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Lithium metal/polymer battery

Tetsuya Osaka^{*}, Toshiyuki Momma

Department of Applied Chemistry, Waseda University, Shinjyuku, Tokyo 169-8555, Japan

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Abstract

Trend and state of the affairs for Li ion polymer battery were summarized. Also the situation of the research and development for the Li metal battery was introduced. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In these decades, the requirement of higher energy density battery grew more and more. In order to satisfy the consumer's requests, many efforts on the development of high energy density battery have been made. The Li ion battery has been shipped from 1992 and attracted both of consumers and researchers. After the first introduction of Li ion battery, the energy density of Li ion battery is growing year by year, while new type battery of Li ion polymer battery is developed with the flexible light features. On the contrary, another effort is also made to realize the battery with the anode of Li metal. The main problem to be solved for the realization of commercial Li metal battery is the achievement of safety. In this paper, the state of affairs of commercial Li ion batteries and the research situation of Li metal battery are reviewed.

2. Circumstance and situation of Li ion battery

In these years, the production of Li ion battery is growing every year as shown in Fig. 1. From the end of 1996, the capacity of production grew extensively exceeding the consumer's demand. The excess supply brought to lower cost of the battery. The main applications of the Li ion batteries are the portable computers and cellular phones. In addition, in these years, the Li ion battery using polymer electrolyte has appeared. In Table 1, the recent development

of Li ion polymer batteries is summarized. The energy densities are not so high for the Li ion polymer battery compared with the Li ion batteries, however, the Li ion polymer battery has merits of reduced thickness and weight of the cell itself. In the field of cellular phones, the energy saving systems brought down the demand for the energy density, while they requested thinner shape, which pushes the appearance of the Li ion polymer battery.

3. Research achievement of Li metal battery

As shown in Fig. 2, for the next generation rechargeable battery, the lithium secondary battery using lithium metal as the anode is the most attractive candidate for higher energy power sources for portable electric devices, electric vehicles, and load leveling systems. There are, however, some disadvantages of the lithium metal anode compared to the carbon anode of Li-ion battery [1,2].

In order to enhance the lithium anode properties, the effect of additives to the liquid electrolyte was studied, e.g. CO₂ [9–13], HF [3,4] and so on. In addition, the dendritic growth of lithium was suppressed in poly(ethylene oxide) (PEO)-based gel electrolyte [5].

The gel electrolyte, which consisted of polymer matrix, organic solvent and supporting electrolyte, was introduced as a novel material in the field of rechargeable battery applications [6–8]. By applying the gel electrolyte to the batteries, the electrolyte solution does not leak out from the cell, and the electrolyte can be prepared as a thin film, which enables to construct a solid state and high energy density battery. In particular, the gel electrolyte demonstrates highly ionic conductivity about 10^{-3} s cm⁻¹ at room temperature

^{*} Corresponding author. Tel.: +81-3-5286-3202; fax: +81-3-3205-2074.
E-mail address: osakatet@mn.waseda.ac.jp (T. Osaka).

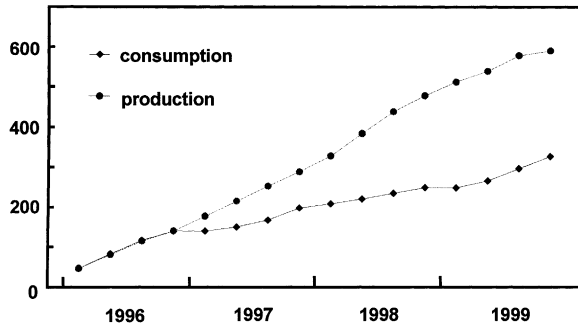


Fig. 1. The production of Li ion battery in Japan from 1996 [18].

and has a sufficient mechanical strength, e.g. poly(acrylonitrile) [9,10], poly(methyl methacrylate) [8,9], a new copolymer of vinylidene fluoride with hexafluoropropylene (PVdF-HFP) [4,12] based gel electrolytes. In 1997, on the basis of these background, the first reliable and practical rechargeable Li-ion plastic battery, which contained the carbon material as an anode, was developed by applying the PVdF-HFP copolymer type gel electrolyte [13].

On the basis of such a circumstance, we applied the PVdF-HFP copolymer type gel electrolyte to the Li metal anode battery, and the high charge–discharge performance of lithium metal anode in the PVdF-HFP gel electrolyte system was demonstrated. Furthermore, the higher performance was obtained by the combination of the CO₂ addition into gel electrolyte.

As described previously [5,14,15], the dendritic deposition was suppressed in the PEO gel electrolytes owing to the immobility of the electrolyte molecules. We assume that the efficiencies for the gel electrolytes depend on the kind of polymer matrix. There are some apparent differences between the PEO and PVdF-HFP gel electrolyte, i.e. the chemical behavior of polymer matrix and the immobility of the electrolyte molecules. It was most likely that the interface between the gel electrolyte and lithium played the most important role in the cycling characteristics. When the poly(tetrafluoroethylene) (PTFE), which has similar chemical structure to the copolymer of PVdF-HFP, became black in color like as carbon by contact with lithium metal, it

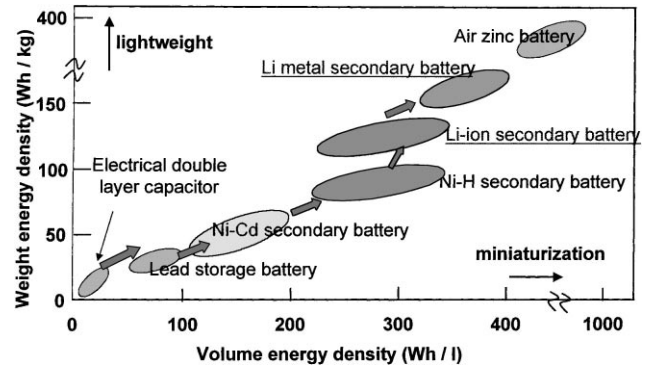


Fig. 2. Trend of energy density of batteries.

seemed that the PTFE polymer was reduced by lithium metal, and lithium surface was covered with lithium compounds. In consideration of this fact, it is probably that the enhancement property for the PVdF-HFP was due to the formation of some protective layers on the lithium by the reductive reaction of PVdF-HFP copolymer by lithium metal.

The effect of CO₂ addition into the PVdF-HFP gel electrolyte and PEO gel electrolyte was also examined. The efficiency was increased by the CO₂ addition. These results confirm that the CO₂ addition is effective not only in the liquid electrolyte but also in the gel electrolyte. Considering the results as reported elsewhere [16], the combination of the PVdF-HFP gel electrolyte and CO₂ addition does enhance effectively the efficiency of lithium anode.

Additionally, the morphology of lithium deposited (charged) in the gel electrolytes was improved. In the case of the PEO gel electrolyte, the morphology became rough gradually by proceeding the cycling. On the contrary, the lithium tested in the PVdF-HFP gel possesses more uniform surface than that in the PEO gel. It was due to the differences in chemical behavior and immobility of the electrolyte molecules. By the addition of carbon dioxide to the PVdF-HFP gel, the surface becomes smooth slightly. Simultaneously, an ac impedance measurement confirmed that the interface resistance was decreased [17,18].

Table 1

List of development for Li ion polymer batteries

	Type	Size (mm, g)	Capacity (mAh)	Energy density		Application, points
				Wh/l	Wh/kg	
Panasonic	Polymer	35 × 62 × 3.6, 16	500	255	125	Cellular
Sony	Polymer	35 × 62 × 3.8, 16	540	270	130	Cellular, MD player
Sanyo	Polymer	35 × 62 × 3.6, 13.5	570	270	155	Cellular
	Li-ion	30 × 48 × 4.8, 13.5	520	290	143	Thin Al case
GS	Polymer	35 × 61 × 3.8, –	500	230	–	
	Li-ion	35 × 62 × 3.6, 12.5	540	290	160	Cellular
Yuasa	Polymer	51 × 75 × 2.0, 13	380	180	105	Audio equipment
Maxell	Polymer	116 × 89 × 3.0, 55	1500	175	100	Mobile PC
Toshiba	Polymer → Li-ion	35 × 62 × 3.6, 13.6	540	260	160	Cellular
NEC-MOLI	Li-ion	32 × 65 × 3.6, 14.3	620	315	165	Cellular

These results suggest that there are possibilities of enhancing the lithium anode properties by selecting and designing host polymer, supporting electrolyte, solvent and additives. Further analyses and discussion should be required for understanding the characteristics of the lithium anode in the PVdF-HFP gel system.

In future, the Li metal secondary battery with higher energy density will be realized on the basis of such scientific and technical developments.

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