R&D on lithium batteries in the USA: high-energy electrode materials

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Abstract

Recent trends in R&D on lithium battery technology in the USA continue to focus on high-performance batteries, polymer electrolyte systems and the development and production of batteries for specialty markets. Research on sol–gel derived amorphous vanadium and manganese oxides as high capacity, high-energy electrode materials has shown these morphologies are capable of reversibly intercalating very large amounts of lithium and they are attractive cathode candidates. Methods to improve the kinetics of these positive electrodes are showing promise. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The primary objective of this paper is to present an overview of recent trends in the field of lithium battery technology in the United States. For the purposes of this study, the lithium battery field is limited to rechargeable batteries that are based on lithium metal anodes, lithium alloy anodes or any of the various types of lithium-ion batteries. A second objective is to describe some of the Corrosion Research Center studies on high-capacity cathode materials.

2. Lithium battery R&D-USA

In Fig. 1 is shown a chronology of trends in the rechargeable consumer battery field, as was reported by Professor Tetsuya Osaka at the 8th IMLB in Nagoya (1996). The indication was that lithium-ion systems would start to dominate this marketplace as we approach the end of this century, but that lithium–metal rechargeable systems would become the accepted, high-performance battery system, early in the next century. During the two years since that conference, lithium-ion battery technology has dominated the area of new advanced rechargeable battery systems. There remain some questions about the future of lithium–metal battery systems. Such systems continue to offer the promise of a higher level of performance, although there are concerns about safety and cycle life.

With respect to lithium battery activities in the US, it is reasonable to conclude that the level of R&D activity is still increasing. Marketing organizations put forth their projections and these have been reported at different meetings or are available by subscription. One measure of the amount of development and production in this field in the US is the number of facilities that have been installed for lithium battery processing. Table 1 shows an estimate of the number of battery dry rooms that have been installed in the US, 76 dry rooms during the past 22 years.

The last column in Table 1 is the nominal rate of installation for each of the three time intervals. During the last 8-year period, dry rooms have been installed at almost twice the rate of the previous decade.

Another indicator of trends in battery R&D activities in the US is the number of national or international symposia dealing with this topic, and the types of papers presented. Table 2 shows a listing of five conferences held in 1998, beginning with the Hawaiian Battery Conference in January (HBC), followed by the 13th Annual Battery Conference on Applications (ABC) held in Long Beach also in January, followed by the 15th International Seminar on Primary and Secondary Batteries (ISB) held in March in Ft. Lauderdale, FL, followed by the 38th Power Sources
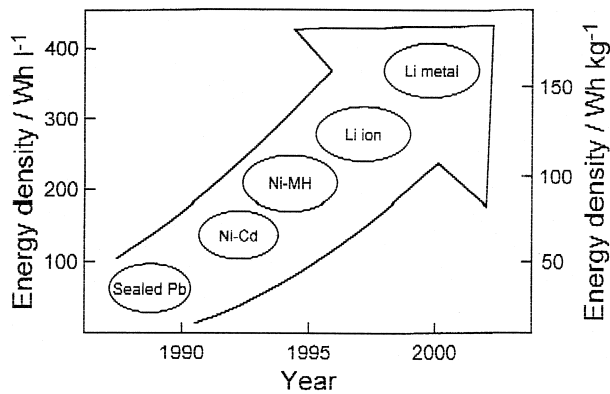
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Fig. 1. Evolution of energy densities for rechargeable batteries (T. Osaka, IMLB-8, Nagoya, Japan, 1996).

Table 2
Lithium battery anodes reported at battery conferences in 1998

Conference in 1998	Percentage of selected references			
	Type of anode			
	Lithium metal	Lithium other	Li-ion carbon	Li-ion other
HBC Hawaii	23	17	40	20
ABC California	0	0	100	0
ISB Florida	19	7	74	0
PSC New Jersey	13	0	84	3
IMLB-9 Scotland	12	6	58	24

Conference (PSC) held in June of this year, at Cherry Hill, NJ, and finally, for comparison, the 9th International Meeting on Lithium Batteries (IMLB-9) held in Edinburgh, Scotland in July.

The conferences listed in Table 2 are not a complete listing of such meetings. For example, the 193rd Meeting of the Electrochemical Society, held in San Diego in May, included sessions on Li batteries, carbon materials for Li-ion batteries and conductive membranes for batteries. Nonetheless, the distribution of papers at the five selected conferences gives some indication of R&D trends. Table 2 suggests that most of the studies favor lithium-ion as opposed to lithium–metal systems.

In Table 3 the same information is shown for metal oxide cathodes. Cobalt oxide positives were included in most of the systems described at those meetings in the US, with strong interest in manganese oxides also being indicated. Interestingly, from the topics of papers listed for the IMLB-9, the majority of papers at this most recent conference deal with manganese oxides or positive materials other than metal oxides. This perhaps is an indication of future trends as opposed to present battery systems in advanced development and production.

Similarly, Table 4 compares these conference papers with respect to the types of electrolytes. Lithium batteries may be classified by the physical state of the electrolyte being liquid or solid. Subcategories include two types of *liquid electrolytes* (inorganic and organic), and three types

that may be termed *solid electrolytes* although the term is somewhat ambiguous. The latter includes polymer–gels, dry polymers and solid inorganic or glassy types of electrolytes. It is seen that liquid organic electrolytes dominate the battery systems, but that polymer gel electrolytes are the next most widely investigated cell type; dry polymer and inorganic have a rather low level of investigation, at least as reported at these meetings.

From this one may conclude that present published studies focus on lithium-ion batteries with liquid organic electrolytes, and the incorporation of cobalt oxide cathodes. A strong interest is also indicated for polymer gel or plasticized electrolyte systems, and manganese oxide cathodes.

A recent market forecast proposed the lithium-ion polymer battery technology will dominate the battery market for portable electronic devices. This projection strongly claims that polymer lithium-ion cell systems will mature and take over the market, replacing the use of the organic liquid systems. Also, in this forecast, lithium-metal anode systems were not mentioned as a factor in the market for portable electronics and consumer products [1].

At the recent 38th Power Source Conference, there was some discussion on the status of lithium battery technology in the US. It was observed that there is limited activity regards the commercialization of consumer batteries based on lithium–metal or lithium-ion cell systems. However, the US continues to maintain an active role in the research

Table 1
Estimated number of battery dry rooms installed in USA

Time interval	Estimated number installed in US	Rate of installation (units/decade)
1976–1979	6	15
1980–1989	26	26
1990–1998	44	49

[a]R.S. Smith, Jr., private communication, 1998.

Table 3
Lithium battery cathodes reported at battery conferences in 1998

Conference in 1998	Distribution of selected references				
	Type of cathode				
	Metal oxide				Other
	V	Co	Ni	Mn	
HBC Hawaii	13%	29%	13%	38%	7%
ABC California	0%	46%	0%	36%	18%
ISB Florida	8%	42%	15%	31%	4%
PSC New Jersey	3%	51%	14%	26%	6%
IMLB-9 Scotland	16%	0%	8%	38%	38%

Table 4
Lithium battery electrolytes reported at battery conferences in 1998

Conference in 1998	Distribution of electrolytes in selected references				
	Type of electrolyte				
	Liquid inorganic	Liquid organic	Polymer gel (plasticized)	Polymer dry	Solid (glass)
HBC Hawaii	0%	67%	22%	4%	7%
ABC California	0%	81%	19%	0%	0%
ISB Florida	0%	70%	18%	12%	0%
PSC New Jersey	3%	61%	30%	6%	0%
IMLB-9 Scotland	7%	52%	27%	7%	7%

and development of these advanced battery systems, and in the development and production of specialty types of batteries. This includes the following:

1. Large cells for military applications
2. Large batteries for the electric vehicle market
3. Specialized batteries for NASA
4. Batteries for medical applications
5. Batteries for small niche markets.

There is considerable work directed towards low temperature electrolytes for special applications, and also high temperature systems that can operate at 150°C. Electrolytes with high voltage windows of stability are under investigation, to be coupled with high energy cathodes. Finally, polymer electrolytes for lithium and lithium-ion batteries continue to be a major area of development.

In conclusion, as far as trends in the US are concerned, the focus continues on high-performance batteries, polymer electrolyte systems and the development and production of batteries for specialty markets. Production of consumer batteries is not being established in any broad sense.

3. High-performance cathode materials

The investigation of research into high-performance cell systems generally is driven by the requisite properties of the electrode and electrolyte materials. The goal is systems that are capable of the following: (a) higher energy density, on both a weight and volume basis; and (b) higher rate capability, so that the high energy density contained within the cell system may be translated into useful energy at rates required by the application.

Low-temperature studies are driven simply by the need to have improved energy and power density at low temperatures and high temperature studies are driven similarly. These conditions dictate types of studies. Cost comes in as a parameter depending on the application. Safety is a function of the intrinsic materials, but is also closely related to the design of the system.

3.1. Organo-sulfur polymer cathode materials

Moltech has reported the use of very high capacity cathode materials based on sulfur polymer compounds.

Specific capacities of 700–1200 mAh/g were reported [2]. They claim to have a performance goal for AA cells of 215 Wh/kg at the C/3 rate. They also report a lithium–metal anode, polymer electrolyte cell, designed into a small 950 mAh prismatic configuration. Energies of 310 Wh/kg and 350 Wh/l with 'high' rate capability are projected.

3.2. Amorphous metal oxide cathode materials

At the University of Minnesota there has been a continuing program on high capacity amorphous cathode materials. This effort was initiated a number of years ago with some work on sol–gel processing of vanadium oxides. A number of papers have reported properties of xerogel, aerogel, and aerogel-like morphologies of vanadium pentoxide [3–8]. More recently, some investigations of amorphous manganese dioxide have been reported [9–11].

The amorphous materials under development at the University of Minnesota are oxides of vanadium and manganese and have demonstrated specific capacities approaching 600 mAh/g. Although these are not as high as the values reported for the organo-sulfur materials, these are considerably higher than the nominal 150 mAh/g that have been reported for crystalline metal oxides based on the lithiated oxides of nickel, cobalt and manganese.
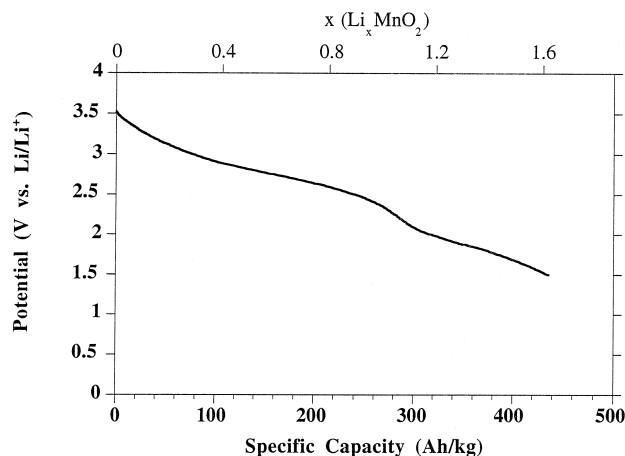

Fig. 2. Voltage vs. capacity (lithium content) curve for a-MnO_2, first discharge, current density = 20 $\mu A/cm^2$.
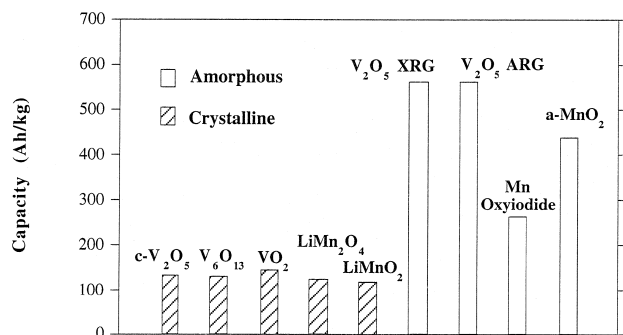
Fig. 3. Comparison of specific capacity of crystalline vs. amorphous metal oxides.

The amorphous vanadium and manganese oxides are prepared by aqueous syntheses, with final drying at normal ambient temperatures. Depending on the drying process one produces a xerogel of surface area 1–10 m^2/g, an aerogel-like material of surface area around 200 m^2/g, or an aerogel with a high surface area of up to 450–500 m^2/g.

The amorphous manganese oxide is synthesized by an aqueous redox sol–gel procedure [9,12,13]. A sodium permanganate solution is reduced with fumaric acid disodium salt, to form colloidal MnO_2 that includes some lower valence species. Addition of sulfuric acid disproportionates the trivalent manganese into the tetravalent metal oxide and the soluble divalent species. The latter are removed by aqueous extraction and the powders are then vacuum-dried. The resultant amorphous material has a porous structure with a surface area of 350 m^2/g. Composite electrodes were prepared by combining this active material with a binder (PTFE) and carbon. The composite was used to make pellet electrodes of about 200 μm thickness and these were tested in liquid electrolyte cells with lithium perchlorate in PC. Electrochemical insertion of lithium-ions was carried out over the potential range of 3.5 V down to 1.5 V, vs. Li/Li^+. Results are shown in Fig. 2. Up to 1.63 lithium-ions per mole of MnO_2 were inserted. This corresponds to about 440 mAh/g. The insertion was carried out at a current density of 20 $\mu A/cm^2$ [9].

The amorphous metal oxides of vanadium and manganese have much higher specific capacities and reversible lithium-ion insertion capacity than do the crystalline forms that have been incorporated into rechargeable cell systems. Fig. 3 illustrates this for a number of materials [11]. Although the high specific capacity is very attractive, the rate capability of these amorphous materials must be improved to increase their usefulness.

In an effort to improve the intercalation kinetics and rate capability of these materials, there has been some investigation of the 'doping' of the V_2O_5 materials with other metal ions such as silver, as reported by Coustier et al. [14]. The electronic conductivity of the doped material is up to 3 orders of magnitude higher than that of the undoped material, and there is a concurrent dramatic enhancement of the Li^+ ion diffusion coefficient, as well. Similar results have also been obtained with copper doped V_2O_5 materials. These very interesting results are being explored further and will be reported in detail at a later time.

Table 5 lists several of the vanadium and manganese oxide intercalation compounds investigated in our laboratory, including V_2O_5 XRG, V_2O_5 ARG, V_2O_5 ARG-like, Ag doped V_2O_5 XRG, and a-MnO_2 materials. All these materials are nearly amorphous or completely amorphous as determined by X-ray powder diffraction, and most of them possess high internal surface areas. All of them have shown high lithium intercalation capacity and high specific energy as determined by constant-current cycling at low current densities or by galvanostatic titration results. The Ag doped V_2O_5 materials also possess much improved kinetic characteristics and rate capability. Two of these materials, the V_2O_5 XRG and the a-MnO_2, are relatively easy and inexpensive to prepare and the industrial scale-up should be quite feasible. Furthermore, the ARG-like materials, although possessing relatively high surface areas, do not require a supercritical drying step for their preparation, in contrast to the ARG materials.

Shown in Fig. 4 are Ragone plots of projected batteries based on these V_2O_5 XRG and a-MnO_2 materials, in comparison to commercial batteries and electrochemical

Table 5
Intercalation compounds studied at the University of Minnesota

Compound	Structure	Surface area (m^2/g)	Li capacity per formula	Specific energy (Wh/kg)	Comments
V_2O_5 XRG	Nearly amorphous	1–10	4	1250[a]	Easy to prepare, scale-up feasible
V_2O_5 ARG	Nearly amorphous	450	4	1700[b]	Supercritical drying required
V_2O_5 ARG-like	Nearly amorphous	200	4	1250[a]	No Supercritical drying required
Ag doped V_2O_5 XRG	Nearly amorphous	1–10	4	1500[b]	Fast kinetics
a-MnO_2	Amorphous	350	> 1.6	1050[a]	Easy to prepare, scale-up feasible

[a]Obtained at low rate, C/100–200 for 2 Li per V or Mn; current density = 2.5–5 mA/g.
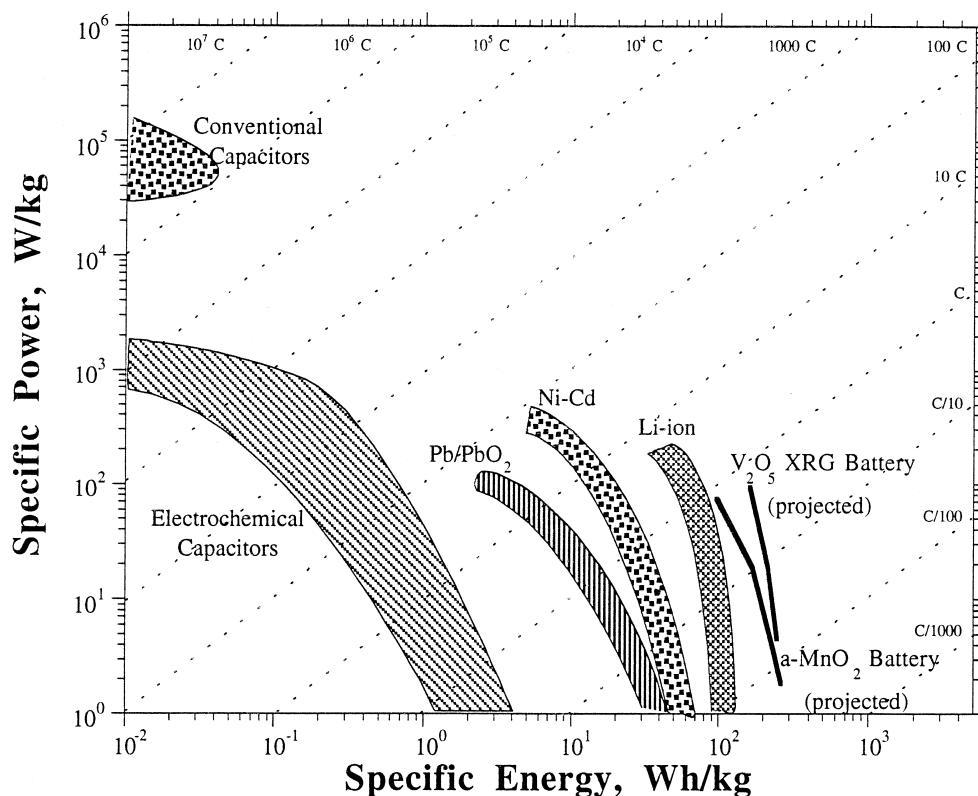[b]Obtained from galvanostatic titration results.

Fig. 4. Ragone plots of projected batteries based on V_2O_5 XRG and a-MnO$_2$, and commercial batteries and capacitors.

capacitors. Using the empirical rule that the projection of specific energy per kilogram of battery is 20–30% of the value per kilogram of active cathode material, we would expect to have viable cell systems with specific energies in the range of 200–350 Wh/kg for the batteries.

Amorphous structures offer a unique combination of properties. In our laboratory we are also investigating the reversible insertion of polyvalent cation species into amorphous metal oxide structures [15]. The XRG materials do not insert such species, but surprisingly the higher surface area ARG materials are exhibiting reversible insertion of Mg^{+2}, Zn^{+2} and Al^{+3}. These offer unique possibilities for other types of non-lithium metal, high-energy cell systems.

4. Conclusion

Work on advanced battery systems in the US is continuing to look at high-performance electrodes and cell systems, and also considerable effort is directed toward polymeric electrolyte materials. The investigations of very high capacity cathode materials are beginning to show promise for practical batteries based on lithium and lithium-ion systems. Some spin-off from these investigations is also showing promise for high energy systems based on negative materials other than lithium.

References

[1] N.J. Fairfield, PR Newswire, June 23, 1998.
[2] J. Broadhead, T.A. Skotheim, The 15th International Seminar on Primary and Secondary Batteries, March 2–5, 1998, Ft. Lauderdale.
[3] D.B. Le, S. Passerini, A.L. Tipton, B.B. Owens, W.H. Smyrl, J. Electrochem. Soc. 142 (1995) L102.
[4] H.K. Park, W.H. Smyrl, M.D. Ward, J. Electrochem. Soc. 142 (1995) 1068.
[5] S. Passerini, D. Chang, X. Chu, D.B. Le, W.H. Smyrl, Chem. Mater. 7 (1995) 780.
[6] A.L. Tipton, S. Passerini, B.B. Owens, W.H. Smyrl, J. Electrochem. Soc. 143 (1996) 3473.
[7] D.B. Le, S. Passerini, J. Guo, J. Ressler, B.B. Owens, W.H. Smyrl, J. Electrochem. Soc. 143 (1996) 2099.
[8] F. Coustier, S. Passerini, W.H. Smyrl, J. Electrochem. Soc. 145 (1998) L73.
[9] J.J. Xu, A.J. Kinser, B.B. Owens, W.H. Smyrl, Electrochem. Solid State Lett. 1 (1998) 1.
[10] J.J. Xu, A.J. Kinser, B.B. Owens, W.H. Smyrl, Abstract 81, p. 94, The Electrochemical Society Meeting Abstracts, Vol. 97-1, Montreal, Quebec, Canada, May 4–9, 1997.

[11] L.H. Manhart, B.B. Owens, W.H. Smyrl, J.J. Xu, Proceed, 38th Power Sources Conf., Cherry Hill, NJ, 1998.

[12] S. Bach, M. Henry, N. Baffer, J. Livage, Solid State Chem. 88 (1990) 325.

[13] H.P. Stadniychuk, M.A. Anderson, T.W. Chapman, J. Electrochem. Soc. 143 (1996) 1629.

[14] F. Coustier, S. Passerini, W.H. Smyrl, Solid State Ionics 100 (1997) 247.

[15] D.B. Le, S. Passerini, F. Coutier, J. Guo, T. Soderstrom, B.B. Owens, W.H. Smyrl, Chem. Mater. 10 (1998) 682.