Chapter 24
A Look at the Future

24.1 Introduction

When considering what changes and new developments are possible, or even likely, in the years ahead, it is realistic to consider a quotation attributed to Thomas A. Edison:

> Making predictions can be rather precarious, especially when they have to do with the future.

Nevertheless, several things are rather obvious. One is that the need for energy storage will certainly grow substantially. This is not just due to the natural growth of all the technologies in which storage is an important component, but also to important changes in the energy production and utilization landscape. There is a greatly increased emphasis upon energy production methods based upon energy sources other than the various fossil fuels. But energy production from such sources is typically periodic, or at least intermittent, rather than continuous. Chief among these are the various solar technologies, and those based upon the use of the wind and tidal flows. Their use will surely increase in future years.

But in addition, the pressure for increased efficiency in the use of current energy sources is growing rapidly. An obvious example is the push toward the development of hybrid and plug-in hybrid, vehicles.

As an aside, it is interesting that official US Department of Energy targets typically assume that new technologies will need to meet the same requirements as those of the current technologies that they are expected to supplant. An example of this is that electrically and fuel cell-powered vehicles are expected to meet the long-range ability of current large, internal combustion vehicles. They also often assume that driving habits in the future will be about the same as those at the present time.

On the other hand, more and more of the public's attention is being given to the fact that a very large fraction of the actual vehicle use involves relatively short range daily commuter trips, for which limited range vehicles, whether battery or

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fuel cell-powered, would be perfectly satisfactory. Occasional longer trips would require the use of a different type of vehicle, of course. It is not unreasonable to think in terms of either two-car families, or the occasional rental of a long-distance vehicle when necessary.

The picture is not the same in all parts of the world. As can be seen in the discussion of several technologies in previous chapters, there are a number of directions in which progress has been greater in other countries than in the USA.

A large fraction of the government financial support of research and development activities related to energy technologies comes through, or is greatly influenced by, the Department of Energy, and especially, ARPA-E, in the USA. This leads to a concentration of work in a relatively small number of directions.

Recently the US Department of Energy decided to terminate efforts to develop hydrogen fuel cell – powered vehicles. In contrast, significant progress in that direction has been made in Japan and Europe, with significant numbers of demonstration vehicles on the road. This is mentioned in Chap. 22.

Some time ago it was decided to terminate work in the USA on both solid electrolyte and molten salt electrolyte elevated temperature batteries. As mentioned in Chap. 22, large sodium/sulfur solid electrolyte batteries are now being produced in Japan for use in large-scale storage facilities connected to the electrical distribution grid, and ZEBRA cells, which also have solid electrolytes, are now being produced in Switzerland for use for vehicle propulsion.

A large fraction of the long-range research in both government and university laboratories in the USA is aimed at advanced energy storage technologies that seem to be more applicable to small, high-tech portable, rather than larger-scale stationary, applications. Work on the latter is primarily concentrated on demonstration projects.

24.2 Emerging Technological Directions

Although most of the attention given to energy storage technology at the present time seems to be focused upon needs related to portable devices, such as computers and telephones, further development and increased use of larger systems is imperative.

Several of these are discussed in Chap. 22, and it can be seen that there is a regeneration of interest in elevated temperature battery systems for use in both large stationary applications and vehicles. Recent progress in both directions has been made outside of the USA, in Japan and Switzerland.

Flow batteries are now being commercially produced and sold by Gildemeister in Germany (who bought Cellstrom in Austria), Redflow in Australia, and Prudent Energy in China, as well as several other firms. The one American company producing such systems, VRB, went bankrupt several years ago, and its technology was purchased by Prudent Energy. Increased research and development activities in this area are now underway in the USA, primarily as the result of the stimulus provided by governmental funding through ARPA-E.

New alternatives are also emerging. One of these, that is actually still in the research stage, is the concept of the use of multilayer liquid battery systems that is mentioned in Chap. 22. It is too early to judge its significance.

Another approach to very large scale energy storage that has begun to get a lot of attention in the last few years, initially in Europe, but now also in the USA [1], may become very important. It involves the use of the sensible heat in relatively inexpensive molten salts as thermal storage media in conjunction with large solar systems. It can be used to periodically supply large amounts of energy to the electrical distribution grid so as to reduce the time-dependent variations in the demand placed upon the major electrical utilities. This is a type of load leveling, and could have a major effect on the cost of electrical energy, especially in areas such as the state of California, in which the demand varies by up to 50 %, depending upon the time of day.

Such a system involves the use of long parabolic reflectors to focus the sun's radiation upon tubes that carry a moving fluid. This fluid transfers the heat to a large molten salt bath, whose sensible heat acts as the storage system. This heat is then fed into a Rankine cycle steam turbine to produce electricity when needed.

The material that is initially heated by sunlight is sometimes called "solar oil," and is typically a synthetic organic material, a 50/50 mixture of the organic materials diphenyl oxide and biphenyl oxide. It has a low freezing point, 12 °C, so there is little danger than it might solidify, and it can be used up to about 400 °C. It transfers heat to a less expensive molten salt, such as the 50/50 eutectic mixture of $NaNO_3$ and KNO_3, that is sometimes called "solar salt." This salt melts at 221 °C, is stable up to about 500 °C, and has a heat capacity about half of that of water. It can be stored in large tanks, and supplies heat as needed to the steam turbine.

Typical prices are 0.5–1 dollar per kg of nitrate salts, and 3–4 dollars per kg for the low-melting organic heat transfer oils. As might be expected, efforts are being undertaken to find less expensive heat transfer media to replace the organic *solar oil*, or even a single material that can be used to handle the total thermal transfer and storage system in order to avoid the need for oil-to-salt heat exchangers. In addition, it would be desirable to be able to operate at higher temperatures, where the steam turbine is more efficient. It is important that the heat transfer material does not freeze inside the solar collector system or associated piping, of course. These nitrate salts are not corrosive, and can be readily contained in a number of metals and alloys.

Data on the compositions and minimum operating temperature of some of the nitrate molten salt materials that have been investigated are included in Table 24.1.

The important factors in the consideration of new technological approaches and systems related to large scale applications are different from those that are important in the smaller, and perhaps more high-tech applications. Both initial and lifetime costs are of great importance. In addition, as systems get larger, there will inevitably be more emphasis on safety, for larger problems can evolve into major disasters.

Table 24.1 Compositions and liquidus temperatures of several nitrate salts

Mol% Li	Mol% Na	Mol% K	Mol% Ca	Liquidus temp. (°C)
	66	34		238
	50	50		221
	21	49	30	133
30	18	52		120
31		58	11	117

24.3 Examples of Interesting New Research Directions

24.3.1 *Organic* Plastic Crystal *Materials*

The use of organic phase change materials for the storage of thermal energy is discussed in Chap. 3. The examples that were mentioned all involved the use of their heat of fusion. There are also some organic materials that undergo solid-state reactions, and exhibit *plastic crystal* behavior. They include some amines and polyalcohols that have large values of solid state phase transition enthalpy and low enthalpies of fusion [2, 3]. This topic is discussed in [4].

24.3.2 Organic Electrode Materials for Lithium Batteries

Present approaches to lithium ion batteries involve the use of metal alloys and inorganic materials as electrode reactants, as discussed in Chaps. 18 and 19. There have been several recent investigations of the potential of the use of organic materials for in this application [5–7]. A recent example is the use of polycarbonyl materials [8]. One of the advantages of these materials is that it is possible to tune the reaction potential. On the other hand, their solubility in electrolytes can be a problem. However, it is believed that this can be alleviated by increasing the molecular weight and increasing the magnitude of negative charge.

24.3.3 New Materials Preparation and Cell Fabrication Methods

As in a number of other areas of both science and technology, there is currently a lot of interest in the synthesis of nano-sized materials, and their potential use in connection with energy storage technologies.

The advantages of the use of small-dimensioned particles as electrode reactants in batteries are quite obvious in situations in which either the large surface area or the solid-state diffusion distance play an important role in controlling the kinetic behavior of electrodes.

But small nanowires can have an additional advantage in the case of some electrode materials that can have very large capacities. A particularly interesting example is the lithium-silicon alloy system. Under equilibrium conditions at elevated temperatures up to 4.2 lithium atoms can react per silicon atom [9], resulting in a theoretical electrode capacity of 4200 mAh g^{-1}. But the volume changes by about 400 % upon insertion and extraction of lithium of so much lithium, and this results in pulverization and capacity fading [10].

However, synthesizing silicon in the form of nanowires that are spaced apart makes it possible to accommodate such large volume changes without mechanical damage. This has been done by [11] and [12], who used the vapor–liquid–solid (VLS) method.

Using this method, it is possible to grow silicon nanowires on metallic substrates, such as stainless steel, so that each wire is attached to the current collector, avoiding the problem of the loss of electronic contact often found with particulate reactants.

The VLS method was first used in connection with the growth of whiskers for entirely different purposes [13]. It has subsequently been used for the growth of a number of other materials [14–19].

Another method that can be used for the formation of large numbers of nanowires employing a special chemical etching procedure has also been recently reported [20]. This is done by electrochemically etching silicon to form macropores, followed by uniform chemical etching to increase their diameter to the point that adjacent pores touch. The result is the formation of a large number of parallel fine nanowires, or pillars, of silicon. Galvanic deposition of copper onto the substrate results in a structure in which the wires are encased in copper at the bottom.

Innovative methods are also being pursued for the synthesis of positive electrode materials and their incorporation in novel electrode structures in high-energy batteries in a number of laboratories. These often involve variants of wet chemistry. One particular interesting method involves the formation of very fine particle oxides by use of a polymer precursor decomposition method [21–23], and a modification involving the use of citric acid [24].

In addition to the synthesis of fine reactant materials, there is a significant interest in methods to coat them with protective, yet electrochemically transparent layers. Another variant is the use of nanofibers to support thin layers of reactant material. One example is the deposition of amorphous silicon coatings onto carbon nanofibers [25].

24.3.4 Batteries with Physically Moving Electrode Structures

A very different approach to reversible energy storage has emerged in the last few years that involves a type of lithium ion battery containing a mechanically flowing semisolid material containing fine reactive particles [26–28]. It can be considered to be a type of flow battery in which the reactant materials are actually fine particles suspended in a viscous liquid. This novel approach is being developed by students and associates of Prof. Yet-Ming Chiang at MIT, and commercialization is being pursued by the new company 24M Technologies.

The label “sludge” has been used to describe the slurry-type of electrode structure that is made electronically conductive by co-suspending nanoscale conductive carbon black particles with the reactant particles.

One example is an aqueous lithium—ion system based upon the $LiTi_2(PO_4)_3$—$LiFePO_4$ couple in a 1 M $LiNO_3$ aqueous electrolyte with a pH of 11–12. In this case the maximum voltage is limited by the range of stability of water (roughly 1 V).

In this type of configuration there is a rather complex relationship between the mass flow behavior and the electrochemical efficiency, and there are inevitable mechanical pumping losses when using high viscosity semisolid electrodes.

Flow suspensions with high viscosity and non-Newtonian rheology benefit from use of an “intermittent flow” mode, in which the electrochemically active region of the cell is replenished in discrete steps, followed by electrochemical cycling. This results in lower mechanical energy dissipation than the use of a continuous flow mode operation.

A principal advantage of this novel approach, which is illustrated schematically in Fig. 24.1, is the ability to provide volumetric capacities an order of magnitude or more greater than that of conventional aqueous chemistries.

This is thus a type of flow battery that combines the high energy density of rechargeable batteries using solid storage electrodes with the architectural advantages of redox flow batteries.

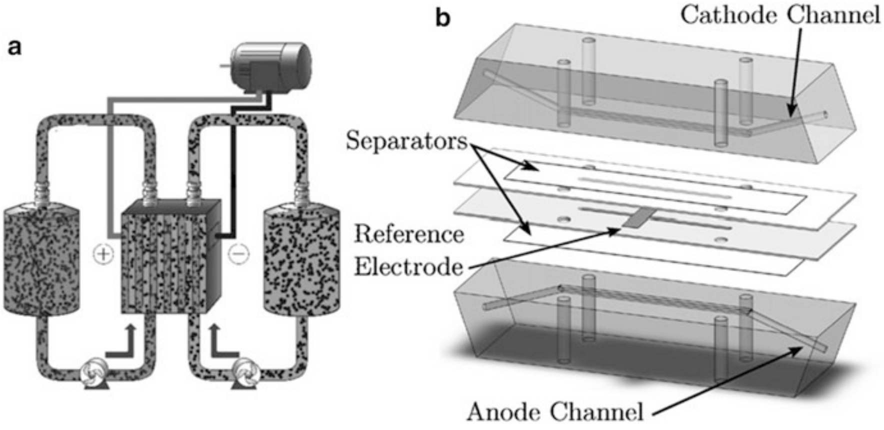

Fig. 24.1 Schematic diagram of a semisolid flow cell, and a model of a laboratory configuration showing the anode and cathode flow channels, separators, and reference electrode [28]

24.3.5 Alternate Electrolytes

There is a growing interest in the use of aqueous electrolytes in lithium systems, primarily for application in moderate-to-large systems in which low cost, high rate, and safety are of particular interest [29–34].

New electrolytes are also being investigated. One group of these that is drawing a lot of attention includes materials called *ionic liquids*. These are molten salts that have low melting temperatures [35–39]. This is accomplished by having one or both of the ions have complicated high entropy structures that are hard to crystallize. These typically contain large organic groups with rather low symmetry. It appears that some of these materials are stable in the presence of lithium battery electrode components.

24.3.6 Interesting New High Power, Long Cycle Life Battery

Early work on a new type of battery chemistry suddenly became visible in April, 2015 [40]. It involved an aluminum metal foil anode and either a pyrolytic graphite foil cathode or a 3-dimensional graphitic foam cathode. The electrolyte used was a nonflammable ionic liquid: $AlCl_3$/1-ethyl-3-methylimidazolium chloride, [(EMIm) Cl], that transports aluminum chloride anions. It was vacuum-dried so that it contained less than 500 ppm of residual water.

This system operates by the electrochemical deposition and dissolution of aluminum at the anode, and the reversible insertion of chloroaluminate anions into the graphite at the cathode. This mechanism is illustrated schematically in Fig. 24.2.

The reaction equations are:

$$4\,Al_2Cl_7^- + 3\,e^- = Al + 7\,AlCl_4^- \tag{24.1}$$

and

$$C_n + AlCl_4^- = C_n(AlCl_4) + e^- \tag{24.2}$$

Where n is the molar ratio of carbon atoms to intercalated anions in the graphite.

On the cathode side, $AlCl_4^-$ is reversibly intercalated into the graphite structure up to a capacity of 60–66 mAh per gram of graphite mass. On the anodic side of the cell metallic aluminum and $AlCl_4^-$ are transformed into $Al_2Cl_7^-$ during discharging, and the reverse reaction takes place on charging.

This cell has been shown to have relatively flat charge and discharge curves at about 2 V, a high coulometric efficiency, and a capacity of 60–70 mAh per gram, as shown in Fig. 24.3.

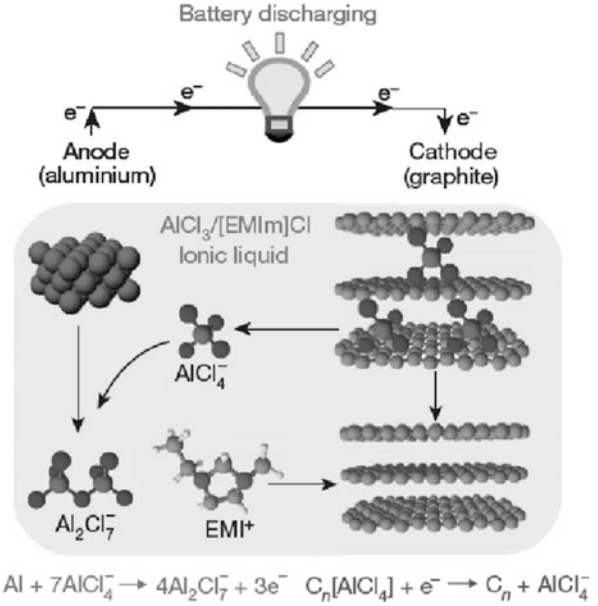

Fig. 24.2 Schematic representation of the operation of the aluminum/graphite battery [40]

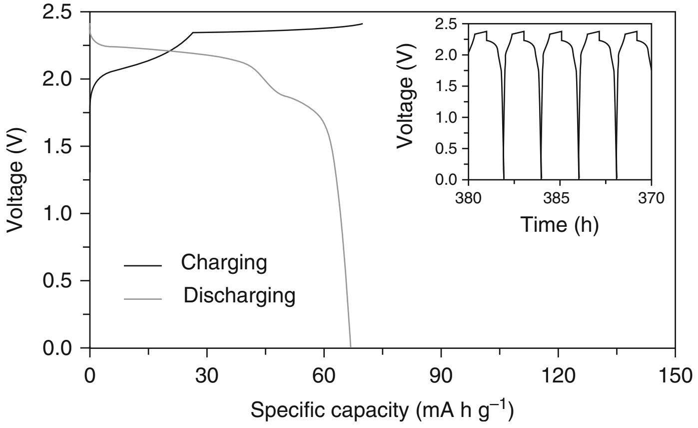

Fig. 24.3 Galvanostatic charge–discharge curves of an Al/pyrolytic graphite cell at a current density of 66 mA/g [40]

The consistency of the charging and discharging behavior of the aluminum/pyrolytic graphite cell up to 200 cycles at a current of 66 mA per gram is demonstrated in Fig. 24.4.

However, such cells showed reduced capacities at rates higher than 1C, and this was thought to be due to slow transport of the relatively large chloroaluminate anions through the graphite layer structure.

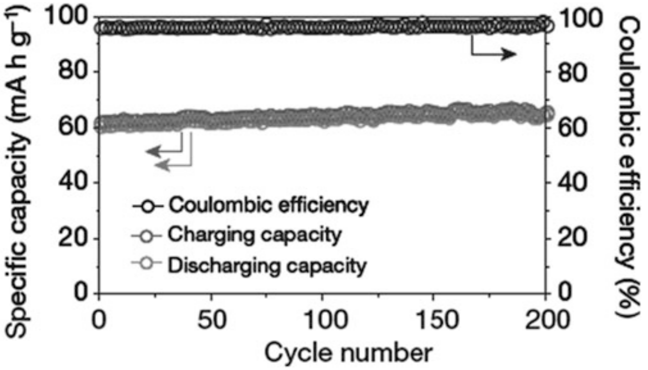

Fig. 24.4 Cycling behavior at 66 mA/g [40]

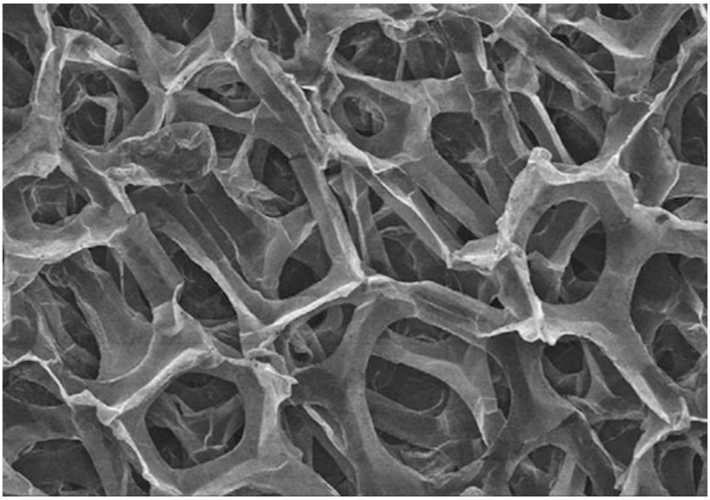

Fig. 24.5 Porous structure of the graphitic foam electrode [40]

Subsequent experiments were performed using very fine-structured porous, and flexible, graphitic foam that was produced by chemical vapor deposition upon a nickel foam template. The microscopic structure of this material is shown in Fig. 24.5. This allows the reaction to take place over a very large (internal) surface area, and makes very high rates of charge and discharge possible.

The very high surface area cathode makes it possible to operate at surprisingly high currents, with total charging times as short as 1 min at a current density of 4 A/g, which is equivalent to a specific power of about 3 kW per kg. This behavior is shown in Fig. 24.6. A cycle life of more than 7500 cycles without appreciable decay is shown in Fig. 24.7.

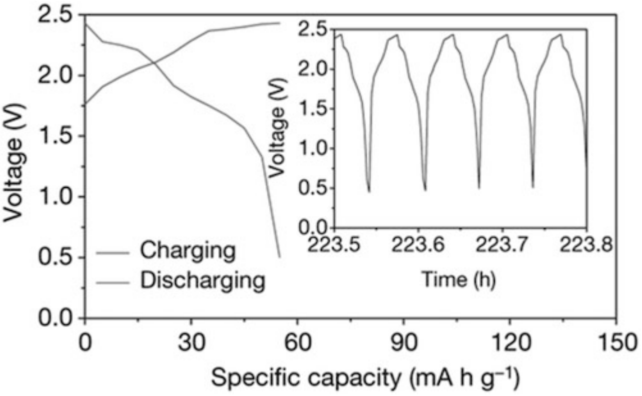

Fig. 24.6 Galvanic charge and discharge curves at a current density of 4 A/g [40]

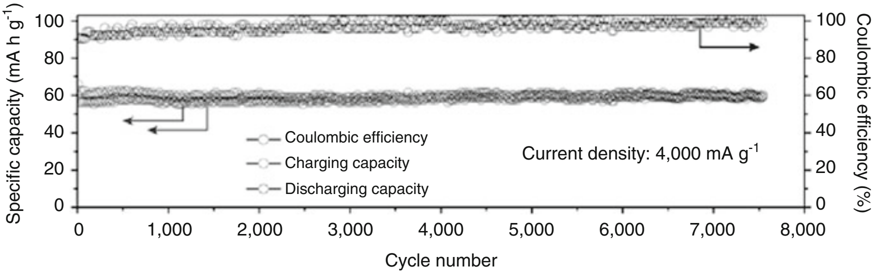

Fig. 24.7 Long-term stability of an Al/graphitic foam cell [40]

The aluminum dissolution and deposition efficiencies were reported to be very high, 98.6–99.8 %. No dendrite formation was found upon charging the aluminum electrode, even at these very high rates, up to a charging voltage cutoff of 2.45 V.

However, it was reported that reduced efficiency was observed when charging to higher voltages. The presence of larger amounts of water in the electrolyte also caused a reduced Coulombic efficiency. These observations are consistent with earlier reports on aluminum electrode behavior in a similar electrolyte [40].

The specific energy of this new type of battery is not especially high, about 40 Wh/kg, which is comparable to current lead-acid and Ni-MH batteries. But when using the highly porous graphitic foam in the cathode, the power density can be unusually high, about 3 kW/kg, which is in the range of supercapacitors.

24.4 Final Comments

Energy storage is becoming increasingly important. There are two general reasons for this. One is the recognition of the inevitable depletion of nonrenewable fossil fuels such as oil, and the need to shift, at least partially, away from today's dependence upon them as the primary energy source, and toward the use of alternate energy sources.

In addition, there is growing concern about the pollution resulting from the use of the major current sources. This may be relieved, at least in part, by the use of some of the alternative sources.

On the smaller scale, there are an increasing number of relatively small portable electrically powered devices that have to carry their energy sources with them. This results in the need for improvement in electrochemical battery or portable fuel cell technology.

The author hopes that this book will be helpful in providing an understanding of the different methods by which energy can be stored.

He also wishes to applaud, and cheer on, all those who have contributed to the current state of knowledge of energy storage science and technology.

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