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# **BATTERIES, OTHER SECONDARY CELLS**

The proliferation of portable electronic devices has fueled rapid market growth for the rechargeable battery industry. Miniaturization of electronics coupled with consumer demand for lightweight batteries providing ever longer run times continues to spur interest in advanced battery systems. Interest also continues to run strong in electric vehicles (EVs) and the large auto manufacturers continue to develop prototype EVs. It is clear that advances in battery technology are required for a widely acceptable EV. Advanced batteries continue to play a strong role in other applications such as load leveling for the electric utility industry and satellite power systems for aerospace.

The goal of advanced battery research is to develop batteries that supply a high number of watthours in a small volume (volumetric energy density) and at low weight (gravimetric energy density). Obviously this increase in energy density must be achieved in a manner that is manufacturable, safe, and of acceptable cost. There has been a significant growth in the number of advanced battery systems in development and several systems are either nearing commercial viability or have been introduced as commercial products in specific applications.

### 1. Ambient Temperature Lithium Systems

Traditionally, secondary battery systems have been based on aqueous electrolytes. Whereas these systems have excellent performance, the use of water imposes a fundamental limitation on battery voltage because of the electrolysis of water, either to hydrogen at cathodic potentials or to oxygen at anodic potentials. The application of nonaqueous electrolytes affords a significant advantage in terms of achievable battery voltages. By far the most actively researched field in nonaqueous battery systems has been the development of practical rechargeable lithium batteries (1). These are systems that are based on the use of lithium [7439-93-2] metal, Li, or a lithium alloy, as the negative electrode (see Lithium and lithium compounds).

The use of lithium as a negative electrode for secondary batteries offers a number of advantages (2). Lithium has the lowest equivalent weight of any metal and affords very negative electrode potentials when in equilibrium with solvated lithium ions resulting in very high theoretical energy densities for battery couples. These high theoretical energy densities have prompted a wealth of research activity in a wide variety of experimental battery systems. However, realization of the technology to commercialize these systems has been slow.

A key technical problem in developing practical lithium batteries has been poor cycle life attributable to the lithium electrode (3). The highly reactive nature of freshly plated lithium leads to reactions with electrolyte and impurities to form passivating films that electrically isolate the lithium metal (4). This isolation results in less than 100% current efficiency for cycling of the lithium electrode, hence limiting cycle life (5). A goal of research for practical rechargeable lithium systems has been to improve the cycling efficiency of the lithium electrode in aprotic electrolytes.

The choice of battery electrolyte is of paramount importance to achieving acceptable cycle life because of the high reducing power of the metallic lithium. The formation of surface films on the lithium electrode (6) imparts the apparent stability of the electrolyte to the electrode. It is critical to determining lithium cycling efficiency. In addition to providing a stable film in the presence of lithium, the electrolyte must satisfy additional requirements including good conductivity, being in the liquid range over the battery operating temperature, and electrochemical stability over a wide voltage range. Solubility of the electrolyte sult in the solvent system is important in achieving good conductivity (7). In order to satisfy the various electrolyte system requirements, the use of mixed solvent electrolytes (8) or ethylene carbonate [96-49-1],  $C_2H_4O_3$ , –propylene carbonate [108-32-7],  $C_4H_6O_3$ , mixed solvent systems (9). Typical electrolyte salts include lithium perchlorate [7791-03-9], LiClO<sub>4</sub>, lithium hexafluoroarsenate [29935-35-1], LiAsF<sub>6</sub>, or lithium tetrafluoroborate [14283-07-9], LiBF<sub>4</sub> (10). The progress in the development of liquid electrolyte systems that provide near 100% current efficiencies for cycling of lithium has played a critical role in the emergence of rechargeable lithium as a commercially viable technology.

A second class of important electrolytes for rechargeable lithium batteries are solid electrolytes. Of particular importance is the class known as solid polymer electrolytes (SPEs). SPEs are polymers capable of forming complexes with lithium salts to yield ionic conductivity. The best known of the SPEs are the lithium salt complexes of poly(ethylene oxide) [25322-68-3] (PEO),  $-(CH_2CH_2O)_n$ , and poly(propylene oxide) [25322-69-4] (PPO) (11–13). Whereas a number of experimental battery systems have been constructed using PEO and PPO electrolytes, these systems have not exhibited suitable conductivities at or near room temperature. Advances in the 1980s included a new class of SPE based on polyphosphazene complexes suggesting that room temperature SPE batteries may be achievable (14, 15).

The lithium or lithium alloy negative electrode systems employing a liquid electrolyte can be categorized as having either a solid positive electrode or a liquid positive electrode. Systems employing a solid electrolyte employ solid positive electrodes to provide a solid-state cell. Another class of lithium batteries are those based on conducting polymer electrodes. Several of these systems have reached advanced stages of development or initial commercialization such as the Seiko Bridgestone lithium polymer coin cell.

The most important rechargeable lithium batteries are those using a solid positive electrode within which the lithium ion is capable of intercalating. These intercalation, or insertion, electrodes function by allowing the interstitial introduction of the  $Li^+$  ion into a host lattice (16, 17). The general reaction can be represented by the equation:

$$x \operatorname{Li}^+ + x e^- + \operatorname{MY}_n \xrightarrow{\longrightarrow} \operatorname{Li}_x \operatorname{MY}_n$$

where  $MY_n$  represents a layered compound. A large number of inorganic compounds have been investigated for their ability to function as a reversible positive electrode in a lithium battery. Intercalation electrodes have found wide application in systems employing both liquid or solid electrolytes. The theoretical electrochemical characteristics of the most advanced of these electrode systems are described in Table 1.

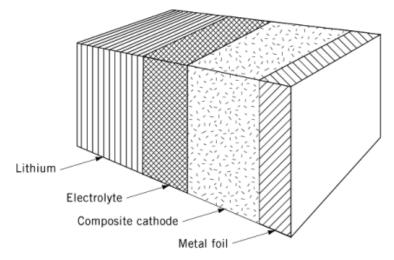
### 1.1. Solid Electrolyte Systems

Whereas there has been considerable research into the development of solid electrolyte batteries (18–21), development of practical batteries has been slow because of problems relating to the low conductivity of the solid electrolyte. The development of an all solid-state battery would offer significant advantages. Such a battery would overcome problems of electrolyte leakage, dendrite formation, and corrosion that can be encountered with liquid electrolytes.

The general configuration of one system that has reached an advanced stage of development (22) is shown in Figure 1. The negative electrode consists of thin lithium foil. The composite cathode is composed

	Operating voltage range, V	Energy density	
Battery couple		Wh/kg	Wh/L
Li–CoO <sub>2</sub>	4.4–2.5	766	2700
Li–MnO <sub>2</sub>	3.5 - 2.0	415	553
$Li-V_2O_5$	3.5 - 2.0	541	1304
Li–TiS <sub>2</sub>	2.6 - 1.6	473	1187
Li–NbSe <sub>3</sub>	2.1 - 1.5	436	1600
Li–MoS <sub>2</sub>	2.3–1.3	233	882

Table 1. Theoretical Energy Densities for Rechargeable Lithium Systems



**Fig. 1.** Configuration for a solid polymer electrolyte rechargeable lithium cell where the total thickness is 100  $\mu$ m.(Courtesy of Mead Corp.)

of vanadium oxide [12037-42-2],  $V_6O_{13}$ , mixed with polymer electrolyte. Demonstration batteries have been constructed having energy densities of 320Wh/L. A key to the technology is a unique radiation cross-linked polymer electrolyte which shows good conductivity at ambient temperatures (23).

A new all solid-state lithium battery employing a positive electrode comprised of organosulfur polymers,  $-(SRS)_n$ , has been reported (24). During discharge of the battery, current is produced by cleavage of the sulfur–sulfur bonds in the polymer, depolymerizing the polymer. On charge, the process is reversed and the disulfides are polymerized back to their original form. This use of a polymerization–depolymerization reaction for a battery electrode is unique and this electrode is expected to offer significantly improved rate capability over intercalation electrodes. The organosulfur electrodes provide excellent stability and reversibility, which should result in long cycle life. Cells constructed to date have employed a PEO electrolyte and hence require operation at elevated temperature (25).

#### 1.2. Coin and Button Cell Commercial Systems

Initial commercialization of rechargeable lithium technology has been through the introduction of coin or button cells. The earliest of these systems was the Li–C system commercialized by Matsushita Electric Industries (MEI) in 1985 (26, 27). The negative electrode consists of a lithium alloy and the positive electrode consists of activated carbon [7440-44-0], carbon black, and binder. The discharge curve is not flat, but rather slopes from

about 3 V to 1.5 V in a manner similar to a capacitor. Use of lithium alloy circumvents problems with cycle life, dendrite formation, and safety. However, the system suffers from generally low energy density.

More recently, commercial introduction of a rechargeable  $\text{Li}-V_2O_5$  coin cell having significantly higher energy density than the previous Li–C cell has been announced (28). This system employs a Li–Al alloy negative electrode coupled with a vanadium pentoxide [1314-62-1],  $V_2O_5$ , positive electrode. The cell voltage on discharge is 3 V. This cell is claimed to have twice the energy density of a conventional Ni–Cd cell (29).

A rechargeable coin cell that employs a lithium salt electrolyte but avoids the use of a metallic lithium negative electrode has been commercially introduced by Toshiba. This cell employs a material called linear-graphite hybrid (LGH) in lieu of a lithium electrode to avoid formation of lithium dendrites. LGH is synthesized by carbonizing organic aromatic polymers. The LGH electrode is coupled with an amorphous  $V_2O_5$  positive electrode to give a battery with a working voltage of 3 V to 1.5 V (30). A similar system employing pyrolytic carbon as a negative electrode has also been reported (31).

A significant development in commercial acceptance of rechargeable lithium was the introduction by Sanyo of rechargeable Li–MnO<sub>2</sub> coin and button batteries (32, 33). Manganese dioxide [1313-13-9] is an attractive positive electrode system because of its relatively high and flat discharge voltage and the low cost of MnO<sub>2</sub>. The widespread use of Li–MnO<sub>2</sub> primary batteries demonstrates the utility of this system. However, the rechargeability of the MnO<sub>2</sub> conventionally employed in primary cells was not sufficient to yield practical secondary cells. The breakthrough came in the modification of the crystal structure of the MnO<sub>2</sub> to improve rechargeability by a lithiation reaction (34). This modified MnO<sub>2</sub>, referred to as composite dimensional manganese oxide (CMDO), is coupled with a Li–Al alloy having special additives to give excellent cycle life and stress resistance to prevent cracking and blistering of the alloy during cycling (35).

#### 1.3. Advanced Systems

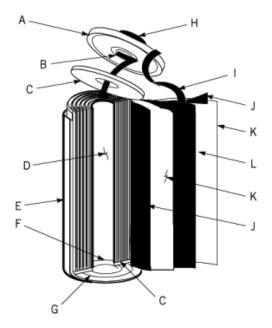
Applications for the coin and button secondary lithium cells is limited. However, researchers are working to develop practical "AA"-sized and larger cells. Several systems have reached advanced stages of development.

The first commercially available lithium "AA" cell was introduced in the early 1980s by Moli Energy Ltd. This cell, known as the Molicel, employs a molybdenum disulfide [1317-33-5], MoS<sub>2</sub>, positive electrode coupled with a pure Li negative one (36). The cell is constructed in a spirally wound configuration using a microporous separator (Fig. 2). The cells have an open circuit voltage of about 2.3 V when fully charged. The discharge curve slopes, with a midpoint voltage of 1.2 V when discharged. The sloping discharge curve allows indication of state of charge (37). Cell capacity is about 600 mA for "AA" cells. Cycle life was found to be strongly dependent on operating conditions including depth of discharge, recharge and discharge currents, and voltage limits on charge and discharge. However, cycle lives of 300 cycles or more were achieved under normal cycling conditions (38).

One of the most widely studied intercalation electrode materials is titanium disulfide [12039-13-3],  $TiS_2$ . A number of factors make  $TiS_2$  attractive for secondary lithium cells including good rate capability, high theoretical energy density, and a highly reversible intercalation reaction (39). Very high cycle lives have been demonstrated for  $TiS_2$  electrodes (40). One of the earliest efforts to develop commercial lithium cells employed  $TiS_2$  (41).

The development of "AA" Li–TiS<sub>2</sub> cells combines the excellent properties of TiS<sub>2</sub> and a proprietary method for preparing polymer bonded electrodes (42) to give a flexible, high capacity bonded electrode. Using this technology, "AA" cells have been constructed giving 1.05Ah capacity at a voltage of 2.3 V to 1.6 V on discharge. Using excess Li for the negative electrode, cycle lives of 200 cycles are claimed for this cell. Other advantages are a good high rate capability (up to C rate), good gravimetric energy density, and very low self-discharge (43).

A rechargeable lithium "AA" cell employing niobium triselenide [12034-78-5], NbSe<sub>3</sub>, as the positive electrode material has been developed (44, 45). The key to this system was a method for thermally growing NbSe<sub>3</sub> fibers that can then be pressed onto a current collector to provide a very high energy density electrode.



**Fig. 2.** Configuration for spirally wound rechargeable lithium cell. A, Cap; B, cathode tab; C, insulating disk (2); D, mandrel; E, can; F, ball; G, safety vent; H, glass-to-metal seal (with center pin); I, anode tab; J, cathode; K, separator; L, anode. Courtesy of Moli Energy Ltd.

No binder or additional conductive material is required. The excellent properties of this electrode also allow for higher discharge currents than those typically available for rechargeable lithium systems. Discharge rates in excess of C rate have been demonstrated. "AA" cells employing this technology give capacities of 1.1Ah when cycled between 2.4 and 1.4 V. Cycle lives of over 250 cycles have been demonstrated for this cell (46).

An "AA" Li– $MnO_2$  cell was announced in the late 1980s, however, this system was not commercialized (47, 48). This cell is claimed to offer considerable advantages over the conventional Ni–Cd system, offering higher energy density, high operating voltage, high rate capability, and excellent cycle life. A comparison of the parameters of these cells is shown in Table 2 (47).

An advanced Li–MnO<sub>2</sub> battery under the trade name Molicel<sup>2</sup> has been developed by Moli Energy Ltd. (49). The cell has a nominal voltage of 3 V, allowing replacement of two NiCd cells with one Molicel<sup>2</sup>, hence significantly reducing battery pack size and volume. Production "AA" cells demonstrate a nominal capacity of 600mAh for an energy density of 100Wh/kg. Cycle life for this cell is reported to be typically 200 cycles (50).

Other solid cathode systems that have been widely investigated include those containing lithium cobalt oxide [12190-79-3],  $LiCoO_2$  (51), vanadium pentoxide [1314-62-1],  $V_2O_5$ , and higher vanadium oxides, eg,  $V_6O_{13}$  (52, 53).

In addition to cells employing solid positive electrodes, a rechargeable lithium cell employing sulfur dioxide [7446-09-5], SO<sub>2</sub>, as a liquid electrode has been developed (54). The widespread use of primary Li–SO<sub>2</sub> batteries, particularly by the U.S. military, led to a strong interest in developing a rechargeable version. The cell electrolyte for this system consists of liquid sulfur dioxide and lithium tetrachloroaluminate [14024-11-4], LiAlCl<sub>4</sub>, salt. The overall cell chemistry of the rechargeable system involves the reduction and oxidation of a complex which forms between LiAlCl<sub>4</sub>, SO<sub>2</sub>, and the carbon that is employed as the current collector for the positive electrode. Specifications for a prototype Li–SO<sub>2</sub> "C"-sized cell are shown in Table 3 (54). Advantages for this system include very high energy densities, a flat running voltage, and the ability to sustain limited

	Cell system		Parameter ratio Li–MnO <sub>2</sub> /Ni–Cd	
Parameter	Li–MnO <sub>2</sub>	Ni–Cd		
cell weight, g	16.0	25.0	0.65	
operating voltage, V	$2.8^a$	$1.2^b$	2.3	
cutoff voltage, V	2.0	1.0		
energy at 0.8 W discharge, Wh	2.03	0.85	2.4	
self-discharge after 1 mo	1%	25%	0.04	
cycles (% $DOD^c$ )				
at 0.85Wh/cycle	1000	500	2	
	(40%)	(100%)		
at 1.3Wh/cycle	400			
	(64%)			
at 1.7Wh/cycle	200			
	(84%)			

<sup>*a*</sup> Average voltage.

<sup>b</sup> Nominal voltage.

<sup>c</sup> DOD = depth of discharge

Parameter	Value
open circuit voltage, V	3.2
operating voltage, at C/6, <sup>b</sup> V	3.0
energy, Wh	5.4
volumetric energy density, Wh/L	220
gravimetric energy density, Wh/kg	134
operating temperature, °C	-30 to $40$
cycle life, cycles	50
discharge rate	$C/1.8^{b,c}$
charge rate	$C/18^{b,d}$
charge retention after 9 mo	100%

<sup>*a*</sup> Where the nominal capacity is **1.8Ah** to 2 V.

 $^{b}$  Where C is the current required to discharge the cell in 1 hour.

 $^{c}_{d} C/1.8 = 1 A.$  $^{d}_{d} C/18 = 0.1 A.$ 

overcharge. The principal drawback has been safety concerns over potential cell ruptures on cycling resulting from internal short circuits.

A related system employs a copper(II) chloride [7447-39-4], CuCl<sub>2</sub>, electrode in a sulfur dioxide electrolyte (55). "AA" cells of nominal capacity of 500mAh at a discharge voltage of 3.4–3.0 V were constructed. Cycle life for this cell is claimed to be 200 cycles. The high voltage of this system offers a significant energy density advantage over conventional Ni-Cd systems.

The discharge performance characteristics of advanced rechargeable lithium "AA" cells and the Ni-Cd cell are illustrated in Figure 3. Whereas it is clear that a number of lithium systems offer energy capacities of significant improvement over conventional Ni-Cd cells, several critical issues remain for cell development before lithium technology gains widespread application. Cycle life continues to be a limitation to most technologies. Unlike Ni-Cd, there is no overcharge or overdischarge protection for the rechargeable lithium cells which generally must be recharged only within closely defined voltage limits. This presents a problem particularly in the design of multicell battery packs. Experiments using electrolyte additives to provide overcharge protection

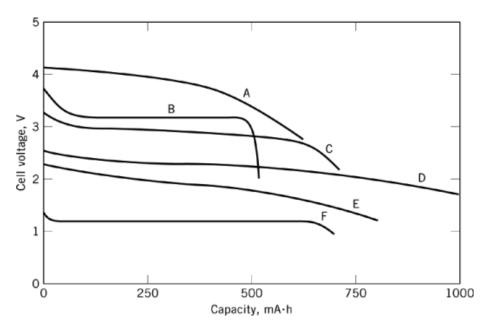


Fig. 3. Cell voltage profiles as a function of discharge capacity for rechargeable "AA" cells: A, Li ion; B, Li–SO<sub>2</sub>; C, Li–MnO<sub>2</sub>; D, Li–TiS<sub>2</sub>; E, Li–MoS<sub>2</sub>; F, Ni–Cd.

have been carried out (56), but this concept has not been demonstrated in advanced cell designs. Additionally, the high reactivity of lithium metal continues to pose serious safety concerns among battery manufacturers and users. Incidences of lithium cells exploding and/or igniting or venting with flame during use have highlighted the need for extensive safety testing of lithium-containing batteries prior to the widescale commercialization of this technology.

A lithium ion rechargeable cell has apparently been developed in response to safety concerns over the  $Li-MnO_2$  cell. This technology is expected to be used for camcorder battery packs. The technical details of this battery have not been reported, but it is understood that the negative electrode consists of a carbon material capable of undergoing an insertion reaction with  $Li^+$  ion (57). This electrode is coupled with an insertion positive electrode such as lithium cobalt oxide (58). The resulting cell has a nominal operating voltage of 3.6 V, three times that of NiCd, providing a significant advantage in energy density (see Fig. 3) for multicell battery packs. The cell is claimed to be capable of rapid charge, discharge rates up to 2C, and 1200 cycles (59).

### 2. High Temperature Systems

#### 2.1. Lithium–Aluminum/Metal Sulfide Batteries

The use of high temperature lithium cells for electric vehicle applications has been under development since the 1970s. Advances in the development of lithium alloy-metal sulfide batteries have led to the Li-Al/FeS system, where the following cell reaction occurs.

$$2 \operatorname{LiAl}_{x} + \operatorname{FeS} \rightleftharpoons \operatorname{Fe} + \operatorname{Li}_{2}S + 2x \operatorname{Al}$$

The cell voltage is 1.33 V to give a theoretical energy density of 458Wh/kg (60). The cell employs a molten salt electrolyte, most commonly a lithium chloride [7447-41-8]/potassium chloride [7447-40-7], LiCl–KCl eutectic mixture. The cell is generally operated at 400–500°C. The negative electrode is composed of lithium–aluminum alloy, which operates at about 300 mV positive of pure lithium. The positive electrode is composed of iron sulfide [1317-37-9] mixed with a conductive agent such as carbon or graphite. Electrodes are constructed by cold pressing powder onto current collectors (61).

Development of practical and low cost separators has been an active area of cell development. Cell separators must be compatible with molten lithium, restricting the choice to ceramic materials. Early work employed boron nitride [10043-11-5], BN, but a more desirable separator has been developed using magnesium oxide [1309-48-4], MgO, or a composite of MgO powder–BN fibers. Corrosion studies have shown that low carbon steel or stainless steel are suitable for the cell housing as well as for internal parts such as current collectors (62).

Li–Al/FeS cells have demonstrated good performance under EV driving profiles and have delivered a specific energy of 115Wh/kg for advanced cell designs. Cycle life expectancy for these cells is projected to be about 400 deep discharge cycles (63). This system shows considerable promise for use as a practical EV battery.

A similar system under development employs iron disulfide [12068-85-8], FeS<sub>2</sub>, as the positive electrode. Whereas this system offers a higher theoretical energy density than does Li–Al/FeS, the FeS<sub>2</sub> cell is at a lower stage of development (64, 65).

#### 2.2. Sodium-Sulfur

The best known of the high temperature batteries is the sodium [7440-23-5]–sulfur [7704-34-9], Na–S, battery (66). The cell reaction is best represented by the equation:

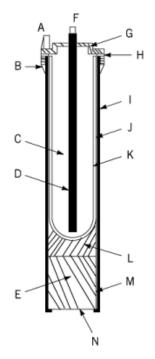
$$2 \text{ Na} + 3 \text{ S} \implies \text{Na}_2 \text{S}_3$$

occurring at a cell voltage of 1.74 V, to give a specific energy of 760Wh/kg. The cell is constructed using a solid electrolyte typically consisting of  $\beta$ -alumina [1344-28-1],  $\beta$ -Al<sub>2</sub>O<sub>3</sub>, ceramic, although borate glass fibers have also been used. These materials have high conductivities for the sodium ion. The negative electrode consists of molten sodium metal and the positive electrode of molten sulfur. Because sulfur is not conductive, a current collection network of graphite is required. The cell is operated at about 350°C. A typical cell design is shown in Figure 4. The outer cell case is constructed from mild steel. The  $\beta$ -alumina separator tube fits inside the cell case with a small gap in between. The positive electrode of molten sulfur is placed inside the alumina tube with a carbon current collector. The molten sodium is stored below the cell and is wicked into the space between the separator and outer cell casing. The mild steel case acts as the negative electrode current collector (67).

The Na–S battery couple is a strong candidate for applications in both EVs and aerospace. Projected performance for a sodium–sulfur-powered EV van is shown in Table 4 for batteries having three different energies (68). The advantages gained from using a Na–S system rather than the conventional sealed lead–acid batteries are evident.

The Na–S system is expected to provide significant increases in energy density for satellite battery systems (69). In-house testing of Na–S cells designed to simulate midaltitude (MAO) and geosynchronous orbits (GEO) demonstrated over 6450 and over 1400 cycles, respectively.

Difficulties with the Na–S system arise in part from the ceramic nature of the alumina separator: the specific  $\beta$ -alumina is expensive to prepare; and the material is brittle and quite fragile. Separator failure is the leading cause of early cell failure. Cell failure may also be related to performance problems caused by polarization at the sodium/solid electrolyte interface. Lastly, seal leakage can be a determinant of cycle life. In spite of these problems, however, the safety and reliability of the Na–S system has progressed to the point where pilot plant production of these batteries is anticipated for EV and aerospace applications.



**Fig. 4.** Construction of a sodium–sulfur battery. A, Negative terminal; B, springs plus graphite felt; C, sulfur; D, carbon; E, sodium reservoir; F, positive terminal; G, insulator; H, aluminum sealing gaskets; I, steel case; J, film of sodium; K,  $\beta$ -alumina tube; L, carbon felt; M, wick; N, aluminum can (67).

	Battery			
Parameter battery energy, kWh	Lead–acid 40.0	Sodium-sulfur		
		40.0	60.0	85.0
range, km	84.0	113.0	169.0	242.0
max payload, t	0.9	1.7	1.6	1.6
battery weight, kg	1250.0	330.0	424.0	580.0

Table 4. Electric Vehicle Battery Performance

A battery system closely related to Na–S is the Na–metal chloride cell (70). The cell design is similar to Na–S; however, in addition to the  $\beta$ -alumina electrolyte, the cell also employs a sodium chloroaluminate [7784-16-9], NaAlCl<sub>4</sub>, molten salt electrolyte. The positive electrode active material consists of a transition metal chloride such as iron(II) chloride [7758-94-3], FeCl<sub>2</sub>, or nickel chloride [7791-20-0], NiCl<sub>2</sub>, (71, 72) in lieu of molten sulfur. This technology is in a younger state of development than the Na–S.

### 3. Miscellaneous Systems

Rechargeable cells employing aluminum [7429-90-5], Al, as a negative electrode in room temperature molten salts have been investigated. Aluminum has a very high electrochemical equivalent weight producing a high energy density, yet aluminum is much less reactive than lithium, alleviating many of the safety issues of lithium electrode systems. The aluminum electrode has been shown to be very reversible in room temperature

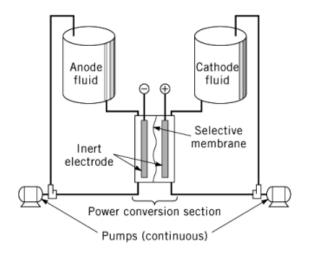


Fig. 5. Schematic for a redox flow battery (78).(Courtesy of Plenum Press.)

molten salts based on aluminum chloride [7446-70-0], AlCl<sub>3</sub>–organic quaternary ammonium salt mixtures (73). Positive electrodes include intercalation (74) and metal sulfide ones (75, 76).

Redox flow batteries, under development since the early 1970s, are still of interest primarily for utility load leveling applications (77). Such a battery is shown schematically in Figure 5. Unlike other batteries, the active materials are not contained within the battery itself but are stored in separate tanks. The reactants each flow into a half-cell separated one from the other by a selective membrane. An oxidation and reduction electrochemical reaction occurs in each half-cell to generate current. Examples of this technology include the iron–chromium, Fe–Cr, battery (79) and the vanadium redox cell (80).

Other flow batteries investigated for both electric vehicle application and utility load leveling include zinc [7440-66-6]–chlorine [7782-50-5], Zn–Cl<sub>2</sub>, Zn–Br<sub>2</sub>, batteries (78, 81, 82).

### 4. Economic Aspects

As of this writing, there is little commercialization of advanced battery systems. Small rechargeable lithium button cells have been commercialized, however, by Sanyo, Matsushita (Panasonic), and Toshiba. These cells are intended for original equipment manufacturer (OEM) use in applications such as memory backup and are not available to the general consumer.

Efforts to commercialize larger versions of rechargeable lithium cells have been frustrated by concerns over product safety. Moli Energy Ltd. briefly introduced "AA" Li– $MoS_2$  cells for OEM use in laptop computers and cellular phones. However, safety issues resulted in a product recall and a halt to commercialization of this product.

Efforts to develop commercially viable EV versions of advanced battery systems continue. The ultimate goal is to develop battery technology suitable for practical, consumer-acceptable electric vehicles. The United States Advanced Battery Consortium (USABC) has been formed with the express purpose of accelerating development of practical EV batteries (83).

### BIBLIOGRAPHY

"Batteries and Electric Cells, Secondary (Other Cells)" in *ECT* 3rd ed., Vol. 3, pp. 663–670, by J. B. Doe, ESB Technology, Co.

#### **Cited Publications**

- 1. M. Hughes, N. A. Hampson, and S. A. G. R. Karunathilaka, J. Power Sources 12, 83-144 (1984).
- 2. E. Yeager, in E. Yeager, *Proceedings of the Workshop on Lithium Nonaqueous Battery Electrochemistry*, Vol. **80–7**, The Electrochemical Society, Inc., Cleveland, Ohio, 1980, 1–12.
- 3. V. R. Koch, J. Power Sources 6, 357–370 (1981).
- 4. M. Garreau, J. Power Sources 20, 9–17 (1987).
- 5. A. Dey, Thin Solid Films 43, 131–171 (1977).
- 6. S. B. Brummer, in Ref. 2, 130–142.
- 7. Y. Matsuda, J. Power Sources 20, 19–26 (1987).
- 8. K. M. Abraham, J. Power Sources 14, 179-191 (1985).
- 9. J. R. Stiles, New Mater. New Processes 3, 89-91 (1985).
- 10. J. Gabano, Prog. Batt. Solar Cells 8, 149–162 (1989).
- 11. M. Armand, Solid State Ionics 9, 10, 745-754 (1983).
- 12. A. Hooper, in K. M. Abraham and B. B. Owens, eds., *Materials and Processes for Lithium Batteries*, Vol. 89–4, The Electrochemical Society, Inc., Cleveland, Ohio, 1980, 15–32.
- 13. P. E. Harvey, J. Power Sources 26, 23-32 (1989).
- 14. Chem. Eng. News, 23, 24 (Nov. 5, 1984).
- 15. K. M. Abraham, M. Alamgir, and S. J. Perrotti, J. Electrochem. Soc. 135, 535, 536 (1988).
- 16. K. M. Abraham, J. Power Sources 7, 1-43 (1981 and 1982).
- 17. A. D. Yoffe, Solid State Ionics 9, 10, 59–70 (1983).
- 18. B. Scosati, A. Selvaggi, and B. Owens, Prog. Batt. Solar Cells 8, 135-137 (1989).
- 19. A. Hammou and A. Hammouche, Electrochimica Acta 33, 1719, 1720 (1988).
- 20. F. Bonino, M. Ottaviani, and B. Scrosati, J. Electrochem. Soc. 135, 12-15 (1988).
- 21. A. Hooper and J. North, Solid State Ionics 9, 10, 1161–1166 (1983).
- 22. D. Shackle, 4th International Seminar on Lithium Battery Technology and Applications, Deerfield Beach, Fla., Mar. 1989.
- 23. U.S. Pat. 4,830,939 (May 1989), M. Lee, D. Shackle, and G. Schwab.
- 24. Science News 136, 342 (1989).
- 25. M. Liu, S. Visco, and L. DeJonghe, in S. Subbarao and co-workers, eds., *Rechargeable Lithium Batteries*, Vol. **90–5**, The Electrochemical Society, Inc., Cleveland, Ohio, 1980, 233–244.
- N. Koshiba and K. Momose, in Y. Matsuda and C. Schlaikjer, eds., Practical Lithium Batteries, JEC Press, Inc., 1988, 79–81.
- 27. K. Momose, H. Hayakawa, N. Koshiba, and T. Ikehata, Prog. Batt. Solar Cells 6, 56, 57 (1987).
- 28. JEC Battery Newsletter, (1), 7 (Jan./Feb. 1989).
- 29. Japan Component News 7(2), 4–6 (Feb. 1990).
- 30. K. Inada and co-workers, in Ref. 26, 96-99.
- 31. M. Mohiri and co-workers, J. Power Sources 26, 545-551 (1989).
- 32. U.S. Pat. 4,748,484 (July 19, 1988), N. Furukawa, T. Saito, and T. Nohma (to Sanyo Electric Co., Ltd.).
- 33. U.S. Pat. 4,904,552 (Feb. 27, 1990), N. Furukawa, T. Saito, and T. Nohma (to Sanyo Electric Co., Ltd.).
- 34. T. Nohma, T. Saito, and N. Furukawa, J. Power Sources 26, 389-396 (1989).
- 35. J. Carcone, 3rd International Rechargeable Battery Seminar, Deerfield Beach, Fla., Mar. 1990.
- 36. Technical Brochure, Moli Energy Ltd., Burnaby, British Columbia, Canada.
- 37. J. Stiles, in Ref. 26, 74–78.
- 38. F. C. Laman and K. Brandt, J. Power Sources 24, 195–206 (1988).
- 39. E. J. Frazer and S. Phang, J. Power Sources 6, 307-317 (1981).

- D. H. Shen and co-workers, Extended Abstract 49, Vol. 87–2, 172nd Meeting of the Electrochemical Society, Honolulu, Hawaii, Oct. 1987.
- 41. U.S. Pat. 4,084,046 (Apr. 1978), M. S. Whittingham (to Exxon Corp.).
- 42. U.S. Pat. 4,731,310 (Mar. 1988), M. Anderman and J. Lundquist (to W. R. Grace & Co.).
- 43. M. Anderman and J. Lundquist, *Extended Abstract* 49, Vol. 87–2, 172nd Meeting of the Electrochemical Society, Honolulu, Hawaii, Oct. 1987.
- 44. U.S. Pat. 3,864,167 (Feb. 4, 1975), J. Broadhead, F. J. DiSalvo, and F. A. Trumbore.
- 45. B. Vyas, 33rd International Power Sources Symposium, Cherry Hill, N.J., June 1988.
- 46. F. Trumbore, 4th International Meeting on Lithium Batteries, Vancouver, Canada, May 1988.
- 47. JEC Battery Newsletter (2), 26, 27 (1988).
- 48. U.S. Pat. 4,828,834 (May 1989), T. Nagaura and M. Yokokawa (to Sony Corp.).
- 49. U.S. Pat. 4,959,282 (Sept. 1990), J. Dahn and B. Way (to Moli Energy, Ltd.).
- 50. Product Literature, Moli Energy Ltd., Burnaby, British Columbia, Canada.
- 51. E. Plichta and co-workers, J. Power Sources 21, 25-31 (1987).
- 52. K. Wiesener and co-workers, J. Power Sources 20, 157–164 (1987).
- 53. K. West, B. Zachua-Christiansen, M. Ostergard, and T. Jacobsen, J. Power Sources 20, 165-172 (1987).
- 54. A. N. Dey, K. C. Kuo, P. Piliero, and M. Kallianidis, J. Electrochem. Soc. 135, 2115–2120 (1988).
- 55. C. Cecilio and co-workers, 4th International Seminar on Lithium Battery Technology and Applications, Deerfield Beach, Fla., Mar. 1989.
- 56. W. Behl and D. Chin, J. Electrochem. Soc. 135, 16-25 (1988).
- 57. U.S. Pat. 4,668,595 (May 1987), A. Yoshino, K. Sanechika, and T. Nakajima (to Sony Corp.).
- 58. Jpn. Pat. 01 122 562, (to Sony Corp.).
- 59. JEC Battery Newsletter, (2), 9–12 (1990).
- 60. E. J. Cairns, in E. J. Cairns, *Comprehensive Treatise of Electrochemistry*, Vol. **3**, Plenum Press, New York, 1981, Chapt. 11.
- 61. R. W. Glazebrood and M. J. Willars, J. Power Sources 8, 327-339 (1982).
- P. A. Nelson, 4th International Seminar on Lithium Battery Technology and Applications, Deerfield Beach, Fla., Mar. 1989.
- 63. P. A. Nelson and H. Shimotake, Prog. Batt. Solar Cells 6, 150-154 (1987).
- 64. T. D. Kaun, in Ref. 25, 294-306.
- 65. T. D. Kaun and co-workers, Proc. of the 25th IECEC 3, 335-340 (1990).
- 66. J. L. Sudworth and A. R. Tilley, The Sodium Sulfur Battery, Chapman and Hall Ltd., 1985, and references therein.
- 67. D. Pletcher, Industrial Electrochemistry, Chapman and Hall Ltd., 1984, 272-274.
- 68. P. Bindin, Proc. 20th IECEC Conf. 2, 1111-1114 (Aug. 1985).
- 69. S. Wolanczyk and S. Vukson, Proc. 25th IECEC Conf. 3, 122-124 (Aug. 1990).
- 70. R. J. Bones, J. Coetzer, R. C. Galloway, and D. A. Teagle, J. Electrochem. Soc. 134, 2379–2382 (1987).
- 71. R. C. Galloway, J. Electrochem. Soc. 134, 256, 257 (1987).
- 72. R. J. Bones, S. D. Brooker, and F. L. Cullen, J. Electrochem. Soc. 136, 1274-1277 (1989).
- 73. J. S. Wilkes and co-workers, Frank J. Seiler Laboratory Technical Report, FJSRL-TR-81-011, ADA 107,989, Oct. 1981.
- 74. P. R. Gifford and J. B. Palmisano, J. Electrochem. Soc. 135, 650-654 (1988).
- 75. V. R. Koch, 3rd International Rechargeable Battery Seminar, Deerfield Beach, Fla., Mar. 1990.
- 76. N. Talami and N. Koura, J. Electrochem. Soc. 136, 730, 731 (1989).
- 77. M. Bartolozzi, J. Power Sources 27, 219-234 (1989) and references therein.
- 78. J. McBreen, in Ref. 60, Chapt. 10.
- 79. R. F. Gahn, N. H. Hagedorn, and J. A. Johnson, Proc. 20th IECEC 2, 91-97 (Aug. 1985).
- 80. M. Skyllas-Kazacos and F. Grossmith, J. Electrochem. Soc. 134, 2950–2953 (1987).
- 81. F. Will and H. S. Spacil, J. Power Sources 5, 173-188 (1980).

- 82. A. Leo and A. Charkey, Proc. 20th IECEC 2, 63–69 (Aug. 1985).
- 83. F. Jamerson, *DOE Automotive Technology Development Contractors' Coordination Meeting*, Vol. **2**, Dearborn, Mich., Oct. 28, 1991.

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