 600 Solves the Small Cell Power and Battery Dilemma. Available online: Https://www.alpha.ca/cellect (accessed on 8 December 2017).
8. Young, K.; Ng, K.Y.S.; Bendersky, L.A. A Technical Report of the Robust Affordable Next Generation Energy Storage System-BASF Program. *Batteries* **2016**, *2*, 2. [CrossRef]
9. Young, K.; Chang, S.; Lin, X. C14 Laves phase metal hydride alloys for Ni/MH batteries applications. *Batteries* **2017**, *3*, 27. [CrossRef]
10. Young, K.; Cai, X.; Chang, S. Reviews on the Chinese Patents regarding nickel/metal hydride battery. *Batteries* **2017**, *3*, 24. [CrossRef]
11. Chang, S.; Young, K.; Lien, Y. Reviews of European patents on nickel/metal hydride batteries. *Batteries* **2017**, *3*, 25. [CrossRef]
12. Chang, S.; Young, K.; Nei, J.; Fierro, C. Reviews on the U.S. Patents regarding nickel/metal hydride batteries. *Batteries* **2016**, *2*, 10. [CrossRef]
13. Ouchi, T.; Young, K.; Moghe, D. Reviews on the Japanese Patent Applications regarding nickel/metal hydride batteries. *Batteries* **2016**, *2*, 21. [CrossRef]
14. Young, K.; Ouchi, T.; Nei, J.; Chang, S. Increase in the surface catalytic ability by addition of palladium in C14 metal hydride alloy. *Batteries* **2017**, *3*, 26. [CrossRef]
15. Chang, S.; Young, K.; Ouchi, T.; Nei, J.; Wu, X. Effects of boron-incorporation in a V-containing Zr-based AB_2 metal hydride alloy. *Batteries* **2017**, *3*, 36. [CrossRef]
16. Young, K.; J. Nei, J.; Wan, C.; Denys, R.V.; Yartys, V.A. Comparison of C15- and C15-predominated AB_2 metal hydride alloys for electrochemical applications. *Batteries* **2017**, *3*, 22. [CrossRef]
17. Abdul, J.M.; Chown, L.H.; Odusote, J.K.; Nei, J.; Young, K.; Olayinka, W.T. Hydrogen storage characteristics and corrosion behavior of $Ti_{24}V_{40}Cr_{24}Fe_2$ alloy. *Batteries* **2017**, *3*, 19. [CrossRef]
18. Young, K.; Ouchi, T.; Nei, J.; Koch, J.M.; Lien, Y. Comparison among constituent phases in superlattice metal hydride alloys for battery applications. *Batteries* **2017**, *3*, 34. [CrossRef]
19. Young, K.; Ouchi, T.; Nei, J.; Yasuoka, S. Fe-substitution for Ni in misch metal-based superlattice hydrogen absorbing alloys—Part 1. Structural, hydrogen storage, and electrochemical properties. *Batteries* **2016**, *2*, 34. [CrossRef]
20. Meng, T.; Young, K.; Hu, C.; Reichman, B. Effects of alkaline pre-etching to metal hydride alloys. *Batteries* **2017**, *3*, 30. [CrossRef]
21. Young, K.; Wang, L.; Yan, S.; Liao, X.; Meng, T.; Shen, H.; Mays, W.C. Fabrications of high-capacity alpha-$Ni(OH)_2$. *Batteries* **2017**, *3*, 6. [CrossRef]
22. Nei, J.; Young, K.; Rotarov, D. Studies on MgNi-based metal hydride electrode with aqueous electrolytes composed of various hydroxides. *Batteries* **2016**, *2*, 27. [CrossRef]
23. Yan, S.; Young, K.; Ng, K.Y.S. Effects of salt additives to the KOH electrolyte used in Ni/MH batteries. *Batteries* **2015**, *1*, 54–73. [CrossRef]
24. Yan, S.; Nei, J.; Li, P.; Young, K.; Ng, K.Y.S. Effects of Cs_2CO_3 additives in KOH electrolyte used in Ni/MH batteries. *Batteries* **2017**, *3*, 41. [CrossRef]
25. Meng, T.; Young, K.; Beglau, D.; Yan, S.; Zeng, P.; Cheng, M.M.-C. Hydrogenated amorphous silicon thin film anode for proton conducting batteries. *J. Power Sources* **2016**, *302*, 31–38. [CrossRef]

26. Meng, T.; Young, K.; Wong, D.F.; Nei, J. Ionic liquid-based non-aqueous electrolytes for nickel/metal hydride batteries. *Batteries* **2017**, *3*, 4. [CrossRef]
27. Young, K.; Koch, J.M.; Wan, C.; Denys, R.V.; Yartys, V.A. Cell performance comparison between C14- and C15- predominated AB_2 metal hydride alloys. *Batteries* **2017**, *3*, 28. [CrossRef]
28. Koch, J.M.; Young, K.; Nei, J.; Hu, C.; Reichman, B. Performance comparison between AB_5 and superlattice metal hydride alloys in sealed cell. *Batteries* **2017**, *3*, 35. [CrossRef]
29. Meng, T.; Young, K.; Nei, J.; Koch, J.M.; Yasuoka, S. Fe-substitution for Ni in misch metal-based superlattice hydrogen absorbing alloys—Part 2. Ni/MH battery performance and failure mechanism. *Batteries* **2017**, *3*, 28. [CrossRef]
30. Yan, S.; Meng, T.; Young, K.; Nei, J. A Ni/MH pouch cell with high-capacity $Ni(OH)_2$. *Batteries* **2017**, *3*, 38. [CrossRef]
31. Zelinsky, M.A.; Koch, J.M.; Young, K. Performance comparison of rechargeable batteries for stationary applications (Ni/MH vs. Ni-Cd and VRLA). *Batteries* **2018**, *4*, 1. [CrossRef]
32. Liu, Y.; Young, K. Microstructure investigation on metal hydride alloys by electron backscatter diffraction technique. *Batteries* **2016**, *2*, 26. [CrossRef]
33. Shen, H.; Young, K.; Bendersky, L.A. Clean grain boundary observations in multi-phase metal hydride alloys. *Batteries* **2016**, *2*, 22. [CrossRef]
34. Yan, S.; Young, K.; Zhao, X.; Mei, Z.; Ng, K.Y.S. Electron backscatter diffraction studies on the formation of superlattice metal hydride alloys. *Batteries* **2017**, *3*, 40. [CrossRef]