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Fibrous zinc anodes for high power batteries

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Abstract

This paper introduces newly developed solid zinc anodes using fibrous material for high power applications in alkaline and large size zinc–air battery systems. The improved performance of the anodes in these two battery systems is demonstrated. The possibilities for control of electrode porosity and for anode/battery design using fibrous materials are discussed in light of experimental data. Because of its mechanical integrity and connectivity, the fibrous solid anode has good electrical conductivity, mechanical stability, and design flexibility for controlling mass distribution, porosity and effective surface area. Experimental data indicated that alkaline cells made of such anodes can have a larger capacity at high discharging currents than commercially available cells. It showed even greater improvement over commercial cells with a non-conventional cell design. Large capacity anodes for a zinc–air battery have also been made and have shown excellent material utilization at various discharge rates. The zinc–air battery was used to power an electric bicycle and demonstrated good results.

Keywords: Zinc; Fibres; Anode; Batteries; Fuel cells

1. Introduction

Zinc has been a material of choice for battery anodes since the invention of the battery 200 years ago. It possesses a unique set of attributes including low equilibrium potential, electrochemical reversibility, stability in aqueous electrolytes, low equivalent weight, high specific energy, high volumetric energy density, abundance, low cost, low toxicity, and ease of handling [1]. The low equilibrium potential and high over potential for hydrogen reaction makes zinc the element with the lowest standard potential among all the elements that can be efficiently reduced from aqueous electrolytes [2].

There are several important commercial zinc based battery systems currently available in the market, Zn–MnO_2, Zn–AgO, and Zn–air. Each of the systems has its own unique advantages in certain market sectors. Zn–MnO_2 primary battery, zinc–carbon and alkaline, is the most common battery system due to its low cost and convenience of use. It is the largest in terms of number of cells produced worldwide every year and the second largest in market share only after the lead–acid battery. The Zn–AgO battery has the highest energy per unit of weight and volume of any commercially available aqueous secondary battery. The high energy and the capability of operating efficiently at extremely high rates make the zinc–silver battery a high performance battery suitable for demanding military and space applications. The Zn–air battery has a very high energy owing to the fact that it does not contain cathodic active material within the battery. It has the highest energy density among primary battery systems available in the marketplace.

Despite the widespread use of zinc–manganese dioxide alkaline batteries, their performance is not adequate for a range of new power demanding electronic devices. The energy utilization in high rate applications is very low for digital cameras, e.g. less than one-third of the usable energy in the cells. Fig. 1 illustrates the utilization efficiency versus power for the alkaline battery in the context of application and market status. It shows that the alkaline battery is ideal for low drain applications due to its high utilization efficiency. For high rate applications, the market is currently dominated by rechargeable and lithium primary battery systems.

The high rate of discharge performance of the alkaline battery needs to be significantly improved to be used for high power applications. Much industrial development effort has been made in this direction as indicated by the number of applica-

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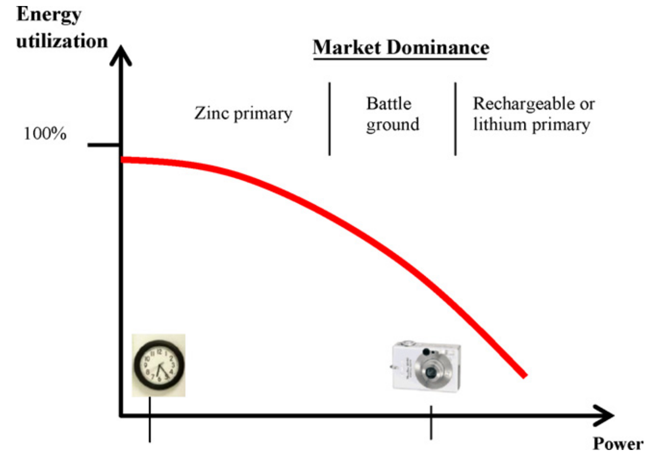

Fig. 1. Schematic illustration of the performance of the alkaline battery in terms of energy utilization and power.

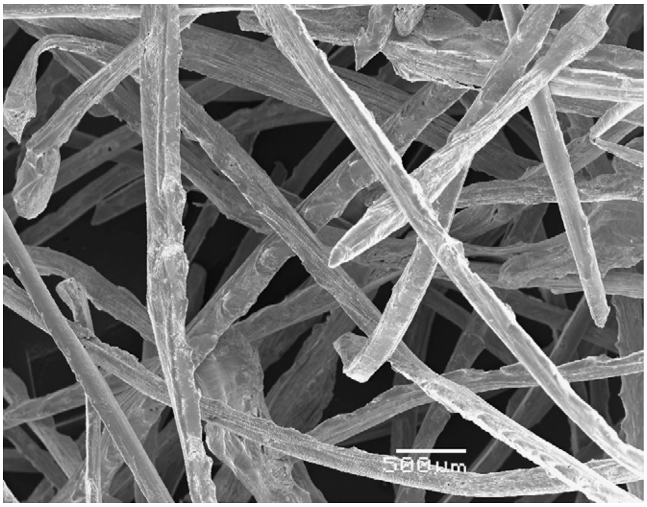

Fig. 2. An SEM image of a typical sample of zinc fibres.

tions that are filed each year. Various approaches have been attempted to improve the performance of zinc anodes such as using multi-modal particle size distribution [4,5], particle agglomerates [6,7], different forms of particulates such as zinc ribbons, flakes or needles [8–10], and increasing the interface area between the anode and the cathode with non-conventional designs [11,12]. Some newly developed batteries even use nickel oxy-hydroxide as the cathode material, which has more noble potential and better discharging characteristics in comparison to the conventional manganese dioxide [13].

Large format zinc–air batteries have great potential in motive power applications such as scooters, bicycles, and buses [3]. There has been a significant effort to develop large systems in the last 10 years. Due to the high power requirement, the anodes in these systems typically use dendritic forms of zinc powder. Dendrite powder is electroplated from alkaline electrolyte and has a very high surface area, about 100 times higher than atomized powder. Dendritic powder can also be pressed and formed into a solid plate without gelling due to the mechanical interlocking among branches of powder particles. However, due to the high surface area and because it is made in a wet condition, the dendritic anode is not suitable for long-term storage. Also, without reinforcement from a strong current collector, the anode is mechanically weak.

Fibrous materials were suggested long ago as having advantages over powders [14]. Several different concepts for making zinc fibres and using fibrous materials to make anodes have been proposed in some recent literature [8,15]. However, these concepts have not been put into practice. Accordingly, there is no technical information on the properties and performance of fibrous zinc materials.

Teck Cominco has developed a new way to make zinc anodes using fibrous materials for high power applications of alkaline batteries and large size zinc–air cells. The experimental results for improved performance of the anodes in these two battery systems will be shown in this paper. The versatility of anode/battery design using fibrous materials and the flexibility of controlling electrode porosity will also be discussed.

2. Experimental

Zinc fibres were produced by a spin cast method in which wheels with a sharp edge turn over the surface of a molten zinc bath and spin out strands of zinc fibres [16]. Fig. 2 shows an example of zinc fibres. The fibres can be further processed into various physical forms such as sheet, rod, bar, and plate which can have various thicknesses and lengths with controlled mass, density, and porosity. Anodes of certain shapes can be made from these different forms of material. Fig. 3 shows a rod form of anode designed for an AA alkaline cell and a plate form of anode for a large size zinc–air cell.

Fig. 3. A rod form of fibrous electrode for an AA cell and a plate form of anode for a large mechanically rechargeable zinc–air cell.

Fig. 4. Photographs of an electric bicycle and its zinc–air battery power source.

The fibrous anodes were tested for discharge performance in C cells. Commercial C cells used for the testing were cut open at the negative end. The gelled zinc anode was extracted and replaced with a fibrous anode. The weight of the zinc was equivalent to the zinc in the gelled anode of the C cell, about 11.5 g; 5.5 g of 35% KOH as the electrolyte was then added into the cell. The cut end with the current collector was then put back into the cell. The cell thus assembled was clamped onto a rack which provided the physical stability of the testing cell. Discharge testing was conducted at room temperature.

Two different sizes of cells were used to test the performance of fibrous anodes in the zinc–air system. The small zinc–air cell was made of Teflon with air cathode windows on both sides. The windows were each 2.5 cm × 4 cm, giving a total anode/cathode interface area of 20 cm^2. The cathode was obtained commercially from Evionyx Inc. The separator was a CELGARD polymer type. The electrolyte was 35% KOH and was added in sufficient amounts to fully immerse the zinc anode. The large zinc–air cells, supplied by Powerzinc Inc., were designed for electric bicycles. Fig. 4 shows the battery along with an electric bicycle. The battery has 11 cells with a nominal voltage of 12 V and a usable energy of 700 Wh.

3. Results and discussion

3.1. *Performance in alkaline cell*

Fig. 5 shows a discharging curve at 1 A continuous current for a C cell constructed with a fibrous anode in comparison to that for an original commercial C cell. The cell with the fibrous anode performed considerably better than the commercial cell. Taking the capacity at 0.8 V as a measurement, the cell with the fibrous anode had about 30% more capacity than the commercial cell. The test cell showed higher voltage than the commercial cell, and the difference increased with time, indicating that the potential loss is less in the fibrous anode, particularly near the end of discharge.

The electrochemical behaviour of an alkaline cell during discharge has distinctive regions in which certain processes are dominant in determining the loss of working voltage of the cell [17]. As shown in Fig. 6, the voltage drop immediately after imposing the discharging current is largely due to polarization of the anode and cathode surfaces, the gradual decaying of the voltage after the initial stage mainly attributed to the potential decay of the MnO_2 cathode, and, near the end of discharge, the rapid drop of potential is mainly due to passivation of the zinc anode because the current density on the zinc surface becomes very high. The fact that the potential drops much slower near the end of discharge for fibrous anodes than for zinc powder anodes may indicate a lower current density for fibre anode than zinc powder. Thus, it implies that the fibrous form of zinc has a better electrical contact among individual pieces of zinc than the powder form. It is interesting to note that the discharging

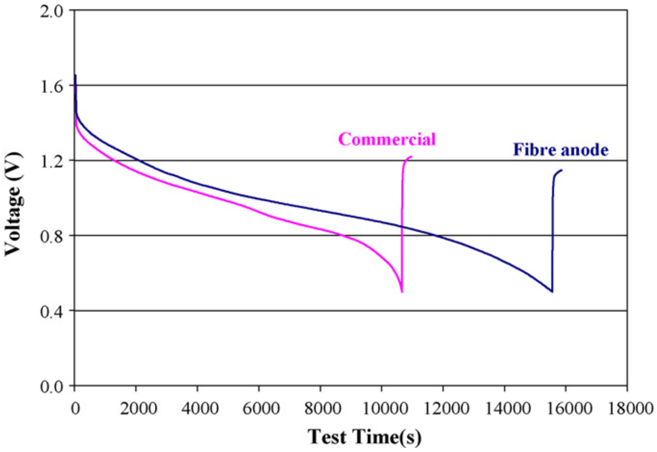

Fig. 5. Discharge curves for an original commercial C cell and a cell using an anode made of zinc fibres.

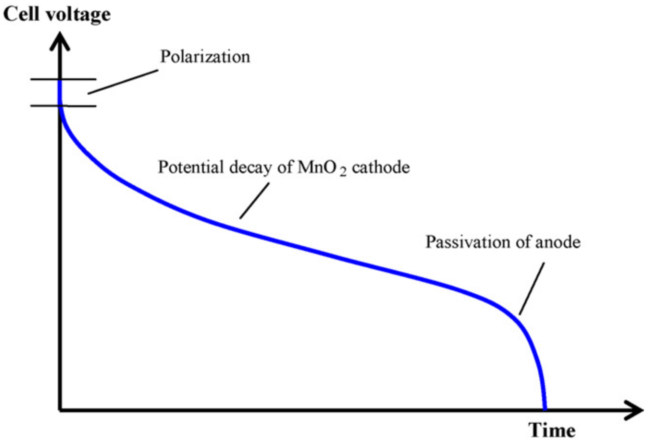

Fig. 6. Dominant processes that are responsible for the potential decay in different regions during discharge of an alkaline cell.

capacity of the fibre anode is about 50% more than the powder anode if the end voltage of discharging is at 0.5 V.

3.2. Control of porosity and distribution of porous space

From a system perspective, the dimension, shape of anode and cathode, anode/cathode interface area, separator material, amount and composition of electrolyte, material and design of current collector, and properties of electrodes are all important in the performance of batteries and fuel cells. With respect to the properties of electrodes, the important parameters are specific surface area (defined as the total physical surface area per unit of weight, $m^2 g^{-1}$), effective surface area (the amount of surface area that is electrochemically active), surface activity, porosity, electrical conductivity, and mechanical stability. Many of these characteristics are determined by the distribution of solid and porous space in the given volume of the space that is determined by the design of the battery and the characteristics of the materials.

Porosity and distribution of porous space in electrodes are very important for the performance of the electrodes inside the batteries. Their control is determined by the form of material and the design of the electrodes. For a given form of material, the porosity for optimum performance is determined by physical and chemical properties, such as reactivity, conductivity, and mechanical property. In the case of alkaline batteries, the current zinc anode material is in the form of atomized powder which relies on gelling to control porosity. If the porosity is too low, the anode may not have good reactivity and, if it is too high the anode may have poor conductivity. The zinc powder used for alkaline battery applications, before being mixed with electrolyte, typically has a density of 3–3.5 $g\,cm^{-3}$, which is about 42–50% zinc volume, or 50–58% porosity. To reach the porosity required for alkaline cells to perform well, which is typically about 70%, manufacturers use a gelling agent to make the mix of zinc powder and electrolyte such that the zinc particles are not densely packed but somewhat suspended in the electrolytic gel. However, for a given powder (certain shapes of particles and particle size distributions), there is only a narrow porosity range in which the particles can be suspended without losing electrical contact between the particles.

Since gelling will cause reduction in particle connectivity and, thus, anode conductivity, the amount of gelling and, therefore, the extent of porosity control is limited. Although gelling provides immobilization of electrolyte and powder particles, the gelled anode is still a paste and does not have the same mechanical integrity as a solid. Furthermore, ionic conductivity and, thus, discharging performance is typically negatively affected by gelling. In addition, gelling adds cost to manufacturing both in terms of material and extra processing steps. Removal of the need for gelling is by itself an improvement in alkaline battery manufacturing and applications as indicated by battery manufacturers [18].

In practice, the lowest zinc powder volume percentage is generally no less than 28% in the zinc anode paste (a mix of zinc powder, KOH, additives, and gelling agents) in order to match the positive electrode's rate of electrochemical output and to provide sufficient particle-to-particle and particle-to-current collector contact to maintain the zinc anode's electrical conductance [8]. Below this amount, voltage instability occurs and the performance becomes sensitive to shock and vibration. If the zinc powder volume in the anode is too high, e.g. higher than 50%, the space between the particles is insufficient for storing electrolyte and zinc dissolution product, which is a mix of zinc oxide, hydroxide, and some elemental zinc.

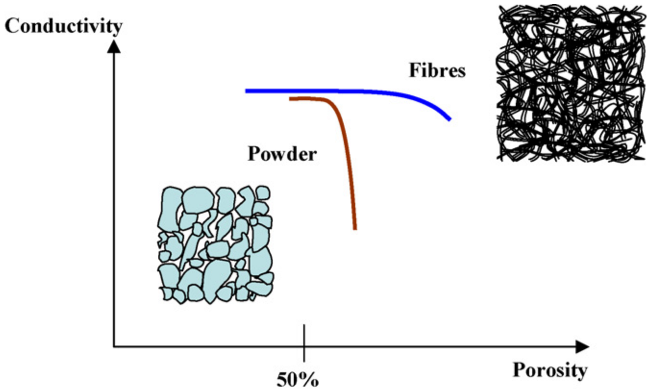

Fig. 7. Qualitative relationship between conductivity and porosity for powder electrodes and fibrous electrodes.

Anodes made of fibrous materials have a greater advantage in that porosity can vary a much greater range than in powder anodes without compromising the conductivity of the anode as schematically illustrated in Fig. 7. Stable solid electrodes of various densities can be readily made from zinc fibres; laboratory samples were made with densities ranging from as low as 0.46 $g\,cm^{-3}$ to as high as 6 $g\,cm^{-3}$. Fig. 8 shows the experimental data for the effect of mass on discharging capacity and utilization efficiency of fibrous anodes in C cells. Capacity increases with increasing mass while efficiency of material utilization decreases. The efficiency for 6 g anodes is near 50% while that for 14 g anodes is less than 25%. The possibility of varying mass and porosity without any gelling agent is a significant advantage for fibrous materials in designing zinc anodes.

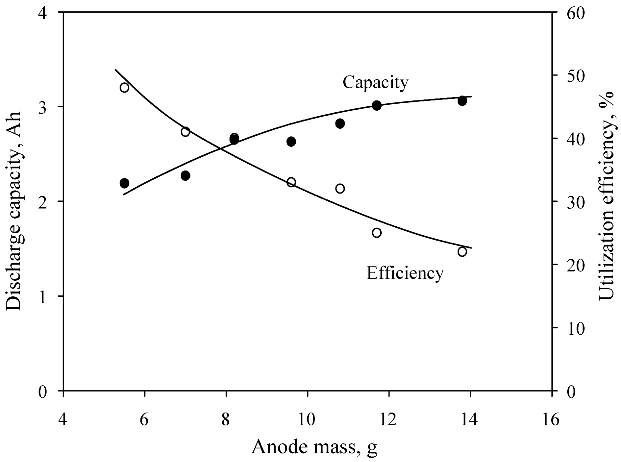

Fig. 8. Effect of anode mass on discharging capacity, and material efficiency of the anodes made of fibrous zinc in a C cell.

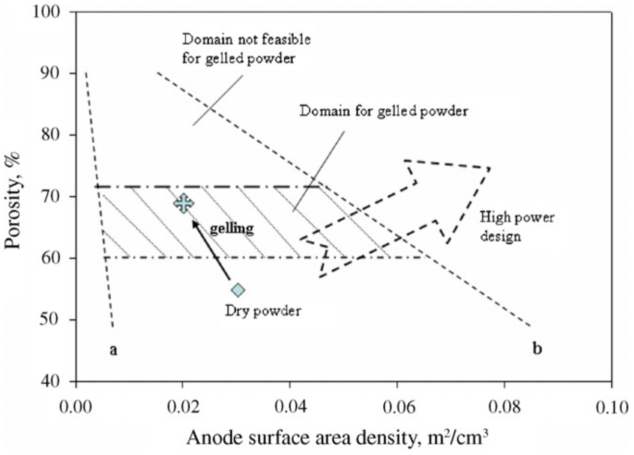

Fig. 9. Possible range for porosity and surface density for atomized zinc and solid porous electrodes. Relationship between porosity and density of effective surface area for anodes made of atomized zinc powder and fibrous zinc. Lines a and b represent materials with equal specific surface area; material b has a larger specific surface area than material a. For a given specific area, the higher the porosity, the lower the surface area density. The effective surface area is calculated based on assumption of geometric shape for spherical powder particles and cylindrical fibres.

Fig. 9 further illustrates the large difference in design possibilities for powder and fibre materials with respect to surface area density, which is defined as specific surface area divided by volume of materials. The diamond symbol denotes the porosity and surface area density of a typical dry powder, about 55%. If higher porosity is desired, for example 68%, one must use gel to bring the porosity from the position of the diamond to that of the star. Porosity significantly higher than 70% can cause problems in anode conductivity and materials initialization efficiency as powder particles lose contact at high porosity. This is not the case for fibrous anodes which can have porosity much higher than 70%. In anode design, porosity must be considered together with specific surface area; the former is controlled by packing density while the latter is controlled by the size of particulates. Generally, anodes for high rate applications have designs that have both high porosity and surface area density, indicated by the arrow in Fig. 9.

3.3. Performance in zinc–air cell

Fig. 10 shows the discharging curves for a fibrous anode and for a gelled atomized powder anode in a zinc–air cell. Both anodes have the same amount of zinc, about 8 g, and occupy the same volume in the cell. The powder anode had a discharge capacity of 3.68 Ah while the fibre anode had a discharge capacity of 5.08 Ah, about 38% more. The fibre anode had a very high material utilization, 86%, while the powder anode had a material utilization of only 60%. Cell voltage with the fibre anode during discharge is also significantly higher than that of the powder anode. The high discharging voltage, in combination with the longer discharging time, resulted in an even higher discharging energy for the fibre anode; 5.29 Wh as compared to 3.55 Wh for the powder anode, or about 49% higher.

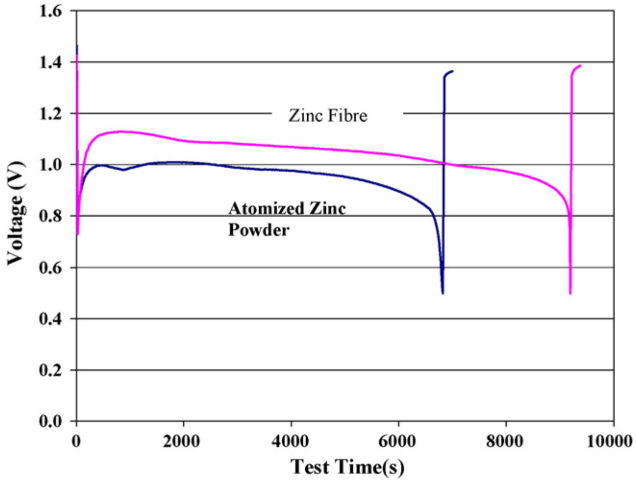

Fig. 10. Discharging curves for a gelled atomized zinc powder anode and a fibrous zinc anode in a laboratory test cell at an anode/cathode interface current density of 100 mA cm^{-2}.

The discharging curve of a zinc–air cell, as shown in Fig. 10, is rather flat in comparison to that of the alkaline cell shown in Fig. 5. Since the kinetics of the air cathode can be assumed to be more or less constant throughout the discharging period, the slight decay in voltage indicates that the polarization of the zinc anode and the ionic resistance of the electrolyte increased only slightly and rather steadily over the entire discharging period. On the other hand, the large voltage loss of the alkaline cell during discharge, as shown in Fig. 5, is largely due to the potential decay of the MnO_2 cathode [17].

Large size anodes were fabricated for the mechanically rechargeable zinc–air battery of Powerzinc used to power electric bicycles. Fig. 11 shows the discharging performance of zinc fibre anodes in comparison to dendritic zinc anodes. At a 10 A continuous discharging current, the capacity is about 72 Ah, similar for the two anodes, yielding a utilization efficiency of more than 90%. Except for short periods at the beginning and at the end, the cell voltages of the two cells during the entire discharging range were essentially identical. Since dendritic zinc has a very large surface area, about two orders of magnitude larger than fibrous zinc, the similar discharging

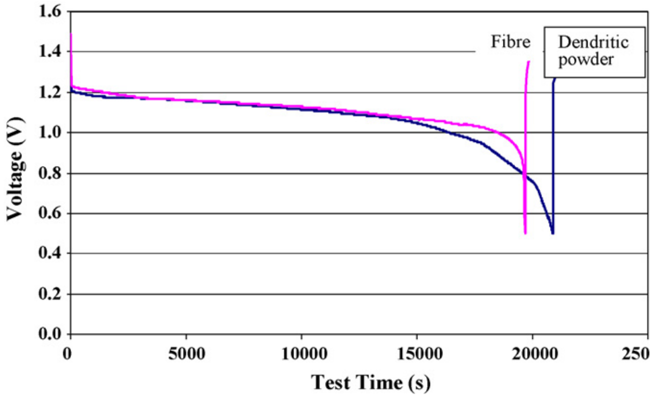

Fig. 11. Discharging curves for a fibrous zinc anode and a dendritic powder anode at a continuous discharge current of 10 A.

performance may indicate the better connectivity of the fibrous material.

Tests were also conducted for other discharging profiles. In a test profile simulating bicycle riding with a discharging current of 5.1 A for 2.5 min followed by 8.5 A for 2.5 min and 18.8 A for 0.5 min and 1 min rest, the discharging capacity of the fibrous anode was found to reach 78%. In another test with cycles of 1 h discharging at 10 A and then rest for 23 h, which simulates the effect of daily rest on the anode/cell, the discharging capacity was found to be about 85%. These tests show that fibrous anodes can have good discharging performance under various practical application conditions that may be encountered by a bicycle.

Field testing was conducted on an electric bicycle powered by zinc–air batteries using fibrous anodes. The electric bicycle was ridden on the streets for about 30 km day^{-1} to a total of 160 km, which was within the specifications of the electric bike (150–200 km). Most electric bicycles currently available on the market use lead–acid batteries as the power source, which typically allow 30–50 km of riding per recharge. This means that the zinc–air battery can last three to five times longer than the lead–acid battery which allows the possibility for daily bike-riders to recharge the battery only once a week.

Fibrous zinc has several advantages over dendritic zinc. Zinc fibre is made in a dry condition and can be stored in air for a long time without degradation. Dendritic zinc cannot be stored for a long time without significant degradation caused by corrosion since it has a large surface area and is produced in a wet condition. To avoid losing much capacity due to corrosion, dendritic anodes must be used shortly after being produced.

Another advantage for mechanically rechargeable battery applications is the mechanical integrity of the anode made of fibrous zinc in comparison to that made of dendritic powder. Fibres can be pressed together as a solid object with significant strength while pressed powder is weak without a support frame such as a current collector. An anode plate made of pressed dendritic powder without a supporting frame can easily break under vibration and impact of certain force. In contrast, anodes made of fibres can be bent to 90° or more without breaking. Such mechanical integrity could allow more flexibility in transportation and handling of anodes for mechanically rechargeable batteries.

3.4. *Design possibilities for fibrous anodes*

There is a great range of possibilities for anode design with fibrous materials. Fig. 12 shows some of the examples that can be easily made from fibrous material but are rather difficult to make with other types of materials such as the powder form of materials. For example, using a die to define the shape of an anode, one can design non-round shaped anodes for alkaline batteries to have better performance for high rate discharge performance. Fig. 13 shows, as an example, the discharging curve of a prototype alkaline C cell with non-conventional design; the discharge capacity is about 80% higher than the original commercial cell. In particular, a wound cell made of layered anode and cathode sheets can be constructed for consumer alkaline batteries by using zinc fibres as illustrated in Fig. 12c. Wound cell design, due to the large interface area between anode and cathode, has superior electrochemical kinetics compared to the conventional cylindrical ring-rod design of alkaline batteries.

For plate forms of anodes, such as those used in mechanically refuelable batteries or fuel cells, the anode can be designed for certain density distribution, either uniformly or non-uniformly across the area (Fig. 12). The anode can also have varied density from the middle to the edge, from the top to the bottom, or in selected areas. For example, an anode can have a denser edge than the middle to give the mechanical stability of the anode but also provide the lower density in the middle area for higher porosity to store electrolyte. The varied density from the top to

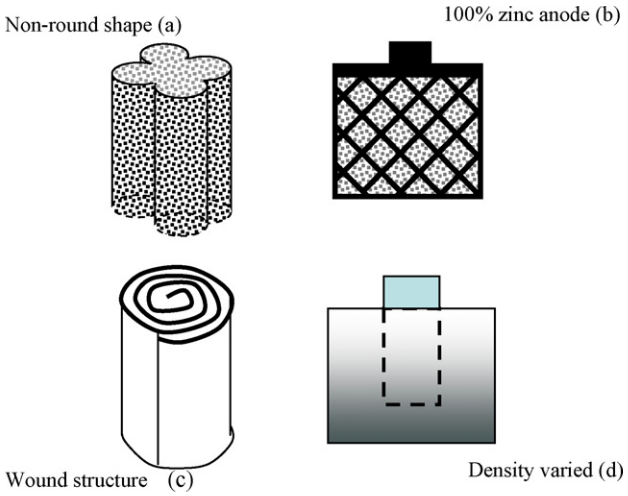

Fig. 12. Schematics of several anode examples to illustrate the design possibilities of anodes made of fibrous zinc: (a) non-round solid anode, (b) 100% zinc anode with the current collecting grid also made of zinc fibres, (c) wound design of electrode assembly using anode sheet made of zinc fibres, and (d) anode with density varying from the top to the bottom.

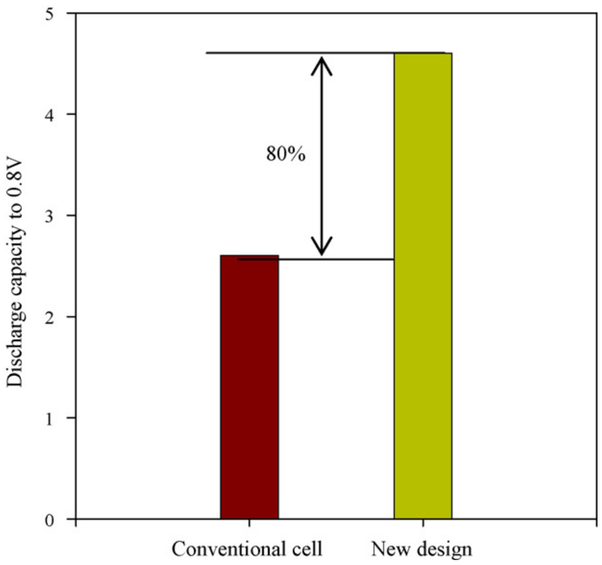

Fig. 13. Discharge capacity comparison of an original commercial C cell and a C cell constructed with a non-conventional cell design using zinc fibres.

the bottom (Fig. 12d) provides the possibility for the case where a variation of electrolyte density or temperature from the top to the bottom can be compensated.

To enhance the mechanical stability of the anode, it is also possible to make a narrow and dense grid to serve as the current collector as shown in Fig. 12b. The density of the denser area (i.e. grid and current collector) can be as high as $6.5\,\mathrm{g\,cm^{-3}}$, which is close to that of the bulk form of zinc (density of zinc is $7.13\,\mathrm{g\,cm^{-3}}$). Under sufficient stress, fine zinc fibres can be turned into continuous metal sheet, meaning the fibres are fused together under the mechanical work. The denser grid not only provides mechanical strength to the anode but also provides better current conductivity for the anode because the dense zinc grid is distributed over the entire anode surface and is in continuity with the current collector. The thickness and density of the grid can vary depending on mechanical strength and electrical conductivity required for the anode.

To form a metal grid from fibrous zinc allows the possibility to form a current collector directly from the active material and removes the need to have a separate current collector made of a foreign metal such as copper. This could have the potential benefit of lower production costs and lack of foreign metal contamination and corrosion loss due to galvanic action between zinc and other metals. Zinc has a relatively good conductivity among common metals. Laboratory testing of prototype anodes made of 100% zinc, including the current collector, showed that the anode could perform as well as the anode with a copper current collector.

4. Summary

Zinc is one of the most commonly used battery electrode materials and zinc anodes in these different systems still have much potential for improvement. Novel solid porous zinc anodes using fibrous material for applications in the alkaline battery and the large size zinc–air battery have been developed. The solid fibrous anodes have a good physical stability and connectivity among individual fibres, which ensures good electrical conductivity, mechanical stability, and design flexibility for controlling mass distribution, porosity and effective surface area. Experimental data on prototypes of anodes indicated that such anodes can provide 20% more capacity in alkaline cells at high discharging currents compared to commercially available cells. In a non-conventional design, it showed as much as an 80% improvement over a commercial cell. Large capacity anodes (70 Ah) have also been tested for the mechanically rechargeable zinc–air battery, which demonstrated 90% material utilization at 1/7 C discharge rate. The zinc–air battery using these anodes was used to power an electric bicycle, and preliminary results showed that it allowed the bike to run for 160 km.

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