



Preparation and Electrochemical Performance of 1.5 V and 3.0 V-Class Primary Film Batteries for Radio Frequency Identification (RFID)

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ABSTRACT :

1.5 V and 3.0 V-class film-type primary batteries were designed for radio frequency identification (RFID) tag. Efficient fabrication processes such as screen-printings of conducting layer (25 μm), active material layer (40 μm for anode and 80 μm for cathode), and electrolyte/separator/electrolyte layer (100 μm), were adopted to give better performances of the 1.5 V-class film-type Leclanché primary battery for battery-assisted passive (BAP) RFID tag. Lithium (Li) metal is used as an anode material in a 3.0 V-class film-type $\text{MnO}_2\|\text{Li}$ primary battery to increase the operating voltage and discharge capacity for application to active sensor tags of a radio frequency identification system. The fabricated 3.0 V-class film-type Li primary battery passes several safety tests and achieves a discharge capacity of more than 9 mAh cm^{-2} .

Keywords : 1.5 V batteries for battery-assisted passive RFID tag; 3.0 V-class batteries for active sensor RFID tag; Primary film batteries; Screen-printing process; Discharge capacity.

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1. Introduction

Recent progress of radio frequency identification (RFID)/sensor node (SN) technology, which can be envisioned that the world will be covered by ubiquitous sensor networks (USN),¹⁾ greatly requires a thin and flexible power source. Whatever the power source has any type of primary or rechargeable battery, it should be eco- and human-friendly, which is adequate for clean ubiquitous lifestyle. For BAP tags of RFID system, for instance, the thin, flexible, environmentally benign power source will be much better if it would be very cheap because the BAP tags may be used with great amount in the administrative control of physical distribution or large-scale logistics. PowerPaper^{®2)} is an example for the purpose, which is a printed primary battery consisting of Zn// MnO_2 electrodes, an aqueous

electrolyte solution,³⁾ and a self-forming separator.⁴⁾

The printed Leclanché battery usually uses poly(ethylene terephthalate) (PET) as a substrate and packaging film. This is because PET has excellent mechanical strength for roll-to-roll process and good coating property due to hydrophilic functional groups like carbonyl-, ester-, and ether group on the film surface. Even though such an excellent property, it has been identified that PET's O_2 and H_2O permeability sharply increases through the film when its surfaces are directly contacted with aqueous electrolytes,⁵⁾ which leads to electrolyte drying and self reaction by oxygen within the cell. This is because the PET does not have selective permeability and barrier property to moisture and gaseous components and the PET film based primary battery does not meet good shelf life of more than two years.⁶⁾ Such reactions of hydrogen formation and polarization surely lead to the reduction of electromotive force between electrodes.

In this paper, a multi-layered design of packaging film defending the moisture evaporation, as well as shielding selectively other gaseous components, is introduced to

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improve the battery durability (or shelf life) and eventually the safety. We also designed aqueous gel electrolytes having neutral pH zone by introducing a gelling and counteracting agent. In addition, it should be noteworthy that a screen printing technique is also employed to achieve an efficient battery-making process, e.g., when coating directly conducting layer (plays as a current collector) and active material layer in sequence on the packaging film substrate.

In contrast to 1.5 V-class film-type primary batteries discussed in a previous part, a Li anode is a very promising means of enlarging the discharge capacity due to its inherent electrical capacity; note that the theoretical capacity of Li metal is about 3860 mAh g^{-1} . For this study, a thin Li metal layer ($20 \mu\text{m}$ thickness) on a copper foil current-collector is designed for use as the anode of a film-type primary battery. The nominal voltage and discharge capacity per active area are expected to be 3.0 V and greater than 3.0 mAh cm^{-2} , respectively. The use of Li metal as an anode, however, may involve safety problems such as smoke, fire, and explosion, due to the chemical instability of Li in a moist environment. For safety reason, therefore, a new multi-layered aluminum pouch is used as a package film for perfect shielding from moisture or gaseous components in air. To ensure long-term stability, a pre-plasticized polymer electrolyte film is combined with a nonaqueous electrolyte solution. Note that the factors described above influence the safety and performance of 3.0 V-class film-type Li primary batteries.

2. Experimental procedure

2.1. Preparation of 1.5 V film-type Leclanché primary battery

Multi-layered polymer films of less than $85 \mu\text{m}$ thickness were first designed to optimize the permeability by considering some physical data of individual polymers.⁷⁾ Low density polyethylene (LDPE), oriented polypropylene (OPP), Nylon 6, and PET film were combined to produce multi-layered packaging film, LDPE/Nylon 6/PET/OPP. In order to optimize the aqueous gel electrolytes, ionic conductivities for various electrolytes with different pH's and different concentrations were evaluated from the impedance spectra, which were already obtained using a frequency response analyzer (Solartron HF 1225). Zinc powder (average diameter $< 70 \mu\text{m}$) used as anode active material was supplied from Umicore Shanghai Co. Electrolytic manganese dioxide powder (EMD, average diameter $< 30 \mu\text{m}$) as cathode active material was from Mitsui

Mining & Smelting Co. Cell fabrication was started by screen-printing a conductive paste on the inner surface of the multi-layered film LDPE/Nylon 6/PET/OPP. The surface resistance was measured using a four-point probe method to determine the optimum thickness of the conducting layer. Two types of Leclanché primary battery in nominal sizes ($55 \text{ mm} \times 55 \text{ mm}$ for Type A, $33 \text{ mm} \times 28 \text{ mm}$ for Type B) were then fabricated by screen printing the cathode and anode slurries separately on the conducting layer with pre-sized masks. The cathode slurry consisted of EMD (90 wt.%) as an active material, carbon black (5 wt.%) as a conductive agent, 40 wt.% aqueous emulsion of styrene-butadiene rubber (2.5 wt.%) as a binder, and 2 wt.% viscous aqueous solution of carboxyl methylcellulose (2.5 wt.%) as a thickener. The anode slurry consisted of same materials and compositions to cathode slurry, except for Zn (90 wt.%) as an active material. Active material layer printed on the conducting layer has the thickness of $80 \mu\text{m}$ in cathode and $40 \mu\text{m}$ in anode. An adhesive electrolyte gel was then screen-printed separately on the cathode and anode layers. The film-type primary battery was finally fabricated by inserting a cellulose separator ($100 \mu\text{m}$ thick) between the cathode and anode and finally sealing homogeneously the outer surface edges of packaging film as shown in Fig. 1. Total thickness of the film-type battery was less than $700 \mu\text{m}$. The discharge capacity of the film-type primary battery was examined by using a cycler (Toscat-3000, Toyo Systems).

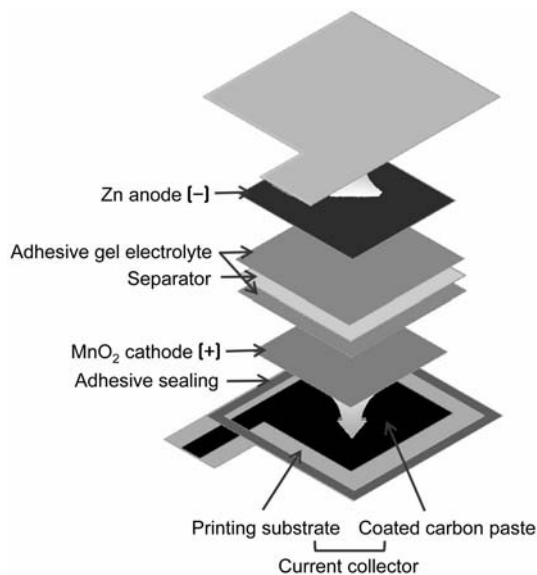


Fig. 1. Cell configuration of 1.5 V primary film battery.

2.2. Preparation of 3.0 V-class film-type Li primary battery

A 20 μm thick homogeneous lithium layer was designed for efficient utilization of a lithium anode. Following this design, Sidrabe Inc. in Latvia supplied a lithium metal anode sheet produced by lithium deposition on a copper foil (15 μm thick).⁸⁾ Electrolytic manganese dioxide powder (MnO_2 , battery grade, average diameter < 300 nm) from the Mitsui Mining & Smelting Co was used as cathode active material. We also used a cathode slurry, which consisted of MnO_2 (90 wt%) as an active material, carbon black (5 wt%) as a conductive agent, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, KynarFlex 2801, Atochem) (5 wt%) as a binder, and *N*-methyl-2-pyrrolidone as a solvent. We produced two types of lithium primary battery in nominal size (34 mm \times 60 mm for Type A and 30 mm \times 28 mm for Type B) by sequentially superimposing an aluminum foil (15 μm thick) as a cathodic current collector, an MnO_2 cathode (95 μm thick), a gel-type polymer electrolyte sheet consisted of PVdF-HFP (30.8 wt%) as a matrix, hydrophobic fumed silica (SiO_2) (7.6 wt%) as an inorganic filler, non-aqueous electrolyte solution (61.6 wt%) (1 M LiPF_6 dissolved in an equal-weight mixture of ethylene carbonate (EC) and propylene carbonate (PC)), a lithium anode, and a copper foil as an anodic current collector as shown in Fig. 2. We also examined the discharge capacity and surface temperature evolution during the discharge process by using a cyler (Toscat-3000, Toyo Systems) and then a thermocouple apparatus attached to the surface of the battery. The discharge rate was set to 0.1 C-rate.

3. Results and Discussion

3.1. 1.5 V thin and flexible primary batteries for BAP tag

We have designed adhesive gel electrolytes based on aqueous 4.6 M NH_4Cl solution. As shown in Fig. 3, polyethyleneimine ($(-\text{CH}_2\text{CH}_2\text{NH}-)_n-$, PEI) as highly water soluble and base polymer has been added to 4.6 M NH_4Cl aqueous electrolytes (●, pH 4.4) as a function of PEI content ranged from 13.7 wt% to 50 wt% in order to give deliquescent property and to shift pH value to neutral pH zone (■). It shows the highest ionic conductivity of 2.1×10^{-1} S/cm and pH as 8.2 at 4.6 M NH_4Cl (aq.)/13.7 wt% PEI at 25°C. Finally we have added a thickener, Carbopol 940 which is high molecular weight polyacrylic acid to previously optimized electrolyte solution. By adding the thickener, the electrolytes become

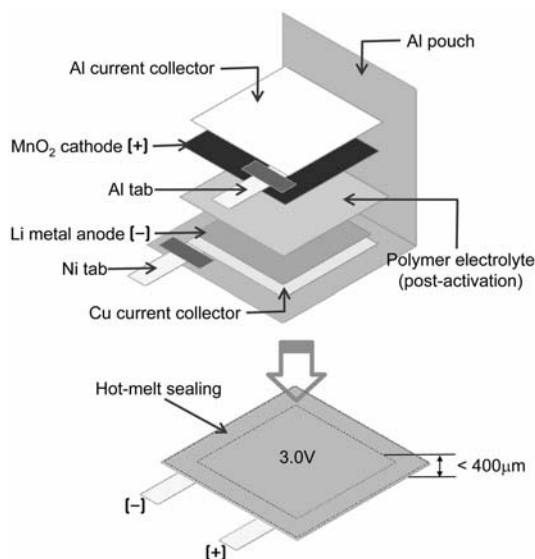


Fig. 2. Design of 3.0 V-class Al pouch cell based on Li/ MnO_2 .

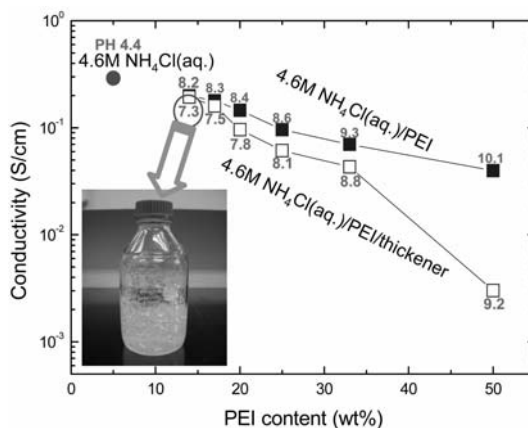


Fig. 3. Ionic conductivities of 4.6 M NH_4Cl (aq.)/PEI/thickener gel electrolytes as a function of PEI content.

abruptly gelled and the viscosity significantly increased until no fluid flow due to the acid-base interaction between the polymers (□). At 4.6 M NH_4Cl /13.7 wt% PEI/3.7 wt% Carbopol 940 based on NH_4Cl (aq.) and PEI mixture (green circle), it shows the optimum gel electrolyte condition of the highest ionic conductivity as 1.94×10^{-1} S/cm and neutral pH value of 7.3 with very adhesive and deliquescent property.

The control of conducting layer thickness is an important condition in the screen-printing step of cell fabrication because the conducting layer plays the role of current collector adequately adjustable to the particular cell performance.⁹⁾ Qualitatively considering, for instance, the

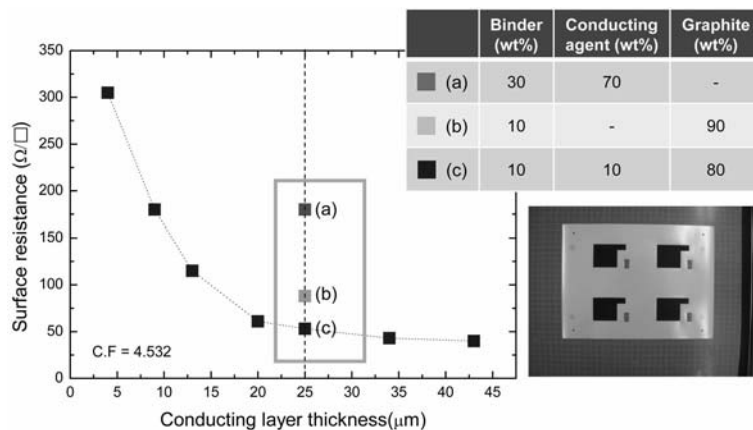


Fig. 4. Surface resistance with conducting layer thickness and carbon paste composition.

thin layer (highly conductive) corresponds to the stable cycle performance with low current rate, whereas the thick layer (comparatively resistive) to the high-rate characteristics. However, Fig. 4 shows the opposite trend that the surface resistance decreases with the increase in the conducting layer thickness (■). This is because the resistance measured by four point-probe method on layer surface is confused with the one measured across the thickness. Comprehensively considering overall cell thickness, the surface resistance maintains constant at the conducting layer thickness (in the range of 20–43 μm), which is highly required for high-rate characteristics of the cell. Meanwhile, the surface resistance increases even more than 6 times with the decrease in the conducting layer thickness (in the range of 4–12 μm), guaranteeing a stable cycle performance.

Electrochemical performances of the film-type primary batteries are shown in Fig. 5. Discharge capacity values appeared are 25 and 6 mAh (2.5 mAh cm^{-2} in reduced by active areas) for Type A ($55 \text{ mm} \times 55 \text{ mm}$) and Type B ($33 \text{ mm} \times 28 \text{ mm}$), respectively in Fig. 5(a). These reduced values per active areas are much higher than the similar-sized commercial PowerPaper® batteries.²⁾ The resultant Type B (1.5 V, Leclanché MnO_2 ||adhesive aqueous electrolytes||Zn, 8 mAh) primary film battery has a RF-Identification length of around 15 m between tag and reader, which is very adequate for simple and stable power supply of BAP tags for RFID, as shown in Fig. 5(b).

3.2. 3.0 V-class film-type Li primary batteries for sensor tag

For the perfect shielding, we prepared a multilayered

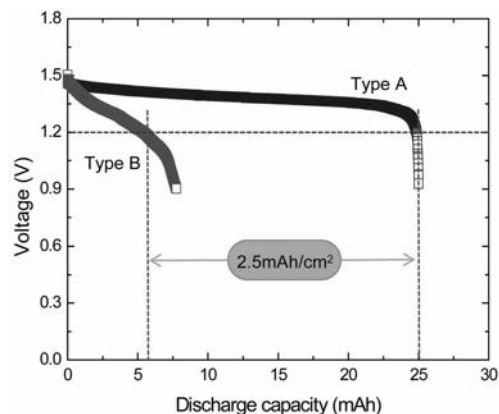


Fig. 5. (a) Discharge capacities of 1.5 V film battery at 25°C

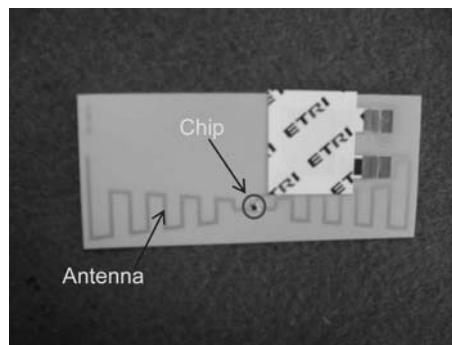


Fig. 5. (b) ETRI's BAP tag and 1.5 V film battery.

aluminum pouch as a packaging film, as shown in Fig. 6; the pouch improves the battery safety and shelf-life by reducing the self-discharge rate. For the Nylon 6/Al/PP pouch, we used the aluminum film (30 μm thick) as the

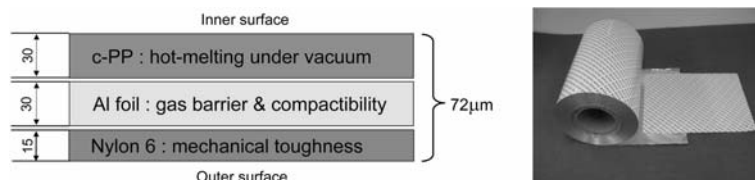


Fig. 6. New thin Al pouch for vacuum sealing method.

middle layer of the pouch on account of its superior shielding against moisture and atmosphere. We then used Nylon 6 film (12 μm thick) as the upper layer of the aluminum film to provide mechanical strength and to insulate the aluminum against breakage problems that arise from bending or folding. According to the physical data,⁷⁾ Nylon 6 has superior impermeabilities to moisture and gaseous components and also exhibits a higher tensile strength than other conventional polymer films, such as PE and PP. In addition, the outer surface of Nylon 6 layer is anti-electrostatically treated to improve the battery safety. The undrawn PP film (20 μm thick) is used as the lower layer of the aluminum film to provide easier thermal fusion at a moderate temperature ($< 130^\circ\text{C}$) and to prevent an internal short circuit due to swelling from the electrolyte solution. This composition of the Nylon 6/Al/PP pouch obviously produces perfect shielding and thereby limits the degradation (or decomposition) of electrodes and electrolyte components. In addition, the Nylon 6/Al/PP pouch maintains thin, sharp, and clear folded traces. Such good bending and folding characteristics indicate more effective molding of the packaging pouch. The suggested Nylon 6/Al/PP is a promising packaging pouch for a film-type lithium primary battery.

As shown in Fig. 7(a), the discharge curves for the film-type lithium primary batteries show nominal voltage plateaus at 3.0 V, which is twice as high as those of an alkaline primary battery. The measured discharge capacity values were 160 mAh for Type A (34 mm \times 60 mm) and 48 mAh for Type B (28 mm \times 30 mm) or 9.4 mAh cm^{-2} and 11.0 mAh cm^{-2} , respectively, when reduced by active areas. These reduced values per active area are much higher than those of similar-sized commercial PowerPaper[®] batteries.²⁾ Such high energy densities may prolong the shelf-life of the power source for a high-quality active RFID sensor tag system. The evolution of surface temperature during the discharging process also appears to be very stable, with a narrow temperature difference in the range of $\pm 1^\circ\text{C}$ as shown in Fig. 7(b). In addition, as shown in Fig. 7(c), the resultant 3.0 V-class primary film battery

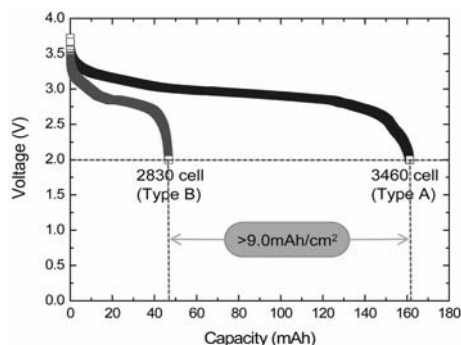


Fig. 7. (a) Discharge capacities of 3.0 V-class film battery at 25°C.

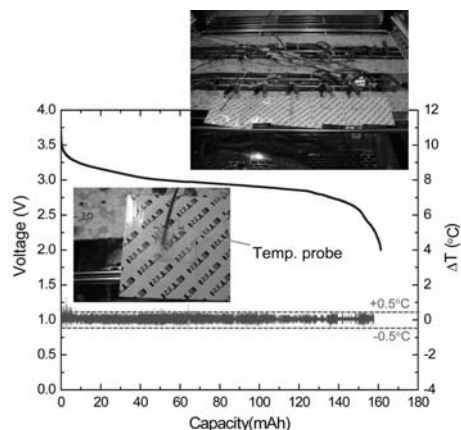


Fig. 7. (b) Temperature change of 3460 cell surface during the discharge process at 25°C.



Fig. 7. (c) ETRI's sensor tag and 3.0 V-class film battery.

(type A), including the Nylon 6/Al/PP packaging pouch, has a nominal thickness of 500 μm , which is adequate for use as a simple and stable power supply in semi-active RFID sensor tag.

4. Conclusions

We designed the 1.5 V-class film-type Leclanché batteries by adopting multi-layered packaging film, NH_4Cl based adhesive aqueous electrolytes, and novel fabrication steps to improve the barrier and selective permeation property, ionic conductivity, and shelf life, respectively. The novel 3.0 V-class film-type primary battery with a lithium anode and a non-aqueous nonaqueous electrolyte was fabricated with a newly designed Nylon 6/Al/PP pouch for perfect shielding. The proposed film-type primary batteries have a wide range of application, particularly where

thin, flexible power sources are required, as in the case of BAP and sensor RFID tag.

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