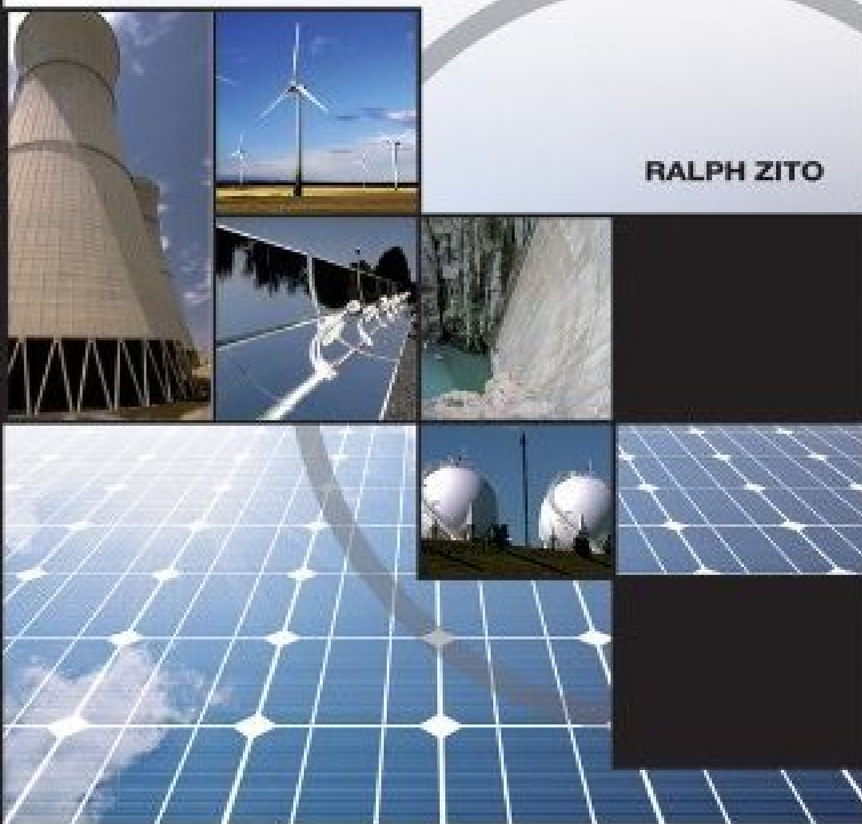
ENERGY STORAGE

A NEW APPROACH

RALPH ZITO



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Preface

The main purpose of this book is to present a different phenomenological approach to practical energy storage. Throughout the book, a main thread of the problems associated with the generation, transmission, conversion, and storage of energy is proposed, and various technologies are addressed primarily from a phenomenological viewpoint. The exploration of new processes is a major part of the continual search for improved means of the generation and storage of energy.

Although some mathematical developments are presented, this book is not intended as a text on thermodynamics or electrochemistry. Certainly, thermodynamics is employed and generous use is made of mathematical tools, but this is not a text directed toward the development or teaching of such principles. It is assumed that the reader possesses some knowledge of elementary classical physics and mathematics and differential calculus in order to easily understand some of the details of thermodynamics and diffusion processes upon which the mechanisms of concentration cell operations are based.

This book presents a broad review of energy technology only in summary fashion in order to provide a background so that the concentration cell approach will be viewed in context with other available means of energy storage. It is necessary to cover a reasonable portion of these subjects in order to make this narrative understandable as an alternative presentation. The rationale behind the concentration cell approach should become apparent as the reader moves through the arguments and reviews.

The primary aim is to suggest and describe an alternative approach to energy storage other than the ones that have been pursued in the past, especially so vigorously within the past thirty to forty years.

The recognized need for improved and practical ways to store large quantities of energy for later use, such as in load leveling for the electric power utilities, has resulted in innumerable programs sponsored by the Atomic Energy Commission, the Energy Research and Development Administration, and the present Department of Energy.

However, many of the concepts regarding the processes at electrode surfaces evolved during the prolonged writing of this book, and the mathematics was developed subsequent to the experiments with laboratory cells described here. The work is hardly complete, and much still needs to be explained. Our astonishment was significant when we first observed the large voltages produced in symmetrical cells with electrodes of large micro-areas.

Hopefully, this book will engender interest in acquiring a basic understanding and stimulate further explorations into other, alternative methods of storing energy that may have been largely overlooked, such as the class of phenomena generally referred to in electrochemistry as "concentration cells." There is much opportunity to store energy in an efficient and easily reversible fashion. Since this type of cell makes use of the colligative properties of substances, many different combinations of materials can be employed in such cells.

The first five parts are devoted to a general discussion of energy issues and the presentation of tutorial information.

The author gathered most of the data and operation and construction details during the various development projects undertaken in redox and concentration types of cell and battery development. Much of the technical information, performance data, and design parameters were obtained while the author was with the Westinghouse Electric Co. Research Center in Pittsburgh, the General Electric Co., the Research and Development Center in Schenectady, NY, and the Technology Research Laboratories, Inc. in Durham, NC.

The practical application aspects of a category of phenomena in physics and electrochemistry have been largely overlooked. That category is the source of electric potentials that can be produced from concentration differences of the same chemical ionic species opposite electrode surfaces.

The only practical answer to all-around energy storage needs may lie in the application of the class of phenomena referred to as electrochemical concentration cells. The electrical potential results from structured cells with intense differences in concentration of the same elemental (chemical) specie at two different oxidation states. Storage continues to be a main concern in the whole spectrum of energy related issues.

There is no question regarding the efficacy or scientific soundness of the principles employed for storing energy in this fashion. The approach is well beyond such serious concerns. The questions that remain are those regarding the ultimate practicality and competitiveness with respect to other methods of reversible energy storage in such matters as its ultimately achievable efficiency, cost, and energy density.

The information presented in this book is the result of forty years of search and experimental researching for a method of storing energy in a reversible, dependable, and life-long manner. Research has largely been centered on the electrochemistry of what has in recent years become known as redox systems. Both static and full flow electrolyte systems have been explored. The resultant system that satisfied most, if not all, of the imposed practical requirements and appeared to offer the least limited performance with future development was the concentration cell – a significant departure from the normal path of such studies.

This mechanism for storage is based upon Nernst's equation for the chemical potential that can be derived from the ratio of concentrations of the same ionic substance at opposing electrodes in an electrochemical cell.

There are two further volumes planned in this series on energy storage, the first of which, tentatively titled, *Concentration Cells: Fabrication Methods and Materials*, is due to be published by Wiley-Scrivener in September 2011. The aim of this second volume will be to provide the engineer and scientist with the most comprehensive coverage of the concentration cell yet written, with a view toward employing the concentration cell in the storage of energy on a large scale.

Dedications and Acknowledgements

I am taking advantage of this written opportunity to express my deep appreciation and thanks to some of the many people who have made writing this book possible. With their participation and contributions over the years in research and development programs at TRL, Inc. and GEL, Inc., they have made many contributions to accumulating more experience with these energy technologies. It is not practical to even attempt to list all those individuals who, over many years, have designed and constructed experimental hardware, from which we have learned how to cope with a multitude of related problems, and who have made writing this book possible.

In particular, I would like to acknowledge the following for their direct influences on the developments. Special thanks go to Prof. Richard S. Morse and Prof. David Ragone at MIT, who both launched this whole area of redox systems in Cambridge, MA in 1968. Also, I would like to thank Keith Poulin for his administrative and managerial skills, Graham Wilson, whose fertile imagination, combined with his engineering capabilities, resulted in most of our very early hardware display devices, Joseph O. Dixon for his engineering skills, faith, and confidence, D. Morris for his problem solving, tenacity, and positive attitude, and Prof. Charles Harman from Duke University for his technical and personal support and patience.

There are so many people, including my dedicated secretaries over the years, Phoebe Rasmussen, Sarah Tortora, and Patricia Pearson, who need to be commended for staying with us through difficult situations. Others include the many shop and laboratory people who coped with rather messy conditions in handling such materials as graphite and carbon black and unfriendly electrolytes in large quantities.

I would like to thank one individual in particular, Sir John Samuel, who has steadfastly maintained a confidence in our technical accomplishments and has been responsible for obtaining much needed support for our programs.

This book reflects only a tiny portion of all the work from so many others who preceded its writing and made writing it possible.

1

Introduction

All the discussions and dire announcements in technical literature during recent years have certainly made everyone aware of the "energy problem." There is not much doubt that we are confronted with this problem and that it is an issue of domestic and international importance. The critical issues concerning the availability of energy sources and their efficient use are rapidly becoming vitally important. Increasing population, in conjunction with the greater-than-ever energy and materials demands that people are making in order to increase their comfort, travel, etc., is indeed causing greater stress. All of these require not only an increased availability of energy but also more effective ways of utilizing what is available.

The main efforts of research and development have been directed towards the development of new alternatives or finding more primary sources of energy. For the present, and until the discovery of a new class of phenomena, we have a fairly good idea of what can be accomplished. We know what alternative sources are possible – alternative presumably to petroleum products. Yet, none of them are nearly as attractive for portable or motive power unless we significantly lower our criteria.

It would appear that sources of energy are plentiful on planet Earth. However, they are often locally unavailable, too bulky, too unpredictable (solar and wind), and/or too dangerous to be portable. An effective method for storing energy would greatly reduce the problem and would provide low-cost energy for everyone. It seems that not nearly as much attention or support has been directed toward the problem of storage as that which has been directed toward generation. Perhaps this difference is due to the absence of many promising approaches to accomplishing the latter. This book presents a different approach and aims to stimulate additional efforts toward the search and development of better storage.

There are not many attractive choices for storage, and most are not portable or cheap. We cannot carry windmills around – they are huge and dangerous. A waterfall, due to topographical considerations, is not available everywhere, and its size is immense for the intermittent power and energy produced.

Batteries are the least obtrusive and the most predictable limited secondary sources, but they are not practical as large-scale primary or secondary sources. Windmills and photovoltaic cells are almost useless without either storage or the assistance of an electric utility power grid, which operates on nuclear power or coal fuel. It would appear that the energy source trap has merely changed shape.

Ideally, high energy and power density "batteries" of some sort that are charged by nuclear or fossil fuel would be a good solution to smoothing the irregularities in the distribution and availability for the planet's population. The term "batteries" used here only refers to some mechanism for practical storage. So far, the most promising is probably an electrochemical method. Compressed air, metal springs, flywheels, etc., all have very serious drawbacks. Most generating facilities are not portable, nor would most people wish to live with them in their midst.

Storing energy in its many forms in nature is a vital part of all processes as well as life itself on Earth. As one explores these processes and their importance to us, we can gradually make observations that lead to some revealing conclusions.

One of our purposes is to examine the general area of energy storage and to identify the key mechanisms that have significant roles in nature and civilization. Then we will develop a description and a reasonably detailed understanding of why we need to store energy and how the various mechanisms we employ work to satisfy these needs. Most of this book is devoted to electrochemical processes and, in particular, full flow electrolyte cells that are frequently referred to as redox batteries.

In a very general sense, there are only three purposes for the storage of energy: to make an energy supply portable from essentially non-portable sources, to store from an ongoing source for use at a later time, and to change the ratio of power-to-energy, as accomplished by flywheels, capacitors, etc.

All applications of energy storage can be put into one or more of these categories. Certainly, if we wish to power a portable power tool or an electric automobile, a hydroelectric plant is hardly practicable. However, if we use the energy produced by the hydroelectric station and store part of what is not immediately needed in an electric battery, it becomes a practical situation for the electric vehicle. Nuclear energy sources are hardly portable on a small scale. But in similar fashion, as for non-portable hydroelectric stations, storing portions of the generated energy in some sort of device such as a battery could become useful in mobile electric vehicles.

In the second instance, we might have the need to store solar energy during the daylight hours for use after sunset to power lights, etc. There are many cases where the convenience factor is not met – where the generation or the source of energy is occurring at a time that does not coincide with the need or application time.

It must be noted here that when we refer to energy we are essentially referring to the "capacity to do work" in the classic sense of *Force* × *Distance*. This capacity is being transferred from one source to a device that is capable of storing that capacity for work to be used at a later time.

The storage of energy in one form or another for later use has been extremely important not only to mankind but also to virtually every form of life. Storing energy in the form of chemical structures, such as carbohydrates, enables life forms to survive for periods of time between food intake activities.

Obviously, all activity and motion are manifestations of exchanges of energy from one level to another. The exchange of potential energy for kinetic energy of motion for falling objects is a simple example. Few energy-expending actions make use of prompt sources. It can be argued that even the processes that produce solar radiation make use of energy that was stored at some earlier stages of cosmic evolution.

An energy bank deposit must be made at an earlier time for energy to be in an available and usable form at the time of demand.

This stored, but temporarily unavailable energy is usually not in a form that is needed for the specific operations at the demand time. Hence, there is usually a conversion mechanism accompanying the stored energy device in order for the energy reserve to be useful. There are many examples that can illustrate this simple, but basic, premise. They are presented in a later section of this book. In biochemical processes, the stored carbohydrates, perhaps in the form of sugars, are oxidized in order to produce the heat necessary to sustain life.

Chapter 3 lists other, simpler forms of energy storage that are familiar to all of us. At the outset, I would like to make clear the major purpose of this book. Its purpose is to emphasize the importance of this general approach to energy storage as a rather new technical viewpoint wherein the physical principles employed are basic to all matter. Perhaps the best example of this is the mechanical and thermal behavior of gas compression.

This book focuses on a single and particular class of artificial means of energy storage, a general class of energy conversion known as electrochemical processes. More specifically, this book concentrates on aqueous systems that are largely compatible with ambient conditions of temperature, pressure, and a chemical environment. Some mention will be made to these other systems and devices, but only in passing, so that we may retain a better perspective regarding in placing the electrochemical systems of prime interest here. The reasons for this selection will become clear as the argument develops and as some background information associated with major application criteria is provided.

In the chapters to follow, I outline the requirements of our energy needs and establish a background of information upon which we can more clearly assess the various storage options available to us. However, the primary purpose is the description of a new approach. The science is not new, but it has received scant attention as a possibility for reducing our energy problems.

The first three sections describe the background and rationale of electrochemical storage and, more specifically, redox types of systems, based on first-hand knowledge in developing earlier attempts at large-scale energy storage for load leveling and standby power. Justifications for redox systems for large-scale, bulk energy, stationary storage applications will also be identified.

The first six chapters present not only a general background of energy requirements, competitive methods for storage, and a description of the basics of concentration cell operations, but they also provide sufficient information to comprehend this different approach to storage along with some justifications for taking that technical direction. However, in order to fully appreciate the important details of cell operational mechanisms, it is necessary to delve a bit into the various key processes of diffusion and transport processes. This entails rather lengthy and tedious mathematical analyses. I have collected and placed the major portion of such activities in Chapters 8 and 9.

A significant amount of space is devoted to explaining the thermodynamics of the concentration cell, and the explanations of the operating principles are numerous. Moreover, keeping track of the materials transport mechanisms and the source of electric potential can be confusing. However, in order to contend with the many aspects of present day energy technology, it is important to have a working knowledge and comprehension of the basic underlying physics. This book is directed to those readers who would like to have an appreciation of the wide vistas of energy technology and wish to acquire enough understanding to make independent evaluations of modern trends in such matters as conservation, fossil fuels versus solar energy, and so on.

The purpose of this book is to stimulate interest in the subject of energy and the dynamics of the physical world around us. Some mathematics are employed where it is necessary in order to establish quantitative energy relationships in solving problems or in the design of devices. The purpose of the mathematics is to provide those who have the interest and skills with a more in-depth understanding of the factors and limitations of the physical world as we now know it.

There are also many excellent texts written on energy, theoretical mechanics, and the mathematics of theoretical physics. Some of these are listed in the accompanying bibliography.

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Comments on Classical Mechanics

The concept of energy is elusive and more than a bit mysterious. It is constantly being re-examined for greater understanding. It's an idea or concept of which nearly everyone thinks they have some understanding. It is interesting to note how we refer to the idea by such phrases as "burning excess energy," "using a lot of energy," or "someone has a lot of energy," as if it were a fuel of some sort. The repetition of the word, as with most concepts, conveys a vague feeling of comfort with the notion, and that we indeed have a grasp of it.

Frequently, in ordinary conversation or in more popular literature, the term energy is confused with or substituted for force. This confusion dates back many centuries beginning with man's attempts to comprehend physical phenomena and the world around him. Even after the beginning of what is known as the scientific method, attributed to Galileo, much about the subject has confounded our comprehension. In the next pages I will address the issue of what energy is.

We are never actually able to observe the quantity named "energy," but its effects are certainly, and easily observable. Perhaps this also adds to the mystery of energy. Lindsay and Margenau presented