

Methods for the reduction of shape change and dendritic growth in zinc-based secondary cells

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Abstract

The widespread adoption of alkaline zinc-based secondary systems has been hindered by two inherent problems associated with the charge reaction. These are commonly referred to as shape change and dendrite growth. This review examines the attempts that have been made to lessen their effects and, hence, ultimately arrive at a working, cycleable secondary zinc-based battery.

Introduction

The reactions and electrochemistry of zinc in alkaline electrolytes have been the subject of a number of previous reviews [1–6]. Some of the properties that make zinc such an attractive material in primary form have, however, hindered its adoption in secondary systems, the main cause being the high solubility of zinc in the strong alkaline electrolytes normally employed in these systems. The problem manifests itself in two main forms of failure mechanism, i.e., shape change (a redistribution of active material, culminating in capacity losses), and dendritic growth, promoting eventual cell failure due to short circuiting. These drawbacks lead to poor cycle life, particularly when compared with traditional rival systems such as lead–acid and nickel–cadmium.

Considerable research effort has been spent on discovering ways of either eliminating, or at least minimising, the effects of these problems. The research can be divided into four distinct categories, viz.,

- (i) Additions to the electrode.
- (ii) Additions to the electrolyte.
- (iii) Development and improvement of separators.

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- (iv) Miscellaneous techniques such as pulse charging, electrode vibration and flowing electrolyte.

This review will attempt to indicate which methods have found most favour in the battery industry in recent years. Although it must be noted that many of the approaches have been employed, in some form or another, for several years. At the same time, the electrochemistry and theory behind certain methods will be explained.

Electrode additions

The incorporation of an additive within the active material of the electrode during its fabrication, is an extensively used method of zinc cycle-life enhancement. One of the most commonly used additives, in both primary and secondary systems, is that of mercury [2, 7, 8]. It has long been known that in aqueous alkali, dissolution of zinc and the evolution of hydrogen occur simultaneously as the anodic and cathodic reactions responsible for 'self-discharge'. This corrosion of the zinc active material is obviously detrimental to the performance of the battery, causing a reduction in capacity that must be minimised. This can be achieved by the addition of an inhibitor which possesses a hydrogen overvoltage which is higher than that of zinc. Mercury is one such additive chosen to perform this role, typically as 1–4% of the paste weight in the form of HgO. For the purpose of inhibiting self-discharge, mercury has been found to be extremely effective [8–11]. Unfortunately, the effect of amalgamation has also been found to be detrimental on the cycling performance of zinc anodes. In particular, it has been reported that the rate of shape change increases with the addition of this metal. Thus, a considerable amount of research has been undertaken into finding a suitable substitute for mercury that would also be capable of reducing the rate of self-discharge whilst maintaining or reducing that of shape change [11, 12].

The effect of various additives in pasted zinc electrodes has been studied in great detail by McBreen and Gannon [13, 14]. They found that the most successful additives were heavy metals (e.g., Pb, Cd, Tl and In) added to the paste mix in the form of their oxide/hydroxides (which are reduced to the metal prior to the reduction of zincate). The beneficial effect of these additives on shape change was attributed to a substrate effect, and that additives such as PbO, In(OH)₃ and Tl₂O₃ increase the polarisability of the electrode which, in turn, improves current distribution and decreases shape change. The adverse effect of HgO was attributed to a decrease in polarisability.

Himy and Wagner [11, 12] also found that lead, cadmium and thallium decreased shape change, in agreement with the results of McBreen and Gannon [13, 14]. In addition, they performed tests on paste formulations which contained two additives. Using such mixtures shape change was considerably decreased, due to a synergistic relationship occurring with these binary compounds. Despite these findings, and the drawbacks associated with it, mercury still finds a high level of use due to its excellent corrosion

inhibiting properties, the latter usually outweighing any deleterious effects on shape change. However, there is currently a trend amongst battery manufacturers to replace mercury with other metals such as thallium and indium [11–13] (see Table 1).

Another series of additives which has received attention in recent years is that of the alkaline-earth-metal oxides or hydroxides. Of these the most promising, at the present time, is calcium. The chemistry of zinc electrodes containing calcium hydroxide has been the subject of many investigations [15–20]. The improvement in cycle life observed in calcium-containing electrodes can be attributed to the formation of calcium zincate, $\text{Ca}(\text{OH})_2 \cdot 2\text{Zn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, which is insoluble [18]. Thus, the migration of zincate away from the electrode is minimised, which, in turn, decreases shape change. However, the incorporation of $\text{Ca}(\text{OH})_2$ can result in a decrease in zinc utilisation, and it has been reported that for optimum efficiency the molar ratio of $\text{Ca}(\text{OH})_2$ to ZnO must be greater than 0.5 to 1.0 [19]. Magnesium and aluminium hydroxides are also thought to function in a similar manner to calcium, i.e., by forming an insoluble species which prevents migration of the zincate species. Another electrode additive which has been found to give beneficial effects on cycling is bismuth oxide at up to 10% Bi_2O_3 [21–23]. McBreen and Gannon [21] suggested that one reason for this improvement is that the crystal growth at the electrode surface is influenced by the bismuth to such an extent that an active deposit is made and maintained. In conjunction with this, it was also suggested that bismuth provides a conductive matrix of needle-like deposits, within the electrode during cycling, hence preventing densification. One final series of inorganic additives to receive attention in recent years is that of titanium salts, usually as the oxide or titanate [24, 25]. In particular, Berchelli and Chireau [24] patented an electrode that specified using between 0.2 and 1.8 wt.% of titanate mixed homogeneously throughout the electrode in the form of fibres that also improve the mechanical strength. Charkey [25] observed that potassium titanate created a stable concentration gradient of $\text{Zn}(\text{OH})_4^{2-}$ within the electrode pores, and as such resulted in improved capacity retention.

Organic additions have also received considerable attention during recent years, and of these polymeric additives have dominated. Their main advantages are essentially mechanical, i.e., binding the electrode, and also structural by providing a stable network to retain the zinc active material, thus slowing shape change. The most extensively used polymeric addition is that of polytetrafluoroethylene, PTFE [26–29]. Small additions of this polymer have been shown to engender a high degree of mechanical stability whilst still maintaining an open network. Other polymer systems have been utilised, though to a lesser extent. Of these, poly(vinyl alcohol) [2, 30] and poly(ethylene) [31] have received the most attention. Hampson and McNeil [32–34] have recently performed a large study of polymer-bound zinc electrodes, observing both potential and cycle-life parameters. In high concentration (i.e., >10%) all polymers tend to shield the active material and as a result reduce the electrode cycle life and capacity. Of the polymers studied

TABLE 1
Patented electrode additives for secondary zinc cells

Electrode additives			Brief details/comments	Patent No.
Author(s)	Company			
T. Ueda, Y. Ishikura <i>et al.</i>	Sanyo Electric Co. Ltd.	Ca(OH) ₂ in paste and coated on surface. Paste also contains calcium lignosulphate	JK 63 155 556	
T. Ueda, Y. Ishikura <i>et al.</i>	Sanyo Electric Co. Ltd.	Ca(OH) ₂ particle size optimised at 50–250 μm	JK 63 126 163	
Y. Fujiwara, Y. Ishikura <i>et al.</i>	Sanyo Electric Co. Ltd.	In oxide or hydroxide coated with silicic acid	JK 63 26 952	
Y. Ishikura, Y. Fujiwara <i>et al.</i>	Sanyo Electric Co. Ltd.	Sodium lignosulphonate (4%)	JK 62 287 569	
T. Ueda, Y. Ishikura	Sanyo Electric Co. Ltd.	Hydroxycarboxylic acids or their salts e.g., sodium gluconate (0.5%)	JK 62 241 262	
S. Furukawa, K. Inoue <i>et al.</i>	Sanyo Electric Co. Ltd.	In oxide/hydroxide plus Sr hydroxide (5%)	JK 62 66 571	
S. Furukawa, K. Inoue <i>et al.</i>	Sanyo Electric Co. Ltd.	Two layer electrode; zinc powder in surface layer only; both layers with In ₂ O ₃ and Ca(OH) ₂	JK 62 11 022	
S. Furukawa, S. Murakami <i>et al.</i>	Sanyo Electric Co. Ltd.	In or TI oxide/hydroxide plus oxide/hydroxide of Ga, Cd,Pb-Sn,Bi or Ag	JK 61 96 666	
K. Inoue, M. Nogami	Sanyo Electric Co. Ltd.	Outer layer having 2–4 times In oxide than inner layer. Layer improves cycle life through even In distribution	JK 61 101 955	
S. Furukawa, S. Murakami <i>et al.</i>	Sanyo Electric Co. Ltd.	In oxide plus Ga oxide	JK 61 811 967	
S. Furukawa, K. Inoue	Sanyo Electric Co. Ltd.	Regenerated cellulose powder	JK 61 91 872	
K. Inoue, M. Nogami	Sanyo Electric Co. Ltd.	In or TI oxide/hydroxide plus LiOH (optimised at 0.1 → 0.8 wt.%)	JK 61 118 968	
T. Shirogami, K. Inada	Toshiba Corp.	Paste containing Ca(OH) ₂ and Bi ₂ O ₃	JK 61 06 500	
H. Tsuji	Furukawa Electric Co.	Poly(vinyl alcohol) plus Ca(OH) ₂ , Ba(OH) ₂ , TiO ₂ , ZrO ₂ and/or MgO	Jk 60 20 853	

S. Furukawa, S. Murakami	Sanyo Electric Co. Ltd.	In and Tl oxide in electrode plus In and Li ions in electrolyte	JK 60 185 372
	Sanyo Electric Co. Ltd.	Anode having higher binder concentration at edges than at centre	JK 60 08 964
	Sanyo Electric Co. Ltd.	SBR rubber at edges of electrode	JK 60 97 559
	Mitsubishi Electric Corp.	Isoprene-isobutylene rubber binder (5%) instead of PTFE	JK 60 89 073
	Sanyo Electric Co. Ltd.	In plus one or more oxides of Hg, Pb, Cd, Tl, Sn or Bi for improved cycle life	JK 60 84 768
	Mitsubishi Electric Corp.	HgO addition plus Al ₂ O ₃	JK 60 56 368
	Sanyo Electric Co. Ltd.	In concentration higher at edges than centre	JK 60 14 758
	Sanyo Electric Co. Ltd.	CdO and PTFE resin which was higher at edges than centre	JK 60 14 757
	Sanyo Electric Co. Ltd.	In ₂ O ₃ found to improve cycle life over In metal	JK 59 186 257
	Sanyo Electric Co. Ltd.	Tl oxide and In oxide plus P.V.A. (1%)	JK 59 189 563
	Sanyo Electric Co. Ltd.	In ₂ O ₃ addition enhances effect of Ti ₂ O ₃	JK 59 18 956
	Sanyo Electric Co. Ltd.	In and In hydroxide plus alkaline earth silicate e.g., calcium silicate	JK 59 71 260
	Sanyo Electric Co. Ltd.	P.V.A. and In found to improve cycle life	JK 59 66 060
	Toshiba Corp	Chopped polyimide fibres (0.5 wt.%)	JK 59 03 027
	Toyota Central R&D	Zinc complexing agent(2,3,7-trihydroxyfluorine)	JK 58 17 895
	Sanyo Electric Co. Ltd.	Zinc anode with (2-15%) oxide of Sn and In (In:Sn 0.25:10)	JK 58 176 870
	Sanyo Electric Co. Ltd.	Zinc anode with (2-15%) oxide of Cd and Sn (Cd:Sn 0.25:10)	JK 58 176 871
	Sanyo Electric Co. Ltd.	Mix of carbon fibre and TiO ₂ (1:1 mix)	JK 53 163 172
	Sanyo Electric Co. Ltd.	In oxide and Sn oxide (Sn inhibits densification of anode)	JK 58 163 158

(continued)

TABLE 1 (continued)

Electrode additives		Brief details/comments	Patent No.
Author(s)	Company		
	Sanyo Electric Co. Ltd.	Cd oxide and Sn oxide	JK 58 163 159
	Sanyo Electric Co. Ltd.	In oxide or hydroxide and In metal	JK 58 163 160
	Sanyo Electric Co. Ltd.	In oxide and carbon fibre	JK 58 163 161
	Sanyo Electric Co. Ltd.	Ti oxide and Sn oxide/hydroxide	JK 58 163 162
	Sanyo Electric Co. Ltd.	Expanded graphite	JK 58 165 250
	Sanyo Electric Co. Ltd.	In hydroxide	JK 58 137 966
	Sanyo Electric Co. Ltd.	Cd and In compounds coated on edges of electrode	JK 58 137 964
	Sanyo Electric Co. Ltd.	Cu oxide (2-10%) improves battery life. Ca(OH) ₂ also in paste	JK 58 119 159
	Matsushita Electrical Ltd.	Na polyacrylate (0.5-2.5%) and C.M.C (2-4%)	JK 58 87 759
	Toshiba Battery Co. Ltd.	Isobutene-maleic anhydride co-polymer	JK 58 73 954
	Furukawa Battery Co.	Cu or CuO to prevent dendrites	JK 58 71 561
R. A. Jones	General Motors Corp.	Ca(OH) ₂ , Pb ₃ O ₄ and cellulose fibres	US Pat 4 358 517
	Toshiba Corp.	Bi ₂ O ₃ (30%) and Ca(OH) ₂ (10%) added	J.T.K. 82 13 102
H. Viadyanathan	Energy Research Corp.	ZnF ₂ or Zn titanate added	US Pat 4 304 828
R. R. Witherspoon, S. G. Meibuhr	General Motors Corp.	CaSi ₂ O ₅ (5-15%)	US Pat 4 312 931
J. Sandera, A. Touskova <i>et al.</i>	Tokyo Shibura Electric Co.	Bi, Bi ₂ O ₃ and/or Bi(OH) ₂ (~3%)	J.T.K. 81 29 345
A. S. Berchelli, R. F. Chireau	Yardney Electric Corp.	ZnF ₂ and/or Zn oxalate	Czech 184 504
		Alkali earth titanate compounds (e.g., Na titanate)	Australian 505 367
H. Tsuji	Furukawa Battery Co.	TiO ₂ (5%) of particle size 0.5 μm	JK 79 122 838

T. Shirokami, K. Inada	Tokyo Shibura Electric Co.	Ca(OH) ₂ , Bi ₂ O ₃ and nonionic surfactant (Triton X-100)	JK 79 41 429
K. Ohsawa, K. Fujiwara <i>et al.</i>	Furukawa Electric Co.	Mn or its oxide (0.1 → 20%)	JK 79 16 631
A. S. Berchelli, R. F. Chirea	Yardney Electric Co.	Potassium titanate in silver-zinc cells	US Pat 4 041 221
Y. Tsuburaya, Y. Maki	Hitachi Maxell Ltd.	Na polyacrylate (0.7 → 2.5 parts/1 part ZnO)	JK 76 142 644
T. Ohira, H. Kumano	Matsushita Electrical Ltd.	Ca(OH) ₂ added	JK 76 121 741
T. Takamura, Y. Kaneda	Tokyo Shibura Electric Co.	Bi ₂ O ₃ , In ₂ O ₃ and poly(acrylic acid) Na salt as binder	JK 74 112 125

by these workers only polycarbonate was found to be competitive with PTFE in terms of cycle-life performance. The addition of a polymer alone does not engender any electrical conductivity to the matrix. Therefore, other additions have been made in order to rectify this situation. In particular various carbons and graphites have been investigated for this purpose, due to their conducting properties. Duffield [35–37] carried out work with graphite additions and found that the cycle life could be significantly improved, in contrast to results obtained by Sandera *et al.* [38]. Duffield attributed this difference to the particle size of graphite used by Sandera, which was large (150 μm). Duffield found that the smaller the particle size used, the better the performance of the cell. He postulated that the beneficial effect was due to a physical entrapment of soluble zincate species during discharge within the electrode matrix. This occurs until a supersaturation takes place and precipitation of zinc oxide follows. Thus it can be seen that the graphite/PTFE matrix acts more as a retardant to shape change, rather than a complete prevention (as zinc will eventually escape into the solution). Other organic additives which have been successfully utilised in secondary zinc cells are surface-active agents, such as emulphogenes [39]. These tend to reduce shape change and densification by being adsorbed onto the zinc surface.

Electrolyte additions

An alternative way of improving the cycle life of the zinc electrode is to incorporate additives in the electrolyte. It is obvious that in this situation the concentration of the additive is also determined by its own solubility, hence, with some materials, only small additions can be made. Consideration must also be given to the effect that the additive will have on the performance of the counter-electrode. Electrolyte additions promote improvements to cycle life by similar mechanisms to those of electrode additions, namely: reduction of electrode corrosion, shape change and dendritic growth. They are used extensively in the metal-finishing industry to modify deposit characteristics. One would therefore expect that the exchange of knowledge and information from one technology to another would readily occur. However, this is true to only a limited extent, as most plating baths operate at much less concentrated alkaline solutions than those encountered in battery systems (e.g., 2 M sodium hydroxide solution compared to 6–7 M potassium hydroxide). This difference helps explain why certain levellers and brighteners, which work exceedingly well in the metal-finishing industry, fail to be of any significant use in modifying zinc deposits in battery systems.

The addition of lead ions to the electrolyte has long been used as a method of influencing the zinc deposit morphology. Mansfield and Gilman [40] reported that lead inhibited the growth of dendrites by blocking the sites which were active for dissolution and deposition, thus dissolution only occurs at macroscopic crystal defects. The morphology of the deposit was found to be affected by lead, in that it consisted of smooth, rounded dendrites

on many small crystallites, as opposed to the classical side-branched monocrytal dendrites obtained in lead-free electrolyte. Diggle and co-workers [41–43] found that the effectiveness of lead was potential dependent (suggesting that the inhibiting species was partially charged), and at high enough concentration ($> 10^{-4}$ M) could totally suppress dendritic growth. Tin salts have also been investigated in a similar way and have been found to exhibit properties favourable for deposit morphology enhancement [44–46]. The effect was attributed to blocking of active sites, similar to the mode of action of lead. Lithium hydroxide is a very common addition to the electrolyte, to extend the capacity of the nickel counter electrode. However, Flerov [47, 48] believed that the presence of LiOH also had a beneficial effect on the zinc electrode, as it could stabilise supersaturated zincate solutions and therefore prevent zinc passivation.

Numerous other electrolyte additives have been suggested, and their respective patents applied for (see Table 2). These include: silicate [48–50], ferro- or ferricyanide [51], phosphate [52–54], borate [52], arsenate [52] and fluoride [54, 55]. Silicate is thought to inhibit the dissolution of zinc by adsorbing it on to its surface, thus reducing the amount of charge needed to cause passivation. The other additives listed above all cause a reduction in the solubility of the discharged zincate species either by reducing the number of free hydroxyl ions, as with the fluoride, or by causing precipitation of zinc oxide in the vicinity of the electrode. Thornton and Carlson [56] investigated a number of alternative electrolytes, and found that there were no zinc anions which formed insoluble zinc compounds at pH values compatible with nickel electrodes. They therefore suggested that the most useful electrolytes were those which would have minimal hydroxyl concentration with the maximum conductivity, usually achieved by the addition of highly soluble salts such as phosphate, borate and fluoride. Nichols *et al.* [57] found that by using fluoride and borate solutions the cycle-life capacity and shape change could indeed be improved by use of such electrolytes. However, increased cell resistance and lower electrode utilisation were also noted by these workers. This compromise between cycle life and energy density must thus play a part in the selection of additives.

Organic electrolyte additions have also been investigated. In particular quaternary ammonium salts have been reported to influence zinc deposit morphology [41, 42, 44, 58, 59]. The proposed mechanism for this action suggests that the large organic cationic species undergo specific adsorption at active growth centres, thus blocking deposition at these sites. The deposition therefore occurs at other less favourable sites, hence producing a more even deposit. This, in turn, leads to an improved cycle life through reduction in dendritic growth. Other organic compounds that have been tested as electrolyte additions include various surfactants [60, 61], thiourea [46, 62] and poly(ethylene glycol) [62, 63]. These probably function in a similar manner to the quaternary ammonium salts.

One final modification that can be made to the electrolyte is the addition of a cellulose- or starch-based derivative to cause a general gellation. The

TABLE 2
Patented electrolyte additives for secondary zinc cells

Electrolyte additives		Patent No.	
Author(s)	Company	Brief details/comments	
S. Furukawa, K. Inoue	Sanyo Electric Co. Ltd.	Fe ³⁺ ions (0.1 mM) in electrolyte, In/TI in electrode	JK 62 110 269
S. Furukawa, K. Inoue	Sanyo Electric Co. Ltd.	Ge ⁴⁺ ions (0.1 mM) in electrolyte, In/TI in electrode	JK 62 108 467
S. Furukawa, K. Inoue	Sanyo Electric Co. Ltd.	K ₃ PO ₄ (1–7%)	JK 62 165 878
S. Furukawa, K. Inoue	Sanyo Electric Co. Ltd.	LiOH (0.5 M)	JK 60 225 372
S. Furukawa, S. Murakemi	Sanyo Electric Co. Ltd.	In(OH) ₃ (0.1 mM) and LiOH (M)	JK 60 185 372
S. Furukawa, S. Murakemi	Sanyo Electric Co. Ltd.	In(OH) ₃ (0.1 mM) and Co(OH) ₂ (0.1 M)	JK 60 185 373
	Pentel Co. Ltd.	Dithiocarbamic acid or its derivatives, e.g., K N,N'-diethyldithiocarbamate	JK 60 240 639
	Matsushita Electrical Ltd.	1 or more compounds of Al, Ga, In, TI (up to 0.8%) in CMC gel	JK 59 103 278
	Fuji Electrochem Co. Ltd.	Chromate in electrolyte, active material in CMC gel	JK 59 51 476
	Sanyo Electric Co. Ltd.	CdO (100 g l ⁻¹) addition	JK 58 158 875
	Agency of Industrial Sciences and Technology	Te oxide (500 mg l ⁻¹) and Pb oxide (500 mg l ⁻¹) in 9 M KOH	J.T.K. 82 05 025
E. J. Carlson	General Electric Co.	KOH(5–10%) with KF(5–15%) and K ₃ PO ₄ (10–20%)	US Pat. 4 273 841
M. Eisenberg	Electrochimica Corp.	K ₃ PO ₄ or borate salt	UK Pat. 4 224 391
B. Furuhashi	Nakamura Kazuo	Sr(OH) ₂ ·8H ₂ O (5 g l ⁻¹) added for dendrite prevention	JK 78 133 734
R. Fukuhara, S. Oshimura <i>et al.</i>	Hirachi-Maxell Ltd.	Electrolyte containing alkali soluble amine/urea or thiourea derivative having unpaired electrons	JK 78 00 839 78 00 840 78 00 841

K. Ohsawa	Furukawa Electric Co.	Polycationic polymer	JK 75 43 435
H. Ikeda, N. Furukawa <i>et al.</i>		In and TI compounds addition	JK 75 65 832
Y. Ikeda, T. Ohhira	Matsushita Electric Co.	Benzylidimethyldodecylammonium chloride (5%)	JK 75 96 845
Y. Ikeda, T. Ohhira	Matsushita Electric Co.	In and Te (500 mg l ⁻¹)	JK 75 118 231
Y. Ikeda, T. Ohhira	Matsushita Electric Co.	Poly(oxyethylene)dodecyl ether and lignosulphonate to electrode and/or electrolyte	JK 75 96 844
K. Ohsawa	Furukawa Electric Co.	Ioene polymer addition (e.g., <i>N,N'</i> -dimethylpiperazine-1,5-dibromo pentane polymer)	JK 75 139 939
T. Ikeda, T. Ohhira	Matsushita Electric Co.	Fluoride ions (2 g l ⁻¹) additions	JK 75 26 040 041 044

gelled electrolyte will inhibit the rapid movement of zincate species and this should, in theory, cause a reduction in shape change and dendritic growth. However, one major problem that may arise when using this system is that the internal cell resistance may be significantly increased due to the reduced ionic mobility. Primary zinc systems use gelled electrolytes extensively [2, 64], and so a transfer of technology should be possible.

Separators

Separator material is used in virtually all zinc battery systems, primarily as a means of keeping the positive and negative electrodes apart. Initially separators took the form of a cellulose film, usually wrapped around the electrode two or three times. However, as time has progressed the use and complexity of separator systems has developed to a point where multilayers of differing materials are nowadays in common use. Broadly speaking though, the basic functions of these systems still remain the same, namely, to act as an electrolyte reservoir and wick, and to interpose a gap between the two electrodes, thus preventing a short circuit. The selection of the correct separator system is therefore of vital importance to the successful operation of a battery. In addition to the basic requirements listed above, there are also certain others which a separator must meet for successful operation. These are: that it should be

- (i) resistant to degradation by either the electrolyte and/or active materials,
- (ii) high in ionic conductivity and low in electrical resistance,
- (iii) effective in preventing migration of particles between electrodes,
- (iv) easily wettable by the electrolyte,
- (v) mechanically strong and flexible enough to withstand battery fabrication,
- (vi) preferably relatively inexpensive.

Lundquist [65] recently characterised the various types of separators employed in Ni–Zn cells. A list of patented systems gleaned from the literature is given in Table 3.

As previously mentioned, cellophane was the first material to be successfully employed as a separator in a practical secondary silver–zinc cell [66]. Unfortunately cellophane is not stable in alkaline solutions and it is also prone to undergo oxidative degradation in silver–zinc cells, thus limiting battery life and performance. Considerable research and development has been undertaken into both improving the properties of cellulosic materials and also finding suitable replacements. Modifications to the cellulose film have included treatment with sodium borohydride [67] to improve chemical stability by reducing the number of aldehyde groups. Anti-oxidants such as phenylene–diamine [68] have also been suggested as a method of improving oxidation resistance.

The search for a suitable replacement for cellulose has progressed along two distinct paths, one being the development of grafted and radiation cross-

TABLE 3
Patented separator materials for secondary zinc cells

Author(s)	Company	Separators	Patent No.
Y. Fujiwara, Y. Ishikura	Sanyo Electric Co. Ltd.	Brief details/comments	
		Anode sprayed with 1:1 dispersion of MgO:Zn to give 50 μm layer	JK 62 22 369
M. Matsui		Porous chloroprene-rubber coated on electrode by dipping	JK 60 53 422
S. Poa	US Dept. of Energy Japan Storage Battery Co. Hitachi Maxell Ltd.	Microporous separator of tertiary C ₅₋₁₀ alkyl amine Electrode wrapped in Teflon-Ni powder-coated microporous bag	US Pat. 580 982 JK 59 71 258
	Japan Storage Battery Co.	Vinylon sheet coated with alkali earth hydroxide and PTFE or polyacrylate	JK 59 16 394
	Sanyo Electric Co. Ltd.	Two poly(propylene) bags--inner one coated at edges with Ni	JK 59 83 363
	Japan Storage Battery Co.	Polyacetylene wrap (CH) _x	JK 58 198 855
	Sanyo Electric Co. Ltd.	Ni-coated separators--carbonyl Ni better than Ni plate	JK 58 126 666 667
	Yusa Battery Co.	Cd on anode face of separator	JK 57 162 275
	Yusa Battery Co.	Zinc anode covered with dispersion of 80 parts MgO:20 parts PTFE	JK 57 163 963
	Yusa Battery Co.	Coating of di-Me polysiloxane with hydrophilic groups	JK 82 86 670
	Toshiba Corp.	Non-woven acrylo-nitro-vinyl chloride co-polymer coated with 10% PVA/1.2% H ₃ BO ₃	JK 82 20 667
G. F. Schmidt, R. E. Weber	Kimberly-Clark Corp.	Non-woven poly(propylene) coated with hydrophilic wetting agent (Strodex PK90), a K salt of organophosphoric acid ester, and butyl rubber latex and then cured	Fr. Demande FR 2 486 312

(continued)

TABLE 3 (continued)

Author(s)	Company	Separators	Patent No.
		Brief details/comments	
L.-C. Hsu, W. H. Phillip <i>et al.</i>	N.A.S.A.	Crosslinked copolymer of vinyl alcohol and unsaturated carboxylic acid	US Pat. Appl. 282 298
M. G. Dodin, A. Charkey	Energy Research Corp.	Polyamide and wettable polymer with filter reactive to zinc e.g., CeO ₂ , Ca(OH) ₂ , Mg(OH) ₂ , Ba(OH) ₂ , Al(OH) ₃ , ZnF ₂ , or Zn(BO ₃) ₂	Euro. Pat. EP 40 826
T. Sakai, H. Furukawa <i>et al.</i>	Sanyo Electric Co. Ltd.	Zinc anode coated with a carbon black-Ca(OH) ₂ mixture	JK 79 129 331
S. Sekido, T. Ohhira	Matsushita Electrical Co.	Ni-Zn cell with separator containing Ca(OH) ₂	US Pat. 3 976 502
R. F. Chireau	Yardney	Interspacer of separator contains 50-95% of titanate material such as K ₂ TiO ₆	US Pat. 4 034 144
T. Takamura, Y. Kanada <i>et al.</i>	Tokyo Shibura Electric Co.	Polyamide separator - electrode contains alkali earth metal oxide/hydroxide	Ger Offen. 2 433 487
K. Ohsawa	Furukawa Electric	Zinc anode dipped in polycationic polymer e.g., 20% poly (N,N-dimethyldiallylammonium)chloride	JK 75 77 839
H. Forst, W. Vielstich		Anode coated with synthetic latex e.g., styrene acrylate latex	Ger Offen. 2 360 026

linked polyalkenes [67, 70], the other being the use of inorganic separators [71–73]. The radiation polymers consist of a film of the polyalkene which is then cross-linked to give a uniform three dimensional structure. This creates a more tortuous pathway for any penetrating species, i.e., dendrite bridging is delayed. Grafting of the film, and exposing it to radiation is performed to increase conductivity in potassium hydroxide, and also oxidation resistance. However, one disadvantage of these separators compared to cellulose, is that they do not swell when wetted, which, in turn, allows the electrodes themselves to expand on cycling, hence accelerating shape change. Other non-cellulosic separator systems which have been proposed are poly(vinyl alcohol) membranes [70]; these do swell in hydroxyl solutions to form a dense gel, but their mechanical strength is poor and consequently their use is mainly in conjunction with other systems. Polymer blends consisting of an aromatic heterocyclic polymer and another polymer have also been investigated with some reported success [74].

The final class of separator system which has been utilised in secondary zinc systems is that of inorganic separators. These were developed mainly for silver–zinc cells in space and military applications; their cost would therefore prove prohibitive for everyday civilian use. Initially, rigid separators were manufactured from aluminosilicate compositions [75], but it was soon realised that flexible separators would have a much greater use and appeal. The formulations for these were based upon those developed for the rigid separators, but with a suitable polymer addition to engender flexibility. The initial results showed that rigid separators give increased cycle life compared to cellulose types, whereas flexible ones gave slightly less. Further work on the later separators has since improved this situation somewhat.

The application of certain substances on the surface of the membrane has also been suggested, i.e., the so-called 'coated separators' [76–79]. These include a metallic-nickel coating on the zinc side of the separator, causing the dendrites to be destroyed on contact with the nickel [76, 77]. However, this method only delays penetration, it does not totally prevent it. Another coated separator suggested, consists of a copolymer of acrylonitrile and poly(vinyl chloride) with a coating of PVA containing inorganic additions [78]. This separator has been reported to be resistant to zincate ion penetration.

At present, the main direction of separator research is into the use of combined systems, which are proving more effective than single separators. However, although separators have progressed greatly with the research dedicated to them, it is probably fair to say that they still have not advanced far enough to meet all the requirements in terms of improving cycle life.

Other methods

One method of improving the cycle life of zinc batteries, which has received increasing interest in recent years, is that of modifying the charging current profile. This can be achieved by a variety of methods, viz., pulsing

the current, superimposing a.c. current on d.c., periodically reversing the current, and multi-component pulse charging. The reasons behind the use of pulsed current charging for the prevention of dendrites has been summarized by Bennion [80]. The application of a high current peak creates a high surface overvoltage, and thus activates a large number of nucleation sites. The following rest period allows local zinc concentration gradients to relax by diffusion into the depleted diffusion layer. Thus a more uniform deposit is obtained by electrodeposition from a replenished diffusion layer. Arouet  *et al.* [81] reported that the effect of pulsed d.c. current on the electrodeposition of zinc was to produce a thicker, more compact deposit by appropriate choice of current density and the pulse on: off ratio. Smithrick [82] conducted pulse current charging on zinc–nickel cells, but found no evidence of any improvement over constant current charging. McBreen *et al.* [83] suggested that at the frequencies employed by Smithrick, double layer effects eliminated any advantages of diffusion relaxation. Wagner [84, 85] confirmed this result stating an optimum frequency to be 5–8 Hz, and the rest: pulse ratio to be 3:1. Katz *et al.* [86] also reported similar results, observing a two-to-three-fold improvement in capacity loss versus constant current charging. The second modification to the charging regime that can be employed is the superimposition of an a.c. current on a constant d.c. waveform. Chin and Venkatesh [87] performed such experiments with the deposition of zinc from an acidic zinc chloride solution, finding that the number of nucleation sites increased with the pulse current. The third alternative, of reversing the current, is only effective when the deposition is rate determining. When the reaction is activation controlled, little or no effect is obtained. Obviously, the deposition period must last longer than the dissolution one in this method.

The final method of modifying the charging waveform is to use a multi-component pulse current. This consists of a deposition current, a dissolution current and a rest period. Appelt and Jurewicz [88, 89] and also Binder and Kordesh [90] have claimed beneficial effects when using such a waveform. It must be remembered, however, that the time required for charging when using these modified waveforms is much longer than when using constant current—in the case of the optimised pulse current suggested by Wagner and Almerini [85], this can be four times longer.

Other miscellaneous ways of improving cell performance are vibrating the electrode [91, 92] and flowing (or pumping) the electrolyte. The patented ‘Vibrocel’ [93] has not found commercial success, probably due to the expense in the construction of the cell. Flowing electrolytes are utilised in zinc–halogen cells, but not in alkaline ones [5]. The mechanism by which both of the above operate is mass transport enhancement, also any dendrites formed tend to be broken off by the agitation/circulation of electrolyte.

Conclusions

This review has outlined the practical attempts that have been undertaken to alleviate both shape change and dendritic growth in zinc-based secondary

cells. The three main methods of reducing these drawbacks, namely, electrode additions, electrolyte additions, and separators all show promise. Electrode additions generally function by limiting the migration of zinc species from the vicinity of the zinc anode during discharge or by improving the current distribution on charging. The former may be achieved by physical entrapment or by localised precipitation of zinc-containing species. Electrolyte additions generally function in one of two ways. They either enhance the charging reaction by promoting a more ordered zinc electrodeposition or they inhibit the dissolution of the zinc during discharge by either adsorption or by reducing the solubility of discharged zincate species. Separator materials function by providing a barrier to discharged zinc species whilst still allowing the passage of charge. The two are not mutually exclusive but do make the choice of separator material critical. Present day materials are complex, often laminated in structure, forming a separator system rather than a single layer.

Clearly, the drive to limit dendritic growth and shape change is still continuing and if eventually successful, will probably lead to a functional, cycling, secondary zinc-anoded cell. At present polymeric electrode additions such as PTFE [26–29] appear promising, whilst electrolyte additions such as borate, phosphate, silicate, etc. [48–55] can inhibit dissolution or reduce the solubility of discharged species and thus make passivation more favourable. Clearly, this could lead to reduced utilisation which could be alleviated by increased electrode porosity. Zinc ions which are lost to the solution can be electrodeposited in a more coherent manner with the use of addition agents such as quaternary ammonium compounds [41, 42, 44, 58, 59]. At present none of the main methods to improve zinc cyclability seems to be totally successful, and perhaps the answer lies in a combined approach of all three methods as typified by the work of Sato *et al.* [78].

Reference

- 1 A. Fleischer and J. J. Lander (eds.), *Zinc–Silver Oxide Batteries*, Wiley, New York, 1971.
- 2 R. V. Bobker, *Zinc in Alkali Batteries*, The Society for Electrochemistry, University of Southampton, U.K., 1973.
- 3 R. D. Armstrong and M. F. Bell, *Electrochemistry*, Specialist Periodical Reports, Vol. 4, The Chemical Society, 1974, p. 1.
- 4 J. McBreen and E. J. Cairns, in H. Gerisher and C. W. Tobias (eds), *Adv. Electrochem. Electrochem. Eng.*, Vol. 11, Wiley, New York, 1978, p. 273.
- 5 J. McBreen, *J. Electroanal. Chem. Interfacial Electrochem.*, 168 (1984) 415.
- 6 R. J. Brodd and V. E. Ledger, in A. J. Bard (ed.), *Encyclopedia of Electrochemistry of the Elements*, Vol. 5, Marcel Dekker, New York, 1976.
- 7 C. M. Shepard and H. C. Langelan, *J. Electrochem. Soc.*, 114 (1967) 8.
- 8 D. P. Gregory, P. C. Jones and D. P. Redfern, *J. Electrochem. Soc.*, 119 (1972) 1288.
- 9 T. P. Dirkse and R. Timmer, *J. Electrochem. Soc.*, 116 (1969) 162.
- 10 R. N. Snyder and J. J. Lander, *Electrochem. Technol.*, 3 (1965) 161.
- 11 A. Himy and O. C. Wagner, *Proc. 27th Power Sources Symp., Atlantic City, NJ, 1976*, p. 135.
- 12 O. C. Wagner and A. Himy, *Proc. 28th Power Sources Symp., Atlantic City, NJ, 1978*, p. 167.

- 13 J. McBreen and E. Gannon, *Electrochim. Acta*, 26 (1981) 1439.
- 14 J. McBreen and E. Gannon, *J. Electrochem. Soc.*, 130 (1983) 1980.
- 15 E. G. Gagnon, *J. Electrochem. Soc.*, 133 (1986) 1989.
- 16 E. G. Gagnon and B. S. Hill, *J. Electrochem. Soc.*, 137 (1990) 377.
- 17 D. M. McArthur, *20th I.E.C.E.L. Proc., Miami, FL, 1985*, Paper 859054.
- 18 R. A. Sharma, *J. Electrochem. Soc.*, 135 (1988) 1875.
- 19 E. G. Gagnon and Y. M. Wang, *J. Electrochem. Soc.*, 134 (1987) 2091.
- 20 A. Charkey, *Eur. Patent No. 0 048 009* (1981).
- 21 J. McBreen and E. Gannon, *J. Power Sources*, 15 (1985) 169.
- 22 C. Biegler, R. L. Deutscher, S. Fletcher, S. Hua and R. Woods, *J. Electrochem. Soc.*, 130 (1983) 2303.
- 23 R. L. Deutscher, S. Fletcher and J. Galea, *J. Power Sources*, 11 (1984) 7.
- 24 A. S. Berchelli and R. F. Chireau, *U. S. Patent No. 4 041 221* (1977).
- 25 A. Charkey, *Proc. 26th Power Sources Symp., Atlantic City, NJ, 1974*, p. 87.
- 26 J. Goodkin, *Proc. 22nd Power Sources Symp., Atlantic City, NJ, 1968*, p. 79.
- 27 A. Charkey, in D. H. Collins (ed.), *Power Sources 4*, Oriel, Newcastle upon Tyne, 1973, p. 93.
- 28 Energy Research Corp., *Br. Patent No. 1 476 550* (1977).
- 29 A. Duffield, P. J. Mitchell, N. Kumar and D. W. Shield, *J. Power Sources*, 15 (1985) 93.
- 30 S. P. Poa and S. J. Lee, *J. Appl. Electrochem.*, 9 (1979) 307.
- 31 M. Cenek, O. Kouril, J. Sandera, Tousekova and M. Calábek, in D. H. Collins (ed.), *Power Sources 6*, Academic Press, London, 1977, p. 215.
- 32 N. A. Hampson and A. J. S. McNeil, *J. Power Sources*, 15 (1985) 245.
- 33 N. A. Hampson and A. J. S. McNeil, *J. Power Sources*, 15 (1985) 261.
- 34 N. A. Hampson and A. J. S. McNeil, *J. Power Sources*, 15 (1985) 61.
- 35 A. Duffield, P. J. Mitchell, D. W. Shield and N. Kumar, in L. J. Pearce (ed.), *Power Sources 11*, Taylor and Francis, Hampshire, U.K., 1986, p. 253.
- 36 A. Duffield, *Ph.D. Thesis*, Loughborough University of Technology, U.K., 1986.
- 37 A. Duffield, *Chem. Ind.* 2 (1988) 88.
- 38 J. Sandera, A. Tousekova, M. Cenek and O. Kouril, *28th Meet. I.S.E.*, 28 (1977) 381.
- 39 J. A. Keralla and S. J. Lander, *Electrochem. Technol.*, 6 (1968) 202.
- 40 F. Mansfield and S. Gilman, *J. Electrochem. Soc.*, 117 (1970) 588.
- 41 J. W. Diggle and A. Damjanovic, *J. Electrochem. Soc.*, 119 (1972) 1649.
- 42 J. W. Diggle and A. Damjanovic, *J. Electrochem. Soc.*, 117 (1970) 65.
- 43 J. O' M. Bockris, J. W. Diggle and A. Damjanovic, *1st Quart. Rep. to NASA, Contract NGR 39-010 002*, 1969.
- 44 F. Mansfield and S. Gilman, *J. Electrochem. Soc.*, 117 (1970) 1154.
- 45 I. N. Justinijanovic, J. N. Jovicevi and A. R. Despic, *J. Appl. Electrochem.*, 3 (1973) 193.
- 46 J. E. Oxley, *NASA Rep. CR-377*, 1966.
- 47 N. N. Flerov, *J. Appl. Chem. (U.S.S.R.)*, 30 (1955) 1326.
- 48 N. N. Flerov, *J. Appl. Chem. (U.S.S.R.)*, 33 (1960) 134.
- 49 A. Marshall and N. A. Hampson, *J. Electroanal. Chem. Interfacial Electrochem.*, 50 (1974) 292.
- 50 J. S. Drury, N. A. Hampson and A. Marshall, *J. Electroanal. Chem. Interfacial Electrochem.*, 50 (1974) 292.
- 51 J. D. H. Julian, *U. K. Patent No. GB 2 083 683 A* (1982).
- 52 M. Eisenberg, *U. S. Patent No. 4 224 391* (1980).
- 53 G. Feuillade and P. Cord, *U. S. Patent No. 3 849 199* (1974).
- 54 E. J. Carlson, *U. S. Patent No. 4 273 841* (1981).
- 55 R. F. Thornton, *U.S. Patent No. 4 247 610* (1981).
- 56 R. F. Thornton and E. J. Carlson, *J. Electrochem. Soc.*, 127 (1980) 1448.
- 57 J. T. Nichols, F. R. McLarnon and E. J. Cairns, *Chem. Eng. Commun.*, 38 (1985) 357.
- 58 P. Ruetschi, *U. S. Patent No. 3 160 520* (1964).
- 59 G. D. Wilcox and P. J. Mitchell, *J. Power Sources*, 32 (1990) 31.
- 60 T. P. Dirkse and R. Shoemaker, *J. Electrochem. Soc.*, 115 (1968) 784.

- 61 C. Cachet, Z. Chami and R. Wiart, *Electrochim. Acta*, 32 (1987) 465.
- 62 G. D. Wilcox and P. J. Mitchell, *J. Power Sources*, 28 (1989) 345.
- 63 E. Frackowiak and M. Kiciak, *Electrochim. Acta*, 33 (1988) 441.
- 64 N. C. Cahoon, in G. W. Heise and N. C. Cahoon (eds.), *The Primary Battery*, Vol. 2, Wiley, New York, 1971.
- 65 J. T. Lundquist, *J. Membrane Science*, 13 (1983) 337.
- 66 H. André, *Bull. Soc. Fr. Electriciens*, 1 (1941) 132.
- 67 C. M. Rosser and R. A. Glinski, *U. S. Patent No. 3 224 907* (1965).
- 68 C. Oberholzer, A. J. Salkin and E. Weiss, *2nd and 3rd Quart. Rep. to NASA, Contract NA 5-2860*, 1963.
- 69 K. V. Lovell and L. B. Adams, Royal Military College of Science, *Tech. Note PD/25/81*, 1981.
- 70 D. W. Sheibley, M. A. Mazo and O. D. Gonzalez-Sanabria, *J. Electrochem. Soc.*, 130 (1983) 255.
- 71 D. W. Sheibley, *NASA Tech. Mem., TM X-3199*, 1975.
- 72 W. H. Philipp and C. E. May, *NASA Tech. Mem., TM X-3357* 1976.
- 73 D. W. Sheibley, *NASA Tech. Mem., TM X-3465* 1976.
- 74 I. A. Angres, W. P. Kilrov and J. V. Duffy, *Proc. 28th Power Sources Symp., Atlantic City, NJ, 1978*, p. 162.
- 75 C. Berger and F. C. Arrance, *U. S. Patent No. 3 379 569* (1968).
- 76 O. C. Wagner, A. Almerini and R. L. Smith, *Proc. 29th Power Sources Symp., Atlantic City, NJ, 1981*, p. 237.
- 77 A. Himy and O. C. Wagner, *U. S. Patent No. 4 192 908* (1980).
- 78 Y. Sato, M. Kanda, H. Niki, M. Heno, K. Murata, T. Shirogami and T. Takamura, *J. Power Sources*, 9 (1983) 147.
- 79 A. Franklin, G. D. Wilcox and P. J. Mitchell, unpublished work.
- 80 D. N. Bennion, Review of membrane separators and zinc-nickel oxide battery development, *D.E. 83 011 663* (1980).
- 81 S. Aroueté, K. F. Blurton and H. G. Oswin, *J. Electrochem. Soc.*, 116 (1969) 166.
- 82 J. J. Smithrick, *Proc. 15th Int. Soc. Am. Inst. Aeronautics Astronautics, New York, 1980*, p. 1203.
- 83 J. McBreen, E. Gannon, D. T. Chin and R. Sethi *J. Electrochem. Soc.*, 130 (1983) 1641.
- 84 O. C. Wagner, *Rep. No 5*, U. S. Army Electronics R & D Command, Fort Monmouth, 1982.
- 85 O. C. Wagner and A. Almerini, *Proc. 31st Power Sources Symp., Atlantic City, NJ, 1984*, p. 255.
- 86 M. H. Katz, T. C. Adler, F. R. McLarnon and E. J. Cairns, *J. Power Sources*, 22 (1988) 77.
- 87 D. T. Chin and S. Venkatesh, *J. Electrochem. Soc.*, 128 (1981) 1439.
- 88 K. Appelt and K. Jurewicz, *J. Power Sources*, 5 (1980) 235.
- 89 K. Appelt and K. Jurewicz, *Electrochim. Acta*, 27 (1982) 1701.
- 90 L. Binder and K. Kordesh, *Electrochim. Acta*, 31 (1986) 255.
- 91 M. B. Liu, G. M. Cook, N. P. Yao, J. R. Selman, *J. Electrochem. Soc.*, 129 (1982) 913.
- 92 O. Von Krusentierna, in D. H. Collins (ed.), *Power Sources 6*, Academic Press, London, 1977, p. 303.
- 93 Exide Management and Technology Company, Annu. Rep. for 1979 on Ni/Zn batteries for electric vehicle propulsion, *ANL/OEPM-79-12*, 1980.