Overview of battery systems

1

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Contents

1.1 Introduction

Electrochemical storage systems will increasingly gain in importance in the future. This is true for the energy supply of computers and mobile phones that are becoming more and more sophisticated and smaller. It is also true for power tools and electric vehicles as well as, on a larger scale, for stationary storage of renewable energy. This Chapter will provide an overview of today's most common electrochemical storage systems. It will discuss two primary systems, which in general cannot be recharged, or only in limited fashion. Among other things, problems

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of rechargeability are discussed, using the example of the anode materials zinc (for aqueous electrolytes) and lithium (for non-aqueous electrolytes). In terms of rechargeable systems, the whole spectrum from lead-acid batteries to rechargeable nickel-based or sodium-based batteries to lithium-ion batteries is covered. Redox flow-batteries also are discussed, as are electric double-layer capacitors. This will enable the reader to gain an insight into lithium-ion technology's competing and complementary technologies. The latter will be presented in other chapters of this book.

1.2 Primary systems

1.2.1 Cells with zinc anodes

One of the first cells of technical importance was the Leclanché cell (1866), which supplied railroad telegraphs and electric bells with electricity.

As with the current advanced zinc-carbon and alkaline cells, its anode material was metallic zinc. One reason for the employment of zinc is its high specific charge of 820 Ah/kg and, for employment in aqueous electrolytes, the high negative voltage of – 0.76 V vs. a standard hydrogen electrode (SHE). If combined with a manganese dioxide (MnO_2) cathode, a cell voltage of 1.5 V is achieved. The internal resistance of these cells, which are mainly used as device batteries, causes a low current capability.

The high specific charge of zinc is also advantageous in zinc-air cells, usually employed in hearing aids. In combination with diffusing oxygen from the air it enables the production of cells with high energy densities of more than 450 Wh/kg.

Unfortunately, these cells exhibit a limited electrochemical rechargeability. The reason is the morphologically poor plating ability of zinc. In spite of intensive research it was not possible to improve the dendritic precipitations of zinc. The Electric Fuel Corp. tried a different approach, namely to substitute the used anodes with new ones. These cells were employed in the nineties during a fleet test of the Deutsche Post (German postal service).

1.2.2 Cells with lithium anodes

Lithium is the perfect material for anodes: It is a very light element and has a specific charge of 3,862 Ah/kg. In addition to that, it features an extremely negative redox potential of – 3.05 V vs. SHE. Specific energies of more than 600 Wh/kg are achievable. However, aqueous electrolytes cannot be used due to the high reducing power of lithium. The electrolytes must be based on organic solvents. In most commercial lithium-metal batteries the cathode consists of manganese dioxide. This enables voltages of more than 3 V. Such cells are used in cameras and watches, for example. Cells with other cathode materials, e.g., thionyl chloride or sulfur dioxide, are employed in electronic energy meters and heat cost allocators as well as in medicine and the military. Since a few years, a new system has found its way into photography applications as a high-quality and powerful replacement for alkaline manganese cells. This system features cathodes made of iron sulfide (FeS_2) and a voltage of 1.5 V, which is similar to that of regular alkaline batteries.

Usually, metallic lithium cells are considered to be non-rechargeable, since the morphology of the electrochemically plated lithium is unsuitable for charging and discharging processes. Dendritic growth of the lithium precipitations through the separator might be induced, causing short circuits with the cathode and subsequent fires. At the end of the eighties, a recall of such problematic rechargeable lithium-metal batteries had to be undertaken by Moli Energy. Since then, the professional world has been skeptical toward this technology.

In spite of that, the French company Bolloré successfully uses lithium-metal polymer systems in more than 3,500 vehicles on the street. Their rechargeable batteries with capacities of 30 kWh exhibit a metallic lithium anode, a polymer electrolyte made of polyethylene oxide (PEO) that prevents dendritic growth.

1.3 Secondary systems

1.3.1 Lead-acid battery

The lead-acid battery is the oldest rechargeable storage system among the systems that are technically relevant today. First investigated in the middle of the 19th century, it has been continually developed all the way to today's valve-regulated lead-acid batteries (VRLA). The active materials of the lead-acid battery are lead and lead oxide (PbO_2) on parallel grid plates. The electrolyte is aqueous sulfuric acid. Its cell voltage of more than 2 V is quite high for an aqueous system. In the newest developments the battery is a closed-system, maintenance-free battery with a fixed electrolyte. In lead-acid gel batteries the electrolyte is gelled by means of adding silica (SiO_2). In absorbent glass mat (AMG) batteries it is physically bound in glass mats.

Due to the high weight of lead (equivalent to 259 Ah/kg), only 30 to 40 Wh/kg are achievable. Although the cycling stability for complete cycles (state of charge 0 to 100 %) is low, it is still possible to charge the lead-acid battery with high currents for short periods of time. This is used in the application as a starter battery in automobiles. The sulfation of the lead into electrically non-conductive lead sulfate ($PbSO_4$) with large particles that occurs as a reaction product on both the anode and the cathode raises the internal resistance. This leads to a deterioration of the battery. The lead-acid battery still has a share of more than 90 % in the battery market. This is due to the low production costs (material, technology) and the high recyclability.

1.3.2 Nickel-cadmium and nickel metal hydride batteries

Nickel-based rechargeable batteries were first developed around 1900: nickel-iron batteries by T. Edison and nickel-cadmium batteries by W. Jungner. The cathode material of both types of batteries is nickel oxide hydroxide (NiO[OH]). The electrolyte is 20 % caustic potash. While the nickel-iron battery never really took off, the rechargeable nickel-cadmium battery was developed into an extremely powerful system. Cadmium demonstrates a high specific charge of 477 Ah/kg and a cell voltage of 1.2 V. Based on these values, specific energies of 60 Wh/kg are reachable. Recent rechargeable batteries are produced using winding technology with active materials on thin current collector foils or lattices. They show a very high current capability and outstanding low-temperature characteristics, even up to – 40 °C.

Due to EU regulations for the usage of cadmium, it is only allowed in medical and safety-relevant applications, also in power tools with high power requirements.

In 1990, Sanyo commercialized the nickel metal hydride batteries. The cadmium was substituted by a hydrogen storage alloy made of nickel and noble earths. It has been possible to triple the specific energy of the cells since their introduction, to 80 Wh/kg. Both nickel-based battery systems feature an internal chemical overcharging and overdischarging protection. They are therefore suitable for battery packs without sophisticated electronics. Consumer electronics has since seen a squeezing out of the nickel metal hydride batteries by the lithium-ion batteries. Now, most nickel metal hydride batteries are used in hybrid vehicles.

1.3.3 Sodium-sulfur and sodium nickel chloride batteries

Both are battery systems for application at high temperatures of 250 to 300 °C. Sodium has a very high specific charge of 1,168 Ah/kg and a very negative voltage curve (– 2.71 V vs. SHE), which is perfect for an anode.

The cathode material of the sodium-sulfur battery is sulfur. Therefore, both electrode materials are liquid at operating temperature. The separator is a solid ceramic made of aluminum oxide (sodium-β-aluminate), which is sodium ion-conductive. At 300 °C, this ceramic exhibits a conductivity for sodium ions that is similar to that of aqueous electrolytes. The nominal voltage of the cells differs in relation to the state of charge due to the formation of various sodium sulfides as reaction products. It lies between 1.78 and 2.08 V, while the specific energy reaches 200 Wh/kg. One advantage of the production of this battery type is the low price of the materials. The high operating temperatures and the subsequent thermal losses correspond to a self-discharging of the battery. This is why it ideally is used as large stationary energy storage system in the MW range. This technology was used in cars in the nineties, e.g., in the BMW E1 and the Ford Ecostar EV.

The sodium nickel chloride battery (“ZEBRA battery”) is a safer variant of sodium batteries since it demonstrates a (limited) tolerance toward overcharging and overdischarging, among other things. Its design is similar to that of the sodium-sulfur battery with an aluminum-oxide ceramic that is sodium ion-conductive. The cathode however consists of a porous nickel matrix as current collector with nickel chloride ($NiCl_2$). The nickel chloride is impregnated with sodium chloroaluminate ($NaAlCl_4$), which functions as a second electrolyte in the form of a molten salt at 250 °C. The specific energy of the cells is around 120 Wh/kg for a nominal voltage between 2.3 and 2.6 V. Its inverse structure (liquid sodium on the outside) is advantageous when compared to the sodium-sulfur battery. It enables the usage of low-cost rectangular steel housings instead of nickel housings. Assembly is facilitated by the fact that it is possible to insert the battery materials in an uncharged state as sodium chloride and nickel. Therefore, the charged active materials are not generated until the first charging cycle.

The sodium nickel chloride batteries are used in short runs of electric vehicles and in special applications. Examples: The first specimens of the Smart ForTwo electric drive were equipped with batteries made by FIAMM SoNick.

1.3.4 Redox-flow batteries

Redox-flow batteries are related to fuel cells in that both electroactive components (for the anode and cathode reaction) are fed into an electrochemical vessel (cell stack) for the reaction from two outside holding tanks. This results in an enormous advantage of redox-flow batteries: It is possible to scale energy content (size of the tanks) and power (size of the vessel) independently of each other. Vanadium-redox batteries (VRB) are of practical use. This technology uses the dissolved vanadium salts as active materials in varying oxidation states. The anodic and cathodic regions are isolated from each other by a separator. This separator is impermeable to electrolytes and is made of a proton-conducting plastic foil, e.g., Nafion®. Contrary to fuel cells it is possible to electrochemically regenerate the "consumed" active material solutions in the vessel. The specific energies are relatively low at around 10 Wh/kg. This is caused by the aqueous, diluted vanadium salt solutions and the elaborate system technology. Therefore, these batteries are currently restricted to usage in the stationary energy storage area.

1.3.5 Electric double-layer capacitors

Electric double-layer capacitors (or "Supercaps", according to their NEC brand name) are similar in structure to standard batteries: The electrodes are made of metallic current collector foils that are coated with particles and separated by a thin electrolyte-soaked separator. However, the charge storage is not achieved by chemical redox reactions like in batteries. It is rather accomplished by means of an electrostatic separation of charge at the electrochemical double a layer between the particles and the electrolyte. Highly porous active carbons with a large specific surface are employed to attain larger surfaces. Also, organic electrolytes such as acetonitrile and suitable conducting salts are employed. They enable higher voltages with subsequent higher specific energies than those of aqueous electrolytes, up to the 5 Wh/kg range. Due to their manner of storage the electric double-layer capacitors achieve a high cycle number of around 1 million. This is the main advantage of this system. Another one is the very high power densities of more than 20 kW/kg. This enables charging and discharge times of less than 20 seconds. They are used for instance in wind turbines, where they power the off-grid blade angle control, and for the boosting/recuperation of railway vehicles, saving around 30 % energy.

1.3.6 Lithium-ion batteries

Above, I mentioned the critical deposition of metallic lithium. In order to prevent this, intercalation compounds of lithium as anode materials were developed in the eighties. Using this technology should result in zero metallic lithium. Instead, lithium ions are charge carriers in the electrolyte and act as counterions to compensate the electrical current flow through the consumer load. The lithium ion is very small, allowing for a multitude of intercalation compounds, which exhibit electrochemical potentials from almost – 3 V to more than 2 V vs. SHE. Intercalation compounds in the lower voltage range are suitable for anodes, graphite or lithium alloys with silicon and tin, for instance. Compounds of lithium with carbon, idealized as lithium graphite (LiC_6), have a specific charge of 372 Ah/kg at a voltage of – 2.9 V vs. SHE. However, due to the fact that these are employed in unlithiated form (as opposed to the lithium-metal battery, the lithium-ion battery is assembled uncharged), the challenge arose to find a cathode material that already contained the necessary lithium: $LiCoO_2$ with 137 Ah/kg and 0.8 V vs. SHE. This material and a compatible electrolyte made of organic carbonates and lithium hexafluorophosphate ($LiPF_6$) were the components for the first lithium-ion battery with an average voltage of around 3.6 V. SONY commercialized the lithium-ion battery in 1991. This was the advent of that system for consumer applications and portable PCs and it took a decade to squeeze out the standard nickel metal hydride technology. The energy density up to 250 Wh/kg for high-energy consumer cells and the possible several hundred cycles have made the lithium-ion battery the undisputed champion. Only with this technology was it possible to achieve the current proliferation of smartphones and tablets. In the beginning of their development, the power density of these high-energy cells was considerably inferior to that of, particularly, nickel-cadmium batteries. This is the reason why they only have been employed in high-power devices such as power tools from 2005 on. Hybrid vehicles, especially plug-in hybrid vehicles, have seen a considerable increase in the use of these systems recently, as well. In the meantime, prototypes are being developed for their employment as stationary energy storage systems to stabilize the grid voltage or to store the fluctuating renewable energies' electricity.

1.4 Outlook

This overview of the varying current technically relevant storage systems has examined the different characteristics of rechargeable batteries based on lead, nickel, and sodium, of redox-flow batteries as well as electric double-layer capacitors. It has also given a short introduction to lithium-ion batteries.

Lithium-ion batteries will eventually satisfy most requirements thanks to their versatility and will, in part, replace some of the established battery systems. Apart from evolutionary improvements will new developments, especially those based on lithium-sulfur batteries and possibly (in the long run) those based on lithium-air batteries, fulfill the increasingly demanding consumer wishes with their very high energy densities.

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