batteries

MDPI

Review

Reviews on Chinese Patents Regarding the Nickel/Metal Hydride Battery

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Abstract: Both the patents issued and applications filed in China regarding nickel/metal hydride (Ni/MH) battery technology are reviewed in the article. Selective works from 39 battery manufactures, 9 metal hydride alloy suppliers, 13 $Ni(OH)_2$ suppliers, 20 hardware suppliers, 19 system integrators, universities, and 12 research institutes are included. China being the country that produces the most Ni/MH batteries is relatively weak in the innovation part of intellectual properties when compared to the US and Japan. However, it produces very many patents in the areas of cell structure optimization and production processes. Designs of high-capacity, high-power, and low-cost cells are compared from different manufacturers.

Keywords: nickel metal hydride battery; Chinese Patent; metal hydride alloy; nickel hydroxide; Chinese battery manufacturer

1. Introduction

The nickel/metal hydride (Ni/MH) battery is an important technology for consumer portable electronics, stationary, and transportation applications [1–3]. Even with the strong competition from the rival Li-ion battery [4–7], Ni/MH still finds its niche market in replacing nickel-cadmium (NiCd) and primary batteries [8–10]. China has been the country that has produced the most (>70%) of the consumer-type Ni/MH batteries for the world since the turn of the century. China has also started to produce Ni/MH batteries for hybrid electrical vehicles produced domestically [11]. While the main mission for the Chinese companies is to make a profit from selling products, many of them have devoted resources to the research and development of Ni/MH batteries—from raw materials, components, the cell, the battery pack, to various applications. Since the intellectual properties belonging to foreign companies have already been reviewed in two prior publications [12,13], only those filed by domestic companies are covered in this article. Three different types of patents are allowed in China: invention patent, utility model, and proactive. In this review, we focus mainly on the invention part unless the content is unique and important. The discussions are classified by the functions of those companies owning the patent right from the battery manufacture, metal hydride (MH) alloy producer, $Ni(OH)_2$ producer, other hardware producer, and system integrator. The relationship between these companies is illustrated in Figure 1. These Chinese issued patents and patent applications can be found online with the English translation of the abstract on the official

site of the State Intellectual Property Office of the People's Republic of China (SIPO) [14]. The full patent application in Chinese can be accessed from the website of the patent search engine—SooPAT as well [15]. The patent application number starts with the year of application, for example 200510087099. The issued patent has a shorter number such as 01242474.

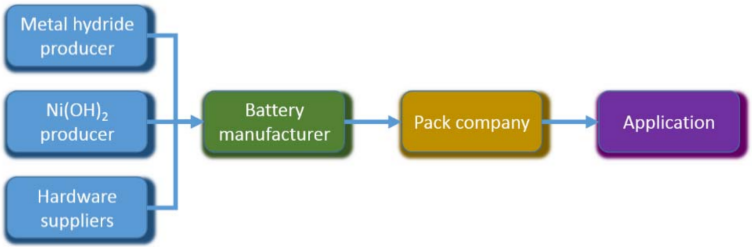


Figure 1. Schematic diagram showing the supply chain for the nickel/metal hydride (Ni/MH) battery industry.

2. Nickel/Metal Hydride (Ni/MH) Battery Manufacturer

In 2012, 74% of the consumer type Ni/MH batteries were produced in China [16]. More than half of them were from the top four manufacturers: Gold Peak (GP, Hong Kong, China), Shenzhen HighPower (SZHP, Shenzhen, Guangdong, China), Corun (Changsha, Hunan, China), and Suppo (Anshan, Liaoning, China) (Figure 2). Brief introductions of the Chinese domestic Ni/MH battery manufacturers are listed in Table 1 and their main inventions in the area of Ni/MH batteries are reviewed in the next few sections. They are mainly located in Guangdong province, especially in the Shenzhen Special District, which just borders Hong Kong (Figure 3). The details of the Ni/MH battery fabrication process were discussed before [12] and a summary flow chart is illustrated in Figure 4.

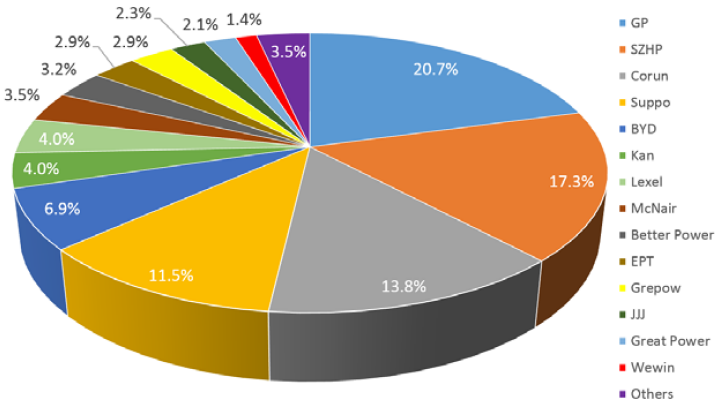


Figure 2. Market share of Chinese domestic Ni/MH battery manufacturer in 2012 [16].

Table 1. Brief introduction of the Chinese Ni/MH battery manufacturers included in this review.

Company Name	Established Date	Headquarter	Main Products	Trademark
Gold Peak 金山/超霸	1964	New Territory, Hong Kong	Ni/MH, Li-ion, primary	GP Batteries
HighPower 豪鹏	2001	Shenzhen, Guangdong	Ni/MH, Li-ion	highpower
Corun 科力远	1998	Changsha, Hunan	Ni/MH	CORUN
Suppo 三普	1996	Anshan, Liaoning	Ni/MH	SUPPO

Table 1. *Cont.*

Company Name	Established Date	Headquarter	Main Products	Trademark
BYD 比亚迪	1995	Shenzhen, Guangdong	Car, Li-ion, Ni/MH	
Kan 凯恩	1993	Suichang, Zhejiang	Ni/MH	
Lexel 力可兴	1997	Shenzhen, Guangdong	Ni/MH	
McNair 迈科	2000	Dongguan, Guangdong	Li-ion, Ni/MH	
BetterPower 倍特力	2002	Shenzhen, Guangdong	Ni/MH, Li-ion	
EPT 量能	2001	Shenzhen, Guangdong	Ni/MH	
Grepow 格瑞普	1998	Shenzhen, Guangdong	Ni/MH, Li-PO	
JJJ 三捷	1989	Jiangmen, Guangdong	Ni/MH, NiCd	
Great Power 鹏辉	2001	Guangzhou, Guangdong	Ni/MH, Li-ion, Li-PO	
Wewin 能一郎	2003	Shenzhen, Guangdong	Li-PO, Ni/MH, Li-ion	
TMK 三俊/大别山	2002	Shenzhen, Guangdong	Ni/MH	
Baosheng 宝生	2006	Chengdu, Sichuan	Ni/MH	
Huangyu 环宇	1982	Xinxiang, Henan	Li-ion	
Fengbiao 沣标/朗泰通	1999	Shenzhen, Guangdong	Ni/MH	
Tianneng 天能	1986	Changxin, Zhejiang	Li-ion, Ni/MH	
Wankaifeng 万凯丰	2010	Mianning, Sichuan	Ni/MH, metal hydride powder	
REO 稀奥科	2001	Baotou, Inner Mongolia	Ni/MH	
BST Power 电科电源	2002	Shenzhen, Guangdong	Ni/MH, NiCd, Li-ion	

Table 1. *Cont.*

Company Name	Established Date	Headquarter	Main Products	Trademark
Zhengda 淄博正大	2009	Zebo, Shandong	Ni/MH	
CENS 赛恩斯	1999	Suzhou, Jiangsu	Ni/MH, NiCd	
Jintion 劲鑫	2002	Quanzhou, Fujian	Ni/MH. NiCd	
Jinhui 金辉	2003	Dongguan, Guangdong	Ni/MH, Li-ion, Li-PO	
Troily 创力	1999	Xinxiang, Henan	NiFe, Ni/MH, NiZn	
Innovation 亿诺	2011	Liuan, Anhui	Ni/MH, Li-PO	
Cel 塞尔	1996	Huaian, Jiangsu	Ni/MH, Li-PO, Li-ion	
Bofuneng 博富能	2003	Shenzhen, Guangdong	Ni/MH, Li-ion, Li-PO	
Ryder 瑞鼎	2005	Shenzhen, Guangdong	Ni/MH, NiCd, charger	
DFEI 德飞	2011	Dali, Shanxi	Ni/MH, Li-ion	
Wintonic 云通	1998	Guangzhou, Guangdong	Ni/MH, Li-ion	
Oceansun 海太阳	2002	Shenzhen, Guangdong	Li-PO, Ni/MH	
Shida 实达	1996	Foshan, Guangzhou	Li-PO, Ni/MH	
Sanik 新力	1995	Foshan, Guangzhou	Ni/MH	
PeaceBay 和平海湾	1996	Tianjin, Tianjin	Ni/MH	
Unitech 联科	2002	Shenzhen, Guangdong	Ni/MH, NiCd, Li-ion	
Taiyi 太一	1996	Zhuhai, Guangdong	Ni/MH	

Figure 3. Locations of domestic Chinese Ni/MH battery manufacturers.

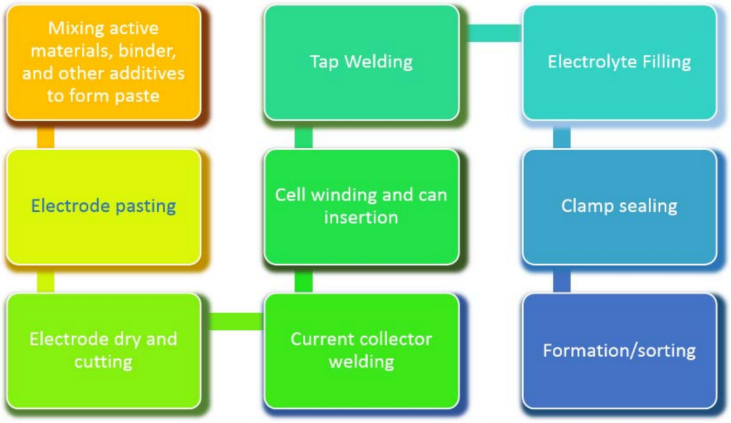


Figure 4. A flow chart showing the Ni/MH battery fabrication processes of a typical manufacturer.

2.1. Gold Peak (GP)

GP obtained two Chinese Patents on the different thicknesses of active material applied on the negative electrode (thicker on the current collector side) to improve the utilization [17] and design of an auto-winding machine [18]. GP also applied patents on a rupture mechanism ensuring a good gas release path when venting occurs [19] (Figure 5), with two separators with different lengths to prevent electrical shortage [20], and a negative electrode with one side scratched to increase the current connectivity to the cell can [21].

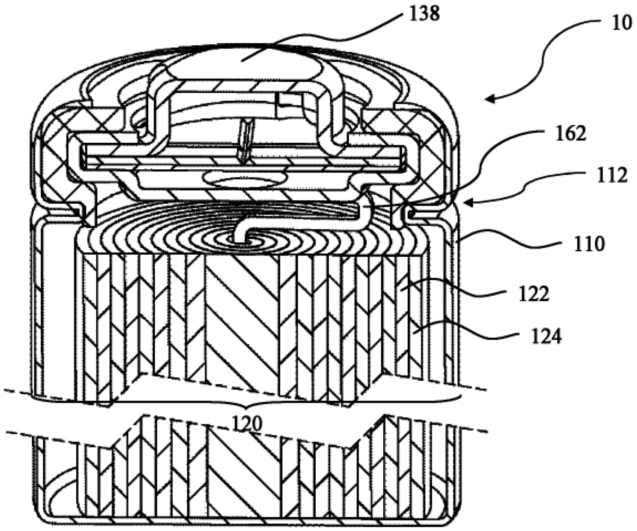


Figure 5. Schematic diagram of a new venting cap design with 10: battery, 138: vent cap, 162: conductive lead, 112: groove, 110: cell can, 122: positive electrode, 124: negative electrode, and 120: electrode assembly [19].

2.2. Shenzhen HighPower

SZHP filed 65 Chinese Patent Applications and was granted 63. In the positive electrode area, a Ni-plated perforated steel (NPPS) as the substrate [22], and a γ-CoOOH coating to extend the cycle life and tolerate overcharge [23] were disclosed. In the negative electrode area, a Ni-coated carbon nanotube as active material [24], a low Pr and Nd AB_5 MH alloy [25], and a hydroxypropyl methylcellulose coating to reduce corrosion [26] were shown. In the electrolyte area, a soluble bromide was added to extend the storage period [27]. In the cell assembly, a multi-cell parallel-connected configuration [28], a multi-venting hole cap design [29], a positive electrode current collector [30], a tap design to self-melt during cell short-circuit [31], a safety short-circuit conduit to prevent explosion [32], a serviceable (electrolyte refilling) cell design [33], an ultra-thin design [34] and a double current-collector design to reduce the cost and production complexity [35] (Figure 6) were introduced. In the fabrication methods, a wet pasting machine [36], a centrifugal electrolyte filling station [37], a capacity sorting machine [38], a tap spot-welding machine [39], and a battery performance testing machine [40] were proposed.

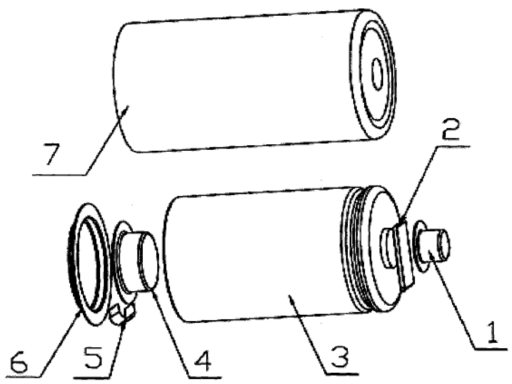
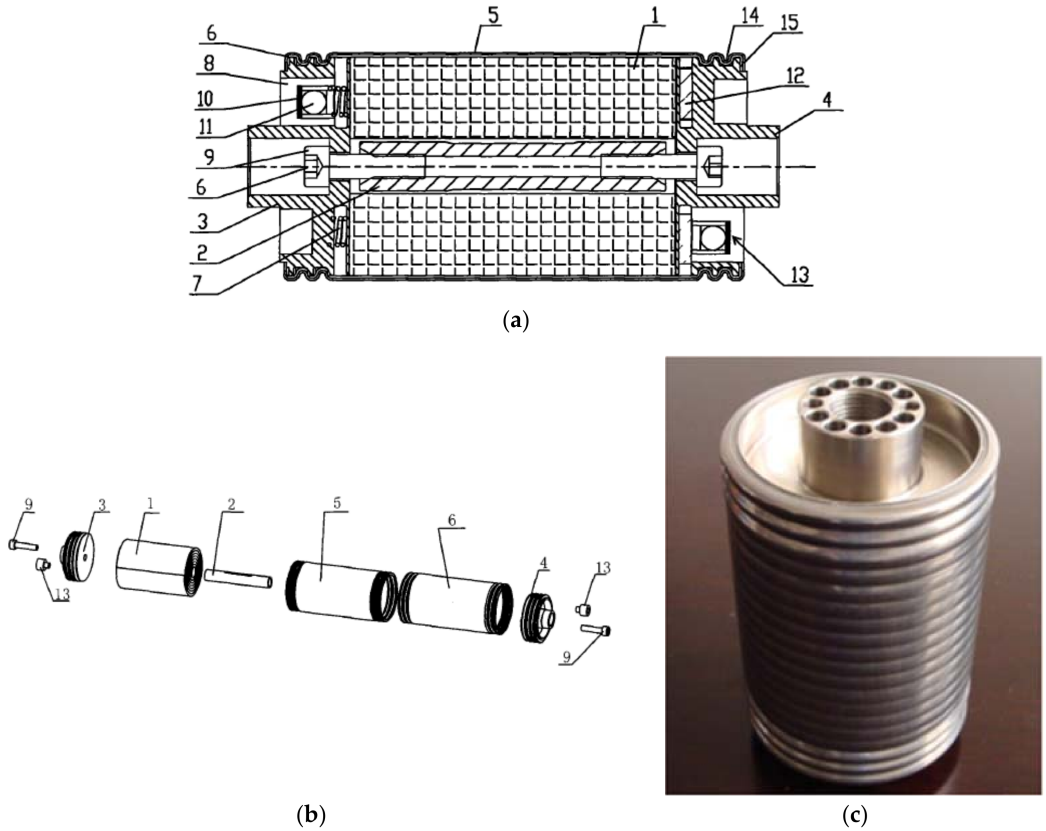


Figure 6. Schematic diagram of a low-cost current collector design with 1: positive terminal, 2: Ni tap, 3: cell assembly, 4: negative electrode bottom plate, 5: Ni tap, 6: negative terminal, and 7: plastic case [35].

2.3. Corun

Corun filed 42 Chinese Patent Application in the area of Ni/MH battery and 18 of them were granted. In the positive electrode area, an extended area covered with a metal wire outside the active material [41], Ca, Y, Co additives [42], and a phosphate [43] and a fluoride [44] coating for high-temperature application were disclosed. In the negative electrode area, a new design of two single-sided electrodes [45] and an electrode composed of single- and double-side coated segments [46] were advocated. In the electrolyte, a tungstate additive for high-temperature charge acceptance [47] was invented. In the cell assembly area, a Ni-plate placed at the bottom of the cell as the negative electrode current collector with a Ni- or Cu-foam in between to increase the high-power capability [48,49], and new type of venting cap designs [50,51] were displayed. A new type of high heat-dissipation battery was proposed with a central conducting rod [52,53] (Figure 7). The production line inventions include an electrode sorting and classification system [54], a battery activation and sorting system [55], an automatic venting cap production machine [56], an automatic electrolyte filling station [57], and a new type of formation process [58].



(**a**) (**b**) (**c**)

Figure 7. (**a**) A cross-section, (**b**) a side-view of a high heat-dissipation cell design, and (**c**) a real photograph with 1: electrode assembly, 2: central rod, 3: positive electrode terminal, 4: negative electrode terminal, 5: case, 6: insulator plastic cover, 7: spring, 8: safe valve base, 9: screw, 10: vent cap, 11: rubber ball, 12: rubber washer, 13: safety valve, 14: groove, and 15: clamp seal [53].

2.4. Suppo

Suppo filed 10 Chinese Patent Applications and was granted six of them. Suppo patented a liquid phase oxidation method to produce a pre-charged NiOOH positive electrode [59], a perforated Cu-substrate for negative electrode [60], a long-life over-stoichiometric AB_x ($5.05 \leq x \leq 5.5$) MH alloy [61], and a design of a low self-discharge battery [62] (Figure 8).

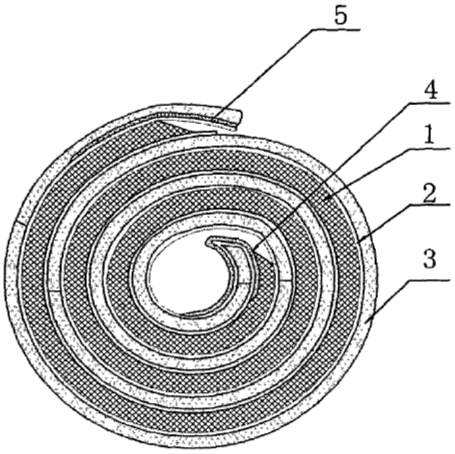


Figure 8. A cross-section view of a low self-discharge cell with an extra spacer at the end of electrode and 1: negative electrode, 2: separator, 3: positive electrode, 4: spacer, and 5: spacer [62].

2.5. BYD

BYD (Shenzhen, Guangdong, China) filed the largest number of Patent Applications in China regarding the Ni/MH battery with 108 applications filed and 84 of them granted. In the positive electrode area, a LiOH solution sprayed Co-coated $Ni(OH)_2$ [63], a Ti-additive to improve the high-temperature charging efficiency [64], a metallic V, Ti, Mo, Mn, Nb, Hf, Zr, Y, or Ta powder additive to improve the capacity and self-discharge performance [65], a poly-oxyalkylene and/or polyhydric alcohol to improve the uniformity in capacity and cycle stability [66], an Al_2O_3, $Al(OH)_3$ or Al-containing salt additives [67], a CoOOH coating [68], a CoO mixture [69] and a depolarizer [70] to increase the charging efficiency and cycle life, and a second coating besides the Co oxides containing the oxide (hydroxide) of Mg, Ba, Zn, Ca, Ti, Al, Ta, Mn, Y, Cr, Cd, Sr, and La-family rare earth element [71] were suggested. In the negative electrode area, surface treatment of $NaBH_4$ [72], NaH_2PO_2 [73], Ni-ion containing solution [74], surface activation by ball milling with alkaline solution [75], Ni or other noble metal [76] coatings, CoO/Co_3O_4 composite additives [77], Y-Ni (or Co) alloy additive to improve the cycle life [78], Cu- [79], Ni- [80], and carbon [81] fine particles coated on the NPPS substrate, addition of Y-containing compounds [82] and tetrapropyl orthosilicate [83], and a metallic thin film on the surface to promote the oxygen recombination during over-charge [84] were proposed. A porous oxide from Ni, Y, Mn, Co, W, Fr, Pb, or Mo was advocated as additives to both positive and negative electrodes to improve the low-temperature performance [85]. In the separator area, a new type of high-temperature (up to 400 °C) material [86] and a new hydrophilic polymer filling [87] were introduced. In the electrolyte area, both an S-containing soluble additive introduced to solve the short-circuit and leakage problems [88] and a gel-type electrolyte for preventing freeze in low-temperature [89] were disclosed. In the cell assembly area, an elongated seal ring [90–92] (Figure 9), a new design of vent cap [93], a venting hole with an oval shape [94], and a multi-layer current collector made of Ni, Cu, stainless steel, Cu and Ni layers [95] were presented. In the alloy design, BYD patterned a NdMgNiAl alloy with a stoichiometry between 3.2 and 3.9 [96], a dual-phase AB_5-based alloy containing a Ti (Zr)-Ni secondary phase [97], a LaNiCuFeCoMnAl alloy containing at least two alkaline earth metals [98], and a RENiCuFeMnSn alloy where RE (rare earth) contains 40–85 wt% La [99] were revealed.

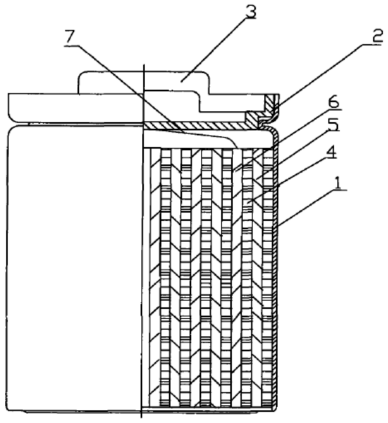


Figure 9. A schematic diagram of a cell with an elongated seal ring and 1: cell wall, 2: sealing ring, 3: vent cap, 4: separator, 5: positive electrode, 6: negative electrode, and 7: tap [91].

2.6. Kan

Kan (Suichang, Zhejiang, China) filed 16 Chinese Patent Applications related to the Ni/MH battery and obtained 13 of them. A MH alloy particle distribution of $D10 \geq 3$ μm, $D50 \leq 80$ μm, and $D90 \leq 130$ μm was claimed to have good high-power capability [100]. An insulator layer was coated on the positive electrode to prevent short-circuit from burr [101]. In the cell assembly, a high-power battery design was repetitively shown in several applications [102–105] (Figure 10). In the fabrication area, an electromagnetic-coupled winder [106], a device for shunting negative electrode [107], an electrode collecting apparatus [108], a connection apparatus to reduce the stress in the automatic spot-welder [109], and an automatic venting cap pressing machine [110] were patented.

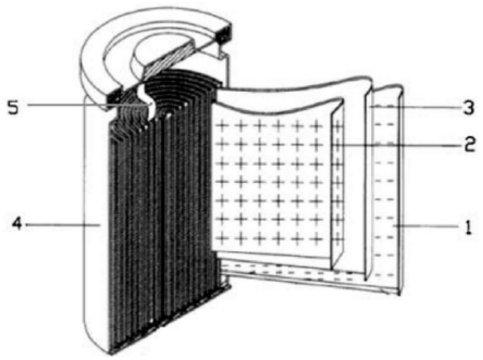


Figure 10. A schematic diagram of a high-power cell design with 1: can, 2: positive electrode, 3: separator, 4: negative electrode, and 5: tap having more than 4 welding spots to the positive electrode [100].

2.7. Lexel

Lexel (Shenzhen, Guangdong, China) filed 13 Chinese Patent applications and received 10 of them as granted. Lexel proposed a composite additive (2% ErO_2, 2% TiO_2, 1% $Ca(OH)_2$) to the positive electrode to increase the energy conversion efficiency during trickle charge [111]. Lexel also advocated the use of oxide or hydroxide of Ti, Y, Er, Tm, Yb, Rf, Ca, or Ba to improve the self-discharge characteristic [112]. In the production facilities, Lexel patented a cell impedance measuring apparatus [113], a cell thermo-resistivity measuring apparatus [114], a cell cleaning machine [115], and a scraping mechanism to remove extra MH powder [116]. In the cell design area, Lexel patented a low-temperature cell [117], a low-cost battery [118], and a high-capacity battery [119] (Figure 11).

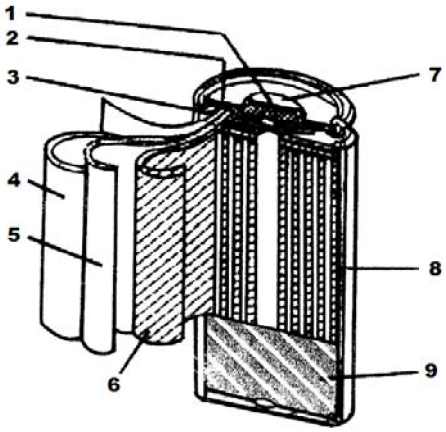


Figure 11. Schematic diagram of a low-cost battery design with 1: rubber, 2: vent cap, 3: plastic gasket, 4: positive electrode, 5: separator, 6: negative electrode, 7: positive terminal, 8: steel can, and 9: space filler [119].

2.8. McNair

McNair (Dongguan, Guangdong, China) disclosed Er, U, and Yb oxides or hydroxides additives in the positive electrode and boron compound in the electrolyte to improve the high-temperature charging efficiency [120], a positive electrode containing 3.7%–4.3% Zn, 1.3%–1.7% Co-co-precipitated $Ni(OH)_2$ with 6% CoO and 1%–10% metallic Ni for a fast charging battery [121], and an additive composed of oxide, hydroxide, fluoride, sulfide, and chloride of Ca, Mn, Er, Y, Yb, and B in the positive electrode with a negative electrode made from superlattice MH for the low self-discharge battery [122].

2.9. BetterPower

There are totally 65 Chinese Patent Applications filed by BetterPower (Shenzhen, Guangdong, China) and 52 got granted. In the positive electrode preparation, an addition of Ca into the paste [123], a vacuum-suction cleaning of the tab area [124], and a Sn-coating Ni-foam [125] were proposed. In the negative electrode preparation, an alkaline pre-activation [126] and an extra current collector layer on the electrode surface [127] were disclosed. In the cell assembly, new materials for the sealing ring [128] and rubber stopper [129], an Al-Cu alloy solder [130], a multi-layer separator [131], a graphite, Ni powder, acetylene black coating inside the wall of the can [132], a varying can wall thickness [133], an open-cell activation method [134], soft oval-shape [135] and cylindrical [136] pouch cells, an automatic powder cleaning station [137], and an automatic folding station [138] were included. A product design of a 9 V battery pack from BetterPower was also granted [139].

2.10. EPT

EPT (Shenzhen, Guangdong, China) filed 52 Chinese Patent Applications on the Ni/MH battery and received 37 of them granted, which cover a fabrication method of a high-capacity cell by adopting electrodes with varying thicknesses [140], a battery with AB_3 MH alloy and pre-oxidized $Ni(OH)_2$ which does not require activation [141], a positive electrode fabrication method using ultrasound atomization [142], a negative electrode containing styrene-butadiene rubber (SBR) or polytetrafluoroethylene (PTFE) as binder [143], a high-power design with additional negative electrode current collector made of Ni-foam [144], and new designs of vent cap [145], sealing ring [146], and current collector [147].

2.11. Grepow

Grepow (Shenzhen, Guangdong, China) filed 21 Chinese Patent Applications and had 10 granted. In the negative electrode area, a Ni-rich (>65%) surface layer prepared by electrodeless plating was

introduced to improve the low-temperature/high-rate performance [148]. Fabrication methods for a low-capacity battery [149], a high-power battery [150] (Figure 12), a wide temperature range battery [151], and a low-impedance battery [152] were also disclosed by Grepow. A combination of battery and heating device was proposed to overcome the low-temperature hurdle of the Ni/MH battery [153,154]. Grepow advocated removing the extra active material in the negative electrode area contacting the can [155] and the related fabrication apparatus [156].

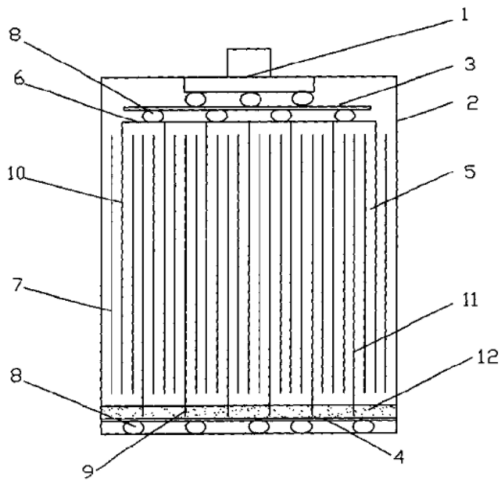


Figure 12. Schematic diagram of a high-power cell with 1: vent cap, 2: cell case, 3: current collector plate, 4: negative electrode plate, 5: electrode assembly, 6: positive electrode plate, 7: separator, 8: spot welding, 9: negative electrode, 10: positive electrode, 11: wound negative electrode, and 12: metallic foam [150].

2.12. JJJ

JJJ (Jiangmen, Guangdong, China) filed nine Chinese Patent Applications and seven of them were accepted. JJJ's inventions include a basic cylindrical cell design [157] (Figure 13), an electrolyte filling apparatus [158], an automatic cell sealing machine [159], a sealing ring coating apparatus [160], a negative electrode waste recycling method [161], a new type of vent cap [162], a low-capacity D-cell design [163], and a current collector design for a high-power battery [164].

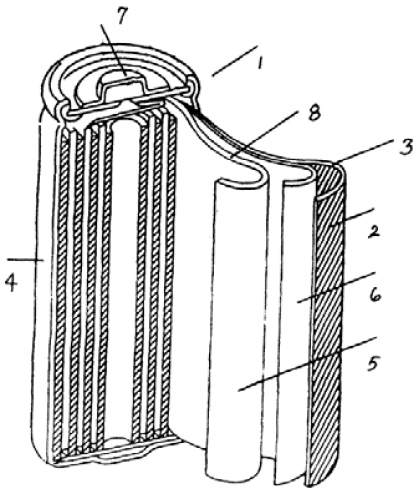


Figure 13. Schematic diagram of a basic structure of a cell with 1: Ni/MH battery, 2: negative electrode, 3: negative substrate, 4: can, 5: positive electrode, 6: separator, 7: vent cap, and 8: positive substrate [147].

2.13. Great Power

Great Power (Guangzhou, Guangdong, China) filed six Chinese Patent Applications and three were allowed. Their inventions include a positive electrode containing CoO, Co, Ni, acetylene black, TiO_2, Y_2O_3, PTFE, and carboxymethyl cellulose [165], a positive electrode substrate using steel web and superfine graphite powder [166], a new type of vent cap [167], and a tri-layer design of negative electrode with a metal plate in between [168].

2.14. Wewin

Only one Chinese Patent Application was filed by Wewin (Xianning, Hubei, China) and is about negative active material using a low-Co AB_5/MgNi composite MH [169].

2.15. Other Battery Manufacturers

Besides the 14 main Chinese Ni/MH manufacturers reported above, there are other smaller companies in China also contributing to the Chinese Patents for the Ni/MH battery and their inventions are summarized in this section. Some of them may be already out of business but their Patent Applications are still reviewed here. Among them, TMK (Shenzhen, China) filed 14 Chinese Patent Applications and received half of them granted. TMK introduced a Ni/MH battery pack with an inspection function [170,171] and a self-balance circuitry [172], a charger preventing overcharge [173], a battery with a good heat dissipation capability [174,175], a control circuitry to prevent over-discharge [176], a low-cost cylindrical cell [177], and a prismatic battery for electrical vehicles (EV) [178]. In the component area, TMK disclosed a new negative electrode current collector [179], a new type vent cap [180], a high-power current collector [181], and a Cu and Ni-coated stainless steel substrate for the negative electrode [182]. In the production facilities, TMK also invented a fixed position electrode holding apparatus [183], a centrifugal electrode dryer [184], and a heated electrolyte filling station [185].

Baosheng (Chengdu, Sichuan, China) applied for 11 Chinese Patents which covered the topics of a high-Fe (3–26 at%) AB_5 MH alloy [186], a Ni/MH battery module for an electrical bus [187], a high-temperature Ni/MH battery with W-containing electrolyte and Ti and Y-added positive electrodes [188], and a high-power Ni/MH battery [189] (Figure 14).

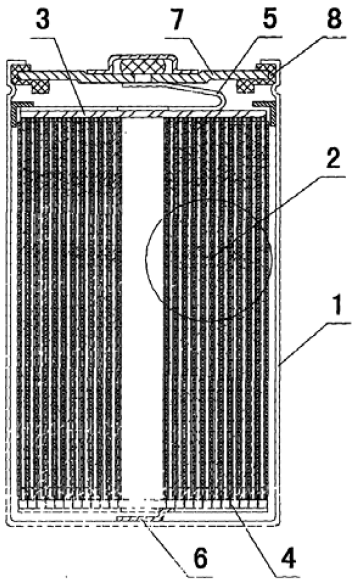


Figure 14. Schematic diagram of a high-power cell with 1: can, 2: electrode assembly, 3: positive electrode, 4: negative electrode, 5: positive current collector, 6: negative current collector, 7: vent cap, and 8: sealing ring [189].

Huanyu (Xinxiang, Henan, China) disclosed an antioxidant made from boric acid [190], a tri-layer separator [191], a Cu-foam [192], a Fe-foam [193], and a Ni-plated expanded-steel [194] (Figure 15) substrates for the negative electrode, and a gas atomization fabrication method of MH powder [195] in their Chinese Patent Applications.

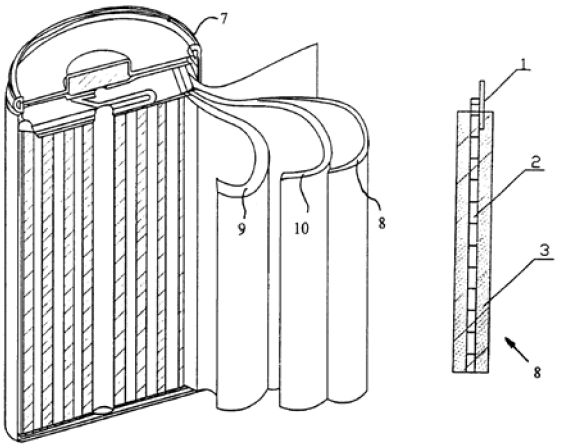


Figure 15. Schematic diagram of a special current collector design with 1: tap, 2: substrate, 3: metal hydride powder, 7: can, 8: negative electrode, 9: positive electrode, and 10: separator [194].

Fengbiao (Shenzhen, Guangdong, China) applied a Chinese Patent mainly in the area of the high-power Ni/MH battery [196–201]. They also proposed a single prismatic cell [202], a multi-prismatic battery pack [203], a low-cost/low-capacity battery [204], a large-capacity battery [205], a wide temperature range battery [206,207] (Figure 16), and a negative electrode recycling apparatus [208] in their additional applications.

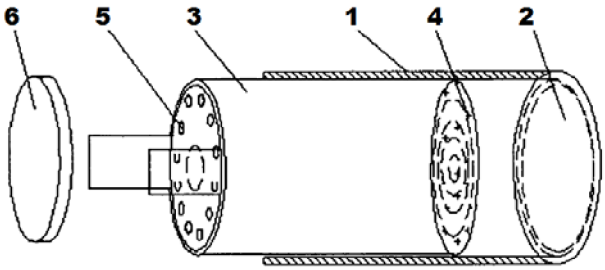


Figure 16. Schematic diagram of a wide temperature range cell with 1: can, 2: Ni-foam mat, 3: electrode assembly, 4: Cu-web with spikes, 5: positive current collector, and 6: vent cap FB [206].

Tianneng (Changxing, Zhejiang, China) invented a bi-polar prismatic Ni/MH battery [209] (Figure 17), a high-power prismatic module [210], a positive electrode fabrication method placing a PTFE layer between the active material and the foam substrate [211], a Y_2O_3-containing low-temperature battery [212], and a Na_3WO_4 containing high-temperature battery [213]. Wangkaifeng (Mianning, Sichuan, China) also owns Chinese Patents about prismatic Ni/MH batteries [214–216] (Figure 18).

Rare-earth ovonic (REO) Ni/MH Power Battery (Baotou, Inner Mongolia, China) filed Chinese Patents on HEV-used battery modules [217] and connectors [218], an EV-used battery module [219], an activation process [220], a short-circuit inspection apparatus [221], a paste mixing apparatus [222], a pasting machine [223,224], an electrode softener apparatus [225], an electrode pressing unit [226], an electrode delivery mechanism [227], a positive current collector ultrasound spot-welder [228], a new type of a sealing ring design [229,230], and an interconnecting mechanism in a battery module [231].

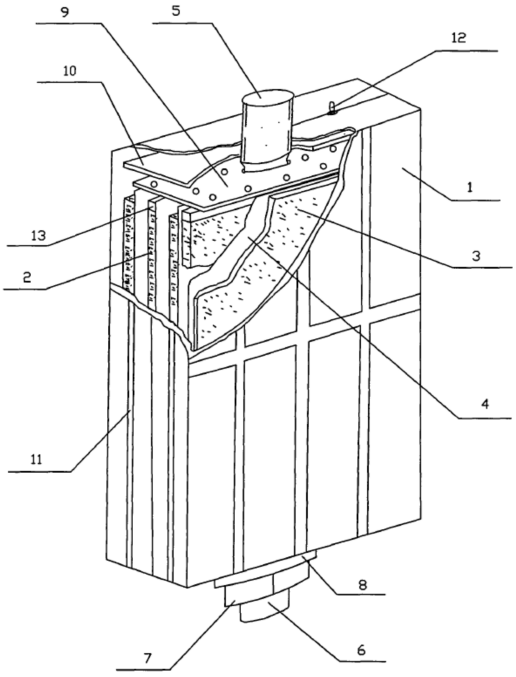


Figure 17. Schematic diagram of a bipolar/prismatic cell with 1: resin case, 2: positive electrode, 3: negative electrode, 4: separator, 5: positive terminal, 6: negative terminal, 7: screw, 8: washer, 9: positive current collector, 10: sealing plate, 11: liquid conduit slot, 12: safety venting valve, and 13: bare substrate [209].

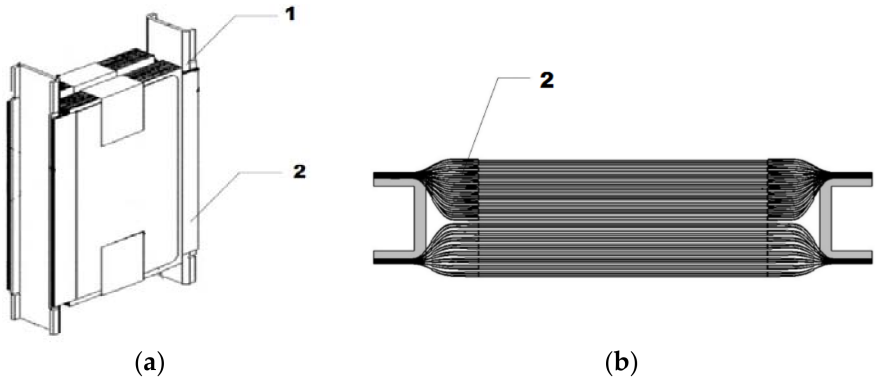


Figure 18. (**a**) A schematic diagram and (**b**) a cross-section view of a prismatic cell with 1: current collector and 2: tab [215].

BST Power (Shenzhen, Guangzhou, China) filed 16 Chinese Patent Applications and had six granted, which cover the areas of: a high-power battery [232], a wide-temperature range battery [233], a high-temperature overcharge-resistant battery [234], a high-temperature and long life battery [235], a low-capacity battery [236], a flat supporting mechanism for transferring a battery during assembly [237], a method to raise the venting pressure of the safety valve [238], an anti-electrolyte spitting design of the cell [239], a gel-type electrode [240], a new tap design to increase the current collection capability [241], a fast electrolyte-filling station [242], and a powder removal apparatus in the positive electrode softening machine [243].

Zhengda (Zibo, Shandong, China) disclosed a high-power Ni/MH battery with a carbon nanotube coated negative electrode and a Co/Y/Ce hydroxide coated positive electrode [244] (Figure 19), a high-capacity cell design [245] (Figure 20), a constant power charger [246], a prismatic cell design [247–249], and a battery sealing mechanism [250,251] in their Chinese Patent applications.

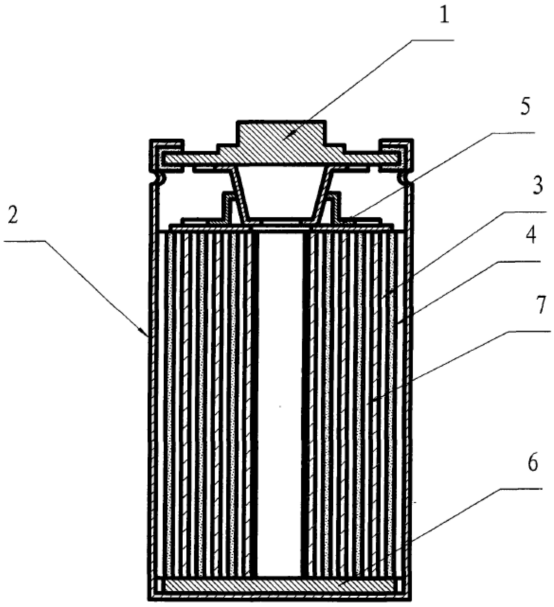


Figure 19. Schematic diagram of a high-power cell with 1: vent cap, 2: can, 3: positive electrode coated with co-precipitated hydroxide of Co, Y, and Ce, 4: negative electrode coated with carbon nanotube, 5: negative current collector, 6: positive current collector, and 7: separator [244].

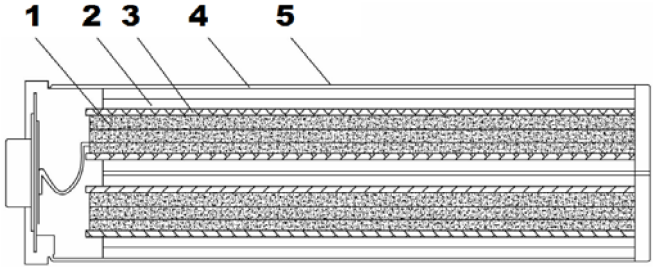


Figure 20. Schematic diagram of a high-capacity cell with 1: positive electrode (three layers), 2: negative electrode (three layers), 3: separator, 4: PTFE anti-corrosion film, and 5: can [245].

Suzhou CENS (Suzhou, Jiangsu, China) filed Chinese Patent Applications on the following subjects: a low-capacity/high-power Ni/MH battery [252], a high-power Ni/MH battery [253], a battery pack connection [254] with a temperature modulation unit [255], a water cooling mechanism [256], and a safe charging device [257].

Jintion (Quanzhou, Fujian, China) owns Chinese Patents in the areas of a high-capacity/high-power [258], high-power [259,260] (Figure 21), low-capacity [261], γ-CoOOH coated high-temperature [262], and β-CoOOH coated long storage [263] Ni/MH batteries, a Y_2O_3 added positive electrode [264], and a new welding design between tap and Ni-foam [265]. It also applied Chinese Patents in these areas as well: a high-power positive electrode with nano-size conductive additives [266], a composite separator for low self-discharge and high-rate applications [267], an electroplating S-containing coating on the negative electrode [268], a high-temperature battery with W-containing additives in the positive electrode [269], a nylon/grid/polypropylene (PP) tri-layer separator [270], and a fast-charge/high-power battery [271].

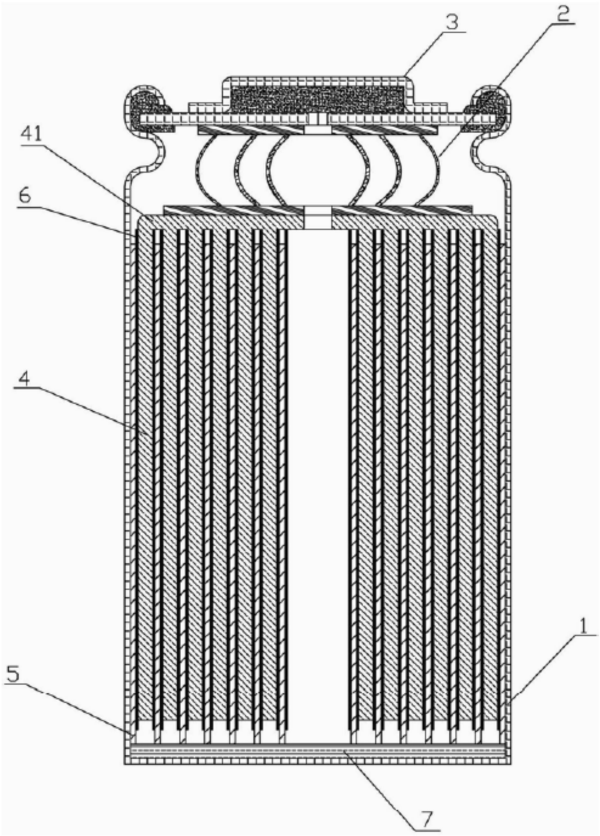


Figure 21. Schematic diagram of a high-capacity/high-power cell with 1: can, 2: current collector, 3: vent cap, 4: positive electrode, 5: negative electrode, 6: separator, 7: Ni-foam, and 41: Ni-foam [260].

Jinhui (Dongguan, Guangdong, China) owns Chinese Patents in the areas of new type button cells [272,273], a low-impedance button cell [274], and a low-cost button cell [275].

Troily New Energy (Xinxiang, Henan, China) has one Chinese Patent granted on a coated positive electrode [276] and one still in examination on a $NaBO_2 \cdot H_2O$ containing electrode for high-temperature application [277].

Innovation New Energy (Liuan, Anhui, China) filed 28 Chinese Patent Applications and had 11 of them granted with the following scope: plastic wrappings for regular [278], low self-discharge [279], high-capacity [280], high-power [281], and high-temperature [282] batteries, sealing glues for regular [283], high-capacity [284], high-temperature [285], low self-discharge [286], and high-power [287] batteries, a positive electrode for a wide temperature-range application [288], a high-temperature/high-power battery [289], a low self-discharge battery [290], a high-capacity non-winding type battery [291] (Figure 22), a high-voltage protection apparatus [292], an energy-efficient battery [293], a high heat-dissipation battery [294], an over-charge protected low-power dissipation battery [295], and an environmentally friendly high-capacity battery [296].

Cel (Huaian, Jiangsu, China) owns two Chinese Patents on a gel coating apparatus for electrode fabrication [297] and a powder scraping apparatus for a dry pasted positive electrode [298].

Bofuneng (Shenzhen, Guangdong, China) owns two Chinese Patents on a prismatic design [299] and an environmental protection cell design [300].

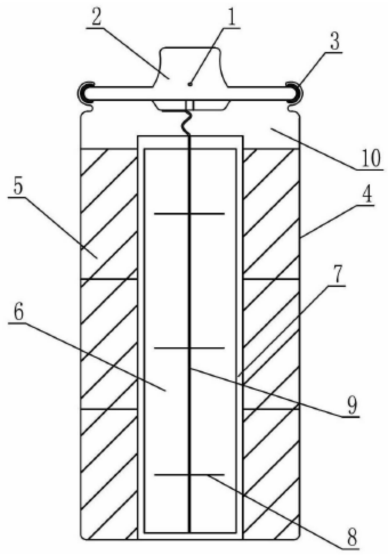


Figure 22. Schematic diagram of a high capacity/non-winding cell with 1: vent hole, 2: cap, 3: sealing ring, 4: can, 5: negative electrode, 6: positive electrode, 7: separator, 8: current collector, 9: tap, and 10: electrolyte [291].

Ryder (Shenzhen, Guangdong, China) owns six Chinese Patents in the subjects of a high-voltage connector design [301], a high-power Ni/MH battery [302,303] (Figure 23), a non-winding battery design [304], a large capacity battery with attached charging unit [305], and a high-voltage module with a high heat dissipation capability [306].

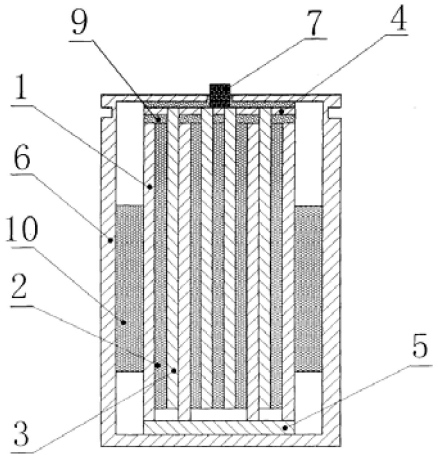


Figure 23. Schematic diagram of a high-power cell with 1: negative electrode, 2: separator, 3: positive electrode, 4: positive current collection, 5: negative current collector, 6: can, 7: cap, 9: insulator, and 10: insulator [302].

DFEI (Dali, Shanxi, China) owns five Chinese Patents in an extra paste removal apparatus in the negative electrode fabrication [307], a dust-removal tape on the positive electrode [308], a high-power design [309] (Figure 24), an automatic transport, vacuum, and de-burr apparatus [310], and a paste stirring apparatus for preparing a positive electrode [311].

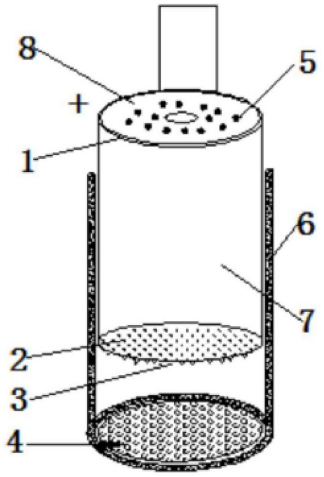


Figure 24. Schematic diagram of a high-power cell with 1: positive current collector plate, 2: Cu mesh, 3: burr, 4: Ni foam, 5: welding spot, 6: insulator, 7: cell, and 8: positive terminal [309].

Wintonic (Guangzhou, Guangdong, China) owns five Chinese Patents on a cylindrical design [312], a nano-carbon containing negative electrode [313], a dual-shell high-temperature can design [314], a high-current positive electrode [315], and a sub-C positive electrode [316].

Oceansun (Shenzhen, Guangdong, China) disclosed a paste positive electrode fabrication method [317], a low-capacity Ni/MH battery [318], and a high-power design [319] in their failed Chinese Patent Applications.

Shida (Foshan, Guangzhou, China) disclosed the following technical ideas in their Chinese Patent Applications: a multi-tab high-power Ni/MH battery [320], a side-folded expanded metal for the electrode substrate [321], and a dry-compaction method for electrode fabrication [322]. Sanik (Foshan, Guangzhou, China) is another Ni/MH battery manufacture in the same city. However, they only filed four patents on the Ni-Fe rechargeable battery and the associated Ni-electrodes.

PeaceBay (Tianjin, China), a company with technology transfer from Toshiba (Tokyo, Japan), filed some early Chinese Patents (all obsolete now) in the areas of fabrications of positive electrodes [323,324], methods of making [325] and winding [326] Ni-foam as positive electrode substrate, a fabrication method for negative electrode [327], a MH/carbon nanotube composite [328] and a MgNi-based alloy [329] as negative active materials, a high-capacity cell design [330] (Figure 25), a reclaiming method of deteriorated MH power [331], and a recycling method for both electrodes [332].

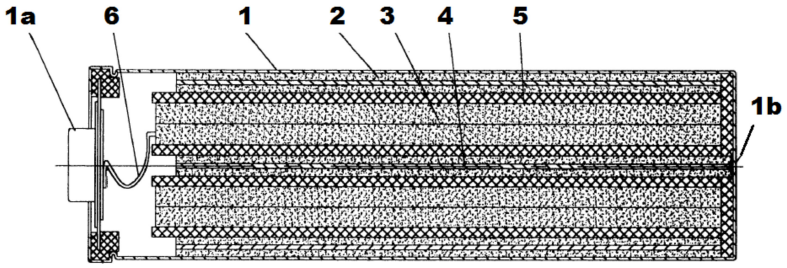


Figure 25. Schematic diagram of a high-capacity cell with 1: can, 1a: positive terminal, 1b: negative terminal, 2: negative electrode, 3: positive electrode, 4: central rod, 5: separator, and 6: current collector [330].

Unitech (Shenzhen, Guangdong, China) filed eight Chinese Patent Applications to cover a protective layer on positive electrode [333], a slot-containing positive electrode [334], a PTFE-coated negative electrode [335], a high-capacity cell design [336], a low-capacity cell design [337], a new cell winding structure [338], and a design of a pasting machine [339].

Taiyi (Zhuhai, Guangzhou, China) has a Chinese Patent proposing a powder container with at least one step inside for the preparing of dry compacted electrode on an expanded metal or a porous metal substrate [340] which was used in some litigation procedures in China. It also applied another application in formation apparatus but is not valid now [341].

3. Metal Hydride Alloy Producer

Chinese MH alloy producers made more than 90% of the MH alloy for Ni/MH battery application (7300 tons in 2016). The top four largest manufactures, Xiamen Tungsten (Xiamen, Fujian, China), Doublewin (Sihui, Guangdong, China), REO Metal Hydride (Baotou, Inner Mongolia, China), and Jiangxi Tungsten (Nanchang, Jiangxi, China) supplied more than 70% of the domestic market in 2016 (Figure 26). Their main product is the rare-earth based AB_5 MH alloy made either by conventional induction melting and casting (Doublewin and REO) or by strip casting (Xiamen Tungsten and Jiangxi Tungsten) (Figure 27). All of them are now working on the high-capacity superlattice MH alloys.

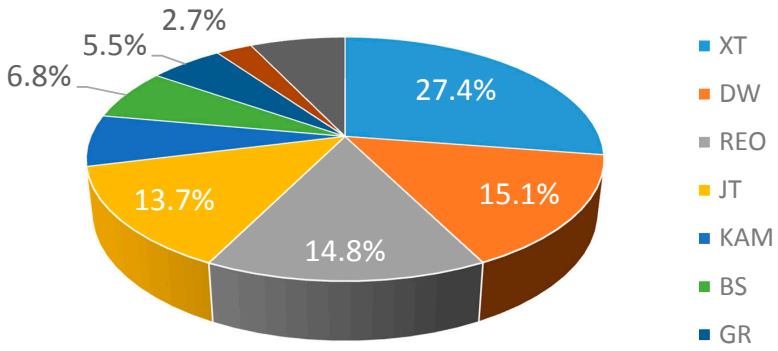


Figure 26. Market shares of MH alloys produced in China in 2016. XT: Xiamen Tungsten, DW: Doublewin, REO: Rare-earth Ovonic, JT: Jiangxi Tungsten, KAM: Kingpowers Advanced Materials, BS: Baotou Santoku, GR: Gansu Rare-earth, and WG: Weishan Gangyan Rare-earth Material.

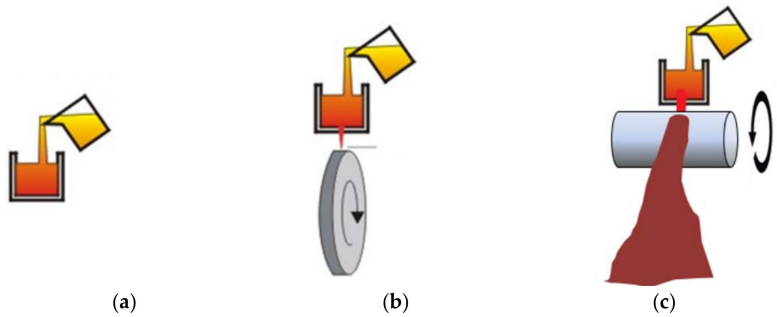


Figure 27. Schematics for (**a**) a conventional melt-and-cast, (**b**) a melt-spin, and (**c**) a strip casting MH alloy fabrication methods.

3.1. Xiamen Tungsten

Xiamen Tungsten, also called Amoi Wuye, has 14 Chinese Patent Applications and had 10 of them granted. In the alloy composition, it disclosed Cu-containing low-cost [342,343], low-Co [344], Co-free and low-Ni [345], Pr-Nd free low self-discharge [346], Mg-containing high-capacity ($\geq$355 mAh g^{-1}) [347], hypo-stoichiometric [348] and Co-free hyper-stoichiometric AB_5 MH alloys [349], and La-Gd [350] and La-Y [351] based A_2B_7 MH alloys. In the alloy production area, it proposed a strip casting of 0.1–0.3 mm thin flake [352–354] (Figure 28) and an electrode fabrication method using Mg-based MH alloy [355].

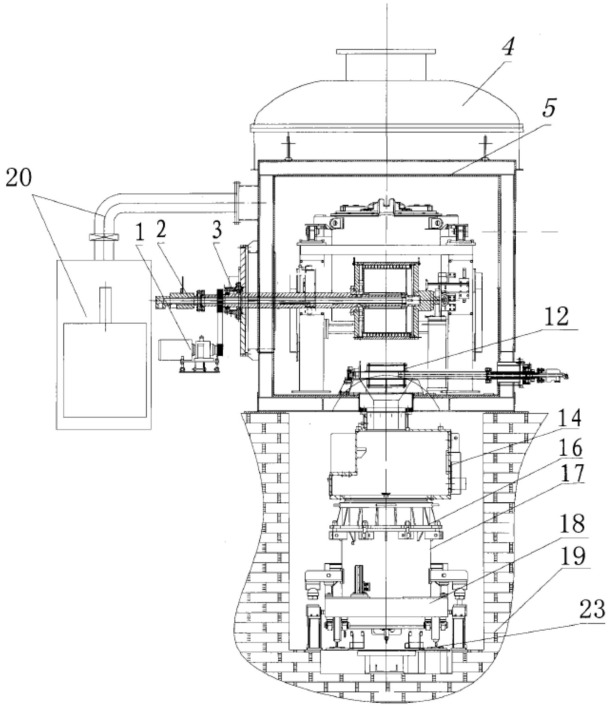


Figure 28. A schematic diagram for a mass-production strip-casting furnace with 1: strip casting motor, 2: rotation coupler, 3: strip casting axis, 4: top cover, 5: furnace, 12: rotating cooling rod, 14: collection box, 16: inside container, 17: outside container, 18: cart, 19: floor foundation, 20: vacuum pump and conduit, and 23: a railing system [354].

3.2. Doublewin

Doublewin filed eight Chinese Patent Applications and all were approved. Their inventions cover mostly the MH alloy production processes, such as a dust collection unit in the powder mixer [356] and in the ingot collection unit [357], an impurity removal unit in the sieving device [358], a cooling mold design [359], a quick electrode fabrication method for alloy quality control [360], and an automatic vacuum casting apparatus [361]. Doublewin also patented MH alloy formula in a (Ag, Sr, Ge)-modified A_2B_7 with improved capacity and low-temperature performance [362] and a (Ag, Sr, Ge, Au) modified AB_5/A_2B_7 mixture [363].

3.3. REO Metal Hydride

REO Metal Hydride filed eight Chinese Patents on MH materials and related fabrication methods which cover a La-rich, Sm-containing superlattice MH alloy [364,365], La-rich, Y, Zr, or Gd-containing over-stoichiometric AB_5 MH alloys [366], an electropolymerized polyaniline coating to protect the alloy surface [367], and a sintered AB_5/AB_3 composite [368].

3.4. Jiangxi Tungsten

Jiangxi Tungsten Haoyun Technology has one issued Chinese Patent on an acid pre-etching process for preparing the negative electrode [369].

3.5. Kingpowers

Kingpowers (Anshan, Liaonining, China) used to be sister company of Suppo and has eight issued Chinese Patents on the alloy formula in a low-Co and (Pr, Nd) free AB_5 MH alloy [370,371] and a Mg-containing A_2B_7 MH alloy [372–374], the alloy production process in annealing [375], and recycling processes from alloy slag [376] and spent batteries [377].

3.6. Others

Guansu Rare-earth (Baiyin, Gansu, China) only has one Chinese Patent Application on a powder grinding, sifting, and mixing process and was rejected [378].

Weishan Gangyan (Jining, Shandong, China) filed 12 Chinese Patent Applications covering areas of a fabrication method of a Ti-containing [379–381] A_2B_7 MH alloy, a nano-graphite/RE_2Mg_{41} type MH composite [382], and a powder packing system [383]. None of them are valid now.

Beijing HarmoFinerY Technology (Beijing, China) owns Chinese Patents of (La, Ce, Dy)-based [384] and (La, Nd, Dy)-based [385] A_2B_7 MH alloys. It also filed a patent about a (La, Y)-based low-temperature A_2B_7 MH alloy.

Vapex (Zhuhai, Guangdong, China) filed 16 Chinese Patent Applications and had 13 granted. In the alloy formula area, Vapex patented a Cu-containing low-Co [386], a Dy-containing [387], a Pt-containing [388], a Fe-containing [389], a Nb-containing [390], a Ga-containing [391], a Sn-Cu containing [386] AB_5 MH alloys, and a Mg-containing A_5B_{19} MH alloy [392]. In the alloy fabrication area, Vapex proposed an induction melting of A_2B_7 alloy in a controlled Mg-vapor [393]. Besides, it also owns patents in the new design of a current collector [394–397], a high-temperature battery design [32], and a Ni/MH battery for solar cell application [398].

4. $Ni(OH)_2$ Producer

The original spherical shape $Ni(OH)_2$ used as the positive electrode active material in the Ni/MH battery was first used in Yuasa (Takatsuki, Osaka, Japan) which was supplied by Tanaka Chemical Co. (Fukui, Japan) [13]. Nowadays in China, almost all spherical shape $Ni(OH)_2$ is produced by the domestic suppliers using a continuous stirring single reactor co-precipitation process invented by Ovonic Battery Co. (Troy, MI, USA) [399]. The top five manufactures, Jinchuan (Lanzhou, Gansu, China), Kingray (Changsha, Hunan, China), Cologne (Xinxiang, Henan, China), Jien (Jilin, Jilin, China), and Aland (Wuwei, Anhui, China) held more than 65% of the market share in 2013 (5.1×10^7 kg , Figure 29). Their contributions to the Ni/MH intellectual properties are summarized in this section.

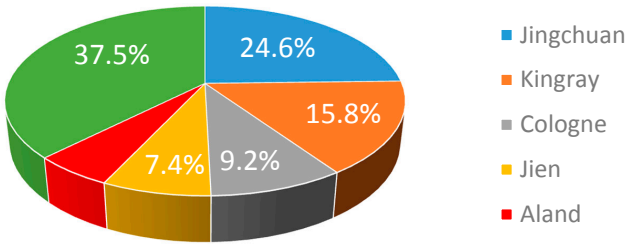


Figure 29. Market shares of Chinese domestic spherical $Ni(OH)_2$ producers in 2013 [13].

4.1. Jinchuan

Jingchuan applied four Chinese Patent Applications on $Ni(OH)_2$ and received one of them. The applications mainly covered the chemical co-precipitation process of making spherical particles [400], a sulfate removal process [401], and a Fe removal process [402].

4.2. Kingray

Kingray New Materials Science and Technology, now Minmetals Capital Co., did not file any Chinese Patent Application on $Ni(OH)_2$.

4.3. Cologne

Cologne filed seven Chinese Patent Applications about $Ni(OH)_2$ and had three of them granted, which cover the areas of a chemical co-precipitation method of making spherical $Ni(OH)_2$ powder [403],

a $Ni(OH)_2$ specifically design for high-temperature battery [404], a Co-coated $Ni(OH)_2$ [405], an eletrolytically coated CoOOH on $Ni(OH)_2$ [406,407], and a chemically precipitated CoOOH on $Ni(OH)_2$ [408].

4.4. Jien

Jien owns one Chinese Patent on a mechanical alloying method to coat Co on $Ni(OH)_2$ [409] and one application is still in the examination stage on a Co-coated $Ni(OH)_2$ for high-temperature applications [410].

4.5. Aland

Aland filed 16 Chinese Patent Applications related to $Ni(OH)_2$ and had six of them granted. The scope of these applications covers a gaseous phase [411,412], a liquid phase [413], and a continuous [414] oxidation to prepare a Co-coated $Ni(OH)_2$, a chemical co-precipitation of (Ni, Zn, Mn, Al)$(OH)_2$ [415], a Y, Yb, and Ca containing $Ni(OH)_2$ for high-temperature applications [416], a new method of making $Ni(OH)_2$ with cyclic amine-containing ionic liquid [417], a reactor for making high-power $Ni(OH)_2$ [418], an oxidizer for high-power Co-coated $Ni(OH)_2$ [419], a reactor for making $Co(OH)_2$ coated $Ni(OH)_2$ [420,421], a microwave dryer [422], an electrochemical/chemical pre-charge station for $Ni(OH)_2$, [423], a static impedance measuring apparatus for Co-coated $Ni(OH)_2$ [424], and a scrap recycling process to treat Co-coated $Ni(OH)_2$ [425].

4.6. Others

Zhonghong (Shaoguan, Guangdong, China) owns one Chinese Patent on the chemical co-precipitation of spherical $Ni(OH)_2$ [426] and also has one in the examination stage for the method of making Co-coated $Ni(OH)_2$ [427]. Liyuan (Changsha, Hunan, China), a subsidiary of Corun, owns one Chinese Patent on a chemical co-precipitation method for making spherical $Ni(OH)_2$ powder [428]. Jintian (Xiangtan, Hunan, China) owns one Chinese Patent on the preparation process of the γ-CoOOH coated $Ni(OH)_2$ [429]. Changyu (Jiangmen, Guangdong, China) owns Chinese Patents in the area of a high-capacity and high discharge voltage $Ni(OH)_2$ [430], a high-temperature $Ni(OH)_2$ [431], a Co-coated $Ni(OH)_2$ drying machine [432], and a spherical $Ni(OH)_2$ production method [433,434]. It also filed Chinese Patents on the subjects of a reactor producing $Ni(OH)_2$ [435], a Co-coating reactor for $Ni(OH)_2$ [436], and a γ-CoOOH coating method [437]. Zhongdao Energy Development (Anding, Hainan, China) owns a Chinese Patent on a (Co, Al) hydrotalcite containing positive electrolyte [438]. Zhongjin Metal Powder (Wuxi, Jiangsu, China) has two Chinese Patents on a nano-structured CoOOH [439] and a β-$Co(OH)_2$ [440]. Yixing Xinxing Zirconium (Yixing, Jiangsu, China) owns a patent on a high-temperature battery with CaF_2, ZnO, $Ba(OH)_2$, Er_2O_3, Y_2O_3, and Zr-compound additives for the positive electrode [441], It also filed Chinese Patents in the areas of a Zr co-precipitated $Ni(OH)_2$ [442] and a rinsing apparatus for spherical $Ni(OH)_2$ [443]. GEM (Shenzhen, Guangdong, China) has one Chinese Patent on a non-stoichiometric $Co_{1.02\sim2}O$ additive to increase the electrochemical activity of $Ni(OH)_2$ [444].

5. Other Hardware Suppliers

Besides the active materials from both electrodes ($Ni(OH)_2$ and MH alloy), there is other hardware used in Ni/MH batteries may also protected by Chinese Patents. Instead of grouping by companies, we listed the inventions from various companies under each part category in this section.

5.1. Ni Foam

The Ni-foam used as the substrate mainly for the positive electrode was first patented by INCO (Toronto, ON, Canada, now Vale Canada Limited) with a chemical vapor deposition (CVD) process from nickel carbonyl onto polymer foam which was removed later on by a sintering process [445].

This costly CVD deposition process was replaced by an electrode plating on the polymer form coated with a carbon-containing substance in China. Dr. Zhong, Chairman of Corun, owns a few Chinese Patents on the electroplating container for the continuous fabrication of Ni-foam [446] and a rough surface of Ni-foam [447] which were used in litigation against INCO in China [448]. His company, Liyuan (Changsha, Hunan, China) filed Chinese Patents in the areas of a high-strength Ni-foam [449, 450], a special structured Ni-foam [451], a carbon nanotube coated Ni-foam [452], a Ni-foam design for vehicle use [453], a multi-stage deposited Ni-foam for HEV use [454], a Ni-foam for high-power application [455], a Ni/Co-foam [456], a Fe-foam [457], a crystallization method for deposited Ni [458], a continuous electroplating apparatus [459], and a recycling procedure for making fine Ni powder from Ni-form waste [460].

Tianyu (Heze, Shandong, China) filed Chinese Patent Applications on the subjects of a Ni-alloy foam for high-power application [461,462], an electroplating Ni-foam [463], a super thick Ni- (or Cu-foam) [464], a purification process for Ni-foam [465], a high-uniformity Ni-foam production method [466,467], a low-face density and high-porosity Ni-foam [468], a high efficiency vacuum apparatus [469], and a raw material preparation method for improvement of Ni-foam uniformity [470].

Tiangao (Dalian, Liaoning, China) owns one Chinese Patent on a new type of electroplating basin for Ni-foam [471] and has one in examination about a super high-density Ni-foam [472].

5.2. Separator

The regular separator used in the Ni/MH battery is treated by acrylic acid (white) and a special sulfonated separator (brown) originally patented by Japan Vilene Co. (Tokyo, Japan) [13] has the advantage of low self-discharge since no trace of nitrogen-containing ion is left. Kangjie (Changzhou, Jiangsu, China) filed Chinese Patent Applications on a low-cost and high-yield sulfonation process [473], a multi-layer nylon-based separator [474], and a grafted polyethylene (PE) separator [475]. Lianyou Jinhao (Laizhou, Shandong, China) also has sulfonated separator patents [476–478]. Besides it also filed Chinese Patent Applications on a separator grafting apparatus [479], a separator pore size measurement apparatus [480], and a separator winding machine [481]. Lingqiao Environment Protection Equipment Works (Shanghai, China) has a Chinese Patent on a PP/PTFE/PP composite separator for a Ni/MH battery [482]. Jianxiang Shunxin Technology (Beijing, China) owns a Chinese Patent of a wet impedance measuring apparatus [483]. Meite Environmental Protection Material (Xianyang, Xi'an, China) filed one patent about a low-cost grafting method for making a separator [484]. Kegao (Luoyang, Henan, China) filed one Chinese Patent Application on a high-power separator with high gas permeability and small thermal contraction [485]. Rongsheng (Yizheng, Jiangsu, China) filed one application for its separator manufacturing process [486].

5.3. Stainless Steel Can

Shanghai Jinyang (Shanghai, China) owns Chinese Patents on an incoming parts organizer [487], an electroplating process [488], a dehydration station [489], a water-saving washing station [490], a plating quality control [491] and a thermal energy recycling mechanisms [492] for plating Ni on a stainless steel can. It also applied for Chinese Patents on the automatic plating apparatus [493]. Fujian Jinyang (Sanmin, Fujian, China) field Chinese Patents about double-plating [494] and triple-plating [495] Ni on a stainless steel can. Donggang (Wuxi, Jiangsu, China) filed a Chinese Patent on a can with gradual cylinder wall thickness [496]. Hugang Electronics (Zhangjiagang, Jiangsu, China) claimed an electroplating/chemical plating combination method [497]. Haiyang (Nantong, Jiangsu, China) filed two Chinese Patent Applications on a case with an easy heat dissipation capability [498,499].

5.4. Negative Electrode Substrate

Zhongjin Gaoneng (Shenzhen, Guangdong, China) has three Chinese Patents on the punching die for the fabrication of a perforated non-ferrous metal belt [500], one for the high-power

perforated stainless steel substrate [501] and one for the regular NPPS belt [502] for the negative electrode substrate of a Ni/MH battery. Besides, it filed a patent on the fabrication method of NPPS [503]. Jiejing (Dongguan, Guangdong, China) also filed an application for an automatic electroplating apparatus for NPPS [504]. Shuzhen (Shanghai, China) filed an application on the Cu-web used as substrate material for a negative electrode [253]. Kingdom Sifang Metal Product (Qinhuangdao, Hebei, China) owns a Chinese Patent to fabricate NPPS [505]. Shenjian Metallurgical Equipment (Shanghai, China) filed an application on a non-metal fiber/Ni composite material for high-strength/light-weight substrate [506].

6. Applications

Ni/MH batteries were first used in consumer-type applications, such as cell phone, notebook computer, other portable electronic devices (walkman, personal data assistant, etc.), and dry cell replacement. Facing competition from the lighter Li-ion battery, the Ni/MH battery moved to the transportation propulsion type of applications, especially for hybrid electrical vehicles (HEV) and EV. Recently, due to the longevity and wide-temperature tolerance of the Ni/MH battery, it also entered stationary type of applications, for example, uninterrupted power supply (UPS), grid-pairing storage systems, and the EV charging station. The Chinese Patents on the application of Ni/MH area are reviewed here.

6.1. Consumer Type

A few common uses of the Ni/MH battery in consumer application are shown as examples in Figure 30. There are many Chinese inventions on this use of the Ni/MH battery. Some examples are: a moisture-protection battery case [507], a power supply for illumination in a mine [508,509], a power supply with monitoring and communication functions [510], a high-speed power tool [511,512], a new type of flashlight [513], an LED flashlight [514], a pager [515], a portable power modulator [516], a rechargeable radio frequency identification card [517], a portable vacuum cleaner [518], a kinetic energy rechargeable infrared detector [519], a remote humidifier [520], a wall-climbing vacuum cleaner [521], a robot used in a mine [522–525], a trimmer [526], and a wearable battery capacity extender [527].

Figure 30. Examples of Ni/MH batteries in consumer applications: (**a**) retailer, (**b**) cordless phone, (**c**) vacuum cleaner, (**d**) power drill, (**e**) shaver, (**f**) toothbrush, (**g**) flashlight, (**h**) solar lamp, and (**i**) remote control for game console.

6.2. Transportation Type

In the transportation area, the Ni/MH battery dominates the HEV market. Three HEVs made in China are shown in Figure 31: a Camry by Guangzhou Auto (Guangzhou, Guangdong, China), a Prius by First Automobile Works (FAW, Changchun, Jilin, China), and an EC7 by Geely Auto (Hangzhou, Zhejiang, China). In the Chinese Patent Applications in this area, an optimized range-extended HEV design [528], a forced-air-cooled HEV battery module [529], a heat dissipation unit [530,531], a temperature-regulated HEV battery system [532], and a HEV-use battery module [533,534] are available. Besides, Qineng (Yangzhong, Jiangsu, China) filed nine Chinese Patent Applications on the fabrication of an HEV-used Ni/MH battery and module [535–543]. In the EV application, inventions like a high-capacity Ni/MH battery pack [544,545], a high-capacity EV battery [546–548], an EV-used battery module [549–551], an overload protection for an EV battery [552], a pulse-based cycle life testing method for EV application [553], a battery management system for EV with Ni/MH [554], a large-capacity prismatic cell design [555–558] and a cylindrical Ni/MH battery [559] for EV application, an MH alloy designed for EV application [556], a battery module for EV [550,551], a Ni/MH battery pack [560], a special high-power cylindrical cell design [561–564], and an EV charging method [565] were demonstrated. In other transportation areas, a lawn mower [566], a fork lift truck [567], a solar-cell powered car, boat, or plane [568], a wind-powered car [569], an underwater propeller [570], a battery assembly for an E-bicycle [571–575], and a fast-charge moving cart [576] can be found.

(**a**) (**b**) (**c**)

Figure 31. Examples of Ni/MH batteries in transportation applications: (**a**) a Camry HEV (Guangzhou Auto), (**b**) a Prius HEV (FAW), and (**c**) an EC7 HEV (Geely Auto).

6.3. Stationary Type

In the un-interrupted power supply (UPS) applications, a video recording system with self-supporting power supply [577], a firefighting emergent light [578], a high-rise building emergency power system [579], a charging circuitry [580], and a mobile communication tower [581] are listed. In the energy storage associated with solar and wind energy, a solar cell/battery combination [582–585], and a Ni/MH rechargeable by solar power [398], a solar charger [586], a light emitting diode (LED) solar lamp [587], a solar rechargeable flashlight [588], and a solar-charged EV battery [589] are included. An example of a solar station equipped with Ni/MH energy storage is shown in Figure 32. In grid-companion energy storage, an energy distribution and EV used charging station [590], a monitoring system for energy storage [591], a double-source power unit [592], a monitoring system [593], a micro-grid Ni/MH system [594], a mega-watt class energy storage system [595], and an energy balancing system for Ni/MH storage [596] were introduced.

(**a**) (**b**)

Figure 32. Example of Ni/MH batteries in alternative energy storage applications: (**a**) a solar cell system and (**b**) the accompanying Ni/MH battery pack installed and tested in Qinghai Plateau. (Courtesy of TMK).

7. Universities and Research Institutes

Many Chinese universities and state-owned research institutes have worked in the Ni/MH battery area, especially those involved in the 863 special project [597]. We reviewed the status of the Patent Applications of a few representative examples and present them here.

7.1. Beijing Institute of Technology

Beijing Institute of Technology (Beijing, China) filed four Chinese Patent Applications related to the Ni/MH battery and had one granted. Their invention covers the areas of a NiO-containing positive electrode [598], an inner-pressure reduction additive [599,600], and a battery non-destructive regeneration method [601].

7.2. Beijing University of Chemical Technology

Beijing University of Chemical Technology (Beijing, China) filed six Chinese Patent Applications about $Ni(OH)_2$ and had two of them granted. The inventions are composed of an activated graphene/needle-shaped $Ni(OH)_2$ composite [602], nano-thin films of α-$Ni(OH)_2$ [603] and β-$Ni(OH)_2$ [604], a nano-structured/doped α-$Ni(OH)_2$ [605], an electrochemical/chemical process of making doped nano-$Ni(OH)_2$ [606], a low-cost fabrication method of nano-$Ni(OH)_2$ using oxygen in air [607], and a nano-C/$Ni(OH)_2$ composite [608].

7.3. Tsinghua University

Tsinghua University (Beijing, China) owns one Chinese Patent on an estimation of state-of-charge based on a standard battery model [609]. It also applied for the following inventions: a real-time estimation of the temperature difference between inside and outside of a cell [610], a magnetic treatment of MH alloy to improve its high-rate performance [611], and an air-cooled apparatus for an HEV-used Ni/MH battery module [612].

7.4. Tianjin University

Tianjin University (Tianjin, China) filed four Chinese Patents Application on these subjects: a negative electrode surface treatment to improve electrochemical performance [613], an apparatus to measure inner pressure of a Ni/MH cell [614], a tri-cellulose acetate/metal oxide composite separator [615], and α-$Ni(OH)_2$ prepared by a ball-milling process [616].

7.5. Nankai University

Nankai University (Tianjin, China) filed patents jointly with Peacebay. It also filed patents on their own in the areas of a C_{60} or boron nitride added negative electrode [617], electrode recycling methods [332], a large-capacity EV-used Ni/MH battery [555], and a negative electrode pasting line [618].

7.6. Tianjin Polytechnic University

Tianjin Polytechnic University (Tianjin, China) has two Chinese Patents on a sulfonated separator [619,620].

7.7. Shanghai Jao Tong University

Shanghai Jao Tong University (Shanghai, China) has one Chinese Patent on a primary (non-rechargeable) Ni/MH battery and withdrew one on a Ni/MH battery with a self-heat-dissipation mechanism [621].

7.8. Donghua University

Donghua University (Shanghai, China) has two Chinese Patents on a composite separator [622] and a nano-coating separator [623].

7.9. Jilin University

Jilin University (Changchun, Jilin, China) filed five Chinese Patent Applications on MH alloy/graphene [624], MH alloy/Co_3O_4 [625], and MH alloy/nanoporous Ni [626] composite negative electrodes, a fast cycle life estimation method for MH alloy with a super long life [627], and a MoS_2 surface treatment for MH alloy [628].

7.10. Yanshan University

Yanshan University (Qinhuangdao, Hebei, China) mainly worked with REO MH Alloy Company in their inventions. In addition, it also filed Chinese Patent Applications on the subjects of a single phase Nd-Mg-Ni-based $PuNi_3$ MH alloy [629] and a surface polypyrrole treatment to improve the electrochemical performance of MH alloy [630] by itself.

7.11. Sichuan University

Sichuan University (Chengdu, Sichuan, China) owns two Chinese Patents on a Nd-free/low-temperature AB_5 MH alloy [631] and a low-Co LaPrCe-Ni based AB_5 MH alloy [632]. It also filed one application on an Nd-free A_2B_7 MH alloy [633].

7.12. University of Electronic Science and Technology of China (UESTC)

UESTC (Chengdu, Sichuan, China) owns three Chinese Patents in the areas of TiO_2 [634], Al_2O_3 ceramic [635], and NiO_2 [636] coatings on a positive electrode.

7.13. Zhejiang University

Most of the Chinese Patents from Zhejiang University are associated with KAN Battery. Zhejiang University (Hangzhou, Zhejiang, China) filed 45 Chinese Patent Applications themselves on an amorphous Mg-Ni [637] and a Ti-Cu-Ni [638] MH alloy as negative electrode active materials and ionic nitridation [639] and B-diffusion [640] methods to improve the anti-corrosion properties of the Mg-based alloy surface.

7.14. Zhejiang Normal University

Zhejiang Normal University (Hangzhou, Zhejiang, China) filed Chinese Patent Applications in the following subjects: a new binder [641], a new electrolyte additive [642], tartaric [643] and mucus [644] salts containing positive electrodes, and a saccharic salt containing a positive electrode [645].

7.15. South East University

South East University (Wuxi, Jiangsu, China) owns two Chinese Patents on a weak acid surface treatment for MH alloy [646] and a high-capacity Mg-Co based MH alloy [647]. It also filed two applications in the areas of an Mg-Pd-Co MH alloy [648] and a recycling method of a spent battery [649].

7.16. Henan Polytechnic University

Henan Polytechnic University (Jiaozuo, Henan, China) filed two Chinese Patent Applications on a fabrication method of RE-Mg-B MH alloy [650] and a multi-phase Mg-based MH alloy [651].

7.17. Guangdong University of Technology

Guangdong University of Technology (Guangzhou, Guangdong, China) owns three Chinese Patents on a graphene-based [652] and a nano-carbon composite [653] high-capacity negative electrodes for high-power battery, and a heat measuring apparatus for a high-power cylindrical cell [654]. It also applied patents in the areas of α-$Ni(OH)_2$ [655], nano-$Ni(OH)_2$ [656], and a multi-element doped nano α-$Ni(OH)_2$ [657,658].

7.18. South China University of Technology

South China University of Technology (Guangzhou, Guangdong, China) owns one Chinese Patent on a Sm-containing A_2B_7 MH alloy [659]. It also filed applications based on a multilayer thinfilm electrode [660], a thin-film electrode [661], and a Sm-containing Pr, Nd-free MH alloy [662].

7.19. Lanzhou University

Lanzhou University (Lanzhou, Gansu, China) filed one Chinese Patent Application on a three-dimensional cellular $Ni(OH)_2$ [663].

7.20. Institute of Metal Research (IMR) in the Chinese Academy of Sciences

IMR (Shenyang, Liaoning, China) filed four Chinese Patents in the areas of a Ni-foam using vacuum evaporation [664], a thick electrodeposition Ni-foam [665], and a nano-carbon decorated current collector for the negative electrode [666].

7.21. Changchun Institute of Applied Chemistry (CIAC) in the Chinese Academy of Sciences

CIAC (Changchun, Jilin, China) filed five Chinese Patents in the areas of a La-based AB_3 MH alloy [667,668], a high-power negative electrode with active carbon or graphite additives [669], a safe design of a button cell [670], and a battery/supercapacitor composite negative electrode [671].

7.22. Shanghai Institute of Microsystem and Information Technology (SIMIT) in the Chinese Academy of Sciences

SIMIT (Shanghai, China) filed Chinese Patents in the areas of a method for improving the long-term storage performance of a Ni/MH battery [672], a high-capacity Ti-V-based MH alloy [673], and a bipolar battery design [674].

7.23. Dalian Institute of Chemistry and Physics (DICP) in the Chinese Academy of Sciences

DICP (Dalian, Liaoning, China) filed a Chinese Patent on a conductive polymer/AB_3 MH alloy composite [675].

7.24. General Research Institute for Nonferrous Metals (GRINM)

GRINM (Beijing, China) filed 11 Chinese Patents to cover a high-capacity, long-life, and high-power A_2B_7/A_5B_{19} based MH alloy [676], a low self-discharge Ce_2Ni_7/Cd_2Co_7 based MH alloy [677], a long life Pr (Nd) free A_2B_7 (>85%) MH alloy [678], a Nd-free low-temperature AB_5 MH alloy [679], a conducting composite for negative electrode [680], a zirconia based separator [681], high-temperature/high-power positive electrode active materials [682,683], a disordered composite positive electrode active material for power application [684], a Ni, Al $(OH)_2$-based positive electrode [685], RE_2O_3-based additives to positive electrodes [686], and a $Ni(OH)_2$ for high-temperature/high-power application [687].

7.25. Guangzhou Research Institute of Non-Ferrous Metals (GZRINM)

GZRINM (Guangzhou, Guangdong, China) filed four Chinese Patents on a low self-discharge Nd-based A_2B_7 MH alloy [688], a La, Sm-based A_2B_7 MH alloy [659], a Co-free AB_5 MH alloy [689], and a low-temperature MH alloy containing a secondary $CeCo_4B$ phase [690].

7.26. Baotou Rare Earth Research Institute (BRERI)

BRERI (Baotou, Inner Mongolia, China) owns a Chinese Patent on a Y-containing A_2B_7 MH alloy [691]. Besides, it also applied for the following inventions: Y containing A_5B_{19} [692] and AB_3 [693] MH alloys, Zr, Ti-modified AB_3 [694], A_2B_7 [695], and A_5B_{19} MH alloys [696], a Y-Ni based MH alloy [697], an amorphous Mg-Ni alloy [698], and a method to improve the capacity stability of Mg-based MH alloy [699].

7.27. National Engineering Research Center for Nanotechnology (NERCN)

NERCN (Shanghai, China) applied for two Chinese Patents on a superlattice MH alloy/BCC alloy composite [700] and an addition of acetylene back to the negative electrode [701].

7.28. Guilin Geology and Mining Academe (GGMA)

GGMA (Guilin, Guangxi, China) has one Chinese Patent on a fabrication method of a paste used in the negative electrode [702].

7.29. Changsha Research Institute of Mining and Metallurgy (CRIMM)

CRIMM (Changsha, Hunan, China) owns a Chinese Patent in the Ce, Co-coated $Ni(OH)_2$ composite material [703].

7.30. China Electronics Technology Group Corporation (CETC) 18th Research Institute

CETC (Tianjin, China) owns one Chinese Patent on a chemical fabrication method of $Ni(OH)_2$ [704] and applied one on the Ni/MH battery with a temperature control apparatus [705].

7.31. Central Iron & Steel Research Institute (CISRI)

CISRI (Beijing, China) applied Chinese Patents in the areas of W-containing high-capacity and V-high-temperature AB_5 MH alloys [706,707], a single-role quench method to prepare MH alloy for high-temperature application [708], a fabrication of a Ni/MH battery [709], an MH alloy pulverization by hydrogenation [710], and an electrolysis method of making misch metal for the raw material of MH alloy [711].

8. Comparisons

So far, we have reviewed Ni/MH battery-related patents (applications) filed in the USA (371) [12], Japan (275) [13], and China (692). The areas of these patents (applications) are categorized into negative electrode (metal hydride alloy), positive electrode ($Ni(OH)_2$), battery structure, manufacturing facilities, applications, and others (other parts, charging algorithm, recycling, etc.) and are plotted in Figure 33. While the US Patents are distributed evenly in each category, Japanese and Chinese Patents are heavy on the negative electrode and battery structure, respectively (Figure 33). As for the assignees, almost all US Patents are from foreign companies and domestic research institutes and those for Japan and China Patents are from several sources: Battery companies, MH alloy suppliers, spherical nickel hydroxide suppliers, vendors of other parts, universities, and research institutes (Figure 34).

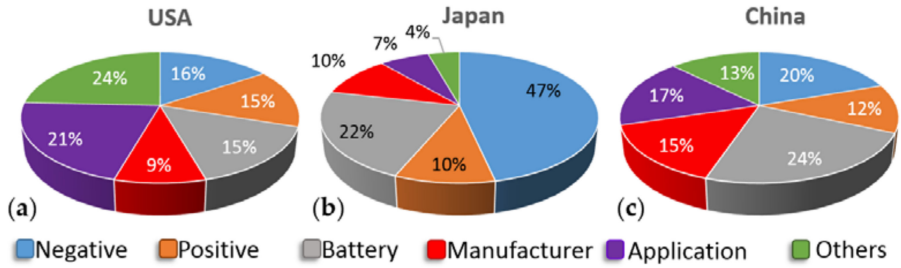


Figure 33. Areas of Patents (Applications) in (**a**) USA, (**b**) Japan, and (**c**) Chinese from negative electrode components (MH alloy), positive electrode component (nickel hydroxide), battery structure, manufacturing facilities, applications, and other areas.

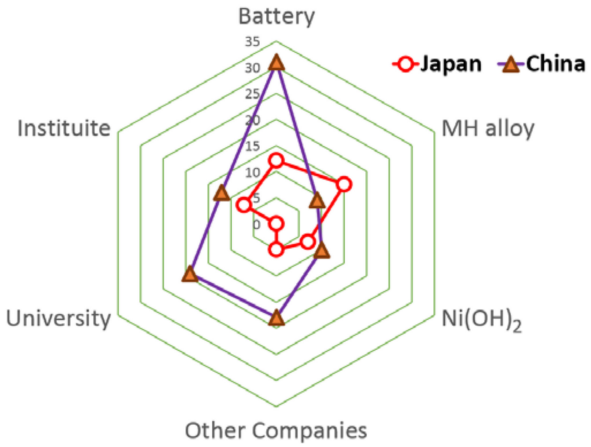


Figure 34. Comparison of numbers of company/institute contributing to the Patents (Applications) in Japan and China.

9. Conclusions

692 Chinese Patent Applications in the nickel/metal hydride battery area are summarized in this review articles categorized by their assignees: battery manufacturers, metal hydride alloy manufacturers, nickel hydroxide manufactures, vendors of other marts, universities, and state-owned research institutes. Some representative schematic diagrams of cell structure designs are included to stimulate new ideas in this area.

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Abbreviations

Ni/MH	Nickel/Metal Hydride
NiCd	Nickel-Cadmium
HEV	Hybrid Electrical Vehicle
MH	Metal Hydride
SIPO	State Intellectual Property Office of the People's Republic of China
GP	Gold Peak
SZHP	Shenzhen HighPower
Li-PO	Lithium-Polymer
NPPS	Ni-Plated Perforated Steel
RE	Rare Earth
SBR	Styrene-Butadiene Rub
PTFE	Polytetrafluoroethylene
EV	Electrical Vehicle
REO	Rare-Earth OVONIC
PP	Polypropylene
CVD	Chemical Vapor Deposition
PE	Polyethylene
UPS	Un-Interrupted Power Supply
LED	Light Emitting Diode
UESTC	University of Electronic Science and Technology of China
CIAC	Changchun Institute of Applied Chemistry
SIMIT	Shanghai Institute of Microsystem and Information Technology
DICP	Dalian Institute of Chemistry and Physics
GNINM	General Research Institute for Nonferrous Metals
GZRINM	Guangzhou Research Institute of Non-Ferrous Metals
BRERI	Baotou Rare Earth Research Institute
NERCN	National Engineering Research Center for Nanotechnology
GGMA	Guilin Geology and Mining Academe
CRIMM	Changsha Research Institute of Mining and Metallurgy
CETC	China Electronics Technology Group Corporation
CISRI	Central Iron & Steel Research Institute

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