



Short communication

3.0 V-class film-type lithium primary battery with highly improved energy density

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ABSTRACT

Lithium 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. A 20- μm thick lithium layer deposited homogeneously on a copper foil is prepared for the purpose of controlling the efficient utilization and lithium handling. A plasticized gel polymer electrolyte filled with SiO_2 particles is also used to enhance the electrochemical stability and safety of the battery. A lithium primary battery with a lithium anode and a nonaqueous electrolyte is fabricated for the first time in the form of a film with a newly designed Nylon 6/Al/polypropylene pouch for perfect shielding. The fabricated 3.0 V-class film-type lithium primary battery passes several safety tests and achieves a discharge capacity and an energy density of more than 9 mAh cm^{-2} and 470 Wh L^{-1} , respectively.

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1. Introduction

The world will eventually be covered with smart sensor networks as a result of the technological progress of wireless communications, sensing, and computations [1]. Accordingly, the high-voltage, high-capacity requirements of film-type primary batteries are increasing enormously because the ubiquitous era in the near future will have to deal with massive information for the chip-embedded sensor tags of radio-frequency identification (RFID) systems. For instance, a high-power primary battery can increase the sensing distance of RFID sensor tags; and this capability is efficient for the administrative control of physical distribution systems or large-scale logistics. In contrast to 1.5 V-class film-type primary batteries, such as the Leclanché battery [$\text{MnO}_2\|\text{ZnCl}_2$ or $\text{NH}_4\text{Cl}\|\text{Zn}$] from PowerPaper[®] [2] and the alkaline manganese battery ($\text{MnO}_2\|\text{KOH}\|\text{Zn}$) discussed in a previous study [3], a lithium anode is a very promising means of enlarging the discharge capacity due to its inherent electrical capacity; note that the theoretical capacity of lithium metal is about 3860 mAh g^{-1} .

For this study, a thin lithium metal layer (20 μm thick) on a copper foil current-collector is designed for use as the anode of a film-type primary battery. To the best of our knowledge, the idea of using lithium in a film-type primary battery (thinner than 500 μm) for improved safety is a novel suggestion. The nominal voltage and

discharge capacity per active area are expected to be 3.0 V and greater than 3.0 mAh cm^{-2} (the target value), respectively. The use of lithium metal as an anode, however, may involve safety problems such as smoke, fire, and explosion, due to the chemical instability of lithium in a moist environment. For safety reasons, therefore, a new multi-layered aluminum pouch is used as a packaging 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 lithium primary batteries.

2. Experimental

The multi-layered aluminum pouch prepared for the lithium anode, polymer electrolyte and MnO_2 cathode consisted of three main film layers of Nylon 6 (12 μm thick), aluminum foil (30 μm) and undrawn polypropylene (PP, 20 μm thick) in sequence from the outer to the inner surfaces. Polyethylene-based adhesive layers, each with a thickness of 5 μm , were inserted between the three layers of film after lamination. The compositions and thicknesses are shown in Fig. 1 with images of the Nylon 6/Al/PP pouch. The physical properties of the Nylon 6/Al/PP pouch, as well as a conventional aluminum pouch (poly(ethylene terephthalate) (PET)/Al/PP, 120 μm thick) for comparison, were tested in terms of moulding ability, bending and folding properties, and the thermally fused temperature. The moulding ability in particular was confirmed by checking the pouch state after oil-pressing in a mould

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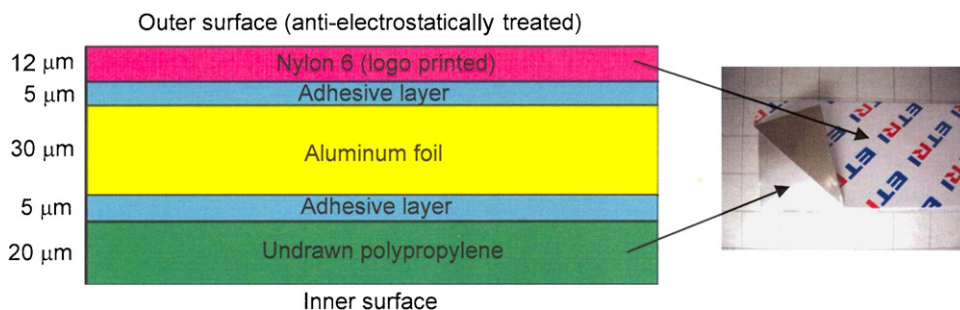


Fig. 1. Composition and thickness of components in packaging pouch (Nylon 6/Al/PP). Images of outer and inner surfaces are included.

(28 mm × 30 mm × 1 mm). To measure the bending characteristics (or flexibility) after the pouches had been bent 90°, the bending angle, as well as the thickness and area of the bent portion of each pouch, was observed. The folding characteristics when the pouches were folded 180° were also investigated.

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). Electrolytic manganese dioxide powder (MnO_2 , battery grade, average diameter <300 nm, Mitsui Mining & Smelting Co.) was used as the cathode active material. A cathode slurry was also employed and 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. The prepared MnO_2 cathode had a thickness of 95 μm and an electrode density of ca. 52 mg cm^{-2} , which corresponds to a MnO_2 loading of ca. 47 mg cm^{-2} . A gel-type polymer electrolyte was prepared by casting a slurry, which consisted of PVdF-HFP (30.8 wt.%) as a matrix, hydrophobic fumed silica (SiO_2) (7.6 wt.%) as an inorganic filler, a nonaqueous electrolyte solution (61.6 wt.%) (1 M LiPF_6 dissolved in an equal-weight mixture of ethylene carbonate (EC) and propylene carbonate (PC)), and acetone as a solvent (see Fig. 2). The room temperature ionic conductivity of the gel polymer electrolyte was determined from complex impedance spectra measured with a frequency response analyzer (Solartron HF 1225 Gain-Phase Analyzer) in a frequency range of 0.1 Hz to 100 kHz. A conductivity cell (2 cm × 2 cm) was also used and comprised two stainless-steel electrodes on each side of the polymer electrolyte film.

Two types of lithium primary battery of nominal size 34 mm × 60 mm for Type A and 30 mm × 28 mm for Type B, as shown in Fig. 4, were assembled by sequentially superimposing an aluminum foil as a cathodic-current-collector, a MnO_2 cathode, a polymer electrolyte, a lithium anode, and a copper foil as an anodic current-collector. The active areas were 32 mm × 53 mm for Type

A and 23 mm × 19 mm for Type B. The superimposed electrodes were inserted into the multi-layered aluminum pouch, which was pre-moulded to a depth of 1 mm. To complete the fabrication of the film-type cells, a nonaqueous electrolyte solution (1 M LiPF_6 dissolved in an equal-weight mixture of EC and dimethyl carbonate (DMC)) was injected as a post-activation additive and the edge of the multi-layered aluminum pouch was vacuum sealed. The amount of post-activation additive injected was the same weight as the PVdF-HFP matrix in the gel-type polymer electrolyte.

To check for safety, external short-circuit and nail penetration (internal short-circuit) tests [4,5] were conducted on the film-type lithium primary batteries. The discharge capacity and surface temperature evolution during discharging process were examined by using a cycler (Toscat-3000, Toyo Systems) and a thermocouple apparatus attached to the surface of the battery. Discharge was set at the 0.1 C-rate. The open-circuit voltage was also measured for about a year in order to examine the self-discharge characteristics of the film-type lithium primary batteries.

3. Results and discussion

The use of a lithium metal anode has the advantage of producing a higher electrical capacity; and a very small amount of lithium is adequate for efficient utilization. Bulk lithium metal is, however, generally difficult to handle due to its softness and sticky nature at ambient temperature. Thus, the thin-film lithium metal anode sheet is coated on a copper foil substrate with a thickness of less than 20 μm to allow easy handling and efficient utilization. A thickness of 20 μm can be obtained from a rough estimation of the utilization of the lithium metal anode that is assumed to be 10% of the theoretical capacity. The volumetric capacity of 10% of the theoretical lithium capacity is calculated as follows: $(3860 \text{ mAh g}^{-1}) \times (0.534 \text{ g cm}^{-3}) \times (0.1) = 206 \text{ mAh cm}^{-3}$, where 0.534 g cm^{-3} refers to the density of lithium metal at room temperature. The minimum thickness required for the target capacity density of 3 mAh cm^{-2} when the volumetric

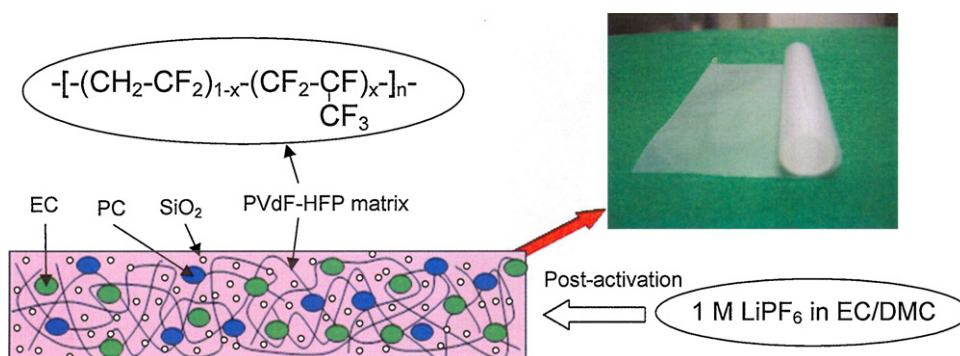


Fig. 2. Image of gel-type polymer electrolyte and schematic illustration of its composition.

capacity is used is then calculated as follows: $(3 \text{ mAh cm}^{-2}) \div (206 \text{ mAh cm}^{-3}) = 0.146 \text{ cm} = 14.6 \text{ }\mu\text{m}$. If it is assumed that the minor effect of lithium consumption by side-reactions corresponds to about $5 \text{ }\mu\text{m}$, the final minimum thickness is found to be $20 \text{ }\mu\text{m}$. Siderabe Inc. in Latvia accepted this design and produced a $20\text{-}\mu\text{m}$ thick lithium metal anode sheet by using homogeneous vapour deposition with a Li pilot coater [6] on a copper foil substrate ($15 \text{ }\mu\text{m}$ thick) as an anodic current-collector. In addition, thinner and more flexible batteries than the type proposed in this work are also possible for wider use in RFID systems if the degree of utilization of the lithium metal anode exceeds 10%; that is, a lithium layer thinner than $20 \text{ }\mu\text{m}$ is developed.

Another concern over the use of a lithium metal anode is the chemical instability of lithium, especially in a moist environment; this instability may cause safety problems such as overheating, fire, and even explosions. Moreover, because the operating voltage rises to 3.0V with a lithium anode and nonaqueous organic electrolyte components, the film-type cells must be shielded perfectly from the atmosphere and from moisture to ensure they are as safe as aqueous 1.5V alkaline batteries [3]. For perfect shielding, a multi-layered aluminum pouch was fabricated as a packaging film, as shown in Fig. 1; the pouch improves battery safety and shelf-life by reducing the self-discharge rate. For the Nylon 6/Al/PP pouch, an aluminum film ($30 \text{ }\mu\text{m}$ thick) was employed as the middle layer of the pouch on account of its superior shielding against moisture and atmosphere. A Nylon 6 film ($12 \text{ }\mu\text{m}$ thick) served as the upper layer of the aluminum film to provide mechanical strength and to insulate the aluminum against breaking problems that may arise from bending or folding. According to the physical data [7], Nylon 6 has superior impermeability 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 the Nylon 6 layer is anti-electrostatically treated to improve battery safety. An undrawn PP film ($20 \text{ }\mu\text{m}$ thick) was 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 structure of the Nylon 6/Al/PP pouch obviously provides perfect shielding and thereby limits the degradation (or decomposition) of electrodes and electrolyte components.

From the properties of the packaging pouch compared in Table 1, it can be seen that the Nylon 6/Al/PP pouch is superior for all mechanical deformations and thermofusion temperatures. The

Table 1
Comparison of packaging pouch properties.

	PET/Al/PP ($120 \text{ }\mu\text{m}$)	Nylon 6/Al/PP ($72 \text{ }\mu\text{m}$)
Molding ability ^a	Not molded	Molded
90° bending	Well bent	Excellently flexible
180° folding	Not folded	Well folded
Thermofusion temperature ^b ($^\circ\text{C}$)	135–150	<130

^a Checking pouch state after oil-press moulding with a $28 \text{ mm} \times 30 \text{ mm} \times 1 \text{ mm}$, mould.

^b Temperature required for obtaining complete thermally fused product in thermal fusion process.

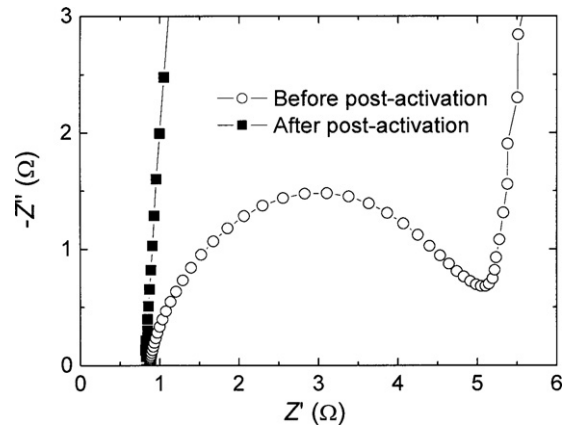


Fig. 3. Complex impedance spectra of gel-type polymer electrolytes before and after post-activation.

conventional PET/Al/PP pouch cannot be moulded to a desired shape when the process is conducted in a shallow mould with a depth of 1 mm because the pouch has a relatively large thickness of $120 \text{ }\mu\text{m}$. By contrast, the Nylon 6/Al/PP pouch shows superior mouldability; that is, the desired shape can be easily attained in a mould with a depth of 1 mm because the pouch is only $72 \text{ }\mu\text{m}$ thick. The bending characteristics of the Nylon 6/Al/PP pouch are also superior to those of the PET/Al/PP pouch. In particular, when bent at 90° , the PET/Al/PP pouch has a wide non-uniform bending portion whereas the Nylon 6/Al/PP pouch has narrow uniform bending por-

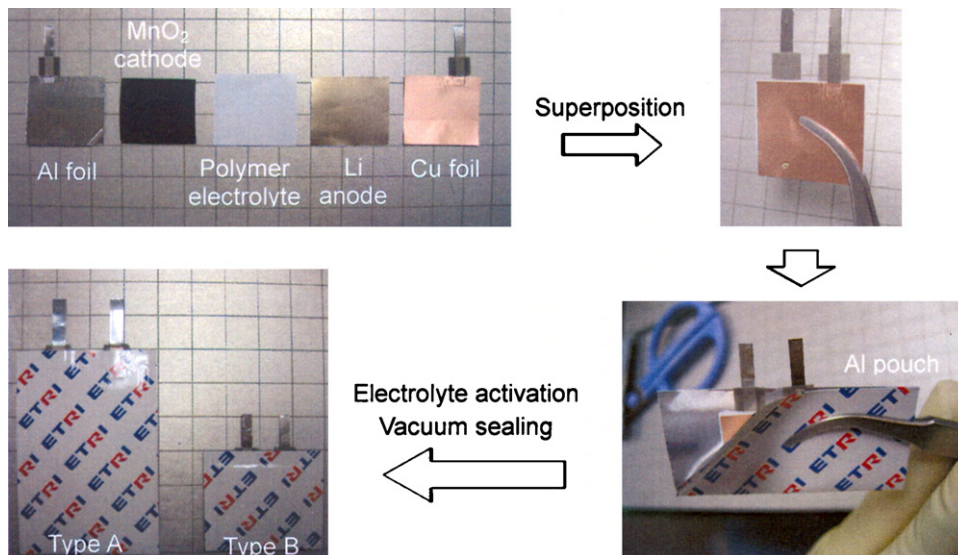


Fig. 4. Schematic of fabrication procedure for film-type lithium primary batteries.

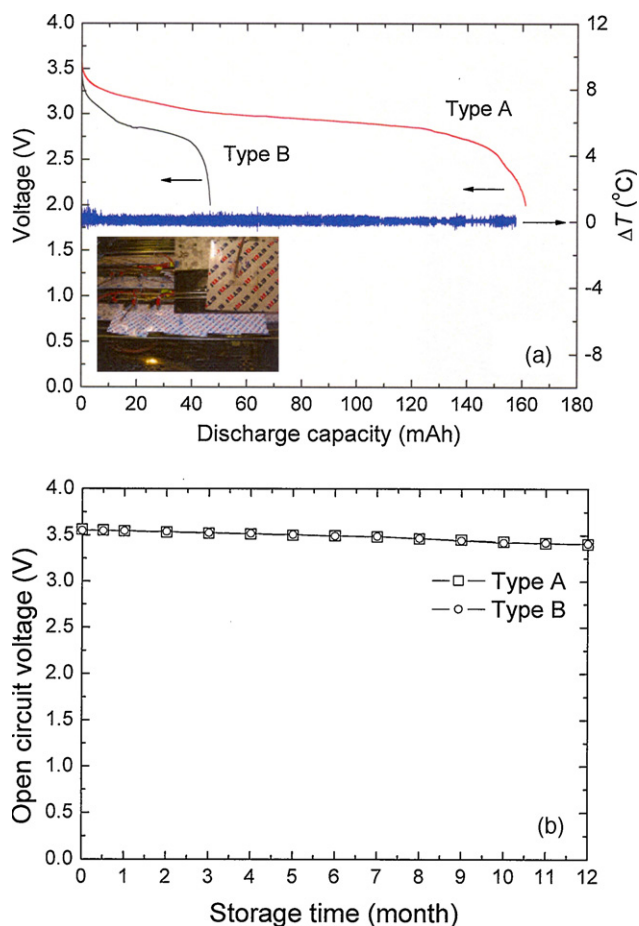


Fig. 5. (a) Discharge curve and surface temperature evolution, (b) self-discharge pattern of film-type lithium primary batteries (Types A and B). Inset in (a) shows image of temperature-measuring apparatus using thermocouples.

tions. Due to its large thickness, the PET/Al/PP pouch does not show any clear trace or shape of the folded portion after being folded 180°. By contrast, the Nylon 6/Al/PP pouch maintains thin, sharp and clear folded traces. Good bending and folding characteristics indicate more effective moulding of the packaging pouch. Thus, a film-type battery with a favourable shape can be manufactured.

When the packaging pouches are thermally fused, the thermofusion temperature must be near or higher than the melting point of the innermost layer film. In addition, when the thickness of the innermost layer film is increased, the fusion time is longer and the fusion temperature is higher. For the thicker PET/Al/PP pouch, the temperature of heat transfer and fusion is comparatively high. For the Nylon 6/Al/PP pouch, however, the fusion occurs in a temperature range of 120–130°C, which is near the melting point of the innermost PP layer because heat transfer is easily achieved due to the thin PP layer. If the thermofusion temperature is excessively high, the metal film will be heated and the battery temperature will increase. The polymer materials in the pouch may subsequently melt and thereby cause degradation of the electrode and electrolytes, volatilization of the electrolyte components and, eventually, a severe decline in battery performance and durability [8]. Thus, the thermofusion temperature must be kept as low as possible. In short, the suggested Nylon 6/Al/PP is a promising packaging pouch for a film-type lithium primary battery.

The gel polymer electrolyte, shown schematically in Fig. 2, is very similar to the PVdF-HFP/SiO₂ system [9]. The addition of silica particles can enhance mechanical strength and improve interfacial compatibility between the electrode and electrolyte. The inclu-

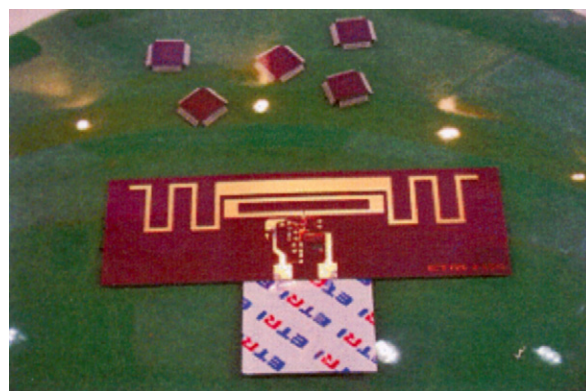


Fig. 6. Active sensor tags with antenna structure for RFID, powered by 3.0V-class film-type lithium primary batteries.

sion of organic solvents such as EC and PC essentially leads to the formation of a slightly sticky gel that ensures intimate contact with the electrode surface. The organic solvent also improves the lithium ion mobility within the gel polymer electrolyte. As shown in Fig. 3, gel-type polymer electrolytes show very low resistances in the conductivity cell (between two stainless-steel electrodes). It is also noteworthy that a liquid-like behaviour, corresponding a linear spectra part, is obviously exhibited after post-activation by an addition of 1 M LiPF₆/EC:DMC = 1:1 (w/w). As a result, the ionic conductivity of the gel polymer electrolyte at room temperature is estimated to be $7.2 \times 10^{-4} \text{ S cm}^{-1}$ before rising and $3.6 \times 10^{-3} \text{ S cm}^{-1}$ after post-activation by the additional electrolyte solution. These ionic conductivity values may be sufficiently good for practical application in the electrolyte solution in a lithium primary battery.

The precise fabrication steps, as shown in Fig. 4, enable the production of thin-film cells (Types A and B) with a total thickness of less than 500 μm. Compact and precise processing ensures good film-type batteries with optimum performance and improved safety. Incidents of flame fire and explosion may occur with lithium batteries when conventional processing techniques are used without the suggested packaging pouch and gel polymer electrolyte. The Types A and B batteries in this work both passed the external short-circuit and nail penetration safety tests without showing any heat, fire or explosion.

As shown in Fig. 5, the discharge curves of the film-type lithium primary batteries each exhibit a nominal voltage plateau at 3.0V, which is twice as high as that of an alkaline primary battery. The discharge capacity values are 160 mAh for Type A and 48 mAh for Type B (or 9.4 and 11.0 mAh cm⁻², respectively, when related to active areas). These reduced values per active area are much higher than those of similar-sized commercial PowerPaper® batteries [2]. Much higher energy densities can be calculated from the discharge capacity, operating voltage, and battery dimensions. The energy densities expressed are:

$$\begin{aligned} \text{for Type A, } & (160 \text{ mAh}) \quad (3.0 \text{ V}) / [(3.4 \text{ cm} \times 6.0 \text{ cm}) \\ & (500 \mu\text{m})] = 470.6 \text{ Wh L}^{-1} \\ \text{for Type B, } & (48 \text{ mAh}) \quad (3.0 \text{ V}) / [(3.0 \text{ cm} \times 2.8 \text{ cm}) \\ & (500 \mu\text{m})] = 342.9 \text{ Wh L}^{-1}. \end{aligned}$$

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 $\pm 1^\circ\text{C}$. The self-discharge patterns for the batteries over a year are given in Fig. 5(b). The patterns are superior to those of conventional alkaline batteries because the Nylon

6/Al/PP packaging pouch prevents the gel polymer electrolyte components from becoming dry. In addition, as shown in Fig. 6, the resultant film-type lithium primary battery, 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 source in active and semi-active RFID sensor tags.

4. Concluding remarks

In this study presents a novel 3.0 V-class lithium primary battery ($\text{MnO}_2||\text{Li}$) with a Nylon/Al/PP packaging pouch, a gel polymer electrolyte filled with fumed silica, and novel fabrication steps that improve the shielding property, ionic conductivity, and electrochemical performances of the cells. A 20- μm thick lithium layer deposited homogeneously on a copper foil has been prepared for efficient utilization and lithium handling. A plasticized gel polymer electrolyte is also used to enhance electrochemical stability and battery safety. The novel film-type primary battery

with a lithium anode and a nonaqueous electrolyte is fabricated with a newly designed Nylon 6/Al/polypropylene pouch for perfect shielding. The proposed film-type lithium primary batteries have a wide range of application where thin, flexible power sources are required, as in the case of active and semi-active RFID sensor tags.

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