

# 1

## Introduction

The world is witnessing increasing requirements for energy to meet the needs of modern society. Due to the drastic climate warming around the world, developing innovative sustainable clean energy (wind, tidal, solar energy, etc.) with high energy efficiency is extremely important. However, various renewable energy to electricity are quite fluctuating over time, and developing reliable energy storage systems is an important way to solve these challenges. Therefore, to satisfy the increasing social and industrial demands, better electrochemical energy storage devices should be used.

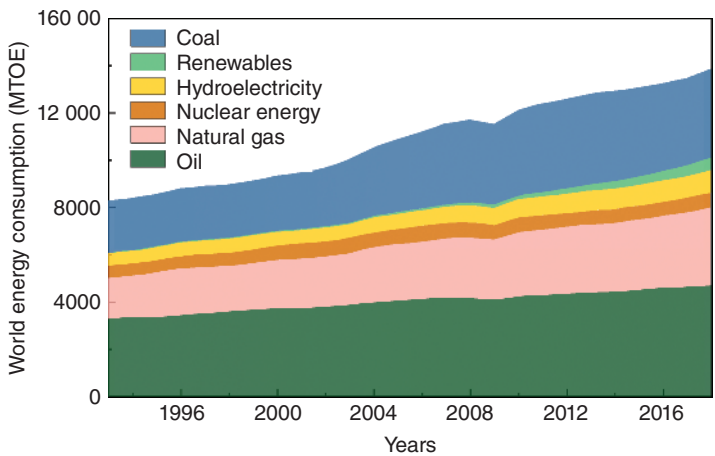
On this point, searching for novel electrochemical energy storage system with exceptional electrochemical properties for energy storage is essential. In this chapter, we will first give a brief introduction toward various electrochemical energy storage devices, including electrochemical capacitors (ECs) and lithium ion batteries (LIBs).

### 1.1 Energy Conversion and Storage: A Global Challenge

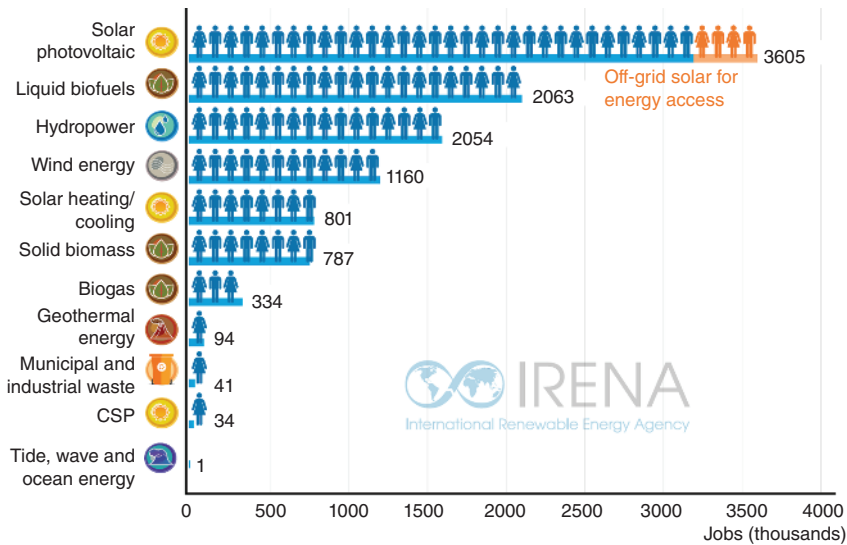
Nobel chemistry prize winner Richard Smalley had said: “Energy is the single most important problem facing humanity today and energy is the largest enterprise on Earth” [1]. Nowadays, the energy generation still mainly relies on fossil fuels (oil, coal, and gas), which occupy 80% of total energy needs in the world. On the other hand, the fossil fuels are still to be the dominant primary energy resources for many years in the future. Therefore, limited supplies of the fossil fuels make it imperative that combustion-based energy sources should be replaced by clean and renewable energy [2]. These sustainable energies mainly include hydropower, solar, wind, geothermal, and tidal energy.

Figure 1.1 shows the global energy consumption. In 2018, the growth rate of global energy consumption is 2.9%, which was the highest rate since 2010. Although fossil energy still occupies the most energy consumption around the world, the renewable energy also made a significant increase in recent years [4]. Gas and renewables have the most obvious increase among various energy sources since 2010 [3].

More importantly, the renewable energy sector also has significant social and economic impact. In 2018, at least 11 million people were employed in the renewable energy sector around the world. Compared with the data in 2016, the growth rate



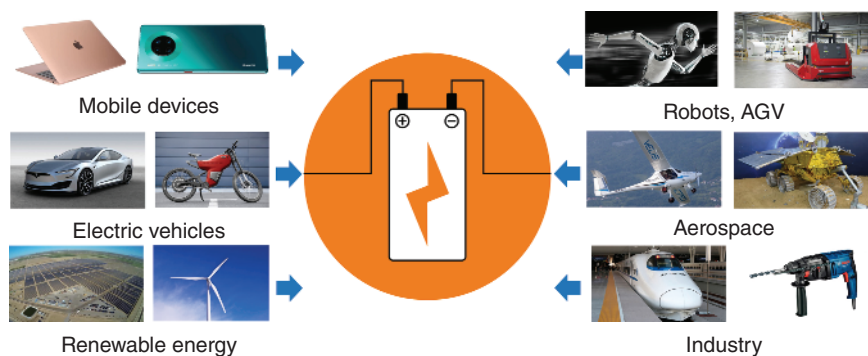
**Figure 1.1** Amounts of global energy consumption.



**Figure 1.2** Global renewable energy employment indexed by technology. Source: International Renewable Energy Agency [4]. © 2018, IRENA - International Renewable Energy Agency.

of employment was 5.3% [4]. As shown in Figure 1.2, the top five employment in the renewable energy sector on the list includes solar photovoltaic, liquid biofuels, hydropower, wind energy, and solar heating.

Electricity has been considered as the most effective way to explore and utilize various renewable energies effectively. Compared with other forms of energy, electricity has many obvious advantages as follows [5]: (i) Convenience: electricity can be easily transformed into the desired forms of energy, such as heat, light, and mechanical energy. (ii) Easy control: electricity can simply be operated and tuned.



**Figure 1.3** Application of electrochemical energy storage, AGV (automated guided vehicles).

(iii) Flexibility: electricity can be easily transferred by transmission line. (iv) Cheap: compared with other forms of energy, electricity is an economical form, which has been widely used for domestic and industrial applications. (v) Low transmission loss: electricity can be easily transmitted with high efficiency from the power plant to the user.

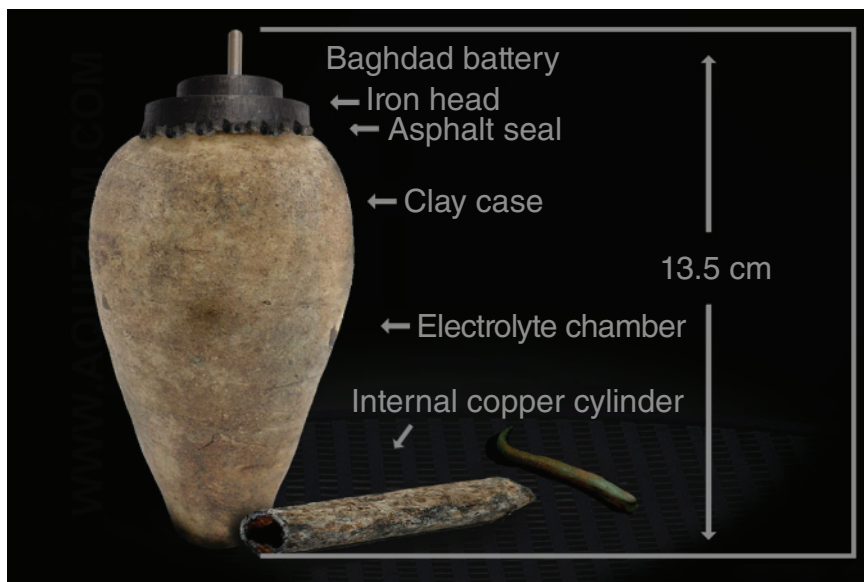
Although electricity has many advantages, the renewable energy-based electricity is quite fluctuating over time. For example, the clouds constantly alter the output of solar energy systems and wind cannot blow at a fixed speed. Unfortunately, grid has a fixed frequency of 50 Hz, which was determined by turbines in power plants. These must be matched to avoid the fluctuation of grid. Therefore, the clean energy-based electricity requires to be stored and delivered for commercial usage.

As a result, renewable energy calls for the development of electricity storage devices. Among these various electrochemical energy storage systems, ECs and various batteries have showed great potential not only in the powering portable electronics but also in the transportation sector.

As shown in Figure 1.3, various electrochemical energy storage has been widely used in every aspect in our daily life, such as aerospace (satellites, rockets, and aircrafts), transportation (cars, trains, and ships), portable electronic gadgets (mobile phones, laptops, and digital cameras), and industry fields [6]. The ever-growing advancement of electrochemical energy storage technology has greatly promoted the development of human society. It can be anticipated that electrochemical energy storage materials and technology play more important role in human life.

## 1.2 Development History of Electrochemical Energy Storage

As shown in Figure 1.4, the first electrochemical energy storage chemistry in history is Baghdad battery, which consisted of a ceramic pot, a tube of copper, a rod of iron, and vinegar electrolyte. This ancient battery has ~2.0 volts of electricity [8].



**Figure 1.4** Replica of Baghdad battery found in Iraq. Source: Aquiziam [7].

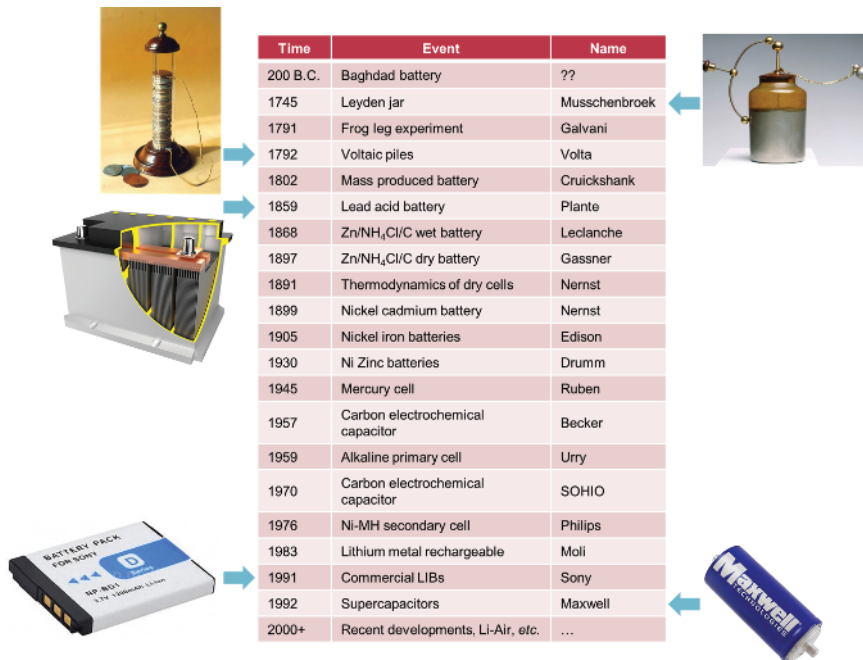
The first modern battery was invented by the Italian scientist Volta in 1799, which was called as “Volta pile.” This battery was a stack of Ag and Zn disks, and the metal disks were separated by salt water-soaked cloth [9]. Volta found that the single pile could only produce 1.0–2.0 volts of electricity. To increase the voltage output, several “Volta piles” could be constructed side by side. The processes that occur in the device were later demonstrated by Humphry Davy and Michael Faraday, which described that it is the occurrence of chemical reactions that is responsible for the production of electricity [9].

This finding marked the emergence of the electrochemistry. Consequently, the research and development of various electrochemical energy storage systems became active in the nineteenth and twentieth centuries.[10] The simple history of electrochemical energy storage is shown in Figure 1.5.

### 1.3 Classification of Electrochemical Energy Storage

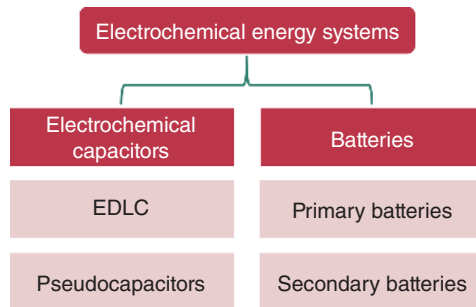
The electrochemical energy storage has almost penetrated every aspect in our daily life, which can efficiently store and convert energy reversibly between chemical energy and electrical energy in an environmentally friendly way.

There are many requirements that electrochemical energy storage needs to fulfill for various application fields, such as portable electronics, electric vehicles (EVs), and power tools. The main requirements for different electrochemical energy storage include high gravimetric/volumetric energy density, long cycle life, low cost, safety, and easy fabrication [11]. These attributes are mainly determined by the intrinsic properties of the materials and chemistry constituting the electrochemical



**Figure 1.5** Development of various electrochemical energy storage.

**Figure 1.6** Classification of electrochemical energy storage. EDLC, electric double-layer capacitors.



energy storage [12]. Based on the charge storage mechanism, the electrochemical energy storage technology has two main categories: ECs and batteries, as shown in Figure 1.6.

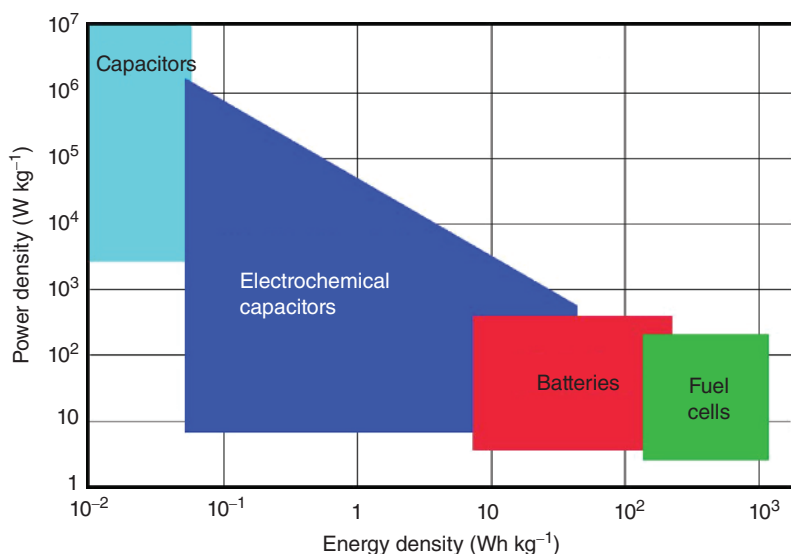
As shown in Figure 1.6, ECs have two mechanisms to store electricity: double-layer capacitance and pseudocapacitance. Double-layer capacitance is based on ionic adsorption, whereas pseudocapacitance is an electrochemical process. Electrochemical batteries have two broad categories, primary and secondary batteries. A primary battery is one that cannot easily be recharged after one use. An example of a primary battery is the dry cell, which was commonly used to power remotes and clocks. In such cells, a Zn container acts as the negative and a carbon rod acts as the positive. A secondary battery can be recharged to their original pre-discharge status, such as LIBs, NiCd, and NiMH batteries.

## 1.4 LIBs and ECs: An Appropriate Electrochemical Energy Storage

Batteries can store energy through reversible redox reactions in the bulk phase electrodes, whereas ECs can store amounts of energy at the electrolyte–electrode interface or through redox reactions on the surface of electrode [13, 14]. As shown in Figure 1.7, a battery usually deliver higher energy density and lower power density than that of ECs, whereas ECs are advantageous and potential candidates in a wide range of applications due to their high power densities ( $>10 \text{ kW kg}^{-1}$ ), exceptional reversibility (90–95%), and ultra-long life span ( $>100\,000$  cycles) [15].

Among various secondary batteries, such as Pb-acid, Ni-Cd, and NiMH batteries, LIBs possess higher energy density and cycle life and have reasonably attracted the biggest commercial and research interest. LIBs have been widely used to power the portable electronics and have also enabled the rapid development of EVs and renewable energy sources. Compared with other secondary batteries, LIBs show many outstanding properties, such as high voltage and energy density, better cycle life, light weight, and low self-discharge rate [16]. Therefore, the development of LIBs has been a hotspot both in industry and in academy. In 2019, the Noble Prize in Chemistry rewards the study of the LIBs to Drs. M. Stanley Whittingham, John B. Goodenough, and Akira Yoshino.

The LIBs concept emerged in the 1970s and was finally commercialized by Sony in the 1990s [17, 18]. The foundation of LIB began during the oil crisis by Stanley Whittingham, who found that  $\text{TiS}_2$  can accommodate lithium ions at a molecular level [19–21].



**Figure 1.7** Power density as a function of energy density for various electrochemical energy storage. Source: Libich et al. [13].

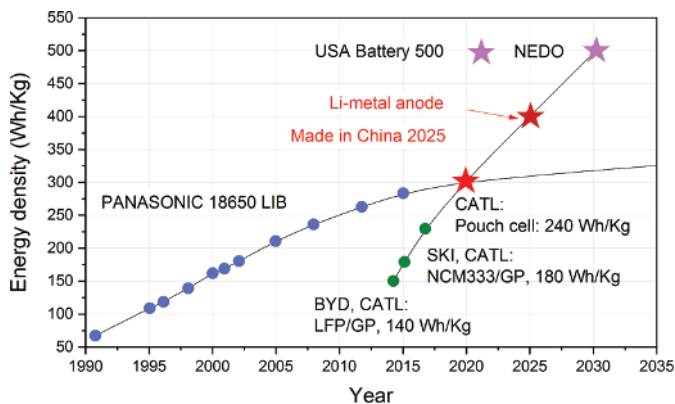
Lithium is the lightest metal (relative atomic weight is 6.94), and it has the lowest potential ( $-3.04$  vs. standard hydrogen electrode, SHE); this property enables LIBs with higher energy density than that of other secondary battery [22]. Since 1970s, metallic lithium has been used as the negative material for lithium primary batteries. Unfortunately, metallic lithium is not suitable for secondary lithium batteries due to the uncontrolled lithium dendrite during cycling, which can pierce the separators to cause inner short-circuit, eventually causing smoking, firing, and explosion [23, 24].

The basic concept of “Rocking chair battery” was proposed in the late 1970s, which used a layer compound to replace the common lithium metal as negative electrode [16, 25]. In this configuration, lithium exists in an ionic state rather than a metal state; the lithium deposition can be greatly suppressed during the electrochemical process. Therefore, the safety of battery can be remarkably improved. According to this concept, Megahed and Scrosati [26] used  $\text{LiWO}_2$  as the negative,  $\text{V}_2\text{O}_5$  as the positive, and  $1 \text{ mol l}^{-1} \text{ LiClO}_4/\text{PC}$  (propylene carbonate) as the electrolyte to confirm this rocking chair battery concept. However, the obtained LIB still showed low specific capacity and poor cycling, which failed to be commercialized. When a metal oxide rather than a metal sulfide acted as the positive, Dr. John Goodenough predicted that the positive may have greater potential. After a systematic investigation, he showed that  $\text{LiCoO}_2$  can produce as high as four volts potential in 1980 [27]. The finding of  $\text{LiCoO}_2$  was a revolutionary breakthrough and would result in more powerful batteries. In 1986, Auborn and Barberio [28] also assembled an LIB with  $\text{LiCoO}_2$  as the positive electrode,  $\text{MoO}_2$  as the negative electrode, and  $1 \text{ mol l}^{-1} \text{ LiPF}_6/\text{PC}$  as the organic electrolyte. However, this battery has the intrinsic problems, such as low operating voltage and sluggish diffusion of lithium ions in the negative electrode.

In the following years, the research and development of LIBs did not make significant progress. Until 1985, with the positive of Goodenough as a basis, Akira Yoshino constructed the first commercial LIB. Rather than the reactive metal lithium as the negative, petroleum coke was used as the negative electrode and  $\text{LiCoO}_2$  acted as the positive electrode to construct a new, high-voltage LIB [16]. This combination of positive and negative materials greatly extended the cycle life of LIBs and significantly improved its safety and voltage. This innovative design opened the door for the large-scale commercialization of LIBs, which has been regarded as a milestone in the history.

Since its commercialization in 1991, LIBs have entered every aspect in our daily life and are the foundation of a wireless, fossil fuel-free society. The better LIBs have been an ongoing goal to satisfy future demands ranging from small-scale consumer electronics to large-scale EVs and grid storage. As shown in Figure 1.8, the energy density of 18 650 cylindrical cells slowly increased from  $\sim 70$  to  $\sim 300 \text{ Wh kg}^{-1}$  [29]. Nowadays, LIBs of  $240\text{--}300 \text{ Wh kg}^{-1}$  level have been commercialized and widely used in EVs. To develop better LIBs, major countries in the world have been invested lots of resources to conduct extensive and in-depth research in this field. For example, the “Battery 500” project was supported by the Department of Energy of United States to set a goal to achieve  $500 \text{ Wh kg}^{-1}$  in 2021. The “New Generation Battery” plan was also funded by New Energy and Industrial Technology





**Figure 1.8** The history, current status, and development of LIBs. (NEDO, The New Energy and Industrial Technology Development Organization; GP, graphite; LFP,  $\text{LiFePO}_4$ ; NCM333,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ; CATL, Contemporary Amperex Technology, Co. Ltd., Ningde, China; BYD, BYD Company Limited, Shenzhen, China; SKI, SK Innovation Co., LTD., Korea.)

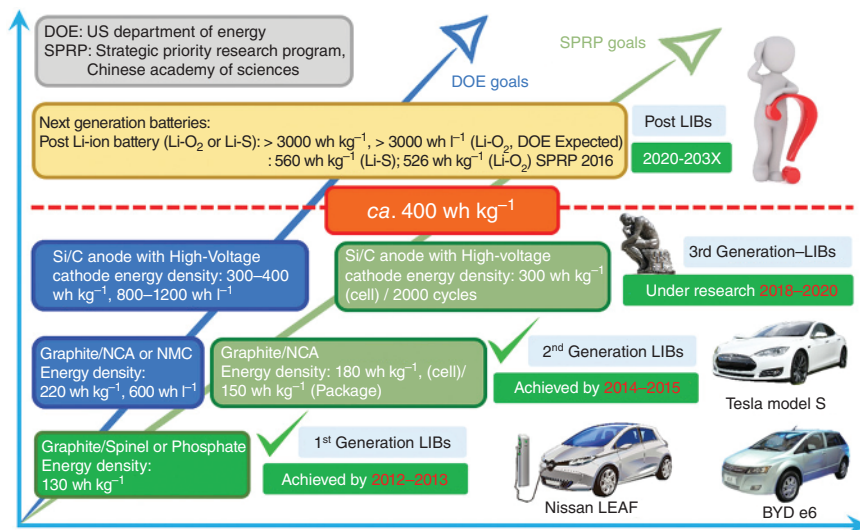
Development Organization (NEDO) of Japan and planned to achieve  $500 \text{ Wh kg}^{-1}$  in 2030. In China, “Strategic Priority Research Program for Electric Vehicles with long range” was released by the Chinese Academy of Sciences (CAS). “Made in China 2025” project launched by the Chinese government set a goal to achieve 300 and  $400 \text{ Wh kg}^{-1}$  of LIBs in 2020 and 2025, respectively (as shown in Figure 1.8) [29].

In summary, a better volumetric/gravimetric energy density, lower cost, better safety, and cycle life are still important requirements to power mobile devices and improve the driving range of EVs. On the other hand, various renewable energies also require to be stored and delivered for commercial applications. In summary, these two problems call for developing appropriate LIBs to meet these requirements.

Figure 1.9 shows the general trends for the present automobile battery research and development objectives with respect to the employed materials of negative, electrolyte, and positive. As shown in Figure 1.9, the energy density of first-generation LIBs for EVs is  $\sim 130 \text{ Wh kg}^{-1}$ , which is based on  $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$ ,  $\text{LiMn}_2\text{O}_4$ , and graphite materials. By far, the second-generation LIBs, which are based on the high-capacity  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  (NMC) or  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA)-positive [31] and graphite materials, normally show practical energy densities up to c.  $240 \text{ Wh kg}^{-1}$  and was subsequently commercialized in TESLA Model S, shown in Figure 1.9. According to both Department of Energy (DOE) and SPRP (Strategic Priority Research Program) projects, a  $400 \text{ Wh kg}^{-1}$  is the roof-top in the third-generation LIBs due to the limitation in the capacity of conventional LIBs configuration. To achieve higher energy density, post LIBs chemistry has also been investigated, such as Li-S, Li-Air, and other systems.

ECs are another important electrochemical energy storage devices, which first appeared in the middle of the twentieth century. Generally, ECs can be regarded as a complementary role for LIBs. In 1957, the first type of ECs was invented by Becker of General Electric. It was found that its capacitance is considerably higher than





**Figure 1.9** Progress of battery technologies based on DOE and SPRP projects. Source: Hong et al. [30]. Reproduced with permission of Wiley.

conventional capacitor due to the high specific surface area of porous carbon [13]. In 1969, a non-aqueous electrolyte was used in porous carbon-based ECs by Sohio, which enhanced the upper potential to 3 V [32]. Then in 1971, the capacitance behavior of RuO<sub>2</sub> films was investigated by Trasatti and Buzzanca et al. [33]. In 1980s, Conway et al. [32, 34, 35] also conducted lots of investigations on the RuO<sub>2</sub> type of EC, which shows a surface-redox pseudocapacitance. This field has been very active since about 1990s. Among various materials, carbon materials with high specific surface area, including activated carbons (ACs), carbon aerogels, carbon nanotubes (CNTs), and graphene, are unique class of materials for electric double-layer capacitors (EDLC)-type ECs and have been applied and investigated [36–38].

The energy storage mechanism in ECs takes place through either ion adsorption at the electrode/electrolyte interface or reversible faradaic reactions [13, 32, 39]. Based on their mechanisms of charge storage, ECs are classified into four broad categories. The first type includes electric double-layer capacitors or so-called EDLC ECs. The second type is pseudocapacitors or Faradaic ECs, which is based on reversible Faradic reactions. The third is called hybrid ECs. Hybrid ECs combines both previous EDLC and pseudocapacitors. The fourth category represents hybrid EC-LIBs devices, which is based on the combination of ECs, reversible faradic reactions, and LIB-type materials [40].

In Chapter 2, we will also give a brief introduction toward the mechanism of ECs. Table 1.1 shows summarization and comparisons of the important performances between LIBs and ECs. The important performances include energy and power density, self-discharge rate, cycle life, and the working temperatures. ECs can produce ultra-high power density and cycle performances, whereas LIBs usually possess higher gravimetric/volumetric energy density.

**Table 1.1** Comparison between ECs and LIBs.

Performances	ECs			LIBs
	EDLC EC	Pseudo EC	Hybrid EC	
Charge time (s)	1–10	1–10	100	600
Cycle performance	1 000 000	100 000	500 000	500–2000
Cell voltage (V)	0–2.7	2.3–2.8	2.3–2.8	3.6
Energy density (Wh kg <sup>-1</sup> )	3–5	10	180	250
Price (USD/kWh)	–10 000	–10 000		–140
Operating temperature (°C)	–40–65	–40–65	–40–65	–20–60
Self-discharge per month (%)	60	60		4
Electrolytes	Aprotic/protic	Protic	Aprotic	Aprotic

Source: Libich et al. [13].

Based on Table 1.1, ECs and LIBs can provide unique solution to the electrochemical energy storage and could be considered as complementary technologies. Therefore, LIBs and ECs are the dominant electrochemical energy storage systems in modern society.

Performances of LIBs and ECs strongly linked with the electrode materials used. With the booming development of materials, the performance of LIBs and ECs has also been progressing rapidly. In Chapter 2, the main part will be focused on materials of LIBs and ECs as the current advanced electrochemical energy storage.

## 1.5 Summary and Outlook

Renewable energy sources, such as wind, solar tide, and geothermal, become extremely important in our modern society. Renewable energy sources must be first converted to secondary electricity before utilization. Therefore, developing electricity storage systems can be available to meet demand whenever needed would be the breakthrough in electricity distribution. Among electrochemical energy storage systems, ECs and LIBs have displayed great potential not only in portable electronics but also in the renewable energy transportation sector. ECs and LIBs have their own advantages; ECs can produce ultra-high power density and cycle life, whereas LIBs usually possess higher gravimetric/volumetric energy density.

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