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Review

Lithium and lithium ion batteries for applications in microelectronic devices: A review

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HIGHLIGHTS

- Chemistry and electrochemistry in lithium-based microbatteries.
- Recent concept and cell design towards different applications.
- Future perspectives of microbattery development.

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ABSTRACT

Batteries employing lithium chemistry have been intensively investigated because of their high energy attributes which may be deployed for vehicle electrification and large-scale energy storage applications. Another important direction of battery research for micro-electronics, however, is relatively less discussed in the field but growing fast in recent years. This paper reviews chemistry and electrochemistry in different microbatteries along with their cell designs to meet the goals of their various applications. The state-of-the-art knowledge and recent progress of microbatteries for emerging micro-electronic devices may shed light on the future development of microbatteries towards high energy density and flexible design.

1. Introduction

1.1. Overview of lithium and lithium ion batteries and need for micro-sized batteries

High energy lithium and lithium ion batteries are playing a key role in the advent of the information age and will continue to expand their applications in many different aspects in the foreseeable future [1]. Batteries based on lithium chemistry are categorized in two groups, primary batteries and secondary (rechargeable) batteries. For primary batteries, metallic lithium is directly adopted as the anode whereas a variety of cathode materials have been used including manganese dioxide [2], carbon fluoride (CF_x) [3], and silver vanadium oxide (SVO) [4]. A typical secondary lithium battery, or so called lithium-ion battery employs intercalation compound such as graphite as the anode. Cathode side also uses intercalation materials such as lithium cobalt dioxide ($LiCoO_2$), while Li^+ ions transport back and forth between cathode and anode during operating [5]. The most commonly used electrolyte is $LiPF_6$ dissolved in EC/DMC [6,7]. Depending on the specific application, the solutes and solvents can be tuned to meet energy/power ratio and operation temperature requirements.

Compared to other battery chemistries, lithium chemistry provides much higher power and energy densities in both gravimetric and volumetric terms [8], which are the most important parameters for applications in portable electronics such as smart phones, digital cameras and laptops. In addition, many lithium batteries have lower self-discharge rates and hence longer shelf lives. There has been a strong drive for vehicle electrification by using lithium

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ion battery technologies (LIBs) and several models of commercial PHEVs and EVs have hit the markets. In recent years, with the continuous cost reduction, lithium ion batteries become highly competitive to the aqueous redox flow batteries for large-scale (grid) energy storage applications.

The most common commercial LIBs used in the aforementioned applications are in the forms of cylindrical cells, pouch cells or coin cells. These batteries are generally bulk in size. For instance, the 18650 cylindrical cell is 65.2 mm long and 18.6 mm in diameter. The smallest coin cell (ML421) is about 5 mm in diameter. A much less discussed area of lithium-based batteries is microbatteries. The rapid development of electronic and information technology towards the directions of multifunctionality, high integration and high power drives the electronic devices towards miniaturization [9]. Lithium microbatteries are the ideal energy storage devices for biological/medical devices (pacemaker, hearing aid, defibrillator, in vivo imaging, etc.) [10] and self-powered microelectronics (miniature transmitters, sensors, actuators, etc.) [11]. These devices are sometimes on the millimeter scale or less (Fig. 1). Unfortunately, commercial coin cells are still routinely used in these applications due to the lack of commercial cells of smaller sizes so the reduction in size and the improvement in the capability of microsystems are presently limited by the size, capacity and power of their on-board power supplies. To bridge the gap, scientists at Pacific Northwest National Laboratory (PNNL) recently developed micro-sized lithium primary batteries with high energy density for Juvenile salmon acoustic telemetry system (JSATS) [12]. Panasonic commercialized industry's smallest pin-type batteries (bottom-right figure in Fig. 1) with similar design in 2014 for targeted applications in wearable devices, electronic pens and medical devices [13]. These batteries combine small sizes and high specific capacity (Table 1) and hence are positive signs of progress in the microbattery field to meet short-term goals. The long-term goal of microbattery research will likely be defined by the fast growth of microelectromechanical systems (MEMS) technology that demands for even higher power, higher energy on a smaller scale [14]. Similar to bulk-size batteries, lithium microbatteries can be either primary or secondary. As the microbatteries in most applications are difficult to service (for instance, replace), the rechargeability can effectively increase the service life of a battery. Ultimately, service-free, continuously-powered devices may be realized through a combination of micro energy harvesting systems and rechargeable microbatteries.

1.2. Traditional batteries for micro-applications

Bulk-size lithium ion batteries normally consist of composite electrodes and liquid electrolytes. As the size of the battery shrinks, the fabrication process for composite electrodes and the use of liquid electrolyte become increasingly incompatible with the required microfabrication process. The parasitic weight in the downsized batteries also increases at the same time. As a result, microbatteries differ greatly from bulk-size LIBs in their architecture design and material choices. Since the composite electrode design works well with a wide range of electrode materials, the research focus of bulk-size batteries is on materials development, i.e. optimizing the electrochemical couples, improving the stability of electrolytes and developing new lithium chemistry (lithium sulfur, Si anode, etc.) [8,15,16]. For microbattery research, the focus is more on innovative fabrication procedures and novel architectures of electrodes or full cells [17–19].

Thin-film batteries adopting two-dimensional (2D) planar design are the most popular traditional batteries for micro-applications. An individual cell consists of thin, dense layers of battery components fabricated by various deposition methods (Fig. 2a). The operating principle of thin-film batteries is similar to bulk-size batteries with composite electrodes, except that the diffusion paths are much shorter. Since only active (electrode) materials are used in the electrode layers (in contrast to composite electrodes in bulk-size cells), the electronic and ionic conduction within the electrodes are entirely dependent upon the intrinsic properties of electrode materials. As a result, the thicknesses of electrodes are limited to a few microns to avoid loss of power and poor electrode utilization. For the electrolyte layer, solid-state

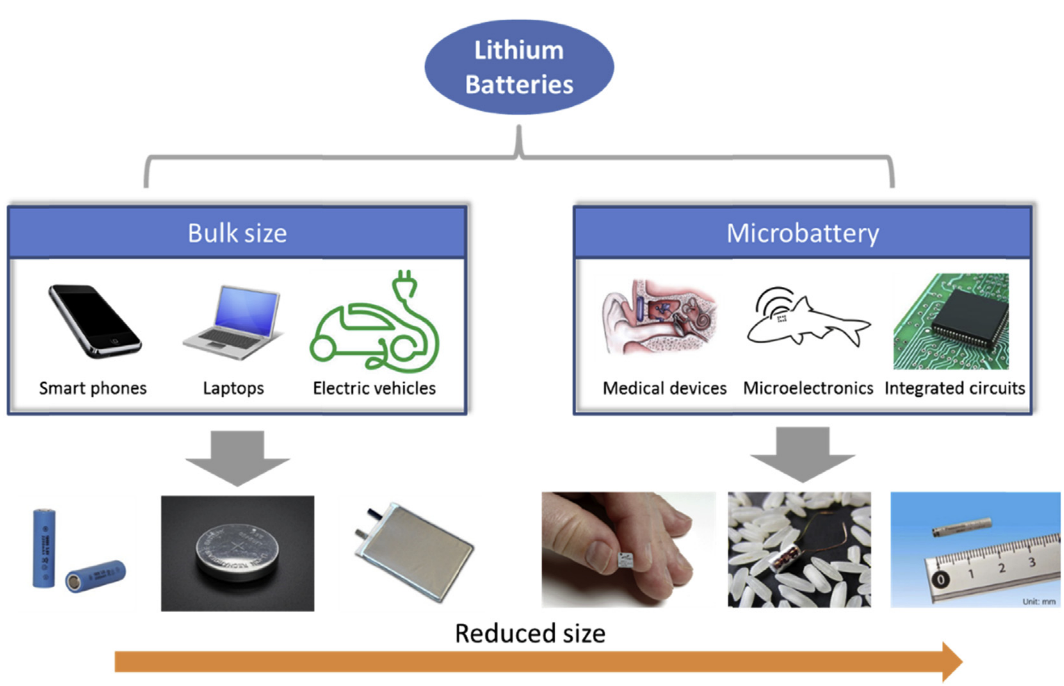

Fig. 1. Examples of lithium battery applications and the form of cells used.