Book Review

High energy non-aqueous batteries

Edited by A. Cisak and L. Werblan, published by Ellis Horwood, Chicester, UK, 1st edn., 1993, 262 pp., US$ 110.00, ISBN 13-388596-8.

Perhaps the least satisfactory aspect of this book is its title, which only poorly describes its contents. Although other electrochemical systems are mentioned briefly, the text essentially concerns the theoretical and practical aspects of lithium secondary cells with liquid electrolytes; a bias that is acknowledged by the authors in the preface.

A cursory glance at the periodic table shows that lithium has the highest theoretical energy density as a battery anode but realising that energy in a practical system is hampered by the metal's high reactivity. Even for non-aqueous solvents with so-called stable electrolytes it appears that a thin surface passivating film is formed on the lithium metal which hinders the re-plating of the metal on recharge.

The obvious choice for the cathode, on energy grounds, is fluorine but the major practical difficulties of handling this reactive gas and its compounds (such as BrF_3) in a cell preclude its use in practical applications. Transition metal sulfides and oxides show the most promise as cathodes but still suffer from cycleability problems.

Despite these unresolved difficulties the authors consider these systems to be the best candidates for high energy batteries and alternative systems, such as Li–Al/FeS_2, Na/S and Li/polymer electrolyte are only mentioned in passing. Specialist applications such as thermal batteries are not within the scope of the text.

Chapter 1 is a short historical review of the development of chemical power sources but concentrates mainly on primary systems, the important secondary systems lead/acid and Ni/Cd not being mentioned, despite the book's main emphasis on secondary batteries.

Chapters 2 to 4 consider in detail the basic physical chemistry required to describe and understand these systems. Reversible equilibrium thermodynamics is described with particular reference to its implications in non-aqueous electrolytes, for instance the use of a hydrogen reference electrode is still possible because of the easy solvation of protons, and the Pt/H_2 electrode potential is largely independent of solvent.

The double-layer theory of Helmholtz and Gouy–Chapman, the Buttler–Volmer equation, Tafel plots and the Arrhenius equation are all reviewed. A brief description is given of the double layer at the semiconductor electrode/electrolyte interface and its differences from the metal/electrolyte interface; a consequence of different charge carrier density.

The thermodynamics of irreversible processes look at ion transport – the theory of Onsager–Prigogine and Glansdorf and charge transport via Debye–Huckel and Onsager equations.

This extensive theoretical section reviews the classical theories required to understand electrochemical power sources including how these theories have been improved and advanced over recent years. It covers a substantial proportion of the book, occupying 100 pages out of the total of 250. The references are comprehensive so that any aspect can be followed up with further reading if required. It is helpful

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that this section is not considered in isolation but developed and discussed with particular reference to the lithium/non-aqueous electrolyte system.

Chapters 5 to 7 are devoted to the three main components of a working cell, the anode, the cathode and the electrolyte. The chapter on anode materials discusses mainly lithium and its alloys such as Li/Al and Li/Mg although Ca, Mg and Na are also discussed as possible anode materials. The section on cathode materials considers metal sulfides such as FeS, CuS and TiS_2 to be of main interest with some discussion on metal oxides (noticeably V_6O_{13} is absent), CF_n (for primary systems) polyacetylene, SO_2 and thionyl chloride.

The solvents used for the electrolyte solutions are grouped according to protonating power and a table of 38 solvents with properties is listed. It would appear that none of these are stable in the presence of lithium, particularly at the high charging voltages seen by cells, and all rely on passivating films to reduce lithium corrosion.

The final chapter covers cell characteristics. The thermodynamics of cells and a section on cell energy losses are followed by a table listing 58 systems that have been investigated together with some electrical characteristics. This is expanded in the text by discussion of cells based on Li/metal sulfide systems, C- and CF_n-based cathodes, polyacetylene and $SOCl_2$, SO_2Cl_2 and SO_2 systems.

The authors conclude that the prospects for secondary lithium cells of high energy density are good, particularly using lithium alloy anodes and mixed metal sulfides/oxides as cathodes. Cell design to minimise internal resistance is stressed.

The book is well translated from the original Polish under the editorship of T.J. Kemp and proves to be a very readable text. The only criticism of the translation is the use of the terms disposable cells and storage batteries to describe primary and secondary cells, respectively. It is well referenced, containing a total of 600 references which include work up to 1991 and is relatively free from typographical errors although some (e.g., pp. 98, 99, 124, 206, 244, 248, 257, 258) do occur.

It is written as an academic text and concentrates on the theoretical concepts of high energy systems rather than the practical problems of designing cells to realise the benefits mentioned. It mentions very little on the testing of practical cells and nothing in the areas of possible applications, cell design, safety, disposal problems, cycling of strings of cells, effects of overcharge, self discharge, abuse resistance, etc.

This book would be an ideal addition to the library of people researching new lithium secondary chemistries but would be of more limited use for those involved in the design of practical cells or those engaged in non-lithium systems.

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