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A secondary, coplanar design Ni/MCM-41/Zn microbattery

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Abstract. A secondary Ni/Zn microbattery (~200 µm thick) has been developed in a coplanar electrode configuration. The cell is essentially of a circular shape (~30 mm in diameter) consisting of a fine circular ring (cathode) and a circle (anode) split apart (~800 µm). Unlike the stacking cell architecture, coplanar configuration offers simple design, ease of fabrication and eventually cost saving. The use of MCM-41 mesoporous silica as the membrane separator cum electrolyte reservoir enables the successful implementation of coplanar configuration. The fabrication of Ni/Zn microbattery first begins with electrodeposition of zinc (Zn) and nickel hydroxide (Ni(OH)$_2$) thin films onto patterned FR4 printed circuit board, followed by deposition of zinc oxide (ZnO) slurry onto the zinc active layer, and finally ends by multiple drop-coating procedures of MCM-41 from its precursor solution at ambient temperature. Once a potassium hydroxide (6 M KOH)/MCM-41 electrolyte-separator mixture is incorporated, the cell is sealed with an acrylic sheet and epoxy adhesive. The fabricated microbatteries were capable to sustain around 130 deep charge-discharge cycles. When rated at 0.1 mA, the energy density of the microbattery was around 3.82 Wh l$^{-1}$ which is suitable for low rate applications and storage for micro energy harvesters such as piezoelectric generators.

1. Introduction
MCM-41 material stands out due to its highly unusual pore texture resulting from long-range ordering, extremely high surface areas in the order of 1000 m$^2$ g$^{-1}$ and very large pore volume i.e. 1 cm$^3$ g$^{-1}$ [1-4]. The mesoporous material also possesses the properties of adjustable hydrophobicity and very good thermal stability [5]. The MCM-41 structure on the nanometer scale is reported as a hexagonal stacking of porous tubes of uniform diameter. Its pore diameters have sizes from about 1.5 to 10 nm [4, 6, 7].

The zinc-air cells fabricated by Saputra et al. [8] employed MCM-41 silica membrane as separator-cum-electrolyte reservoir; the membrane was dip-coated on a Zn foil or Zn electrodeposits. The cells possessed a maximum power density of 32 mW cm$^{-2}$ and an energy density of 360 Wh l$^{-1}$. The transformation of MCM-41 silica into gel-like MCM-50 after 24 hours in controlled exposure of 6-M KOH solution was reported in [9]. Soon after, Mohd Zawi et al. [10] employed the MCM-41 silica membrane as separator in Zn/MnO$_2$ Leclanché button cells. The cells were able to produce a maximum power of 0.7 mW and 1.3 mW for monopolar and bipolar configurations, respectively, rated at current densities of 0.44 and 0.76 mA cm$^{-2}$. However, the cells were quite thick i.e. ~2 mm. The viability of MCM-41 incorporated in the primary cells drive us to test the material in the Ni/Zn secondary battery system which is more challenging due to concerns of a pressure build-up from gas evolution and dendritic growth of Zn.
Humble et al. [11] fabricated Ni/Zn microbatteries for use in autonomous microsystem applications, employing a side-by-side electrode design. The cell had a footprint area of 0.02 cm$^2$ and could produce power in the range of 1 – 2 mW. The cell had a capacity of 0.389 mAh cm$^{-2}$ at a current density of 2.5 mA cm$^{-2}$, which corresponds to 55 Wh l$^{-1}$ of specific energy. Although the performance was remarkable, the cell runtime was only around 11 minutes, i.e. the cell was discharged with only 10% of depth of discharge (DOD). A Ni/Zn microbattery fabricated with a three dimensional (3D) architecture was reported by Chamran and co-workers [12]. The microbattery consisted of interdigitated electrode post arrays with a footprint area of 0.25 cm$^2$. Despite its high surface area, the cell could only sustain 6 cycles of charge and discharge due to the severe etching of the Zn electrode by the KOH. The microbattery was charged and discharged at 10 µA and the capacity on the sixth cycle was 0.0025 mAh cm$^{-2}$.

The commonly used microbattery substrates includes epoxy-coated silicon [11], polycrystalline alumina [13], silica (on silicon) [14] and glass [12, 15], while the current collectors used were usually electron-beam evaporated [11] or electroplated [12] zinc and nickel metals, or pyrolyzed carbon [14]. However, some of these processes prevent mass production of microbattery fabrication and involve applications at high temperatures, which thus increase fabrication cost.

In this paper, a relatively simple microbattery fabrication route comprising photolithography, electrodeposition and drop-coating is presented, using copper (Cu) printed circuit board (PCB) (an easily obtained material) as current collector cum microbattery substrate. The microbattery had a coplanar (side-by-side) electrode configuration which further simplified the fabrication steps. The secondary Ni/MCM-41/Zn electrochemical system has been selected for the test. MCM-41 serves as the membrane separator cum KOH electrolyte reservoir.

2. Experimental Procedures

**Microbattery Fabrication.**

![Figure 1 Schematic diagram of microbattery design.](image)

The cell’s current collector was patterned on a FR4 PCB substrate by photolithography processes (Figure 1). Next, Zn and Ni(OH)$_2$ thin films were electrodeposited successively to form the anode and cathode, respectively. The electrodeposited Zn was later coated with zinc oxide (ZnO) slurry (~50 µm). Once dried, the entire area of cell including the anode-cathode interface area was coated with MCM-41 thin film by successive drop-coating procedures (a total of 6 layers) of the precursor solution, intercepted by drying in ambient conditions. The KOH electrolyte was applied in the form of a KOH/MCM-41 solution/powder mixture (weight ratio of 70:30). Finally, the microbattery was capped using a Perspex® sheet and thereafter sealed with an epoxy adhesive; the depth of well of the cap was 200 µm.
Synthesis of MCM-41 Silica Thin Film and Powder. Two forms of MCM-41 were used in the microbattery fabrication, i.e. thin film and powder. Sol-gel method was employed for the synthesis. The MCM-41 thin film was formed from the precursor solution. In a typical synthesis, the precursor solution was prepared by mixing a quaternary ammonium surfactant, cetyltrimethylammonium bromide (CTAB, CH₃(CH₂)₃N(Br)(CH₃)₃; Merck, Germany) as an organic template, hydrochloric acid (HCl; J.T. Baker, Thailand), ethanol (C₂H₅OH, Systerm) as a solvent, distilled water (H₂O) and tetraethyl orthosilicate (TEOS, Si(OCH₃)₄; Merck, Germany) as a silica source, with a molar ratio of 0.05 CTAB: 1.0 TEOS: 0.5 HCl: 25 C₂H₅OH: 75 H₂O and stirring at 200 rpm, at a room temperature of 30 °C for about one hour [8]. On the other hand, MCM-41 powder was synthesized by mixing CTAB, sodium hydroxide (NaOH, Sigma-Aldrich, Sweden), distilled water and TEOS, with a molar ratio of 0.05 CTAB: 1.0 TEOS: 0.5 NaOH: 100 H₂O, and stirring at 200 rpm, heating the mixture on a hotplate at around 50 °C for 15 hours. The white precipitate of the MCM-41 powder was separated by filtration, rinsed with distilled water and dried at 100 °C.

Electrodeposition of Zn and Ni(OH)₂ Thin Films. Zn electrodeposits were prepared by cathodic reduction of an electrolytic bath comprising of 2 M zinc chloride (ZnCl₂) (50 vol. %) and 3 M ammonium chloride (NH₄Cl) (50 vol. %) galvanostatically (12.43 mA/cm²) for 60 minutes, at room temperature.

Ni(OH)₂ electrodeposits were prepared from an electrolytic bath of 1.8 M nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) (49.4 vol. %), 0.075 M sodium nitrate (NaNO₃) (16.6 vol. %) and absolute ethanol (34 vol. %), reduced cathodically (4.40 mA/cm²) for 180 minutes at room temperature.

The electrodepositions were performed using an Autolab PGSTAT302N (Eco Chemie B.V., Netherlands) potentiostat/galvanostat and the working electrode-counter electrode separation distance was fixed at 2.45 cm.

Cell Testing. Galvanostatic charge-discharge cycling test was performed on the assembled microbattery cells using a Neware battery testing system, model BTS-5V100mA (NEWARE Technology Ltd., China) at a room temperature of 30 °C to determine the performance of the secondary Ni/Zn microbattery. The cells were charged at 1.0 mA for 2 hours, left at open circuit potential for 5 minutes before being discharged at 0.1, 0.2 and 0.3 mA, respectively, until the potential reached 0.49 V. The steps were repeated for as many cycles until the cell failed.

3. Results and Discussion

Cell Dimensions. Based on the FE-SEM cross sectional observations (not shown here), the apparent thickness (excluding the cap and substrate) of the coplanar-designed microbattery was ca. 195 μm, i.e. comprising the Cu layer (30 μm), Zn electrodeposits (65 μm) and ZnO layer (~50 μm) and KOH/MCM-41 layer (~50 μm); the thickness of Ni(OH)₂ electrodeposits (27 μm) is not included since the anode was much thicker than the cathode and the electrodes were arranged side-by-side. The footprint area of the microbattery was 6.41 cm² and thus its effective volume was 0.128 cm³.

Electrochemical Performance of the Microbatteries. The discharge capacity and efficiency profiles of the microbattery discharged at 0.1 mA (denoted as MB-0.1) are shown in Figure 2; the profiles correspond to the 1st cycle until the 134th cycle (complete failure) of the charge-discharge cycling. The first 16 cycles show that the capacity increases by 11.8 times the capacity of the 1st cycle. The increase in capacity for the first few cycles was related to the gradual transformation of Ni(OH)₂ to nickel oxyhydroxide (NiOOH) [12]; the 17th cycle could be the point in which the cell was fully charged. The capacities for cycles 17th to 43rd fluctuate considerably from 8.93 to 15.83 mAh g⁻¹. The trend for cycles 44th to 59th is stabilizing, showing good point-to-point continuity, with an average capacity of 14.82 mAh g⁻¹; this corresponds to a value of 0.07 mAh cm⁻², i.e. when normalized by the total area of the microbattery including the anode-cathode separation
area. Cycles from the 76th to the 80th show a descending trend before the capacity continues to fluctuate in the remaining cycles.

Figure 2 Discharge capacity and efficiency profiles of the microbattery discharge at 0.1 mA as a function of cycle number.

Figure 3 shows some of the discharge curves of MB-0.1; the number accompanying each curve denotes the corresponding cycle number. In the beginning the discharge curve shows the typical Ni-based battery discharge curves featuring distinct plateaus and slopes (refer to cycle number 8, 13, 17, 25 and 32). Then, the sagging of the plateaus took place i.e. the plateau diminishes and is substituted with a slope (refer to cycle number 53 and 66), implying the onset of polarization. It could be due to the resistance or concentration polarization as the electrolyte was in the “semi-dry” or gel form. As the ion mobility are greatly reduced when the electrolyte is gelled, the cell becomes sensitive to water loss resulting from electrolysis and heat generated during repeated charge cycles. Discharge curves from the 66th cycle onwards evolve substantially as “bulges” and grow in size successively before the cell failed completely. The cell energy and power output varies from 0.388 – 0.577 mWh and 0.091 – 0.129 mW, respectively.

Figure 3 Discharge curves of the microbattery discharged at 0.1 mA for the selected cycle numbers.
The discharge capacity and efficiency profiles of the microbattery discharged at 0.2 mA (MB-0.2), as a function of cycle number are shown in Figure 4. The profile of MB-0.2 is better than MB-0.1 since it has more cycles with increasing capacity trend (in the early stage), i.e. 26 cycles as compared to only 17 cycles for MB-0.1, and the capacity of MB-0.2 does not fluctuate as much as that of MB-0.1. However, the increase in capacity up to the 16\textsuperscript{th} cycle is only 4.4 times the capacity of the 1\textsuperscript{st} cycle while for MB-0.1 the increment after 16 cycles is 11.8 times the capacity of the 1\textsuperscript{st} cycle. The capacities of MB-0.2 between the 27\textsuperscript{th} to the 49\textsuperscript{th} cycles fluctuate between 11.07 to 14.00 mAh g\textsuperscript{-1} and later stabilizes with a mean value of 10.91 mAh g\textsuperscript{-1} (53\textsuperscript{rd}-68\textsuperscript{th} cycle). From then onwards, the cell capacity starts to decrease (cycle number 76 to 91), fluctuates considerably starting from the 112\textsuperscript{th} cycle until the failure cycle (138\textsuperscript{th}).

Figure 4 Discharge capacity and efficiency profiles of the microbattery discharge at 0.2 mA as a function of cycle number.

Figure 5 shows some of the discharge curves of MB-0.2 with similar features of MB-0.1 as described above. Overall, however, MB-0.2 possesses higher power output i.e. 0.157 – 0.252 mW, but lower energy output i.e. 0.284 – 0.389 mWh. The average capacity for cycles from the 53\textsuperscript{rd} to the 86\textsuperscript{th} is 11.3 mAh g\textsuperscript{-1} or 0.05 mAh cm\textsuperscript{-2}.
Figure 5 Discharge curves of the microbattery discharged at 0.2 mA for the selected cycle numbers.

When the discharge current was increased to 0.3 mA (MB-0.3), the cell could only sustained 11 cycles of charge-discharge cycling before failed completely (Figure 6). The discharge curves of figure 6 clearly illustrate the onset of polarization from the early cycles indicating 0.3 mA is the limiting discharge load of the cell.

![Discharge curves of the microbattery discharged at 0.3 mA for the selected cycle numbers.](image)

Figure 6 Discharge curves of the microbattery discharged at 0.3 mA for all cycle numbers.

The use of MCM-41 membrane separator enables the successful implementation of co-planar configuration Ni/Zn microbattery. The membrane could be prepared sufficiently thin simply by employing drop-coating procedures which make it compatible with existing microfabrication processes. Unlike polymeric membrane separator that requires additional layer as electrolyte reservoir, MCM-41 material essentially serves as a cell separator, ionic exchange membrane and electrolyte reservoir. Its transformation into lamellar MCM-50 gel has probably limited the cell’s high discharge rate capability. Although the Ni/Zn microbattery could sustain more than 100 deep charge-discharge cycles, the discharge load could not exceed 0.3 mA. As such the microbattery of the present co-planar configuration is suitable for low discharge rate applications. Among the potential applications are as a power source for remote sensing devices and power storage for piezoelectric energy harvesters.

One cell design aspect to be implemented is to coat the bare copper substrate with an inert, conducting material such as carbon. This is due to the poor electrochemical stability of copper in the highly-concentrated KOH electrolyte [16, 17]. In fact, XRD measurements on dismantled cells show the evidence of dissolved copper and cupric oxide (CuO) (results are not presented here) due to the caustic alkaline surround.

4. Conclusions
A secondary Ni/Zn microbattery of co-planar design has been fabricated onto a FR4 printed circuit board. The use of inorganic MCM-41 membrane separator permits the cell to be designed sufficiently thin (ca. 200 µm). The preparation processes adopted for the cell fabrication are compatible with existing manufacturing processes involving printed circuit board, thus potentially cost saving. The microbattery demonstrated an acceptable cycling stability performance (> 130 cycles) and was tested under a high depth of discharge and long cycling period (exceeded one month).

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