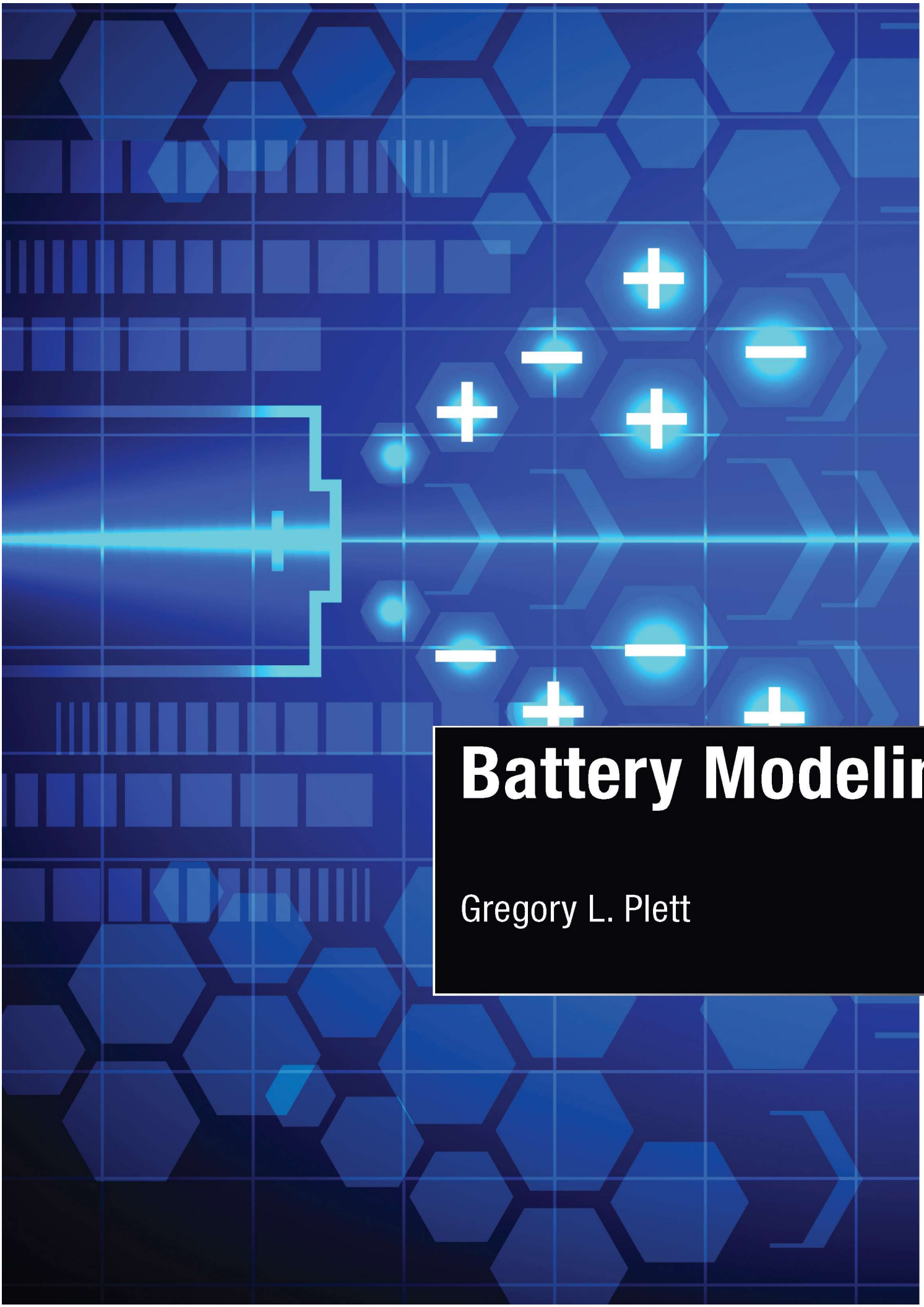

BATTERY MANAGEMENT SYSTEMS

Battery Modeling

Gregory L. Plett

VOLUME I

Battery Management Systems

Volume I

Battery Modeling

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Contents

Preface

This book constitutes the first volume in what is planned to be a three-volume series describing battery management systems. The intent of the series is not to be encyclopedic; rather, it is to put forward only the current best practices, with sufficient fundamental background to understand them thoroughly.[1]

This first volume focuses on deriving mathematical sets of equations or *models* that describe how battery cells work, inside and out. The second volume applies equivalent-circuit style models to solve problems in battery management and control. The third volume shows how physics-based models can also be used to solve problems in battery management and control, leading to better results.

This particular volume is organized in the following way:

- Chapter 1 introduces the fundamental definitions pertaining to battery systems and gives an overview of how they work.
- Chapter 2 derives empirical models based on using linear circuits as an analog to input–output battery-cell behaviors.
- Chapter 3 presents the fundamental physics needed to understand physics-based internal battery-cell behaviors and derives microscale models.
- Chapter 4 introduces volume averaging as a means to convert microscale models to continuum-scale models, leading to the well-known pseudo-two-dimensional porous-electrode model.
- Chapter 5 reviews state-space models as the ultimate form of our development and develops the "discrete-time realization algorithm" (DRA) as a method for creating a state-space model.
- Chapter 6 derives cell-level discrete-time physics-based state-space models of similar computational complexity to the circuit models in Chapter 2, but able to predict internal cell behaviors in addition to input–output behaviors.
- Chapter 7 shows how a coupled electrochemical–thermal model can be derived—introducing concepts in heat generation and heat flux—leading to a physics-based reduced-order model of thermal effects.

[1] Certainly, what is meant by "best practices" is at least somewhat subjective, and I may well have overlooked approaches and methodologies that are better in some applications than those described herein. Perhaps I should say "best" from my own point of view, given what I happen to have tried, in application domains and problems I have attempted to address.

- Appendix A is a bonus chapter that applies the techniques from Chapters 3 through 7 to create a discrete-time physics-based state-space model of a supercapacitor.

The intended audience for this material is someone with an undergraduate degree in engineering—principally electrical or mechanical. Readers having a different background may find some of the material too basic (because they have studied it before, whereas engineering students have not) or not descriptive enough (because they are missing some background that would typically be encountered in an engineering degree program). Both problems have a remedy, although the solution to the second involves background research to become proficient in an unfamiliar discipline—not an easy undertaking.

The mathematical intensity—particularly for the topics presented in Chapters 3 through 7—can be intimidating even to someone having the intended background. However, I have found that the student who is willing to take the time to work the equations by hand, side by side with the derivations in the book, is able to validate every step and thus conquer the material. For the reader who is interested primarily in a higher-level understanding, the main derivation results to be proven are shared at the beginnings of the most mathematical chapters (i.e., Chapters 3, 4, and 7). The derivations themselves are necessary to understand the genesis of these results, but not to be able to implement the final equations in a simulation or some other application, and so may be skimmed on a preliminary reading.

The content in this book has been taught multiple times to students of diverse backgrounds in *ECE5710: Battery Modeling, Simulation, and Identification* at the University of Colorado Colorado Springs. Lecture videos are available at `http://mocha-java.uccs.edu/ECE5710/index.html`. As the lecture videos sometimes explain the concepts of this book in a somewhat different way, the additional perspective may be an advantage to the learner.

I am greatly indebted to a number of my students and colleagues who have assisted me over the years in understanding and developing the theory and methods presented in this work. Dr. Kan-Hao Xue prepared the first draft of the derivations in Chapter 3. Drs. Amit Gupta and Xiangchun Zhang explained to me the concepts of volume-averaging that are presented in Chapter 4. Dr. Mark Verbrugge introduced me to the pioneering work of Dr. Kandler Smith, which is the foundation of the work presented in Chapters 5 through 7 (and Dr. Smith himself was kind enough to answer questions I had on his work). Dr. Jim Lee developed the DRA presented in Chapter 5 and was the first to implement cell-scale optimum reduced-order models using the DRA, as presented in Chapter 6. Mr. Matt Aldrich developed the reduced-order thermal models in

Chapter 7. Finally, Dr. Al Mundy was the first to implement reduced-order supercapacitor models using the DRA techniques presented in Appendix A. My colleague and friend Dr. M. Scott Trimboli has also been a great encourager of this work and a true pleasure to work with.

Despite my best intentions, there are certain to be errors and confusing statements in this book. Please feel free to send me corrections and suggestions for improvements.

1
Battery Boot Camp

This book is all about developing a mathematical understanding of how electrochemical—and especially lithium-ion—battery cells work. This kind of knowledge is helpful when designing cells, when selecting cells to be used in an application, and for knowing how to use cells properly in an application. For some of these tasks, a high-level qualitative understanding is sufficient; however, for others, detailed quantitative insight into cell operation is critical. Here, we're interested in both levels, with the ultimate goal of being able to predict both internal and external cell operational variables to a degree that enables optimized battery-pack controls.

This book has mission-critical single-cell or large battery-pack applications in mind, as these applications justify both the complexity of the models to be developed and an investment in advanced control methods that use the models, since such methods can prolong battery-pack life and improve total system performance. Example applications include battery systems for hybrid and electric vehicles or for utility-scale grid storage, backup, and frequency regulation. However, much of the material that is covered also applies to smaller battery packs, such as for personal electronics, and much of the material can also be applied to chemistries different from lithium-ion.

The three main foci of the book are:

1. *Modeling*: Deriving mathematical expressions that describe how battery cells work, both internally and externally. After several stages of development, the final models will comprise coupled sets of discrete-time ordinary difference equations (ODEs) that are functions of unknown but measurable or identifiable *parameter* values. The input to the models will be the cell current; the output will include cell voltage and possibly cell internal electrochemical states as well.
2. *Simulation*: Using computer tools to predict how a battery cell will respond to an input stimulus. The equations of the battery model are used to predict cell voltage and possibly internal

battery-cell states. We will see simulations involving different degrees of fidelity applied to different cell-length scales. We will describe simulations that use the finite-element software platform COMSOL Multiphysics®, and we will give code to implement cell models in MATLAB®.[1]

3. *Identification*: Determining the values of model parameters, using data obtained via lab tests, to cause the model simulated predictions to match measured performance as closely as possible.

[1] COMSOL Multiphysics is a registered trademark of The COMSOL Group, and MATLAB is a registered trademark of The MathWorks. From now on, these products will be referred to simply as COMSOL and MATLAB, respectively.

This chapter very quickly covers a lot of background material relating to battery terminology, function, and general application.[2] Later chapters will systematically develop models of battery-cell dynamics at different length scales for different kinds of application and show how to use these models to simulate performance and how to identify model parameters.

[2] Much of the content of this chapter is adapted from the excellent Web site: `http://www.mpoweruk.com/`.

1.1 Preliminaries

Cells are the smallest individual electrochemical unit and deliver a voltage that depends on the combination of chemicals and compounds chosen to make the cell.[3] Single-use cells are called *primary cells* and rechargeable cells are called *secondary cells*. *Batteries* or *battery packs* are made up from groups of cells.[4] The schematic symbols for a cell and a battery are shown in Fig. 1.1.

[3] The National Electrical Code, document NFPA-70 defines a cell as "The basic electrochemical unit, characterized by an anode [i.e., negative electrode] and a cathode [i.e., positive electrode], used to receive, store, and deliver electrical energy."

[4] IEEE standard 446 defines a battery as "Two or more cells electrically connected for producing electric energy."

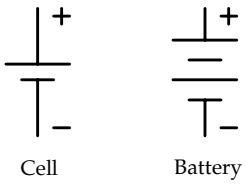


Figure 1.1: Schematic symbols for a cell and a battery.

Technically, a cell is different from a battery, but many people (including me, at times) use the term *battery* to describe any electrochemical energy source, even if it is a single cell, and this can lead to confusion. I will attempt to use the terms *cell* or *battery cell* consistently to refer to an individual electrochemical unit, and reserve the terms *battery* (used by itself) and *battery pack* to refer to an electrically connected group of cells. Note that it is not always obvious whether the correct term should be *cell* or *battery* since batteries are sometimes packaged in a single physical unit. For example, automotive "12 V" lead-acid batteries internally comprise six "2 V" cells wired in series;[5] also, many high-capacity lithium-ion batteries consist of a number of cells wired in parallel in a single package.

[5] Cells deliver a range of voltage depending on conditions such as temperature and how much charge they are holding. Table 1.1 lists the voltage of a single lead-acid cell as 2.1 V, which is more accurate under many conditions than the more commonly cited figure of 2 V, but either figure is roughly correct unless more specific operational factors are specified. One purpose of the models developed in this book is to be able to predict cell voltage under very general operating conditions.

Cell voltage depends a number of factors, as we will find out. The manufacturer-specified *nominal voltage* is "The value assigned to a cell or battery of a given voltage class for the purpose of convenient designation. The operating voltage of the cell or battery may vary above or below this value."[6] Cells with lead-acid (PbA) chemistry have a nominal voltage of 2.1 V; nickel-cadmium (NiCd) cells have a nominal voltage of 1.35 V; and nickel-metal-hydride (NiMH) chemistries

[6] From the National Electrical Code, document NFPA-70.

have a nominal voltage of 1.2 V (cf. Table 1.1). Most lithium-based cells have nominal voltages over 3 V.

CELLS STORE AND ARE ABLE TO DELIVER electrical charge to power a load circuit. The cell *nominal charge capacity* specifies the quantity of charge, in ampere-hours (Ah) or milliampere-hours (mAh), that a cell is rated to hold.[7] The cell's nominal energy capacity (see below) is a different quantity. Both definitions of capacity have merit and can be computed from one another. However, as our focus in this book is on creating models that relate a cell's input current (i.e., rate of change of charge) to its internal electrochemical state and output voltage, charge capacity turns out to be the more relevant concept. Unless otherwise mentioned, the term *capacity* will refer to charge capacity and not to energy capacity in this book.

Related to the cell's charge capacity, the *C rate* is a relative measure of cell current. It is the constant-current charge or discharge rate that the cell can sustain for 1 hour—it is simply the nominal ampere hour rating of the cell multiplied by $1\,\mathrm{h}^{-1}$. For example, a fully charged 20-Ah cell should be able to deliver 20 A (a "1C" rate) for 1 h or 2 A (a "C/10" rate) for about 10 h before the cell is completely discharged. If the cell is discharged at a 10C rate, it will be completely discharged in about 6 minutes. Note that the relationship between C rate and discharge time is not strictly linear, primarily because of the internal resistance of the battery cell and incomplete utilization of the active materials when the cell is exercised at high rates. In fact, a cell discharged at a 10C rate will reach a minimum operational voltage before 6 minutes has elapsed, but a cell discharged at a C/10 rate may be operated somewhat more than 10 h before reaching the minimum voltage.

A CELL STORES *energy* in electrochemical form, which it can later release to do work. The cell *nominal energy capacity* is the quantity of electrical energy in watt hours (Wh) or kilowatt hours (kWh) that the cell is rated to hold and is computed as the cell's nominal voltage multiplied by its nominal charge capacity.[8] For example, a 2 V, 10-Ah lead-acid cell has an energy storage capacity of roughly 20 Wh. It is important to note that energy and power are different quantities for a particular rate of discharge. *Power* is the instantaneous rate at which energy is being released. Power is measured in watts (W) or kilowatts (kW). The maximum power that a cell can deliver is limited by the cell's internal resistance and is not an easy value to quantify. Power is usually regulated by enforcing minimum and maximum limits on cell terminal voltage.

[7] Note that the SI unit for charge is the coulomb (C) and that $1\,\mathrm{Ah} = 3,600\,\mathrm{C}$, which is quite a lot of charge! The SI unit is not often used, probably because it is such a small amount of charge relative to the capacity of most cells.

[8] The SI unit for energy is the joule (J), where $1\,\mathrm{J} = 1\,\mathrm{W\,s}$. A joule is a pretty tiny unit of energy compared to what a typical battery holds, which is probably why the SI unit is not usually used when working with batteries.

When cells are connected in *series*, the battery voltage is the sum of the individual cell voltages, by Kirchhoff's voltage law. However, by Kirchhoff's current law, the charge capacity of the series-connected battery is the same as the charge capacity of an individual cell since the same current passes through all of the cells. As an example, consider the battery in Fig. 1.2, which is constructed from three 2 V, 20-Ah cells connected in series. The battery voltage will be 6 V, the battery charge capacity will be 20 Ah, and the battery energy capacity will be 120 Wh.

When cells are connected in *parallel*, the battery voltage is equal to the cells' voltage, by Kirchhoff's voltage law. However, by Kirchhoff's current law, the charge capacity is the sum of the cells' charge capacities since the battery current is the sum of all the cell currents. For example, consider the battery in Fig. 1.3, which is constructed from five 2 V, 20-Ah cells connected in parallel. The battery will have a voltage of 2 V, a charge capacity of 100 Ah, and energy capacity of 200 Wh.

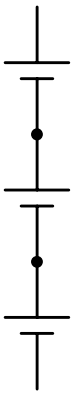


Figure 1.2: Three cells connected in series.

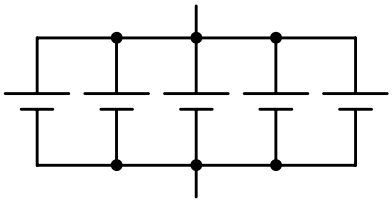


Figure 1.3: Five cells connected in parallel.

Specific energy and *energy density* are measures of the maximum amount of stored energy per unit weight or volume, respectively. For a given weight, a higher specific energy cell design will store more energy, and for a given storage capacity, a higher specific energy cell will be lighter. For a given volume, a higher energy density cell chemistry will store more energy, and for a given storage capacity, a higher energy density cell will be smaller.

In general, higher energy densities and higher specific energies are obtained by using more reactive chemicals. The downside is that more reactive chemicals tend to be less stable and may require special safety precautions. Further, the quality of the active materials used in cell construction matters, with impurities limiting cell performance that can be achieved and with construction flaws reducing safety. Cells from different manufacturers with similar cell chemistries and similar construction may yield different performance. Cell construction also matters: overhead from packaging decreases the energy densities.

1.2 *How cells work*

Cells are built from a number of principal components. These include a negative electrode, a positive electrode, the electrolyte, and a separator. Certain types of cells also have current collectors that are distinct from the electrodes themselves. Fig. 1.4 shows a schematic of a lithium-ion cell, but the basic idea applies generally.

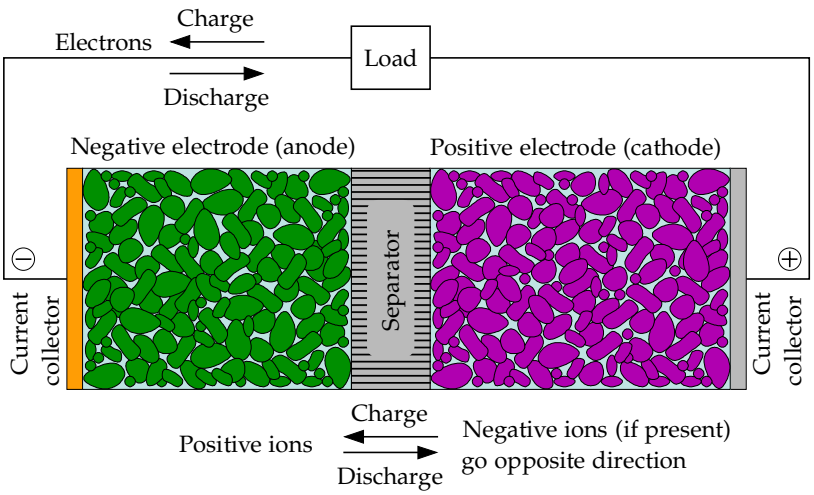


Figure 1.4: Schematic diagram of lithium-ion cell.
(Based on Fig. 1 of Stetzel, K., Aldrich, L., Trimboli, M.S., and Plett, G., "Electrochemical state and internal variables estimation using a reduced-order physics-based model of a lithium-ion cell and an extended Kalman filter," *Journal of Power Sources*, 278, 2015, pp. 490–505.)

The *negative electrode* in an electrochemical cell is often a pure metal, or an alloy, or even hydrogen. For example, the negative electrode of a lead-acid cell is pure lead.[9] Table 1.1 lists negative-electrode materials for common types of cells.

[9] This is realized in a practical lead-acid cell by spreading a lead paste on a lead-alloy grid.

Electrochemistry	Negative electrode	Positive electrode	Electrolyte	Nominal voltage
Lead acid	Pb	PbO_2	H_2SO_4	2.1 V
Dry cell	Zn	MnO_2	$ZnCl_2$	1.6 V
Alkaline	Zn	MnO_2	KOH	1.5 V
Nickel cadmium	Cd	NiOOH	KOH	1.35 V
Nickel hydrogen	H_2	NiOOH	KOH	1.5 V
Nickel zinc	Zn	NiOOH	KOH	1.73 V
Silver zinc	Zn	Ag_2O	KOH	1.6 V
Zinc air	Zn	O_2	KOH	1.65 V

Table 1.1: Components of some common electrochemical cells.
(Adapted from Table 1.2 in Linden, D., *Handbook of Batteries*, Linden, D. and Reddy, T.B. eds., 3d, McGraw-Hill, 2002.) The nominal voltages are representative only. For example, the open-circuit voltage of a lead-acid cell is related to the specific gravity of its electrolyte. Most vented lead-acid cells have a specific gravity of 1.215 and an open-circuit voltage of 2.05 V. Most valve-regulated lead-acid (VRLA) cells have a specific gravity of 1.3 and an open-circuit voltage of 2.15 V.

During discharge, the negative electrode gives up electrons to the external circuit, a process by which the electrode is *oxidized:* oxidation of a species involves the loss of electrons or, equivalently, an increase in the oxidation state of the species (it becomes more positively charged). During charge, the negative electrode accepts electrons from the external circuit and is *reduced:* reduction of a species involves the gain of electrons or, equivalently, a decrease in its oxidation state (it becomes more negatively charged). Thus, the chemical processes that occur in an electrochemical cell are sometimes called reduction–oxidation or *redox* reactions.[10]

The negative electrode is often called the *anode*. Technically, the

[10] A mnemonic that may be helpful is "OIL RIG," which stands for "oxidation is loss (of electrons) and reduction is gain (of electrons)." Not a very "green" acronym for a "green" subject!

anode is the electrode where oxidation occurs. So, the negative electrode is really the anode only when the cell is discharging and is actually the cathode when the cell is charging! But this gets pretty confusing, so most people call it the anode regardless of whether the cell is being charged or discharged. To minimize this confusion, this book will avoid the term *anode* and will use the term *negative electrode* instead.

THE *positive electrode* in an electrochemical cell is often a metallic oxide, sulfide, or oxygen. For example, the positive electrode of a lead-acid cell is made from pure lead dioxide, often formed from a lead-oxide paste applied to a lead-alloy grid. Table 1.1 lists positive-electrode materials for common types of cells.

During discharge, the positive electrode accepts electrons from the external circuit, a process by which the electrode is reduced. During charge, the positive electrode gives up electrons to the external circuit and is oxidized.

The positive electrode is often called the *cathode*, but again, there are problems with this description. Technically, the cathode is the electrode where reduction occurs. So, the positive electrode is really the cathode only when the cell is discharging and is actually the anode when the cell is charging! Again, to minimize confusion, this book will avoid the term *cathode* and will use the term *positive electrode* instead.

THE *electrolyte* is an ionic conductor that provides the medium for internal ionic charge transfer between the electrodes.[11] The electrolyte most often comprises a liquid *solvent* containing dissolved chemicals (the *solute*) that provide this ionic conductivity (although solid polymer electrolytes are also possible). The chemistries listed in Table 1.1 use *aqueous* electrolytes, where the solvent is water, and the ionic charge transfer is accomplished via either an *acid* (H_2SO_4), a *base* (KOH), or a *salt* ($ZnCl_2$). Cells using aqueous electrolytes have terminal voltages limited to less than about 2 V because the oxygen and hydrogen in water dissociate in the presence of higher voltages. Lithium-ion cells must use nonaqueous electrolytes as their overall voltages are well above 2 V.

During discharge, positively charged ions or *cations* move through the electrolyte toward the positive electrode, and negatively charged ions or *anions* (if present) move through the electrolyte toward the negative electrode. During charge, the opposite occurs: cations move toward the negative electrode and anions move toward the positive electrode.

[11] The electrolyte must be an electronic insulator (it cannot conduct electrons). If it were an electronic conductor, a complete circuit would form internal to the cell, which would cause the cell to *self-discharge* or *short-circuit*.

The *separator* physically isolates the positive and negative electrodes. It is an ionic conductor but an electronic insulator. Its function is to prevent internal short circuiting between the two electrodes, which would cause the cell to rapidly self-discharge and become useless.

Current collectors, if present, are electronic conductors onto which the electrode materials are adhered or with which the electrode materials are mixed. The current collectors take no part in the chemical reactions of the cell, but instead either allow simple electronic connection to materials that may otherwise be very difficult to connect to a cell terminal, or are included to reduce the electronic resistance of an electrode. In a lithium-ion cell, for example, the negative-electrode current collector is usually made from copper foil, and the positive-electrode current collector is usually made from aluminum foil. The current collector in the positive electrode of a dry cell is carbon.[12]

[12] Dry cells are sometimes called *zinc carbon* cells, and the positive electrode is sometimes identified as carbon. But, this is not actually true, as carbon takes no part in the chemical reaction—it serves only to collect current and reduce resistance of the manganese dioxide mix.

The observant reader will note the conspicuous absence of two very important chemistries in Table 1.1—nickel-metal hydride and lithium-ion cells. The principle of operation of these two advanced types of cell is somewhat different from the chemical processes that we are describing in this section, and so detailed discussion is reserved until Sections 1.4 and 1.5. For now, it is sufficient to note that these cells also have negative electrodes, positive electrodes, electrolyte, and a separator.

1.2.1 *The discharge process*

Electrochemical potential energy at the negative electrode favors a chemical process that would release electrons into the external circuit and positively charged ions into the electrolyte. Also, electrochemical potential energy at the positive electrode favors a chemical process that would accept electrons from the external circuit and positively charged ions from the electrolyte. The resulting electrical pressure or potential difference between the terminals of the cell is called the *cell voltage* or *electromotive force* (EMF).

This stored potential energy can be released and converted to useful work only when pathways are available for electrons and positively charged ions to travel from the negative electrode to the positive electrode. The electrolyte provides an always-available medium for positive-ion movement, but the separator prevents electron movement within the cell (hence preventing an internal short circuit). In order for electrons to move, an external electrical circuit must be completed, connecting the negative and positive electrodes electronically. When a circuit is completed, the cell *discharges* its energy through the

circuit, or *load*, and converts the stored chemical potential energy into electrical energy.

1.2.2 *The charge process*

In *primary cells*, this electrochemical reaction is not reversible. During discharge, the chemical compounds are permanently changed and electrical energy is released until the original compounds are completely exhausted. Primary cells can be used only once.

In *secondary* or *rechargeable cells*, the electrochemical reaction is reversible. The original chemical compounds can be reconstituted by the application of an electrical potential across the electrodes that is higher than the cell's own electrical potential. This injects energy into the cell, causing electrons and positive ions to move from the positive electrode back to the negative electrode, thus storing charge.

Secondary cells can be discharged and recharged many times. During charge, cations move from the positive to the negative electrode through the electrolyte, and electrons move from the positive to the negative electrode through the external circuit. The energy injected into the cell transforms the active chemicals to their original state.

1.3 *Materials choice*

The voltage generated across the terminals of a cell is directly related to the types of materials used in the positive and negative electrodes. When designing and analyzing a cell, it is often convenient to consider the electrodes separately. However, it doesn't make sense to talk about the voltage of an electrode by itself. Voltage is a *difference* in potential, and when dealing with a single electrode, what two potentials are being differenced?

There is a similar problem in the field of electrical circuit analysis. The solution in that case is to arbitrarily select a point in the circuit whose potential is defined to be "zero volts" or "ground," against which all other potentials in the circuit are measured. We apply the same basic solution when analyzing an electrochemical electrode. We consider a potential difference between the electrode under study and a hypothetical reference electrode, which may or may not be a part of the actual cell being designed or analyzed. Often, this reference is chosen to be in terms of the *standard hydrogen electrode,* and the potential at which $2H^+ + 2e^-$ spontaneously converts to $H_{2(g)}$ is defined to be zero volts.[13]

The electrode potentials of some common electrode half reactions, known as an *electrochemical series*, are shown in Table 1.2. Compounds

[13] Although, we will see that with lithium-ion cells, the reference is often chosen to be with respect to Li^+/Li, or the potential at which $Li^+ + e^-$ spontaneously converts to $Li_{(s)}$.

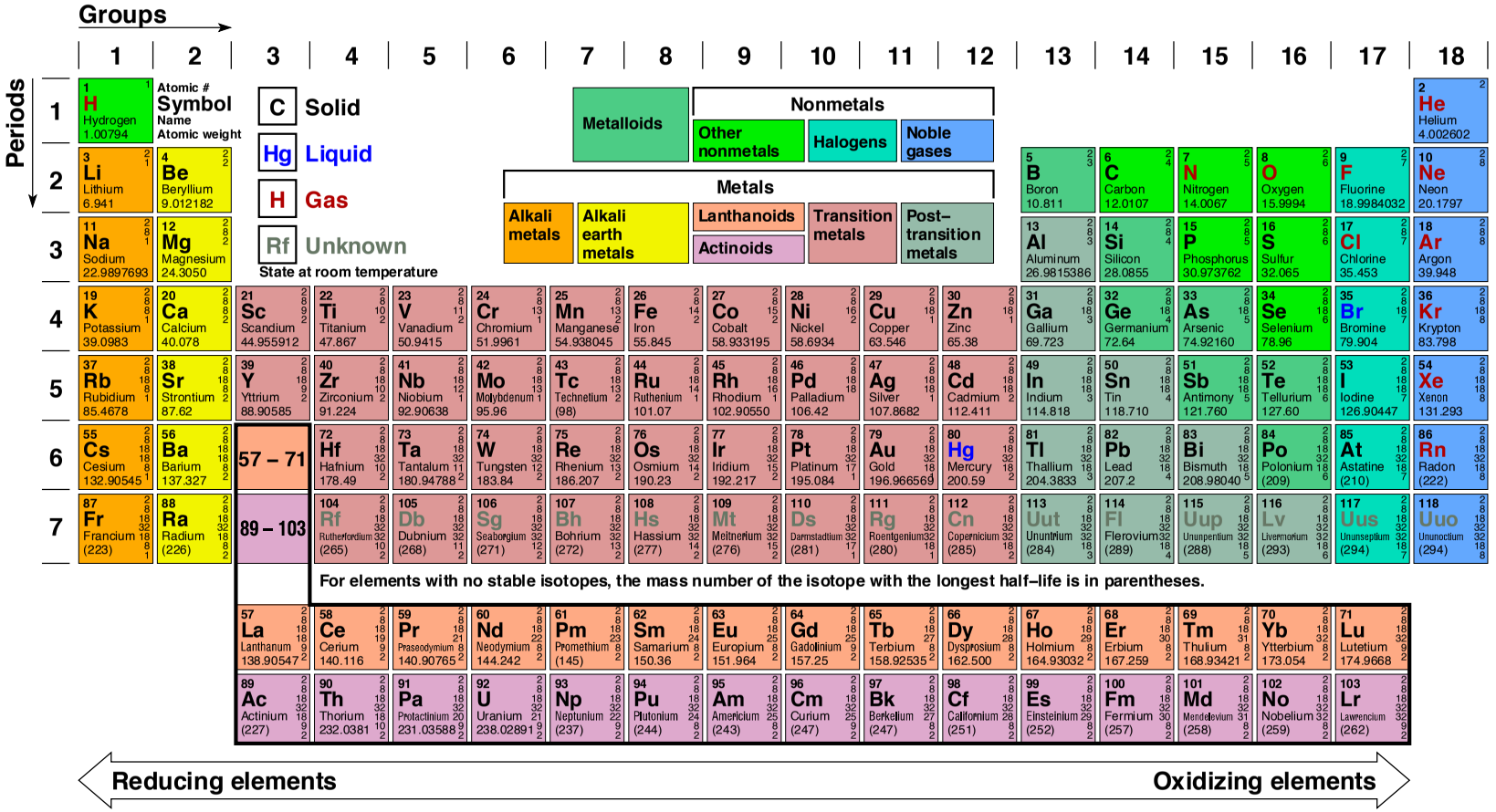


Figure 1.5: Periodic table of the elements.

with more negative electrode potentials are used for negative electrodes and those with more positive electrode potentials for positive electrodes. The larger the difference between the electrode potentials of the negative and positive electrodes, the greater the cell voltage.

The values for the table entries are reduction potentials. Fluorine, $F_{2(g)}$, has the most positive number in the table, indicating that it reduces most easily, and therefore is the best oxidizing agent of those listed. Lithium, $Li_{(s)}$, has the most negative number in the table, indicating that it would rather undergo oxidation (and hence is the strongest reducing agent of those listed). If we were to create a cell combining the top and bottom reactions, the cell voltage would be $2.87\,V - (-3.04\,V) = 5.91\,V$ (but so far we cannot, since there is no known electrolyte that will withstand that high a voltage without decomposing).

The electrochemical series is good for quantitative analysis, but an exhaustive table of all possible oxidation/reduction reactions is unwieldy and not necessarily intuitive. For qualitative analysis, we may consider the periodic table of the elements, such as in Fig. 1.5, where the relative reducing and oxidizing capabilities of the elements are indicated by the arrow below the table.

Each box in the periodic table corresponds to a particular element. The number in the top-left of each box is the element's *atomic number* (the number of protons in the nucleus of the atom). The number in the bottom-left of the box is the *atomic weight*, or the ratio of the average mass per atom of the element to 1/12 of the mass of an atom of ^{12}C. The series of numbers to the right of each box is arrangement of electrons in orbitals or shells in a *Bohr* or *classical model* of the atom.[14] Some examples of the electron orbital occupancies are shown in Fig. 1.6.

[14] It is still common to speak of shells despite the advances in understanding of the quantum-mechanical nature of electrons. For the purpose of this book, an understanding of the Bohr model is sufficient.

Cathode (reduction) half-reaction	Standard potential E^0 (volts)
$Li^+ + e^- \Rightarrow Li_{(s)}$	−3.01
$K^+ + e^- \Rightarrow K_{(s)}$	−2.92
$Ca^{2+} + 2e^- \Rightarrow Ca_{(s)}$	−2.84
$Na^+ + e^- \Rightarrow Na_{(s)}$	−2.71
$Zn^{2+} + 2e^- \Rightarrow Zn_{(s)}$	−0.76
$2H^+ + 2e^- \Rightarrow H_{2(g)}$	0.00
$Cu^{2+} + 2e^- \Rightarrow Cu_{(s)}$	0.34
$O_{3(g)} + 2H^+ + 2e^- \Rightarrow O_{2(g)} + H_2O_{(l)}$	2.07
$F_{2(g)} + 2e^- \Rightarrow 2F^-$	2.87

Table 1.2: Standard potentials of electrode reactions at 25 °C. (Condensed from Table 2.2 in Broadhead, J. and Kuo, H.C., *Handbook of Batteries*, D. Linden and T.B. Reddy, eds., 3d, McGraw-Hill, 2002.)

The elements in the table are color-coded to highlight elements that behave in similar ways to each other. For example, we see that the strong reducing elements are grouped to the left, while the strong oxidizing elements are grouped to the right. Elements within each individual *group* (generally) have the same number of *valence electrons*, or number of electrons in their outer *valence shell* (but, transition metals are a little strange). Because the number of valence electrons determines how the atom reacts chemically with other atoms, elements within a particular group tend to have similar chemical properties. All the elements in any one *period* have the same number of electron shells or orbits, which corresponds to the number of possible energy levels of the electrons in the atom. The period number corresponds to the number of electron shells.

Atoms with one or two valence electrons more than a closed shell are highly reactive because the extra electrons are easily removed to form positive ions. Reducing agents have a surplus of valence-shell electrons, which they donate in a redox reaction, becoming oxidized. *Alkaline metals*, group 1, have only one valence electron, and *alkaline earth metals*, group 2, have only two valence electrons, so elements in these groups are highly reactive.

Atoms with one or two valence electrons fewer than a closed shell are also highly reactive because of a tendency either to gain the missing electrons and form negative ions, or to share electrons and form covalent bonds. Oxidizing agents have a deficit of valence-shell electrons and accept electrons in a redox reaction, becoming reduced. *Halogens*, group 17, are short only one valence electron, and so are highly reactive.

When the outer electron shell is full, as in the *noble gases* in group 18, there are no "free" electrons available to take part in chemical reactions. This is the lowest energy state for a species, and hence these atoms tend to be chemically nonreactive or *inert*.

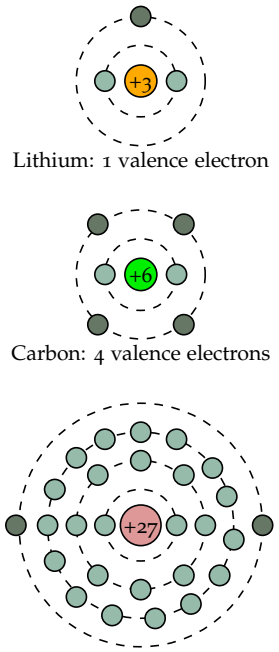


Figure 1.6: Schematic of some elements, showing electron configurations in different shells, and highlighting the number of valence electrons.

1.4 *Insertion electrode cells*

Relatively recently, new cell chemistries have been developed using alternative chemical reactions to the traditional redox scheme. *Metal hydride* cells, such as nickel-metal hydride, depend on the ability of some metals to absorb large quantities of hydrogen without chemically changing the composition of the metal itself (much like a sponge absorbs water without undergoing a chemical change). These metallic alloys, termed *hydrides*, can provide a storage sink for hydrogen, which can reversibly react in battery-cell chemistry. Such metals or alloys are used for the negative electrodes. The positive electrode is nickel hydroxide (NiOOH) as in NiCd batteries. The electrolyte,

which is also a hydrogen-absorbent aqueous solution such as potassium hydroxide (KOH), takes no part in the reaction but serves to transport hydrogen H^+ ions (protons) between the electrodes. As we will see in the next section, lithium-ion cells work in a similar way.

1.5 Lithium-ion cell preview

This book focuses on lithium-ion cells (although much that we cover is quite general and could be applied to other chemistries). Lithium-ion cells have several advantages over other chemistries:

- They operate at higher voltages than other rechargeable cells, typically about 3.7 V for lithium-ion versus 1.2 V for NiMH or NiCd. Because of this, they tend to have higher energy density also.
- The higher voltage means that a single cell can often be used in a particular application rather than multiple NiMH or NiCd cells in series. While NiCd and NiMH do not require battery management circuitry for safe operation, all battery packs can potentially benefit from battery management: the battery management circuitry for lithium-ion can be simplified by this reduced cell count.
- Lithium-ion cells also have a lower self-discharge rate than other types of rechargeable cells. NiMH and NiCd cells can lose anywhere from 1–5 % of their charge per day, even if they are not installed in a device. Lithium-ion cells, on the other hand, will retain most of their charge even after months of storage.

Lithium-ion cells are at a disadvantage to other chemistries in other respects:

- Lithium-ion cells are more expensive than similar capacity NiMH or NiCd cells. This is in part because they are presently manufactured in much smaller numbers than NiMH or NiCd. As volumes increase, prices are expected to come down.
- Lithium-ion cells are very sensitive to overcharge and often include special circuitry that prevents damage by disconnecting the cell from the circuit if an attempt is made to operate the cell outside of its design voltage range. This adds to the cost and complexity of manufacture, and to the complexity of battery chargers. The cost of the protection circuitry may not scale as favorably with volume as the cost of the manufacturing process itself, and as it is possible for the circuitry itself to fail, the reliability of the overall battery system can be degraded.
- Lithium-ion cells are not available in standard cells sizes (AA, C, and D) like NiMH and NiCd cells.[15] And, different lithium-ion

[15] Note that the Energizer® "e² Lithium" is not a lithium-ion cell. It is a standard nonrechargeable 1.5 V galvanic cell with lithium/iron-disulfide (Li/FeS_2) chemistry.

cells in the reasonably common "18650" or "26650" form factors may internally comprise different types of lithium-ion electrochemistry that are not compatible with each other. So, because of their different shapes and sizes and internal chemistries, each type of lithium-ion cell tends to require a specific matching charger designed to accommodate it. This means that lithium-ion battery chargers are more expensive and more difficult to find than NiMH and NiCd battery chargers.[16]

[16] In some applications, such as stationary battery systems for the telecom industry, standard chargers are specified, which largely mitigates this disadvantage.

Lithium-ion cells work differently from the electrochemical cells that we looked at earlier in this chapter. Traditional electrochemical cells depend on redox reactions that chemically change the reacting species at the electrode surfaces. Consider, for example, a lead-acid cell. On discharge, lead (Pb) from the negative electrode reacts with HSO_4^- in the electrolyte, producing hydrogen ions (protons), emitting two electrons to the external circuit, and forming solid lead sulfate ($PbSO_4$) crystals on the surface of the negative electrode. We can write,

$$Pb_{(s)} + HSO^-_{4(aq)} \Rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^-.$$

In the positive electrode, lead oxide (PbO_2) and HSO_4^- from the electrolyte react with hydrogen ions, consuming electrons and forming solid lead sulfate crystals on the surface of the positive electrode. We can write,

$$PbO_{2(s)} + HSO^-_{4(aq)} + 3H^+_{(aq)} + 2e^- \Rightarrow PbSO_{4(s)} + 2H_2O_{(l)}.$$

Lithium-ion cells work differently. Like NiMH cells, they are insertion-electrode cells. Lithium does not react with the electrode materials, per se. Instead, lithium is either absorbed from the electrolyte and inserted into the structure of the electrode material (a process called *intercalation*), or is expelled from the electrode material into the electrolyte (*deintercalation*), depending on the direction of current flow.

For this to work, the electrodes must have two key properties. First, they must have open-crystal structures, pervaded with empty pathways or "corridors" that are large enough for lithium to move through freely. Thus, lithium can be inserted into the vacancies in the structure from the electrolyte, can be removed from the vacancies in the structure, and is free to move among the vacant spaces within the crystalline structure. Second, the electrodes must also be able to deliver or accept compensating electrons to/from the external circuit at the same time.

The crystal structure itself is not changed chemically by the insertion or removal of lithium. However, structural changes of the crystal lattice can occur. For example, small volume changes, generally on

the order of about 10 % or less, are observed as lithium is added or removed. The presence of lithium can also cause nonuniform distortions to the shape of the crystalline structure, and these *phase transitions* can sometimes result in permanent damage to the material. To compensate, the cell is designed to be operated in regimes where these distortions are minimized.

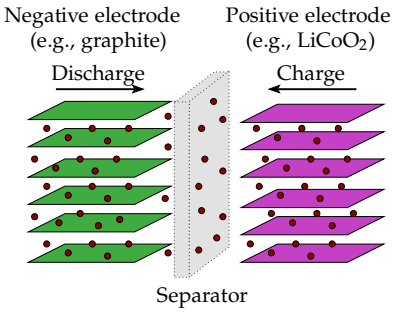


Figure 1.7: Simplified schematic of lithium-ion cell operation.

We begin describing lithium-ion cell operation using the simplified schematic of Fig. 1.7. (We will refine this understanding as the chapter proceeds.) In the figure, the negative and positive electrodes are drawn as crystal structures comprising layers of electrode material. Lithium, drawn as small spheres, can be added to or removed from the spaces between the layers.

Within the electrodes, lithium is stored as independent charge-neutral atoms. Each lithium atom's valence electron is very loosely shared with neighboring atoms in the crystal structure. As such, the lithium is not tightly bonded in one place and is actually quite free to move around. Lithium enters and exits the surface of the electrode, but diffuses within the layered open crystal structure to equalize the concentration of lithium within the vacant spaces of the electrode.

During discharge, lithium atoms at the surface of the negative electrode give up electrons—which travel through the external circuit—and become positive lithium ions, Li^+—which exit the crystal structure of the electrode and dissolve into the electrolyte. We can write, $Li \Rightarrow Li^+ + e^-$. Conversely, lithium ions proximate to the surface of the positive electrode receive electrons from the external circuit, and the resulting charge-neutral lithium atoms enter the crystal structure of the electrode. We can write, $Li^+ + e^- \Rightarrow Li$.

The process is completely reversible. Thus the lithium ions pass back and forth between the electrodes during charging and discharging. This has given rise to the terms *rocking chair*, *swing*, or *shuttlecock* cells to describe lithium-ion cells. The intercalation mechanism is much gentler than an electrochemical reaction, so lithium-ion cells have much longer lives than other secondary cells.

Until now, we have treated lithium-ion cell electrodes as homogeneous crystalline blocks. However, this is not actually the case. Instead, the electrodes are manufactured from millions of small electrode particles. This is done to increase the surface area of the electrodes, allowing easier lithium entrance/egress, decreasing overall cell resistance, and enhancing power delivery capability. For example, Fig. 1.8 shows a scanning electron microscope (SEM) image of a lithium-ion cell's negative electrode comprising graphite particles. The two images are of the same material at different magnifications.

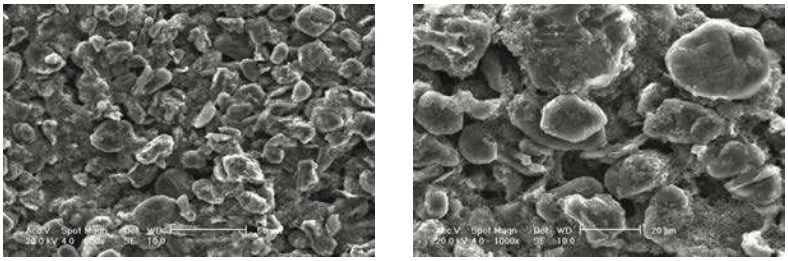


Figure 1.8: Scanning electron microscope (SEM) images of MTI-brand mesophase carbonaceous spheres (graphite).
(Images courtesy Sangwoo Han.)

Fig. 1.9 shows an SEM image of a positive electrode comprising lithium-manganese-oxide particles. The two images are of the same material at different magnifications. We see that the particles have distinctly different shape and size from the graphite particles.

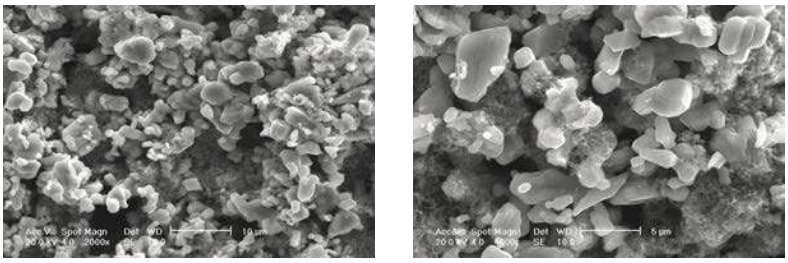


Figure 1.9: SEM images of Aldrich-brand lithium manganese oxide (LMO).
(Images courtesy Sangwoo Han.)

Fig. 1.10 shows cross-sections of an electrode. On the left, the electrode has been sliced by a razor blade; on the right, a focused ion beam (FIB) was used to mill a more precise cross-section, cutting through particles in the process. We see that the electrode structure is quite porous—electrolyte fills the pores between particles.

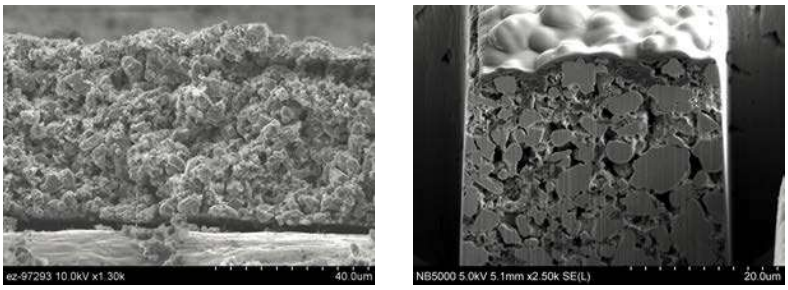


Figure 1.10: Focused ion beam (FIB) image of profile of LMO electrode (left) and FIB milled slice of LMO (right).
(Images courtesy Sangwoo Han.)

Mixed in with the primary electrode materials are binders, such as polyvinylidene fluoride (PVdF), to adhere the particles together, and conductive additives, such as carbon black, to enhance electron conduction, which is otherwise poor, especially in positive electrode materials. These additives are not "active" portions of the cell chemistry, and so are not always mentioned when discussing the composition of lithium-ion cells, but they are always present.[17]

[17] The images shown above are of an electrode with a 90:5:5 ratio of active material to carbon black to PVdF.

1.5.1 *Negative electrodes*

We now begin to describe the materials that are commonly used as electrodes for lithium-ion cells. Presently, the vast majority of commercial lithium-ion cells use some form of graphite (C_6) for the negative-electrode material. Graphite comprises multiple graphene layers, in which hexagonal C_6 structures are tightly bonded together. The graphene layers are stacked loosely on top of each other, held together only by weak van der Waals forces; lithium intercalates between these layers. This is shown in Fig. 1.11, where carbon atoms are drawn as gray spheres joined by covalent bonds to neighboring carbon atoms in the graphene layers, and the lithium atoms are drawn as purple spheres. There is sufficient room between the graphene layers for the lithium atoms to be able to move freely.

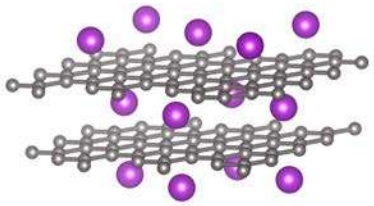


Figure 1.11: Atomic structure of lithiated graphite.
(Drawn with VESTA. See, Momma, K. and Izumi, F., "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *Journal of Applied Crystallography*, 44, 1272–1276 (2011).)

Several different forms of graphite are used in lithium-ion cells. Two examples are illustrated in Fig. 1.12, where the lines depict graphene segments, and lithium is able to reside in the voids between graphene layers. The difference is in the degree of uniformity of the graphene layers within the microstructures of the particles. Natural and synthetic graphite tends to be the most uniform; natural "hard" or disordered carbons are less uniform, having many small pockets of graphene layers, arranged in random configurations. The different types of graphite have different voltage properties, capacities, and aging characteristics, but operate in essentially the same fashion.

The maximum amount of lithium that can be stored in graphite is one atom of lithium per six atoms of carbon; the minimum amount is zero. Therefore, when talking about the degree of lithiation of a graphite electrode, we use notation Li_xC_6, where $0 \leq x \leq 1$. Clearly, when viewed at the atomistic level, there is either a single lithium atom or no lithium atom at all for any given C_6 site. But, when the entire electrode is considered, some fraction of the total number of C_6 sites is occupied, and that fraction is the value of x. When the cell is charged, the negative electrode is highly lithiated, and x is close to 1. When the cell is discharged, the negative electrode is largely depleted of lithium, and x is close to zero.

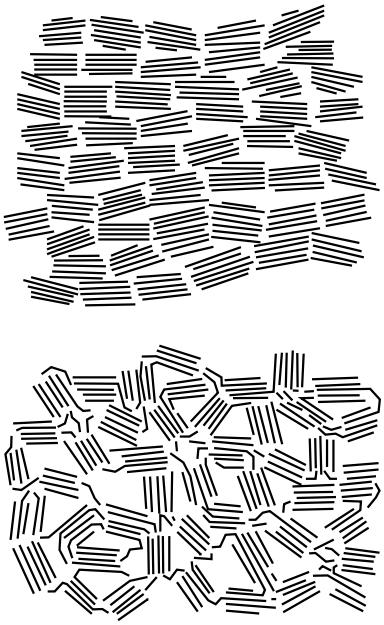


Figure 1.12: Microstructure of natural graphite (top) and hard carbon (bottom).
(Adapted from Fig. 4 in Wakihara, M. "Recent developments in lithium ion batteries," *Materials Science and Engineering R33*, 2001, 109–134, with permission from Elsevier.)

Alternative materials are being investigated for use as negative electrodes. Lithium titanate ($Li_4Ti_5O_{12}$, also known as *lithium titanate oxide* or *LTO*) allows much faster charging—without harmful side reactions—than graphite. The suppression of side reactions also yields cell lifetimes of many tens of thousands of charge/discharge cycles. However, the use of LTO also results in a cell voltages being reduced by about 1.4 V with respect to an equivalent cell having a graphite negative electrode and thus yields lower energy density. Silicon structures are also being researched, with the potential of

much higher energy densities than graphite since up to four atoms of lithium can be stored per atom of silicon. However, this causes very large changes in the volume of the silicon structures when lithium intercalates, leading to rapid structural breakdown and poor cell lifetimes. At this point it remains to be seen what technology will replace graphite negative electrodes in the future.

1.5.2 *Positive electrodes*

There is much more variability in the choice of materials to be used in positive electrodes for lithium-ion cells. In 1980, John B. Goodenough discovered that lithium cobalt oxide (Li_xCoO_2, also known as *LCO*) was a viable intercalation compound. Fig. 1.13 shows the crystal structure of LCO. The blue spheres represent cobalt atoms, the red spheres represent oxygen atoms, and the purple spheres represent lithium atoms. The amount of lithium in the structure is variable, but the cobalt-oxygen structures are fixed, and these are drawn as linked blue polyhedra (specifically, octahedra) to highlight the fact that the layers of cobalt oxide do not change—only the degree of lithiation of the structure can change. It is because of these layers, which behave somewhat like graphene in graphite, that this material is often called a *layered cathode*. A difference is that the lithium atoms in LCO act like pillars in the structure, keeping the cobalt-oxide layers apart. If too much lithium is removed, then the crystal structure collapses, and lithium can no longer enter between the layers. To avoid this collapse, only about half the theoretic capacity is usable ("x" in Li_xCoO_2 is permitted to use only about half of its theoretic range of 0 to 1).

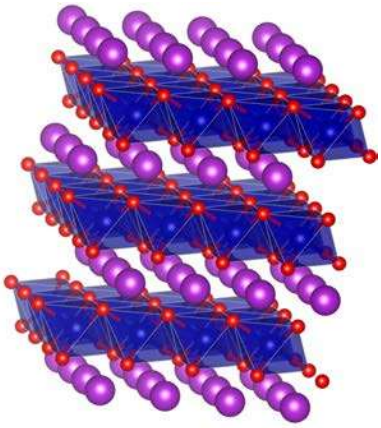


Figure 1.13: Crystal structure of lithium cobalt oxide (LCO).
(Drawn with VESTA. See, Momma, K. and Izumi, F., "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *Journal of Applied Crystallography*, 44, 1272–1276 (2011).)

LCO is commonly used in lithium-ion cells for portable electronics but suffers some problems when trying to scale up to larger cells for grid storage and vehicular applications. The principal problem is that cobalt is rare, toxic, and expensive. Nickel can be substituted for the cobalt sites, resulting in higher energy density (higher voltages at same capacity), but the resulting cell is not very stable thermally (it tends to catch fire). Aluminum, chromium, and manganese can be substituted as well, resulting in somewhat different properties. Often, a combination of transition metals is used. For example, a lithium nickel manganese cobalt oxide (NMC) electrode comprises a blend of nickel, manganese, and cobalt, which retains the layered structure, and has properties from all three constituent metals. A lithium nickel cobalt aluminum oxide (NCA) electrode blends nickel, cobalt, and aluminum.

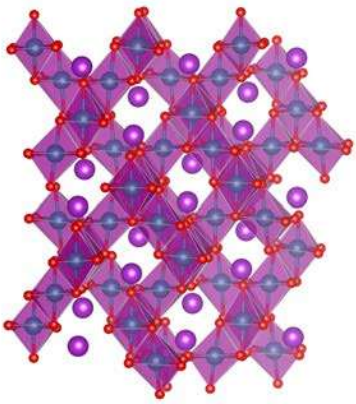


Figure 1.14: Crystal structure of lithium manganese oxide (LMO).
(Drawn with VESTA. See, Momma, K. and Izumi, F., "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *Journal of Applied Crystallography*, 44, 1272–1276 (2011).)

In 1983, Goodenough and Thackery proposed lithium manganese oxide ($Li_xMn_2O_4$, or LMO) as an alternate intercalation compound. This structure is drawn in Fig. 1.14. Manganese is drawn as blue

spheres, oxygen as red spheres, and lithium as purple spheres. The manganese oxide forms octahedral crystals in a pattern known as a *cubic spinel* structure, which is quite complicated and difficult to view in a two-dimensional projection. An interesting feature of this structure is that there are tunnels through it from each side, allowing lithium movement from front to back, from left to right, and from top to bottom.[18] These degrees of freedom make it easy for lithium to move within the structure, decreasing the resistance of the cell.

[18] For this reason, this material is said to have a "three-dimensional" or 3D structure. By referring back to Fig. 1.13, we see that LCO has a two-dimensional structure, and by looking forward to Fig. 1.15, we see that LFP has a one-dimensional structure.

The value of "x" in $Li_xMn_2O_4$ typically varies between 0 and 1, but can go as high as 2. Values of x greater than one are usually avoided because the structure of LMO becomes unstable in acidic conditions when highly lithiated—the crystal structure disintegrates as manganese is attacked by the acid and dissolves into the electrolyte. Additives can be introduced to the electrolyte to neutralize acidity to help prevent this, but the "art" of additive design is presently in the realm of black magic and trade secrets. Despite this serious limitation, LMO is common because it is less expensive and safer than LCO and has similar energy-storage densities.

More recently, in 1997, Goodenough proposed *olivine* style phosphates as a third major category of positive-electrode material. Lithium iron phosphate (Li_xFePO_4, or LFP) is the most common in this family. Its crystal structure is drawn in Fig. 1.15, where iron is represented by brown spheres, phosphorus by gray spheres, oxygen by red spheres, and lithium by purple spheres. Within this overall crystal structure, FeO_6 forms the brown octahedra, and PO_4 forms the gray tetrahedra.

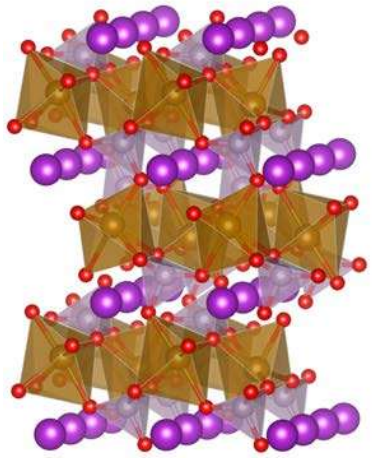


Figure 1.15: Crystal structure of lithium iron phosphate (LFP).
(Drawn with VESTA. See, Momma, K. and Izumi, F., "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *Journal of Applied Crystallography*, 44, 1272–1276 (2011).)

Lithium is free to move only in one-dimensional linear tunnels, which makes this material quite resistive. In order to compensate for this high resistance, the electrode particle size is usually chosen to be very small, minimizing the diffusion length (and hence resistance). LFP is quite popular due to the material's low-cost, low-toxicity, and very stable voltage profile. However, it also produces a lower cell voltage—by about 0.5 V—than other common positive-electrode materials and hence also a lower energy density. The amount of lithium by mass in LFP is also low, resulting in lower specific energies.

Alternative materials are being investigated for use as positive electrodes. Many of these are doped with vanadium, which tends to yield higher cell voltages. However, at present, the challenge is to develop an electrolyte that will function properly as a lithium ion conductor, but will not break down at the higher voltages.

1.5.3 *Electrolyte: Salt and solvent*

The electrolyte is the media that conducts ions between electrodes. It comprises either a salt, an acid, or a base that is dissolved in a solvent. Since lithium reacts violently with water, the electrolyte in a lithium-ion cell is composed of nonaqueous organic solvents plus a lithium salt and acts purely as an ionic conducting medium, not taking part in the chemical reaction. The most commonly used salt is lithium hexafluorophosphate ($LiPF_6$), which disassociates in the solvent into Li^+ and PF_6^-, but other candidates include $LiBF_4$ and $LiClO_4$.

Common solvents include ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC). The chemical structure of each of these is drawn in Table 1.3. A distinguishing feature of each is the double-bonded oxygen at the top of the molecule, which has a slight negative charge. To compensate, the remainder of the molecule has a slight positive charge. This polarization is what supports ionizing the salt in the solution and conduction of an ionic current.

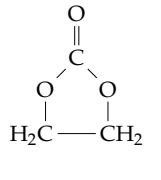
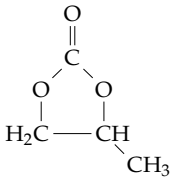
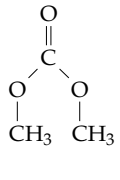
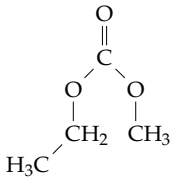
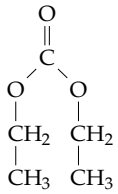
EC	PC	DMC	EMC	DEC
				

Table 1.3: Formulation of solvents commonly found in lithium-ion cells.

The solvent does not participate in the chemical processes of the cell, so we typically ignore it in our models (different solvents have different properties with regard to aging, low-temperature performance, and so forth, so the choice is important, but it doesn't factor in directly). So, we often talk about the salt as being the same thing as the electrolyte, even though the electrolyte also includes the solvent.

1.5.4 *Separator*

The separator in a lithium-ion cell is a permeable membrane with holes large enough to let lithium ions pass through unimpeded, but small enough that the negative- and positive-electrode particles do not make contact through the holes (which would short-circuit the cell). It is also an electronic insulator. An SEM image of a separator is shown in Fig. 1.16. To get a feel for the relative size of the pore

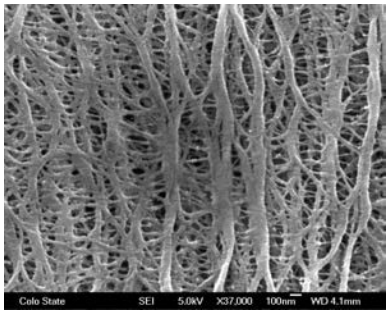


Figure 1.16: SEM image of raw separator material.
(Image courtesy Colorado State University.)

openings in the separator compared to an active-material particle, an atomic force microscopy (AFM) image of a lithium-manganese-oxide particle on top of a typical separator material is shown in Fig. 1.17. The fibrous nature of this particular type of separator is evident, where the pores are smaller than the most obvious depressions between the fibers. The vast scale differences between particle size and pore size of the separator material is also quite apparent. The separator is typically on the order of 20 μm thick; pore size is on the order of 50 Å; and this particular particle's size is on the order of 5 μm in diameter.

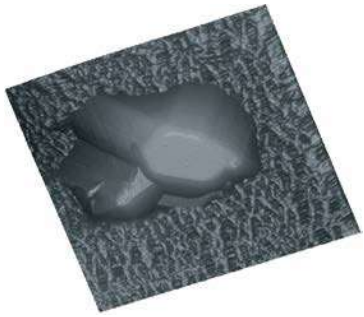


Figure 1.17: Lithium-manganese-oxide particle on top of separator material. (Image courtesy Sangwoo Han.)

1.6 *Manufacturing*

Some idea of how lithium-ion cells are manufactured can aid understanding how they work. The basic elements are the same for all kinds of lithium-ion cell, but there are some variations based on form factor:

- *Cylindrical* cells are ... cylindrical, and are encased in metal cans.
- *Prismatic* cells are ... prismatic, and are also encased in metal cans.
- *Pouch* cells are also flat and are encased in soft pouches.

Some examples of each form factor are shown in Fig. 1.18. In each case, the cells all contain one or more negative and positive electrodes (which are electrically connected inside the cell, forming a single logical negative and positive electrode), separator(s), and electrolyte (as previously discussed). Cylindrical cells are historically most common, but prismatic and pouch cells are finding heavy use for high-capacity battery applications to optimize the use of volume in high-capacity battery packs, since the more rectangular shapes pack together better.

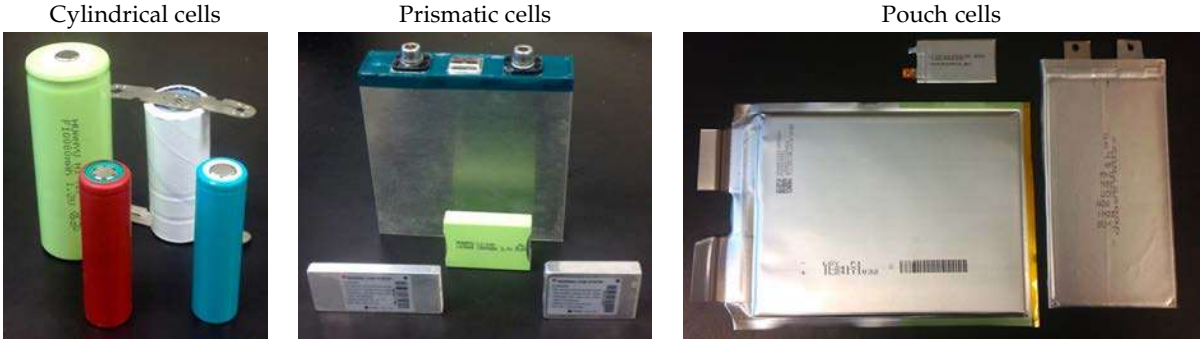


Figure 1.18: Different common form factors for lithium-ion cells.

1.6.1 *Electrode coating*

The negative and positive electrodes in lithium-ion cells are of similar form and are made by similar processes on similar or identical equipment. The active electrode materials are coated on both sides of thin metallic foils (the foils are on the order of 20 μm thick) that act as the current collectors, conducting the current into and out of the cell. This is illustrated in Fig. 1.19.

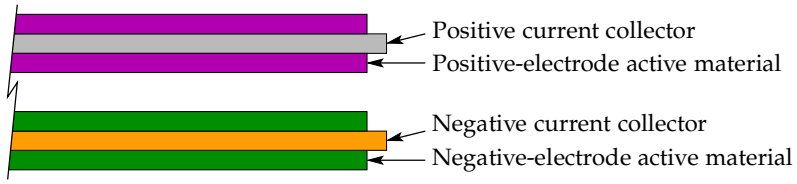


Figure 1.19: Electrode active material coats both sides of metal foil current collector.

Both negative- and positive-electrode active materials are delivered to the factory in the form of black powder.[19] To the untrained eye they are nearly indistinguishable. Because contamination between negative- and positive-electrode materials would ruin a cell, great care must be taken to prevent these materials from coming into contact with each other. For this reason the different electrodes are usually processed in different rooms.

[19] Green and purple coloring for the negative- and positive-electrode active materials, respectively, is used in this book purely for illustrative purposes. Orange and gray are used to represent copper and aluminum current collectors, respectively.

The metal electrode foils are delivered on large reels, typically about 0.5 m wide, with copper for the negative-electrode current collector and aluminum for the positive-electrode current collector. These reels are mounted directly on the coating machines where the foil is unreeled as it is fed into the machine through precision rollers.

The electrode active materials are mixed with a conductive binder and a solvent to form a slurry that is spread on the surface of the foil. A knife edge is located just above the foil, and the thickness of the electrode coating is controlled by adjusting the gap between the knife edge and the foil. (The thickness of the two electrodes will generally be different as the volumetric energy densities of the materials is generally different.) After being coated on both sides, the foil is fed directly into a long drying oven to evaporate the solvent from the slurry and to bake the electrode material onto the foil. As the coated foil exits the oven it is re-reeled. The process as described so far is accomplished by an electrode coating machine, which might look something like the illustration in Fig. 1.20.

The coated foils are subsequently fed into a *calendaring* (i.e., pressing) and slitting machine. Calendaring is done to compress the electrode active material, compacting the spaces between particles, pressing out porosity. Slitting cuts the foil into narrower strips of the desired width. Later they are cut to length. Any burrs on the edges

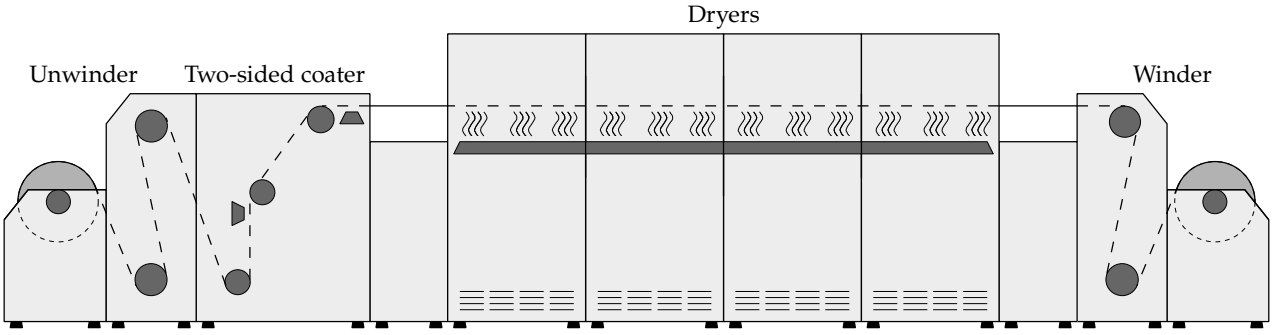


Figure 1.20: Electrode coating machine.

of the foil strips could give rise to internal short circuits in the cells so the slitting machine must be very precisely manufactured and maintained. The calendaring and slitting is accomplished by a machine that might look something like the illustration in Fig. 1.21.

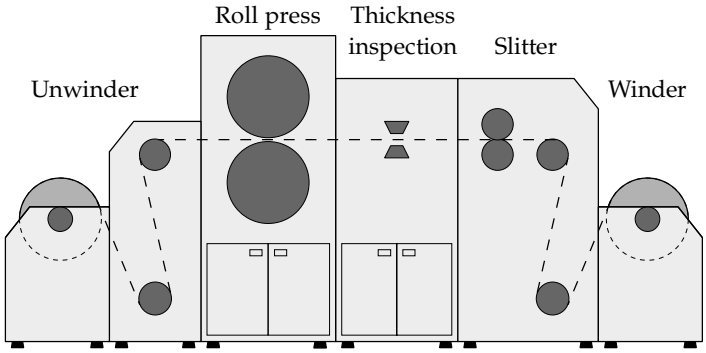


Figure 1.21: Calendaring and slitting machine.

1.6.2 *Cell assembly*

The electrodes are now ready to be assembled into cells. For cylindrical cells, the negative- and positive-electrode foils are cut into two long strips that are wound on a cylindrical mandrel, together with the separator that keeps them apart, to form a structure called a *jelly roll*. A cutaway diagram of a cylindrical cell is illustrated in Fig. 1.22. The mandrel is attached directly to the positive-electrode current collector and becomes the cell's positive terminal; the negative-electrode current collector is attached to the cell's negative terminal.

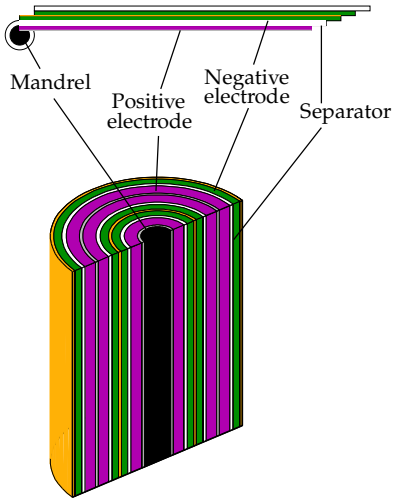


Figure 1.22: Construction of a cylindrical cell.

Prismatic cells are constructed similarly, but by winding the electrode-coated current-collector foils on a flat mandrel instead of a cylindrical mandrel. This is illustrated in Fig. 1.23. The flat mandrel causes the jelly-roll structure to be more prismatic than cylindrical in shape; once inserted into its can, the external appearance is prismatic.

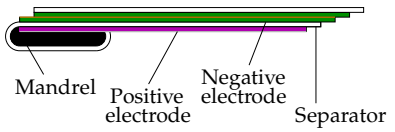


Figure 1.23: Construction of a prismatic cell.

The next stage is to connect the electrode structure to the terminals

and any internal electronic safety devices, and to insert this subassembly into a metal can. The can is then sealed via laser welding or ultrasonic heating, retaining a small opening. Electrolyte is injected into this opening, and the opening is closed. Addition of the electrolyte must be carried out in a *dry room* since the electrolyte reacts with water. Lithium hexafluorophosphate ($LiPF_6$), for instance, one of the most commonly used electrolyte salts, reacts with water to form toxic hydrofluoric acid (HF), which can attack the positive-electrode active materials and lead to premature cell failure. Afterward, the cell is given an identification code with a label or by printing a batch or serial number directly on the case. The final assembly is accomplished by a machine that might look something like the illustration in Fig. 1.24.

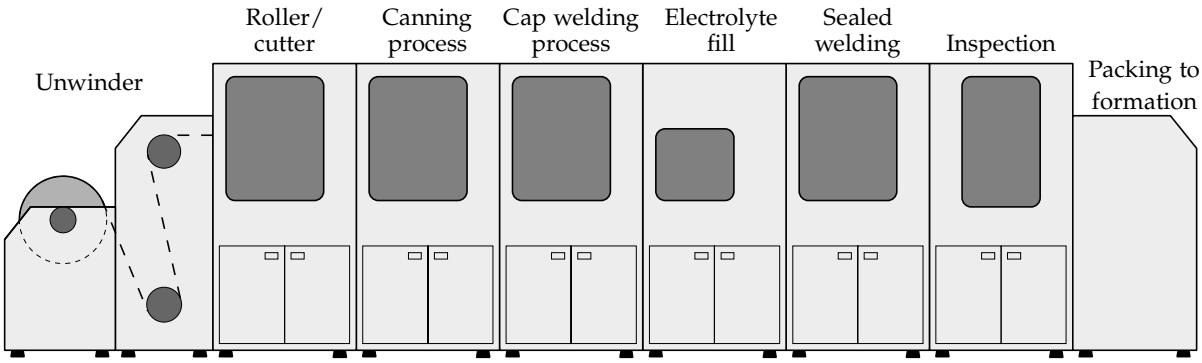


Figure 1.24: Cell construction machine.

Construction of pouch cells is somewhat different. Instead of winding long electrode strips around a mandrel, electrode plates are stamped out of the reels of electrode-coated foil. Negative- and positive-electrode plates are alternately stacked, with separator material between them, as shown in Fig. 1.25. All negative-electrode tabs are welded in parallel and to the cell's negative terminal; all positive-electrode tabs are welded in parallel and to the cell's positive terminal.

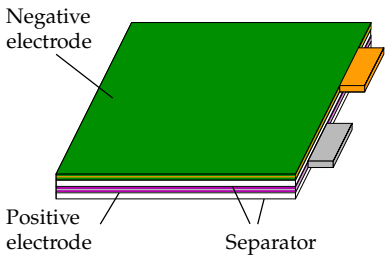


Figure 1.25: Stacked construction of a pouch cell.

1.6.3 Formation

Lithium-ion cells are fabricated in a completely discharged state (all of the lithium is in the positive electrode). So, once the cell assembly is complete, the cell must be put through at least one precisely controlled charge cycle to activate the working materials, transforming them into their usable form. This first charge begins with a low voltage and builds up gradually until the cell is fully charged. This is called the *formation process.*

THE ORGANIC SOLVENTS used in most lithium-ion cells naturally tend to react violently with graphitic negative electrodes. This would appear to be a "deal breaker," but it turns out that the reaction is self-limiting. The process can be compared to what happens when aluminum is exposed to air. Aluminum reacts rapidly with oxygen to form a film of aluminum oxide on its surface. This aluminum oxide prevents oxygen from reaching the underlying aluminum metal and so inhibits further reaction. In lithium-ion cells, the reaction of the solvent with the graphite in the negative electrode creates a passivating film on the surface of the graphite, known as the *solid electrolyte interphase* (SEI) layer, which is electrically insulating yet provides sufficient ionic conductivity for lithium to intercalate into and deintercalate out of the electrode particles readily. This SEI layer inhibits solvents from reaching the underlying graphite and so protects the graphite from further reaction.

The SEI is both a blessing and a curse. It is necessary for the proper safe operation of the cell, but it also increases the resistance of the cell and consumes lithium when being formed, decreasing the cell's capacity. Fortunately, once the SEI film is formed during the first charge cycle, it remains fairly stable and tends to grow only slowly as the cell is used. Even so, SEI growth is considered one of the principal aging mechanisms that lead to the cell wearing out.

DURING CELL FORMATION, data are also collected from the charger and recorded. The spread of the performance measurements across many cells gives an indication of whether the manufacturing process is under control. Although not the prime purpose of formation, the process allows a significant percentage of early-life cell failures due to manufacturing defects to occur in the manufacturer's plant rather than in the customers' products.

Tight tolerances and strict process controls are essential throughout the manufacturing process. Contamination, physical damage, and burrs on the electrodes are particularly dangerous because they can cause penetration of the separator and give rise to internal short circuits in the cell. There are no protection methods that can prevent or control this. Cleanliness is essential to prevent contamination, and cells are normally manufactured in clean-room conditions, with controlled access to the assembly facilities via air showers.

1.7 Failure modes

This book focuses on the operation of ideal cells, with the ultimate direction leading toward battery controls. To be able to effect optimal battery controls, however, an understanding of the potential cell

failure modes is essential. Failures occur because of cell design faults, poorly controlled manufacturing processes, aging, uncontrolled operations, and abuse. Battery controls can't do too much about the first two (it's too late!), but can do something about the others. Here, we briefly look at some qualitative aspects relating to postmanufacture cell failure.

1.7.1 "Normal" aging

Cell performance naturally deteriorates gradually with time due to unwanted chemical side reactions and physical changes to the active chemicals. Aging is generally irreversible and eventually results in cell failure. The following are some examples of causes (not all chemistries are susceptible to all of these mechanisms).

Corrosion refers to deterioration due to chemical interaction with the environment. It is a catch-all term for any number of undesirable side reactions that can occur within a cell. Some examples include reaction between the solvent and the current collectors and reaction between the solvent and the electrode active and inactive materials. In some cases, products of these reactions can themselves have a corrosive effect on other cell components.

Lithium-ion cells having graphitic negative electrodes are prone to a particular kind of corrosion known as *passivation*. The solvent in the electrolyte is not chemically stable at the high voltages found in most lithium-ion cells, and it reacts with the graphite particles. This forms a passivation layer of reaction products on the surface of the particles, which is known as the *solid–electrolyte interphase* or SEI film. This film protects the graphite against further reaction, greatly slowing down the process of passivation. However, SEI continues to grow at a slow rate throughout the cell's lifetime.

Some chemistries naturally produce gaseous products when charging, which ideally return to their prior aqueous state when discharging. However, if the gases leak due to a breach in the cell enclosure, capacity is lost. In many cases this can also be dangerous as in some cells the released gases are explosive (e.g., lead-acid cells give off oxygen and hydrogen when overcharged). In sealed cells, pressure buildup can lead to the rupture or explosion of the cell, unless the cell has a release vent to allow the escape of the gasses.

Chemical redox cells are also naturally susceptible to *crystal formation*. When material is removed from an electrode during discharge, it will not generally return to the same location when the cell is recharged. Instead, crystal structures will tend to form on the electrode surfaces. As the crystals grow, this reduces the effective surface

area of the electrodes, increasing resistance and hence decreasing their ability to deliver high power.

A particular example of crystal growth is when metallic *dendrites* form at the surface of an electrode. These treelike structures can grow through the separator, causing an increase in the cell's self-discharge rate or even a short circuit. For example, in lithium-ion cells, low-temperature operation or overcurrent during charging can cause deposition of lithium metal on the negative-electrode particles, leading to the growth of lithium dendrites.

Charging and discharging intercalation-based electrodes causes volume changes, which stress the electrodes and can lead to cracking of the active materials. In some lithium-ion positive-electrode materials, it can cause structural collapse, which prevents the electrode from intercalating or deintercalating lithium. Strains on the binder materials and conductive additives can lead to loss of contact between particles, increasing resistance.

Any of these causes lead to one or more of the following undesirable effects:

- *Increased internal impedance*: The resistance of the cell tends to increase as it ages. This limits the power that the cell is capable of delivering, leading to *power fade*.
- *Reduced capacity*: The capacity of a cell tends to decline as it ages. In some chemistries, some capacity can be recovered through reconditioning the cell by subjecting the cell to one or more deep discharges, but the general trend is in the downward direction. The decline of capacity over time is known as *capacity fade*.
- *Increased self-discharge*: Due to electrode swelling, which puts pressure on the separator; dendritic growth, which penetrates the separator; or local overheating, which melts and thins the separator, the self-discharge rate of a cell tends to increase as it ages as well.

Aging processes are generally accelerated by elevated temperatures. The best way to extend a cell's life is to maintain its temperature in an acceptable range.[20]

[20] A good rule of thumb for lithium-ion chemistries is that if you are comfortable at a certain temperature, the cell is also "comfortable" at that temperature. If it's too hot or too cold for your tastes, it's probably too hot or too cold for the cell as well.

1.7.2 *Uncontrolled operating conditions and abuse*

Good battery cells are not immune to failure, which can be provoked by the way they are used or abused. "Bad things" to do to a cell include using an unsuitable charging profile and/or overcharging, and exposing it to high ambient or storage temperatures.

Cells will also fail when subjected to physical abuse such as dropping, crushing, puncture, impact, immersion in fluids, freezing, or contact with fire, any of which could happen to an automotive

battery during an accident, for instance. It is generally accepted that a cell is not required to survive all these trials; however, it should not itself cause an increased hazard or safety problem in these circumstances.

There are several possible failure modes associated with the complete breakdown of the cell, but it is rarely possible to predict which one will occur. It depends very much on the circumstances.

- *Open-circuit failure*: This is a fail-safe mode for the cell but possibly not for the application. Once the current path is cut and the cell is isolated, further damage to the cell is limited. This may not suit the user, however. If one cell of a multicell series-connected battery fails open-circuit, then the whole battery will be out of commission.
- *Short-circuit failure*: If one cell of a series-connected battery fails because of a short circuit, the rest of the cells may be slightly overloaded, but the battery will continue to provide power to its load. This may be important in emergency situations.

  Short circuits may be external to the cell or internal within the cell. The *battery management system* (BMS) should be able to isolate cells from an external short, but there's not much the BMS can do to rescue a cell from an internal short circuit. However, the BMS and pack design must be able to prevent a single-cell failure from spreading to other cells; precautions include, for example, careful fusing, contactor control, and venting.

Within the cell there are different degrees of failure.

- *Hard short circuit*: Solid connection between electrodes causes extremely high current flow and complete discharge, resulting in permanent damage to the cell. The cell voltage collapses to 0 V, and the cell effectively acts as a resistor in the overall circuit.
- *Soft short circuit*: This is caused by small localized contact between electrodes. It may be self-correcting due to melting of the small regions in contact caused by the high current flow, acting as a local fuse, and interrupting the short-circuit current. A cell with a soft short is still operational, but has a high self-discharge rate.
- *Explosion and/or fire*: The rate of chemical reactions tends to double for every 10 °C increase in temperature. If the heat generated by these reactions cannot be removed as quickly as it is generated, this can lead to a further increase in temperature and set up a self-sustaining uncontrolled positive feedback known as *thermal runaway*, leading to a destructive result (fire/explosion). This is to be avoided at all costs, and the battery pack must incorporate protection circuits or devices to prevent it.