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ELECTROCHEMICAL ENERGY STORAGE

(Prepared for <u>Encyclopedia</u> <u>of</u> <u>Physics</u>)

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I. INTRODUCTION

Energy storage is important in alleviating discrepancies between energy supply and energy demand. These discrepancies may be either temporal or spatial, or both. Energy storage is already being used in many applications, varying in size from a few milliwatt-hours (e.g., electric watches and calculators) to many gigawatt-hours (pumped hydro-electric storage). Energy may be stored in many ways, including storage as potential energy in the earth's gravitational field (raising a weight), kinetic energy (a spinning flywheel), thermal energy (heating a substance), chemical energy (carrying out a reversible chemical reaction), or electrochemical energy (carrying out a reversible electrochemical reaction). This article deals with the storage of energy by means of electrochemical reactions which can be carried out in both forward and reverse directions. The devices which provide this capability are called rechargeable (or secondary[*]) electrochemical cells. Cells may be connected in series and/or parallel to form arrays called batteries[**].

There are many current applications for electrochemical energy storage devices, varying from aerospace (batteries for satellites' on-board power, recharged by solar cells; starting batteries for aircraft) to military (communications equipment, torpedoes, submarines) to industrial (electric fork-lift trucks, other electric vehicles) to consumer (battery-powered appliances, automobile batteries). Future applications that are providing incentive for

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[*]Primary electrochemical cells are based upon reactions that cannot be reversed; the cells are discarded after a single discharge.

[**]Often the term battery is misused in place of cell.

current research and development include energy storage for electric utility systems (megawatt hours), for solar and wind-powered electric systems (kilowatt hours to megawatt hours), and for electric vehicles (tens of kilowatt hours).

The charateristics of rechargeable batteries that are important in many applications include the specific energy (energy stored per unit battery mass, Wh/kg), the specific power (power delivered per unit battery mass, W/kg), the cycle life (number of discharge-charge cycles before failure), the lifetime (time to failure), and the cost (usually expressed as $/kWh of energy storage capability). Of course, it is desirable to have batteries of high performance, long life, and low cost. The scientific implications of these goals are shown in Table 1.

There are a number of fundamental characteristics that enable the achievement of the goals of Table 1. The desired characteristics for each of the three essential parts of a cell (the negative electrode, the positive electrode, and the electrolyte) are listed in Table 2. A large electronegativity difference between the reactants, and small equivalent weights yield a high theoretical specific energy for a cell:

$$\text{Theoretical specific energy} = \frac{-\Delta G}{\Sigma \gamma_i M_i}$$

where γ_i is the number of moles of reactant i, M_i is the molecular weight of reactant i, and ΔG is the Gibbs free energy change for the overall cell reaction. The theoretical specific energy is a useful guide in the selection of cells for applications in which high specific energy is important (e.g., mobile uses). For cells with solid reactants, it can be expected that 20-25% of the theoretical specific energy will be obtained from well-designed cells. A plot of the theoretical specific energy for a number of cells is shown in Figure 1.

A careful examination of Figure 1 reveals that the cells with the highest theoretical specific energy generally involve reactants that are not stable in contact with an aqueous electrolyte (Li, Na), whereas those of lower specific energy are compatible with aqueous electrolytes (Pb, Cd, Fe, NiOOH, etc.). This feature results in the subdivision of rechargeable cells into two major

categories: those with aqueous electrolytes, which operate at ambient temperature, and those with non-aqueous electrolytes, most of which operate at high temperatures (for reasons given below).

II. AMBIENT-TEMPERATURE RECHARGEABLE CELLS

Rechargeable cells that operate at ambient temperature in almost all cases make use of aqueous electrolytes. The use of aqueous electrolytes limits the choice of electrode materials to those that do not react with the water in the electrolyte at an unacceptably high rate. This consideration eliminates the alkali metals (e.g., Li, Na, K) and the alkaline earth metals (e.g., Mg, Ca, Ba) from consideration, even though they have low electronegativities and low equivalent weights, and other desirable properties called for in Table 2. Those materials that are sufficiently stable with aqueous electrolytes, have acceptably low electronegativities, take part in electrochemical reactions that can be reversed, and have other desirable properties as negative electrodes include: Pb, Cd, Fe, and Zn. The elements that have high electronegativities are in groups V, VI, and VII of the periodic chart of the elements. These have been used as elements (e.g., Cl_2, Br_2) or as compounds (metal oxides such as PbO_2, $NiOOH$, AgO) in positive electrodes.

The lists of negative and positive electrode reactants given above can be used to select pairs of electrodes to make cells, along with suitable electrolytes. Aqueous electrolytes are usually strongly acidic (e.g., H_2SO_4) or strongly alkaline (e.g., KOH) in order to maximize the electrolytic conductivity, which contributes to achieving a low cell resistance and therefore a high specific power capability. The cells that are currently available, or are under development include $Pb/H_2SO_4/PbO_2$, $Cd/KOH/NiOOH$, $Fe/KOH/NiOOH$, $Zn/KOH/NiOOH$, $Cd/KOH/AgO$, $Zn/KOH/AgO$, $Zn/ZnBr_2-KCl/Br_2$, $Zn/ZnCl_2/Cl_2$.

The Pb/PbO_2 cell is the most wide-spread and least expensive of all those currently available. Its most common use is for starting, lighting, and ignition purposes in automobiles. The automobile battery stores almost 1 kWh. With about 10^8 automobiles in the U.S., nearly 10^8 kWh of energy is stored in these batteries. For electric vehicle applications, the specific energy of Pb/PbO_2 at 25-40 Wh/kg is too low -- 70 Wh/kg is needed for an urban driving range of 150 km (a common goal). For electric utility energy storage, the cost of Pb/PbO_2 (~\$100/kWh) is too high, and the cycle life is too low.

The Cd/NiOOH cell, with its very long cycle life and ruggedness has found various military and aerospace applications that do not require storage of much energy (there is a limited supply of Cd, and it has a high cost). A significant consumer market for use in small battery-powered appliances has also developed.

The Fe/NiOOH cell, also known as the Edison cell, has disappeared from the marketplace, largely because of its high cost. There are now efforts to develop a lighter-weight, lower-cost Fe/NiOOH cell for electric vehicle propulsion, but its modest specific energy of 40-50 Wh/kg, and its low efficiency (~60%) limit its applicability for electric automobiles or stationary energy storage.

The Zn/NiOOH cell has a very attractive specific energy of 70-75 Wh/kg, but the short cycle life of the Zn electrode (<300 cycles) has prevented it from achieving wide application. Research and development efforts aimed at improving the Zn electrode continue.

The Cd/AgO and Zn/AgO cells offer higher specific energy than their NiOOH counterparts, but the high cost of Ag limits them to military, aerospace, and specialty applications usually requiring the storage of small amounts of energy.

In recent years, Zn/halogen systems with flowing electrolyte plus reactant streams have been under development. These systems may be of acceptably low cost (less than \$100/kWh) because they rely heavily on such inexpensive materials as carbon and polymers. The specific energies are in an intermediate range (about 60 Wh/kg for Zn/Br_2 and 70 Wh/kg for Zn/Cl_2). The safe storage of halogens is an important issue for these systems. Chlorine is stored as an ice-like material $Cl_2 \cdot 8H_2O$ at temperatures below 9°C. Bromine is stored as a chemical complex formed from quaternary ammonium organic salts. This complex is a dense, oil-like liquid which spontaneously separates from the electrolyte. These Zn/halogen flow batteries are more complex than other batteries, and probably will not be acceptable for mobile applications if alternative batteries of similar specific energy are available. Stationary applications are good possibilities, especially if efficiencies above 70% are achieved.

There has been a great deal of research devoted to non-aqueous ambient-temperature rechargeable cells, especially those using Li electrodes, with the hope of achieving 100-200 Wh/kg. This has been a difficult research area because all of the electrolytes investigated have been thermodynamically unstable in contact with lithium. Consequently, the lithium electrode has not been capable of being recharged very many times before failure, and there have been some explosions resulting from rapid reactions of lithium with the electrolyte. In addition, only a few candidate positive-electrode materials have shown the ability to be recharged repeatedly. One of these is TiS_2, a layered crystal that permits the entry of Li atoms between its crystal planes. Research continues on rechargeable, ambient-temperature lithium cells, but none are available yet.

III. HIGH-TEMPERATURE SYSTEMS

It has been found that the alkali metals, which promise high specific energy, can be used more readily at elevated temperatures than at ambient temperature. This is the case because elevated-temperature operation permits the use of stable molten-salt or ceramic electrolytes which have high conductivities for alkali metal cations. For various chemical reasons, molten salt electrolytes are used with the lithium electrode, and ceramic electrolytes are used with the sodium electrode. The positive electrodes are sulfur or compounds containing sulfur. These cells operate at 350-475°C, and large batteries would be kept at operating temperature by means of efficient thermal insulation to contain the heat produced by the battery in its normal operation.

An example of the molten-salt cells is the $Li_4Si/LiCl-KCl/FeS_2$ cell. The compound Li_4Si is used instead of lithium because it is a light-weight solid, whereas Li is liquid at temperatures above 180°C, and is therefore difficult to control in the cell. The same is true for solid FeS_2 as compared to sulfur, which melts at 118°C. The LiCl-KCl eutectic electrolyte melts at 352°C, and the cell is operated at about 450°C. The theoretical specific energy of this cell is 960 Wh/kg, as shown in Figure 1. Practical values as high as 180 Wh/kg have been reported for single laboratory cells. Only a few small laboratory batteries have been built, but many large cells and some multi-kWh batteries of LiAl/LiCl-KCl/FeS cells have been demonstrated. This system is

quite similar to $Li_4Si/LiCl-KCl/FeS_2$, but it has a much lower specific energy (about 100 Wh/kg vs. 180-200 Wh/kg).

Molten-salt cells may find application for stationary energy storage, and for electric vehicles with high duty cycles, so that thermal cycling to ambient temperature is only infrequently required. In addition to high specific energy, these cells have inexpensive reactants. If the high-temperature corrosion problems can be overcome, molten-salt cells may be attractive.

The ceramic-electrolyte cells are best exemplified by the $Na/Na_2O \cdot 8Al_2O_3/S$ cell. The electrolyte is called beta alumina, and can conduct sodium ions in the crystallographic planes perpendicular to the C axis. The purity and crystal size of the electrolyte are critical to achieving long life and high performance. This cell operates at 350°C, and uses liquid Na and liquid S as the reactants. A graphite felt material serves to collect the current in the non-conductive sulfur. The electrolyte is used in a tube form, with one reactant inside, the other outside.

The ceramic electrolye is made from materials which are basically inexpensive, but the purity, quality control, and manufacturing conditions have made the process extremely expensive, and a major topic for continued development. The electrolyte should be strong, very dense (>97% of theoretical), of low resistivity (<10Ω-cm), have controlled crystal size and structure and be highly pure.

Thousands of single cells of various sizes up to 100-200 Ah have been tested, as well as several multi-kWh batteries, and one 75-100 kWh battery. With additional development of the electrolyte, work on sulfur corrosion, and cost reduction, the Na/S cell could find applications similar to those mentioned above for Li_4Si/FeS_2.

IV. SUMMARY AND OUTLOOK

The several rechargeable cells discussed above are listed with some of their important characteristics in Table 3. It is clear from this table that none of the systems presently meets the goals for the major energy storage applications of electric automobiles (>70 Wh/kg, >100 W/kg, >300 cycles,

<$100/kWh), or energy storage for electric utilities (>70% efficiency, 80 kWh/m^2 floor space, >2000 cycles, 10 years life, <$50/kWh). There are other applications that may be filled by the newer systems, once developed. Batteries are already ubiquitous for storage of small amounts of energy (less than a few kWh); they may expand their applicability to many MWh.

Suggested Additional Reading

E.J. Cairns, in Materials for Advanced Batteries, D.W. Murphy and J. Broadhead, eds., Plenum Publishing Corporation, New York (1982).

J.R. Birk, EPRI Journal, p. 6, October, 1981.

D.L. Douglas and J.R. Birk, in Annual Review of Energy, 5, 61 (1980).

F.R. Kalhammer, Scientific American, 241, No. 6, 56 (December, 1979).

E.J. Cairns, in Energy and Chemistry, R. Thompson, ed., Royal Society of Chemistry, London (1981).

E.J. Cairns and E.H. Hietbrink, in Comprehensive Treatise of Electrochemistry, V. 3, J.O'Bockris, B.E. Conway, E. Yeager, and R.E. White, eds., Plenum Publishing Corporation, New York, 1981, p. 421.

E.J. Cairns, ibid., p. 341.

E.J. Cairns, in Proceedings of the 3rd International Symposium on Molten Salts, G. Mamantov, M. Blander, and G.P. Smith, eds., The Electrochemical Society, Pennington, New Jersey, 1981, p. 138.

Table 1

General Goals for Batteries

	Implication
High Specific Energy	High cell voltage Low equivalent weight High utilization of active material
High Specific Power	High cell voltage Rapid reactions Rapid mass transport Low internal resistance
Long Life	Reversible reactions Low corrosion rates Negligible rates of side reactions
Low Cost	Inexpensive, plentiful materials Simple manufacturing processes High efficiency Little or no maintenance

Table 2

Desirable Characteristics of Systems for High-Performance Electrochemical Cells

Characteristic	Negative electrode reactant	Positive electrode reactant	Electrolyte
Electronegativity	Low (~1)	High (>1.5)	--
Equivalent weight (g/g-equiv.)	Low (<30)	Low (<30)	Low* (<30)
Conductivity (ohm^{-1} cm^{-1})	High (>10^4)	High (>10^4)	High (>1)
Electrochemical Reaction Rate (i_o, A/cm^2)	High (>10^3)	High (>10^3)	High (>10^3)
Solubility in electrolyte (mol %)	Low (<0.1)	Low (<0.1)	—
Mass transport rate (equiv./sec-cm^2)	High (>10^4)	High (>10^4)	High (>10^4)

* A more important criterion for the electrolyte is low density.

Table 3

Status of Some Rechargeable Batteries

Cell	Voltage	Theor. Wh/kg	Actual Wh/kg	Actual W/kg	Cycle Life	Cost $/kWh	Comments
Ambient Temperature							
$Pb/H_2SO_4/PbO_2$	2.1	175	25-41	50-100	300-800	100	Available now.
$Cd/KOH/NiOOH$	1.3	202	40-50	200+	500-2000	>100	Available; expensive.
$Fe/KOH/NiOOH$	1.4	267	40-50	100	500+	>100	Batteries on test; low efficiency.
$Zn/KOH/NiOOH$	1.7	326	60-75	150	100-300	>100	Cells and modules; short Zn life.
$Cd/KOH/AgO$	1.4-1.1	257	50-65	200+	500	≥100	Available, very expensive.
$Zn/KOH/AgO$	1.8-1.5	432	80-110	200+	100	≥100	Available, very expensive.
$Zn/ZnBr_2-KCl/Br_2$	1.8	323†	60	75	400+	**	Batteries on test; little life data; projected 35$/kWh.
$Zn/ZnCl_2/Cl_2·8H_2O$	2.1	405	66	70	1400*	**	Complex system; batteries on test.
High-Temperature							
$LiAl/LiCl-KCl/FeS$	1.3	458	60-100	60-100	300+	**	Small batteries on test.
$Li_4Si/LiCl-KCl/FeS_2$	1.8,1.3	944	120-180	100+	700	**	Single cell status.
$Na/Na_2O·8Al_2O_3/S$	2.0	758	100-160	60-130	250-1500	**	S corrosion problems; expensive ceramic; batteries on test.

*1 kWh system, with electrolyte maintenance.

**Too early to predict; not available now.

†Includes weight of complexing agent.
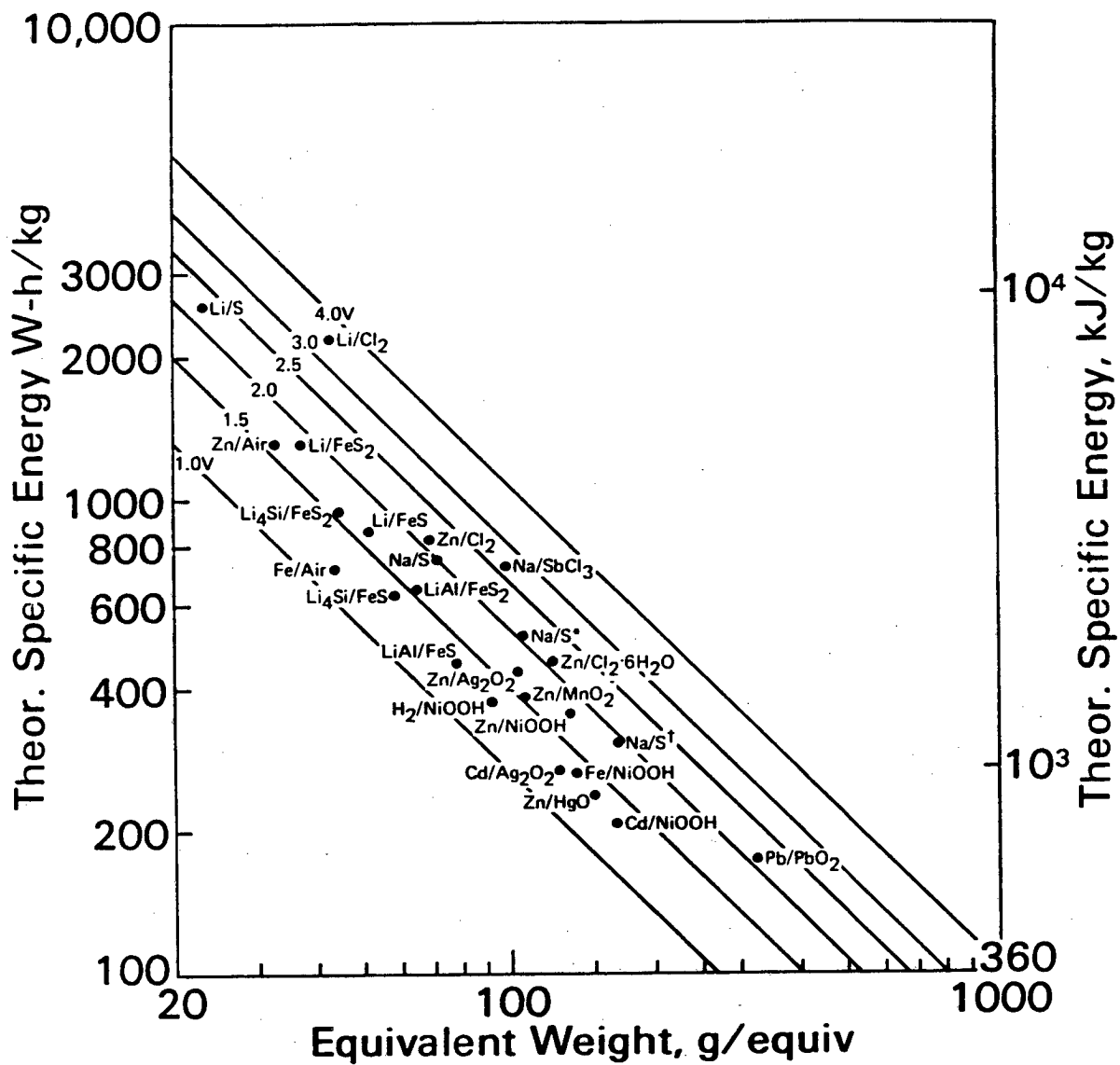
Figure 1. Theoretical specific energy of candidate cells. Lines are for cell voltages from 1V to 4V, as labeled.