# New structures of thin air cathodes for zinc–air batteries

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## Abstract

Thin composite cathodes for air reduction were manufactured using microfibre-based papermaking technology. The electrodes have a thin structural design, less than 0.15 mm in thickness. Composite cathode materials for oxygen reduction applications were fabricated by entrapping carbon particles in a sinter-locked network of 2–8 $\mu$m diameter metal fibres. The thin structure not only results in electrodes that are 30–75% thinner than those commercially available, but also offers an opportunity for custom-built air cathodes optimized for high-rate pulse applications. Using a thin composite structure for the air cathode in a zinc–air battery that is part of a zinc–air/ capacitor hybrid is likely to increase the pulse capability of the hybrid power system. The thin cathode structure provides a better, more efficient three-phase reaction zone. In a half-cell test, the ultrathin air cathode generated more than 1.0 V vs Zn/ZnO for a current of 200 mA cm$^{-2}$. Half-cell, full-cell and pulse-power tests revealed that thin composite cathodes have a better rate and pulse performance than the air cathodes commonly used.

## 1. Introduction

Metal–air batteries or fuel cells typically use carbon-based electrodes for electrochemical conversion [1–5]. In the most commonly used cathode designs, the oxygen electrode is based on a three-phase reaction zone. Because oxygen is poorly soluble at atmospheric pressure, a three-phase reaction zone is required to provide oxygen in concentrations suitable for higher current densities [6]. The cathode structure in zinc–air button cells usually includes a catalyst layer, metallic mesh screen, hydrophobic membrane and diffusion membrane, and air-distribution layer [7]. A new approach has been developed at Auburn University where fibrous metal–carbon composite electrodes and capacitors are fabricated using metal fibres, carbon fibres and/or powders, and cellulose fibers in a paper making process [8–13]. Kohler et al. [11] used stainless steel fibers and carbon fibre bundles to fabricate composite metal–carbon electrodes. The sintered composite electrode structure shows a surface area of about 760 m$^2$ g$^{-1}$ of carbon. Ahn et al. [2, 13] reported the fabrication of fibre composite structures and successfully utilized them for oxygen reduction in an alkaline electrolyte. Smith demonstrated that a composite oxygen electrode was used effectively for the electrochemical production of hydrogen peroxide [14]. Poole and his coworkers [9, 15] produced composite air electrodes by entrapping activated carbon fibers and/or powders

in a sinter-locked network of 2–8 $\mu$m diameter metal fibres.

For most gas-depolarized electrodes the PTFE content is no more than 30%, so that the active layer is only partly wetted by the electrolyte. The barrier layer is normally unsintered porous PTFE film. Zinc–air batteries were not commercially feasible until the development of Teflon, which allowed the oxygen electrode to operate efficiently. With Teflon, the oxygen electrode could be made thinner, which ultimately allowed the commercialization of the zinc–air button cells. The thin structural design has found applications in the hearing aid, pulse power, cell phone and fuel cell markets [16–18].

The microfibre-based composite oxygen electrode offers many advantages over current commercially available designs, making it possible to design three-dimensional structures for both the active layer and current collection. This paper describes a thin structural design for composite air cathodes. The fabrication process, microstructure, polarization curves in a half-cell and a pulse test in Zn–air cells are also discussed in detail.

## 2. Experimental details

### 2.1. *Fabrication of microfibrous nickel–carbon composite structures*

The general wet-lay procedure developed in this laboratory has been described in detail in previous publications

[8–12]. The present process combined cellulose, micrometre (dia.) sized metal fibres, and Black Pearl carbon particles (Cabot Corporation) in an aqueous slurry. Nickel fibres (Memtec America) were chopped to 2–3 mm in length and had diameters of 2, 4, and 8 $\mu$m. Cellulose fibres (Georgia Pacific) were 30–60 $\mu$m in width and had lengths between 100 and 1000 $\mu$m. The carbon fibres, nickel fibres, and cellulose fibres were stirred at 50 Hz in about 1 litre of water for 3 min. The dispersed fibre mixture with carbon particles was collected on a sheet mold to form the wet paper composite preform. The paper was then pressed at about 400 kN m$^{-2}$ and allowed to dry in air at a temperature of 45 °C. The SEM micrograph of a composite sheet (Figure 1(a)) shows an oxygen electrode composite preform containing cellulose, carbon particles and different diameter nickel fibres (2, 4 and 8 $\mu$m). The electrode preforms and/or nickel meshes were placed between metal screens held together either with a U-shaped quartz clip or nickel wires. A large quartz tube (70 mm dia. × 320 mm length) was used as a reactor for sintering. The atmosphere for sintering was controlled to be hydrogen at a flow rate of 10 cm$^3$ min$^{-1}$ with a total pressure of 101.3 kPa. SEM micrographs of sintered fibre substrates are shown in Figure 1(b,c). The small nickel fibres (2, 4 and 8 $\mu$m) shown in the structure are well sintered at their contact points to form an interlocking metal network. Along with a sintered expanded nickel foil on the electrolyte side for current collection, the overall thickness can range from 0.13 to 0.50 mm. The schematic drawing of the new structure design is shown in Figure 2. This paper-making technique offers an opportunity for the development of cathode layering structures.

### 2.2. Preparation of thin composite air cathodes

#### 2.2.1. Fabrication process of composite air cathodes

After sintering, manganese catalyst was impregnated into the activated carbon for the decomposition of peroxide. Manganese hydroxide was added into the pores of carbon particles to promote peroxide decom-
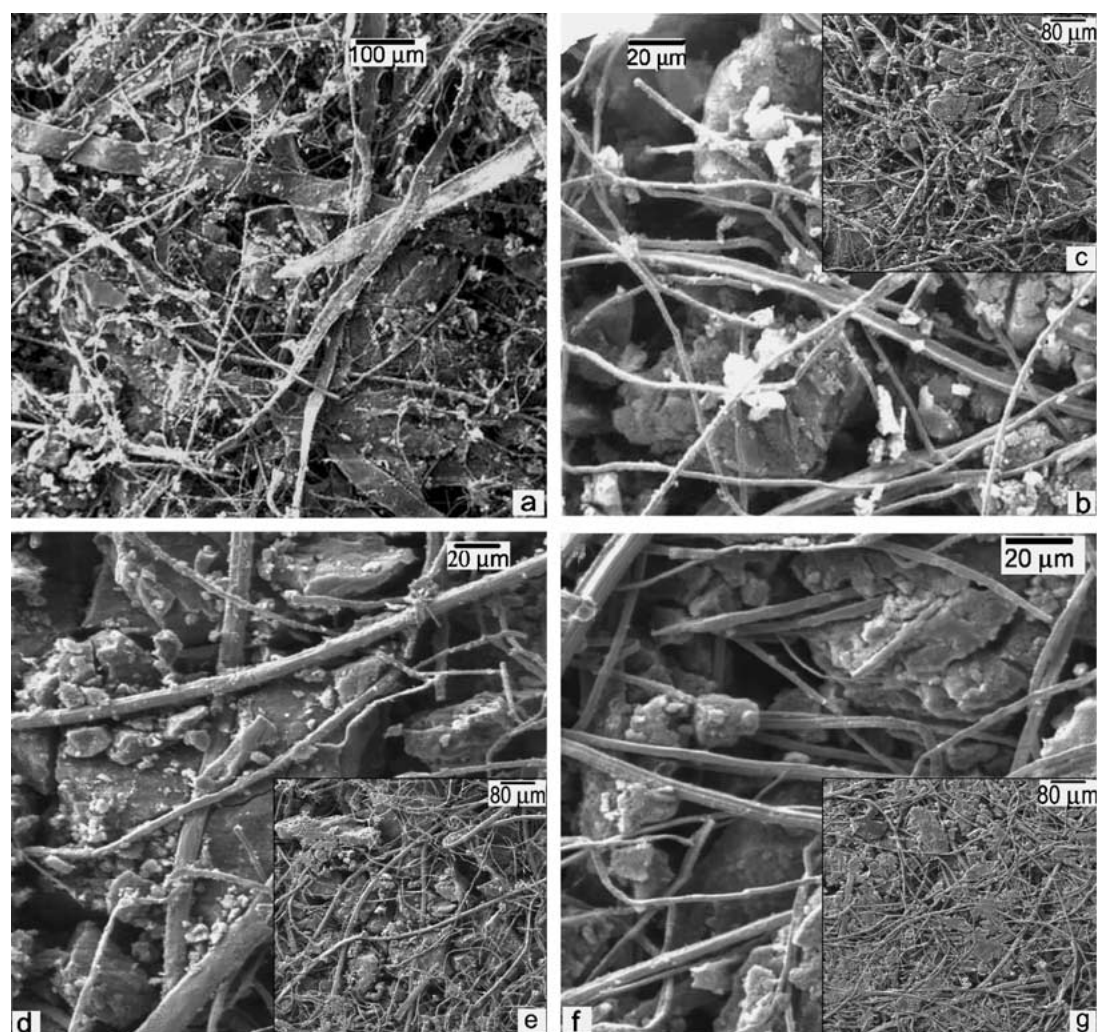


*Fig. 1.* SEM micrograph of microfibre-based composite structures with carbon particles and manganese catalysts. (a) Air cathode preform made from 2, 4 and 8 $\mu$m nickel fibres, carbon particles and cellulose fibres, (b, c) sintered composite substrate containing activated carbon particulate, (d, e) 2, 4 and 8 $\mu$m diameter mixed composite structure after loading of Mn(OH)$_2$, (f, g) Teflon-treated air cathodes (Mn/Teflon loaded).
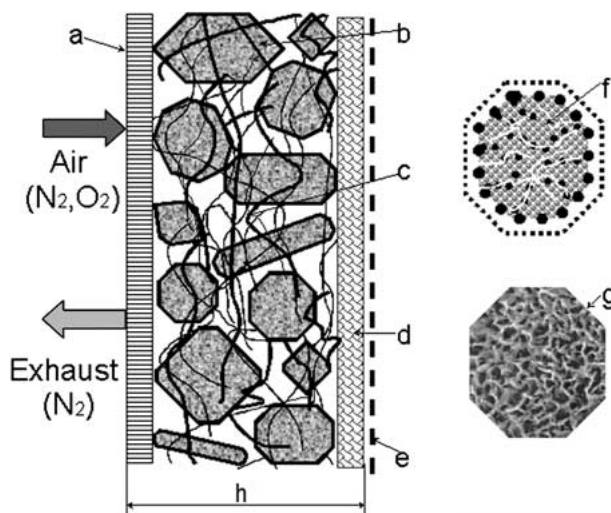
Fig. 2. Schematic drawing of a thin microfibre-based composite air cathode. (a) Gas side layer of pressed Teflon film, (b, c) catalytic layer (b active catalytic carbon particle, c mixed diameter microfibres), (d) current collecting layer (microfibrous substrate), (e) electrolyte, (f, g) carbon-particle catalytic unit encapsulated by porous Teflon film (f hydrophilic carbon particle, g porous hydrophobic PTFE film), and (h) total thickness of the composite air cathode.

position [19]. Sample dipping solutions were adjusted by using a solution of manganese nitrate and 30 wt% potassium hydroxide each for about 5 min. This step was repeated two to four times until the required loading level of manganese hydroxide was obtained [15].

The structure after manganese impregnation is depicted in Figure 1(d,e), which shows that catalyst loaded particles are supported on the fibrous network. The structure was then completely dried and dipped in 12 wt % dispersion of PTFE for 5 min at room temperature and dried at 110 °C for 1 h. The dip-coated electrode is shown in Figure 1(f,g). The electrode was then heated to 350 °C for 20 min to remove the surfactants. Finally, Teflon film was lightly pressed onto the gas side of the electrode to control weeping of electrolyte through the composite structure.

The composition of the thin air electrode originally consisted of 5.86 mg cm$^{-2}$ carbon black and 1.67 mg cm$^{-2}$ mixed diameter nickel fibres. A single layer preform was pressed onto Xmet and then sintered to form a thin composite structure. After proper catalyst and Teflon loading into the structure, the electrode was pressed at 15.17 MPa onto a porous Teflon film, with a nickel screen that supported the electrode structure

acting as a current collector. The finished air electrode was pressed to a design thickness between 0.13 and 0.33 mm. The electrode thickness was measured by a micrometer (Mitutoyo Electronic Micrometer, No. 293-721-30).

### 2.2.2. Manufacturing development of thin air cathodes

Samples, including one-foot square preforms, carrying carbon particles were sintered in a 40 foot belt furnace at the center for Microfibrous Materials Manufacturing in a hydrogen-reducing atmosphere at temperatures from 925 to 1125 °C for 30 min. Typical data for the air electrodes tested, which were each cut from a 60 mm × 100 mm sample, is shown in Table 1. If the nickel mesh was used, this added a weight of 11.0 mg cm$^{-2}$. The expanded nickel mesh is the heaviest component for current collection. Small diameter nickel fibres (2 or 4 $\mu$m) were used to replace the thicker 8 $\mu$m diameter fibres to fabricate thinner composite air cathodes.

Microfibrous composite cathodes were also prepared as one-foot square samples by using a sheet forming paper machine. The manganese loading level obtained from three repetitions of the dipping/soaking process was 2.4 mg cm$^{-2}$. After soaking in 12% PTFE dispersion for the first time, thin composite electrodes were dried at 85 °C overnight. Table 2 lists the loading level of PTFE particles and the scaled-up results for one-foot square air cathodes.

### 2.3. Electrochemical measurements in half-cells

Experiments were carried out in a plastic half-cell (Quickcell™, Electrosynthesis, Inc.) as shown in Figure 3. The active geometric area of the working electrodes was either 1.3 or 2.7 cm$^2$. Air at an overpressure of about 1.245 kPa was fed into the gas chamber behind the air cathode to be tested. A platinum disc was used as a counter electrode. An Hg/HgO electrode was used as a reference electrode. The electrolyte was usually either 26% or 35% KOH. Polarization curves were recorded galvanostatically using an EG&G model 273 potentiostat/galvanostat. A simple zinc reference electrode (Zn/ZnO) was also made to measure the potential of the air cathode. IR-compensation was done through the built-in current interrupt routine in the EG&G potentiostat. Half-cell galvanostat measurements were performed using the air cathodes that were constructed as described above. The data collected for potential versus current

Table 1. Typical parameters of a thin composite cathode in comparison with a commonly used air electrode*

| Cathodes for air (O$_2$) reduction | Thin composite cathode (0.15 mm thick) | | Paste composition for common air cathode [16] |
|---|---|---|---|
| Manganese catalyst | 0.43 mg cm$^{-2}$ Mn(OH)$_2$ | (6.4%) | 22% $\gamma$-MnO$_2$ |
| PTFE loading | 0.62 mg cm$^{-2}$ | (9.3%) | 26% Teflon particle |
| Ni fibre loading | 0.96 mg cm$^{-2}$ | (14.4%) | – |
| Carbon loading | 4.67 mg cm$^{-2}$ | (70.0%) | 52% carbon particle |

* No Teflon film is pressed on the cathode. The weight loading of 0.038 mm nickel mesh is 11.0 mg cm$^{-2}$ if present.

*Table 2.* One-foot square scaled-up samples of composite air cathodes and physical parameter comparison between thin composite cathodes and a commercial air cathode

| Electrode | $W_0$ | $W_{Mn}$ | $W_{PTFE}$ /mg cm$^{-2}$ | $W_{Film}$ | $W_{Finished}$ | Thickness /mm | Mesh | Layer |
|---|---|---|---|---|---|---|---|---|
| 1130-1 | 21.47 | 2.41 | 1.500 | – | failed | – | Delker expanded | 2 |
| 0131-1 | 19.66 | 1.74 | 0.905 | – | 26.65$^\dagger$ | 0.152* | Delker expanded | 2 |
| 0131-2 | 8.83 | 1.77 | 0.667 | 4.34 | 15.58 | 0.165 | – | 3 |
| 0205-3 | 21.44 | 2.41 | 1.164 | – | 29.35$^\dagger$ | 0.191*$^{,\ddagger}$ | Delker expanded | 2 |
| 0205-4 | 8.85 | 1.23 | 0.985 | – | 15.40$^\dagger$ | 0.152*$^{,\ddagger}$ | – | 2 |
| Commercial-C | – | – | – | – | 88.70 | 0.394 | woven | 3 |

* No Teflon film was pressed on the electrode.
$^\dagger$ Weight of the finished electrode was estimated based on weight of 4.34 mg cm$^{-2}$ Teflon film.
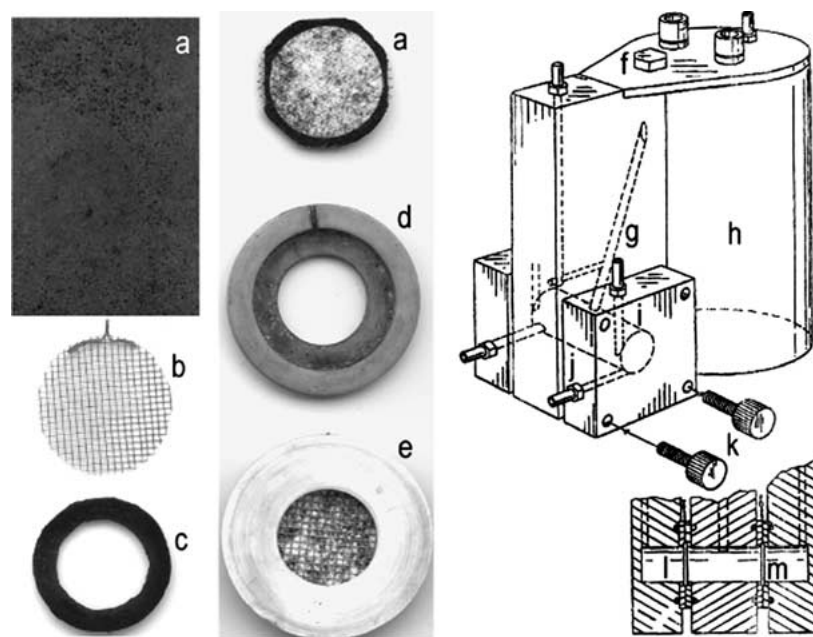$^\ddagger$ Finished electrode was not pressed.



*Fig. 3.* Composite air cathode and half-cell test apparatus of Quickcell™. (a) Two sides of microfibre-based composite cathodes, (b) nickel mesh current collector, (c) rubber cushion, (d, e) Teflon holder, (f) port for the reference electrode, (g) electrode gas-evolving outlet, (h) electrolyte reservoir, (i, j) inlet and outlet of gas reactant, (k) tightening screws, (l, m) composite working and platinum counter electrodes.

density were used to create polarization curves for the air electrodes.

### 2.4. *Pulse tests in zinc–air cells*

The zinc anodes were prepared from polymer gel, zinc powder, Teflon™ (polytetrafluoroethylene dispersion, a hydrophobic polymer resin, Dupont), and trace amounts of PbO. The amount of polymer gel was controlled at roughly 5 wt % [15]. The zinc paste also contained some zincate, which is the soluble form of zinc hydroxide. The amount of zinc in the battery determined its capacity. The theoretical capacity of the zinc electrode was 0.825 Ah g$^{-1}$ of zinc [4]. Zinc electrodes consisted of 81% zinc powder and 19% additives. The zinc–air cell was set up with a working area of 2.69 cm$^2$ (18.5 mm dia.). Pulse tests on the zinc–air cells and capacitor hybrids were conducted in the laboratory. An EG&G potentiostat/galvanostat (model 273) was set up

and connected to a computer by a GPIB-PCIIA card from National Instruments. A program was edited for the current pulse test. The voltage drop of either 10, 20, 40, or 60 mV was kept constant across the zinc–air cell. The pulse current across the cell was obtained both without and with a capacitor. The pulse time was 0.5 ms and the rest time was 3.5 ms during pulse tests. Data were collected at 50 $\mu$s intervals between two data samples.

### 3. Results and discussion

#### 3.1. *Composite air electrode and its ultrathin structure*

##### 3.1.1. *Structure of microfibre-supported composite cathodes*
A highly opened pore structure, a low amount of Teflon binding, and fibre strengthening leading to cathode flexibility and improved conductivity are the unique
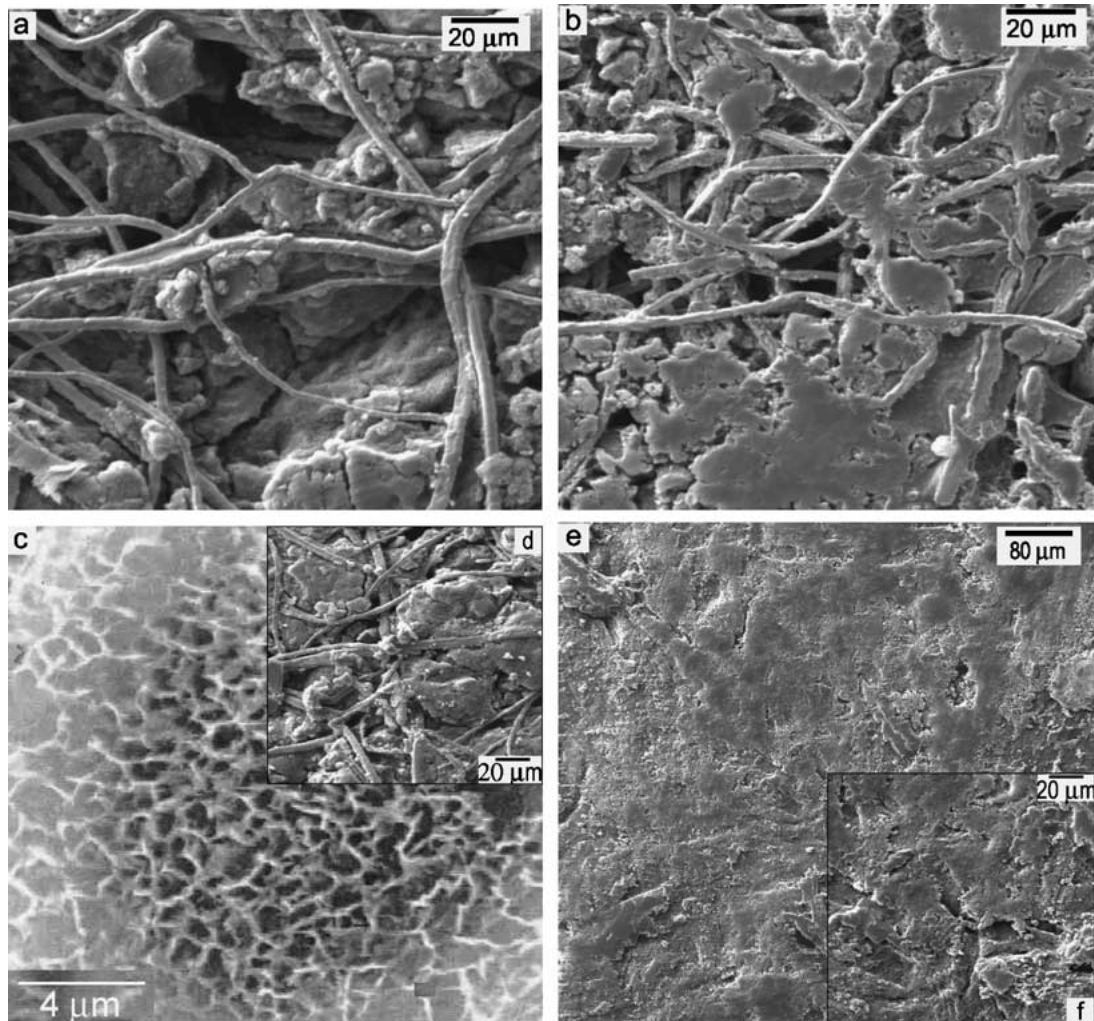
*Fig. 4.* SEM micrograph of the composite air cathodes and the Commercial-C air cathodes. (a) Finished composite air cathode (350 °C post-treated after Teflon dipping, (b) finished cathode composite structure with PTFE overloaded, (c) porous microstructure of Teflon film on the carbon surface, (d) tested thin composite cathode having a normal discharge potential, (e, f) a Commercial-C air cathode, where Figure 4(f) (conventional cathode structure) has the same scale as Figure 4(d) (microfibre-based composite structure).

features of composite cathode designs. Finished cathode structures are shown in Figure 4(a,b). Small amounts of Teflon coating produce a porous thin film on the composite particles. This increases the gas–liquid interfacial area and gives much more opportunity for oxygen dissolution and diffusion at the reaction zone. However, if PTFE is overloaded (Figure 4(b)), the cathode becomes hydrophobic, producing an electrode that is mass-transfer inhibited in the liquid phase. The electrolyte cannot permeate into the electrode, which is evident in its high overpotential.

### 3.1.2. *Microstructure comparison with commonly used air cathodes*

A schematic drawing of a thin air cathode is shown in Figure 2. Either the expanded nickel mesh or the microfibrous substrate can serve as the current collector while increasing the electrode strength. Typically, a thin air cathode design uses a three-layer structure consisting of an active reduction layer, a current collecting layer, and a PTFE film layer. In a common cathode design, Teflon particles bind the carbon particles and also allow diffusion of oxygen into the cathode. The carbon particles provide a conductive path for electrons. This type of cathode is based on a three-phase reaction zone. In this zone, oxygen is reduced on the surface of the activated carbon and the electrolyte contains $OH^-$ ions and water. However, for the composite cathode, a Teflon porous film was coated on the carbon surface as shown in Figure 4(c). The micropore structure is clearly shown on the surface of the composite cathode and the measured pore diameter is between 0.35 and 0.71 $\mu$m. The finished composite cathodes, which were approximately 0.15 mm thick (Figure 4(d)), were tested and had a normal discharge potential with acceptable performance. The Commercial-C air cathode in Figure 4(e,f) is commonly shown as a paste-pressing dense structure. In comparison with the Commercial-C air cathode (Figure 4(f)) at the same scale, the composite cathode (Figure 4(d)) provides opportunities for better electron transfer across the metal network, lower mass transfer resistance in the liquid phase, and more gas diffusion passages in its open-pored

structure. Due to its ultrathin feature, product removal or diffusion out of the composite pores is much easier than for the commonly used dense structure. The microfibrous metal network has a larger surface area that contributes when collecting current. The composite cathode (0.15 mm, 16.8 mg cm$^{-2}$) has a fivefold weight reduction due to being 2.5 times thinner than the thick Commercial-C electrode (0.40 mm, 88.7 mg cm$^{-2}$). The thin structure design gives the cathode advantages due to its light weight and reduced volume.

The physical parameter comparison of two types of electrodes is shown in Table 1. The thin composite structure has a lower loading level for both Teflon and catalysts. More carbon and less Teflon particles increase the electronic conductivity and improve the mass transfer performance in the liquid phase. This feature of the lightweight composite cathode makes it possible to minimize the amount of expensive catalysts required in high power applications. Current theory for the composite air cathode suggests that an improved three-phase reaction zone exists around the carbon particle unit, where the ultrathin electrolyte film wraps around the activated sites but is in turn surrounded by a porous layer of Teflon film. The cathode, which has a highly opened microporous structure, potentially provides an opportunity for the development of a high performance gas diffusion electrode that can operate at a much higher current density.

### 3.1.3. Cathode thickness and layering structures

The air electrode usually uses a gas supply layer and is laminated together with a nickel mesh current collector at the gas side [20]. For a thin cathode such as these used in fuel cells, it has a thickness of about 0.25 mm but its structure is based on an expensive thin-film catalyst layer (for example, platinum ink print or paint, less than 0.10 mm) coated on a porous graphite paper (~0.18 mm, Toray, TGP-006) [21] or directly on the Nafion™ membrane. The conventional cathode for zinc–air cells can be as thick as 0.40 to 0.50 mm. The composite structure can be made with a thickness of 0.15 to 0.33 mm, and commonly uses a much cheaper manganese catalyst in air cathodes for Zn–air cells.

The layering structures for several different types of air cathodes are shown in Figure 5. Using gradient hydrophobicity in the different layers, the composite structure can control the depth of electrolyte permeation. The approach used for the fabrication of carbon-based electrodes is unique and allows for maximum flexibility of the structure. A single composite active layer may serve directly as an air cathode if an outside conductive mesh or gas distribution bipolar plate is used to collect current (e.g. the electrode in the fuel cells).

### 3.2. Polarization performance in half-cell tests

Without PTFE dipping, even if the electrode was loaded with catalyst and pressed with a Teflon film, the cathode had poor oxygen-reduction ability. Once Teflon was
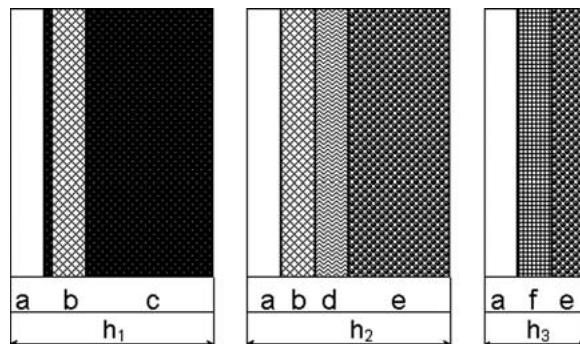
*Fig.* 5. Layering configurations of different air cathodes. $h_1$ commonly used commercial cathode, 0.40 mm; $h_2$ thick composite electrode structure, 0.25–0.50 mm; $h_3$ layering design of thin composite air cathode, 0.15 mm. (a) hydrophobic Teflon film, (b) expanded nickel mesh, (c) paste-pressing active catalytic layer, (d) inert connecting layer, (e) microfibre-based composite active layer, and (f) small diameter nickel-fibre substrate.

loaded, the curves went up due to an improvement of mass transfer in the gas phase and the resulting decrease in the electrode polarization. Manganese and cobalt catalysts greatly increase the electrode ability for oxygen reduction (Figure 6, where 1Mn10 means that the electrode was dipped once in 10 wt % Mn(NO$_3$)$_2$) and PTFE coating is the most important step that contributes to the electrode performance. After loading the manganese or cobalt catalyst and dipping in the Teflon solution, the cathodes obtained the best performance in comparison with the electrodes with either Teflon or catalyst loaded. This demonstrates that PTFE has much more influence than the catalyst on the overall reduction process of the oxygen electrode. Therefore, a composite cathode with carefully selected hydrophobicity and hydrophilicity provides a large interfacial area for oxygen diffusion and dissolution in the electrolyte films. Oxygen transfer into the cathode microstructure is necessary for gas dissolution or absorption for further reduction at the moistened active sites on the solid surface. In the half-cell test shown in Figure 7, the thin cathodes have a better performance than the Commer-
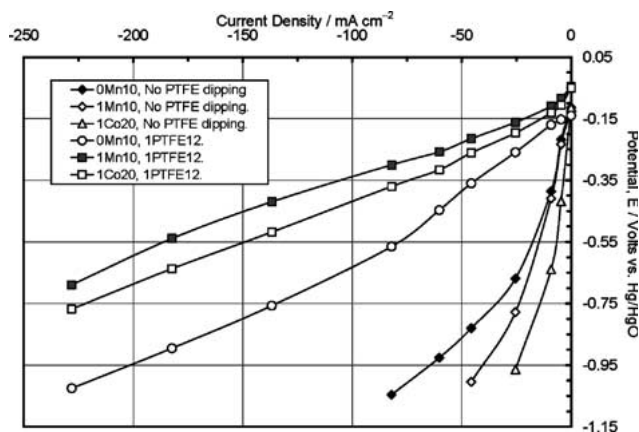
*Fig.* 6. Polarization curves of various thin composite cathodes for air reduction (35% KOH, 1.245 kPa of air over pressure, 23 °C).
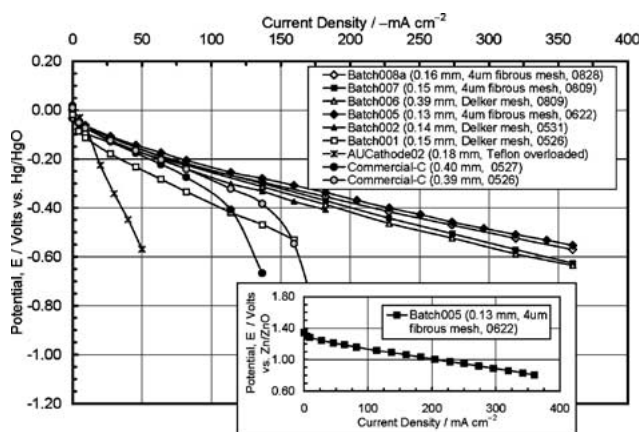
Fig. 7. Polarization curves of composite air cathodes in comparison with the Commercial-C air cathode (26% KOH, 1.245 kPa of air overpressure, 23 °C).



Fig. 8. Zinc–air cell performance at different discharge current densities in comparison with the Commercial-C air cathode.

cial-C air cathode, especially at higher current densities (>50 mA cm$^{-2}$). The thin electrode (0.13 mm) operating at 200 mA cm$^{-2}$ maintains a potential of about 1.0 V vs Zn/ZnO. The potential of the commercial electrodes drops dramatically at current densities between 100 and 200 mA cm$^{-2}$. This result indicates that commercial air cathodes still have a great deal of scope for further improvement, especially for higher rate applications.

### 3.3. Pulse testing in the Zn–air cells

Using a nickel electrode, the zinc electrode was charged to 60 mAh. The composite air cathode and the charged zinc electrode were used to evaluate the Zn–air cell performance. The ZincAir01 cell was made with a 0.13 mm thin air cathode, the cathode in the ZincAir01a cell was a 0.40 mm thick Commercial-C electrode, and the ZincAir02 cell was assembled with a 0.33 mm composite electrode, but its zinc anode was also treated with a PTFE dispersion and a polymer gel binder. The test results on rate performance are shown in Figure 8. The thin cathode had a better performance at a higher current density than the Commercial-C electrode. The thinner design is also most attractive for smaller button cell batteries, where even a small reduction in cathode thickness represents a large percent age of the total battery.

Tests on zinc–air cells and capacitor hybrids were performed for a series of four pulses, as shown in Figures 9 and 10. The air cathodes made by the composite technique were tested for thickness of 0.14 and 0.33 mm. When a 10 mV pulse voltage drop was applied, the 0.33 mm thick electrode experienced a lower current pulse drop due to its higher loading of catalyst and greater number of active sites for oxygen reduction. The pulse current was higher than for the Commercial-C electrodes (Figure 9). For the higher 60 mV pulse voltage drop, the 0.33 mm thick electrode showed the highest pulse current. The pulse drop was
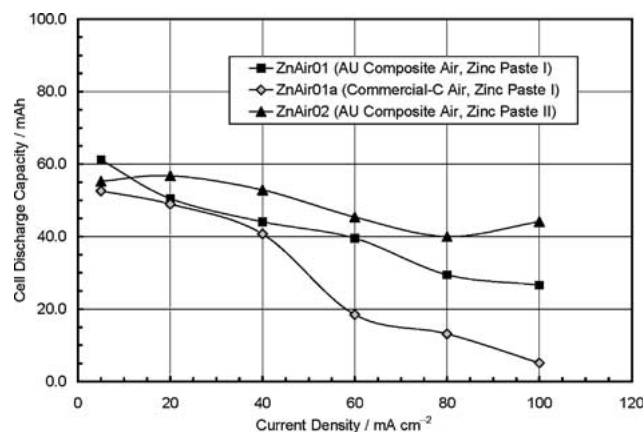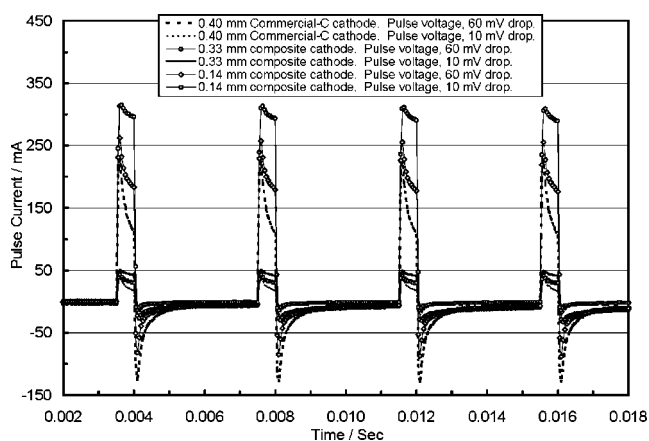


Fig. 9. Pulse curves of the composite air cathodes in comparison with the Commercial-C air cathode in zinc–air cells. Pulse voltage, 10 and 60 mV drops.

only 20 mA compared to the 150 mA drop of the commercial-C cathode. When a 10 F capacitor was added to the circuit, the experimental data (data not shown) demonstrated that the 0.33 mm composite cathode outputted 700 mA pulse current, but the commercial-C electrode only produced a 580 mA pulse current. The thin cathode (0.14 mm) provides a higher pulse current and also has a better flat pulse curve in comparison with the commercial-C electrode.

The difference for a higher pulse current (60 mV pulse voltage drop) was that the ultrathin cathode had a 200 mA minimum pulse current and the commercial-C cathode had only about a 100 mA minimum pulse current. After a 10 F capacitor was added in the thin cathode circuit, as shown in Figure 10, the pulse current increased from about 210 to 550 mA. This demonstrates that the thin cathode of 0.14 mm thick has a better current pulse curve; that is, 50% less pulse current drop than the 0.40 mm thick Commercial-C electrode. As a whole, the wet-lay process is a vast improvement over the slurry-pasting manufacturing process,
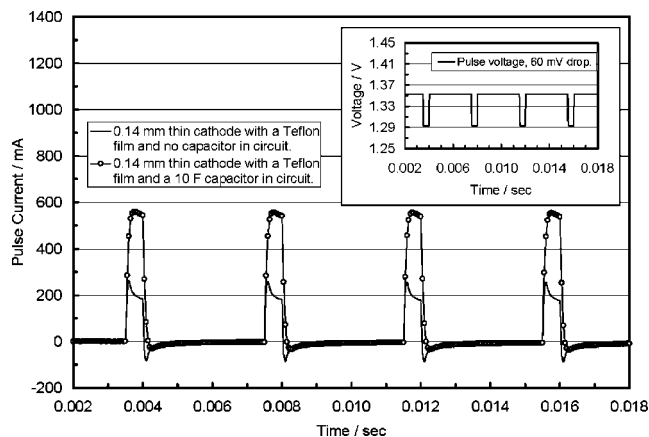
*Fig. 10.* Voltage pulse across the zinc–air cell and current pulse curves of the thin composite cathode in zinc–air cells. Pulse voltage, 60 mV drop.

providing both better electrode performance and pulse capability.

## 4. Conclusion

For the thin composite cathode, conductivity inside the electrode is no longer dependent on low porosity to provide carbon particle contacts as for commonly used cathodes. This new approach to electrode construction offers the opportunity to fabricate thin, high-performance composite cathodes. The thin electrode design, from 0.13 to 0.33 mm, not only offers electrodes that are 30–75% thinner than those commercially available, but also offers an opportunity for custom-built air cathodes optimized for high-rate pulse applications. The test results demonstrate that the thin composite cathodes have a better performance than the existing Commercial-C electrodes. The thin composite cathode has the unique features of a highly open porous structure and highly efficient catalysed units supported within the microfibrous network. Using thin air cathodes in zinc–air batteries as part of a zinc–air/ultracapacitor hybrid improves the pulse capability of the hybrid power system. The thin composite structure improves the cathode pulse performance compared to the cathodes currently used cathodes and will find numerous applications in a variety of electronic devices that require a high pulse power supply.

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