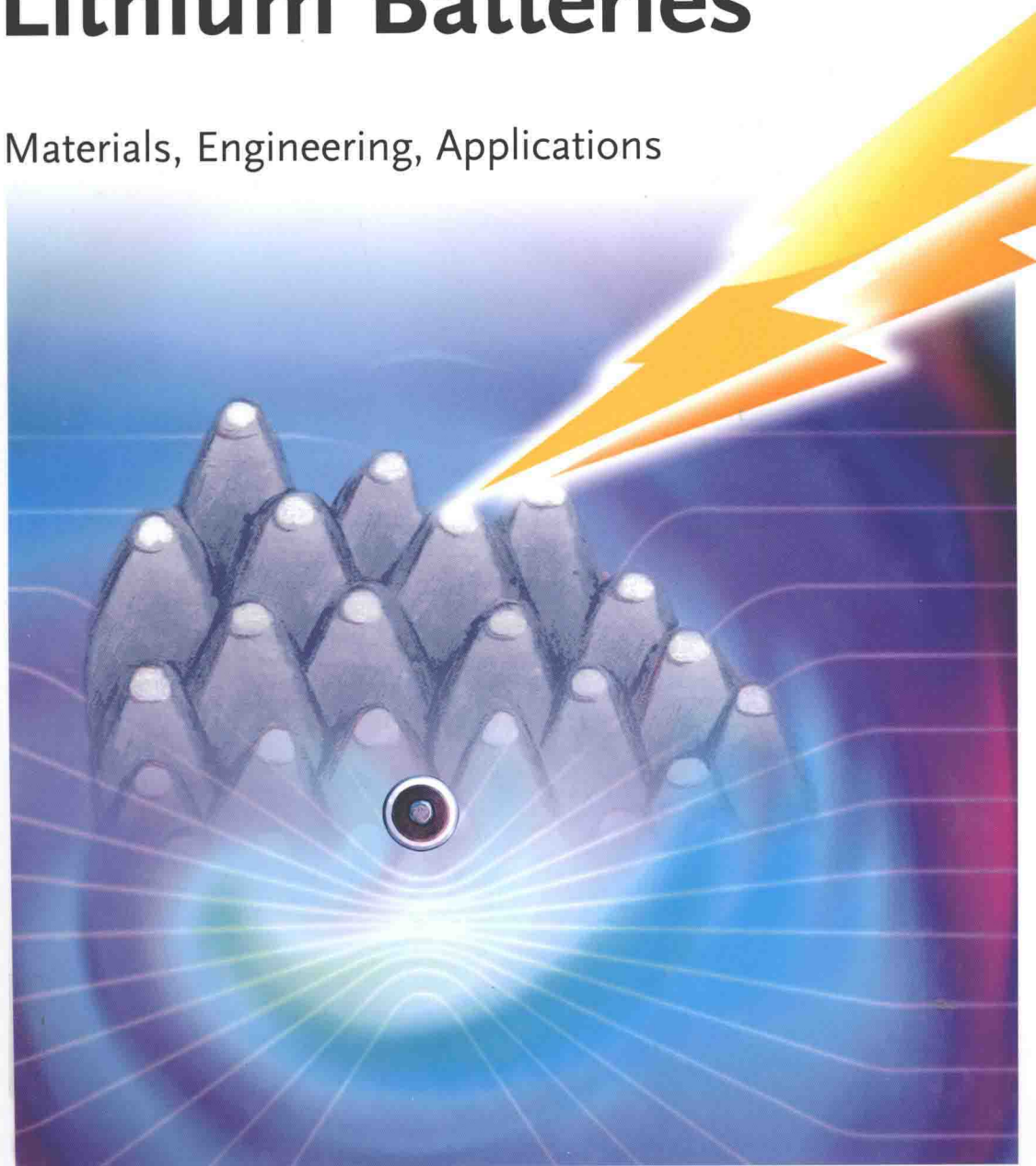


Edited by K. E. Aifantis,  
S. A. Hackney, and R. V. Kumar

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# High Energy Density Lithium Batteries

Materials, Engineering, Applications



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Materials, Engineering, Applications

*Edited by*

*Katerina E. Aifantis, Stephen A. Hackney,  
and R. Vasant Kumar*



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### The Editors

**Dr. Katerina E. Aifantis**

Aristotle University of Thessaloniki  
Laboratory of Mechanics and Materials  
P.O. Box 468  
52124 Thessaloniki  
Greece

and

Physics Department  
Michigan Technological University  
1400, Townsend Drive  
Houghton, MI 49931  
USA

**Prof. Stephen A. Hackney**

Materials Science and Metallurgy  
Michigan Technological University  
1400, Townsend Drive  
Houghton, MI 49931  
USA

**Dr. R. Vasant Kumar**

University of Cambridge  
Department of Materials Science  
and Metallurgy  
Pembroke Street  
Cambridge, CB2 3QZ  
United Kingdom

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## Preface

Modern society is characterized by a constant need for energy. In the past century, the majority of this energy has been supplied by fossil fuels. Fossil fuels are not only used in the thermal generation of electricity, but oil products are also relied upon for rapid transportation. The oil shock of 2008 and the concerns of possible global climate change have brought into question this reliance on petroleum and there has been a discernable shift towards developing technologies that can convert alternative energy sources, such as solar, wind and nuclear into electricity. It is just as important, however, to develop, at the same pace, technologies that can store this energy in a portable form. Portable energy allows for the increasing interconnectivity of people around the world through rapid communication and transportation. The portable energy afforded by high energy density batteries has not only made possible a variety of personal communication, entertainment and computational devices, but has found use in biomedical implantable devices such as pacemakers. Recently, this portable energy has also begun to influence battery applications in transportation. The improvement of battery science and technology is, therefore, a critical link in transitioning from fossil fuels to alternative energy sources. In particular, the emerging field of nanotechnology promises not only higher energy density batteries, but also rechargeable batteries with longer lifetimes.

It is this need for high density energy storage devices that prompted us to edit the present book. Although batteries are essential to everyone from a very young age, their explicit study is not custom during college education. The present book, therefore, starts out with an introductory chapter that familiarizes the reader with the basic electrochemical processes and properties of batteries. In continuing, Chapters 2 and 3 give a historic outline of the development of primary and secondary (rechargeable) batteries, where the highly preferred properties of Li batteries are illustrated. To further motivate the reader about the importance of continuous research on secondary Li chemistries, Chapter 4 describes the current and potential application of Li batteries, focusing on how they can be used for powering electric vehicles. The remaining chapters, therefore, elaborate on technological developments that are currently being undertaken for improving cathodes, anodes and electrolytes for rechargeable Li batteries; the common characteristic of all these components is their nanoscale structure. This book is, therefore, appropriate

not only for advanced undergraduates and graduates, but also for battery developers (Chapters 4-8). Chapter 8 in particular is a collection of recent studies that are concerned with the limited theoretical works of the last decade that try to predict, using mechanics, the optimum materials chemistries for next generation anodes and cathodes. Such theoretical considerations, must be accounted for, in order to develop next-generation electrodes, as experiments and theory go hand in hand for obtaining the most efficient product. And despite the fact that plethora experimental studies are concerned with anode and cathode materials, theoretical works that try to predict their damage during charging and discharging, by employing known theoretical models, are well below twenty.

In fact, it was this attempt of interpreting damage and fracture in Li-electrodes that initiated the collaboration of Katerina Aifantis and Stephen Hackney, 9 years ago, when the latter posed this research problem to the former who was his undergraduate student at the time. They soon realized that their theoretical predictions were in agreement with experimental data and were in fact able to employ their design criteria for fabricating promising Sn/C nanostructured anodes. This urged them to make the importance of theoretical input known to a larger audience, through publication of a book, and that is why the present book concludes with a chapter devoted to theoretical issues of Li batteries. In searching for a third editor that could contribute by providing more complete information on the operation of electrochemical cells, they decided to ask R. Vasant Kumar, not only due to his expertise, but also due to his thorough web-based lecture notes.

In order to ensure continuity throughout the book we wrote or co-wrote the majority of the chapters ourselves and we constantly communicated with our authors, whom we would like to gratefully acknowledge for their thoroughness and promptness. In this connection we would like to thank Dr. Emmanuel Stratakis of the IESL-FORTH, Crete, Greece, for providing SEM images of his Si-microstructures on which Katerina E. Aifantis based the cover influenced by the paintings of her artist mother. KEA would also to thank the European Research Council (ERC Starting Grant 211166) for currently supporting her research on nanostructured materials, including Li-anodes, as well as her mentor: Professor E.C. Aifantis (father), and PhD advisors J.R. Willis & J.Th.M. De Hosson. The Editors would also like to acknowledge use of materials from the University of Cambridge web-based teaching and learning package on "Batteries".

In concluding this preface we would like to mention that the past two decades have not only seen considerable improvements in performance of the well-established types of secondary batteries but also witnessed the introduction of new types of batteries. Over the same period many new applications for such batteries have also taken place in wide ranging applications. This is by no means the end of the story. In the near future new chemistries may emerge within the secondary battery technology resulting in applications we have not even imagined at this stage.

*Katerina E. Aifantis, Stephen A. Hackney, R. Vasant Kumar*

## List of Contributors

### ***Katerina E. Aifantis***

Aristotle University of  
Thessaloniki  
Laboratory of Mechanics and  
Materials  
P.O. Box 468  
52124 Thessaloniki  
Greece

Michigan Technological  
University  
Physics Department  
1400, Townsend Drive  
Houghton, MI 49931  
USA

### ***Martin L. Dunn***

University of Colorado  
Department of Mechanical  
Engineering  
Boulder, CO 80309  
USA

### ***Stephen A. Hackney***

Michigan Technological  
University  
Department of Materials Science  
and Engineering  
Houghton, MI 49931  
USA

### ***Seok Kim***

Pusan National University  
Department of Chemical and  
Biochemical Engineering  
San 30, Jangjeon-dong,  
Geumjeong-gu  
Busan 609-735  
South Korea

### ***R. Vasant Kumar***

University of Cambridge  
Department of Materials Science  
and Metallurgy  
Cambridge, CB2 3QZ  
UK

### ***Kurt Maute***

University of Colorado  
Aerospace Engineering Science  
Boulder, CO 80309  
USA

### ***Soo-jin Park***

Inha University  
Department of Chemistry  
253, Yonghyun-dong, Nam-gu  
Incheon 402-751  
South Korea

***Thapanee Sarakonsri***

Chiang Mai University  
Department of Chemistry  
Chiang Mai 50200  
Thailand

***Min-Kang Seo***

Inha University  
Department of Chemistry  
253, Yonghyun-dong, Nam-gu  
Incheon 402-751  
South Korea



## Contents

**Preface** *XIII*

**List of Contributors** *XV*

|          |  |           |
|----------|--|-----------|
| <b>1</b> | <b>Introduction to Electrochemical Cells</b>           | <b>1</b>  |
|          | <i>R. Vasant Kumar and Thapanee Sarakonsri</i>         |           |
| 1.1      | What are Batteries?                                    | 1         |
| 1.2      | Quantities Characterizing Batteries                    | 3         |
| 1.2.1    | Voltage  | 4         |
| 1.2.2    | Electrode Kinetics (Polarization and Cell Impedance)   | 7         |
| 1.2.2.1  | Electrical Double Layer                                | 7         |
| 1.2.2.2  | Rate of Reaction                                       | 8         |
| 1.2.2.3  | Electrodes Away from Equilibrium                       | 8         |
| 1.2.2.4  | The Tafel Equation                                     | 8         |
| 1.2.2.5  | Example: Plotting a Tafel Curve for a Copper Electrode | 9         |
| 1.2.2.6  | Other Limiting Factors                                 | 11        |
| 1.2.2.7  | Tafel Curves for a Battery                             | 11        |
| 1.2.3    | Capacity   | 13        |
| 1.2.4    | Shelf-Life   | 14        |
| 1.2.5    | Discharge Curve/Cycle Life                             | 14        |
| 1.2.6    | Energy Density   | 15        |
| 1.2.7    | Specific Energy Density                                | 15        |
| 1.2.8    | Power Density  | 16        |
| 1.2.9    | Service Life/Temperature Dependence                    | 16        |
| 1.3      | Primary and Secondary Batteries                        | 17        |
| 1.4      | Battery Market   | 19        |
| 1.5      | Recycling and Safety Issues                            | 20        |
|          | References   | 25        |
| <b>2</b> | <b>Primary Batteries</b>                               | <b>27</b> |
|          | <i>Thapanee Sarakonsri and R. Vasant Kumar</i>         |           |
| 2.1      | Introduction   | 27        |
| 2.2      | The Early Batteries                                    | 27        |

|          |  |           |
|----------|--|-----------|
| 2.3      | The Zinc/Carbon Cell   | 31        |
| 2.3.1    | The Leclanché Cell   | 31        |
| 2.3.2    | The Gassner Cell   | 32        |
| 2.3.3    | Current Zinc/Carbon Cell   | 33        |
| 2.3.3.1  | Electrochemical Reactions  | 34        |
| 2.3.3.2  | Components   | 35        |
| 2.3.4    | Disadvantages  | 36        |
| 2.4      | Alkaline Batteries   | 36        |
| 2.4.1    | Electrochemical Reactions  | 38        |
| 2.4.2    | Components   | 38        |
| 2.4.3    | Disadvantages  | 39        |
| 2.5      | Button Batteries   | 40        |
| 2.5.1    | Mercury Oxide Battery  | 40        |
| 2.5.2    | Zn/Ag <sub>2</sub> O Battery                                       | 41        |
| 2.5.3    | Metal–Air Batteries  | 42        |
| 2.5.3.1  | Zn/Air Battery   | 44        |
| 2.5.3.2  | Aluminum/Air Batteries   | 45        |
| 2.6      | Li Primary Batteries   | 46        |
| 2.6.1    | Lithium/Thionyl Chloride Batteries                                 | 47        |
| 2.6.2    | Lithium/Sulfur Dioxide Cells                                       | 48        |
| 2.7      | Oxyride Batteries  | 49        |
| 2.8      | Damage in Primary Batteries  | 50        |
| 2.9      | Conclusions  | 52        |
|          | References   | 52        |
| <b>3</b> | <b>A Review of Materials and Chemistry for Secondary Batteries</b> | <b>53</b> |
|          | <i>R. Vasant Kumar and Thapanee Sarakonsri</i>                     |           |
| 3.1      | The Lead-Acid Battery  | 54        |
| 3.1.1    | Electrochemical Reactions  | 56        |
| 3.1.2    | Components   | 57        |
| 3.1.3    | New Components   | 60        |
| 3.2      | The Nickel–Cadmium Battery   | 63        |
| 3.2.1    | Electrochemical Reactions  | 65        |
| 3.3      | Nickel–Metal Hydride (Ni-MH) Batteries                             | 66        |
| 3.4      | Secondary Alkaline Batteries                                       | 67        |
| 3.4.1    | Components   | 67        |
| 3.5      | Secondary Lithium Batteries  | 68        |
| 3.5.1    | Lithium-Ion Batteries  | 70        |
| 3.5.2    | Li-Polymer Batteries   | 73        |
| 3.5.3    | Evaluation of Li Battery Materials and Chemistry                   | 74        |
| 3.6      | Lithium–Sulfur Batteries   | 76        |
| 3.7      | Conclusions  | 80        |
|          | References   | 80        |

|          |   |            |
|----------|---|------------|
| <b>4</b> | <b>Current and Potential Applications of Secondary Li Batteries</b>   | <b>81</b>  |
|          | <i>Katerina E. Aifantis and Stephen A. Hackney</i>                    |            |
| 4.1      | Portable Electronic Devices   | 81         |
| 4.2      | Hybrid and Electric Vehicles  | 82         |
| 4.3      | Medical Applications  | 85         |
| 4.3.1    | Heart Pacemakers  | 85         |
| 4.3.2    | Neurological Pacemakers   | 86         |
| 4.4      | Application of Secondary Li Ion Battery Systems in Vehicle Technology | 87         |
| 4.4.1    | Parallel Connection   | 91         |
| 4.4.2    | Series Connections  | 93         |
| 4.4.3    | Limitations and Safety Issues   | 97         |
|          | References  | 100        |
| <b>5</b> | <b>Li-Ion Cathodes: Materials Engineering Through Chemistry</b>       | <b>103</b> |
|          | <i>Stephen A. Hackney</i>   |            |
| 5.1      | Energy Density and Thermodynamics                                     | 103        |
| 5.2      | Materials Chemistry and Engineering of Voltage Plateau                | 111        |
| 5.3      | Multitransition Metal Oxide Engineering for Capacity and Stability    | 119        |
| 5.4      | Conclusion  | 126        |
|          | References  | 126        |
| <b>6</b> | <b>Next-Generation Anodes for Secondary Li-Ion Batteries</b>          | <b>129</b> |
|          | <i>Katerina E. Aifantis</i>   |            |
| 6.1      | Introduction  | 129        |
| 6.2      | Chemical Attack by the Electrolyte                                    | 130        |
| 6.3      | Mechanical Instabilities during Electrochemical Cycling               | 132        |
| 6.4      | Nanostructured Anodes   | 135        |
| 6.5      | Thin Film Anodes  | 136        |
| 6.5.1    | Sn-Based Thin Film Anodes   | 136        |
| 6.5.2    | Si-Based Thin Film Anodes   | 137        |
| 6.6      | Nanofiber/Nanotube/Nanowire Anodes                                    | 142        |
| 6.6.1    | Sn-Based Nanofiber/Nanowire Anodes                                    | 142        |
| 6.6.2    | Si-Nanowire Anodes  | 143        |
| 6.7      | Active/Less Active Nanostructured Anodes                              | 146        |
| 6.7.1    | Sn-Based Active/Less Active Anodes                                    | 146        |
| 6.7.1.1  | Sn-Sb Alloys  | 146        |
| 6.7.1.2  | SnS <sub>2</sub> Nanoplates   | 148        |
| 6.7.1.3  | Sn-C Nanocomposites   | 149        |
| 6.7.2    | Si-Based Active/Less Active Nanocomposites                            | 151        |
| 6.7.2.1  | Si-SiO <sub>2</sub> -C Composites                                     | 151        |
| 6.7.2.2  | Si-C Nanocomposites   | 153        |

|       |                       |     |
|-------|-----------------------|-----|
| 6.8   | Other Anode Materials | 157 |
| 6.8.1 | Sb-Based Anodes       | 157 |
| 6.8.2 | Al-Based Anodes       | 158 |
| 6.8.3 | Bi-Based Anodes       | 160 |
| 6.9   | Conclusions           | 162 |
|       | References            | 162 |

## 7 Next-Generation Electrolytes for Li Batteries 165

*Soo-Jin Park, Min-Kang Seo, and Seok Kim*

|         |  |     |
|---------|--|-----|
| 7.1     | Introduction   | 165 |
| 7.2     | Background   | 170 |
| 7.2.1   | Li-Ion Liquid Electrolytes   | 170 |
| 7.2.2   | Why Polymer Electrolytes?  | 172 |
| 7.2.3   | Metal Ion Salts for Polymer Electrolytes   | 173 |
| 7.3     | Preparation and Characterization of Polymer Electrolytes                           | 174 |
| 7.3.1   | Preparation of Polymer Electrolytes  | 175 |
| 7.3.1.1 | Molten-Salt-Containing Polymer Gel Electrolytes                                    | 175 |
| 7.3.1.2 | Organic-Modified MMT-Containing Polymer Composite Electrolytes                     | 175 |
| 7.3.1.3 | Ion-Exchanged Li-MMT-Containing Polymer Composite Electrolytes                     | 175 |
| 7.3.1.4 | Mesoporous Silicate (MCM-41)-Containing Polymer Composite Electrolytes             | 176 |
| 7.3.2   | Characterization of Molten-Salt-Containing Polymer Gel Electrolytes                | 176 |
| 7.3.2.1 | Morphologies and Structural Properties   | 176 |
| 7.3.2.2 | Thermal Properties   | 178 |
| 7.3.2.3 | Electrochemical Properties   | 180 |
| 7.3.3   | Characterization of Organic-Modified MMT-Containing Polymer Composite Electrolytes | 185 |
| 7.3.3.1 | Morphologies and Structural Properties   | 185 |
| 7.3.3.2 | Thermal Properties   | 188 |
| 7.3.3.3 | Electrochemical Properties   | 189 |
| 7.3.4   | Ion-Exchanged Li-MMT-Containing Polymer Composite Electrolytes                     | 191 |
| 7.3.4.1 | Structural Properties  | 191 |
| 7.3.4.2 | Thermal Properties   | 192 |
| 7.3.4.3 | Electrochemical Properties   | 193 |
| 7.3.5   | Mesoporous Silicate (MCM-41)-Containing Polymer Composite Electrolytes             | 197 |
| 7.3.5.1 | Morphologies and Structural Properties   | 197 |
| 7.3.5.2 | Thermal Properties   | 200 |
| 7.3.5.3 | Electrochemical Properties   | 201 |
| 7.4     | Conclusions  | 203 |
|         | References   | 205 |

|          |   |            |
|----------|---|------------|
| <b>8</b> | <b>Mechanics of Materials for Li-Battery Systems</b>                            | <b>209</b> |
|          | <i>Katerina E. Aifantis, Kurt Maute, Martin L. Dunn, and Stephen A. Hackney</i> |            |
| 8.1      | Introduction  | 209        |
| 8.2      | Mechanics Considerations During Battery Life                                    | 211        |
| 8.3      | Modeling Elasticity and Fracture During Electrochemical Cycling                 | 214        |
| 8.3.1    | Fracture in a Bilayer Configuration   | 214        |
| 8.3.2    | Elasticity and Fracture in an Axially Symmetric Configuration                   | 216        |
| 8.3.3    | Fracture and Damage Evolution for Thin Film Case                                | 220        |
| 8.3.4    | Fracture and Damage in Fiber-Like/Nanowire Electrodes                           | 223        |
| 8.3.5    | Spherical Active Sites  | 223        |
| 8.3.6    | Stability Plots   | 226        |
| 8.3.7    | Volume Fraction and Particle Size Considerations                                | 227        |
| 8.3.7.1  | Information from Stability Index  | 228        |
| 8.3.7.2  | Griffith's Criterion  | 228        |
| 8.3.8    | Critical Crack Length   | 230        |
| 8.3.9    | Mechanical Stability of Sn/C Island Structure Anode                             | 231        |
| 8.4      | Multiscale Phenomena and Considerations in Modeling                             | 235        |
| 8.4.1    | Macroscale Modeling   | 236        |
| 8.5      | Particle Models of Coupled Diffusion and Stress Generation                      | 239        |
| 8.5.1    | Li <sup>+</sup> Transport During Extraction and Insertion from a Host           | 240        |
| 8.5.2    | Electrochemical Reaction Kinetics   | 242        |
| 8.5.3    | Stress Generation   | 243        |
| 8.5.4    | Representative Results  | 243        |
| 8.6      | Diffusional Processes During Cycling  | 248        |
| 8.6.1    | Multiscale Electrochemical Interactions   | 248        |
| 8.6.2    | Diffusion Stresses in Low Symmetry Composition Fields                           | 252        |
| 8.7      | Conclusions   | 254        |
|          | References  | 254        |
|          | <b>Index</b>  | <b>257</b> |

## 1

## Introduction to Electrochemical Cells

*R. Vasant Kumar and Thapanee Sarakonsri*

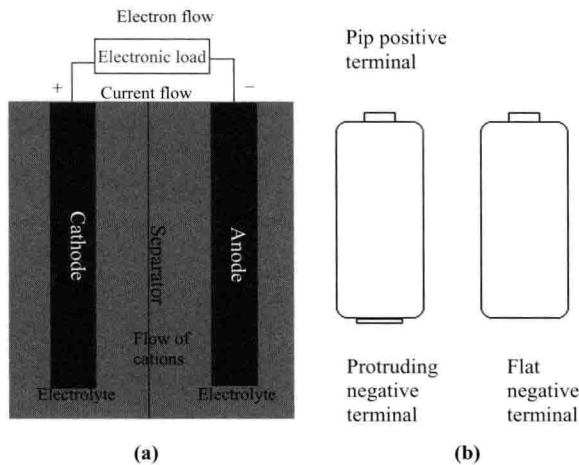
### 1.1

#### What are Batteries?

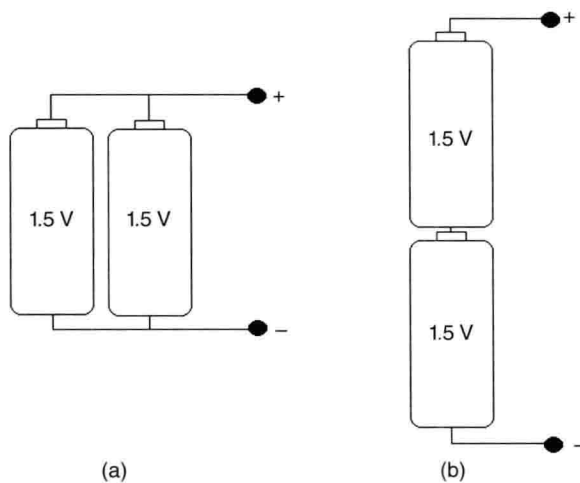
The purpose of this chapter is to provide the basic knowledge on batteries, which will allow for their general understanding. Therefore, after defining their components and structure, an overview of the quantities that characterize these storage devices will be given.

Scientifically batteries are referred to as electrochemical or galvanic cells, due to the fact that they store electrical energy in the form of chemical energy and because the electrochemical reactions that take place are also termed galvanic. Galvanic reactions are thermodynamically favorable (the free energy difference,  $\Delta G$ , is negative) and occur spontaneously when two materials of different positive standard reduction potentials are connected by an electronic load (meaning that a voltage is derived). The material with the lower positive standard reduction potential undergoes an oxidation reaction providing electrons by the external circuit to the material with the higher positive standard reduction potential, which in turn undergoes a reduction reaction. These half reactions occur concurrently and allow for the conversion of chemical energy to electrical energy by means of electron transfer through the external circuit. It follows that the material with the lower positive standard reduction potential is called the negative electrode or anode on discharge (since it provides electrons), while the material with the higher positive standard reduction is called the positive electrode or cathode on discharge (since it accepts electrons).

In addition to the electrodes, the two other constituents that are required for such reactions to take place are the electrolyte solution and the separator. The electrolyte is an ion conducting material, which can be in the form of an aqueous, molten, or solid solution, while the separator is a membrane that physically prevents a direct contact between the two electrodes and allows ions but not electrons to pass through; it therefore ensures electrical insulation for charge neutralization in both the anode and cathode once the reaction is completed. Two final parts required to complete a commercial galvanic cell are the terminals. They are necessary when applying the batteries to electrical appliances with specific holder



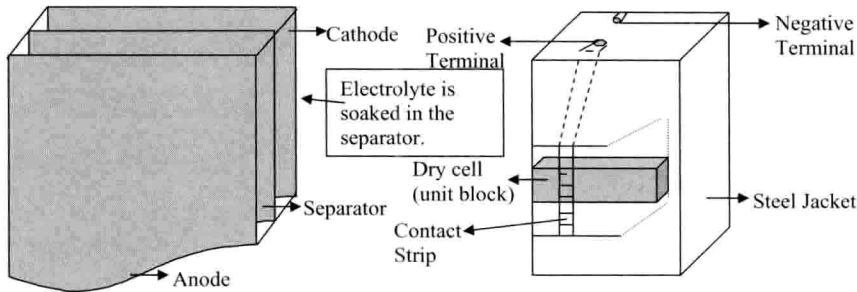
**Figure 1.1** (a) The schematic diagram of a simple galvanic cell. (b) Terminal designs for cylindrical batteries.



**Figure 1.2** (a) An illustration of batteries connected in parallel to obtain double current. (b) An illustration of batteries connected in series to obtain 3 V.

designs in order to prevent short-circuit by battery reverse installation, and they are shaped so as to match the receptacle facilities provided in the appliances. For example, in cylindrical batteries, the negative terminal is either designed so as to be flat, or to protrude out of the battery end, while the positive terminal extends as a pip at the opposite end. A simple galvanic cell is illustrated in Figure 1.1a, while Figure 1.1b shows terminal designs for cylindrical batteries.

In order to meet the voltage or current used in specific appliances, cylindrical galvanic cells are connected in series or parallel. Figures 1.2a, and b represent



**Figure 1.3** (a) Single-flat cell configuration; (b) composite flat cell configuration.

parallel and series connections; parallel connections allow for the current to be doubled, while series connections allow for the voltage to be doubled.

In addition to cylindrical battery cells, as those shown in Figures 1.1 and 1.2, flat battery configurations are also quite common. The biggest impetus for these configurations came from the rapid growth of portable radios, since the flat cells use the space of the battery box more efficiently than cylindrical cells. The electrodes are made in the form of flat plates, which are suspended in the electrolyte and are held immobilized in a microporous separator (Figure 1.3a). The separator also helps in isolating the electrodes, preventing any short-circuiting whereby ions can directly move internally between the anode and cathode. Short-circuiting will result in capacity loss, parasitic reactions, and heat generation. This can also lead to catastrophic situations causing fires, explosions, leakage of materials, and accidents. The configuration of Figure 1.3a can be scaled up to very large sizes, for high currents and large storage capacities, by placing each cell inside a plastic envelope and stacking them inside a steel jacket. Connector strips are used to collect and connect the positive and the negative electrodes to a common positive and negative terminal; a sketch of such a cell compaction is shown in Figure 1.3b.

Both cylindrical and flat cells come in various sizes so that they can fit a wide range of portable appliances and devices. Table 1.1 summarizes the various battery sizes that are available commercially.

## 1.2 Quantities Characterizing Batteries

Upon operation of galvanic cells, meaning that the device is on power mode, it is said that the galvanic cell is discharged and electrons flow, through an external circuit, from the anode to the cathode, which as a result attains a negative, and consequently cations are attracted from the anode to the cathode to which they diffuse through the electrolyte. The electrochemical reactions that take place upon operation of different batteries are shown in Table 1.2, whereas the quantities that characterize batteries are defined in Table 1.3.



**Table 1.1** Dimensions of commercially available battery sizes [1].

| Battery size      | Diameter (mm) | Height (mm)    |
|-------------------|---------------|----------------|
| N                 | 12            | 30.2           |
| AAA               | 10.5          | 44.5           |
| AA                | 14.5          | 50.5           |
| C                 | 26.2          | 50             |
| D                 | 34.2          | 61.5           |
| F                 | 32.0          | 91.0           |
| Flat cells        |               |                |
| Length (mm)       | Width (mm)    | Thickness (mm) |
| 24                | 13.5          | 6.0            |
| 43                | 43            | 6.4            |
| Rectangular cells |               |                |
| 48.5              | 26.5          | 17.5           |

In order to better understand the differences between various materials chemistries, some of the quantities in Table 1.3 are further elaborated in the following pages.

### 1.2.1

#### Voltage

The theoretical standard cell voltage,  $E^0(\text{cell})$  can be determined using the electrochemical series and is given by the difference between the standard electrode potential at the cathode,  $E^0(\text{cathode})$ , and the standard electrode potential at the anode,  $E^0(\text{anode})$  [2] as

$$E^0(\text{cathode}) - E^0(\text{anode}) = E^0(\text{cell}) \quad (1.1)$$

The standard electrode potential,  $E^0$ , for an electrode reaction, written (by convention) as a reduction reaction (i.e., involving consumption of electrons), is the potential generated by that reaction under the condition that the reactants and the products are in their standard state in relation to a reference electrode. (A reactant or product is defined to be in its standard state when the component in a condensed phase is at unit activity and any component in the gas phase is at a partial pressure of 1 atmosphere.) In aqueous systems, the standard hydrogen potential is taken as the universal reference electrode, whose potential is defined as zero. In practical terms, the standard hydrogen electrode can be constructed by passing pure hydrogen at one atmosphere over an electrode of platinized platinum, where a high surface area of platinum is deposited on a platinum foil or plate, which is dipped into an acid solution of unit activity of  $\text{H}^+$  ions, corresponding to 1 M acid solution. A list containing selected standard electrode potentials at 298 K in an aqueous