

RECENT ADVANCES IN LITHIUM BATTERY TECHNOLOGY

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ABSTRACT

Portable electronics such as cellular telephones and laptop computers have produced a surge in battery development and the introduction of rechargeable lithium battery systems. The most dramatic improvement in rechargeable battery technology was the introduction of the lithium-ion battery in 1990. Today, the sale of lithium-ion systems dominates the rechargeable battery market. The cell voltage for any battery system is determined by the selection of the anode and cathode materials, and the electrolyte determines the chemistry of the system and the rate of the electrode reactions. Applications of lithium batteries range from cardiac pacemakers to thermal batteries for military operations. Various types of lithium batteries are discussed. The next major improvement in lithium battery technology will likely be the use of solid polymer electrolytes that provide a truly all-solid-state battery.

I. INTRODUCTION

Portable electronics such as cellular telephones and laptop computers have produced a recent surge in battery development and the introduction of rechargeable lithium battery systems. The annual battery production today exceeds \$30 billion and is estimated at 15 units per person throughout the developed countries of the world.

All battery systems can be described in terms of three basic components: (1) the anode material, (2) the cathode material, and (3) the electrolyte as illustrated in Fig. 1. The electrode reaction at the anode (oxidation) releases electrons that flow through an external circuit to the cathode. The electrode reaction at the cathode (reduction) accepts the electrons. The cell circuit is completed by the transport of ions across the electrolyte [1]. The equilibrium cell voltage (E) and the Gibbs free energy (ΔG) for the cell reaction are related by

$\Delta G = -zFE$, thus the cell voltage for any battery system is determined by the selection of the anode and cathode materials [2]. The electrolyte determines the chemistry of the system and the rate of the electrode reactions.

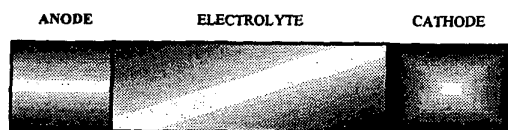


Fig. 1. Basic Components of Battery Systems

Batteries are often classified as primary (non-rechargeable) or secondary (rechargeable) depending on their capability of being electrically recharged. This is determined mainly by the reversibility of the anodic and cathodic electrode reactions. A familiar example of a primary battery is the flashlight battery consisting of a zinc anode (Zn) and a manganese dioxide (MnO_2) cathode represented as Zn/MnO_2 . The alkaline-manganese dioxide cell uses a potassium hydroxide (KOH) aqueous electrolyte, thus this widely used battery can be represented by $Zn/KOH/MnO_2$ analogous to Fig. 1. A well-known example of a secondary battery is the lead-acid battery used in automobiles. This rechargeable battery consists of a lead (Pb) anode, a sulfuric acid (H_2SO_4) electrolyte, and a lead dioxide (PbO_2) cathode and can be represented by $Pb/H_2SO_4/PbO_2$.

The primary battery is a convenient, relatively inexpensive power source for portable electronics, lighting, toys and many other applications. The general advantages of primary batteries are good shelf life, high energy density, little (if any) maintenance and ease of use. Secondary batteries offer rechargeability, high power densities, high discharge rates, flat discharge curves, and good low temperature performance. Their charge retention is poorer than most primary batteries, although any lost capacity is readily restored by recharging.

A special type of primary battery is the reserve battery where a key component is separated from the rest of the battery until the battery is activated. Chemical deterioration or self-discharge is thereby essentially eliminated, and the battery is capable of long-term storage [1]. The electrolyte is usually the component that is isolated. In other systems, such as thermal batteries, the battery is inactive until it is heated to melt a solid electrolyte, which then becomes ionically conductive. The reserve battery design is used to meet extremely long or environmentally severe storage requirements.

Thermal batteries, for example, are used to deliver high power for short periods of time in missiles, torpedoes, and other weapon systems [1].

Lithium metal is very attractive as a battery anode material because of its light weight, high voltage, and good conductivity. Because of these outstanding features, the use of lithium in both primary and secondary batteries has greatly increased since 1980.

II. PRIMARY LITHIUM BATTERIES

The reactivity of lithium metal in aqueous solutions requires the use of non-aqueous electrolytes for lithium batteries. Polar organic liquids are the most common electrolyte solvents such as propylene carbonate (PC), ethylene carbonate (EC), acetonitrile (AN), and dimethylsulfoxide (DMSO).

An interesting twist for primary lithium batteries is the use of inorganic solvents such as thionyl chloride (SOCl_2) and sulfuryl chloride (SO_2Cl_2) as both the electrolyte solvent and the active cathode material. This is possible because a passivating film forms on the lithium surface which protects it from further reaction. The passivating layer conducts lithium ions and is often referred to as the Solid Electrolyte Interphase or SEI. This SEI formation is actually present in many battery systems and is an important factor in the performance [2]. It is now well established that in lithium batteries, the anode is always covered by a SEI passivating layer [2].

The lithium/thionyl chloride (Li/SOCl_2) system has one of the highest cell voltages (3.6 V) and energy density of any battery system. Energy densities of about 500 Wh/kg and 900 Wh/dm³ (1 dm³ = 1000 cm³ = 61.0 in³) have been achieved with low rate cells [1]. The basic reactions in the Li/SOCl_2 battery are given in Table 1. The thionyl

chloride system originally suffered from a chemical instability that led to an explosion hazard as well as a voltage delay due to the protective LiCl film on the anode. Most of these problems have been resolved, and Li/SOCl_2 cells have been fabricated in a variety of sizes, shapes, and designs. Low-rate cells are used commercially for memory backup and other applications requiring a long operating life. Wide application in consumer-orientated products is still limited because of the relatively high cost and lingering concerns with the safety and handling of Li/SOCl_2 batteries. The higher-rate Li/SOCl_2 batteries are used mainly in military applications where high energy density is needed to fulfill important mission requirements. The $\text{Li}/\text{SO}_2\text{Cl}_2$ system is not as widely used as the Li/SOCl_2 system because of a cell voltage that is sensitive to temperature variations, a lower capacity at low temperatures, and a higher self-discharge rate [1]. A related system is the lithium/sulfur dioxide (Li/SO_2) primary battery that is used mainly in military applications. This system has an energy density up to 280 Wh/kg. The Li/SO_2 cell is especially noted for its capability to handle high current or high power requirements and for its excellent low-temperature performance [1].

Thermal batteries were developed in the early 1940s by German scientists and are used mainly for weapon applications. Thermal batteries are primary reserve batteries that employ inorganic salt electrolytes which are nonconductive solids until the system is activated by suddenly supplying sufficient thermal energy to melt the electrolyte. The shelf life of an unactivated thermal battery is 10 years or longer because there is no self-discharge, thus no maintenance is required. The characteristics of thermal batteries make them ideally suited for missiles, bombs, torpedoes and many other military operations [1]. The high operating temperatures of molten salt electrolytes provide high peak-power densities for thermal batteries that exceed 10,000 W/dm³ [1].

Major changes in thermal battery technology are rare due mainly to the lack of any significant commercial applications. The German scientists used a calcium metal anode, a LiCl-KCl electrolyte (mp = 352°C), and a calcium chromate cathode, i.e., $\text{Ca}/\text{LiCl-KCl}/\text{CaCrO}_4$. This remained the main thermal battery design until 1980 when lithium or lithium-alloy anodes were introduced along with the iron disulfide cathode. This $\text{Li}/\text{LiCl-KCl}/\text{FeS}_2$ thermal battery system has not changed significantly

Table 1. Features of the Lithium-Thionyl Chloride Battery

$\text{Li} / \text{SOCl}_2$ (E = 3.6 V)
Anode Reaction:
$4 \text{Li} + 4\text{Cl}^- \rightarrow 4 \text{LiCl} + 4\text{e}^-$
Cathode Reaction:
$2 \text{SOCl}_2 + 4\text{e}^- \rightarrow \text{S} + \text{SO}_2 + 4\text{Cl}^-$
Cell Reaction:
$4 \text{Li} + 2 \text{SOCl}_2 \rightarrow 4 \text{LiCl} + \text{S} + \text{SO}_2$

over the past 21 years. Disadvantages of this thermal battery system include a low cell voltage (2.0 V), a low energy density (44 Wh/kg), and a high operating temperature (450-600°C). A new molten nitrate electrolyte system for thermal batteries has been developed at China Lake [3]. The $\text{LiNO}_3\text{-KNO}_3$ electrolyte (mp = 124°C) along with new cathode materials offers high cell voltages (3 V or higher), higher energy densities (100 Wh/kg), and lower operating temperatures (200-350°C). Prototypes of this new thermal battery system have been investigated for possible missile defense applications [4]. Completely new thermal battery concepts are being explored at China Lake including the use of a solid polymer electrolyte for the conduction of lithium ions at high temperatures (200-350°C). Another concept is the use of LiOH-KOH (mp = 210°C) as the electrolyte. The use of new electrolyte systems is a neglected area of thermal battery research.

Another example of a lithium primary battery is the lithium/iodine cell that is widely used in medical applications such as cardiac pacemakers [1]. Lithium and iodine are consumed, and their reaction product, LiI , serves as the cell separator and electrolyte. This battery represented by Li/LiI/I_2 is an example of a solid-electrolyte system. Modern pacemakers using this system can be made as thin as 6 mm. Practical energy densities approaching 1000 Wh/dm³ can be obtained at low discharge rates. Attractive features of the Li/LiI/I_2 batteries are high reliability, low self-discharge, and no gassing during discharge.

III. SECONDARY LITHIUM BATTERIES

In the past, the secondary or rechargeable battery market has been dominated by the sale of lead-acid batteries and nickel-cadmium batteries. The nickel-cadmium battery consists of a cadmium anode, a potassium hydroxide aqueous electrolyte, and a nickel oxyhydroxide cathode, i.e., Cd/KOH/NiOOH . The nickel-metal hydride battery (M(H)/KOH/NiOOH) has gained a significant share of the market in the past 10 years [5]. The nickel-cadmium battery is known for a memory effect described as an apparent reduction in cell capacity resulting from highly repetitive patterns of use. There has been considerable discussion about the cause of this memory effect. However, the memory effect is also observed in nickel-metal hydride batteries. Therefore, it may be concluded that the cause of the

memory effect is the NiOOH cathode material used in both battery systems [6].

It has been a difficult struggle to develop a commercial secondary battery that uses metallic lithium. The electroplating of lithium during recharge forms a porous deposit with a larger surface area than the original metal. Every time the lithium is replated during charge, the surface area increases and a new lithium surface is exposed and then passivated with a new SEI film, consuming lithium. In order to obtain a reasonable cycle life, a fivefold excess of lithium may be required [1].

The introduction of the lithium-ion battery by Sony in 1990 solved the various problems and gave a dramatic improvement in rechargeable battery technology. Today, the sale of lithium-ion systems dominates the rechargeable battery market [5]. The basic features of the lithium-ion secondary battery are given in Table 2. The main improvements for the lithium-ion battery are that this system permits many charge-discharge cycles, has no memory effect, produces high cell voltages (4 V), and high energy density (150 Wh/kg or 300 Wh/dm³). Thus, lithium-ion battery packs for portable electronics are significantly smaller than for other rechargeable battery systems.

Table 2. Features of the Lithium-Ion Battery

Li(C)/LiPF_6 , Organic (EC)/ $\text{Li}_{(1-x)}\text{CoO}_2$ ($E = 4.0 \text{ V}$)
Anode Reaction:
$x \text{ Li(C)} \rightarrow x \text{ Li}^+ + x e^-$
Cathode Reaction:
$\text{Li}_{(1-x)}\text{CoO}_2 + x \text{ Li}^+ + x e^- \rightarrow \text{LiCoO}_2$
Cell Reaction:
$x \text{ Li(C)} + \text{Li}_{(1-x)}\text{CoO}_2 \rightarrow \text{LiCoO}_2$

In the lithium-ion system, carbon materials which can reversibly accept and donate significant amounts of lithium ($\text{Li:C} = 1:6$) are used for the anode, Li(C) , instead of metallic lithium [1]. The carbon host protects the lithium, and the lithium intercalation during charge and discharge is nearly 100% reversible. Intercalation compounds consisting of transition metal oxides such as LiCoO_2 are the most suitable cathode materials for lithium-ion batteries. Lithium ions are inserted interstitially into the host lattice during discharge and subsequently extracted during recharge with little or no structural modification of the LiCoO_2 [1]. In effect, lithium ions move from the anode to the cathode during the battery discharge and then reverse their direction

during recharging. The concept of lithium ions moving back and forth has led to the name of "rocking-chair" for the lithium-ion battery.

IV. FUTURE OUTLOOK

The theoretical energy density of any battery system can be calculated from the thermodynamics of the cell reaction and the quantity of electricity (coulombs) obtained from the active materials (anode and cathode). This, however, neglects the weight due to the electrolyte, the battery case, and all other battery components. The theoretical and actual experimental energy densities of various battery systems are present in Table 3. It is readily apparent from Table 3 that the lithium battery systems offer

Table 3. Theoretical and Practical Energy Densities of Various Battery Systems.

System	Theoretical (Wh/kg)	Practical Wh/kg	Wh/dm ³	Percent of Theoretical
*Pb/H ₂ SO ₄ /PbO ₂ (Lead-Acid)	170	35	90	21%
*Cd/KOH/NiOOH (Nickel-Cadmium)	209	50	90	24%
Zn/KOH/MnO ₂ (Alkaline)	336	65	135	19%
*MH/KOH/NiOOH (Nickel-Metal Hydride)	380	60	80	16%
Li/LiCl-KCl/FeS ₂ (Thermal)	490	44	90	9%
*Li(C)/EC/ Li _(1-x) CoO ₂ (Lithium-Ion)	525	150	220	29%
Li/LiI/I ₂ (Pacemaker)	560	250	1000	45%
Li/SO ₂ (Sulfur Dioxide)	1120	280	440	25%
Li/SOCl ₂ (Thionyl Chloride)	1480	500	900	34%

* Secondary (rechargeable) batteries

the highest theoretical energy density as well as the highest actual energy densities. Furthermore, the percent of the theoretical energy density actually obtained is significantly higher for the lithium battery systems except for the thermal battery that requires added pyrotechnic materials and insulation. It is expected that most future improvements in battery technology will involve lithium batteries. Nevertheless, considerable progress continues to be made that involves the improvement of older battery

technologies such as the lead-acid battery where energy densities of 45 to 55 Wh/kg are projected [6]. Significant improvements in the neglected area of thermal batteries can also be expected [3,4].

The new technology of lithium-ion batteries will continue to improve. There are prospects of increasing the energy density of lithium-ion batteries to perhaps 200 to 250 Wh/kg [7]. This will likely involve the use of new cathode materials, light weight construction, and new anode and electrolyte development [7]. Perhaps the next major improvement in lithium battery technology will be the use of solid polymer electrolytes that transport lithium ions. This would provide a truly all-solid-state battery.

The use of lithium batteries for electric vehicles is expected to increase, but the cost needs to be reduced significantly. The gasoline engine, however, remains a formidable competitor because it offers 3000 Wh/kg of gasoline. A battery replacement for the gasoline engine would require a 10-fold weight increase. Hybrids involving batteries, fuel cells, as well as the gasoline engine are more likely to meet the automotive need.

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